Quantum Mechanics 3

22. August. 2006

2005 Winter Session

Hatsugai

Contents

PartI Scattering Theory 6

1 Scattering Theory in One Dimention 6

1.1 Transfer Matrix Method 6

1.1.1 Transfer Matrix for Scattering State and Bound State 6

1.1.2 The Transfer Matrix and the Scattering Matrix 12

1.2 The Green's Function and Scattering Integral Equations 16

1.3 Levinson's Theorem in One Dimension 22

2 The Scattering Theory in Three Dimention 29

2.1 The Scattering Amplitude and the Differntial Cross Sections 29

2.2 Lippmann-Schwinger Equation and the scattering Amplitude 33

2.3 Born Approximation 35

2.4 Partial Wave Decomposition 37

2.4.1 The Schroedinger Equation in Spherical Symmetric Field . . 37

2.4.2 Phase Shift 45

2.4.3 Lograrithmic Differntiation and the Phase Shift 48

2.4.4 Jost Function and the Bound States 50

3 Time-dependent Scattering Theory 54

3.1 Lippmann-Schwinger Equation 54

3.2 Optical Theory 59

PartII Relativistic Quantum Mechanics 62

4 Special Relativity (Classical Theory) 62

4.1 Lorentz Transformation 63

4.2 Effects of Free Particles 67

4.3 Particle Motion in Electromagnetic Field (Lagrange Formulation) . 70

4.4 Particle Motion in Electromagnetic Field (Hamilton Formulation) . 77

5 Dirac Equations 82

5.1 Deriving the Dirac Equation 82

5.2 Symmetry of Dirac Equation 85

5.2.1 The Lorentz Invariance 88

5.3 The Plane-wave Solutions for the Free Dirac Equation 93

5.3.1 In the Case of $m \neq 0$ 95

5.4 The Non-relativistic Limit 96

PartIII Quantum Mechanics of ManyParticle System 102

6 Second Quantization and Interaction 102

6.1 The Classical Equation of Motion for a Single Particle 102
6.2 (First) Quantization of a Single Free Particle 103
6.3 First Quantization of Many Particle Systems 105
6.4 Many-particle Quantum Mechanics and the Symmetry by Particle Switching 106
6.5 First Quantization of N-Free Particles System 108
6.6 Second Quantization 111
6.7 Operator and the Interactoin in Second Quantization Formalism . . 114

7 Single-particle States and Mean-field Approximations in Fermion Systems 118

7.1 Single-particle Orbit and Unitary Transformation of Fermi Operator 118
7.2 Total Energy of Single-particle States 120
7.3 Mean Field Equations: Hartree-Fock Equations 124

8 The Single-particle State and Mean Field Approximation in Electron Spin System 129

8.1 Hamiltonian of Many-particle System 129
8.2 Spin-orbital Function 129
8.3 The Total Energy of Single-particle States 130
8.4 The Hartree-Fock Equation in Electron Systems 131

PartIV Electronic Structure of Many-Electron Atoms 133

9 Periodic Table and One-electronic Level of Atoms 133

9.1 One-electronic Level Structure of a Hydrogen-like Atom 133
9.2 The Hamiltonian in Many-electron Atoms 143
9.3 Periodic Law of the Elements and the Shielding Effect 144

10 Electron Configurations and Multiplet Structures 147

10.1 Multiplet Terms and Perturbation Theory 147
10.2 Angular Momentum Operator, Spin-orbital Function, and Second Quantization 155
10.3 Some Concrete Examples of Multiplet Terms and the Method of Trace158

10.3.1 $(1s)(2s)$ . . . 158
10.3.2 $(1s)(1s)$ . . . 162
10.3.3 $(1s)(2s)(3s)$ . . . 162
10.3.4 $(2p)(3p)$ . . . 163
10.3.5 $(2p)^2$ . . . 166
10.3.6 pd . . . 168
10.3.7 pds . . . 168
10.4 Electron-hole Transformation and the Multiplet $(nl)^x$ . . . 168
10.4.1 Multiplet $(nl)^x$ . . . 168
10.4.2 Electron-hole Transformation . . . 169
10.5 Hund 's Rule . . . 171
10.6 Spin-orbit Interaction . . . 172

PartV Interaction of Light and Matter 179

11 Classical Electromagnetic Field 179
11.1 Maxwell 's Equation . . . 179
11.2 The Vector Potential and Scalar Potential . . . 181
11.3 Classical Field Equations . . . 188
11.4 Field Momentum . . . 192
11.5 Angular Momentum of the Field . . . 194

12 The Interacting Particle System and Electromagnetic Field as Field Quantity 196
12.1 Lagrangian Density and Equation of Motion . . . 196
12.2 Energy-momentum Tensor and the Conservation Law . . . 198

13 Quantization of Electromagnetic Field and the Charged Particles 200
13.1 Hamiltonian . . . 202
13.2 Momentum . . . 203

14 Interaction of Electromagnetic Field with Matter 204
14.1 Fermi 's Golden Rule . . . 206
14.2 Transition Matrix Elements and Dipole Transition . . . 208
14.3 Light Emission . . . 212
14.4 Light Absorption . . . 213

PartVI Appendix 214

A Separation of Variables for Hel,holtz Equation in Polar Coordinates 214

B Spherical Function 215

B.1 Legendre Differential Equation 215

B.2 Associated Legendre Differential Equation 216

B.3 Spherical Function 216

C Spherical Bessel Function 217

C.1 Spherical Bessel Function 217

PartI

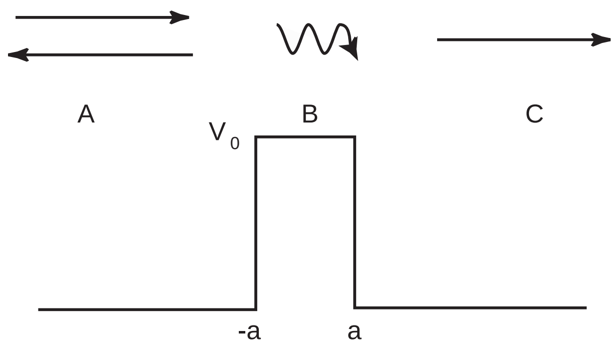
Scattering Theory

1 Scattering Theory in One Dimention

In this section, we present the basics of scattering theory as we demonstrate some examples of scattering in one-dimensional systems shown in the figure below, describing a left-moving incident particle on a potential barrier.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi(x,t) &= H\Psi(x,t) \\ H &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x) \end{aligned}$$

$$V(x) = \begin{cases} V_0 & x \in [-a,a] \\ 0 & \text{otherwise} \end{cases}$$



We assume that the time dependent variable in the wavefunction is separable (stationary state).

$$\begin{aligned} \Psi(x,t) &= e^{-i\omega t}\Psi(x) \\ H\Psi(x) &= E\Psi(x), \quad E=\hbar\omega \end{aligned}$$

1.1 Transfer Matrix Method

1.1.1 Transfer Matrix for Scattering State and Bound State

Let us divide the system shown in the figure above into three regions: A: $(-\infty,-a)$, B: $[-a,a]$, C: (a,∞). For the solutions int the regions (r =A, B, C), we can write with the wave number k_r for which the potential is constant.

$$\Psi_r(x) = \xi^+ e^{ik_r x} + \xi^- e^{-ik_r x}, \quad \frac{\hbar^2 k_r^2}{2m} = E - V_r$$

We define the former wavefunction as Ψ_1 and the latter as Ψ_2, and the junction conditions for the wavefunction when $x = \xi$ can be $\Psi_1(\xi) = \Psi_2(\xi)$ and $\Psi_1'(\xi) = \Psi_2'(\xi)$, which we can further write down as:

$$\begin{aligned} \xi_1^+ e^{ik_1\xi} + \xi_1^- e^{-ik_1\xi} &= \xi_2^+ e^{ik_2\xi} + \xi_2^- e^{-ik_2\xi} \\ k_1(\xi_1^+ e^{ik_1\xi} - \xi_1^- e^{-ik_1\xi}) &= k_2(\xi_2^+ e^{ik_2\xi} - \xi_2^- e^{-ik_2\xi}) \end{aligned}$$

In matrix representation, we can write

$$\boldsymbol{M}_\xi(k_1) \begin{pmatrix} \xi_1^+ \\ \xi_1^- \end{pmatrix} = \boldsymbol{M}_\xi(k_2) \begin{pmatrix} \xi_2^+ \\ \xi_2^- \end{pmatrix}$$

$$\boldsymbol{M}_\xi(k) = \begin{pmatrix} e^{ik\xi} & e^{-ik\xi} \\ ke^{ik\xi} & ke^{-ik\xi} \end{pmatrix}, \quad \boldsymbol{M}_\xi^{-1}(k) = \begin{pmatrix} \frac{1}{2}e^{-ik\xi} & \frac{1}{2k}e^{-ik\xi} \\ \frac{1}{2}e^{ik\xi} & -\frac{1}{2k}e^{ik\xi} \end{pmatrix}$$

Thus, we rewrite the equations to give

$$\begin{pmatrix} \xi_1^+ \\ \xi_1^- \end{pmatrix} = \boldsymbol{T}_\xi(k_1, k_2) \begin{pmatrix} \xi_2^+ \\ \xi_2^- \end{pmatrix} \qquad \boldsymbol{T}_\xi(k_1, k_2) = \boldsymbol{M}_\xi^{-1}(k_1)\boldsymbol{M}_\xi(k_2)$$

We repeatedly use the above equation particularly in our present case to yield

$$\begin{pmatrix} \xi_A^+ \\ \xi_A^- \end{pmatrix} = \boldsymbol{T} \begin{pmatrix} \xi_C^+ \\ \xi_C^- \end{pmatrix}, \quad \boldsymbol{T} = \boldsymbol{T}_{-a}(k_{out}, k_{in})\boldsymbol{T}_a(k_{in}, k_{out})$$

Thus,

$$\frac{\hbar^2 k_{out}^2}{2m} = E, \quad \frac{\hbar^2 k_{in}^2}{2m} + V_0 = E$$

We can solve the scattering problems for more complicated scatterer in the same way we showed above. Let us now consider two different boundary conditions.

- Boundary condition I: $\Psi(x) \sim e^{ikx}, \quad x \to \infty$ Recall that an asymptotic form of the time-dependent wavefunction where $x \to +\infty$ is $e^{i(kx-\omega t)}$, so the waves (i.e., only the scattering waves) traveling toward the positive direction on x axis are what required in the limit $x \to +\infty$. Such states are called the scattering states, and require the conditions $\xi_C^- = 0, \ (\xi_C^+ = 1)$. The scattering states always exist whenever energy E is positive (E ¿ 0). For the reflection coefficient $\mathcal{R}$ and the transmission coefficient $\mathcal{T}$,

$$\begin{pmatrix} \xi_A^+ \\ \xi_A^- \end{pmatrix} = \boldsymbol{T} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} T_{11} \\ T_{21} \end{pmatrix}$$

giving $\xi_A^+,\ and \xi_A^-$ thus, we obtain

$$\begin{aligned}\mathcal{R} &= \frac{\xi_A^-}{\xi_A^+} = \frac{T_{21}}{T_{11}} \\ \mathcal{T} &= \frac{1}{\xi_A^+} = \frac{1}{T_{11}}\end{aligned}$$

.

(Note that the reflection rate is $|\mathcal{R}|^2$ and the transmission rate is $|\mathcal{T}|^2$.) Furthermore, there is a relation between the transmission coefficient and the reflection coefficient, which can be written

$$|\mathcal{T}|^2 + |\mathcal{R}|^2 = 1$$

We may generally explain the above relation by studying the Wronskians of the differential equation. Suppose we have the potential V that is real and whose solution is $\Psi(x)$ then, its complex conjugate $\Psi^*(x)$ can also be the solution. The Schroedinger equation does not contain the first-order derivatives; thereby Wronskians $W(x) = W(\Psi(x), \Psi^*(x))$ is independent of x.

[1] Asymptotically we can write

$$\psi(x) = e^{ikx} + \mathcal{R}e^{-ikx} \quad x \approx \mathcal{T}e^{ikx} \quad x \approx \infty$$

from which we evaluate the Wronskians to give $W() = W(\infty)$, revealing indeed that we have $|\mathcal{T}|^2 + |\mathcal{R}|^2 = 1$. As another way to express the above,

[1]Consider the solutions for the differential equation of $f(x)$

$$f'' + p(x)f' + q(x)f = 0$$

from which we write the Wronskians for the two solutions f_1 and f_2,

$$W(x) = W(f_1, f_2) = \det\begin{pmatrix} f_1 & f_2 \\ f_1' & f_2' \end{pmatrix}$$

Thus,

$$W' = \det\begin{pmatrix} f_1 & f_2 \\ f_1'' & f_2'' \end{pmatrix} = \det\begin{pmatrix} f_1 & f_2 \\ -pf_1' - qf_1 & -pf_2' - qf_2 \end{pmatrix} = -pW$$

which leads to

$$W(x) = W(y)e^{-\int_y^x dt p(t)}$$

we define the current J_x in x direction to have

$$\begin{aligned} J_x &= \frac{\hbar}{2mi} W(\psi^*, \psi) \\ &= \frac{\hbar}{2mi} \left(\psi^* \frac{d\psi}{dx} - \frac{d\psi^*}{dx} \psi \right) \end{aligned}$$

and write out the conservation law of J_x to be

$$\frac{dJ_x}{dx} = 0.$$

.

[2]

- Boundary condition II: To satisfy the condition $\int_{-\infty}^{\infty} |\Psi(x)| dx < +\infty$, we will need the pure imaginary wave number; i.e., the energy E is negative. $(E < 0)$ Which we may write

$$k_{out} = i\kappa, \;\; \kappa = \frac{\sqrt{2m|E|}}{\hbar}$$

Furthermore, to avoid the exponential divergence of the wavefunction when we define k_{out}, we will need both $\xi_A^+ = 0$ and $\xi_C^- = 0$. So, we write

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \boldsymbol{T} \begin{pmatrix} \xi_C^+ \\ 0 \end{pmatrix}$$

whose first equation

$$T_{11} = 0$$

gives restriction to the wave number k. This is called the **bound state** in contrast with the scattering state. In our earlier discussion of the scattering

[2] Where $x \approx$,

$$\begin{aligned} W(-\infty) &= \det \begin{pmatrix} e^{ikx} + \mathcal{R}e^{-ikx} & e^{-ikx} + \mathcal{R}^* e^{ikx} \\ ike^{ikx} - ik\mathcal{R}e^{-ikx} & -ike^{-ikx} + ik\mathcal{R}^* e^{ikx} \end{pmatrix} \\ &= \det \begin{pmatrix} e^{ikx} + \mathcal{R}e^{-ikx} & e^{-ikx} + \mathcal{R}^* e^{ikx} \\ 2ike^{ikx} & 2ik\mathcal{R}^* e^{ikx} \end{pmatrix} = \det \begin{pmatrix} e^{ikx} + \mathcal{R}e^{-ikx} & (1 - |\mathcal{R}|^2) e^{-ikx} \\ 2ike^{ikx} & 0 \end{pmatrix} \\ &= 2ik(|\mathcal{R}|^2 - 1) \end{aligned}$$

, while at $x \approx \infty$ we have

$$\begin{aligned} W(\infty) &= \det \begin{pmatrix} \mathcal{T}e^{ikx} & \mathcal{T}^* e^{-ikx} \\ ik\mathcal{T}e^{ikx} & -ik\mathcal{T}^* e^{-ikx} \end{pmatrix} = \det \begin{pmatrix} \mathcal{T}e^{ikx} & \mathcal{T}^* e^{-ikx} \\ 0 & -2ik\mathcal{T}^* e^{-ikx} \end{pmatrix} \\ &= -2ik|\mathcal{T}|^2 \end{aligned}$$

states, we defined the transmission coefficient $\mathcal{T}$ and the reflection coefficient $\mathcal{R}$, from which we understand that the energy and the wave number in the bound states are defined as the

polars in the upper-half of the complex plane k of

the transmission and the reflection coefficient.

The Transfer-matrix Approach to the Scattering Problem in One-dimensional Square-well Potential

Here we discuss specific calculations for the scattering problem in a simple square-well potential. To begin with, we write the transfer matrix for a single boundary [3]

$$\boldsymbol{T}_\xi(k_1,k_2)=\frac{1}{2k_1}\begin{pmatrix}(k_1+k_2)e^{-i(k_1-k_2)\xi} & (k_1-k_2)e^{-i(k_1+k_2)\xi}\\ (k_1-k_2)e^{i(k_1+k_2)\xi} & (k_1+k_2)e^{i(k_1-k_2)\xi}\end{pmatrix}$$

$$\begin{aligned}
\boldsymbol{T} &= \boldsymbol{T}_{-a}(k_o,k_i)\boldsymbol{T}_a(k_i,k_o)\\
&= \frac{1}{4k_ik_o}\begin{pmatrix}(k_o+k_i)e^{i(k_o-k_i)a} & (k_o-k_i)e^{i(k_o+k_i)a}\\ (k_o-k_i)e^{-i(k_o+k_i)a} & (k_o+k_i)e^{-i(k_o-k_i)a}\end{pmatrix}\\
&\qquad\times\begin{pmatrix}(k_i+k_o)e^{-i(k_i-k_o)a} & (k_i-k_o)e^{-i(k_i+k_o)a}\\ (k_i-k_o)e^{i(k_i+k_o)a} & (k_i+k_o)e^{i(k_i-k_o)a}\end{pmatrix}\\
T_{11} &= \frac{e^{i2k_oa}}{4k_ik_o}\left[(k_i+k_o)^2e^{-2ik_ia}-(k_i-k_o)^2e^{2ik_ia}\right]\\
T_{21} &= -\frac{1}{4k_ik_o}(k_i^2-k_o^2)(e^{-2ik_ia}-e^{2ik_ia})\\
T_{12} &= \frac{1}{4k_ik_o}(k_i^2-k_o^2)(e^{-2ik_ia}-e^{2ik_ia})\\
T_{22} &= \frac{e^{-i2k_oa}}{4k_ik_o}\left[(k_i+k_o)^2e^{2ik_ia}-(k_i-k_o)^2e^{-2ik_ia}\right]
\end{aligned}$$

Therefore, int the following case:

3

$$\begin{aligned}
\boldsymbol{T}_\xi(k_1,k_2) &= \boldsymbol{M}_\xi^{-1}(k_1)\boldsymbol{M}_\xi(k_2)\\
&= \frac{1}{2}\begin{pmatrix}e^{-ik_1\xi} & \frac{1}{k_1}e^{-ik_1\xi}\\ e^{ik_1\xi} & -\frac{1}{k_1}e^{ik_1\xi}\end{pmatrix}\begin{pmatrix}e^{ik_2\xi} & e^{-ik_2\xi}\\ k_2e^{ik_2\xi} & -k_2e^{-ik_2\xi}\end{pmatrix}\\
&= \frac{1}{2k_1}\begin{pmatrix}k_1e^{-ik_1\xi} & e^{-ik_1\xi}\\ k_1e^{ik_1\xi} & -e^{ik_1\xi}\end{pmatrix}\begin{pmatrix}e^{ik_2\xi} & e^{-ik_2\xi}\\ k_2e^{ik_2\xi} & -k_2e^{-ik_2\xi}\end{pmatrix}\\
&= \frac{1}{2k_1}\begin{pmatrix}(k_1+k_2)e^{-i(k_1-k_2)\xi} & (k_1-k_2)e^{-i(k_1+k_2)\xi}\\ (k_1-k_2)e^{i(k_1+k_2)\xi} & (k_1+k_2)e^{i(k_1-k_2)\xi}\end{pmatrix}
\end{aligned}$$

- Complete transmission

$$T_{21} = 0$$

that is where we have

$$\sin 2k_i a = \sin \frac{2a\sqrt{2m(E - V_0)}}{\hbar} = 0$$

there will be no reflection $\mathcal{R} = 0$ so, we will have a complete transmission $|\mathcal{T}| = 1$.

- Bound state

$Where E \leq 0$, that is $k_o = i\kappa$ (where κ is real, ($\frac{\hbar^2 k_o^2}{2m} = E$) We look for the solutions for

$$T_{11} = 0$$

, which we find the bound states when

$$\left(\frac{k_i + i\kappa}{k_i - i\kappa}\right)^2 = e^{i4k_i a}$$

- Tunneling

The classical particles cannot pass through a barrier where

$$E < V_0$$

, but if we calculate the transmission rate having considered

$$\begin{aligned} k_i &= i\kappa_i \\ \kappa_i &= \frac{\sqrt{2m(V_0 - E)}}{\hbar} \end{aligned}$$

generally we can obtain $|T| > 0$, meaning that the quantum effect allowed the particles to be passed through the barrier. This is called the tunneling effect. In the case where we have energy of the incident particles that is much smaller in contrast to the potential ($|k_o| << |k_i| = \kappa$) , we can write [4]

$$|\mathcal{T}|^2 \approx \frac{16k_o^2}{\kappa^2}\left(\frac{1}{1 - e^{-4\kappa a}}\right)^2 e^{-4\kappa a}$$

4

$$\begin{aligned} |T_{11}| &= \frac{\kappa}{4k_o}\left[\left(1 + \frac{k_o}{i\kappa}\right)^2 e^{2\kappa a} - \left(1 - \frac{k_o}{i\kappa}\right)^2 e^{-2\kappa a}\right] \\ &= \frac{\kappa}{4k_o}(e^{2\kappa a} - e^{-2\kappa a}) \\ |\mathcal{T}|^2 &= \frac{1}{|T_{11}|^2} = \frac{16k_o^2}{\kappa^2}\frac{1}{(1 - e^{-4\kappa a})^2}e^{-4\kappa a} \end{aligned}$$

thus, lowers the transmission rate of the thickness of the potential barrier by remarkably high speed.

- Delta-function potential

  Where

$$V(x) = g\delta(x)$$

, [5] we consider the limit of

$$V_0 2a \to g, \quad (|V_0| \to \infty, \quad a \to 0)$$

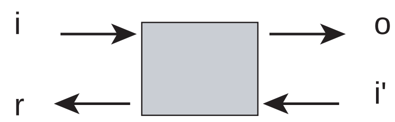
[6] (Note that $\frac{2m}{\hbar^2} g \equiv \tilde{g}$)we obtain

$$\begin{aligned} T_{11} &= 1 + i\frac{\tilde{g}}{2k_o}, \quad T_{21} = -i\frac{\tilde{g}}{2k_o}, \\ T_{22} &= 1 - i\frac{\tilde{g}}{2k_o}, \quad T_{12} = i\frac{\tilde{g}}{2k_o} \end{aligned}$$

Thus, giving

$$|\mathcal{T}|^2 = \frac{1}{1 + \left(\frac{\tilde{g}}{2k_o}\right)^2}, \quad |\mathcal{R}|^2 = \frac{\left(\frac{\tilde{g}}{2k_o}\right)^2}{1 + \left(\frac{\tilde{g}}{2k_o}\right)^2}$$

1.1.2 The Transfer Matrix and the Scattering Matrix



---

[5]

$$\begin{aligned} V_0 2a &\to g, \quad (|V_0| \to \infty, \quad a \to 0) \\ -k_i^2 2a &\to \frac{2m}{\hbar^2} g \equiv \tilde{g} \quad (-\frac{\hbar k_i^2}{2m} \to V_0) \\ |k_i| &\to \infty, \quad a \to 0, \quad (|k_i| a \to 0) \end{aligned}$$

[6]

$$\begin{aligned} T_{11} &= \frac{1}{4k_i k_o}\left((k_i + k_o)^2 - (k_i - k_o)^2 e^{i4k_i a}\right) \\ &\approx \frac{1}{4k_i k_o}\left(4k_i k_o - (k_i - 0)^2 i4k_i a\right) \\ &= 1 - i\frac{k_i^2 a}{k_o} = 1 + i\frac{\tilde{g}}{2k_o} \\ T_{21} &= -\frac{1}{4k_i k_o}(k_i^2 - 0)(-i4k_i a) \\ &= i\frac{k_i^2 a}{k_o} = -i\frac{\tilde{g}}{2k_o} \end{aligned}$$

Let us suppose the wavefunction with the incidence and reflection from free-space to an arbitrary region shows in the figure above. When we have the wavefunction of the left side $\psi_i e^{ikx} + \psi_r e^{-ikx}$ and the light side $\psi_o e^{ikx} + \psi_{i'} e^{-ikx}$, the consetvation of probability yields an equation. [7]

$$|\psi_i|^2 - |\psi_r|^2 = |\psi_o|^2 - |\psi_{i'}|^2$$

Now we define the one-dimensional scattering matrix S

$$\begin{pmatrix} \psi_r \\ \psi_o \end{pmatrix} = \boldsymbol{S} \begin{pmatrix} \psi_i \\ \psi_{i'} \end{pmatrix}$$

At which $\boldsymbol{S}$ becomes the unitary matrix
[8]

$$\boldsymbol{S}\boldsymbol{S}^\dagger = \boldsymbol{S}^\dagger \boldsymbol{S} = \boldsymbol{I}$$

We further define the transfer matrix $\boldsymbol{T}$ to obtain

$$\begin{pmatrix} \psi_o \\ \psi_{i'} \end{pmatrix} = \boldsymbol{T} \begin{pmatrix} \psi_i \\ \psi_r \end{pmatrix}$$

$$\boldsymbol{T}^\dagger \boldsymbol{J} \boldsymbol{T} = \boldsymbol{J}$$

$$\boldsymbol{J} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

[9]

To provide more details, we define the scattering matrix $\boldsymbol{S}$ (including the multichannel cases)

$$\boldsymbol{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix}$$

[7] Calculation of the Wronskians.

[8] The conservation law

$$|\psi_r|^2 + |\psi_o|^2 = (\psi_r^*, \psi_o^*) \begin{pmatrix} \psi_r \\ \psi_o \end{pmatrix} = (\psi_i^*, \psi_{i'}^*) \boldsymbol{S}^\dagger \boldsymbol{S} \begin{pmatrix} \psi_i \\ \psi_{i'} \end{pmatrix} = (\psi_i^*, \psi_{i'}^*) \begin{pmatrix} \psi_i \\ \psi_{i'} \end{pmatrix}$$

is valid for arbitrary $\psi_i, \psi_{i'}$ thus, $\boldsymbol{S}^\dagger \boldsymbol{S} = \boldsymbol{I}$.

[9] The conservation law is written

$$|\psi_o|^2 - |\psi_{i'}|^2 = (\psi_o^*, \psi_{i'}^*) \boldsymbol{J} \begin{pmatrix} \psi_o \\ \psi_{i'} \end{pmatrix} = (\psi_i^*, \psi_r^*) \boldsymbol{T}^\dagger \boldsymbol{J} \boldsymbol{T} \begin{pmatrix} \psi_i \\ \psi_r \end{pmatrix} = (\psi_i^*, \psi_r^*) \boldsymbol{J} \begin{pmatrix} \psi_i \\ \psi_r \end{pmatrix}$$

,giving

$$\boldsymbol{T}^\dagger \boldsymbol{J} \boldsymbol{T} = \boldsymbol{J}$$

so that we can write

$$\boldsymbol{T} = \begin{pmatrix} t^{\dagger^{-1}} & r' t'^{-1} \\ -t'^{-1} r & t'^{-1} \end{pmatrix}$$

[10] Here we can write

$$\begin{aligned} \boldsymbol{T}^{-1} =& \boldsymbol{J}\boldsymbol{T}^{\dagger}\boldsymbol{J} \\ (\boldsymbol{T}\boldsymbol{T}^{\dagger})^{-1} =& (\boldsymbol{T}^{-1})^{\dagger}\boldsymbol{T}^{-1} = \boldsymbol{J}\boldsymbol{T}\boldsymbol{T}^{\dagger}\boldsymbol{J} \end{aligned}$$

GIven that each pair becomes idential with the non-negative eigenvalues of $\boldsymbol{T}\boldsymbol{T}^{\dagger}$ and $(\boldsymbol{T}\boldsymbol{T}^{\dagger})^{-1}$, all eigenvalues can be written

$$e^{\pm 2x_n}, x_n \geq 0$$

[10]The unitarity can bu expressed in the relation equaitons

$$\boldsymbol{S}^{\dagger}\boldsymbol{S} = \begin{pmatrix} r^{\dagger} & t^{\dagger} \\ t'^{\dagger} & r'^{\dagger} \end{pmatrix} \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} = \begin{pmatrix} r^{\dagger} r + t^{\dagger} t & r^{\dagger} t' + t^{\dagger} r' \\ t'^{\dagger} r + r'^{\dagger} t & t'^{\dagger} t' + r'^{\dagger} r' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad (*1)$$

$$\boldsymbol{S}\boldsymbol{S}^{\dagger} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} \begin{pmatrix} r^{\dagger} & t^{\dagger} \\ t'^{\dagger} & r'^{\dagger} \end{pmatrix} = \begin{pmatrix} r r^{\dagger} + t' t'^{\dagger} & r t^{\dagger} + t' r'^{\dagger} \\ t r^{\dagger} + r' t'^{\dagger} & t t^{\dagger} + r' r'^{\dagger} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad (*2)$$

with the definition of the S matrix we obtain

$$\begin{aligned} \psi_r =& r\psi_i + t'\psi_{i'} \\ \psi_o =& t\psi_i + r'\psi_{i'} \end{aligned}$$

It is clear that if the boundary condition $\psi_{i'} = 0$ is required, t will represent the transmission rate, and$r$, the reflection rate. To obtain the transfer matrix through solving $\psi_o, \psi i'$, we rewrite the first equation

$$\psi_{i'} = -t'^{-1} r\psi_i + t'^{-1}\psi_r$$

and the second equation,

$$\psi_o = t\psi_i - r' t'^{-1} r\psi_i + r' t'^{-1}\psi_r = (t - r' t'^{-1} r)\psi_i + r' t'^{-1}\psi_r$$

The unitarity may give

$$\begin{aligned} 1 =& t t^{\dagger} + r' r'^{\dagger} = t t^{\dagger} + r'(t'^{-1} t') r'^{\dagger} = t t^{\dagger} + r' t'^{-1}(-r t^{\dagger}) \\ =& (t - r' t'^{-1} r) t^{\dagger} \end{aligned}$$

which leads to obtain

$$\psi_o = = t^{\dagger^{-1}}\psi_i + r' t'^{-1}\psi_r$$

$$\begin{pmatrix} \psi_o \\ \psi_{i'} \end{pmatrix} = \begin{pmatrix} t^{\dagger^{-1}} & r' t'^{-1} \\ -t'^{-1} r & t'^{-1} \end{pmatrix} \begin{pmatrix} \psi_i \\ \psi_r \end{pmatrix}$$

$$\boldsymbol{T} = \begin{pmatrix} t^{\dagger^{-1}} & r' t'^{-1} \\ -t'^{-1} r & t'^{-1} \end{pmatrix}$$

The further calculations may yield [11]

$$\left(\boldsymbol{T}\boldsymbol{T}^\dagger + (\boldsymbol{T}\boldsymbol{T}^\dagger)^{-1} + 2\boldsymbol{I}\right)^{-1} = \frac{1}{4}\begin{pmatrix} tt^\dagger & \\ & {t'}^\dagger t' \end{pmatrix}$$

Thus, we know that $\frac{1}{\cosh x_n}$ may give the absolute eigenvalues for $t^\dagger t'$ and${t'}^\dagger t'$. [12]

11

$$\begin{aligned}
\boldsymbol{T}\boldsymbol{T}^\dagger =& \begin{pmatrix} {t^\dagger}^{-1} & r'{t'}^{-1} \\ -{t'}^{-1}r & {t'}^{-1} \end{pmatrix}\begin{pmatrix} t^{-1} & -r^\dagger {{t'}^\dagger}^{-1} \\ {{t'}^\dagger}^{-1}{r'}^\dagger & {{t'}^\dagger}^{-1} \end{pmatrix} \\
=& \begin{pmatrix} {t^\dagger}^{-1}t^{-1} + r'{t'}^{-1}{{t'}^\dagger}^{-1}{r'}^\dagger & -{t^\dagger}^{-1}r^\dagger {{t'}^\dagger}^{-1} + r'{t'}^{-1}{{t'}^\dagger}^{-1} \\ -{t'}^{-1}rt^{-1} + {t'}^{-1}{{t'}^\dagger}^{-1}{r'}^\dagger & {t'}^{-1}rr^\dagger{{t'}^\dagger}^{-1} + {t'}^{-1}{{t'}^\dagger}^{-1} \end{pmatrix} \\
\boldsymbol{T}^{-1} =& \boldsymbol{J}\boldsymbol{T}^\dagger\boldsymbol{J} \\
(\boldsymbol{T}\boldsymbol{T}^\dagger)^{-1} =& (\boldsymbol{T}^{-1})^\dagger \boldsymbol{T}^{-1} = \boldsymbol{J}\boldsymbol{T}\boldsymbol{T}^\dagger\boldsymbol{J} \\
\boldsymbol{T}\boldsymbol{T}^\dagger + (\boldsymbol{T}\boldsymbol{T}^\dagger)^{-1} =& 2\begin{pmatrix} {t^\dagger}^{-1}t^{-1} + r'{t'}^{-1}{{t'}^\dagger}^{-1}{r'}^\dagger & \\ & {t'}^{-1}rr^\dagger{{t'}^\dagger}^{-1} + {t'}^{-1}{{t'}^\dagger}^{-1} \end{pmatrix} \\
=& 2\begin{pmatrix} (tt^\dagger)^{-1} + r'({t'}^\dagger t')^{-1}{r'}^\dagger & \\ & {t'}^{-1}rr^\dagger{{t'}^\dagger}^{-1} + ({t'}^\dagger t')^{-1} \end{pmatrix} \\
=& 2\begin{pmatrix} (tt^\dagger)^{-1} + r'(1 - {r'}^\dagger r')^{-1}{r'}^\dagger & \\ & {t'}^{-1}rr^\dagger{{t'}^\dagger}^{-1} + ({t'}^\dagger t')^{-1} \end{pmatrix} \\
=& 2\begin{pmatrix} ((tt^\dagger)^{-1} + ({{r'}^\dagger}^{-1}{r'}^{-1} - 1)^{-1} & \\ & {t'}^{-1}rr^\dagger{{t'}^\dagger}^{-1} + ({t'}^\dagger t')^{-1} \end{pmatrix} \\
\boldsymbol{T}\boldsymbol{T}^\dagger + (\boldsymbol{T}\boldsymbol{T}^\dagger)^{-1} + 2\boldsymbol{I} =& 2\begin{pmatrix} (tt^\dagger)^{-1} + {{r'}^\dagger}^{-1}{r'}^{-1}({{r'}^\dagger}^{-1}{r'}^{-1} - 1)^{-1} & \\ & {t'}^{-1}(t'{t'}^\dagger + rr^\dagger){{t'}^\dagger}^{-1} + ({t'}^\dagger t')^{-1} \end{pmatrix} \\
=& 2\begin{pmatrix} (tt^\dagger)^{-1} + (1 - r'{r'}^\dagger)^{-1} & \\ & 2({t'}^\dagger t')^{-1} \end{pmatrix} = 4\begin{pmatrix} (tt^\dagger)^{-1} & \\ & ({t'}^\dagger t')^{-1} \end{pmatrix}
\end{aligned}$$

given that

$$\left(\boldsymbol{T}\boldsymbol{T}^\dagger + (\boldsymbol{T}\boldsymbol{T}^\dagger)^{-1} + 2\boldsymbol{I}\right)^{-1} = \frac{1}{4}\begin{pmatrix} tt^\dagger & \\ & {t'}^\dagger t' \end{pmatrix}$$

12

$$(2 + e^{2x_n} + e^{-2x_n})^{-1} = ((e^{x_n} + e^{-x_n})^{-1})^2 = \frac{1}{4\cosh x_n} \equiv \frac{1}{4}\begin{pmatrix} tt^\dagger & \\ & {t'}^\dagger t' \end{pmatrix}$$

1.2 The Green's Function and Scattering Integral Equations

Consider the Schrodinger equation in the form

$$\begin{aligned} (E - H_0(x))\Psi(x) &= V(x)\Psi(x) \\ H_0(x) &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \end{aligned}$$

Suppose we obtained the Green function $G_0(\xi byletting \delta(x)$ to be the Dirac delta function

$$(E - H_0(\xi))G_0(\xi) = \delta(\xi)$$

With homogeneous solution $\phi(x)$

$$(E - H_0(x))\Phi(x) = 0$$

we write the equation

$$\Psi(x) = \Phi(x) + \int_{-\infty}^{\infty} dy G_0(x-y)V(y)\Psi(y) \quad \text{(LS)}$$

[13] Next, we recast the equations above in the form, which clearly show the energy dependence instead of the x space coordinate dependence

$$\begin{aligned} (E - H_0)\Psi &= V\Psi, \\ (E - H_0)G_0(z) &= 1 \\ G_0(E) &= \frac{1}{E - H_0} \\ (E - H_0)\Phi &= 0 \\ \Psi &= \Phi + \frac{1}{E - H_0}V\Psi \\ &= \Phi + G_0 V \Psi \quad \text{(LS)} \end{aligned}$$

[13] We may simply check by making substitution into the Schrodinger equation

The last line of equation is called the Lippmann-Schwinger equation. [14] [15] [16]

---

[14]We consider that the inverse number of the operator $(z - H_0)$ uses the eigenstate $|\epsilon\rangle$ of the energy ϵ for H_0 to be defined as

$$G_0(z) = \sum_\epsilon \frac{1}{z-\epsilon}|\epsilon\rangle\langle\epsilon|$$

Generally, in contrast to the real energy of $z = E$, $G_0(z)$ cannot be defined for its unique property it has. We will instead have to use the limit $z \to E \pm i\delta$ at the end by calculating for the complex energy z. Throughout the proceeding sections, we need to note this as an important fact. The further details of the calculations can be found in the following.

[15]The relation between the formal solution and the coordinate representation can be considered as

$$\begin{aligned}(z - H_0)G_0 =&1\\ \langle x|(z-H_0)G_0|x'\rangle =&\langle x|x'\rangle\\ \int dx'' \int dpdp' \, \langle x|p\rangle\langle p|(z-H_0)|p'\rangle\langle p'|x''\rangle\langle x''|G_0|x'\rangle =&\langle x|x'\rangle\end{aligned}$$

On the one hand, $\langle x|x'\rangle = \delta(x-x')$ is the eigenfunction for the eigenvalue x' of the operator$\hat{x}$ such that we may treat it as $\hat{x}|x\rangle = x|x\rangle$.

$$\hat{x}\langle x|x'\rangle = \int dx'' \, x\langle x|x''\rangle\langle x''|x'\rangle = \int dx'' \, x\delta(x-x'')\delta(x''-x') = x'\delta(x-x') = x'\langle x|x'\rangle$$

For $\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}$ on the other hand, we may treat it as $\hat{p}|p\rangle = p|p\rangle$ because $\hat{p} = -i\hbar\partial_x$ is the eigenfunction of the eigenvalue p for the operator $\hat{p} = -i\hbar\partial_x$. Th completeness and the orthonormality are given

$$\begin{aligned}\int dx'' \, \langle x|x''\rangle\langle x'|x''\rangle^* =& \int dx'' \, \delta(x-x'')\delta(x'-x'') = \delta(x'-x') \quad \textit{completeness}\\ \int dx \, \langle x|x'\rangle^*\langle x|x''\rangle =& \int dx \, \delta(x-x')\delta(x-x'') = \delta(x'-x'') \quad \textit{orthonormality}\\ \int dp \, \langle x|p\rangle\langle x'|p\rangle^* =& \frac{1}{2\pi\hbar}\int dp \, e^{ip(x-x')/\hbar} = \frac{1}{\hbar}\delta((x-x')/h) = \delta(x-x') \quad \textit{completeness}\\ \int dx \, \langle x|p\rangle^*\langle x|p'\rangle =& \frac{1}{2\pi\hbar}\int dx \, e^{-i(p-p')x)/\hbar} = \delta(p-p') \quad \textit{orthonormality}\end{aligned}$$

Thus, we have $\langle x|G_0|x'\rangle = G_0(x,x')$ to write

$$\begin{aligned}\langle p|(z-H_0)|p'\rangle =& \langle p|(z-\frac{\hat{p}^2}{2m})|p'\rangle = \delta(p-p'))(z-\frac{p^2}{2m})\\ \int dx'' \int dpdp' \, \langle x|p\rangle\langle p|(z-H_0)|p'\rangle\langle p'|x''G_0(x'',x') =& \frac{1}{2\pi\hbar}\int dx'' \int dp \, e^{ip(x-x''}(z-\frac{p^2}{2m})G_0(x'',x')\\ =& \left(z+\frac{1}{2m}\frac{d^2}{dx^2}\right)\int dx'' \, \delta(x-x'')G_0(x'',x') = \left(z+\frac{1}{2m}\frac{d^2}{dx^2}\right)G_0(x,x')\end{aligned}$$

Given by the translational symmetry, we have $G_0(x,x') = G_0(x-x')$

We can further write the variation of the Lippmann-Schwinger equation in the

---

[16]Let us summarize different types of normalization for the plane waves.

- L volume $V = L^3$ =boundary condition

  Let us define $\boldsymbol{k}_n = \frac{2\pi}{L}(n_x, n_y, n_z),\ n_i = 0, \pm1, \pm2, \cdots$ to write

$$\begin{aligned}
\langle \boldsymbol{r}|\boldsymbol{n}\rangle =& \psi_n(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_n\cdot\boldsymbol{r}} \\
\langle n|n'\rangle =& \int_V d\boldsymbol{r}\, \psi_n^*(\boldsymbol{r})\psi_{n'}(\boldsymbol{r}) = \delta_{nn'} : normalization \\
\sum_n \langle \boldsymbol{r}|n\rangle\langle n|\boldsymbol{r}'\rangle =& \sum_n \psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}') = \frac{1}{V}\sum_n e^{-i(\boldsymbol{k}_n - \boldsymbol{k}_{n'})\cdot\boldsymbol{r}} \\
=& \frac{1}{(2\pi)^3}\left(\frac{2\pi}{L}\right)^3 \sum_n e^{-i(\boldsymbol{k}_n - \boldsymbol{k}_{n'})\cdot\boldsymbol{r}} = \frac{1}{(2\pi)^3}\int d\boldsymbol{k}\, e^{-i(\boldsymbol{k}_n - \boldsymbol{k}_{n'})\cdot\boldsymbol{r}} \\
=& \delta(\boldsymbol{r} - \boldsymbol{r}') = \langle \boldsymbol{r}|\boldsymbol{r}'\rangle \\
\sum_n |n\rangle\langle n| =& 1 : completeness
\end{aligned}$$

- Take the continuum limit for the wave-number represetation

$$\begin{aligned}
\langle \boldsymbol{r}|\boldsymbol{k}\rangle =& \psi_k(\boldsymbol{r}) = \frac{1}{\sqrt{(2\pi)^3}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \\
means\ |\boldsymbol{k}\rangle =& \sqrt{\frac{V}{(2\pi)^3}}|\boldsymbol{n}\rangle \\
\langle \boldsymbol{k}|\boldsymbol{k}'\rangle =& \frac{1}{(2\pi)^3}\int d\boldsymbol{r}\, \psi_k^*(\boldsymbol{r})\psi_{k'}(\boldsymbol{r}) = \delta(\boldsymbol{k} - \boldsymbol{k}') : normalization \\
\int d\boldsymbol{k}\, \langle \boldsymbol{r}|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\boldsymbol{r}'\rangle =& \int d\boldsymbol{k}\, \psi_k(\boldsymbol{r})\psi_k^*(\boldsymbol{r}') = \frac{1}{(2\pi)^3}\sum_n e^{-i\boldsymbol{k}\cdot(\boldsymbol{r} - \boldsymbol{r}')} \\
=& \delta(\boldsymbol{r} - \boldsymbol{r}') = \langle \boldsymbol{r}|\boldsymbol{r}'\rangle \\
\int d\boldsymbol{k}\, |\boldsymbol{k}\rangle\langle \boldsymbol{k}| =& 1 : completeness
\end{aligned}$$

- For the momentum representation

$$\begin{aligned}
\langle \boldsymbol{r}|\boldsymbol{p}\rangle =& \psi_p(\boldsymbol{r}) = \frac{1}{\sqrt{(2\pi\hbar)^3}} e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \\
Thatis,\ |\boldsymbol{p}\rangle =& \frac{1}{\sqrt{\hbar^3}}|\boldsymbol{k}\rangle = \sqrt{\frac{V}{(2\pi\hbar)^3}}|\boldsymbol{n}\rangle \\
\langle \boldsymbol{p}|\boldsymbol{p}'\rangle =& \frac{1}{(2\pi\hbar)^3}\int d\boldsymbol{r}\, \psi_p^*(\boldsymbol{r})\psi_{p'}(\boldsymbol{r}) = \delta(\boldsymbol{p} - \boldsymbol{p}') : normaliation \\
\int d\boldsymbol{p}\, \langle \boldsymbol{r}|\boldsymbol{p}\rangle\langle \boldsymbol{p}|\boldsymbol{r}'\rangle =& \int d\boldsymbol{p}\, \psi_p(\boldsymbol{r})\psi_p^*(\boldsymbol{r}') = \frac{1}{(2\pi\hbar)^3}\sum_n e^{-i\boldsymbol{p}\cdot(\boldsymbol{r} - \boldsymbol{r}')/\hbar} \\
=& \delta(\boldsymbol{r} - \boldsymbol{r}') = \langle \boldsymbol{r}|\boldsymbol{r}'\rangle \\
\int d\boldsymbol{p}\, |\boldsymbol{p}\rangle\langle \boldsymbol{p}| =& 1 : completeness
\end{aligned}$$

form

$$\begin{aligned}\Psi &= (1 - G_0 V)\Phi = (1 + GV)\Phi \\ G &= \frac{1}{E - H} \\ &= G_0 + G_0 V G = G_0 + G_0(VG_0) + G_0(VG_0)^2 + \cdots\end{aligned}$$

[17] Let us now consider more specified one-dimensional Green's function G_0 via

[17]Here we used the relation

$$\begin{aligned}A(B - A)B &= (AB - 1)B = A - B \\ &= -B(A - B)A = B(B - A)A\end{aligned}$$

The substitution of $A = E - H_0$,and $B = E - H_0 - V$ into the equation above gives

$$-G_0 V G = G_0 - G = -GVG_0$$

hence, we have $(1 - G_0 V)G = G_0$. That is

$$(1 - G_0 V) = GG_0 = (G_0 + GVG_0)G_0 = 1 + GV$$

We also obtain a useful reration

$$G = G_0 + G_0 V G = G_0 + G_0(VG_0) + G_0(VG_0)^2 + \cdots$$

Fourier analysis [18] [19] [20]

[18]Clariy the space coordinate to express

$$G_0(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{ikx} \hat{G}_0(k)$$

so, we can write $\delta(x) = \frac{1}{2\pi} \int dk e^{ikx}$ to give

$$E = \frac{\hbar^2 K^2}{2m}$$

which leads to $(E - H_0)G_0(x) = \delta(x)$ thus $\hat{G}_0(k) = \frac{1}{\sqrt{2\pi}} \left(\frac{2m}{\hbar^2}\right) \frac{1}{K^2-k^2}$

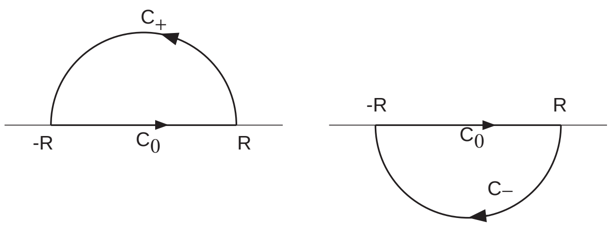
$$G_0(x) = \frac{1}{2\pi} \left(\frac{2m}{\hbar^2}\right) \int_{\infty dk \frac{1}{K^2-k^2} e^{ikx}}$$

In the following, we consider E of the positive and ngative energies.

[19]Where $E \geq 0$, the integral remains indefinite for the unique characteristic observed along the real axis. We now consider expanding the energy E into the complex energy $E \to E \pm i0$. This in fact corresponds to having $K \to K \pm i0$ thus gives

$$\begin{aligned} G_0^{\pm}(x) &= \frac{1}{2\pi} \left(\frac{2m}{\hbar^2}\right) \int_{\infty dk \frac{1}{2K} \left(\frac{1}{k+K\pm i0} - \frac{1}{k-K\mp i0}\right) e^{ikx}} \\ &= \left(\frac{2m}{\hbar^2}\right) i \frac{1}{2K} \times \mp e^{\pm iKx} \quad (x > 0) \mp e^{\mp iKx} \quad (x < 0) \\ &= \left(\frac{2m}{\hbar^2}\right) \frac{\mp i}{2K} e^{\pm iK|x|} \end{aligned}$$

The evaluation of the integral is done via the complex integration along the paaths $C_0 + C_+$ or $C_0 + C_-$ shows in the figure below. Further, we proceed by use of the Jordan's lemma.



When $|f(z)|$ is uniformly 0 on the upper-half/lower-half plane at $|z| \to \infty$, we can write

$$\int_{C_\pm} dz f(z) e^{\pm iaz} \to 0, \quad (R \to \infty, a > 0)$$

[20]Where $E < 0$, we write

$$K = i\kappa = i\frac{\sqrt{2m|E|}}{\hbar}, \quad \kappa > 0$$

which we can use directly to evaluate the integral. Applying a clear case such as $K \to K + i0$ $(E \to$

$$G_0(E) = \begin{cases} \left(\frac{2m}{\hbar^2}\right)\frac{\mp i}{2K}e^{\pm iK|x|}, & K \to K \pm i0 = \frac{\sqrt{2mE}}{\hbar} \pm i0, \quad E \to E \pm i0, E > 0 \\ \left(\frac{2m}{\hbar^2}\right)\frac{-1}{2\kappa}e^{-\kappa|x|}, & \kappa = \frac{\sqrt{2m|E|}}{\hbar}, \qquad E < 0 \end{cases}$$

[21] Where the energy $E > 0$, the Green's function and its homogeneous solution take the traveling waves $\Phi(x) = \frac{1}{\sqrt{2\pi}}e^{ikx}$ of $+x$ direction. the substitution into the Lippmann-Schwinger equation may give

$$\Psi^{\pm}(x) = \frac{1}{\sqrt{2\pi}}e^{ikx} + \left(\frac{2m}{\hbar^2}\right)\frac{(\mp i)}{2k}\int_{-\infty}^{\infty} dyV(y)e^{\pm ik|x-y|}\Psi^{\pm}(y)$$

form which the solutions that satisfy the boundary condition I we discussed in the prior section can be clarilfied to be $\Psi^+(x)$. For this $\Psi^+(x)$ where $x << -a$, we can write

$$\begin{aligned} \Psi^+(x) \approx & \quad \frac{1}{\sqrt{2\pi}}\left(e^{ikx} + e^{-ikx}f(k,)\right) \\ f(k,) \quad = & \quad \left(\frac{2m}{\hbar^2}\right)\frac{-i\sqrt{2\pi}}{2k}\int_{-\infty}^{\infty} dyV(y)e^{iky}\Psi^+(y) \end{aligned}$$

While in $a << x$, we can write

$$\begin{aligned} \Psi^+(x) \approx & \quad \frac{1}{\sqrt{2\pi}}\left(e^{ikx}(1 + f(k,\infty)\right) \\ f(k,\infty) \quad = & \quad \left(\frac{2m}{\hbar^2}\right)\frac{-i\sqrt{2\pi}}{2k}\int_{-\infty}^{\infty} dyV(y)e^{-iky}\Psi^+(y) \end{aligned}$$

which giving the reflection coefficient ($\mathcal{R}$) and the transmission coefficient ($\mathcal{T}$) to be

$$\mathcal{R} = f(k,), \qquad \mathcal{T} = 1 + f(k,\infty)$$

. To obtain more specific form of the equation, we need a specific form of Ψ^+. The approximation of taking $\Psi^+(x) \approx \Phi(x)$ in the right term of the equation is called the Born approximation.

$E + i0$) may give

$$\begin{aligned} G_0^+(x) &= \left(\frac{2m}{\hbar^2}\right)\frac{-i}{2K}e^{iK|x|} \\ &= \left(\frac{2m}{\hbar^2}\right)\frac{-1}{2\kappa}e^{-\kappa|x|} \end{aligned}$$

[21]Note that this solution remains indefinite as we have the linear combination of the homogeneous solution $e^{\pm ikx}$. This indefinition rests on how to take the formal solution as we are discussing in the next section.

The Scattering Problems in One-dimentional Delta-function Potential via Integral Equation

Here we discuss how to solve the scattering problem in the delta-function potential $V(x) = g\delta(x)$ in detail. The scattering integral equation is written

$$\Psi(x) = \frac{1}{\sqrt{2\pi}}e^{ikx} + \left(\frac{2m}{\hbar^2}\right)\frac{(-i)}{2k}\int_{-\infty}^{\infty} dyV(y)e^{ik|x-y|}\Psi(y)$$

$$\Psi(x) = \frac{1}{\sqrt{2\pi}}e^{ikx} - i\tilde{g}\frac{1}{2k}e^{-ikx}\Psi(0), \quad x < 0\frac{1}{\sqrt{2\pi}}e^{ikx} - i\tilde{g}\frac{1}{2k}e^{ikx}\Psi(0), \quad x > 0$$

Let us have $x = 0$ to give

$$\Psi(0) = \frac{1}{\sqrt{2\pi}}\frac{1}{1 + i\tilde{g}\frac{1}{2k}}$$

thus

$$\mathcal{T} = 1 - \frac{i}{2k}\tilde{g}\frac{1}{1 + i\tilde{g}\dfrac{1}{2k}} = \frac{1}{1 + \dfrac{i\tilde{g}}{2k}}, \qquad \mathcal{R} = -\frac{\dfrac{i\tilde{g}}{2k}}{1 + \dfrac{i\tilde{g}}{2k}}$$

1.3 Levinson's Theorem in One Dimension

Now we discuss the Levinson 's theorem, which relates to connecting the number of bound sates to the scattering states. We consider the solutions and the new boundary conditions for the Schroedinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2 f_{\pm\infty}}{dx^2} + V(x)f_{\pm\infty} = Ef_{\pm\infty} = \frac{\hbar^2 k^2}{2m}f_{\pm\infty}$$

- $f_{\infty}(k, x) \to e^{ikx}$, $x \to \infty$
- $f_{-\infty}(k, x) \to e^{-ikx}$, $x \to -\infty$

The integral equations for the solutions above can be obtained via taking the Green's function

$$G_{\infty} = G_1 = -\frac{2m}{\hbar^2}\theta(x' - x)\frac{\sin k(x - x')}{k}$$
$$G_{-\infty} = G_2 = \frac{2m}{\hbar^2}\theta(x - x')\frac{\sin k(x - x')}{k}$$

22 23

[22]Let us consider another way to obtain the Green 's function. Generally, we consider the Green 's function in the second-order differential equation for $y = y(x)$

$$G''(x,x') + p(x)G'(x,x') + q(x)G(x,x') = \delta(x-x'), \ \text{' is the } x \text{ differentials}$$

Suppose we already obtained the independent homogeneous solutions $y_+(x)$, and $y_-(x)$ so we write

$$y_i'' + p(x)y_i' + q(x)y_i = 0, \quad i = +, -$$

Based on the variation of parameter we have

$$G = C_+ y_+ + C_- y_-$$

whichleads to

$$G' = (C_+' y_+ + C_-' y_-) + (C_+ y_+' + C_- y_-')$$

Now requires

$$(C_+' y_+ + C_-' y_-) = 0$$

which yields

$$G'' = (C_+ y_+' + C_- y_-')' = (C_+' y_+' + C_-' y_-') + (C_+ y_+'' + C_- y_-'')$$

so we can write

$$\begin{aligned} G'' + pG' + qG &= C_+(y_+'' + py_+' + qy_+) + C_-(y_-'' + py_-' + qy_-) \\ &\quad + C_+' y_+' + C_-' y_-' = C_+' y_+' + C_-' y_-' = \delta(x-x') \end{aligned}$$

which giving

$$\begin{aligned} \begin{pmatrix} y_+ & y_- \\ y_+' & y_-' \end{pmatrix} \begin{pmatrix} C_+' \\ C_-' \end{pmatrix} &= \begin{pmatrix} 0 \\ \delta(x-x') \end{pmatrix} \\ \begin{pmatrix} C_+' \\ C_-' \end{pmatrix} &= \frac{1}{W} \begin{pmatrix} y_-' & -y_- \\ -y_+' & y_+ \end{pmatrix} \begin{pmatrix} 0 \\ \delta(x-x') \end{pmatrix} = \frac{1}{W} \begin{pmatrix} -y_-\delta(x-x') \\ y_+\delta(x-x') \end{pmatrix} \end{aligned}$$

hence,

$$G(x,x') = \int_{b_-}^{x} dt \frac{-y_+(x)y_-(t)}{W(t)} \delta(t-x') + \int_{b_+}^{x} dt \frac{y_-(x)y_+(t)}{W(t)} \delta(t-x')$$

Note that b_+, and b_- may impose differnt boundary conditions for the integral constants.

[23]We consider some examples for such cases.

Where$b_- = b_+ = x' - 0$

$$G_2(x,x') = \theta(x-x') \frac{-y_+(x)y_-(x') + y_-(x)y_+(x')}{W(x')}$$

Where $b_- = b_+ = x' + 0$

$$G_1(x,x') = \theta(x'-x) \frac{y_+(x)y_-(x') - y_-(x)y_+(x')}{W(x')}$$

For these Green 's function written above, we add each formal solution to determine the integral equations

$$
\begin{aligned}
f_\infty(k,x) &= e^{+ikx} - \frac{2m}{\hbar^2}\frac{1}{k}\int_x^\infty dx' \, \sin k(x-x')V(x')f_\infty(k,x') \\
f_{-\infty}(k,x) &= e^{-ikx} + \frac{2m}{\hbar^2}\frac{1}{k}\int_{-\infty}^x dx' \, \sin k(x-x')V(x')f_{-\infty}(k,x')
\end{aligned}
$$

It is clear that each solution satisfies the boundary conditions.

We now regard the functions $f_{\pm\infty}(k,x)$ as functions of the complex number k to investigate the analyticity. First, given the integral equations we should have the complex number k where

$$\mathrm{Im}\, k > 0$$

which clearly indicates that there are the convergence conditions of the integrals for each term by successive approximation of $f_{\pm\infty}(k,x)$. In fact, the series itself is said to converge while $f_{\pm\infty}(k,x)$ beocmes the regular function of k on the complex plane k and on the upper-half plane.

We make evaluations for the Wronslians in $f_\infty(k,x)$, $f_\infty(-k,x)$, $f_{-\infty}(k,x)$ and $f_{-\infty}(-k,x)$ where $x \to \infty$,

$$
\begin{aligned}
W(f_\infty(k,x), f_\infty(-k,x)) &= -2ik \\
W(f_{-\infty}(k,x), f_{-\infty}(-k,x)) &= 2ik
\end{aligned}
$$

Where$b_- = \infty,\ b_+ = -\infty$

$$
\begin{aligned}
G(x,x') &= \int_x^\infty dt \frac{y_+(x)y_-(t)}{W(t)}\delta(t-x') + \int_{-\infty}^x dt \frac{by_-(x)y_+(t)}{W(t)}\delta(t-x') \\
&= \frac{y_+(\xi_<)y_-(\xi_>)}{W(x')} \\
\xi_> &= \max(x,x'), \quad \xi_< = \min(x,x')
\end{aligned}
$$

specially

$$
\begin{aligned}
(E-H_0)G_0 &= \frac{\hbar^2}{2m}(k^2 + \frac{d^2}{dx^2})G_0'' = \delta(x-x') \\
E = \frac{\hbar^2 k^2}{2m}
\end{aligned}
$$

as $y_\pm(x) = e^{i\pm x}$ $W(y_+, y_-) = \det \begin{pmatrix} e^{ikx} & e^{-ikx} \\ ike^{ikx} & -ike^{-ikx} \end{pmatrix} = -2ik$

- $$\frac{\hbar^2}{2m}G_2(x,x') = \theta(x-x')\frac{\sin k(x-x')}{k}$$
- $$\frac{\hbar^2}{2m}G_1(x,x') = -\theta(x'-x)\frac{\sin k(x-x')}{k}$$

Thus, the solutions are independent where $k \neq 0$. This allows us to expand the equations [24]

$$
\begin{aligned}
f_{-\infty}(k,x) &= c_{11}(k) f_{\infty}(k,x) + c_{12}(k) f_{\infty}(-k,x) \\
f_{\infty}(k,x) &= c_{21}(k) f_{-\infty}(-k,x) + c_{22}(k) f_{-\infty}(k,x)
\end{aligned}
$$

We now consider $x \to \pm\infty$ for tha latter equation above to write in the form

$$
c_{21} e^{ikx} + c_{22} e^{-ikx} \quad (x \to -\infty), \qquad e^{ikx} \quad (x \to \infty)
$$

These are the solutions that satisfy the boundary conditions for the scattering thus, the relation between the transmission coefficient and the reflection coefficient are expressed as

$$
\begin{aligned}
\mathcal{R} &= \frac{c_{22}}{c_{21}} \\
\mathcal{T} &= \frac{1}{c_{21}} = \frac{1}{T_{11}} : Referthetransfermatrix
\end{aligned}
$$

Here we consider the Wronskians for each form of $f_{\mp\infty}(k,x)$ and $f_{\pm\infty}(\pm k,x)$ to derive

$$
\begin{aligned}
c_{11}(k) &= -\frac{1}{2ik} W(f_{-\infty}(k,x), f_{\infty}(-k,x)) \\
c_{12}(k) &= \frac{1}{2ik} W(f_{-\infty}(k,x), f_{\infty}(k,x)) \\
c_{21}(k) &= -\frac{1}{2ik} W(f_{\infty}(k,x), f_{-\infty}(k,x)) \\
c_{22}(k) &= \frac{1}{2ik} W(f_{\infty}(k,x), f_{-\infty}(-k,x))
\end{aligned}
$$

[24]b The successive substitution may give

$$
\begin{aligned}
f_{-\infty}(k) &= c_{11}(k)\big(c_{21}(k) f_{-\infty}(-k) + c_{22}(k) f_{-\infty}(k)\big) + c_{12}(k)\big(c_{21}(-k) f_{-\infty}(k) + c_{22}(-k) f_{-\infty}(-k)\big) \\
&= \big(c_{11}(k)c_{22}(k) + c_{12}(k)c_{21}(-k)\big) f_{-\infty}(k) + \big(c_{11}(k)c_{21}(k) + c_{12}(k)c_{22}(-k)\big) f_{-\infty}(-k)
\end{aligned}
$$

Where $k \neq 0$

$$
c_{11}(k)c_{22}(k) + c_{12}(k)c_{21}(-k) = 1, \quad c_{11}(k)c_{21}(k) + c_{12}(k)c_{22}(-k) = 0
$$

Likewise

$$
\begin{aligned}
f_{\infty}(k) &= c_{21}(k)\big(c_{11}(-k) f_{\infty}(-k) + c_{12}(-k) f_{\infty}(k)\big) + c_{22}(k)\big(c_{11}(k) f_{\infty}(k) + c_{12}(k) f_{\infty}(-k)\big) \\
&= \big(c_{12}(-k)c_{21}(k) + c_{11}(k)c_{22}(k)\big) f_{\infty}(k) + \big(c_{11}(-k)c_{21}(k) + c_{12}(k)c_{22}(k)\big) f_{\infty}(-k)
\end{aligned}
$$

thus,

$$
c_{12}(-k)c_{21}(k) + c_{11}(k)c_{22}(k) = 1, \quad c_{11}(-k)c_{21}(k) + c_{12}(k)c_{22}(k) = 0
$$

Especially the forms of $c_{21}(k)$, the equations are expressed in regular $f_{\pm\infty}(k,x)$ on the upper-half of the complex k plane, and the zero-point k_B on the upper-half of the plane gives the polar of $\mathcal{T}$; i.e., giving the bound states, because $c_{21}(k)$ is also a regular function.

We may also show some other facts for $c_{21}(k)$.

- Where $|k| \to \infty$,$c_{21}(k) = 1 + \mathcal{O}(\frac{1}{k})$

  In $|k| \to \infty$, where the incident energu is large enough, the effects by the potentials can be ignored, so that we understand from the transmission coefficient to take $\mathcal{T} \to 1$ or from the analyticity property.

- The zero-point $c_{21}(k)$ of k_B exists on the imaginary axis, not on th real axis. [25]

[25] It is clear from the discussion of the transfer matrix.

- All the zero-points k_B for $c_{21}(k)$ are in the first-order.Thus, $\dot{c}_{21}(k_B) \neq 0$. [26]

We can integrate $\frac{d}{dk}\log c_{21}(k)$ along the integral path C where the path is ormed by the real axis and the half circle on the upper-half plane. This integration may completely detached ($\frac{\dot{c}_{21}}{c_{21}} = \mathcal{O}(\frac{1}{k^2})$, $|k| \to \infty$ away from the half-circle. From the

[26] At the wave number k_B, in which the bound states are allowed to exist, $f_{\pm\infty}(k_B, x)$ become linearly dependent to each other.

$$\begin{aligned}
c_{21}(k_B) &= 0, \quad c_{11}(k_B)c_{22}(k_B) = 1, \quad c_{11}(k_B) \neq 0, \quad c_{22}(k_B) \neq 0 \\
f_\infty(k_B, x) &= c_{22}(k_B) f_{-\infty}(k_B, x) \\
W(f_\infty(k_B, x), f_{-\infty}(k_B, x)) &= 0
\end{aligned}$$

k differentiation is written by $\dot{}$,

$$\begin{aligned}
\dot{c}_{21}(k_B) &= -\frac{1}{2ik_B}\Big(W(\dot{f}_\infty(k_B, x), f_{-\infty}(k_B, x)) + W(f_\infty(k_B, x), \dot{f}_{-\infty}(k_B, x))\Big) \\
&= -\frac{1}{2ik_B}\left(\frac{1}{c_{22}}W(\dot{f}_\infty(k_B, x), f_\infty(k_B, x)) + c_{22}W(f_{-\infty}(k_B, x), \dot{f}_{-\infty}(k_B, x))\right)
\end{aligned}$$

To evauate this we diffentiate the Schroedinger equation and equation above with respect to k. Which gives,

$$\begin{aligned}
f'' + k^2 f &= \frac{2m}{\hbar^2} V f \\
\dot{f}'' + 2kf + k^2 \dot{f} &= \frac{2m}{\hbar^2} V \dot{f}
\end{aligned}$$

With the potential terms being cancelled in the equation, we can rewrite

$$f''\dot{f} - \dot{f}'' f - 2kf^2 = \frac{d}{dx} W(\dot{f}, f) - 2kf^2 = 0$$

This above equation is used for f_∞ to give $\mathrm{Im}\, k > 0$ $\lim_{x\to\infty} f_\infty(k, x) = 0$ thus

$$W(\dot{f}_\infty, f_\infty) = -2k \int_x^\infty dx' \, [f_\infty(k, x')]^2$$

the same as $\mathrm{Im}\, k > 0$ のとき $\lim_{x\to-\infty} f_{-\infty}(k, x) = 0$

$$W(\dot{f}_{-\infty}, f_{-\infty}) = 2k \int_{-\infty}^x dx' \, [f_{-\infty}(k, x')]^2$$

hence,

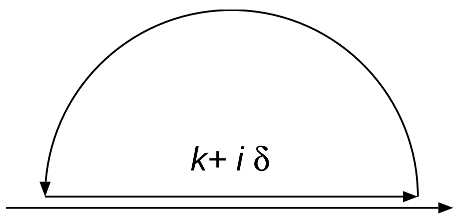
$$\begin{aligned}
\dot{c}_{21}(k_B) &= -\frac{1}{2ik_B}\left(-\frac{1}{c_{22}(k_B)} 2k_B \int_x^\infty dx' \, [f_\infty(k_B, x')]^2 + c_{22}(k_B)(-2k_B) \int_{-\infty}^x dx' \, [f_{-\infty}(k_B, x')]^2 \right) \\
&= -i \int_{-\infty}^\infty dx' [f_\infty(k_B, x') f_{-\infty}(k_B, x')] \\
&= -ic_{22}(k_B) \int_{-\infty}^\infty dx' [f_{-\infty}(k_B, x')]^2 = -i\frac{1}{c_{22}(k_B)} \int_{-\infty}^\infty dx' [f_\infty(k_B, x')]^2
\end{aligned}$$

Thus, $i\dot{c}_{21}(k_B)c_{22}(k_B)$ is not zero for $f_\infty(k_B, x)$.

argument principle, the number of zero-point N for c_{21} on the upper-half plane can be written

$$
\begin{aligned}
N &= \frac{1}{2\pi i}\int_C \frac{d}{dk}\log c_{21}(k) = \frac{1}{2\pi i}\log c_{21}(k+i0)\Big|_{k=-\infty}^{\infty} \\
&= \frac{1}{2\pi}\Big(\mathrm{Arg}\, c_{21}(-\infty+i0) - \mathrm{Arg}\, c_{21}(\infty+i0)\Big) \\
&= \frac{1}{2\pi}\Big(\mathrm{Arg}\, T_{11}(-\infty+i0) - \mathrm{Arg}\, T_{11}(\infty+i0)\Big) \\
&= -\frac{1}{2\pi}\Big(\mathrm{Arg}\, \mathcal{T}(-\infty+i0) - \mathrm{Arg}\, \mathcal{T}(\infty+i0)\Big)
\end{aligned}
$$

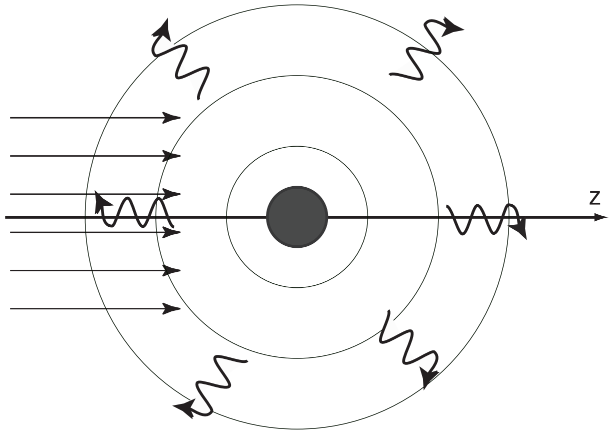
Note that the changes in argument are measured on the straight line in which the argument deviates infinitesimally on the real axis towards the upper-half plane.



The N represents the number of bound states. It is defined by the transmission coefficient $\mathcal{T}$ (more precisely, by what $\mathcal{T}$ is analytic continued to the complex k plane), which provides the scattering information. This is called the Levinson's theorem.

2 The Scattering Theory in Three Dimention

In this section, we discuss the scattering theory in three-dimension by following the methods especially using the integral equation that are introduced in our earlier discussions on one-dimensional scattering theory. More specifically, we consider a spherically-symmetric scatterer at periphery of origin, in which the plane waves incident in z-axis direction.



2.1 The Scattering Amplitude and the Differntial Cross Sections

In such case shown in the figure bove, the boundary condition for the stationary state be

$$\Psi(\vec{r}) \overset{\vec{r}\to\infty}{\longrightarrow} \frac{1}{(2\pi)^{3/2}}\left(e^{ikz} + \frac{f(\theta)}{r}e^{ikr}\right)$$

We can rewrite the above by using $mv = \hbar k\$, and$ $\mathrm{V}_0 = (2\pi)^3$ [27] [28]

[27]We can understand from $\int_{-\pi}^{\pi} dx \ \int_{-\pi}^{\pi} dy \ \int_{-\pi}^{\pi} dz \ |\Psi|^2 = 1$ that $\Psi(\vec{r}) = \frac{1}{(2\pi)^{3/2}}e^{i\vec{k}\cdot\vec{r}}$ has a particle for every volume $v_0 = (2\pi)^3$.

[28]Given

$$\vec{\nabla} f = \frac{\partial f}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial f}{\partial \theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial f}{\partial \phi}\hat{\phi}$$

,

$$\begin{aligned}\Psi_s^*\vec{\nabla}\Psi_s &= \frac{1}{(2\pi)^3}\frac{f^*(\theta)}{r}e^{-ikr}\left(-\frac{f(\theta)}{r^2}e^{ikr}\hat{r} + \frac{f(\theta)}{r}e^{ikr}ik\hat{r} + \frac{1}{r}\frac{\partial f(\theta)}{\partial \theta}\frac{1}{r}e^{ikr}\hat{\theta}\right)\\ &= \frac{1}{(2\pi)^3}\frac{|f|^2}{r^2}ik\hat{r} + \mathcal{O}(\frac{1}{r^2})\end{aligned}$$

$$
\begin{aligned}
\Psi_0 &= \frac{1}{(2\pi)^{3/2}} e^{ikz} \\
\vec{j}_0 &= \left(\frac{\hbar}{2mi}\right)\left(\Psi_0^* \vec{\nabla}\Psi_0 - (\vec{\nabla}\Psi_0^*)\Psi_0\right) = \frac{1}{(2\pi)^3}\frac{\hbar k}{m}\hat{z} = \frac{v}{V_0}\hat{z} \\
\Psi_s &= \frac{1}{(2\pi)^{3/2}}\frac{f(\theta)}{r} e^{ikr} \\
\vec{j}_s &= \left(\frac{\hbar}{2mi}\right)\left(\Psi_s^* \vec{\nabla}\Psi_s - (\vec{\nabla}\Psi_s^*)\Psi_s\right) = \frac{1}{(2\pi)^3}\frac{|f(\theta)|^2}{r^2}\frac{\hbar k}{m}\hat{r} + o(\frac{1}{r^2}) \approx \frac{v}{V_0}\frac{|f(\theta)|^2}{r^2}\hat{r}
\end{aligned}
$$

The boundary condition at infinite distance away is the superposition of the plane waves and the spherical waves.

Let $f(\theta)$ be the scattering amplitude. We can write the differntial scattering cross section $\sigma(\theta)$ given the ratio between the incidene flux per unit area $\Phi_0 = \vec{j}_z \cdot \hat{z}$ snf the scattering flux $\Phi_s = \vec{j}_s \cdot d\vec{S}$ per surface element $d\vec{S} = r^2 d\vec{\Omega}$ ($d\vec{\Omega} = d\Omega\hat{r}$)

$$
\Phi_s = \sigma(\theta) d\Omega \cdot \Phi_0
$$

This gives

$$
\sigma(\theta) = |f(\theta)|^2
$$

Now that we call $\sigma_T = \int d\Omega\sigma(\theta)$ a total scattering cross section.

Now we can express the equation of continuity for the waveunction $\Psi(\vec{r}, t)$, which is the solution for the time-dependent Schroedinger equation,

$$
\begin{aligned}
\frac{\partial\rho(\vec{r}, t)}{\partial t} + \vec{\nabla}\cdot\vec{j}(\vec{r}, t) &= 0 \\
\rho(\vec{r}, t) &= |\Psi(\vec{r}, t)|^2 \\
\vec{j}(\vec{r}, t) &= \frac{\hbar}{2mi}\left(\Psi^*(\vec{r}, t)\vec{\nabla}\Psi(\vec{r}, t) - h.c.\right)
\end{aligned}
$$

[29] This gives the wavefunction for the stationary states, the main forcus of our discussion

$$
\vec{\nabla}\cdot\vec{j}(\vec{r}, t) = 0
$$

[29] We use Schroedinger equation in the forms of time resolution $\partial_t N = \partial_t \int_V d\vec{r}|\Psi(\vec{r})|^2$ for the number of particles N in an arbitrary volume V and write

$$
\begin{aligned}
\partial_t N &= \int d\vec{r}\Big(\dot{\Psi}^*(\vec{r})\Psi(\vec{r}) + \Psi^*(\vec{r})\dot{\Psi}(\vec{r})\Big) = \int_V d\vec{r}\frac{1}{i\hbar}\Big(- H\Psi^*(\vec{r})\Psi(\vec{r}) + \Psi(\vec{r})H\Psi^*(\vec{r})\Big) \\
&= -\left(\frac{\hbar}{2mi}\right)\int_V d\vec{r}\big(- (\nabla^2\Psi^*(\vec{r}))\Psi(\vec{r}) + \Psi^*(\vec{r})\nabla^2\Psi(\vec{r})\big) \\
&= -\left(\frac{\hbar}{2mi}\right)\int_{\partial V} d\vec{S}\big(- (\vec{\nabla}\Psi^*(\vec{r}))\Psi(\vec{r}) + \Psi^*(\vec{r})\vec{\nabla}\Psi(\vec{r})\big) = -\int_{\partial V} d\vec{S}\vec{j}(\vec{r}) \\
\vec{j}(\vec{r}) &= \left(\frac{\hbar}{2mi}\right)\Big[\Psi^*(\vec{r})\vec{\nabla}\Psi(\vec{r}) - (\vec{\nabla}\Psi^*(\vec{r}))\Psi(\vec{r})\Big]
\end{aligned}
$$

which shows that $\vec{j}$ is the current operator so, given that the volume V is the arbitrary volume, Integrate the wquation above over a region bounded by a largy sphere S_R having a radius R with its center located origin. Applying the Gauss theorem to write [30]

---

the equation of continuity

$$\partial_t |\Psi(\vec{r})|^2 + \vec{\nabla} \cdot \vec{j} = 0$$

is obeyed. We can also obtain the above equation directly without using the arbitral characteristics of the volume.

[30]We consider a more unified expression for the behavior of spherical waves at infinite distant away via analytic continuation given the wavefunction in bound states. So, we can write

$$\begin{aligned} \Psi(\vec{r}) &\longrightarrow \frac{1}{(2\pi)^{3/2}} \left(e^{ikz} + \frac{f(\theta)}{r} e^{ik^+ r} \right) \\ k^+ &= k + i0 = k + i\epsilon \end{aligned}$$

We further suppose $R\epsilon >> 1$; i.e., we have the initial system of infinite large then, take the limit of $\epsilon \to 0$ at the end. Thus,

$$\begin{aligned} \Psi &= \frac{1}{(2\pi)^{3/2}} (e^{ikr\cos\theta} + \frac{f}{r} e^{ik^+ r}) \\ V_0 \Psi^* \boldsymbol{\nabla} \Psi \Big|_{r=R} &= (e^{-ikr\cos\theta} + \frac{f^*}{r} e^{-ik^- r})(ike^{ikr\cos\theta} + ik\frac{f}{r} e^{ik^+ r}) \hat{\boldsymbol{r}} \Big|_{r=R} + \mathcal{O}(1/R^2) \\ &= \left(ik\cos\theta + ik\frac{f^*}{R} \cos\theta e^{iR(k\cos\theta - k^-)} + ik\frac{f}{R} e^{-iR(k\cos\theta - k^+)} \right) \hat{\boldsymbol{r}} \\ &= \left(ik\cos\theta + ik\frac{f^*}{R} \cos\theta e^{ikR(\cos\theta - 1) - \epsilon R} + ik\frac{f}{R} e^{-ikR(\cos\theta - 1) - \epsilon R} \right) \hat{\boldsymbol{r}} \\ V_0 \Psi^* \boldsymbol{\nabla} \Psi \Big|_{r=R} - h.c. &= \left(2ik\cos\theta + ik\frac{f^*}{R}(1+\cos\theta) e^{ikR(\cos\theta - 1) - \epsilon R} + ik\frac{f}{R}(1+\cos\theta) e^{-ikR(\cos\theta - 1) - \epsilon R} \right) \hat{\boldsymbol{r}} \end{aligned}$$

In the following equations, the higher-prder terms are ignored $(1/R^2)$,and rewritten

$$\begin{aligned} 0 = &\int_S d\vec{S} \cdot \vec{j}_\infty \\ = &\left(\frac{\hbar}{2mi} \right) \int_S dS \left(\Psi^* \frac{\partial \Psi}{\partial r} - h.c. \right) \\ = &\int_S d\vec{S} (\hat{z} \vec{j}_0 - \hat{z} \vec{j}_0) + \int d\Omega \left[R^2 \cdot \frac{v}{V_0} \frac{|f(\theta)|^2}{R^2} \right] + \mathcal{O}\ (\frac{1}{R}) \\ + &\left(\frac{\hbar}{2mi} \right) \int d\hat{\Omega}\, R^2 \frac{1}{(2\pi)^3} \left(e^{-ikz} (ik) \frac{f(\theta)}{R} e^{ikR}\, \hat{r} + \frac{f^*(\theta)}{R} e^{-ikR} (ik) e^{ikz}\, \hat{z} - h.c. \right) \\ = &\frac{v}{V_0} \int d\Omega |f(\theta)|^2 \\ + &\left(\frac{i\hbar k}{2mi} \right) \int d\Omega\, R^2 \frac{1}{(2\pi)^3} \left(e^{ikR(1-\cos\theta)} \frac{f(\theta)}{R} + \frac{f^*(\theta)}{R} e^{-ikR(1-\cos\theta)} \cos\theta \right. \\ &\qquad \left. + e^{-ikR(1-\cos\theta)} \frac{f^*(\theta)}{R} + \frac{f(\theta)}{R} e^{ikR(1-\cos\theta)} \cos\theta \right) \\ = &\frac{v}{V_0} \int d\Omega |f(\theta)|^2 + \frac{\hbar k}{2m} \frac{1}{(2\pi)^3} R \int d\Omega\, (1+\cos\theta)(f(\theta) e^{ikR(1-\cos\theta)} + f^*(\theta) e^{-ikR(1-\cos\theta)}) \\ = &\frac{v}{V_0} \int d\Omega |f(\theta)|^2 + \frac{\hbar k}{2m} \frac{1}{(2\pi)^3} R 2 \cdot 2\pi \frac{1}{kR} i(f(0) - f^*(0)) + \text{const.} e^{\pm ikR} \end{aligned}$$

31 32

31

$$
\begin{aligned}
\int d\Omega\, e^{ikR(1-\cos\theta)} f(\theta) &= 2\pi f(0)\int_0^\pi d\theta \sin\theta e^{ikR(1-\cos\theta)} f(\theta) \to 2\pi f(0)\int_{-1}^1 dt\, e^{ikR(1-t)}, \quad kR\to\infty \\
&= 2\pi f(0)\frac{1}{-ikR}e^{ikR(1-t)}\Big|_{-1}^{1} = 2\pi f(0)\frac{i}{kR}(1-e^{-2ikR}) \\
&= 2\pi\frac{1}{kR}if(0) + \text{const.}e^{-2ikR} \\
\int d\Omega\, e^{-ikR(1-\cos\theta)} f^*(\theta) &= -2\pi\frac{1}{kR}if^*(0) + \text{const.}e^{2ikR}
\end{aligned}
$$

32 Our discussion in general can be

$$
\begin{aligned}
0 &= \int_S d\vec{S}\cdot\vec{j}_\infty \\
&= \left(\frac{\hbar}{2mi}\right)\int_S dS\left(\Psi^*\frac{\partial\Psi}{\partial r} - h.c.\right) \\
&= \int_S d\vec{S}(\hat{z}\vec{j}_0 - \hat{z}\vec{j}_0) + \int d\Omega\left[R^2\cdot\frac{v}{V_0}\frac{|f(\theta)|^2}{R^2}\right] + \mathcal{O}\,(\frac{1}{R}) \\
&+ \left(\frac{\hbar}{2mi}\right)\int d\hat{\Omega}\, R^2\frac{1}{(2\pi)^3}\left(e^{-ikz}(ik)\frac{f(\theta)}{R}e^{ikR}\,\hat{r} + \frac{f^*(\theta)}{R}e^{-ikR}(ik)e^{ikz}\,\hat{z} - h.c.\right) \\
&= \frac{v}{V_0}\int d\Omega|f(\theta)|^2 \\
&+ \left(\frac{i\hbar k}{2mi}\right)\int d\Omega\, R^2\frac{1}{(2\pi)^3}\left(e^{ikR(1-\cos\theta)}\frac{f(\theta)}{R} + \frac{f^*(\theta)}{R}e^{-ikR(1-\cos\theta)}\cos\theta\right. \\
&\qquad\qquad \left. + e^{-ikR(1-\cos\theta)}\frac{f^*(\theta)}{R} + \frac{f(\theta)}{R}e^{ikR(1-\cos\theta)}\cos\theta\right) \\
&= \frac{v}{V_0}\int d\Omega|f(\theta)|^2 + \frac{\hbar k}{2m}\frac{1}{(2\pi)^3}R\int d\Omega\,(1+\cos\theta)(f(\theta)e^{ikR(1-\cos\theta)} + f^*(\theta)e^{-ikR(1-\cos\theta)}) \\
&= \frac{v}{V_0}\int d\Omega|f(\theta)|^2 + \frac{\hbar k}{2m}\frac{1}{(2\pi)^3}R2\cdot 2\pi\frac{1}{kR}i(f(0)-f^*(0)) + \text{const.}e^{\pm ikR}
\end{aligned}
$$

We can take average of the above at infinitesimal region of R, which we can leave out the last term. Thus,

$$
0 = \frac{v}{V_0}\int d\Omega|f(\theta)|^2 + \frac{v}{V_0}\frac{4\pi}{k}(-)\text{Im}\, f(0)
$$

$$\begin{aligned}
\vec{j}_\infty &= \left(\frac{\hbar}{2mi}\right)\left(\Psi^* \frac{\partial \Psi}{\partial r} - h.c.\right) \\
0 &= \int_S d\vec{S} \cdot \vec{j}_\infty \\
&= \left(\frac{\hbar}{2mi}\right) \int_S dS \left(\Psi^* \frac{\partial \Psi}{\partial r} - h.c.\right) \\
&= \int_S d\vec{S}(\hat{z}\vec{j}_0 - \hat{z}\vec{j}_0) + \int d\Omega \left[R^2 \cdot \frac{v}{V_0}\frac{|f(\theta)|^2}{R^2}\right] + \mathcal{O}\,(\frac{1}{R}) \\
&+ \left(\frac{\hbar}{2mi}\right) \int d\hat{\Omega}\, R^2 \frac{1}{(2\pi)^3}\left(e^{-ikz}(ik)\frac{f(\theta)}{R}e^{ikR}\,\hat{r} + \frac{f^*(\theta)}{R}e^{-ikR}(ik)e^{ikz}\,\hat{z} - h.c.\right)
\end{aligned}$$

We average the above by the infinitesimal area on R to obtain

$$\mathrm{Im}\ f(0) = \frac{k}{4\pi}\int d\Omega |f(\theta)|^2 = \frac{k}{4\pi}\sigma_T$$

Such relation between the forward scattering amplitude and the total cross section of the scatterer is called the optical theorem.

2.2 Lippmann-Schwinger Equation and the scattering Amplitude

We now consider determining the scattering amplitude via the integral equation derived from the Lippmann-Schwinger equation, which we discussed in our previous section. To begin with, we difine the Green's function $G_0(\vec{r}) = G_0^{\pm}(\vec{r}, E)$ of the three-dimentional free-particle system as the solution of the equation

$$\begin{aligned}
(E - H_0(\vec{r}))G_0(\vec{r}) &= \delta(\vec{r}) \\
H_0(x) &= -\frac{\hbar^2 \nabla^2}{2m}
\end{aligned}$$

Specific forms of the equation above can be obtained by using the Fourier analysis in the same way we did to obtain the specific equation form in our previous section. [33]

$$G_0(E) = \begin{cases} G_0^{\pm}(\vec{r}) = & -\left(\frac{2m}{\hbar^2}\right)\frac{1}{4\pi}\frac{e^{\pm iKr}}{r}, \quad K \to K \pm i0 = \frac{\sqrt{2mE}}{\hbar} \pm i0, \quad E \to E \pm i0, E > 0 \\ G_0^{+}(\vec{r}, K \leftarrow i\kappa) = & -\left(\frac{2m}{\hbar^2}\right)\frac{1}{4\pi}\frac{e^{-\kappa r}}{r}, \qquad \kappa = \frac{\sqrt{2m|E|}}{\hbar}, \qquad E < 0 \end{cases}$$

[33] On the one hand where $E \geq 0$, we may write

$$E \pm i0 = \frac{\hbar^2 K_\pm^2}{2m}, \quad G_0^{\pm}(x) = \frac{1}{(2\pi)^{3/2}}\int d^3k \hat{G}_0^{\pm}(\vec{k}) e^{i\vec{k}\cdot\vec{r}}$$

In out present case, we consider the scattering states where $E > 0$, and having the plane wave of $\Phi(\vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{ikz}$ traveling in z-axis direction as homogeneous solution to express the Lippmann-Schwinger integral equation

$$\Psi^{\pm} = \Phi + \frac{1}{E \pm i0 - H_0} V \Psi^{\pm}$$

In more specifin form we can write

$$\Psi^{\pm}(\vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{ikz} - \left(\frac{2m}{\hbar^2}\right) \frac{1}{4\pi} \int d\vec{r}' \frac{e^{\pm ik|r-r'|}}{|\vec{r} - \vec{r}'|} V(\vec{r}') \Psi^{\pm}(\vec{r}')$$

Here we suppose there is the scatterer of a finite size ($V(\vec{r}) \approx 0, r >> a$). We consider the wavefunction at a point, a sufficient distance away from the scatterer.

The equation we initially defined and $\delta(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3k e^{i\vec{k}\cdot\vec{r}}$ yields $\hat{G}_0^{\pm}(\vec{k}) = \left(\frac{2m}{\hbar^2}\right) \frac{1}{(2\pi)^{3/2}} \frac{1}{K^2 - k^2}$ so, we cn write

$$G_0^{\pm}(\vec{r}) = \frac{1}{(2\pi)^3} \left(\frac{2m}{\hbar^2}\right) \int d^3k \frac{1}{K^2 - k^2} e^{i\vec{k}\cdot\vec{r}}$$

This integral is evaluated in the polar coordinated (z-axis in $\vec{r}$ direction) such that

$$\int d^3k \frac{1}{K_{\pm}^2 - k^2} e^{i\vec{k}\cdot\vec{r}} = \int_0^{\infty} dk k^2 \frac{1}{K_{\pm}^2 - k^2} (2\pi) \int_0^{\pi} d\theta \sin\theta e^{ikr\cos\theta}$$

$$= \frac{\pi}{i} \frac{1}{r} \int_{\infty dk \frac{k}{K_{\pm}^2 - k^2} (e^{ikr} - e^{-ikr}) = \frac{\pi}{i} \frac{1}{r} 2 \int_{\infty} dk \frac{-k}{K_{\pm}^2 - k^2} e^{ikr}}$$

$$= \frac{\pi}{i} \frac{1}{r} \int_{-\infty}^{\infty} dk \left(\frac{1}{k + K \pm i0} + \frac{1}{k - K \mp i0} \right) (-e^{ikr}) = \frac{\pi^2}{r} (-2) e^{\pm iKr}$$

Thus,

$$G_0^{\pm}(\vec{r}) = -\left(\frac{2m}{\hbar^2}\right) \frac{1}{4\pi} \frac{e^{\pm iKr}}{r}$$

On the other where $E < 0$, same way we handled the one-dimensional systems, we write

$$K = i\kappa = i\frac{\sqrt{2m|E|}}{\hbar}, \quad \kappa > 0$$

In this case, we may directly evaluate the integral, in which we can apply $K \to K + i0$ ($E \to E + i0$) . Thus,

$$G_0(\vec{r}) = -\left(\frac{2m}{\hbar^2}\right) \frac{1}{4\pi} \frac{e^{-\kappa r}}{r}$$

Having $r >> a \;\; r' \approx a$, we can write [34]

$$\begin{aligned} |\vec{r} - \vec{r}'| &= r - \hat{r}\cdot\vec{r}' + \mathcal{O}(\left(\frac{a}{r}\right)) \\ \frac{a}{|\vec{r} - \vec{r}'|} &= \frac{a}{r} + \mathcal{O}(\left(\frac{a}{r}\right)^2) \end{aligned}$$

which giving

$$\Psi^{\pm}(\vec{r}) = \frac{1}{(2\pi)^{3/2}}\left[e^{ikz} + \frac{e^{\pm ikr}}{r}\left\{-\left(\frac{2m}{\hbar^2}\right)\frac{(2\pi)^{3/2}}{4\pi}\int d\vec{r}' e^{\mp i\vec{k}_r\cdot\vec{r}'}V(\vec{r}')\Psi^{\pm}(\vec{r}')\right\}\right] + \mathcal{O}(\left(\frac{a}{r}\right))$$

Here we note that $\vec{k}_r = k\hat{r}$ is the k-vector in the direction of the scattering. This in fact shows that $\Psi^+(\vec{r})$ is the solution, which satisfies the boundary condition. The scattering amplitude can be given from

$$f(\theta_{\vec{k}_r}) = -\left(\frac{2m}{\hbar^2}\right)\frac{(2\pi)^{3/2}}{4\pi}\int d\vec{r}' e^{-i\vec{k}_r\cdot\vec{r}'}V(\vec{r}')\Psi^{+}(\vec{r}')$$

Note that the incident wave is expressed as
$\Phi_{\vec{k}_z}(\vec{r}) = \frac{1}{(2\pi)^{3/2}}e^{i\vec{k}_z\cdot\vec{r}}, \;\; (\vec{k}_z = k\hat{z})$, we can write [35]

$$\begin{aligned} f(\theta_{\vec{k}_r}) &= -\left(\frac{2m}{\hbar^2}\right)\frac{(2\pi)^3}{4\pi}\langle\Phi_{\vec{k}_r}|V|\Psi^+\rangle \\ &= -\left(\frac{2m}{\hbar^2}\right)\frac{(2\pi)^3}{4\pi}\langle\Phi_{\vec{k}_r}|T|\Phi_{\vec{k}_z}\rangle \\ T &= V + V\frac{1}{E_k - H + i0}V \end{aligned}$$

2.3 Born Approximation

The approximation method that has solution Phi in the right side of $\Psi^{\pm}$ as the lowest order of the successive approximation steps within the integral equation to give a simplest form of approximation

$$\Psi^{\pm} \approx \frac{1}{(2\pi)^{3/2}}e^{ikz} = \frac{1}{(2\pi)^{3/2}}e^{ik\hat{z}\cdot\vec{r}}$$

---

[34]

$$\begin{aligned} |\vec{r} - \vec{r}'| = (r^2 + r'^2 - 2\vec{r}\cdot\vec{r}')^{1/2} &= r(1 - 2\frac{\hat{r}\cdot\vec{r}'}{r} + \frac{r'^2}{r^2})^{1/2} = r(1 - 2\frac{\hat{r}\cdot\vec{r}'}{r} + \mathcal{O}(\left(\frac{a}{r}\right)^2))^{1/2} \\ = r - \hat{r}\cdot\vec{r}' + \mathcal{O}(\left(\frac{a}{r}\right)) \end{aligned}$$

[35] We used $\Psi^+ = (1 + G^+V)\Phi$

Is called the (first) Born approximation. The scattering amplitude in this approximation can be written

$$\begin{aligned} f_B(\theta_{\vec{k}}) &= -\left(\frac{2m}{\hbar^2}\right)\frac{1}{4\pi}\int d\vec{r}e^{i(\vec{k}'-\vec{k})\cdot\vec{r}}V(r) \\ \vec{k}' &= k\hat{z} \end{aligned}$$

Now let us have

$$\vec{K} = \vec{k}' - \vec{k}$$

Calculation is made with the polar coordinates $(\bar{r}, \bar{\theta}, \bar{\phi})$ in $\vec{K}$ direction to give [36]

$$\begin{aligned} f_B(\theta_{\vec{k}}) &= -\left(\frac{2m}{\hbar^2}\right)\frac{1}{4\pi}\int d\bar{\phi}\int d\bar{\theta}\sin\bar{\theta}\int d\bar{r}\bar{r}^2 e^{iK\bar{r}\cos\bar{\theta}}V(\bar{r}) \\ &= -\left(\frac{2m}{\hbar^2}\right)\frac{1}{2}\int d\bar{r}\bar{r}^2\frac{1}{iK\bar{r}}e^{iK\bar{r}\cos\bar{\theta}}\Big|_{\cos\bar{\theta}=-1}^{\cos\bar{\theta}=1}V(\bar{r}) \\ &= -\left(\frac{2m}{\hbar^2}\right)\frac{1}{K}\int drr\sin(Kr)V(r) \end{aligned}$$

The differntial cross section can be written

$$\sigma = \left(\frac{2m}{\hbar^2}\right)^2\left|\frac{1}{K}\int_0^\infty drV(r)r\sin(Kr)\right|^2$$

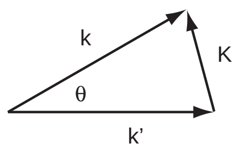
A Case for Born Approximation (Rutherford Scattering)

Consider scattering by Yukawa potential

$$V(r) = \frac{Ae^{-\mu r}}{r}$$

---

[36]



$$K = |\vec{K}| = \sqrt{2k^2(1-\cos\theta)} = 2k\sin\frac{\theta}{2}$$

$$\begin{aligned} dK &= k\cos\theta/2d\theta \\ KdK &= k^2\sin\theta d\theta \\ \sin\theta d\theta &= \frac{1}{k^2}KdK \end{aligned}$$

In which we can write [37]

$$f_B(\theta) = -\frac{2m}{\hbar^2}\frac{A}{K^2+\mu^2}$$

We can rewrite the above equation with $\mu \to 0$, $A = -Ze^2$ to have

$$f_B \overset{\mu\to 0}{\longrightarrow} \frac{m}{2(\hbar k)^2}\frac{Ze^2}{\sin^2\theta/2}$$

This indeed is equivalent to the classical formula of the Rutherford scattering.

2.4 Partial Wave Decomposition

In the following sections we discuss the scattering problems with an approach by the partial wave decomposition. [38]

2.4.1 The Schroedinger Equation in Spherical Symmetric Field

The Schroedinger equation is expressed in the forms

$$\begin{aligned} H\Psi(\vec{r}) &= E\Psi(\vec{r}) \\ H &= \frac{\vec{p}^2}{2m} + V(r) \\ \vec{p} &= \frac{\hbar}{i}\vec{\nabla} \end{aligned}$$

Given that we consider to obtain the its eigenfunction in the following forms

$$\begin{aligned} \Psi(\vec{r}) &= R(r)\ \Theta(\theta)\ \Phi(\phi) \\ x &= r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta \end{aligned}$$

Let the angular momentum be

$$\begin{aligned} \vec{L} &\equiv \vec{r}\times\vec{p} \\ L_i &= \epsilon_{ijk}x_j p_k, \quad x_1 = x, \quad x_2 = y, \quad x_3 = z \end{aligned}$$

37

$$\begin{aligned} \int_0^\infty dr \sin Kr rV(r) &= A\int_0^\infty dr e^{-\mu r}\sin Kr = \frac{A}{2i}\int_0^\infty dr\left(e^{(-\mu+iK)r} - e^{(-\mu-iK)r}\right) \\ &= A\frac{-1}{2i}\left(\frac{1}{-\mu+iK} - \frac{1}{-\mu-iK}\right) = \frac{AK}{K^2+\mu^2} \end{aligned}$$

38 Review the mathematical handbooks for the basic knowledge of the spherical function.

giving [39]

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k$$

This exchange relationship generally makes clear of the fact (from the algebraic relation only) that the simultaneous eigenstates for $\vec{L}^2$ and L_z can be obtained as

$$\begin{aligned}
\vec{L}^2 Y_{\ell m} &= \hbar^2\ell(\ell+1)Y_{\ell m} \\
L_z Y_{\ell m} &= \hbar m Y_{\ell m} \\
m &= -\ell, \ell+1, \cdots, \ell-1, \ell
\end{aligned}$$

Furthermore, we may write [40]

$$\begin{aligned}
\vec{\nabla} &= \vec{e}_r\frac{\partial}{\partial r} + \vec{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} \\
\vec{e}_r &= \frac{\widehat{\partial\vec{r}}}{\partial r} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta), \\
\vec{e}_\theta &= \frac{\widehat{\partial\vec{r}}}{\partial\theta} = (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta), \\
\vec{e}_\phi &= \frac{\widehat{\partial\vec{r}}}{\partial\phi} = (-\sin\phi, \cos\phi, 0), \\
\vec{r} &= \vec{e}_r r
\end{aligned}$$

which gives a clear sense that $\vec{L}$ does not depend on r but depends on θ, and ϕ in

[39] $[x_i, p_j] = x_i p_j - p_j x_i = i\hbar\delta_{ij}$

$$\begin{aligned}
[L_i, L_j] &= \epsilon_{iab}\epsilon_{jcd}[x_a p_b, x_c p_d] = \epsilon_{iab}\epsilon_{jcd}(x_a[p_b, x_c p_d] + [x_a, x_c p_d]p_b) = \epsilon_{iab}\epsilon_{jcd}(x_a[p_b, x_c]p_d + x_c[x_a, p_d]p_b) \\
&= \epsilon_{iab}\epsilon_{jcd}(-i\hbar\delta_{bc}x_a p_d + i\hbar\delta_{ad}x_c p_b) = -i\hbar\epsilon_{iab}\epsilon_{jbd}x_a p_d + i\hbar\epsilon_{iab}\epsilon_{jca}x_c p_b \\
&= i\hbar(\delta_{ij}\delta_{ad} - \delta_{id}\delta_{aj})x_a p_d - i\hbar(\delta_{ij}\delta_{bc} - \delta_{ic}\delta_{bj})x_c p_b \\
&= i\hbar(\delta_{ij}x_a p_a - x_j p_i - \delta_{ij}x_b p_b + x_i p_j) = i\hbar(x_i p_j - x_j p_i) = i\hbar\epsilon_{ijk}L_k \\
&\quad (= i\hbar\epsilon_{ijk}\epsilon_{kab}x_a p_b = i\hbar(x_i p_j - x_j p_i))
\end{aligned}$$

[40] It is cleat that

$$\vec{r} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$$

the function. We can write respsctively, [41]

$$
\begin{aligned}
L_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
L_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
L_z &= -i\hbar\frac{\partial}{\partial\phi} \\
\vec{L}^2 &= -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}
\end{aligned}
$$

We use these specific in the above to determine the eigenvalue $\hbar^2\ell(\ell+1)$ for $\vec{L}^2$. In the first step, let us have $Y_{lm}(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ and write out the equations according to the eigenfunction to have

$$
\begin{aligned}
\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\Theta(\theta)\Phi(\phi) &= -\ell(\ell+1)\Theta(\theta)\Phi(\phi) \\
\frac{1}{\Theta}\sin^2\theta\left\{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\Theta\right\} &= -\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2}
\end{aligned}
$$

41

$$
\vec{L} = \vec{r}\times\vec{p} = -i\hbar\vec{e}_\phi\frac{\partial}{\partial\theta} + i\hbar\vec{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} = -i\hbar(-\sin\phi,\cos\phi,0)\frac{\partial}{\partial\theta} + i\hbar(\cot\theta\cos\phi,\cot\theta\sin\phi,-1)\frac{\partial}{\partial\phi}
$$

$$
\begin{aligned}
L_x^2 =& -\hbar^2\big(\sin\phi\,\partial_\theta + \cot\theta\cos\phi\,\partial_\phi\big)\big(\sin\phi\,\partial_\theta + \cot\theta\cos\phi\,\partial_\phi\big), \quad (\cot\theta)' = -\frac{1}{\sin^2\theta} \\
=& -\hbar^2\big(\sin^2\phi\,\partial_\theta^2 - \frac{1}{\sin^2\theta}\sin\phi\cos\phi\,\partial_\phi + \cot\theta\sin\phi\cos\phi\,\partial_\theta\,\partial_\phi \\
& + \cot\theta\cos^2\phi\,\partial_\theta + \cot\theta\cos\phi\sin\phi\,\partial_\phi\,\partial_\theta \\
& - \cot^2\theta\sin\phi\cos\phi\,\partial_\phi + \cot^2\theta\cos^2\phi\,\partial_\phi^2\big) \\
L_y^2 =& -\hbar^2\big(\cos\phi\,\partial_\theta - \cot\theta\sin\phi\,\partial_\phi\big)\big(\cos\phi\,\partial_\theta - \cot\theta\sin\phi\,\partial_\phi\big) \\
=& -\hbar^2\big(\cos^2\phi\,\partial_\theta^2 + \frac{1}{\sin^2\theta}\sin\phi\cos\phi\,\partial_\phi - \cot\theta\sin\phi\cos\phi\,\partial_\theta\,\partial_\phi \\
& + \cot\theta\sin^2\phi\,\partial_\theta - \cot\theta\sin\phi\cos\phi\,\partial_\theta\,\partial_\phi \\
& + \cot^2\theta\sin\phi\cos\phi\,\partial_\phi + \cot^2\theta\sin^2\phi\,\partial_\phi^2\big) \\
L_x^2 + L_y^2 =& -\hbar^2\big(\partial_\theta^2 + \cot\theta\,\partial_\theta + \cot^2\theta\,\partial_\phi^2\big) \\
L_z^2 =& -\hbar^2\,\partial_\phi^2 \\
\boldsymbol{L}^2 =& -\hbar^2\left(\partial_\theta^2 + \cot\theta\,\partial_\theta + \frac{1}{\sin^2\theta}\,\partial)\phi^2\right) \\
=& -\hbar^2\left(\frac{1}{\sin\theta}\,\partial_\theta(\sin\theta\,\partial_\theta) + \frac{1}{\sin^2\theta}\,\partial)\phi^2\right)
\end{aligned}
$$

We separate the equations above to give

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \{\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\}\Theta = 0$$

The first equations above to give

$$\Phi(\phi) = e^{im\phi}, \quad m = 0, \pm1, \pm2, \pm3, \cdots,$$

The condition for the m is being satisfied given the monodromy of the function. If we require the finite property in the whole region for θ in the function of Θ, we may use the associated Legendre differntial equation to write

$$\Theta(\theta) \propto P_l^{|m|}(\theta), \quad \ell = 0, 1, 2, \cdots, \ m = -\ell, \ell+1, \cdots, \ell$$

[42] With all the iformation we obtained from above, we now determine the normalization constant as in the following form

$$Y_{\ell m}(\theta,\phi) = (-1)^{\frac{m+|m|}{2}}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}P_l^{|m|}(\cos\theta)e^{im\phi}$$

Thus, we can write the orthonormality,

$$\langle Y_{\ell'm'}|Y_{\ell m}\rangle \equiv \int d\Omega Y^*_{\ell'm'}(\theta,\phi)Y_{\ell m}(\theta,\phi) = \delta_{\ell,\ell'}\delta_{mm'}$$

the effects of ladder operator as,

$$L_\pm Y_{\ell m} \;=\; \hbar\sqrt{(\ell\mp m)(\ell\pm m+1)}Y_{\ell m\pm1}$$

and the complex conjugation as,

$$Y^*_{\ell m}(\theta,\phi) = (-)^m Y_{\ell -m}(\theta,\phi)$$

---

[42]With $x = \cos\theta$, we know $\frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -\sin\theta\frac{d}{dx}$ thus, we have $\frac{1}{\sin\theta}\frac{d}{d\theta}\big(\sin\theta\frac{d\Theta}{d\theta}\big) = \frac{d}{dx}\big(\sin^2\theta\frac{d\Theta}{dx}\big) = \frac{d}{dx}\big((1-x^2)\frac{d\Theta}{dx}\big)$ From that we obtain

$$\{(1-x^2)\frac{d\Theta}{dx}\} + \big(\ell(\ell+1) - \frac{m^2}{1-x^2}\big)\Theta = 0$$

(associated Legendre differntial equation)

43

---

[43]Here we demonstrate step-by-step of deriving the spherical harmonics $Y_{\ell m}(\theta,\phi) = \Theta_{\ell m}(\theta)\Phi_m(\phi)$ via algebraic functions alone. First, we have $L_z Y_{\ell m} = m\hbar Y_{\ell m}$, which gives. $\Phi_m = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ We may also write

$$\begin{aligned} L_+ =& L_x + iL_y = \hbar e^{i\phi}(\partial_\theta + i\cot\theta\partial_\phi) \\ L_- =& L_x - iL_y = \hbar e^{-i\phi}(-\partial_\theta + i\cot\theta\partial_\phi) \end{aligned}$$

So, from $L_+ Y_{\ell\ell} = 0$, we can write

$$\Theta'_{\ell\ell} - \ell\cot\theta\Theta_{\ell\ell} = 0, \rightarrow \Theta_{\ell\ell}(\theta) = C_\ell \sin^\ell\theta$$

Normalization may give

$$\begin{aligned} 1 =& |C_\ell|^2 \int_0^\pi d\theta\,\sin\theta\sin^{2\ell}\theta = 2|C_\ell|^2\int_0^{\pi/2} d\theta\,\sin^{2\ell+1}\theta = C_\ell^2 B(\ell+1,1) = |C_\ell|^2\frac{\Gamma(\ell+1)\Gamma(1/2)}{\Gamma(\ell+3/2)} \\ =& |C_\ell|^2\frac{\ell!\Gamma(1/2)}{(\ell+1/2)(\ell-1/2)(\ell-3/2)\cdots(1/2)\Gamma(1/2)} \\ =& |C_\ell|^2\frac{\ell!2^\ell}{(\ell+1/2)(2\ell-1)!!} = |C_\ell|^2\frac{\ell!2^\ell\cdot(2\ell+1)2^\ell\ell!}{(\ell+1/2)(2\ell+1)!} = |C_\ell|^2\frac{2(\ell!2^\ell)^2}{(2\ell+1)!} \\ C_\ell =& e^{i\delta}\sqrt{\frac{(2\ell+1)!}{2}}\frac{1}{\ell!2^\ell} \end{aligned}$$

Thus, we write

$$\begin{aligned} Y_{\ell m-1} =& \frac{1}{\sqrt{(\ell+m)(\ell-m+1)}}e^{-i\phi}(-\partial_\theta + i\cot\theta\partial_\phi)Y_{\ell m} \\ =& \frac{1}{\sqrt{(\ell+m)(\ell-m+1)}}(-)(\partial_\theta + m\cot\theta)\Theta_{\ell m}\Phi_{m-1}(\phi) = \Theta_{\ell m-1}\Phi_{m-1}(\phi) \\ \Theta_{\ell m-1} =& -\frac{1}{\sqrt{(\ell+m)(\ell-m+1)}}(\partial_\theta + m\cot\theta)\Theta_{\ell m} \end{aligned}$$

Here we note that

$$\begin{aligned} \sin^{1-m}\theta\frac{d}{d\cos\theta}(\sin^m\theta\Theta) =& \sin^{1-m}\theta\left(\frac{d\cos\theta}{d\theta}\right)^{-1}\frac{d}{d\theta}(\sin^m\theta\Theta) = -\sin^{-m}\theta(\Theta m\sin^{m-1}\theta\cos\theta + \sin^m\theta\partial_\theta\Theta) \\ =& -(\Theta m\cot\theta + \partial_\theta\Theta) \end{aligned}$$

which giving,

$$
\begin{aligned}
\Theta_{\ell m-1} =& \frac{1}{\sqrt{(\ell+m)(\ell-m+1)}} \sin^{1-m}\theta \frac{d}{d\cos\theta}(\sin^m\theta\Theta_{\ell m}) \\
\Theta_{\ell m-2} =& \frac{1}{\sqrt{(\ell+m-1)(\ell-m+2)}} \sin^{2-m}\theta \frac{d}{d\cos\theta}(\sin^{m-1}\theta\Theta_{\ell m-1}) \\
=& \frac{1}{\sqrt{(\ell+m)(\ell+m-1)\cdot(\ell-m+1)(\ell-m+2)}} \sin^{1-m}\theta \left(\frac{d}{d\cos\theta}\right)^2 (\sin^m\theta\Theta_{\ell m}) \\
\Theta_{\ell m-k} =& \frac{\sqrt{(\ell+m-k)!(\ell-m)!}}{\sqrt{(\ell+m)!(\ell-m+k)!}} \sin^{k-m}\theta \left(\frac{d}{d\cos\theta}\right)^k (\sin^m\theta\Theta_{\ell m}) \\
& Letusnowhavem \to \ell, k \to \ell - mso, werewriteintheform \\
\Theta_{\ell m} =& \frac{\sqrt{(\ell+m)!(0)!}}{\sqrt{(2\ell)!(\ell-m)!}} \sin^{-m}\theta \left(\frac{d}{d\cos\theta}\right)^{\ell-m} (\sin^\ell\theta\Theta_{\ell\ell}) \\
=& e^{i\delta}\sqrt{\frac{2\ell+1}{2}\frac{(\ell+m)!}{(\ell-m)!}} \frac{1}{\ell!2^\ell} \frac{1}{\sin^m\theta} \left(\frac{d}{d\cos\theta}\right)^{\ell-m} (\sin^{2\ell}\theta) \\
& Weespeciallyconsiderm = 0toobtai \\
\Theta_{\ell 0} =& e^{i\delta}\sqrt{\frac{2\ell+1}{2}} \frac{1}{\ell!2^\ell} \left(\frac{d}{d(\cos\theta)}\right)^\ell (\sin^{2\ell}\theta) = e^{i\delta}(-)^\ell \sqrt{\frac{2\ell+1}{2}} \frac{1}{\ell!2^\ell} \frac{d}{d(\cos\theta)}(\cos^2\theta-1)^\ell \\
=& e^{i\delta}(-)^\ell \sqrt{\frac{2\ell+1}{2}} P_\ell(\cos\theta) \\
& so, weput e^{i\delta} = (-)^\ell \\
\Theta_{\ell 0} =& \sqrt{\frac{2\ell+1}{2}} P_\ell(\cos\theta) \\
\Theta_{\ell m} =& (-)^\ell \sqrt{\frac{2\ell+1}{2}\frac{(\ell+m)!}{(\ell-m)!}} \frac{1}{\ell!2^\ell} \frac{1}{\sin^m\theta} \left(\frac{d}{d\cos\theta}\right)^{\ell-m} (\sin^{2\ell}\theta) \\
m \le 0&, \\
\Theta_{\ell m} =& \sqrt{\frac{2\ell+1}{2}\frac{(\ell+m)!}{(\ell-m)!}} \frac{1}{\sin^m\theta} \left(\frac{d}{d\cos\theta}\right)^{-m} P_\ell(\cos\theta) \\
=& \sqrt{\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}} \sin^{|m|}\theta \left(\frac{d}{d\cos\theta}\right)^{|m|} P_\ell(\cos\theta)
\end{aligned}
$$

On the other hand, we have

$$
\begin{aligned}
Y_{\ell m+1} =& \frac{1}{\sqrt{(\ell-m)(\ell+m+1)}} e^{i\phi}(\partial_\theta + i\cot\theta\partial_\phi) Y_{\ell m} \\
=& \frac{1}{\sqrt{(\ell-m)(\ell+m+1)}} (\partial_\theta - m\cot\theta)\Theta_{\ell m}\Phi_{\ell m+1} \\
\Theta_{\ell m+1} =& \frac{1}{\sqrt{(\ell-m)(\ell+m+1)}} (\partial_\theta - m\cot\theta)\Theta_{\ell m}
\end{aligned}
$$

While we can write using the algebraic functions alone, [44]

$$\vec{L}^2 = r^2\vec{p}^2 - r^2 p_r^2, \qquad p_r^2 = -\hbar^2(\partial_r^2 + \frac{2}{r}\partial_r)$$

Thus,

$$\frac{\vec{p}^2}{2m} = \frac{1}{2m}p_r^2 + \frac{1}{2m}\frac{\vec{L}^2}{r^2}$$

$$\sin^{m+1}\theta\frac{d}{d\cos\theta}(\sin^{-m}\theta\Theta) = \sin^{m+1}\theta\left(\frac{d\cos\theta}{d\theta}\right)^{-1}\frac{d}{d\theta}(\sin^{-m}\theta\Theta) = -\sin^m\theta(-\Theta m\sin^{-m-1}\theta\cos\theta + \sin^{-m}\theta\partial_\theta\Theta)$$
$$=(\Theta m\cot\theta - \partial_\theta\Theta)$$

which giving,

$$\begin{aligned}
\Theta_{\ell m+1} =& (-)\frac{1}{\sqrt{(\ell-m)(\ell+m+1)}}\sin^{m+1}\theta\frac{d}{d\cos\theta}(\sin^{-m}\theta\Theta_{\ell m}) \\
\Theta_{\ell m+2} =& (-)\frac{1}{\sqrt{(\ell-m-1)(\ell+m+2)}}\sin^{m+2}\theta\frac{d}{d\cos\theta}(\sin^{-m-1}\theta\Theta_{\ell m+1}) \\
=& (-)^2\frac{1}{\sqrt{(\ell-m)(\ell-m-1)\cdot(\ell+m+1)(\ell+m+2)}}\sin^{m+2}\theta\left(\frac{d}{d\cos\theta}\right)^2(\sin^{-m}\theta\Theta_{\ell m}) \\
\Theta_{\ell m+k} =& (-)^k\frac{\sqrt{(\ell-m-k)!(\ell+m)!}}{\sqrt{(\ell-m)!(\ell+m+k)!}}\sin^{m+k}\theta\left(\frac{d}{d\cos\theta}\right)^k(\sin^{-m}\theta\Theta_{\ell m}) \\
& We put m\to 0, k\to m (m>0) \\
\Theta_{\ell m} =& (-)^m\frac{\sqrt{(\ell-m)!\ell!}}{\sqrt{\ell!(\ell+m)!}}\sin^m\theta\left(\frac{d}{d\cos\theta}\right)^m\Theta_{\ell 0} \\
=& (-)^m\sqrt{\frac{2\ell+1}{2}\frac{(\ell-m)!}{(\ell+m)!}}\sin^m\theta\left(\frac{d}{d\cos\theta}\right)^m P_\ell(\cos\theta)
\end{aligned}$$

$$Now, from P_\ell^{|m|}(\cos\theta) = \sin^{|m|}\theta\left(\frac{d}{d\cos\theta}\right)^{|m|}P_\ell(\cos\theta) we obtain,$$

$$\Theta_{\ell m} = (-1)^{\frac{m+|m|}{2}}\sqrt{\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}}P_\ell^{|m|}(\cos\theta)$$

$$With m\le 0, we can write \Theta_{\ell -m} = (-)^m\Theta_{\ell m}$$

[44] GIven that we have $\vec{r}\cdot\vec{p} = -i\hbar x_i\partial_i = -i\hbar r\frac{x_i}{r}\partial_i = -i\hbar r\frac{\partial x_i}{\partial r}\partial_i = -i\hbar r\partial_r$,

$$\begin{aligned}
\vec{L}^2 &= \epsilon_{ijk}\epsilon_{ilm}x_j p_k x_l p_m = (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})x_j p_k x_l p_m \\
&= x_j p_k x_j p_k - x_j p_l x_l p_j = x_j(x_j p_k - i\hbar\delta_{jk})p_k - x_j(x_l p_l - i\hbar\delta_{ll})p_j \\
&= r^2\vec{p}^2 - i\hbar\vec{r}\cdot\vec{p} - x_j(p_j x_l + i\hbar\delta_{lj})p_l + 3i\hbar\vec{r}\cdot\vec{p} = r^2\vec{p}^2 - (\vec{r}\cdot\vec{p})^2 + i\hbar\vec{r}\cdot\vec{p} \\
&= r^2\vec{p}^2 - r^2 p_r^2 \\
p_r^2 &= \frac{1}{r^2}\left\{(\vec{r}\cdot\vec{p})^2 - i\hbar\vec{r}\cdot\vec{p}\right\} = \frac{\hbar^2}{r^2}\left\{-r\partial_r r\partial_r - r\partial_r\right\} = -\hbar^2(\partial_r^2 + \frac{2}{r}\partial_r)
\end{aligned}$$

Here we suppose $\Psi(\vec{r}) = R(r)Y_{lm}(\theta,\phi)$, the Schroedinger equation may give

$$\begin{aligned} \left\{ -\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) \right. &+& \left. \frac{\ell(\ell+1)}{r^2} + U(r) \right\} R_\ell(r) = k^2 R_\ell(r) \\ \frac{\hbar^2 k^2}{2m} &=& E, \quad \frac{\hbar^2}{2m} U(r) = V(r) \end{aligned}$$

Especially in the case where the potential employs the constant $V = V_0$, we define $x = kr,\ E - V_0 = \frac{\hbar^2 k^2}{2m}$, and write

$$\left\{ \left(\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}\right) + 1 - \frac{\ell(\ell+1)}{x^2} \right\} F_\ell(x) = 0$$

This equation is caled the spherical Bessel equation, and its second-order of the differntial equation has two independent solutions. [45] General solutions of the Schroedinger equaiton can be obtained by using those two independent solutions, and written

$$\Psi(\vec{r}) = \sum_{\ell m} c_{\ell m} R_\ell(r) Y_{\ell m}(\theta,\phi), \quad E = \frac{\hbar^2 k^2}{2m}$$

Here we summarize the requirements for the radial of the wavefunction R_ℓ.

- Behavior at origin periphery

  Where $V(r)$ has no uniqueness at origin periphery [46]

$$R_\ell(kr) \overset{\vec{r}\to 0}{\longrightarrow} (kr)^\ell$$

- Conservation

[45] Either the pairs of the spherical Bessel function $j_\ell(x)$ and the spherical Neumann function $n_\ell(x)$, or the Hankel function of the first kind $h_\ell^{(1)}(x)$ and the Hankel function of the second kind $h^{(2)}\ell(x)$, can be used as the independent solutions.

$$F_\ell(x) = A_\ell j_\ell(x) + B_\ell n_\ell(x) = C_\ell h_\ell^{(1)}(x) + D_\ell h_\ell^{(2)}(x)$$

and more specifically given

$$\begin{aligned} j_\ell(x) &=& (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \left(\frac{\sin x}{x}\right) \overset{x\to 0}{\longrightarrow} \frac{x^\ell}{(2\ell+1)!!} \\ n_\ell(x) &=& -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \left(\frac{\cos x}{x}\right) \overset{x\to 0}{\longrightarrow} -\frac{(2\ell-1)!!}{x^{\ell+1}} \end{aligned}$$

[46] Let us suppose $R_\ell \sim r^n$ at the origin periphery, the Schoedinger equation may give $\{-n(n-1) - 2n + \ell(\ell+1)\}r^{n-2} \sim 0$. From which, we write

$$-n^2 - n + \ell^2 + \ell = (\ell - n)(\ell + n + 1) = 0$$

This gives r^ℓ,and $\frac{1}{r^{\ell+1}}$ yat, the probability amplitude is required not to diverge at the origin.

Especially the case where the potential is the real [47]

$$\det\begin{pmatrix} rR_\ell & rR_\ell^* \\ (rR_\ell)' & (rR_\ell^*)' \end{pmatrix} = 0$$

This becomes the conserved quantity; independent of the coordinate systems. (Consider where $r \to 0$)

2.4.2 Phase Shift

We now consider the potential that is resticted to the finite region. In this case, the region with no potential possesses the free particles, and the wavefunction can be written [48]

$$\Psi(\vec{r}) = \sum_\ell A_\ell \{ S_\ell h_\ell^{(1)}(kr) + h_\ell^{(2)}(kr) \} P_\ell(\cos\theta)$$

---

[47]Suppose we define, $R(x) = x^n \mathcal{R}(x)$ we can write, $R' = nx^{n-1}\mathcal{R} + x^n\mathcal{R}'$, $R'' = n(n-1)x^{n-2}\mathcal{R} + 2nx^{n-1}\mathcal{R}' + x^n\mathcal{R}''$ which giving

$$R'' + 2x^{-1}R' = n(n-1)x^{n-2}\mathcal{R} + 2nx^{n-1}\mathcal{R}' + x^n\mathcal{R}'' + 2nx^{n-2}\mathcal{R} + 2x^{n-1}\mathcal{R}' = x^n\mathcal{R}'' + 2(1+n)x^{n-1}\mathcal{R}' + \cdots$$

If we take $R(x) = x^{-1}\mathcal{R}(x)$, there are no first order differntials for the differntial equation of $\mathcal{R}$ so, Wronskians will be invariable when solutions for the differential equation be $\mathcal{R}_1$, and $\mathcal{R}_2$. Especially in this case, we consider the Wronskians of R and R^* for the real potential, giving

$$\det\begin{pmatrix} rR & rR^* \\ (rR)' & (rR^*)' \end{pmatrix}$$

This does not depend on the coordinate system

[48]The point of measurement for the angle of ϕ can be selected at any points, and therefore, the wavefunction does not depend on ϕ but, depends only on $Y_{\ell m=0}$.

. Let us first define the amplitude A_ℓ of each partial wave as we consider the asymptotic conditions for the point where infinite distance away. We can write [49]

$$\begin{aligned}
\Psi(\vec{r}) &= \frac{1}{(2\pi)^{3/2}} \sum_{\ell=0}^{\infty} \frac{(2\ell+1)}{2} i^\ell \big\{ S_\ell h_\ell^{(1)}(kr) + h_\ell^{(2)}(kr) \big\} P_\ell(\cos\theta) \\
&\longrightarrow \sum_\ell \frac{1}{(2\pi)^{3/2}} \frac{-i(2\ell+1)}{2} \frac{1}{kr} \big\{ S_\ell e^{ikr} - (-1)^\ell e^{-ikr} \big\} P_\ell(\cos\theta)
\end{aligned}$$

[49] The asymptotic form for a large argument can be written

$$j_\ell(x) \stackrel{x\to\infty}{\longrightarrow} \frac{1}{x} \sin\big(x - \frac{\ell\pi}{2}\big), \qquad n_\ell(x) \stackrel{x\to\infty}{\longrightarrow} -\frac{1}{x} \cos\big(x - \frac{\ell\pi}{2}\big)$$

$$h_\ell^{(1)}(x) \stackrel{x\to\infty}{\longrightarrow} (-i)^{\ell+1} \frac{e^{ix}}{x} \qquad h_\ell^{(2)}(x) \stackrel{x\to\infty}{\longrightarrow} (i)^{\ell+1} \frac{e^{-ix}}{x}$$

giving,

$$\Psi(\vec{r}) \longrightarrow \sum_\ell A_\ell \frac{(-i)^{\ell+1}}{kr} \big\{ S_\ell e^{ikr} - (-1)^\ell e^{-ikr} \big\} P_\ell(\cos\theta)$$

We expand the scattering amplitude in terms of the complete set $f(\theta) = \sum_{\ell=0}^{\infty} a_\ell P_\ell(\cos\theta)$, and further expand the incident wave in terms of the partial wave as following

$$e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty} (2\ell+1) i^\ell j_\ell(kr) P_\ell(\cos\theta)$$

$$j_\ell(x) \stackrel{x\to\infty}{\longrightarrow} \frac{1}{x} \sin\big(x - \frac{\ell\pi}{2}\big) = \frac{1}{2ix}\big(e^{ix - i\frac{\ell\pi}{2}} - e^{-ix + i\frac{\ell\pi}{2}}\big) = \frac{1}{2ix}\big((-i)^\ell e^{ix} - i^\ell e^{-ix}\big)$$

From the above, we can express the expansion of the boundary condition at infinity point in terms of the Partial wave in the followin form

$$\begin{aligned}
& \frac{1}{(2\pi)^{3/2}} \left(e^{ikr\cos\theta} + \frac{f(\theta)}{r} e^{ikr} \right) \\
&= \frac{1}{(2\pi)^{3/2}} \frac{1}{2ikr} \sum_{\ell=0}^{\infty} \left\{ (2\ell+1) i^\ell \big((-i)^\ell e^{ikr} - i^\ell e^{-ikr}\big) + 2ika_\ell e^{ikr} \right\} P_\ell(\cos\theta) \\
&= \frac{1}{(2\pi)^{3/2}} \frac{1}{2ikr} \sum_{\ell=0}^{\infty} (2\ell+1) \left\{ \big(1 + \frac{2ika_\ell}{(2\ell+1)}\big) e^{ikr} - (-)^\ell e^{-ikr} \right\} P_\ell(\cos\theta)
\end{aligned}$$

Compare the two equqaions from above and write

$$a_\ell = \frac{(2\ell+1)}{2ik}(S_\ell - 1)$$

$$A_\ell \frac{(-i)^{\ell+1}}{kr} = \frac{1}{(2\pi)^{3/2}} \frac{(2\ell+1)}{2ikr}$$

Thus,

$$A_\ell = \frac{1}{(2\pi)^{3/2}} \frac{(2\ell+1)}{2} i^\ell$$

We use S_ℓ to write the scattering amplitude as

$$f(\theta) = \frac{1}{2ik}\sum_{\ell=0}^{\infty}(2\ell+1)(S_\ell - 1)P_\ell(\cos\theta)$$

Note that this undefined coefficient S_ℓ is called the scattering matrix, which can be difined by the boundary condition of a region with a presence of the potential. We precede the rest of our discussion based on that we assume having defined the coefficient.

Now we apply the conservation law from our earlier discussion to each partial wave ℓ of the radial part, which corresponds to the conservation law for the number of the particle, and gives [50]

$$|S_\ell| = 1$$

Thus,

$$S_\ell = e^{i2\delta_\ell}, \quad \delta\text{: real}$$

Rewrite the asymptotic form as [51]

$$\Psi(\vec{r}) \longrightarrow \frac{1}{(2\pi)^{3/2}}\sum_\ell \frac{(2\ell+1)}{kr} i^\ell e^{i\delta_\ell}\sin(kr - \frac{\pi}{2}\ell + \delta_\ell)P_\ell(\cos\theta)$$

Compare the above with the asymptotic form for no potential,

$$\frac{1}{(2\pi)^{3/2}}e^{ikr\cos\theta} = \frac{1}{(2\pi)^{3/2}}\sum_{\ell=0}^{\infty}\frac{(2\ell+1)}{kr}i^\ell \sin(kr - \frac{\pi}{2}\ell)P_\ell(\cos\theta)$$

This makes us aware that there is a shift in the phase, and the shift occurred as much as δ_ℓ. δ_ℓ is called the phase shift.

50

$$\begin{aligned} 0 &= \det\begin{pmatrix} S_\ell e^{ikr} - (-1)^\ell e^{-ikr} & S_\ell^* e^{-ikr} - (-1)^\ell e^{ikr} \\ ikS_\ell e^{ikr} + ik(-1)^\ell e^{-ikr} & -ikS_\ell^* e^{-ikr} - ik(-1)^\ell e^{ikr} \end{pmatrix} \\ &= \det\begin{pmatrix} S_\ell e^{ikr} - (-1)^\ell e^{-ikr} & S_\ell^* e^{-ikr} - (-1)^\ell e^{ikr} \\ 2ik(-1)^\ell e^{-ikr} & -2ikS_\ell^* e^{-ikr} \end{pmatrix} \\ &= \det\begin{pmatrix} S_\ell e^{ikr} - (-1)^\ell e^{-ikr} & \{|S_\ell|^2 - 1\}(-1)^\ell e^{ikr} \\ 2ik(-1)^\ell e^{-ikr} & 0 \end{pmatrix} = -2ik\{|S_\ell|^2 - 1\} \end{aligned}$$

51

$$\begin{aligned} e^{i(2\delta_\ell + kr)} - e^{i(\pi\ell - kr)} &= e^{i(\delta_\ell + \frac{\pi}{2}\ell)}(e^{i(\delta_\ell + kr - \frac{\pi}{2}\ell)} - e^{i(-\delta_\ell + \frac{\pi}{2}\ell - kr)}) \\ &= e^{i(\delta_\ell + \frac{\pi}{2}\ell)}2i\sin(kr - \frac{\pi}{2}\ell + \delta_\ell) \end{aligned}$$

The total scattering cross section satisfies [52]

$$\sigma_T = \frac{4\pi}{k} f(0) = \sum_\ell \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell$$

This first equation is called the optical theorem. We understand that when $\delta_\ell = (n+\frac{1}{2})\pi, n$: (integer), the scattering cross section of ℓ becomes the largest, while the area becomes 0 when $\delta_\ell = n\pi$.

2.4.3 Lograrithmic Differntiation and the Phase Shift

In determining the phase shift more exactly, let us first consider the junction conditions for the wavefunction within the radius $r = a$ and the wavefunction in radius part; outside the radius, by each partial wave.

$$\begin{aligned} R_\ell^{in}(a) &= R_\ell^{out}(a) \\ R_\ell^{in\prime}(a) &= R_\ell^{out\prime}(a) \end{aligned}$$

We can write the wavefunction of the outer part as

$$R_\ell^{out}(r) = C(S_\ell h_\ell^{(1)}(kr) + h_\ell^{(2)}(kr))$$

Since the noemalization factor C is unknown, the condition we can obtain now is

$$\left.\frac{d\log R_\ell^{in}(r)}{dr}\right|_{r=a} = \left.\frac{d\log R_\ell^{out}(r)}{dr}\right|_{r=a} = k\frac{S_\ell h_\ell^{(1)\prime}(ka) + h_\ell^{(2)\prime}(ka)}{S_\ell h_\ell^{(1)}(ka) + h_\ell^{(2)}(ka)}$$

Here we have

$$h^{(1,2)\prime}(ka) = \left.\frac{dh^{(1,2)}(x)}{dx}\right|_{x=ka}$$

from which we write the effects of the potential for the inner part

$$f_\ell^{in} = \frac{1}{k}\left.\frac{d\log R_\ell^{in}(r)}{dr}\right|_{r=a}$$

[52]

$$\begin{aligned} \sigma_T &= \int d\Omega |f(\theta)|^2 = \frac{1}{4k^2}\sum_\ell (2\ell+1)^2|S_\ell - 1|^2 2\pi \frac{2}{(2\ell+1)} \\ &= \frac{\pi}{k^2}\sum (2\ell+1)|S_\ell - 1|^2 \end{aligned}$$

$$\begin{aligned} f(0) &= \frac{f(0) - f^*(0)}{2i} = \frac{1}{2i}\frac{1}{2ik}\sum (2\ell+1)(S_\ell + S_\ell^* - 2)P_\ell(\cos\theta) \\ &= -\frac{1}{4k}\sum_\ell (2\ell+1)(-1)(1-S_\ell)(1-S_\ell^*) = \frac{1}{4k}\sum_\ell (2\ell+1)|1-S_\ell|^2 = \frac{1}{4k}4\sum_\ell (2\ell+1)\sin^2\delta_\ell \end{aligned}$$

We parametralize the above to write

$$S_\ell = -\frac{h_\ell^{(2)}(ka) f_\ell^{in} - h_\ell^{(2)'}(ka)}{h_\ell^{(1)}(ka) f_\ell^{in} - h_\ell^{(1)'}(ka)}$$

While we have [53]

$$\tan\delta_\ell = \frac{j_\ell(ka) f_\ell^{in} - j'_\ell(ka)}{n_\ell(ka) f_\ell^{in} - n'_\ell(ka)}$$

This indicates that the wavefunction in the outer oart region is defined only by the logarithmic differntiation of the boundary of the scattering region, and not by the details of the potential.

The Low Energy Scattering

In the case for the low energy scattering

$$ka << 1$$

This gives [54] [55]

$$\delta_\ell \propto (ka)^2 \quad \ell = 0 (ka)^{2\ell+1} \quad \ell \geq 1$$

Thus, [56]

$$f(\theta) = \frac{\delta_0}{k}$$

53

$$\tan\delta_\ell = \frac{1}{i}\frac{S_\ell - S_\ell^*}{S_\ell + S_\ell^* + 2}$$

54

$$\begin{aligned}
\tan\delta_\ell &\to -\frac{1}{(2\ell+1)!!(2\ell-1)!!}(ka)^{2\ell+1}\frac{f_\ell^{in} - \ell/(ka)}{f_\ell^{in} + (\ell+1)/(ka)} \\
&= -\frac{1}{(2\ell+1)!!(2\ell-1)!!}\frac{ka f_\ell^{in} - \ell}{ka f_\ell^{in} + \ell + 1}(ka)^{2\ell+1} \\
&\propto (ka)^2 \quad \ell = 0 (ka)^{2\ell+1} \quad \ell \geq 1
\end{aligned}$$

55 This does not apply hor the hard sphere.

56

$$\begin{aligned}
f(\theta) &= \frac{1}{2ik}\sum_{\ell=0}^{\infty}(2\ell+1)(S_\ell - 1)P_\ell(\cos\theta) \\
&\to \frac{1}{2ik}2i\delta_0 = \frac{\delta_0}{k}
\end{aligned}$$

The Hard Sphere Case

Suppose we have a hard sphere of radius $r = a$ we can assume $R(a) = 0$ when $r = a$, and written

$$f_\ell^{in} = \infty$$

Based on the above, we can write

$$\tan \delta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)}$$

Here in particular, we consider the low energy case where $ka << 1$, and using the asymptotic form, which gives [57]

$$\tan \delta_\ell = -\frac{(ka)^{2\ell+1}}{(2\ell+1)!!(2\ell-1)!!}$$

2.4.4 Jost Function and the Bound States

The equation for the partial wave of the radius part in terms of

$$\mathcal{R}(r) = rR(r)$$

can be written as we discussed earlier,

$$\mathcal{R}'' - \left(U(r) + \frac{\ell(\ell+1)}{r^2} \right) \mathcal{R} = -k^2 \mathcal{R}$$

The first order differential terms are absent in the equation above, and that the Wronskians for the equation will become the conserved quantity. Now, let us consider the solutions, which satisfy the three different boundary conditions.

- Solutions in physical term

  Require the regularity at the origin to have normalization

  $$\mathcal{R} = \psi^\ell(k, r) \to r^{\ell+1} \quad (r \to 0)$$

  This is the solution, which we have been discussing expect for the normalization.

57

$$j_\ell(x) \overset{x \to 0}{\to} \frac{x^\ell}{(2\ell+1)!!}$$

$$n_\ell(x) \overset{x \to 0}{\to} -\frac{(2\ell-1)!!}{x^{\ell+1}}$$

- Jost solution

$$\mathcal{R} = f^\ell_\pm(k,r) \to e^{\pm ikr} \quad (k>0, \quad r \to \infty)$$

Here we calculate the Wronskians among these solutions, which giving the conserved quantity for all. Thus, solution is independent of the coordinate systems [58]

$$W(f^\ell_+(k,r), f^\ell_-(k,r)) = -2ik$$

Now, let us write down

$$W(f^\ell_\pm(k,r), \psi^\ell(k,r)) = f^\ell_\pm(k)$$

in which we call

$$f^\ell_\pm(k)$$

the Jost function.

Given the function is the second order, the solution for the physical terms can be multiplied by the Jost solution. Whose coefficient can be given by the Jost function in the form,

$$\psi^\ell(k,r) = \frac{-i}{2k}\{f^\ell_-(k) f^\ell_+(k,r) - f^\ell_+(k) f^\ell_-(k,r)\}$$

Furthermore, we consider the asymptotic form of the solution in the physical terms, and which bein compared with the definition of the scatterin matrix to give [59]

$$f^\ell_\pm(k) = (\pm)^\ell f^\ell(k) e^{\mp i\delta_\ell(k)}$$

Note that

$$S_\ell = (-1)^\ell \frac{f^\ell_-}{f^\ell_+}$$

58

$$W(f^\ell_+(k,r), f^\ell_-(k,r)) = \det\begin{pmatrix} f_+ & f_- \\ f'_+ & f'_- \end{pmatrix} = \det\begin{pmatrix} e^{ikr} & e^{-ikr} \\ ike^{ikr} & -ike^{-ikr} \end{pmatrix} = \det\begin{pmatrix} e^{ikr} & e^{-ikr} \\ 2ike^{ikr} & 0 \end{pmatrix} = -2ik$$

59

$$\psi^\ell(k,r) = \frac{-if^\ell_+(k)}{2k}\left(\frac{f^\ell_-}{f^\ell_+}e^{ikr} - e^{-ikr}\right) \qquad (r \to \infty)$$

The definition of the scattering matrix gives

$$S_\ell = (-1)^\ell \frac{f^\ell_-}{f^\ell_+}$$

Thus,

$$f^\ell_\pm(k) = (\pm i)^\ell f^\ell(k) e^{\mp i\delta_\ell(k)}$$

We consider carrying out the analytic continuation of the wave number k to reach the comlex number with the real energy, we have て

$$k = i\kappa, \qquad \kappa > 0$$

Whose physical terms solution can be

$$\psi(i\kappa, r) \to f^{\ell}_{-}(i\kappa)e^{-\kappa r} - f^{\ell}_{+}(i\kappa)e^{\kappa r}$$

As long as we have

$$f^{\ell}_{+}(k = i\kappa) = 0$$

The solution can be normalized in the whole space thus; the solution represents the bound state. the above equation also indicates that the scattering mtrix possesses the polar in the bound state energy.

$$\frac{1}{S(k = i\kappa)} = 0$$

Since the potential is real, the following symmetric properties are being also obeyed.

- $\psi^{\ell}(k, r) = \psi^{\ell}(-k, r) = \psi^{\ell *}(k, r)$
- $f^{\ell}_{+}(k, r) = f^{\ell}_{-}(-k, r)$ thus giving $f^{\ell}_{+}(k) = f^{\ell}_{-}(-k)$
- $f^{\ell\,*}_{+}(k, r) = f^{\ell}_{-}(k, r)$ giving $f^{\ell\,*}_{+}(k) = f^{\ell}_{-}(k)$

In our discussion of carrying the analytic continuations of the Jost function and the phase shift on the complexplanes, we can observe that the number of the bound states is defined by the phase shift analysis. This we call, Levinson's theorem.

The S-wave Scattering in the Three-dimentional Square Well Potential

Now we consider the function that the wavefunction $\mathcal{R} = rR$ satisfies, and consider especially the case for the s-waves $\ell = 0$.

$$\mathcal{R}'' + (k^2 - U(r))\mathcal{R} = 0$$

For the square well potential we suppose

$$U(x) = \begin{cases} U_0 & r \leq a \\ 0 & \text{otherwise} \end{cases}$$

and we define

$$K^2 = k^2 - U_0$$

Which gives [60]

$$f_0^{in} = \frac{1}{ka}(Ka\cot Ka - 1)$$

Thus, [61]

$$\tan\delta_0 = \frac{ka\cot ka - Ka\cot Ka}{ka + Ka\cot Ka\cot ka}$$

Under the low energy $ka << 1$, we can write [62]

$$\tan\delta_0 = ka\,\frac{1 - a\sqrt{-U_0}\cot a\sqrt{-U_0}}{a\sqrt{-U_0}\cot a\sqrt{-U_0}}$$

For the hard sphere, we have $U_0 \to \infty$, which gives

$$\tan\delta_0 = -ka$$

This matches with our first result. Generally speaking, we may expand the equation above about $a\sqrt{-U_0}$ if we have the potential that is very weak. So, we have

[60] Require the boundary condition

$$\mathcal{R}|_{r=0} = rR|_{r=0} = 0$$

Thus, we write

$$\begin{aligned}
\mathcal{R} &= C\sin Kr \\
\frac{d\log R}{dr} &= \frac{d\log(r^{-1}\mathcal{R})}{r} = -\frac{1}{r} + K\frac{\cos Kr}{\sin Kr} \\
f_0^{in} &= \frac{1}{k}\frac{d\log R}{dr}\bigg|_{r=a} = \frac{1}{ka}(Ka\cot Ka - 1)
\end{aligned}$$

[61]

$$j_0(x) = \frac{\sin x}{x},\quad j_0'(x) = \frac{x\cos x - \sin x}{x^2},\quad n_0(x) = -\frac{\cos x}{x},\quad n_0'(x) = \frac{x\sin x + \cos x}{x^2},$$

From the above, we let $x = ka$, and write

$$\begin{aligned}
\tan\delta_0 &= \frac{j_0(x)f_0^{in} - j_0'(x)}{n_0(x)f_0^{in} - n_0'(x)} = \frac{\frac{\sin x}{x}\frac{1}{x}(Ka\cot Ka - 1) - \frac{x\cos x - \sin x}{x^2}}{-\frac{\cos x}{x}\frac{1}{x}(Ka\cot Ka - 1) - \frac{x\sin x + \cos x}{x^2}} \\
&= \frac{\sin x Ka\cot Ka - x\cos x}{-\cos x Ka\cot Ka - x\sin x} = \frac{ka\cot ka - Ka\cot Ka}{ka + Ka\cot Ka\cot ka}
\end{aligned}$$

[62]

$$\begin{aligned}
Ka &\overset{ka\to 0}{\to} a\sqrt{-U_0} \\
\tan\delta_0 &\overset{ka\to 0}{\to} ka\,\frac{1 - a\sqrt{-U_0}\cot a\sqrt{-U_0}}{a\sqrt{-U_0}\cot a\sqrt{-U_0}}
\end{aligned}$$

63

$$\tan\delta_0 \to -\frac{U_0 k a^3}{3} \approx \delta_0$$

In other words, the gravity may give $\delta_0 > 0$ while the repulsion may give $\delta_0 < 0$. In order to discuss the bound states by the method using the integral equation; that is inndeed the main focus of our present section, recall that we define k, which is defined by $E = \frac{\hbar^2 k^2}{2m}$ in $E < 0$ to be as k を $k \to i\kappa,\ (\kappa > 0)$:

$$\mathcal{R} \approx S_\ell h^{(1)}(kr) + h^{(2)}(kr) = S_\ell h_0^{(1)}(i\kappa r) + h_0^{(2)}(i\kappa r)$$

$$h_0^{(1)}(i\kappa r) = j_0(i\kappa r) + i n_0(i\kappa r) = \frac{e^{-\kappa r}}{i\kappa r}, \quad h_0^{(2)}(i\kappa r) = j_0(i\kappa r) - i n_0(i\kappa r) = \frac{e^{\kappa r}}{i\kappa r},$$

This clearly tells that we need

$$S_\ell \to \infty$$

for the wavefunctions that are not being normalized. We ensured that the energy in the bound state indeed gives the polar of the scattering matrix. In our specific case, we have [64]

$$\tan\delta_0 + i = 0$$

3 Time-dependent Scattering Theory

3.1 Lippmann-Schwinger Equation

In this section we aim to understand the scatering theory in the time-dependent forms, which contrasting with the scattering in the stationary states from our ealier discussions. The Schroedinger equation can be written

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle_S =& H|\Psi(t)\rangle_S \\ H =& H_0 + V \end{aligned}$$

63

$$\cot x = \frac{1}{x} - \frac{1}{3}x \cdots$$

Thus,

$$\tan\delta_0 \to ka\frac{1}{3}(a\sqrt{-U_0})^2 = -\frac{U_0 k a^3}{3}$$

64

$$S_0 = \frac{e^{i\delta_0}}{e^{-i\delta_0}} = \frac{\cot\delta_0 + i}{\cot\delta_0 - i}$$

To be careful with the formal solution at $V = 0$, and we write

$$|\Psi(t)\rangle_S = e^{-iH_0 t/\hbar}|\Psi(t)\rangle$$

This gives, ($|\Psi(t)\rangle$ is called the interaction representation) [65]

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle &= V(t)|\Psi(t)\rangle \\ V(t) &= e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} \end{aligned}$$

Given that we write

$$|\Psi(t)\rangle = U_+(t)|\Psi(-\infty)\rangle$$

Thus, [66]

$$U_+(t) = 1 + \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\, V(\tau)U_+(\tau)$$

Especially in our case, we let

$$|\Psi(+\infty)\rangle = S|\Psi(-\infty)\rangle$$

be given, and have $S = U_+(+\infty)$ thus,

$$S = 1 + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau\, V(\tau)U_+(\tau)$$

65

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle_S &= H_0 e^{-iH_0 t/\hbar}|\Psi(t)\rangle + e^{-iH_0 t/\hbar} i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = (H_0 + V)e^{-iH_0 t/\hbar}|\Psi(t)\rangle \\ i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle &= e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}|\Psi(t)\rangle \\ i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle &= V(t)|\Psi(t)\rangle \\ V(t) &= e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} \end{aligned}$$

66

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}U_+(t) &= V(t)U_+(t) \\ U_+(-\infty) &= 1 \end{aligned}$$

In the integral form we have

$$U_+(t) = 1 + \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\, V(\tau)U_+(\tau)$$

We now consider a case where the interactoin vanishes adiabatically at $t \to \pm\infty$ to have $H \to H_0$. For that we suppose

$$V(t) \to V(t)e^{-0|t|/\hbar} = V^{\epsilon}(t)$$

Under such condition, we take the eigenstate $|\Phi_i\rangle = \frac{1}{\sqrt{(2\pi)^3}} e^{i\boldsymbol{k}_i \cdot \boldsymbol{r}}$ for H_0 for the initial state. [67] [68] Which we write

$$\begin{aligned}|\Psi(-\infty)\rangle =&|\Phi_i\rangle \\ H_0|\Phi_i\rangle =&E_i|\Phi_i\rangle \\ \langle\Phi_i|\Phi_j\rangle =&1_{ij} = \delta(\boldsymbol{k}_i - \boldsymbol{k}_j)\end{aligned}$$

We write the transition probability W_{ji} at $t : -\infty \to +\infty$ as

$$W_{ji} = |\langle\Phi_j|S\Phi_i\rangle|^2 = |S_{ji}|^2$$

Here we define

$$T = S - 1$$

which gives

$$\begin{aligned}i \neq j, \quad W_{ji} = |T_{ji}|^2 \\ T_{ji} =& \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau \, \langle\Phi_j|V^{\epsilon}(\tau)U_{+}^{\epsilon}(\tau)|\Phi_i\rangle \\ =& \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau \, e^{iE_j\tau/\hbar}\langle\Phi_j|Ve^{-iH_0\tau/\hbar}e^{-0|\tau|/\hbar}U_{+}(\tau)|\Phi_i\rangle\end{aligned}$$

Thus, we can write

$$|\Psi_i^{(+)}(E)\rangle = \int_{-\infty}^{\infty} d\tau \, e^{i(E-H_0)\tau/\hbar}e^{-0|\tau|/\hbar}U_{+}(\tau)|\Phi_i\rangle$$

This equation yields,

$$T_{ji} = \frac{1}{i\hbar}\langle\Phi_j|V|\Psi_i^{(+)}(E_j)\rangle$$

---

[67] The wavefunction for the interaction representation at $V = 0$ will be the wavefunction for the stationary states.

[68]

$$\langle\Phi_i|\Phi_j\rangle = \frac{1}{(2\pi)^3}\int d\boldsymbol{r} \, e^{-i(\boldsymbol{k}_i - \boldsymbol{k}_j)\cdot\boldsymbol{r}} = 1_{ij} = \delta(\boldsymbol{k}_i - \boldsymbol{k}_j)$$

The integral equation for U_+ gives [69] [70]

---

[69]

$$
\begin{aligned}
|\Psi_i^{(+)}(E)\rangle &= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar}\left(\int_{-\infty}^{\tau} d\tau'\, V^{\epsilon}(\tau')U_+^{\epsilon}(\tau')\right)|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau' \int_{\tau'}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} V^{\epsilon}(\tau')U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau' \int_{\tau'}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} e^{-0|\tau'|/\hbar} e^{iH_0\tau'/\hbar} V e^{-iH_0\tau'/\hbar} U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau' e^{-0|\tau'|/\hbar} \int_{\tau'}^{\infty} d\tau e^{-0|\tau|/\hbar}\, e^{i(E-H_0)\tau/\hbar} e^{iH_0\tau'/\hbar} V e^{-iH_0\tau'/\hbar} U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau' e^{-0|\tau'|/\hbar} \int_{\tau'}^{\infty} d\tau e^{-0|\tau|/\hbar}\, e^{i(E-H_0)(\tau-\tau')/\hbar} V e^{i(E-H_0)\tau'/\hbar} U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau' e^{-0|\tau'|/\hbar} \int_{0}^{\infty} d\tau e^{-0|\tau|/\hbar}\, e^{i(E-H_0)\tau/\hbar} V e^{i(E-H_0)\tau'/\hbar} U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{0}^{\infty} d\tau e^{-0|\tau|/\hbar}\, e^{i(E-H_0)\tau/\hbar} V \int_{-\infty}^{\infty} d\tau' e^{-0|\tau'|/\hbar}\, e^{i(E-H_0)\tau'/\hbar} U_+^{\epsilon}(\tau')|\Phi_i\rangle \\
&= \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
&\quad + \frac{1}{i\hbar}\int_{0}^{\infty} d\tau e^{-0\tau/\hbar}\, e^{i(E-H_0)\tau/\hbar} V |\Psi_i^{(+)}(E)\rangle
\end{aligned}
$$

[70] Recall the definition of the delta function

$$
\begin{aligned}
\frac{1}{x \pm i0} &= P\frac{1}{x} \mp i\pi\delta(x) \\
\delta(x) &= -\frac{1}{2\pi i}\left(\frac{1}{x+i0} - \frac{1}{x-i0}\right) = \frac{1}{\pi}\mathrm{Im}\,\frac{1}{x-i0}
\end{aligned}
$$

$$
\begin{aligned}
|\Psi_i^{(+)}(E)\rangle = & \int_{-\infty}^{\infty} d\tau\, e^{i(E-E_i)\tau/\hbar} e^{-0|\tau|/\hbar} |\Phi_i\rangle \\
& + \frac{1}{i\hbar} \int_0^{\infty} d\tau e^{-0\tau/\hbar}\, e^{i(E-H_0)\tau/\hbar} V |\Psi_i^{(+)}(E)\rangle \\
= & 2\pi\hbar\delta(E-E_i)|\Phi_i\rangle + \frac{1}{E+i0-H_0} V |\Psi_i^{(+)}(E)\rangle
\end{aligned}
$$

We can write the eqution above in the form

$$
|\Psi_i^{(+)}(E)\rangle = 2\pi\hbar\delta(E-E_i)|\Psi_i^{(+)}\rangle \qquad (*)
$$

This enables us to derive the Lippmann-Schwinger equation

$$
|\Psi_i^{(+)}\rangle = |\Phi_i\rangle + \frac{1}{E+i0-H_0} V |\Psi_i^{(+)}\rangle
$$

Note that $(*)$ is [71]

$$
e^{-iH_0 t/\hbar} U_+(t)|\Phi_i\rangle = e^{-iE_i t/\hbar} |\Psi_i^{(+)}\rangle
$$

The left-hand side of the equation above represents the wavefunction for the Schroedinger representation, while we regard $|\Psi_i^{(+)}\rangle$ as the wavefunction for the stationary states. [72]

$$
\int_0^{\infty} d\tau\, e^{-0\,\tau/\hbar + i(E-H_0)\tau/\hbar} = \int_0^{\infty} d\tau\, e^{i(E+i0-H_0)\tau/\hbar} = -\frac{\hbar}{i} \frac{1}{E+i0-H_0} = -\frac{\hbar}{i}\left(P\frac{1}{E-H_0} - i\pi\delta(E-H_0)\right)
$$

[71]

$$
\begin{aligned}
|\Psi_i^{(+)}(E)\rangle = & \int_{-\infty}^{\infty} d\tau\, e^{i(E-H_0)\tau/\hbar} U_+(\tau)|\Phi_i\rangle \\
= & \int_{-\infty}^{\infty} d\tau\, e^{i(E-E_i)\tau/\hbar} |\Psi_i^{(+)}\rangle \\
e^{-iH_0\tau/\hbar} U_+(\tau)|\Phi_i\rangle = & e^{-iE_i\tau/\hbar} |\Psi_i^{(+)}\rangle
\end{aligned}
$$

[72]The relationship between the state vector $|\Psi(t)\rangle$ in the interaction representation and the state vector $|\Psi(t)\rangle_S$ in the Schroedinger representation gives

$$
e^{-iH_0 t/\hbar} U_+(t)|\Phi_i\rangle = e^{-iH_0 t/\hbar} |\Psi_i(t)\rangle = |\Psi_i(t)\rangle_S = e^{-iE_i t/\hbar} |\Psi_i^{(+)}\rangle
$$

In our last discussion, we let $|\Psi_i(t)\rangle$ prossess the same energy E_i of $|\Phi_i\rangle$. Precisely, we consider the system in the box with the length of each ede to be L. The interaction is adiabactically applied slower than the energy resolution occurring the same time. We assume the interaction to take the limit of $L \to \infty$ knowing that the interaction may give the energy hift of about $1/L^3$ from the fact that the potential is much local.

3.2 Optical Theory

We further write [73]

$$\begin{aligned} T_{ji} \equiv& -2\pi i\delta(E_i - E_j)\boldsymbol{T}_{ji} togive \\ \boldsymbol{T}_{ji} =& \langle\Phi_j|V|\Psi_i^{(+)}\rangle \end{aligned}$$

The scattering probability for $i \to j$ per unit of time can be written [74]

$$w_{ji} = \frac{2\pi}{\hbar}\delta(E_i - E_j)|\boldsymbol{T}_{ji}|^2$$

If the equation above is approximated by $|\Psi_i^{(+)}\rangle \approx |\Phi_i\rangle$, which will be called the Fermi's golden rule.

We write the Green's function first;

$$\begin{aligned} G_0^+ =& \frac{1}{E + i0 - H_0} \\ G^+ =& \frac{1}{E + i0 - H} = \frac{1}{E + i0 - H_0 - V} = [(G_0^+)^{-1} - V]^{-1} = [(1 - VG_0^+)G_0^{+-1}]^{-1} \\ =& G_0^+(1 - VG_0^+)^{-1} = G_0^+ + G_0^+(VG_0^+) + G_0^+(VG_0^+)^2 + \cdots \\ =& G_0^+ + (G_0^+V)G_0^+ + (G_0^+V)^2G_0^+ + \cdots = (1 - G_0^+V)^{-1}G_0^+ \end{aligned}$$

73

$$\begin{aligned} |\Psi_i^{(+)}(E)\rangle =& 2\pi\hbar\delta(E - E_i)|\Psi_i^{(+)}\rangle \\ T_{ji} =& \frac{1}{i\hbar}\langle\Phi_i|V|\Psi_i^{(+)}(E_j)\rangle \\ =& -2\pi i\delta(E_j - E_i)\boldsymbol{T}_{ji} gives \\ \boldsymbol{T}_{ji} =& \langle\Phi_j|V|\Psi_i^{(+)}\rangle \end{aligned}$$

74

$$\begin{aligned} W_{ji} =& 4\pi^2\big(\delta(E_i - E_j)\big)^2|\boldsymbol{T}_{ji}|^2 \\ =& 4\pi^2\delta(E_i - E_j)|\boldsymbol{T}_{ji}|^2(\frac{1}{2\pi\hbar})\int_{-\infty}^{\infty} d\tau\, e^{i(E_i - E_j)\tau/\hbar} \\ =& \frac{2\pi}{\hbar}\delta(E_i - E_j)|\boldsymbol{T}_{ji}|^2\int_{-\infty}^{\infty} d\tau\, 1 \\ w_{ji} =& \frac{W_{ji}}{\int_{-\infty}^{\infty} d\tau\, 1} = \frac{2\pi}{\hbar}\delta(E_i - E_j)|\boldsymbol{T}_{ji}|^2 \end{aligned}$$

Here we rewrite the Lippmann-Schwinger equation:

$$
\begin{aligned}
|\Psi_i^{(+)}\rangle =&|\Phi_i\rangle + G_{0,i}^{(+)}V|\Psi_i^{(+)}\rangle = (1+G_{0,i}^{+}V + (G_{0,i}^{+}V)^2+\cdots)|\Phi_i\rangle = (1+G_i^{+}V)|\Phi_i\rangle,\\
&G_{0,i}^{+} = G_0^{+}(E_i),\ G_i^{+} = G^{+}(E_i)\\
V|\Psi_i^{(+)}\rangle =&V(1+G_i^{+}V)|\Phi_i\rangle \equiv T(E_i)|\Phi_i\rangle\\
T(E) =&V(1+G^{+}(E)V)\\
|\Psi_i^{(+)}\rangle =&\big(1+G_0^{+}(E_i)T(E_i)\big)|\Phi_i\rangle
\end{aligned}
$$

Since $|\Psi_i^{(+)}\rangle$ and $|\Phi_i\rangle$ are linked by a unitary transformation, we can write

$$
\langle\Psi_j^{(+)}|\Psi_i^{(+)}\rangle =\langle\Phi_j|\Phi_i\rangle
$$

While we can write

$$
\boldsymbol{T}_{ji} =\langle\Phi_j|V|\Psi_i^{(+)}\rangle = \langle\Phi_j|T_i|\Phi_i\rangle
$$

which yields to

$$
\langle\Psi_j^{(+)}|\Psi_i^{(+)}\rangle =\langle\Phi_j|\Phi_i\rangle + \langle\Phi_j|G_{0i}^{+}T_i|\Phi_i\rangle + \langle\Phi_j|T_j^{*}G_{0,j}^{+*}|\Phi_i\rangle + \langle\Phi_j|T_j^{*}G_{0,j}^{+*}G_{0,i}^{+}T_i|\Phi_i\rangle
$$

Thus, [75]

$$
-\mathrm{Im}\,\boldsymbol{T}_{ii} =\pi\sum_k \delta(E_i-E_k)|\boldsymbol{T}_{ik}|^2
$$

---

[75]

$$
\begin{aligned}
0 =&\frac{1}{E_i-E_j+i0}\langle\Phi_j|T_i|\Phi_i\rangle + \frac{1}{E_j-E_i-i0}\langle\Phi_j|T_j^{*}|\Phi_i\rangle\\
&+\sum_k\langle\Phi_j|T_j^{*}G_{0,j}^{+*}|\Phi_k\rangle\langle\Phi_k|G_{0,i}^{+}T_i|\Phi_i\rangle\\
=&\frac{1}{E_i-E_j+i0}\langle\Phi_j|T_i|\Phi_i\rangle + \frac{1}{E_j-E_i-i0}\langle\Phi_j|T_j^{*}|\Phi_i\rangle\\
&+\sum_k\frac{1}{E_j-E_k-i0}\frac{1}{E_i-E_k+i0}\langle\Phi_j|T_j^{*}|\Phi_k\rangle\langle\Phi_k|T_i|\Phi_i\rangle\\
=&\left(P\frac{1}{E_i-E_j}-i\pi\delta(E_i-E_j)\right)(\boldsymbol{T}_{ji}-\boldsymbol{T}_{ij}^{*})\\
&+\frac{1}{E_j-E_i-i0}\sum_k\left(\frac{1}{E_i-E_k+i0}-\frac{1}{E_j-E_k-i0}\right)\boldsymbol{T}_{kj}^{*}\boldsymbol{T}_{ki}\\
=&\left(P\frac{1}{E_i-E_j}-i\pi\delta(E_i-E_j)\right)(\boldsymbol{T}_{ji}-\boldsymbol{T}_{ij}^{*})\\
&+\frac{1}{E_j-E_i-i0}\sum_k\left(P\frac{1}{E_i-E_k}-P\frac{1}{E_j-E_k}-i\pi\big(\delta(E_i-E_k)+\delta(E_j-E_k)\big)\right)\boldsymbol{T}_{kj}^{*}\boldsymbol{T}_{ki}\\
=&\left(P\frac{1}{E_i-E_j}-i\pi\delta(E_i-E_j)\right)(\boldsymbol{T}_{ji}-\boldsymbol{T}_{ij}^{*})\\
&-\left(P\frac{1}{E_i-E_j}-i\pi\delta(E_i-E_j)\right)\sum_k\left(P\frac{1}{E_i-E_k}-P\frac{1}{E_j-E_k}-i\pi\big(\delta(E_i-E_k)+\delta(E_j-E_k)\big)\right)\boldsymbol{T}_{kj}^{*}\boldsymbol{T}_{ki}
\end{aligned}
$$

This equation in fact is equivalent to $S^\dagger S = 1$. [76]

The optical theorem written below takes the same value as the equation above. [77]

$$\mathrm{Im}\, f(0) = \frac{k_i}{4\pi} \int d\Omega_k |f(\theta_k)|^2$$

Thus,

$$(\boldsymbol{T}_{ji} - \boldsymbol{T}^*_{ij}) = \sum_k \left(P\frac{1}{E_i - E_k} - P\frac{1}{E_j - E_k} - i\pi\big(\delta(E_i - E_k) + \delta(E_j - E_k)\big)\right) \boldsymbol{T}^*_{kj}\boldsymbol{T}_{ki}$$

Let us have $i = j$, and we obtain

$$2i\mathrm{Im}\, \boldsymbol{T}_{ji} = \sum_k -2i\pi\delta(E_i - E_k)|\boldsymbol{T}_{ki}|^2$$

76

$$\begin{aligned}
(1 + T^\dagger)(1 + T) =& 1 \\
-(T + T^\dagger) =& T^\dagger T \\
2\pi i\delta(E_i - E_j)(\boldsymbol{T}_{ij} - \boldsymbol{T}^\dagger_{ij}) =& -(2\pi i)^2 \sum_k \delta(E_i - E_k)\delta(E_k - E_j)\boldsymbol{T}^\dagger_{ik}\boldsymbol{T}_{kj} \\
2\pi i\delta(E_i - E_j)(\boldsymbol{T}_{ij} - \boldsymbol{T}^*_{ji}) =& 4\pi^2\delta(E_i - E_j)\sum_k \delta(E_i - E_k)\boldsymbol{T}^*_{ki}\boldsymbol{T}_{kj} \\
where i = j, we obtain \quad - \mathrm{Im}\, \boldsymbol{T}_{ii} =& \pi \sum_k \delta(E_i - E_k)|\boldsymbol{T}_{ik}|^2
\end{aligned}$$

77

$$\begin{aligned}
\sum_k \delta(E_i - E_k) =& \int dk\, k_k^2 \delta(\frac{\hbar^2}{2m}(k_i^2 - k_k^2)) \int d\Omega_k \\
=& \frac{2m}{\hbar^2} \int dk\, k_k^2 \frac{1}{2k_k}\delta(k_i - k_k) \int d\Omega_k \\
f(\theta_{ij}) =& -\frac{2m}{\hbar^2}\frac{(2\pi)^3}{4\pi}\boldsymbol{T}_{ij} \\
\mathrm{Im}\, f(0) =& \pi\frac{2m}{\hbar^2} \int dk_k \frac{1}{2k_k}\delta(k_i - k_k)k_k^2 \frac{\hbar^2}{2m}\frac{4\pi}{(2\pi)^3} \int d\Omega_k |f(\theta_k)|^2 \\
=& \frac{k_i}{4\pi} \int d\Omega_k |f(\theta_k)|^2
\end{aligned}$$

PartII
Relativistic Quantum Mechanics

In order to discuss the spin of an electron, the effect arising from relativity must be fully considered. In the following series of sections we sill discuss this important theory of relativity.

4 Special Relativity (Classical Theory)

First, we begin by reviewing the classical relativity theory. We use the following notation:

$$x^\mu = (x^0, x^1, x^2, x^3 = (ct, x, y, z)$$

We write the metric tensors (will be discussed later) in special relativity

$$\begin{aligned} g_{\mu\nu} &= g_{\nu\mu} = \text{diag } (1, -1, -1, -1) \\ g^{\mu\nu} &= g^{\nu\mu} = (g_{\mu\nu})^{-1} = \text{diag } (1, -1, -1, -1) \\ g_{\mu\nu} g^{\nu\rho} &= \delta_\mu{}^\rho \end{aligned}$$

The indices can be raised and lowered as below:

$$a_\mu = g_{\mu\nu} a^\nu$$

This yields

$$g^\mu{}_\nu = g^{\mu\lambda} g_{\lambda\nu} = \delta^\mu{}_\nu$$

More generally, we can express in the notation

$$a_0 = a^0, \; a_1 = -a^1, \; a_= - a^2, \; a_3 = -a^3$$

Which gives

$$a_\mu b^\mu = a^0 b^0 - \vec{a} \cdot \vec{b} = a_0 b_0 - \vec{a} \cdot \vec{b}$$

For

$$\partial_\mu = \frac{\partial}{\partial x^\mu} = \left(\frac{1}{c} \frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

we can write

$$\partial_\mu \partial^\mu = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \Delta = -\Box$$

4.1 Lorentz Transformation

We call the Lorentz transformation for the real linear transformations (coordinate transformations) that conserve the norm $|x|^2 = g_{\mu\nu}x^\mu x^\nu$. (We denote the coordinates of the fixed points in space time, which we measured by another frame to be x^μ, $x'^{\mu'}$.)

$$
\begin{aligned}
x'^{\mu'} &= \Omega^{\mu'}{}_{\nu}x^\nu \\
(\Omega^{\mu'}{}_{\nu})^* &= \Omega^{\mu'}{}_{\nu} \\
|x'|^2 &= |x|^2 \\
g'_{\mu'\nu'}x'^{\mu'}x'^{\nu'} &= g_{\mu\nu}x^\mu x^\nu \\
g'_{\mu\nu} &= g_{\mu\nu} = \text{ diag } (1,-1,-1,-1)
\end{aligned}
$$

From which, we can derive the conditions below. [78] [79] [80]

$$
\begin{aligned}
g_{\lambda\kappa} &= g'_{\mu'\nu'}\Omega^{\mu'}{}_{\lambda}\Omega^{\nu'}{}_{\kappa} \\
\delta^\rho_\kappa &= g^\rho_\kappa = \Omega^{\mu'\rho}\Omega_{\mu'\kappa} = (\Omega_{\mu'}{}^{\rho}\Omega^{\mu'}{}_{\kappa})
\end{aligned}
$$

[78]

$$
\begin{aligned}
g_{\mu\nu}g^{\nu\lambda} =& \delta^\lambda_\mu \\
=& g^\lambda_\mu
\end{aligned}
$$

[79]

$$
\begin{aligned}
x'^{\mu'} &= \Omega^{\mu'}{}_{\nu}x^\nu \\
(\Omega^{\mu'}{}_{\nu})^* &= \Omega^{\mu'}{}_{\nu} \\
g'{}_{\mu'\nu'}x'^{\mu'}x'^{\nu'} &= g'_{\mu'\nu'}\Omega^{\mu'}{}_{\lambda}x^\lambda\Omega^{\nu'}{}_{\kappa}x^\kappa = g_{\lambda\kappa}x^\lambda x^\kappa gives \\
g_{\lambda\kappa} &= g'_{\mu'\nu'}\Omega^{\mu'}{}_{\lambda}\Omega^{\nu'}{}_{\kappa} \\
Thus, \delta^\rho{}_\kappa &= g^{\rho\lambda}g_{\lambda\kappa} \\
&= g^{\rho\lambda}g'_{\mu'\nu'}\Omega^{\mu'}{}_{\lambda}\Omega^{\nu'}{}_{\kappa} \\
&= \Omega^{\mu'\rho}\Omega_{\mu'\kappa}
\end{aligned}
$$

[80] For the arbitrary quantities X, Y, we write

$$
X^\mu Y_\mu = X_\kappa g^{\kappa\mu}Y^\lambda g_{\lambda\mu} = X_\kappa Y^\lambda g^\kappa{}_\lambda = X_\kappa Y^\kappa
$$

The inverse transformation can be written [81]

$$x'^{\mu}\Omega_{\mu}{}^{\kappa} = x^{\kappa}$$

The following relation is also valid: [82]

$$\begin{aligned}\Omega_{\nu\kappa}\Omega^{\rho\kappa} &= \delta^{\rho}_{\nu} \\ &= \Omega_{\nu}{}^{\kappa}\Omega^{\rho}{}_{\kappa} = g^{\rho}_{\nu}\end{aligned}$$

All together, we can express [83]

$$\begin{aligned}(\Omega^{-1})^{\mu}{}_{\nu} &= (\Omega)_{\nu}{}^{\mu} \\ (\Omega^{-1})_{\mu}{}^{\nu} &= \Omega^{\nu}{}_{\mu} \\ (\Omega^{-1})_{\mu\nu} &= \Omega^{\nu\mu} \\ (\boldsymbol{\Omega})_{\mu\nu} &\equiv \Omega_{\mu\nu} \text{として} \\ \tilde{\boldsymbol{\Omega}}\boldsymbol{\Omega} = \boldsymbol{\Omega}\tilde{\boldsymbol{\Omega}} &= \boldsymbol{I}\end{aligned}$$

81

$$\begin{aligned}x'^{\mu}g_{\mu\rho} &= g_{\rho\mu}\Omega^{\mu}{}_{\nu}x^{\nu} = \Omega_{\rho\nu}x^{\nu} \\ x'^{\mu}g_{\mu\rho}\Omega^{\rho\kappa} &= \Omega^{\rho\kappa}\Omega_{\rho\nu}x^{\nu} \\ x'^{\mu}\Omega_{\mu}{}^{\kappa} &= \delta^{\kappa}_{\nu}x^{\nu} = x^{\kappa}\end{aligned}$$

82

$$\begin{aligned}g_{\rho\kappa}x^{\rho}x^{\kappa} &= g_{\rho\kappa}x'^{\nu}\Omega_{\nu}{}^{\rho}x'^{\mu}\Omega_{\mu}{}^{\kappa} = g_{\nu\mu}x'^{\nu}x'^{\mu} \\ g_{\rho\kappa}\Omega_{\nu}{}^{\rho}\Omega_{\mu}{}^{\kappa} &= \Omega_{\nu\kappa}\Omega_{\mu}{}^{\kappa} = g_{\nu\mu} \\ \Omega_{\nu\kappa}\Omega^{\rho\kappa} &= g_{\nu\mu}g^{\mu\rho} = \delta^{\rho}_{\nu}\end{aligned}$$

[83] Let us put

$$(\Omega^{-1})^{\mu}{}_{\nu} = (\Omega)_{\nu}{}^{\mu}$$

This gives

$$\begin{aligned}(\Omega^{-1})^{\mu}{}_{\nu}\Omega^{\nu}{}_{\kappa} &= (\Omega)_{\nu}{}^{\mu}\Omega^{\nu}{}_{\kappa} = \delta^{\mu}_{\kappa} \\ \Omega^{\mu}{}_{\nu}(\Omega^{-1})^{\nu}{}_{\kappa} &= \Omega^{\mu}{}_{\nu}\Omega_{\kappa}{}^{\nu} = \delta^{\mu}_{\kappa}\end{aligned}$$

and furthuer we can write

$$(\Omega^{-1})_{\mu}{}^{\nu} = ((\Omega^{-1})^{-1})^{\nu}{}_{\mu} = \Omega^{\nu}{}_{\mu}$$

The Example pf the Lorentz Transformation

- Rotation *phi* around $z-$ axis

$$\begin{pmatrix} ct'^0 \\ x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\phi & \sin\phi & 0 \\ 0 & -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} ct^0 \\ x \\ y \\ z \end{pmatrix}$$

- Special Lorentz transformation with velocity $v = c\tanh\phi$ in direction of $x-$ axis: [84]

$$\begin{pmatrix} ct' \\ x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cosh\phi & -\sinh\phi & 0 & 0 \\ -\sinh\phi & \cosh\phi & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} ct \\ x \\ y \\ z \end{pmatrix}$$

Tensor

Under the coordinate transformation $x \to x'$, the physical quantity $\mathcal{O}(P)$ in space time p, which follows the transformations described below are called in each name below. (A point in space time $P(\{x^\mu\})$ defined by a coordinate system is $\{x^\mu\}$, while it is defined as $P(\{x'^\mu\})$ by another coordinate system of $'$. This gives the functional relationship $x'^\mu = x'^\mu(\{x^\nu\})$.)

$$\begin{aligned} \frac{\partial x'^{\mu'}}{\partial x^\nu} &\equiv x^{\mu'}_{,\nu} = \Omega^{\mu'}{}_\nu \\ \frac{\partial x^\nu}{\partial x'^{\mu'}} &\equiv x^\nu_{,\mu'} = \Omega_{\mu'}{}^\nu \\ x^{\mu'}_{,\nu} x^\nu_{,\kappa'} &= \frac{\partial x'^{\mu'}}{\partial x^\nu} \frac{\partial x^\nu}{\partial x'^{\kappa'}} = \delta^{\mu'}{}_{\kappa'} \\ x^\mu_{,\nu'} x^{\nu'}_{,\kappa} &= \frac{\partial x^\mu}{\partial x'^{\nu'}} \frac{\partial x'^{\nu'}}{\partial x^\kappa} = \delta^\mu{}_\kappa \end{aligned}$$

[84]FOr this we let $x = 0$ and write

$$\begin{aligned} t' &= t\cosh\phi, \quad x' = -ct\sinh\phi \\ \frac{x'}{t'} &= -c\tanh\phi \end{aligned}$$

This above implies that the system x' is i uniform motion with the velocity $-c\tanh\phi$ to the system x

- Scalar

$$T' = T$$

- Contravariant vector

$$T'^{\mu'} = \frac{\partial x'^{\mu'}}{\partial x^\nu} T^\nu = x^{\mu'}_{,\nu} T^\nu = \Omega^{\mu'}{}_\nu T^\nu$$

- Covariant vector

$$T'_\mu = \frac{\partial x^\nu}{\partial x'^\mu} T_\nu = \Omega_\mu{}^\nu T_\nu$$

- Contravariant of the 1st order and the 2nd order (examples)

$$T'^{\mu_1}{}_{\kappa_1 \kappa_2} = \frac{\partial x'^{\mu_1}}{\partial x^{\nu_1}} \frac{\partial x^{\rho_1}}{\partial x'^{\kappa_1}} \frac{\partial x^{\rho_2}}{\partial x'^{\kappa_2}} T^{\nu_1}{}_{\rho_1 \rho_2} = \Omega^{\mu_1}{}_{\nu_1} \Omega_{\kappa_1}{}^{\rho_1} \Omega_{\kappa_2}{}^{\rho_2} T'^{\nu_1}{}_{\rho_1 \rho_2}$$

- The contraction $A^\mu B_\mu$, for example, of the contravariant vector and covariant vector is the scalar. [85]
- What contracts with the contravariant vector to become a scalar is called the covariant vector.
- The second order covariant tensor is $g_{\mu\nu}$. [86]

[85]

$$A'^\mu B'_\mu = \Omega^\mu{}_\nu A^\nu \Omega_\mu{}^\kappa B_\kappa = \Omega^\mu{}_\nu \Omega_\mu{}^\kappa A^\nu B_\kappa = g^{\mu\rho} \Omega_{\rho\nu} g_{\mu\eta} \Omega^{\eta\kappa} A^\nu B_\kappa = \Omega_{\rho\nu} \Omega^{\rho\kappa} A^\nu B_\kappa = A^\nu B_\nu$$

[86]

$$\begin{aligned} ds'^2 &= g'_{\mu\nu} dx'^\mu dx'^\nu = g'_{\mu\nu} \frac{\partial x'^\mu}{\partial x^\rho} dx^\rho \frac{\partial x'^\nu}{\partial x^\kappa} dx^\kappa \\ ds^2 &= g_{\rho\kappa} dx^\rho dx^\kappa \end{aligned}$$

giving $ds = ds'$ thus,

$$\begin{aligned} g'_{\mu\nu} \frac{\partial x'^\mu}{\partial x^\rho} \frac{\partial x'^\nu}{\partial x^\kappa} &= g_{\rho\kappa} \\ g'_{\mu\nu} &= \frac{\partial x^\rho}{\partial x'^\mu} \frac{\partial x^\kappa}{\partial x'^\nu} g_{\rho\kappa} \end{aligned}$$

4.2 Effects of Free Particles

The action integral is defined as:

$$
\begin{aligned}
S &= -mc\int_a^b ds = \int_{t_a}^{t_b} L\,dt \\
ds^2 &= g_{\mu\nu}dx^\mu dx^\nu \\
L &= -mc\sqrt{g_{\mu\nu}\frac{dx^\mu}{dt}\frac{dx^\nu}{dt}} = -mc^2\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}, \quad \vec{v} = \frac{d\vec{r}}{dt} = \dot{\vec{r}}
\end{aligned}
$$

The Lorentz transformations $x'^\mu = \Omega^\mu{}_\nu x^\nu$ gives ($g' = g$) , and the line element stays invariant $ds = ds'$. This fact implies that the action is being interpreted as Lorentz invariant.

In the non-relativity limit:

$$
L \;\rightarrow\; -mc^2(1-\frac{1}{2}\frac{v^2}{c^2}) = -mc^2 + \frac{1}{2}mv^2
$$

where the kinetic energy is indeed being given, while excluding the constant values in the limit. The momentum can be written

$$
\begin{aligned}
\vec{p} &= \frac{\partial L}{\partial \dot{\vec{r}}} = \frac{\partial L}{\partial \vec{v}} = \frac{m\vec{v}}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} \equiv M\vec{v} \\
M &= \frac{m}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}}
\end{aligned}
$$

and let M be the relative mass. The Hamiltonian H and the energy E can be defined as:

$$
\begin{aligned}
H &= E = \vec{p}\cdot\dot{\vec{r}} - L = \vec{p}\cdot\vec{v} - L \\
&= \frac{mv^2}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} + mc^2\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}} = \frac{mc^2}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} = Mc^2
\end{aligned}
$$

Therefore, in the non-relativity limit, we have

$$
E \;\rightarrow\; mc^2(1+\frac{1}{2}\frac{v^2}{c^2}) = mc^2 + \frac{1}{2}mv^2
$$

which naturally gives the rest energy mc^2 . The following relations can be derived between the energy and the momentum: [87]

$$\begin{aligned} c\vec{p} &= \frac{\vec{v}}{c}E \\ H &= E = c\sqrt{p^2 + m^2c^2} \end{aligned}$$

Especially where super-relativistic $v \approx c$, [88] the relation with $E \approx cp$ particularly with light can be

$$E = cp$$

The canonical equation can be written [89]

$$\begin{aligned} \dot{\vec{r}} &= \vec{v} = \frac{\partial H}{\partial \vec{p}} = \frac{c^2\vec{p}}{E} \\ \dot{\vec{p}} &= -\frac{\partial H}{\partial \vec{r}} = 0 \end{aligned}$$

which giving $\vec{p} = \frac{E\vec{v}}{c^2} = M\vec{v}$ by the first equation, we may make a substitution into the second equation to write

$$\dot{\vec{p}} = \frac{d(M\vec{v})}{dt} = \frac{d}{dt}\frac{m\vec{v}}{\sqrt{1 - \frac{v^2}{c^2}}} = 0$$

[87] We can use

$$\vec{p} = \vec{v}\frac{E}{c^2}$$

to cancel v from the energy equation such that

$$\begin{aligned} E^2(1 - \frac{v^2}{c^2}) &= m^2c^4 \\ E^2(1 - c^2\frac{p^2}{E^2}) &= m^2c^4 \\ E^2 &= m^2c^4 + c^2p^2 \end{aligned}$$

[88]

$$\begin{aligned} \frac{p^2}{E} &\approx \frac{m}{\sqrt{1 - \frac{\vec{v}^2}{c^2}}} = \frac{E}{c^2} \\ E &\approx cp \end{aligned}$$

[89]

$$\dot{\vec{r}} = \vec{v} = \frac{\partial H}{\partial \vec{p}} = c\frac{2\vec{p}}{2\sqrt{p^2 + m^2c^2}} = \frac{c^2\vec{p}}{E}$$

This in fact is an equation of motion.

To discuss the Lorentz invariance in more explicit form, we can use the variation principle to write the differential of the curve 's parameter τ with $'$. Rewrite the action of the curve with common parameter τ, and write the Lagrangian of the common parameter as L ($S = \int_{\tau_a}^{\tau_b} L\, d\tau$). [90] Thus,

$$\frac{\delta L}{\delta x^\mu} = \frac{\partial L}{\partial x^\mu} - \frac{d}{d\tau}\frac{\partial L}{\partial x^{\mu\prime}} = -mc\frac{d}{d\tau}\left(\frac{g_{\mu\nu}x^{\nu\prime}}{\sqrt{g_{\rho\kappa}x^{\rho\prime}x^{\kappa\prime}}}\right) = 0$$

We take parameter τ as $ds = cd\tau$,($x^{\mu\prime}x_\mu{}' = c^2$) that gives (proper time) [91] [92]

$$\frac{d^2x^\kappa}{d\tau^2} \quad = \quad 0$$

From this, we can now consider the free-particle. If we have $\tau = t$, the relational expression for the components of $\mu = 0$ can be written [93]

$$\frac{d}{dt}\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}} = \frac{dE}{dt} = 0$$

indicating that the energy is being conserved. The conservation of momentum can

---

90

$$\begin{aligned} L &= -mc\sqrt{g_{\mu\nu}\frac{dx^\mu}{d\tau}\frac{dx^\nu}{d\tau}} = -mc\sqrt{g_{\mu\nu}x^{\mu\prime}x^{\nu\prime}} \\ \frac{\delta L}{\delta x^\mu} &= \frac{\partial L}{\partial x^\mu} - \frac{d}{d\tau}\frac{\partial L}{\partial x^{\mu\prime}} = -mc\frac{d}{d\tau}\left(\frac{g_{\mu\nu}x^{\nu\prime}}{\sqrt{}}\right) = 0 \end{aligned}$$

91 Let parameter τ be $ds = cd\tau$,($x^{\mu\prime}x_\mu{}' = c^2$) and write

$$\begin{aligned} s = \int_{s_a}^{s} ds = \int_{\tau_a}^{\tau}\sqrt{g_{\mu\nu}\frac{dx^\mu}{d\tau}\frac{dx^\nu}{d\tau}}d\tau = \int_{\tau_a}^{\tau}\sqrt{x^{\mu\prime}x_\nu{}'}d\tau \\ ds = \sqrt{x^{\mu\prime}x_\nu{}'}d\tau = cd\tau \\ x^{\mu\prime}x_\nu{}' = c^2 \end{aligned}$$

92

$$g^{\kappa\mu}\frac{\delta L}{\delta x^\mu} = = -mcg^{\kappa\mu}\frac{d}{d\tau}g_{\mu\nu}x^{\nu\prime} = -mc\delta^\kappa{}_\nu\frac{d^2x^\nu}{d\tau^2} = -mc\frac{d^2x^\kappa}{d\tau^2} = 0$$

93

$$\frac{d}{dt}\frac{c}{c\sqrt{1-\frac{v^2}{c^2}}} = 0$$

be given by $\mu = i = 1, 2, 3$: [94]

$$\frac{d}{dt}\frac{mc\dot{\vec{r}}}{\sqrt{1-\frac{v^2}{c^2}}} = \vec{0}$$

When we let four-momentum be $p_\mu = \dfrac{\partial L}{\partial \dot{x}^\mu}$ as we will cover it in our next section, we have [95]

$$\begin{aligned} p_0 &= -Mc = -\frac{E}{c} \\ p_i &= p_{x,y,z} = \left(\frac{m\dot{\vec{r}}}{\sqrt{1-\frac{v^2}{c^2}}}\right)_i \end{aligned}$$

which giving the covariance of vectors for the Lorentz transform.

4.3 Particle Motion in Electromagnetic Field (Lagrange Formulation)

Let us describe below as the action integral:

$$\begin{aligned} S &= S_0 + S_{el} \\ S_0 &= -mc\int_a^b ds = -mc\int_{\tau_a}^{\tau_b} d\tau\,\sqrt{g_{\mu\nu}x^{\mu\prime}x^{\nu\prime}} = \int_{t_a}^{t_b} dt\,L_0 \\ L_0 &= -mc\sqrt{g_{\mu\nu}\dot{x}^\mu\dot{x}^\nu} \\ S_{el} &= -e\int A_\mu dx^\mu = -e\int_{\tau_a}^{\tau_b} A_\kappa x^{\kappa\prime} d\tau = \int_{t_a}^{t_b} dt\,L_{el} \\ L_{el} &= -eA_\mu\frac{dx^\mu}{dt} = -e\phi + e\dot{\vec{r}}\cdot\vec{A} \end{aligned}$$

94

$$\frac{d}{dt}\frac{-\dot{x}^\mu}{c\sqrt{1-\frac{v^2}{c^2}}} = 0$$

95

$$\begin{aligned} p_\mu &= -mc\frac{g_{\mu\nu}\dot{x}^\nu}{\sqrt{g_{\mu\nu}\dot{x}^\mu\dot{x}^\nu}} \\ p_0 &= -mc\frac{c}{c\sqrt{1-\frac{v^2}{c^2}}} = -Mc = -\frac{E}{c} \\ p_i &= p_{x,y,z} = -mc\frac{-\dot{x}^i}{c\sqrt{1-\frac{v^2}{c^2}}} = \left(\frac{m\dot{\vec{r}}}{\sqrt{1-\frac{v^2}{c^2}}}\right)_i \end{aligned}$$

The four-vector potential can be written

$$A_0 = A^0 = \frac{1}{c}\phi$$
$$A_i = -A^i, \quad A^1 = A_x, A^2 = A_y, A^3 = A_z$$

Where $\dot{x}^\mu = \frac{dx^\mu}{dt}$ is the four-velocity.

Note that the Lorentz invariance of this action is obeyed by the covariant vector A_μ. The covariance of A_μ is obeyed by the observation given by the Maxwell 's equation as well as by the conservation of the electric charge. [96]

In those actions, we use the variation principle in which the equation of motion

[96]The covariance of A_μ is obeyed by the observation because of the Maxwell 's equation and the conservation of the electric charge. From our later discussion, the Maxwell 's equation can be defined by $\vec{B} = \mathrm{div}\,\vec{A}$, $\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi$, which are equivalent to the two equations below:

$$\begin{aligned}\Box\vec{A} &= \Delta\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = \vec{\nabla}(\mathrm{div}\,\vec{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t}) - \mu_0\vec{j} \\ \Delta\phi &= -\frac{\partial}{\partial t}\mathrm{div}\,\vec{A} - \frac{\rho}{\epsilon_0}\end{aligned}$$

Under a condition called the Lorentz (gauge) condition

$$\mathrm{div}\,\vec{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t} = \frac{\partial A^\mu}{\partial x^\mu} = \partial_\mu A^\mu = 0$$

The two equivalent equations we described above can be written

$$\begin{aligned}\Box\vec{A} &= -\mu_0\vec{j} \\ \Box\phi &= -c^2\mu_0\rho\end{aligned}$$

Here we let the four-current j^μ be

$$j_0 = c\rho,\ j^1 = j_x,\ j^2 = j_y,\ j^3 = j_z$$

which giving the Maxwell 's equation

$$\Box A^\mu = -\mu_0 j^\mu$$

.

For the conservation of electric charge

$$0 = \mathrm{div}\,\vec{j} + \frac{\partial\rho}{\partial t} = \partial_\mu j^\mu$$

which is (experimentally) understood to be the Lorentz invariant. This gives the contravariant vector j^μ and A^μ. Note that the Lorentz condition $\partial_\mu A^\mu = 0$ in fact expresses the relation for the scalar, and remains invariant to the Lorentz transformation,

$$\Box\partial_\mu A^\mu = -\mu_0\partial_\mu j^\mu = 0$$

This is compatible with the field equation. Now, the gauge transformation

$$\begin{aligned}\vec{A} \to \bar{\vec{A}} = \vec{A} + \vec{\nabla}\chi \\ \phi \to \bar{\phi} = \phi - \frac{\partial\chi}{\partial t}\end{aligned}$$

can be written

$$A_\mu \to \bar{A}_\mu = A_\mu + \partial_\mu\chi$$

To write $\vec{E}$, $\vec{B}$ in four-form, we let the second order covariant tensor be

$$f_{\mu\nu} \equiv \partial_\mu A_\nu - \partial_\nu A_\mu = -f_{\nu\mu}$$

We may write down

$$\begin{aligned}
f_{01} &= \partial_0 A_1 - \partial_1 A_0 = -\frac{1}{c}\frac{\partial A_x}{\partial t} - \frac{1}{c}\frac{\partial \phi}{\partial x} = \frac{1}{c}E_x \\
f_{02} &= \frac{1}{c}E_y \\
f_{03} &= \frac{1}{c}E_z \\
f_{12} &= \partial_1 A_2 - \partial_2 A_1 = -\frac{\partial A_y}{\partial x} + \frac{\partial A_x}{\partial y} = -B_z \\
f_{13} &= \partial_1 A_3 - \partial_3 A_1 = -\frac{\partial A_z}{\partial x} + \frac{\partial A_x}{\partial z} = B_y \\
f_{23} &= \partial_2 A_3 - \partial_3 A_2 = -\frac{\partial A_z}{\partial y} + \frac{\partial A_y}{\partial z} = -B_x
\end{aligned}$$

Organize the above and rewrite

$$f_{\mu\nu} = \begin{pmatrix} 0 & \frac{E_x}{c} & \frac{E_y}{c} & \frac{E_z}{c} \\ -\frac{E_x}{c} & 0 & -B_z & B_y \\ -\frac{E_y}{c} & B_z & 0 & -B_x \\ -\frac{E_z}{c} & -B_y & B_x & 0 \end{pmatrix}$$

These indeed stay invariant under gauge transformation:

$$\begin{aligned}
\bar{f}_{\mu\nu} &= \partial_\mu \bar{A}_\nu - \partial_\nu \bar{A}_\mu \\
&= \partial_\mu (A_\nu + \partial_\nu \chi) - \partial_\nu (A_\mu + \partial_\mu \chi) = f_{\mu\nu}
\end{aligned}$$

[97] takes the proper-time parameter. In the Lorentz invariant form, we can write

$$
\begin{aligned}
m\frac{d^2x^\rho}{d\tau^2} &= -e\frac{dx_\nu}{d\tau}f^{\nu\rho} \\
f_{\mu\nu} &= \partial_\mu A_\nu - \partial_\nu A_\mu = \begin{pmatrix} 0 & \frac{E_x}{c} & \frac{E_y}{c} & \frac{E_z}{c} \\ -\frac{E_x}{c} & 0 & -B_z & B_y \\ -\frac{E_y}{c} & B_z & 0 & -B_x \\ -\frac{E_z}{c} & 0 & B_x & 0 \end{pmatrix}
\end{aligned}
$$

Rewrite the above as

$$
m\frac{d^2x^\rho}{d\tau^2} = F^\rho
$$

$$
F^\rho = -e\frac{dx_\nu}{d\tau}f^{\nu\rho}
$$

We call F^ρ the four-force. This equation of motion embodies the all four forces

---

97

$$
\begin{aligned}
\frac{\delta L_0}{\delta x^\mu} &= mc\frac{d}{d\tau}\left(\frac{g_{\mu\nu}x^{\nu\prime}}{\sqrt{g_{\alpha\beta}x^{\alpha\prime}x^{\beta\prime}}}\right) \\
\frac{\delta L_{el}}{\delta x^\mu} &= -e\big(\partial_\mu(A_\kappa x^{\kappa\prime}) - \frac{dA_\mu}{d\tau}\big) \\
&= -e\big(\partial_\mu(A_\kappa x^{\kappa\prime}) - x^{\nu\prime}\partial_\nu A_\mu\big) \\
&= -e\big(x^{\kappa\prime}\partial_\mu A_\kappa - x^{\nu\prime}\partial_\nu A_\mu\big) \\
&= -e(\partial_\mu A_\nu - \partial_\nu A_\mu)x^{\nu\prime} = -f_{\mu\nu}x^{\nu\prime} = f_{\nu\mu}x^{\nu\prime}
\end{aligned}
$$

In which we take proper-time parameter, and written

$$
\begin{aligned}
mg_{\mu\nu}\frac{d^2x^\nu}{d\tau^2} + e\frac{dx^\nu}{d\tau}f_{\nu\mu} &= 0 \\
mg^{\rho\mu}g_{\mu\nu}\frac{d^2x^\nu}{d\tau^2} &= -eg^{\rho\mu}\frac{dx^\nu}{d\tau}f_{\nu\mu} \\
m\frac{d^2x^\rho}{d\tau^2} &= -e\frac{dx^\nu}{d\tau}f_\nu{}^\rho = -e\frac{dx_\nu}{d\tau}f^{\nu\rho}
\end{aligned}
$$

We define $\tau = t$, so that

$$
\begin{aligned}
m\frac{d}{dt}\frac{g_{\mu\nu}\dot{x}^\nu}{\sqrt{1-\frac{v^2}{c^2}}} &= e\dot{x}^\kappa f_{\mu\kappa} \\
\frac{d\pi_\mu}{dt} &= e\dot{x}^\kappa f_{\mu\kappa}, \quad (\pi_\mu takesthetimetforthecommonparameter\tau; thatiswhen\tau = t) \\
\pi_\mu &= m\frac{g_{\mu\nu}\dot{x}^\nu}{\sqrt{1-\frac{v^2}{c^2}}} = Mg_{\mu\nu}\dot{x}^\nu = M\dot{x}_\mu \\
\pi_\mu\pi^\mu &= \frac{m^2\dot{x}_\mu\dot{x}^\mu}{1-\frac{v^2}{c^2}} = \frac{m^2(c^2-v^2)}{1-\frac{v^2}{c^2}} = m^2c^2
\end{aligned}
$$

that are not independent but has a linear relation among them: [98]

$$u_\mu F^\nu = 0$$
$$u_\mu = \frac{dx_\mu}{d\tau}$$

Where u^μ is the four-velocity, we can write

$$u^\mu u_\mu = c^2$$
$$u^\mu = (c\frac{dt}{d\tau}, \vec{v}\frac{dt}{d\tau})$$

[99]

With time t, this equation of motion can be written [100]

$$\begin{aligned}\frac{d\pi_\mu}{dt} &= e\dot{x}^\kappa f_{\mu\kappa} \\ \pi_\mu &= m\frac{g_{\mu\nu}\dot{x}^\nu}{\sqrt{1-\frac{v^2}{c^2}}} = M\dot{x}_\mu = mu_\mu \\ \pi_\mu \pi^\mu &= m^2c^2\end{aligned}$$

98

$$\frac{dx_\mu}{d\tau}F^\mu = -e\frac{dx_\mu}{d\tau}\frac{dx_\kappa}{d\tau}f^{\kappa\mu} = 0; antisymmetric of \quad f^{\kappa\mu}$$

99 We can rewrite

$$u^0 = c\frac{dt}{d\tau}$$
$$u^i = \frac{dx^i}{d\tau}$$

$$\sqrt{(\frac{dt}{d\tau})^2 - \frac{1}{c^2}(\frac{dt}{d\tau}\dot{\vec{r}})^2} = 1$$
$$dt\sqrt{1-\frac{v^2}{c^2}} = d\tau$$
$$M\dot{x}^\mu = \frac{m}{\sqrt{1-\frac{v^2}{c^2}}}\dot{x}^\mu = \frac{m}{\sqrt{1-\frac{v^2}{c^2}}}\frac{dx^\mu}{dt} = m\frac{dx^\mu}{d\tau} = mu^\mu$$

100

$$\pi_\mu \pi^\mu = M^2c^2 - \vec{\pi}^2 = m^2c^2$$
$$\vec{\pi} = M\vec{v} = (\pi^1, \pi^2, \pi^3) = (-\pi_1, -\pi_2, -\pi_3)$$

For each component we can write in the forms [101]

$$\begin{aligned}\frac{d(Mc^2)}{dt} &= e\vec{v}\cdot\vec{E}\\ \frac{d\vec{\pi}}{dt} &= e(\vec{E}+\vec{v}\times\vec{B})\\ M^2c^2-\vec{\pi}^2 &= m^2c^2\end{aligned}$$

Now let us rewrite the above:

$$\begin{aligned}M &= \frac{m}{\sqrt{1-\frac{v^2}{c^2}}}\\ \vec{\pi} &= M\vec{v} = (\pi^1,\pi^2,\pi^3) = (-\pi_1,-\pi_2,-\pi_3)\\ \vec{v} &= \dot{\vec{r}}\end{aligned}$$

We can also confirm the equation

$$\vec{v}\cdot\frac{d\pi}{dt} = e\vec{E}\cdot\vec{v} = \frac{dMc^2}{dt}$$

101

$$\begin{aligned}\pi_0 &= \frac{mc\cdot 1}{\sqrt{1-\frac{v^2}{c^2}}} = Mc\\ \pi_1 &= \frac{-m\dot{x}}{\sqrt{1-\frac{v^2}{c^2}}} = -M\dot{x} = -\pi^1 = -\pi_x\\ \pi_2 &= -M\dot{y} - \pi^2 = -\pi_y, \quad \pi_3 = -M\dot{z} = -\pi^3 = -\pi_z\end{aligned}$$

The zeroth component gives

$$\begin{aligned}\frac{d\pi_0}{dt} &= c\frac{dM}{dt} = e\dot{x}^\kappa f_{0\kappa} = \frac{e}{c}(\dot{x}E_x+\dot{y}E_y+\dot{z}E_z)\\ \frac{d(Mc^2)}{dt} &= e\vec{v}\cdot\vec{E}\end{aligned}$$

While the first component gives

$$\begin{aligned}\frac{d\pi_1}{dt} &= -\frac{d(M\dot{x})}{dt} = e\dot{x}^\kappa f_{1\kappa} = e\Big(-\frac{c}{c}E_x - \dot{y}B_z + \dot{z}B_y\Big)\\ \frac{d\pi_x}{dt} &= e(\vec{E}+\dot{\vec{r}}\times\vec{B})_x\\ Lilewisewewrite \quad & \frac{d\pi_y}{dt} = e(\vec{E}+\dot{\vec{r}}\times\vec{B})_y, \quad \frac{d\pi_z}{dt} = e(\vec{E}+\dot{\vec{r}}\times\vec{B})_z\end{aligned}$$

Thus, only $\frac{d\vec{\pi}}{dt} = e(\vec{E}+\vec{v}\times\vec{B})$ remains independent for the equation of motion. [102]

4.4 Particle Motion in Electromagnetic Field (Hamilton Formulation)

We now discuss the particle motion in electromagnetic field by Hamiltonian forms. Where $(\tau = t)$, the canonical momentum is defined as [103]

$$\begin{aligned} p_\mu &= \frac{\partial L}{\partial \dot{x}^\mu} \\ &= -\frac{m\dot{x}_\mu}{\sqrt{1-\frac{v^2}{c^2}}} - eA_\mu = -M\dot{x}_\mu - eA_\mu \end{aligned}$$

102

$$\begin{aligned} \vec{v}\cdot\frac{d\vec{\pi}}{dt} &= e\vec{E}\cdot\vec{v} \\ &= \frac{dM}{dt}\vec{v}^2 + M\vec{v}\cdot\frac{d\vec{v}}{dt} \\ &= \frac{dM}{dt}v^2 + \frac{1}{2}M\frac{dv^2}{dt} \\ &= m\frac{\frac{d}{dt}\frac{v^2}{c^2}}{2(1-\frac{v^2}{c^2})^{3/2}}v^2 + \frac{1}{2}M\frac{dv^2}{dt} \\ &= m\frac{v^2+(1-\frac{v^2}{c^2})c^2}{2(1-\frac{v^2}{c^2})^{3/2}}\frac{d}{dt}\frac{v^2}{c^2} = \frac{m}{2(1-\frac{v^2}{c^2})^{3/2}}\frac{dv^2}{dt} = \frac{dMc^2}{dt} \end{aligned}$$

$$\vec{v}\cdot\frac{d\pi}{dt} = e\vec{E}\cdot\vec{v} = \frac{dMc^2}{dt}$$

103

$$\begin{aligned} p_\mu &= \frac{\partial L}{\partial \dot{x}^\mu} \\ &= -mc\frac{g_{\mu\nu}\dot{x}^\nu}{\sqrt{g_{\mu\nu}\dot{x}^\mu\dot{x}^\nu}} - eA_\mu \\ &= -\frac{m\dot{x}_\mu}{\sqrt{1-\frac{v^2}{c^2}}} - eA_\mu = -M\dot{x}_\mu - eA_\mu \\ &= -\pi_\mu - eA_\mu \end{aligned}$$

$$\begin{aligned} &p_0 = -Mc - eA_0 = -Mc - \frac{e}{c}\phi \\ &p_1 = -M\dot{x}_1 - eA_1 = +M\dot{x} + eA_x \\ &p_2 = -M\dot{x}_2 - eA_2 = +M\dot{y} + eA_y \\ &p_3 = -M\dot{x}_3 - eA_3 = +M\dot{z} + eA_z \end{aligned}$$

Each component can be written in the forms:

$$p_0 = -Mc - \frac{e}{c}\phi$$
$$p_1 = M\dot{x} + eA_x \equiv p_x$$
$$p_2 = M\dot{y} + eA_y \equiv p_y$$
$$p_3 = M\dot{z} + eA_z \equiv p_z$$

$$\vec{p} = \vec{\pi} + e\vec{A}$$

The Hamiltonian H can be defined as [104] [105]

$$\begin{aligned} H &= \sum_{\mu=1,2,3} p_\mu \dot{x}^\mu - L \\ &= c\sqrt{\vec{\pi}^2 + m^2c^2} + e\phi \\ &= c\sqrt{(\vec{p} - e\vec{A})^2 + m^2c^2} + e\phi \end{aligned}$$

---

[104] Giving

$$\begin{aligned} \vec{\pi} &= M\vec{v} = \vec{p} - e\vec{A} \\ M^2c^2 &= \vec{\pi}^2 + m^2c^2 \end{aligned}$$

We may write

$$Mc = \sqrt{\vec{\pi}^2 + m^2c^2}$$

More precisely we can write

$$\begin{aligned} (\vec{p} - e\vec{A})^2 &= M^2v^2 \\ (\vec{p} - e\vec{A})^2 + m^2c^2 &= \frac{m^2v^2}{1 - \frac{v^2}{c^2}} + m^2c^2 = m^2\frac{v^2 + c^2(1 - \frac{v^2}{c^2})}{1 - \frac{v^2}{c^2}} \\ &= m^2\frac{c^2}{1 - \frac{v^2}{c^2}} \\ \sqrt{(\vec{p} - e\vec{A})^2 + m^2c^2} &= \frac{mc}{\sqrt{1 - \frac{v^2}{c^2}}} = Mc \end{aligned}$$

Thus,

$$Mc^2 = c\sqrt{(\vec{p} - e\vec{A})^2 + m^2c^2}$$

[105]

$$\begin{aligned} H &= \sum_{\mu=1,2,3} p_\mu \dot{x}^\mu - L \\ &= \sum_{\mu=0,1,2,3} p_\mu \dot{x}^\mu - p_0\dot{x}^0 - L \\ &= -p_0\dot{x}^0 + p_\mu \dot{x}^\mu - L \\ &= -p_0\dot{x}^0 - M\dot{x}_\mu \dot{x}^\mu - eA_\mu \dot{x}^\mu - (-mc^2\sqrt{1 - \frac{v^2}{c^2}} - eA_\mu \dot{x}^\mu) \\ &= -p_0\dot{x}^0 - M(c^2 - v^2) + mc^2\sqrt{1 - \frac{v^2}{c^2}} \\ &= -p_0\dot{x}^0 = Mc^2 + e\phi \\ &= c\sqrt{\vec{\pi}^2 + m^2c^2} + e\phi \\ &= c\sqrt{(\vec{p} - e\vec{A})^2 + m^2c^2} + e\phi \end{aligned}$$

In the non-relativistic limit $\frac{(\vec{p}-e\vec{A})^2}{2m} << mc^2$ the Hamiltonian can be defined as [106]

$$H \approx mc^2 + \frac{(\vec{p}-e\vec{A})^2}{2m} + e\phi$$

Recall our initial discussion is to formulate a Hamiltonian description of particle motion in electromagnetic field. The canonical equation can be given [107]

$$\begin{aligned}\vec{v} &\equiv \dot{\vec{r}} = \frac{\vec{\pi}}{M} \\ \dot{\vec{p}} &= e\vec{\nabla}(\vec{A}\cdot\vec{v} - \phi)\end{aligned}$$

Now given $\vec{p} = \vec{\pi} + e\vec{A}$, the canonical equation we described above may give the equation of motion which we described earlier:

[106]

$$\begin{aligned}H =& mc^2\sqrt{1 + \frac{1}{m^2c^2}(\vec{p}-e\vec{A})^2} + e\phi \\ \approx& mc^2(1 + \frac{1}{2}(\vec{p}-e\vec{A})^2) + e\phi = mc^2 + \frac{(\vec{p}-e\vec{A})^2}{2m} + e\phi\end{aligned}$$

[107] The canonical equations are written

$$\begin{aligned}\dot{\vec{r}} &= \frac{\partial H}{\partial \vec{p}} \\ \dot{\vec{p}} &= -\frac{\partial H}{\partial \vec{r}}\end{aligned}$$

we direct our attention to the first equation of $Mc = \sqrt{\vec{\pi}^2 + m^2c^2}, \vec{\pi} = \vec{p} - e\vec{A} = M\vec{v}$ and write

$$\begin{aligned}\vec{v} &\equiv \dot{\vec{r}} = \frac{\partial H}{\partial \vec{p}} \\ &= c\frac{\vec{\pi}}{\sqrt{\vec{\pi}^2 + m^2c^2}} \\ &= \frac{\vec{\pi}}{M}\end{aligned}$$

Given $\vec{\pi} = M\vec{v}$, te second equation is written

$$\begin{aligned}\dot{\vec{p}} &= -\frac{\partial H}{\partial \vec{r}} \\ &= c\frac{e\vec{\nabla}(\vec{\pi}\cdot\vec{A})}{\sqrt{\vec{\pi}^2+m^2c^2}} - e\vec{\nabla}\phi, \ (Note\ that\ \vec{\nabla}\ does\ not\ differentiate\ \pi.) \\ &= e(\vec{\nabla}(\vec{A}\cdot\vec{v}) - \vec{\nabla}\phi), \ (Note\ that\ \vec{\nabla}\ does\ not\ differentiate\ v\ as\ we\ express\ normally.) \\ &= e\vec{\nabla}(\vec{A}\cdot\vec{v} - \phi)\end{aligned}$$

$$
\begin{aligned}
\frac{d\vec{\pi}}{dt} &= e\vec{\nabla}(\vec{A}\cdot\vec{v}-\phi) - e\frac{d\vec{A}}{dt} \\
&= e\vec{\nabla}(\vec{A}\cdot\vec{v}-\phi) - e\frac{\partial\vec{A}}{\partial t} - e(\vec{v}\cdot\vec{\nabla})\vec{A} \\
&\qquad (Note\ that\ \vec{\nabla}\ does\ not\ differentiate\ v\ :\ a\ normal\ way\ of\ expression.) \\
&= e\vec{E} + e\big(\vec{\nabla}(\vec{A}\cdot\vec{v}) - (\vec{v}\cdot\vec{\nabla})\vec{A}\big) \\
&= e(\vec{E} + \vec{v}\times\vec{B})
\end{aligned}
$$

Thus, the non-relativistic limit of the above equation speaks for itself. [108]

[108] We consider v is being independent of $\vec{r}$, and given that we have $\vec{A}\times(\vec{B}\times\vec{C}) = (\vec{A}\cdot\vec{C})\vec{B} - (\vec{A}\cdot\vec{B})\vec{C} = \vec{B}(\vec{A}\cdot\vec{C}) - (\vec{A}\cdot\vec{B})\vec{C}$ we can write

$$
\begin{aligned}
\vec{v}\times \mathrm{rot}\,\vec{A} &= \vec{v}\times(\vec{\nabla}\times\vec{A}) \\
&= \vec{\nabla}(\vec{v}\cdot\vec{A}) - (\vec{v}\cdot\vec{\nabla})\vec{A}
\end{aligned}
$$

or

$$
\begin{aligned}
(\vec{v}\times \mathrm{rot}\,\vec{A})_i &= \epsilon_{ijk}v_j\epsilon_{klm}\partial_l A_m = (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})v_j\partial_l A_m \\
&= v_j\partial_i A_j - v_j\partial_j A_i
\end{aligned}
$$

5 Dirac Equations

5.1 Deriving the Dirac Equation

Based on the relativistic Hamiltonian we obtained in the previous section, we continue the procedures of quantization. We first write the classical Hamiltonian

$$H_{cl} \;=\; c\sqrt{(\vec{p}-e\vec{A})^2+m^2c^2}+e\phi$$

to which we make replacement $\vec{p} \to -i\hbar\vec{\nabla}$ and consider the quantum Hamiltonian. Knowing that the root sign included in above equation being somehow difficult, we may write

$$H_{D,cl} \;=\; c\vec{\alpha}\cdot(\vec{p}-e\vec{A})+\beta mc^2+e\phi$$

and use the formal equation of

$$H_{cl} \;=\; H_{D,cl}$$

from which we try determining the Hamiltonian $H_{D,cl}$ that includes no root signs. To explain further, we would like to determine the expansion coefficients $\vec{\alpha}$ and β which satisfy

$$c^2\left\{(\vec{p}-e\vec{A})^2+m^2c^2\right\} \;=\; \left\{c\vec{\alpha}\cdot(\vec{p}-e\vec{A})+\beta mc^2\right\}^2$$

To obtain such coefficients we need to have

$$\begin{aligned}
\alpha_x^2=\alpha_y^2=\alpha_z^2=\beta^2 &= 1\\
\{\alpha_i,\alpha_j\} &= \alpha_i\alpha_j+\alpha_j\alpha_i=0,\ i\neq j\\
\{\alpha_i,\beta\} &= \alpha_i\beta+\beta\alpha_i=0
\end{aligned}$$

The coefficients $\vec{\alpha}$ and β that satisfy the above may be considered the matrix of forth-order. In our case, the Dirac expression described below is considered to be convenient:

$$\begin{aligned}
\alpha_i &= \begin{pmatrix} \boldsymbol{O}_2 & \boldsymbol{\sigma_i} \\ \boldsymbol{\sigma_i} & \boldsymbol{O}_2 \end{pmatrix} \equiv \rho_1\otimes\sigma_i\\
\beta &= \begin{pmatrix} \boldsymbol{I}_2 & \boldsymbol{O}_2 \\ \boldsymbol{O}_2 & -\boldsymbol{I}_2 \end{pmatrix} \equiv \rho_3\otimes\boldsymbol{I}_2
\end{aligned}$$

where $\vec{\sigma}$ and $\vec{\rho}$ are the Pauli matrices

$$\sigma_x=\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\quad \sigma_y=\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\quad \sigma_z=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

They satisfy the following relation [109]

$$\begin{aligned}
\sigma_i\sigma_j &= i\epsilon_{ijk}\sigma_k, \quad (i \neq j) \\
\sigma_i^2 &= \boldsymbol{I}_2 \\
[\sigma_i, \sigma_j] &= 2i\epsilon_{ijk}\sigma_k \\
\mathrm{Tr}\,\sigma_x &= \mathrm{Tr}\,\sigma_y = \mathrm{Tr}\,\sigma_z = 0 \\
\det\sigma_x &= \det\sigma_y = \det\sigma_z = -1 \\
(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) &= (\vec{A}\cdot\vec{B})\boldsymbol{I}_2 + i\vec{\sigma}\cdot(\vec{A}\times\vec{B})
\end{aligned}$$

Here we use the sign $\otimes$ when we describe 4×4 matrices from a set of 2×2 matrix. (Tensor Product):

$$\begin{aligned}
(A\otimes B)_{ia,jb} \equiv& A_{ij}B_{ab} \\
i,j =& 1,2 \quad a,b = 1,2 \\
(i,a),(j,b) =& (1,1),(1,2),(2,1),(2,2)
\end{aligned}$$

Recall the multiplication of the block matrices, we may write

$$(A\otimes B)(C\otimes D) = (AC\otimes BD)$$

In another way, we may also understand from the equation

$$\begin{aligned}
\{(A\otimes B)(C\otimes D)\}_{ia,jb} =& (A\otimes B)_{ia,kc}(C\otimes D)_{kc,jb} \\
=& A_{ik}B_{ac}C_{kj}D_{cb} = (AC)_{ij}(BD)_{ab} \\
=& (AC\otimes BD)_{ia,jb}
\end{aligned}$$

Furthermore, [110]

109

$$\begin{aligned}
(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) =& \sigma_i A_i \sigma_j B_j = \frac{1}{2}\{\sigma_i A_i \sigma_j B_j + \sigma_j A_j \sigma_i B_i\} \\
=& \frac{1}{2}\{\sum_{i=j}(\sigma_i\sigma_j A_i B_j + \sigma_j\sigma_i A_j B_i)\} + \sum_{i\neq j}(\sigma_i\sigma_j A_i B_j + \sigma_j\sigma_i A_j B_i)\} \\
=& \frac{1}{2}\left\{\sum_i 2\sigma_i^2 A_i B_i + \sum_{i\neq j}\sigma_i\sigma_j(A_iB_j - A_jB_i)\right\} \\
=& \vec{A}\cdot\vec{B} + i\frac{1}{2}\epsilon_{ijk}\sigma_k(A_iB_j - A_jB_i) \\
=& \vec{A}\cdot\vec{B} + i\epsilon_{ijk}\sigma_k A_i B_j \\
=& \vec{A}\cdot\vec{B} + i\vec{\sigma}\cdot\vec{A}\times\vec{B}
\end{aligned}$$

110

$$\mathrm{Tr}\,A\otimes B = \sum_{ia}(A\otimes B)_{ia,ia} = \sum_{ia} A_{ii}B_{aa} = \mathrm{Tr}\,A\,\mathrm{Tr}\,B$$

$$
\begin{aligned}
\operatorname{Tr} A \otimes B =& \operatorname{Tr} A \operatorname{Tr} B \\
[A \otimes I, B \otimes C] =& AB \otimes C - BA \otimes C = [A, B] \otimes C
\end{aligned}
$$

The quantization $\vec{p} \to -i\hbar\vec{\nabla}$ via $H_{D,cl}$ is what we call the Dirac Hamiltonian H_D such that the Schroedinger equation is called the Dirac equation and written

$$
\begin{aligned}
H_D &= c\vec{\alpha} \cdot (\frac{\hbar}{i}\vec{\nabla} - e\vec{A}) + \beta mc^2 + e\phi \\
i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) &= H_D \Psi(\vec{r}, t)
\end{aligned}
$$

Here we bring the Dirac matrix $\gamma_\mu,\ \mu = 0, 1, 2, 3$ into the Dirac equation and rewrite which in [111]

$$
\begin{aligned}
\gamma^\mu &= (\gamma^0, \vec{\gamma}) \\
\gamma^0 &= \beta \\
\vec{\gamma} &= (\gamma_x, \gamma_y, \gamma_z) = \beta\vec{\alpha} = (\gamma^1, \gamma^2, \gamma^3) \\
\{\gamma^\mu, \gamma^\nu\} &= 2g^{\mu\nu}
\end{aligned}
$$

Note that the Hermitian for $\vec{\alpha}$ and β can be written

$$
\begin{aligned}
{\gamma^0}^\dagger &= \gamma^0 \\
{\gamma^i}^\dagger &= -\gamma^i
\end{aligned}
$$

We may simplify this in the form

$$
{\gamma^\mu}^\dagger = \gamma^0 \gamma^\mu \gamma^0
$$

[111] For example,

$$
\gamma_1\gamma_1 = \beta\alpha_x\beta\alpha_x = -\beta\beta\alpha_x\alpha_x = -I
$$

Given that we can write the Dirac equation [112]

$$\left\{ i\hbar\gamma^\mu(\partial_\mu + i\frac{e}{\hbar}A_\mu) - mc \right\}\Psi = 0$$
$$(i\hbar\gamma^\mu D_\mu - mc)\Psi = 0$$
$$D_\mu = \partial_\mu + i\frac{e}{\hbar}A_\mu$$

Note that there are four components in the wave function. For $i\hbar\frac{\partial}{\partial t}\Psi = H_D\Psi$, we can write

$$H_D = \gamma^0(-i\hbar c\vec{\gamma}\cdot\vec{\nabla} + mc^2)$$
$$i\hbar c\partial_0\Psi = H_D\Psi$$

5.2 Symmetry of Dirac Equation

The Conservation of Current

Consider now the Dirac equation and whose Hermitian conjugate, which gives [113]

$$\rho = \Psi^\dagger\Psi$$
$$\vec{j} = c\Psi^\dagger\vec{\alpha}\Psi$$

[112]

$$\left\{ i\hbar\frac{\partial}{\partial t} - c\boldsymbol{\alpha}\cdot(\frac{\hbar}{i}\vec{\nabla} - e\boldsymbol{A}) - \beta mc^2 - e\phi \right\}\Psi = 0$$
$$\frac{\gamma^0}{c}\times$$
$$\left\{ \gamma^0(i\hbar\frac{1}{c}\frac{\partial}{\partial t} - e\frac{1}{c}\phi) - \vec{\gamma}\cdot(-i\hbar\vec{\nabla} - e\vec{A}) - mc \right\}\Psi = 0$$
$$\left\{ i\hbar\gamma^0(\frac{\partial}{\partial(ct)} + ie\frac{1}{c\hbar}\phi) + i\hbar\vec{\gamma}\cdot(\vec{\nabla} - i\frac{e}{\hbar}\vec{A}) - mc \right\}\Psi = 0$$
$$\left\{ i\hbar\gamma^\mu(\partial_\mu + i\frac{e}{\hbar}A_\mu) - mc \right\}\Psi = 0$$
$$(i\hbar\gamma^\mu D_\mu - mc)\Psi = 0$$
$$D_\mu = \partial_\mu + i\frac{e}{\hbar}A_\mu$$

[113] The Dirac equation

$$i\hbar\frac{\partial\Psi}{\partial t} = c(-i\hbar\partial_i - eA_i)\alpha_i\Psi + (\beta mc^2 + e\phi)\Psi$$

whose Hermitian conjugate gives

$$-i\hbar\frac{\partial\Psi^\dagger}{\partial t} = c(i\hbar\partial_i - eA_i)\Psi^\dagger\alpha_i + \Psi^\dagger(\beta mc^2 + e\phi)$$

Thus, the equation of continuity

$$\frac{\partial\rho}{\partial t} + \mathrm{div}\,\vec{j} = 0$$

can be written.

In the covariant form we have $\bar{\Psi} = \Psi^\dagger\gamma^0$; the following relation for the conservation of current can be obtained: [114][115]

$$\begin{aligned} \partial_\mu j^\mu &= 0 \\ j^\mu &= \bar{\Psi}\gamma^\mu\Psi \end{aligned}$$

Thus,

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}(\Psi^\dagger\Psi) &= i\hbar(\dot{\Psi}^\dagger\Psi + \Psi^\dagger\dot{\Psi}) \\ &= -ic\hbar\Big\{(\partial_i\Psi^\dagger\alpha_i)\Psi + \Psi^\dagger\alpha_i(\partial_i\Psi)\Big\} \\ &= -ic\hbar\partial_i(\Psi^\dagger\alpha_i\Psi) \end{aligned}$$

and

$$\begin{aligned} \rho &= \Psi^\dagger\Psi \\ \vec{j} &= c\Psi^\dagger\vec{\alpha}\Psi \end{aligned}$$

Hence

$$\frac{\partial\rho}{\partial t} + \mathrm{div}\,\vec{j} = 0$$

[114]Given

$$i\hbar\gamma^\mu(\partial_\mu\Psi) - e\gamma^\mu A_\mu\Psi - mc\Psi = 0$$

the Hermitian conjugate may yield

$$-i\hbar(\partial_\mu\Psi^\dagger)\gamma^{\mu\dagger} - e\Psi^\dagger\gamma^{\mu\dagger}A_\mu - mc\Psi^\dagger = 0$$

Let us have $\bar{\Psi} = \Psi^\dagger\gamma^0$ and write

$$-i\hbar(\partial_\mu\bar{\Psi})\gamma^\mu - e\bar{\Psi}\gamma^\mu A_\mu - mc\bar{\Psi} = 0$$

Therefore the following relation of the conservation of current can be given

$$\begin{aligned} \partial_\mu j^\mu &= 0 \\ j^\mu &= \bar{\Psi}\gamma^\mu\Psi \end{aligned}$$

[115]In order to show the Lorentz invariance we must first show that the current j^μ is the invariant vector. Vice versa, we can say that the Lorentz invariance is being retained by experimentally identifying this conservation.

Conservation of Total Angular Momentum for Free Particles

Here we consider the free particles $\vec{A}=\vec{0}, \phi=0$ in Dirac representation [116]

$$H = c\vec{\alpha}\cdot\vec{p}+\beta mc^2 = c\rho_1\otimes\sigma_i p_i + \rho_3 mc^2$$

where we have

$$\begin{aligned}\vec{L} &= \vec{r}\times\vec{p} \\ L_i &= \epsilon_{ijk} r_j p_k\end{aligned}$$

we may write

$$[\frac{\hbar}{2}\vec{\sigma}+\vec{L}, H] = 0$$

Thus,

$$\begin{aligned}[H,\vec{J}] &= 0 \\ \vec{J} &= \vec{L}+\vec{S} \\ \vec{S} &= \frac{\hbar}{2}\vec{\sigma}\end{aligned}$$

[116]For

$$H = c\vec{\alpha}\cdot\vec{p}+\beta mc^2 = c\rho_1\otimes\sigma_i p_i + \rho_3 mc^2$$

in which

$$\begin{aligned}\vec{L} &= \vec{r}\times\vec{p} \\ L_i &= \epsilon_{ijk} r_j p_k\end{aligned}$$

we may write

$$\begin{aligned}[L_i, H] &= c\rho_1\otimes\sigma_\ell[\epsilon_{ijk}r_j p_k, p_\ell] = i\hbar c\rho_1\otimes\sigma_\ell\epsilon_{ijk}\delta_{j\ell}p_k \\ &= i\hbar c\rho_1\otimes\epsilon_{ijk}\sigma_j p_k = i\hbar c\rho_1\otimes(\vec{\sigma}\times\vec{p})_i\end{aligned}$$

$$\begin{aligned}[AB, C] &= ABC - CAB \\ A[B,C]+[A,C]B &= ABC - ACB + (ACB - CAB)\end{aligned}$$

while we write

$$\begin{aligned}[\sigma_i, H] &= c\rho_1\otimes[\sigma_i,\sigma_\ell]p_\ell \\ &= 2ic\rho_1\otimes\epsilon_{i\ell k}\sigma_k p_\ell \\ &= -2ic\rho_1\otimes(\vec{\sigma}\times\vec{p})_i\end{aligned}$$

Thus,

$$[\frac{\hbar}{2}\vec{\sigma}+\vec{L}, H] = 0$$

where we call $\vec{S}$ the spin, and therefore the total angular momentum $\vec{J}$ becomes the conserved quantity.

Conservation of Energy and Momentum for Free Particles

For the free particles $A^\mu = 0$, we can write

$$\begin{aligned} H_D =& c\rho_1 \otimes \sigma_i p_i + \rho_3 mc^2 \\ [H_D, H_D] =& 0 \\ [H_D, \vec{p}] =& \vec{0} \end{aligned}$$

5.2.1 The Lorentz Invariance

The Lorentz transformation

$$\begin{aligned} x'^\mu &= \Omega^\mu{}_\nu x^\nu \\ x'^\mu \Omega_\mu{}^\kappa &= x^\kappa \end{aligned}$$

gives D_μ, which is transforming as the covariance vector thus, [117] $(D_\mu = D'_\nu \Omega^\nu{}_\mu)$

$$\hat{\gamma}^\mu = \Omega^\mu{}_\nu \gamma^\nu$$

giving [118]

$$(i\hbar\hat{\gamma}^\nu D'_\nu - mc)\Psi(x) = 0$$

117

$$\partial'_\mu = \frac{\partial x^\nu}{\partial x'^\mu}\partial_\nu = \Omega_\mu{}^\nu \partial_\nu$$

$$\partial_\mu = \frac{\partial}{\partial x^\mu} = \frac{\partial x'^\nu}{\partial x^\mu}\frac{\partial}{\partial x'^\nu} = \Omega^\nu{}_\mu \partial'_\nu = \partial'_\nu \Omega^\nu{}_\mu$$

while the covariance of A_μ gives

$$\begin{aligned} A'_\mu(x') &= \Omega_\mu{}^\nu A_\nu(x) \\ A'_\mu(x')\Omega^\mu{}_\kappa &= \Omega_\mu{}^\nu A_\nu(x)\Omega^\mu{}_\kappa = g_{\mu\rho}\Omega^{\rho\nu}A_\nu(x)g^{\mu\tau}\Omega_{\tau\kappa} = \delta_\rho{}^\tau \Omega^{\rho\nu}A_\nu(x)\Omega_{\tau\kappa} \\ &= \Omega^{\rho\nu}A_\nu(x)\Omega_{\rho\kappa} = \delta^\nu{}_\kappa A_\nu(x) = A_\kappa(x) \end{aligned}$$

118

$$\begin{aligned} 0 &= (i\hbar\gamma^\mu D_\mu - mc)\Psi(x) = (i\hbar\gamma^\mu D'_\nu \Omega^\nu{}_\mu - mc)\Psi(x) \\ &= \big(i\hbar(\Omega^\nu{}_\mu \gamma^\mu)D'_\nu \Omega^\nu{}_\mu - mc\big)\Psi(x) \\ &= (i\hbar\hat{\gamma}^\nu D'_\nu - mc)\Psi(x) \end{aligned}$$

Now let us have [119]

$$\{\hat{\gamma}^\mu, \hat{\gamma}^\nu\} = 2g^{\mu\nu}$$

which indicates the existence of the regular matrix Λ, and for all μ we know that there is Λ that satisfies

$$\hat{\gamma}^\mu = \Lambda^{-1}\gamma^\mu\Lambda$$

For the in depth explanation, which is covered in our later discussion, and given the fact, the Dirac equation forms the Lorentz covariance as described in the following: [120]

$$(i\hbar\gamma^\mu D'_\mu - mc)\Psi'(x') = 0$$

Thus,

$$\Psi'(x') = \Lambda\Psi(x)$$

so, we can write

$$x' = \mathcal{L}x, \quad x'^\mu = \Omega^\mu{}_\nu x^\nu$$

Therefore,

$$\Psi'(x') = (\mathcal{L}\Psi)(x') = (\mathcal{L}\Psi)(\mathcal{L}x) = \Lambda\Psi(x)$$

A specific structure of the transformation matrix Here we elaborate on Λ used in our discussion for a specific construction. First, consider the infinitesimal Lorentz transformation

$$\Omega^\mu{}_\nu = g^\mu{}_\nu + \delta\Omega^\mu{}_\nu$$

119

$$\begin{aligned}\{\hat{\gamma}^\mu, \hat{\gamma}^\nu\} &= \Omega^\mu{}_\kappa\Omega^\nu{}_\rho\{\gamma^\kappa, \gamma^\rho\} = 2\Omega^\mu{}_\kappa\Omega^\nu{}_\rho g^{\kappa\rho} \\ &= 2\Omega^\mu{}_\kappa\Omega^{\nu\kappa} = 2g^{\mu\tau}\Omega_{\tau\kappa}\Omega^{\nu\kappa} = 2g^{\mu\tau}\delta_\tau{}^\nu = 2g^{\mu\nu}\end{aligned}$$

120

$$\begin{aligned}&(i\hbar\Lambda^{-1}\gamma^\mu\Lambda D'_\mu - mc)\Psi = 0 \\ &\quad (i\hbar\gamma^\mu\Lambda D'_\mu - mc\Lambda)\Psi \equiv (i\hbar\gamma^\mu D'_\mu - mc)\Psi'(x') = 0\end{aligned}$$

Given that we have up to the degree of first-order $\Omega^{\mu}{}_{\nu}\Omega_{\mu}{}^{\lambda} = g^{\lambda}_{\nu}$ for the infinitesimal quantity, [121] we can write

$$\delta\Omega_{\lambda\nu} = -\,\delta\Omega_{\nu\lambda}$$

Now, let us rewrite $\Lambda^{-1}\gamma^{\mu}\Lambda = \Omega^{\mu}{}_{\nu}\gamma^{\nu}$. To do so, we begin by writing down

$$\begin{aligned}
\Omega^{\mu}{}_{\nu} =& g^{\mu}{}_{\nu} + \delta\Omega^{\mu}{}_{\nu} \\
\Omega^{\mu}{}_{\nu}\gamma^{\nu} =& \gamma^{\mu} + \delta\Omega^{\mu}{}_{\nu}\gamma^{\nu} \\
\Lambda =& I + \delta\Lambda \quad Towhich, wemaywrite \\
(I-\delta\Lambda)\gamma^{\mu}(I+\delta\Lambda) =& \gamma^{\mu} - [\delta\Lambda, \gamma^{\mu}]
\end{aligned}$$

Therefore,

$$\begin{aligned}
\delta\Omega^{\mu}{}_{\nu}\gamma^{\nu} =& -\,[\delta\Lambda, \gamma^{\mu}] \\
\delta\Omega_{\mu\nu}\gamma^{\nu} =& -\,[\delta\Lambda, \gamma_{\mu}]
\end{aligned}$$

and

$$\delta\Lambda = -\,\frac{i}{4}\sigma^{\kappa\nu}\delta\Omega_{\kappa\nu}$$

Given the antisymmetric property of $\delta\Omega_{\mu\nu}$ we suppose

$$\sigma^{\mu\nu} = -\,\sigma^{\nu\mu}$$

without losing the generality, and being aware of the antisymmetric property, we can write

$$\begin{aligned}
\delta\Omega_{\mu\nu}\gamma^{\nu} =& \frac{i}{4}[\sigma^{\kappa\nu}, \gamma_{\mu}]\delta\Omega_{\kappa\nu} \\
[\sigma^{\kappa\nu}, \gamma_{\mu}] =& -\,2i(g^{\kappa}_{\mu}\gamma^{\nu} - g^{\nu}_{\mu}\gamma^{\kappa})
\end{aligned}$$

121

$$\begin{aligned}
g^{\lambda}_{\nu} =& (g^{\mu}{}_{\nu} + \delta\Omega^{\mu}{}_{\nu})(g_{\mu}{}^{\lambda} + \delta\Omega_{\mu}{}^{\lambda}) \\
=& g^{\lambda}_{\nu} + \delta\Omega^{\lambda}{}_{\nu} + \delta\Omega_{\nu}{}^{\lambda} \\
0 =& \delta\Omega^{\lambda}{}_{\nu} + \delta\Omega_{\nu}{}^{\lambda} \\
0 =& \delta\Omega_{\lambda\nu} + \delta\Omega_{\nu\lambda}
\end{aligned}$$

We can show that the following relation for $\sigma^{\mu\nu}$ being satisfied: [122]

$$\sigma^{\mu\nu} = \frac{i}{2}[\gamma^\mu, \gamma^\nu]$$

By integrating the above we obtain [123]

$$\begin{aligned}\boldsymbol{\Omega} &= e^{\boldsymbol{\omega}}, \\ \tilde{\boldsymbol{\omega}} &= -\boldsymbol{\omega}\end{aligned}$$

For the above equations we may write down ($\boldsymbol{\omega}$: real antisymmetric) [124]

---

[122]

$$\begin{aligned}\sigma^{\mu\nu} =& \frac{i}{2}[\gamma^\mu, \gamma^\nu] \\ \because [\gamma^\kappa\gamma^\nu, \gamma^\mu] =& \gamma^\kappa\gamma^\nu\gamma^\mu - \gamma^\mu\gamma^\kappa\gamma^\nu \\ =& \gamma^\kappa(-\gamma^\mu\gamma^\nu + 2g^{\mu\nu}) - \gamma^\mu\gamma^\kappa\gamma^\nu \\ =& -\gamma^\kappa\gamma^\mu\gamma^\nu + 2\gamma^\kappa g^{\mu\nu} - \gamma^\mu\gamma^\kappa\gamma^\nu \\ =& -2g^{\kappa\mu}\gamma^\nu + 2\gamma^\kappa g^{\mu\nu} \\ [[\gamma^\kappa, \gamma^\nu], \gamma^\mu] =& -2g^{\kappa\mu}\gamma^\nu + 2\gamma^\kappa g^{\mu\nu} - (-2g^{\nu\mu}\gamma^\kappa + 2\gamma^\nu g^{\mu\kappa}) \\ =& -4g^{\kappa\mu}\gamma^\nu + 4\gamma^\kappa g^{\mu\nu} \\ [[\gamma^\kappa, \gamma^\nu], \gamma_\mu] =& -4g^\kappa_\mu\gamma^\nu + 4\gamma^\kappa g^\nu_\mu \\ [\frac{i}{2}[\gamma^\kappa, \gamma^\nu], \gamma_\mu] =& -2i(g^\kappa_\mu\gamma^\nu - \gamma^\kappa g^\nu_\mu)\end{aligned}$$

[123]

$$\begin{aligned}\boldsymbol{\Omega} &= e^{\boldsymbol{\omega}} \\ \boldsymbol{\Omega}\tilde{\boldsymbol{\Omega}} &= \boldsymbol{I} gives \\ \tilde{\boldsymbol{\omega}} &= -\boldsymbol{\omega}\end{aligned}$$

To express the components, given

$$(\tilde{\Omega})^\mu{}_\nu = \Omega_\nu{}^\mu$$

which yields

$$\begin{aligned}(\Omega\tilde{\Omega})^\mu{}_\nu =& \Omega^\mu{}_\kappa\Omega_\nu{}^\kappa = \delta^\mu{}_\nu \\ (\Omega^{-1})^\kappa{}_\nu =& \Omega_\nu{}^\kappa \\ (\tilde{\omega})^\mu{}_\nu =& \omega_\nu{}^\mu = -\omega^\mu{}_\nu \\ (e^\omega)^\mu{}_\kappa(e^\omega)_\nu{}^\kappa =& (e^\omega)^\mu{}_\kappa(\tilde{e^\omega})^\kappa{}_\nu = (e^\omega)^\mu{}_\kappa(e^{\tilde{\omega}})^\kappa{}_\nu = \delta^\mu{}_\nu\end{aligned}$$

[124] First we begin with writing down

$$\hat{\gamma}^\kappa = (e^{t\omega})^\kappa{}_\lambda\gamma^\lambda\Big|_{t=1}$$

$$\Lambda = e^{-\frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu}}$$

While [125]

$$\Lambda^\dagger = \gamma^0 \Lambda^{-1} \gamma^0$$

and

$$\Lambda(t) = e^{-\frac{it}{4}\sigma^{\mu\nu}\omega_{\mu\nu}} = e^{-\frac{it}{4}\sigma_\mu{}^\nu \omega^\mu{}_\nu}$$

to give

$$\begin{aligned}
\Gamma^\kappa(t) =& \Lambda(t)^{-1}\gamma^\kappa\Lambda(t) = e^{+\frac{it}{4}\sigma_\mu{}^\nu\omega^\mu{}_\nu}\gamma^\kappa e^{-\frac{it}{4}\sigma_\mu{}^\nu\omega^\mu{}_\nu} \\
\frac{\partial\Gamma^\kappa}{\partial t} =& \frac{i}{4}\Lambda^{-1}[\sigma_\mu{}^\nu, \gamma^\kappa]\Lambda\omega^\mu{}_\nu = \frac{1}{2}\Lambda^{-1}(g^\kappa_\mu\gamma^\nu - g^{\kappa\nu}\gamma_\mu)\Lambda\omega^\mu{}_\nu \\
=& \frac{1}{2}(g^\kappa_\mu\Gamma^\nu - g^{\kappa\nu}\Gamma_\mu)\omega^\mu{}_\nu = \frac{1}{2}(\Gamma^\nu\omega^\kappa{}_\nu - \Gamma_\mu\omega^{\mu\kappa}) = \frac{1}{2}(\Gamma^\nu\omega^\kappa{}_\nu - \Gamma^\mu\omega_\mu{}^\kappa) \\
=& \frac{1}{2}(\Gamma^\nu\omega^\kappa{}_\nu + \Gamma^\mu\omega^\kappa{}_\mu) = \omega^\kappa{}_\mu\Gamma^\mu
\end{aligned}$$

Where $t = 0$, note for $\Gamma^\mu(0) = \gamma^\mu$, the solution of the simultaneous differential equation is given

$$\Gamma^\mu = (e^{t\omega})^\mu{}_\nu\gamma^\nu$$

While $t = 1$, the solution is given

$$\Gamma^\mu(1) = \hat{\gamma}^\mu$$

125

$$\begin{aligned}
\sigma^{\mu\nu\dagger} =& \left(\frac{i}{2}[\gamma^\mu, \gamma^\nu]\right)^\dagger = -\frac{i}{2}[\gamma^{\nu\dagger}, \gamma^{\mu\dagger}] \\
=& \frac{i}{2}[\gamma^{\mu\dagger}, \gamma^{\nu\dagger}] = \gamma^0\frac{i}{2}[\gamma^\mu, \gamma^\nu]\gamma^0 \\
=& \gamma^0\sigma^{\mu\nu}\gamma^0 \\
\Lambda^\dagger =& e^{\frac{i}{4}(\sigma^{\mu\nu})^\dagger\omega_{\mu\nu}} \\
=& \gamma^0 e^{\frac{i}{4}(\sigma^{\mu\nu})\omega_{\mu\nu}}\gamma^0 \\
=& \gamma^0\Lambda^{-1}\gamma^0
\end{aligned}$$

For this Lorentz transformation, we can write the current

$$\begin{aligned}\Psi =&\Lambda^{-1}\Psi' = \gamma^0\Lambda^\dagger\gamma^0\Psi' \\ j^\mu =&\bar{\Psi}\gamma^\mu\Psi \\ =&\Psi^\dagger\gamma^0\gamma^\mu\Psi \\ =&\Psi'^\dagger\gamma^0\Lambda\gamma^0(\gamma^0\gamma^\mu)\Lambda^{-1}\Psi \\ =&\Psi'^\dagger\gamma^0\Lambda\gamma^\mu\Lambda^{-1}\Psi' \\ =&\bar{\Psi}'\Lambda\gamma^\mu\Lambda^{-1}\Psi'\end{aligned}$$

Recall our discussion in the previous section, we can express

$$\begin{aligned}\Omega^\mu{}_\nu\gamma^\nu =&\Lambda^{-1}\gamma^\mu\Lambda \\ \Omega^\mu{}_\nu\Lambda\gamma^\nu\Lambda^{-1} =&\gamma^\mu \\ \Omega_\mu{}^\kappa\Omega^\mu{}_\nu\Lambda\gamma^\nu\Lambda^{-1} =&g^\kappa_\nu\Lambda\gamma^\nu\Lambda^{-1} = \Lambda\gamma^\kappa\Lambda^{-1} = \\ =&\Omega_\mu{}^\kappa\gamma^\mu = \gamma^\mu\Omega_\mu{}^\kappa\end{aligned}$$

Thus, [126]

$$\begin{aligned}j'^\kappa =&\Omega^\kappa{}_\mu j^\mu \\ j'^\mu =&\bar{\Psi}'\gamma^\mu\Psi'\end{aligned}$$

This implies that the current is capable of transforming itself into the invariant vector such that the conservation $\partial_\mu j^\mu = 0$ can be regarded as the Lorentz invariant.

5.3 The Plane-wave Solutions for the Free Dirac Equation

In this section, we consider the solutions for Dirac equation where $A^\mu = 0$. Let us write the Dirac Hamiltonian

$$H =c\vec{\alpha}\cdot\frac{\vec{\nabla}}{i} + \beta mc^2 = c\rho_1\otimes\vec{\sigma}\cdot\vec{p} + \rho_3 mc^2$$

such that the Dirac equation can be written

$$i\hbar c\partial_0\Psi =H\Psi$$

[126]

$$\begin{aligned}j^\mu =&j'^\nu\Omega_\nu{}^\mu \\ \Omega^\kappa{}_\mu j^\mu =&\Omega^\kappa{}_\mu\Omega_\nu{}^\mu j'^\nu = g^\kappa_\nu j'^\nu = j'^\kappa\end{aligned}$$

Rewrite the above and give

$$
\begin{aligned}
\Psi^{(+)}(x) =& e^{-ik_\mu x^\mu} u(k) \\
\Psi^{(-)}(x) =& e^{+ik_\mu x^\mu} v(k) \\
-k^\mu x^\mu =& -k^0 x^0 + k^i x^i = \vec{k} \cdot \vec{r} - \omega t \\
(k_x, k_y, k_z) =& (k^1, k^2, k^3) = (-k_1, -k_2, -k_3) \\
k_0 =& k^0 = \frac{\omega}{c}
\end{aligned}
$$

Thus,

$$
H^2 = (c^2 \vec{p}^{\,2} + m^2 c^4) \mathbf{1}_4
$$

Note the above, and obtain the following relation for the solutions of the plane waves:[127]

$$
\begin{aligned}
\vec{p}\Psi^{(\pm)} =& \pm \hbar \vec{k} \Psi^{(\pm)} \\
H\Psi^{(\pm)} =& \pm E \Psi^{(\pm)} \\
Hu =& + Eu \\
Hv =& - Ev \\
E =& c\hbar k_0 = c\hbar k^0 = \hbar\omega \\
\hbar k_0 =& \sqrt{\hbar \vec{k}^{\,2} + m^2 c^2} \\
k_\mu k^\mu =& \left(\frac{mc}{\hbar}\right)^2
\end{aligned}
$$

127

$$
\begin{aligned}
H^2 =& c^2 \rho^2 \otimes (\vec{\sigma} \cdot \vec{p})^2 + \rho_3^2 m^2 c^4 + 2mc^2 (\rho_1 \rho_3 + \rho_3 \rho_1) \vec{\sigma} \cdot \vec{p} \\
=& (c^2 \vec{p}^{\,2} + m^2 c^4) \mathbf{1}_4
\end{aligned}
$$

or

$$
\begin{aligned}
H =& \gamma^0 (-i\hbar c \vec{\gamma} \cdot \vec{\nabla} + mc^2) \\
H^2 =& \gamma^0 (-i\hbar c \vec{\gamma} \cdot \vec{\nabla} + mc^2) \gamma^0 (-i\hbar c \vec{\gamma} \cdot \vec{\nabla} + mc) \\
=& -\hbar^2 c^2 \gamma^0 \gamma^i \gamma^0 \gamma^j (\vec{\nabla})_i (\vec{\nabla})_j + m^2 c^4 - i\hbar mc^2 (\gamma^i \gamma^0 + \gamma^i \gamma^0)(\vec{\nabla})_i \\
=& -\hbar^2 c^2 (-\gamma^i) \gamma^j (\vec{\nabla})_i (\vec{\nabla})_j + m^2 c^4 \\
=& -\hbar^2 c^2 \vec{\nabla}^2 + m^2 c^4 = c^2 \vec{p}^{\,2} + m^2 c^4
\end{aligned}
$$

$$
\vec{p}\Psi^{(\pm)} = \frac{\hbar}{i} \vec{\nabla} \Psi^{(\pm)} = \frac{\hbar}{i} (\mp i)(k_1, k_2, k_3) \Psi^{(\pm)} = \pm \hbar (k^1, k^2, k^3) \Psi^{(\pm)} = \pm \hbar \vec{k} \Psi^{(\pm)}
$$

While we let $(i\hbar\gamma^\mu\partial_m u - mc)\Psi^{(\pm)} = 0$ given by the Dirac equation $\not{k} = k_\mu\gamma^\mu$ such that [128]

$$
\begin{aligned}
(\hbar\not{k} - mc)u =& 0\\
(\hbar\not{k} + mc)v =& 0
\end{aligned}
$$

5.3.1 In the Case of $m \neq 0$

If we take the inertial system $\vec{v} = 0$, $k^\mu = (\frac{mc}{\hbar}, 0, 0, 0)$ which stays stationary, the complete system $u^\alpha_{\text{rest}}, v^\alpha_{\text{rest}}$,$\alpha = 1, 2$ can be given [129]

$$
\begin{aligned}
u^1_{\text{rest}} =& \begin{pmatrix} 1\\0\\0\\0 \end{pmatrix}, \quad u^2_{\text{rest}} = \begin{pmatrix} 0\\1\\0\\0 \end{pmatrix}, \quad v^1_{\text{rest}} = \begin{pmatrix} 0\\0\\1\\0 \end{pmatrix}, \quad v^2_{\text{rest}} = \begin{pmatrix} 0\\0\\0\\1 \end{pmatrix}\\
\bar{u}^\alpha u^\beta =& \delta_{\alpha\beta}, \quad \bar{v}^\alpha v^\beta = -\delta_{\alpha\beta}, \quad \bar{u}^\alpha v^\beta = \bar{v}^\alpha u^\beta = 0\\
u^\alpha_{\text{rest}} =& \begin{pmatrix} \psi^\alpha_{\text{rest}}\\ 0 \end{pmatrix}, \quad v^\alpha_{\text{rest}} = \begin{pmatrix} 0\\ \chi^\alpha_{\text{rest}} \end{pmatrix}
\end{aligned}
$$

From which we determine the general solutions for the plane waves via Lorentz

---

128

$$
\begin{aligned}
(\pm\hbar\not{k} - mc)\Psi^{(\pm)}(x) =& 0, \quad \not{k} = k_\mu\gamma^\mu\\
(\hbar\not{k} - mc)u =& 0\\
(\hbar\not{k} + mc)v =& 0
\end{aligned}
$$

129

$$
\begin{aligned}
mc(\gamma^0 - 1)u_{\text{rest}} =& mc \begin{pmatrix} 0 &&& \\ & 0 && \\ && -2 & \\ &&& -2 \end{pmatrix} u_{\text{rest}} = 0\\
mc(\gamma^0 + 1)v_{\text{rest}} =& mc \begin{pmatrix} 2 &&& \\ & 2 && \\ && 0 & \\ &&& 0 \end{pmatrix} v_{\text{rest}} = 0
\end{aligned}
$$

transformation. We begin by the equations [130]

$$
\begin{aligned}
\not{a}\not{b} =& -ia_\mu b_\nu \sigma^{\mu\nu} + a_\mu b^\nu \\
\not{k}\not{k} =& k_\mu k^\mu = k^2
\end{aligned}
$$

which gives

$$
\begin{aligned}
u^\alpha =& \frac{1}{mc}(\hbar\not{k} + mc)u^\alpha_{\mathrm{rest}} \\
=& \frac{1}{mc}\begin{pmatrix} (\hbar k_0 + mc)\psi^\alpha_{\mathrm{rest}} \\ \gamma_i \hbar k^i \psi^\alpha_{\mathrm{rest}} \end{pmatrix} = \frac{1}{mc}\begin{pmatrix} (\frac{E}{c} + mc)\psi^\alpha_{\mathrm{rest}} \\ (\vec{\sigma}\cdot\vec{p})\psi^\alpha_{\mathrm{rest}} \end{pmatrix}
\end{aligned}
$$

5.4 The Non-relativistic Limit

The four components spinor can be written by the two components spinor ψ and χ:

$$
\Psi(x) = \begin{pmatrix} \psi(x) \\ \chi(x) \end{pmatrix}
$$

Let us write the Dirac equation in the forms

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\begin{pmatrix} \psi \\ \chi \end{pmatrix} &= \begin{pmatrix} mc^2 + e\phi & cP \\ cP & -mc^2 + e\phi \end{pmatrix}\begin{pmatrix} \psi \\ \chi \end{pmatrix} \\
P &= \vec{\alpha}\cdot\vec{\pi} = \vec{\sigma}\cdot(\vec{p} - e\vec{A})
\end{aligned}
$$

In steady states, we obtain

$$
\begin{aligned}
\psi(x) &= e^{-iEt/\hbar}\psi(\vec{r}) \\
\chi(x) &= e^{-iEt/\hbar}\chi(\vec{r})
\end{aligned}
$$

yielding

$$
\begin{aligned}
(mc^2 + e\phi)\psi + cP\chi &= E\psi \\
cP\psi + (-mc^2 + e\phi)\chi &= E\chi
\end{aligned}
$$

[130]

$$
\begin{aligned}
\not{a}\not{b} =& a_\mu\gamma^\mu b_\nu\gamma^\nu = \frac{1}{2}(a_\mu b_\nu\gamma^\mu\gamma^\nu + a_\nu b_\mu\gamma^\nu\gamma^\mu) = \frac{1}{2}\big(a_\mu b_\nu\gamma^\mu\gamma^\nu + a_\nu b_\mu(-\gamma^\mu\gamma^\nu + 2g^{\mu\nu})\big) \\
=& \frac{1}{2}(a_\mu b_\nu - a_\nu b_\mu)\gamma^\mu\gamma^\nu + a_\mu b^\nu = \frac{1}{2}a_\mu b_\nu[\gamma^\mu, \gamma^\nu] + a_\mu b^\nu \\
=& -ia_\mu b_\nu\sigma^{\mu\nu} + a_\mu b^\nu \\
\sigma^{\mu\nu} =& \frac{i}{2}[\gamma^\mu, \gamma^\nu]
\end{aligned}
$$

To consider the non-relativistic limit

$$e\phi \quad << \quad mc^2, \quad \frac{P^2}{2m} << mc^2, \quad E \approx mc^2$$

we transform the Dirac equation into a much more convenient form

$$W \quad = \quad E - mc^2$$

Thus, given the second equation we can write down

$$\begin{aligned} \chi &= \frac{c}{2M'c^2} P\psi = \frac{1}{2M'c} P\psi \\ 2M'c^2 &= E + mc^2 - e\phi = 2mc^2 + W - e\phi \\ M' &= m + \frac{1}{2c^2}(W - e\phi) \end{aligned}$$

From these equations the Dirac equation can be accurately rewritten in the form [131]

$$(P\frac{1}{2M'}P + e\phi)\psi \quad = \quad W\psi$$

The Lowest Order Approximation

For the lowest order approximation we suppose

$$M' \quad = \quad m$$

This gives (Schroedinger approximation)

$$\begin{aligned} H_{sh}\psi &= W\psi \\ H_{sh} &= \frac{1}{2m}P^2 + e\phi \end{aligned}$$

Here note that [132]

$$P^2 \quad = \quad \vec{\pi}^2 - e\hbar\vec{\sigma}\cdot\vec{B}, \quad \vec{B} = \mathrm{rot}\, A$$

131

$$\begin{aligned} (mc^2 + e\phi)\psi + P\frac{1}{2M'}P\psi &= E\psi \\ (P\frac{1}{2M'}P + e\phi)\psi &= W\psi \end{aligned}$$

132

$$\begin{aligned} P^2 &= (\vec{\sigma}\cdot\vec{\pi})^2 = (\sigma_i\pi^i)(\sigma_j\pi^j) = \vec{\pi}^2 + \frac{1}{2}(\sigma_i\sigma_j - \sigma_j\sigma_i)\pi^i\pi^j \\ &= \vec{\pi}^2 + i\epsilon_{ijk}\sigma_i\pi_j\pi_k = \vec{\pi}^2 + i\epsilon_{ijk}\sigma_i(p_j - eA_j)(p_k - eA_k) \\ &= \vec{\pi}^2 - ie\epsilon_{ijk}\sigma_i(p_jA_k) = \vec{\pi}^2 - ie\epsilon_{ijk}\sigma_i\frac{\hbar}{i}(\partial_jA_k) \\ &= \vec{\pi}^2 - e\hbar\vec{\sigma}\cdot\vec{B}, \quad \vec{B} = \mathrm{rot}\, A \end{aligned}$$

Thus,

$$
\begin{aligned}
H_{sh} &= \frac{(\vec{p}-e\vec{A})^2}{2m} + e\phi + \vec{\mu}\cdot\vec{B} \\
\vec{\mu} &= -\frac{e\hbar}{2m}\vec{\sigma} \\
&= -g\mu_B \vec{S}/\hbar, \quad (\vec{S} = \frac{\hbar}{2}\sigma) \\
Where Borh magneton is\ \mu_B &= \frac{e\hbar}{2m} \\
, and so call\ g\ factor is\ g &= 2
\end{aligned}
$$

.

The Approximation to $\frac{v^2}{c^2}$

In our next step, we raise the order of approximation [133] to

$$
\frac{1}{M'} \approx \frac{1}{m} - \frac{1}{2m^2c^2}(W - e\phi)
$$

Here we make an estimate of $W - e\phi \approx mv^2$, where we take the value up to $\frac{v^2}{c^2}$ such that we can write

$$
P\frac{1}{2M'}P = \frac{P^2}{2m} - \frac{1}{4m^2c^2}WP^2 + \frac{e}{4m^2c^2}P\phi P
$$

and which gives

$$
\left(\frac{P^2}{2m} + e\phi + \frac{e}{4m^2c^2}P\phi P\right)\psi = W(1 + \frac{1}{4m^2c^2}P^2)\psi
$$

Now we consider the normalization condition such that

$$
\chi = \frac{1}{2mc}P\psi
$$

For this we can write

$$
\begin{aligned}
1 &= \int d^3r\, \Psi^\dagger\Psi = \int d^3r\, (\psi^\dagger\psi + \chi^\dagger\chi) \\
&= \int d^3r\, \psi^\dagger(1 + \frac{1}{4m^2c^2}P^2)\psi
\end{aligned}
$$

133

$$
\begin{aligned}
\frac{1}{M'} &= \frac{1}{m}(1 + \frac{1}{2mc^2}(W - e\phi))^{-1} \\
&= \frac{1}{m} - \frac{1}{2m^2c^2}(W - e\phi) + o(\frac{v^2}{c^2}) \\
&\approx \frac{1}{m} - \frac{1}{2m^2c^2}(W - e\phi)
\end{aligned}
$$

Therefore if we let the normalized wavefunction ψ_N in two components to be

$$\begin{aligned} \psi_N &= \Omega\psi \\ 1 &= \int d^3r\, \psi_N^\dagger \psi_N \end{aligned}$$

then we may also have

$$\Omega = 1 + \frac{1}{8m^2c^2}P^2$$

The equation for ψ_N can be given [134] [135]

$$\left(\frac{P^2}{2m} + e\phi - \frac{P^4}{8m^3c^2} - \frac{e}{8m^2c^2}[P,[P,\phi]]\right)\psi_N = W\psi_N$$

When we look into the degree of order, the below indicates that there are the values up to $\frac{v^2}{c^2}$:

$$\begin{aligned} \frac{e}{8m^2c^2}[P,[P,\phi]] &\approx \frac{mv^2(mv)^2}{m^2c^2} = \frac{1}{2}mv^2 \cdot \left(\frac{v^2}{c^2}\right) \\ \frac{1}{8m^3c^2}P^4 &\approx \frac{(mv)^4}{m^3c^2} = \frac{1}{2}mv^2 \cdot \left(\frac{v^2}{c^2}\right) \end{aligned}$$

[134] Given $\{A^2,B\} - 2ABA = A^2B - BA^2 - 2ABA$, $[A,[A,B]] = A(AB-BA) - (AB-BA)A = A^2B - 2ABA + BA^2$ we may use $\{A^2,B\} - 2ABA = [A,[A,B]]$

[135]

$$\begin{aligned} \left(\frac{P^2}{2m} + e\phi + \frac{e}{4m^2c^2}P\phi P\right)\Omega^{-1}\psi_N &= W\Omega\psi_N \\ \Omega^{-1}\left(\frac{P^2}{2m} + e\phi + \frac{e}{4m^2c^2}P\phi P\right)\Omega^{-1}\psi_N &= W\psi_N \\ \left(\frac{P^2}{2m} + e\phi - \frac{P^4}{8m^3c^2} - \frac{e}{8m^2c^2}\{\phi,P^2\} + \frac{e}{4m^2c^2}P\phi P\right)\psi_N + o(\frac{v^2}{c^2}) &= W\psi_N \\ \left(\frac{P^2}{2m} + e\phi - \frac{P^4}{8m^3c^2} - \frac{e}{8m^2c^2}[P,[P,\phi]]\right)\psi_N &= W\psi_N \end{aligned}$$

[136]

$$
\begin{aligned}
P^4 &= [\vec{\pi}^2 - e\hbar(\vec{\sigma}\cdot\vec{B})]^2 \\
[P,\phi] &= [\sigma_j(p_j - eA_j),\phi] = \sigma_j(p_j\phi) = -i\hbar\sigma_j\partial_j\phi
\end{aligned}
$$

In the stationary electric fields, which is given by $\vec{E} = -\vec{\nabla}\phi$, we can write

$$
[P,[P,\phi]] = \hbar^2 \mathrm{div}\,\vec{E} + 2\hbar\vec{\sigma}\cdot\vec{E}\times\vec{\pi}
$$

The approximation (Pauli approximation) can be made to the degree of order we obtained in the above so that we write

$$
\begin{aligned}
H_{pauli}\psi_N &= W\psi_N \\
H_{pauli} &= H_{sh} + H_c \\
H_{sh} &= \frac{1}{2m}(\vec{\pi}^2 - e\hbar\vec{\sigma}\cdot\vec{B})^2 + e\phi = \frac{1}{2m}\vec{\pi}^2 + e\phi - \frac{e\hbar}{2m}\vec{\sigma}\cdot\vec{B} \\
H_c &= -\frac{(\vec{\pi}^2 - e\hbar\sigma\cdot\vec{B})^2}{8m^3c^2} - \frac{e\hbar^2}{8m^2c^2}\mathrm{div}\,\vec{E} - \frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{E}\times\vec{\pi}
\end{aligned}
$$

Now we consider the non-relativistic limit for the classical Hamiltonian, we can write

$$
\begin{aligned}
H_{cl} &= c\sqrt{\vec{\pi}^2 + m^2c^2} + e\phi = mc^2\sqrt{1 + \frac{\vec{\pi}^2}{m^2c^2}} + e\phi \\
&\approx e\phi + mc^2(1 + \frac{1}{2}\frac{\pi^2}{m^2c^2} - \frac{1}{8}\frac{\pi^4}{m^4c^4}) \\
&= e\phi + mc^2 + \frac{\vec{\pi}^2}{2m} - \frac{\vec{\pi}^4}{2m^3c^4}
\end{aligned}
$$

where we define $\vec{\pi}^2 \to \vec{\pi}^2 - e\hbar\vec{\sigma}\cdot\vec{B}$, which includes the effects by the spin, the first term of H_c can be regarded as the correction term for the relativistic kinetic energy. The second term of the equation is called the Darwin term.

136

$$
\begin{aligned}
P^4 &= [\vec{\pi}^2 - e\hbar(\vec{\sigma}\cdot\vec{B})]^2 \\
[P,\phi] &= [\sigma_j(p_j - eA_j),\phi] = \sigma_j(p_j\phi) = -i\hbar\sigma_j\partial_j\phi \\
[P,[P,\phi]] &= -i\hbar[\sigma_i(p_i - eA_i),\sigma_j\partial_j\phi] \\
&= -\hbar^2[\sigma_i\partial_i,\sigma_j\partial_j\phi] + ie\hbar[\sigma_iA_i,\sigma_j\partial_j\phi] \\
&= -\hbar^2\sigma_i\sigma_j\partial_i\partial_j\phi - \hbar^2\sigma_i\sigma_j(\partial_j\phi)\partial_i + \hbar^2\sigma_j\sigma_i(\partial_j\phi)\partial_i + ie\hbar[\sigma_i,\sigma_j]A_i\partial_j\phi \\
&= -\hbar^2\Delta\phi - \hbar^2[\sigma_i,\sigma_j](\partial_j\phi)\partial_i - 2e\hbar\epsilon_{ijk}\sigma_kA_i(\partial_j\phi) \\
&= -\hbar^2\Delta\phi - 2i\hbar^2\epsilon_{ijk}\sigma_k(\partial_j\phi)\partial_i - 2e\hbar\epsilon_{ijk}\sigma_kA_i(\partial_j\phi) \\
&= \hbar^2\mathrm{div}\,\vec{E} - 2i\hbar^2\vec{\sigma}\cdot\vec{E}\times\vec{\nabla} + 2e\hbar\sigma\cdot\vec{A}\times\vec{E} \\
&= \hbar^2\mathrm{div}\,\vec{E} + 2\hbar\vec{\sigma}\cdot\vec{E}\times(\vec{p} - e\vec{A}) \\
&= \hbar^2\mathrm{div}\,\vec{E} + 2\hbar\vec{\sigma}\cdot\vec{E}\times\vec{\pi}
\end{aligned}
$$

For the last term of the equation, when we consider the central force field,
[137]

$$
\begin{aligned}
e\phi(\vec{r}) &= V(r), \quad \vec{A} = \vec{0} \\
H_{LS} &\equiv -\frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{E}\times\vec{\pi} = \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{\sigma}\cdot(\vec{r}\times\vec{p}) \\
&= \left(\frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{s}\cdot\vec{\ell} \\
\vec{s} &= \frac{\hbar}{2}\vec{\sigma} \\
\vec{\ell} &= \vec{r}\times\vec{p}
\end{aligned}
$$

and is called the spin-orbit interaction.

The Time-dependent Case (The Lowest Order)

Given

$$
\Psi = e^{-imc^2t/\hbar}\begin{pmatrix}\psi \\ \chi\end{pmatrix}
$$

Recall our discussion for the steady states, and we direct our attention to the slow mode in energy mc^2 periphery:

$$
\begin{aligned}
mc^2\psi + i\hbar\partial_t\psi &= (mc^2 + e\phi)\psi + cP\chi \\
mc^2\chi + i\hbar\partial_t\chi &= cP\psi + (-mc^2 + e\phi)\chi
\end{aligned}
$$

which gives

$$
\begin{aligned}
i\hbar\partial_t\psi &= e\phi\psi + cP\chi \\
i\hbar\partial_t\chi &= cP\psi + (-2mc^2 + e\phi)\chi
\end{aligned}
$$

We define $mv^2 << mc^2$, $e\phi << mc^2$, the second equation may give

$$
\chi = \frac{cP}{2mc^2}\psi
$$

Thus, we can derive the Schr?dinger equation

$$
\begin{aligned}
i\hbar\frac{\partial\psi}{\partial t} &= H_{sh}\psi \\
H_{sh} &= \frac{P^2}{2m} = \frac{(\vec{p}-e\vec{A})^2}{2m} + e\phi + \vec{\mu}\cdot\vec{B}
\end{aligned}
$$

137

$$
\vec{E} = -\frac{\partial V}{\partial r}\hat{r} = -\frac{1}{r}\frac{\partial V}{\partial r}\vec{r}
$$

PartIII

Quantum Mechanics of ManyParticle System

6 Second Quantization and Interaction

In this section, we discuss an effect of interaction in many-fermion systems by second quantzation approach. We begin with problems of single particles, followed by the discussion of many particle problems of free (no interaction) N- particles then we finally discuss the interactions.

6.1 The Classical Equation of Motion for a Single Particle

To begin with, recall Newton'S equation of motions for a classical particle having a mass m in one-dimentional potenital $V(x)$.

$$m\ddot{x} = -\frac{\partial}{\partial x}V(x)$$

IN analytical mechanical perspective, the Hamiltonian formulation shows the equivalent canonical equation of the above:

$$\begin{aligned} H_{cl}(x,p) &= \frac{\vec{p}^2}{2m} + V, \quad \vec{p} = m\vec{v} = m\dot{x} \\ \frac{\partial H_{cl}}{\partial x} &= -\dot{p} \\ \frac{\partial H_{cl}}{\partial p} &= \dot{x} \end{aligned}$$

Note that the Hamiltonian $H_{cl}(x,p)$ is enpressed as a pair of canonical variables (x,p).

[138] The state of the classical system is specified by each point (x, y, z, p_x, p_y, p_z) in phase space.

Likewise, we can express the three-dimension:

$$m\ddot{\vec{r}} = -\vec{\nabla}V(\vec{r})$$

[138]Show this.

In the Hamiltonian formulation we can write

$$\begin{aligned} H_{cl}(\vec{r},\vec{p}) &= \frac{\vec{p}^2}{2m} + V, \quad \vec{p} = m\dot{\vec{r}} \\ \frac{\partial H_{cl}}{\partial r_i} &= -\dot{p}_i \\ \frac{\partial H_{cl}}{\partial p_i} &= \dot{r}_i, \quad i = x, y, z \end{aligned}$$

6.2 (First) Quantization of a Single Free Particle

A first quantization bases its discussion on the Hamiltonian formalism of analytical mechanics, in which a pair of mutually conjugate canonical variables (x, p) being replaced by an operator in the equation called Schroedinger equation for the wavefunction. In our one-dimensional case, for example, we let 、 $\hat{x}$,$\hat{p}$ be the operators which requires the commutators between the two; i.e., commutation relation:

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

Having completed this procedure of replacement, we formaliza the quantum mechanical Hamiltonian operator H. The following Schroedinger equation for the wavefunction $\Psi(t)$ can be given

$$\begin{aligned} H^{1,Q} &= \frac{\hat{p}^2}{2m} + V(\hat{x}) \\ i\hbar\frac{\partial}{\partial t}\psi &= H^{1,Q}\psi \end{aligned}$$

Note that the wavefunction ψ forms an inner product space $(\cdot, \cdot)$, and contains a complete description of physical reality of the system in the state. We let Hamiltonian be the Hermitian in terms of this inner product $H = H^\dagger$. [139] In these settings, if the physical quantity corresponds to a Hermitian operator $\mathcal{O}$, the expectation value for the observable physical quantity at time t having the wavefunction $\psi(t)$ to describe the physical state of the system can be written

$$Theexpectationvalue = (\psi(t), \mathcal{O}\psi(t))$$

[139] For the arbitrary state vectors Ψ, Φ, we suppose the operator $\mathcal{O}$ and whose Hemitian conjugrate $\mathcal{O}^\dagger$ to satisfy the relation below:

$$(\Psi, \mathcal{O}\Phi) = (\mathcal{O}^\dagger\Psi, \Phi)$$

The Schroedinger equation defines the time expansion of the state vectors of our case. In a concrete representation that is very often used, a basis of (" square integrable ") function space and the inner product are formed:

$$(f, g) = \int_{-\infty}^{\infty} dx\, f^*(x)g(x), \quad \int_{-\infty}^{\infty} dx\, |f(x)|^2 < +\infty, \quad \int_{-\infty}^{\infty} dx\, |g(x)|^2 < +\infty$$

so that

$$\begin{aligned} \hat{x} &= x \cdot \\ \hat{p} &= \frac{\hbar}{i}\frac{\partial}{\partial x} \end{aligned}$$

Under such expression, we can write

$$H^{1,Q} = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

The treatment of $H_{cl} \to H^{1,Q}$ is called the (first) quantization.

Likewise, the three dimensionsformalism can be given

$$\begin{aligned} H^{1,Q} &= -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r}), \\ i\hbar\frac{\partial}{\partial t}\psi(t, \vec{r}) &= H^{1,Q}\psi(t, \vec{r}) \end{aligned}$$

In our specific case, the Hamiltonian is independent of time ($\partial_t H^{1,Q} = 0$) thus, in the stationary state, we suppose a solution of the separation of variables to be written

$$\psi(\vec{r}, t) = e^{-i\epsilon t/\hbar}\phi(\vec{r})$$

The Schroedinger equation is then regarded as the eigenvalue problems:

$$H^{1,Q}\phi_k(\vec{r}) = \left[-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right]\phi_k(\vec{r}) = \epsilon_\lambda\phi_k(\vec{r})$$

Note that in general cases, a certain kind of boundary condition is imposed to the eigenfunction. For the wavefunction which being orthonormalized such that

$$\int d^3r\, \phi_k^*(\vec{r})\phi_{k'}(\vec{r}) = \delta_{kk'}$$

We further formalize a complete system

$$\int d^3r\, \phi_k(\vec{r})\phi_k^*(\vec{r}\,') = \delta(\vec{r} - \vec{r}\,')$$

<u>Example of Free Space</u>

To provide a more concrete example, we suppose $V = 0$ with the system being put inside a box having each edge the length L. If a periodical boundary condition $\phi_\lambda(x+L,y,z) = \phi_\lambda(x,y+L,z) = \phi_\lambda(x,y,z+L) = \phi_\lambda(x,y,z)$ is required, we let k be the label to obtain $\vec{k} = (k_x, k_y, k_z)$ thus,

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}}, \quad \epsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}, \quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \cdots$$

[140]

6.3 First Quantization of Many Particle Systems

In the system of N-particles, we let the coordinates of jth particle be $\vec{r}_j = (x_j, y_j, z_j)$. If there is the potential $V(\vec{r}_1, \cdots, \vec{r}_N)$ existing in the N-particle system, the classical equation of motion can be written

$$m\ddot{\vec{r}}_j = -\vec{\nabla}_j V(\vec{r}_1, \cdots, \vec{r}_N)$$

Whose corresponding Hamilton's equation can be written

$$\begin{aligned} H_{cl} &= \sum_j \frac{\vec{p}_j{}^2}{2m} + V(\vec{r}_1, \cdots, \vec{r}_N) \\ \frac{\partial H_{cl}}{\partial r_j^\alpha} &= -\dot{p}_j^\alpha, \quad \alpha = x, y, z \\ \frac{\partial H_{cl}}{\partial p_j^\alpha} &= \dot{r}_j^\alpha \end{aligned}$$

In the case with no interactions between the particles, we can express

$$V(\vec{r}_1, \cdots, \vec{r}_N) = \sum_j v(\vec{r}_j)$$

In our continuing discussions, we consider no interaction cases followed by discussions of the interaction cases. [141]

[140] Show the orthonormality and completeness.

[141] If we consider in general up to the two-body force, the potential can be written

$$V(\vec{r}_1, \cdots, \vec{r}_N) = \sum_j v(\vec{r}_j) + \frac{1}{2}\sum_{i \neq j} g(\vec{r}_i, \vec{r}_j)$$

In the cases with no existing interactions, the (first) quantization can be performed as:

$$\begin{aligned} H_N^{1,Q} &= \sum_{j=1}^N h_j \\ h_j &= -\frac{\hbar^2}{2m}\vec{\nabla}_j^2 + v(\vec{r}_j), \quad \vec{\nabla}_j = (\frac{\partial}{\partial x_j}, \frac{\partial}{\partial y_j}, \frac{\partial}{\partial z_j}) \\ i\hbar\dot{\Phi}(t, \vec{r}_1, \cdots, \vec{r}_N) &= H_N^{1,Q}\Phi(t, \vec{r}_1, \cdots, \vec{r}_N) \end{aligned}$$

Here h_j is regarded as the operator that acts only on jth particle coordinates and it is called the sinple-particle Hamiltonian. Now we consider for the stationary states, and solve the Schroedinger equation of the N-particle system for the eigenfunction $\Phi_\Lambda(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N)$ and its eigenvalue E_Λ of the N-particle system: (We denote the name label of the eigenvalue in N-particle system by Λ.)

$$H_N^{1,Q}\Phi_\Lambda(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = E_\Lambda\Phi_\Lambda(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

This equation in fact is a partial differential equation such that the solution can be written (by using the method of separation of variables)

$$\begin{aligned} \Phi_{k_1,k_2,\cdots,k_N}(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N) &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N) = \prod_{j=1}^N \phi_{k_j}(\vec{r}_j) \\ E_{k_1,k_2,\cdots,k_N} &= \epsilon_{k_1} + \epsilon_{k_2} + \cdots + \epsilon_{k_N} = \sum_{j=1}^N \epsilon_{k_j} \end{aligned}$$

The eigenfunction label Λ takes the paitrs from k_1 to k_N; i.e., $k_1, k_2, \cdots, k_N$ をとり (note the order). Each $\phi_{k_j}(\vec{r}_j)$ is called the wavefunction of the single-particle state は k_j, which is the eigenfunction having the eigenvalue ϵ_{k_j} known as the single-particle energy of the single-particle Hamiltonian h_j (labeled by k_j). In short, this can be written $h_j\phi_{k_j}(\vec{r}_j) = \epsilon_{k_j}\phi_{k_j}(\vec{r}_j)$。[142]

Note: for a reshuffled state of $k_1, k_2, \cdots, k_N$, we will generally have a different state but the energy will stay the game.

6.4 Many-particle Quantum Mechanics and the Symmetry by Particle Switching

To begin, let us consider a point in the generalized x-coordinates obtained by symmetry operation R, which we suppose to be moving to a point in the coordinates Rx. In this, let symmetry operation O_R for the function $phi(x)$ be defined as:

[142] Confirm the energy of many-particle system is given by the above equation.

$$
\begin{aligned}
O_R\phi(Rx) &= \phi(x) \\
O_R\phi(x) &= \phi(R^{-1}x)
\end{aligned}
$$

Here if we define $\psi(x) = H(x)\phi(x)$, we can write

$$
\begin{aligned}
O_R\{H(x)\phi(x)\} &= O_R\psi(x) = \psi(R^{-1}x) = H(R^{-1}x)\phi(R^{-1}x) \\
O_R\{H(x)\phi(x)\} &= O_R\{H(x)O_R^{-1}O_R\phi(x)\} = O_R H(x) O_R^{-1}\phi(R^{-1}x)
\end{aligned}
$$

Thus, the transformation for $H(x)$ as the operator acting upon the function can be given

$$
H(R^{-1}x) = O_R H(x) O_R^{-1}
$$

This indicates if $H(x)$ is invariable under the symmetry operation R, expressed in the form

$$
\begin{aligned}
H(R^{-1}x) &= H(x) \\
H &= O_R H O_R^{-1} \\
[H, O_R] &= HO_R - O_R H = 0
\end{aligned}
$$

we can use the fact to further discuss the symmetry by the particle-switching in many-particle quantum mechanics. Since it is clear to all that the Hamiltonian $H_N^{1,Q}$ in N-particle system is invariant against the switching of the particles, we can express that by letting the switching operator between the ith and Jth particles be P_{ij} $(i, j = 1, \cdots, N)$:

$$
\left[H, P_{ij}\right] = 0, \quad P_{ij} H P_{ij}^{-1} = H
$$

The above indicates that the many-particle wavefunction of having the simultaneous eigenstate for the energy and the particle-switching such that

$$
\begin{aligned}
H_N^{1,Q}\Phi_\Lambda &= E_\Lambda \Phi_\Lambda \\
P_{ij}\Phi_\Lambda(\cdots, \vec{r}_i, \cdots, \vec{r}_j, \cdots,) &= \Phi_\Lambda(\cdots, \vec{r}_j, \cdots, \vec{r}_i, \cdots,) \\
&= p_{ij}\Phi_\Lambda(\cdots, \vec{r}_i, \cdots, \vec{r}_j, \cdots,)
\end{aligned}
$$

Switching the particle twice enables the particle to switch back to the initial position, and therefore the eigenvalue p_{ij} for P_{ij} satisfies $p_{ij}^2 = 1$ contrasting with $P_{ij}^2 = 1$; i.e., $p_{ij} = \pm 1$. The particle system under $p_{ij} = +1$ is called a boson system (B) while under $p_{ij} = -1$ is called a fermion system (F). This switching characteristic is regarded as one of the fundamental characteristics of the constituent particles. The each wavefunction for boson (B) and fermion system (F) has the characteristics described below:

$$
\begin{aligned}
\Phi_\Lambda(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= +\Phi_\Lambda(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \quad \text{(Boson)}\\
\Phi_\Lambda(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= -\Phi_\Lambda(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \quad \text{(Fermion)}
\end{aligned}
$$

The wavefunctions we obtained for the many-particle system does not satisfy the symmetry described in above. Now we use the linear combination of the degenerate states we noted earlier when we talked about the degenerations, and make the valid wavefunctions that satisfy the symmetry by performing the symmetrizing and anti-symmetrizing of the wavefunctions. The results can be written

$$
\begin{aligned}
\Phi^{\mathrm{B}}_{\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\\
\text{[Boson]} \qquad & \quad +\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+\cdots\\
&= \sum_{\substack{\text{All possible exchange of}\\ k_1,\cdots,k_N}} \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)
\end{aligned}
$$

$$
\begin{aligned}
\Phi^{\mathrm{F}}_{\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\\
\text{[Fermion]} \qquad & \quad -\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+-\cdots\\
&= \sum_{\substack{\text{All possible exchange}\\ P \text{ of } k_1,\cdots,k_N}} (-1)^{\mathrm{P}}\phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)
\end{aligned}
$$

Note that the wavefunctions do not depend of the order $k_1, k_2, \cdots, k_N$ (except for the scalar multiplications). In the fermion system, the existence of the same single-particle states may give the wavefunction to be 0 because of the characteristics of the determinant. In other words, the consistent wavefunction with no-zeros is free of superposition of single-particle states. This is called the Pauli 's exclusion principle.

6.5 First Quantization of N-Free Particles System

In summarizing our discussions up to this point, we denote H_N as $H_N^{1,Q}$ to simplify. The complete system of the orthonormalized eigenfunction of the single free particle Hamiltonian $h(\vec{r})$ can be written in the form [143]

$$\begin{aligned} h(\vec{r})\phi_k(\vec{r}) &= \epsilon_k \phi_k(\vec{r}) \\ \sum_k \phi_k(\vec{r})\phi_k^*(\vec{r}\,') &= \delta(\vec{r}-\vec{r}\,') \quad \textit{completeness} \\ \int d^3r\ \phi_k^*(\vec{r})\phi_{k'}(\vec{r}) &= \delta_{kk'} \quad \textit{orthonormality} \end{aligned}$$

The Schroedinger equations of each fermion and boson system for the (first quantized) Hamiltonian H_N of the N-free particles can be given by

$$\begin{aligned} H_N(\vec{r}_1,\cdots,\vec{r}_N) &= \sum_{i=1}^N h(\vec{r}_i) \\ H_N(\vec{r}_1,\cdots,\vec{r}_N)\Phi_\Lambda^{F,B}(\vec{r}_1,\cdots,\vec{r}_N) &= E_\Lambda \Phi_\Lambda^{F,B}(\vec{r}_1,\cdots,\vec{r}_N) \end{aligned}$$

Whose eigenfunctions satisfy the symmetry condition to the following commutation:

$$\begin{aligned} \Phi_\Lambda^B(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= +\Phi_\Lambda^B(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \quad \text{(Boson)} \\ \Phi_\Lambda^F(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= -\Phi_\Lambda^F(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \quad \text{(Fermion)} \end{aligned}$$

[143] For the completeness, we can write

$$\phi_k(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{ik\cdot\vec{r}}$$

giving

$$\begin{aligned} \sum_k \phi_k(\vec{r})\phi_k^*(\vec{r}\,') &= \frac{1}{\delta k^3}(\delta k)^3 \sum_k \frac{1}{L^3} e^{ik\cdot(\vec{r}-\vec{r}\,')} \\ &= \frac{1}{(2\pi)^3}\int_V dV e^{ik\cdot(\vec{r}-\vec{r}\,')} = \delta^3(\vec{r}-\vec{r}\,') \end{aligned}$$

In each equation above, we introduce the normalization constants to write

$$
\begin{aligned}
\Phi^B_{\Lambda=\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= C_B\Big\{\phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(r_N) \\
&\qquad +\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+\cdots\Big\} \\
&= C_B\sum_P \phi_{k_{P1}}(\vec{r}_1)\phi_{k_{P2}}(\vec{r}_2)\cdots\phi_{k_{PN}}(\vec{r}_N) \\
&\equiv C_B \mathrm{per}\,\boldsymbol{D}(\phi_{k_1}\phi_{k_2}\cdots\phi_{k_N}) \\
\Phi^F_{\Lambda=\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= C_F\Big\{\phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N) \\
&\qquad -\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+-\cdots\Big\} \\
&= C_F\sum_P (-1)^P\phi_{k_{P1}}(\vec{r}_1)\phi_{k_{P2}}(\vec{r}_2)\cdots\phi_{k_{PN}}(\vec{r}_N) \\
&= C_F \det\,\boldsymbol{D}(\phi_{k_1}\phi_{k_2}\cdots\phi_{k_N}) \quad \text{Slater determinants} \\
\{\boldsymbol{D}(\phi_{k_1}\phi_{k_2}\cdots\phi_{k_N})\}_{i,j} &= \phi_{k_i}(\vec{r}_j) \\
E_\Lambda &= \sum_{i=1}^N \epsilon_{k_i}
\end{aligned}
$$

The normalization constants C_B and C_F will be defined later. Let us use to label the eigenfunctions of N-particle systems; the wavefunction is independent of the order $k_1, k_2, \cdots, k_N$ (except for the scalar multiplications). Now, we organize the overlapping parts in $k_1, k_2, \cdots, k_N$ as to change the method in defining the state of N-particle systems from our initially used method of: “ defining the single-particle states which being occupied by particles ” to, “ method of defining the number of overlapping occupations for each single-particle state which is defined by the label k of the single-particle states. ”Further, these overlaps are called the occupation numbers of a single-particle states k. The states of N-particle systems can be determined by defining all possible occupation numbers of the single-particle states k. Therefore, we obtain the occupation number n_k for the single-particle states k, and give $\{n_k\}$ to finally determine the states. In the boson systems, the occupation numbers can be $n_k = 0, 1, 2, 3, \cdots$ while it can become $n_k = 0, 1$ for the fermion systems. (Pauli 's principle) We use this occupation number representation to write the Schroedinger equation and the energy of N-particle system:

$$
\begin{aligned}
H \quad \Phi^{B,F}_{\{n_k\}}(\vec{r}_1,\cdots,\vec{r}_N) &= E_{\{n_k\}}\Phi^{B,F}_{\{n_k\}}(\vec{r}_1,\cdots,\vec{r}_N) \\
E_{\{n_k\}} &= \sum_k \quad \epsilon_k n_k
\end{aligned}
$$

6.6 Second Quantization

We now consider a new form of Schoedinger equation through the following procedures:

$$H_N \quad \rightarrow \quad \mathcal{H} = \sum_k \quad \epsilon_k \hat{n}_k, \qquad \hat{n}_k = d_k^\dagger d_k$$

$$\Phi^{B,F}_{\{n_k\}}(\vec{r}_1, \cdots, \vec{r}_N) \quad \rightarrow \quad |\{n_k\}\rangle = \prod_k |n_k\rangle \equiv \prod_k \frac{1}{\sqrt{n_k!}} (d_k{}^\dagger)^{n_k} |0\rangle$$

The negative sign ? is used for Bosons (commutation relation) while the positive sign + is used for Fermions (anti-commutation relation) in equation $[A, B]_\mp = AB \mp BA$. Thus, we understand that $d_k^\dagger$ and d_k are the creation and annihilation operators which satisfy

$$[d_k^\dagger, d_{k'}^\dagger]_\mp = 0, \quad [d_k, d_{k'}]_\mp = 0, \quad [d_k, d_{k'}^\dagger]_\mp = \delta_{kk'}$$

Take notice of $\hat{n}_k|n_k\rangle = n_k|n_k\rangle$、$|n_k\rangle = \frac{1}{\sqrt{n_k!}}(d_k^\dagger)^{n_k}|0\rangle$ which are derived from the eqquations above, one can write the Schroedinger equation that corresponds to $\mathcal{H}$:

$$\begin{aligned} \mathcal{H}|\{n_k\}\rangle &= E_{\{n_k\}}|\{n_k\}\rangle \\ E_{\{n_k\}} &= \sum_k \quad \epsilon_k n_k \end{aligned}$$

The form of energy can be written in the same form that was given before. Here note that the vacuum $|0\rangle$ is being defined by

$$\begin{aligned} {}^\forall k, d_k|0\rangle &= 0 \\ \langle 0|0\rangle &= 1 \end{aligned}$$

These procedures $H \rightarrow \mathcal{H}$ are called the second quantization.

We can express $|\{n_k\}\rangle$ in which tha label of k decides the one-dimensional order where we denote the order by $\prec$ and obtain $k_1 \prec k_2 \prec k_3 \cdots$ such that

$$\begin{aligned} |\{n_k\}\rangle &= |n_{k_1}, n_{k_2}, n_{k_3}, \cdots\rangle \\ &= \prod_{k_1 \prec k_2 \prec k_3 \cdots} \frac{1}{\sqrt{n_{k_i}!}} (d_{k_1}^\dagger)^{n_{k_1}} (d_{k_2}^\dagger)^{n_{k_2}} (d_{k_3}^\dagger)^{n_{k_3}} \cdots |0\rangle \end{aligned}$$

The normalization of this state is written

$$\begin{aligned} \langle\{n_k\}|\{n_k'\}\rangle &= \delta_{\{n_k\}\{n_k'\}} \\ &= \prod \delta_{n_{k_1}, k_1'} \delta_{n_{k_2}, k_2'} \cdots \end{aligned}$$

In the following discussions, let us express only the non-zero n_k found in $|\{n_k\}\rangle$.

Field Operator

We use the operator which is defined by the so called field operator

$$\hat{\psi}(r) = \sum_k \phi_k(r) d_k$$

and write

$$\begin{aligned}
[\hat{\psi}(\vec{r}), \hat{\psi}^\dagger(\vec{r}')]_\pm &= \delta(\vec{r} - \vec{r}') \\
[\hat{\psi}(\vec{r}), \hat{\psi}(\vec{r}')]_\pm &= 0 \\
[\hat{\psi}^\dagger(\vec{r}), \hat{\psi}^\dagger(\vec{r}')]_\pm &= 0
\end{aligned}$$

The Hamiltonian of the free-particle systems can be written

$$\mathcal{H} = \int d^3 r \hat{\psi}^\dagger(\vec{r})(-\frac{\hbar^2 \vec{\nabla}^2}{2m})\hat{\psi}(\vec{r})$$

This equation represents the first quantization of energy such that the wavefunction corresponds to the operator in the form; the reason why we call " second quantization. "It should be clear to most of us by now that the Hamiltonian for the general single-particle can be discussed in the same manner. The general treatment for the operators will be discussed later yet; we can still obtain the Hamiltonian that corresponds to the energy based on the knowledge we have obtained up to this point.

In our next step, we consider how to treat the state vectors. The relation between the state vector $|\{n_k\}\rangle$ by second quantization formalism and the many-particle wavefunction in first quantization can be written [144]

$$\begin{aligned}
\Phi_{\{n_k\}}(\vec{r}_1, \cdots, \vec{r}_N) &= \langle \vec{r}_1, \cdots, \vec{r}_N | \{n_k\} \rangle \\
|\vec{r}_1, \cdots, \vec{r}_N\rangle &\equiv \frac{1}{\sqrt{N!}} \hat{\psi}^\dagger(\vec{r}_1) \cdots \hat{\psi}^\dagger(\vec{r}_N)|0\rangle = \frac{1}{\sqrt{N!}} \prod_{j=1}^{N} \hat{\psi}^\dagger(\vec{r}_j)|0\rangle
\end{aligned}$$

[144] For fermions:

$$\begin{aligned}
\langle \vec{r}_1, \cdots, \vec{r}_N | \{n_k\} \rangle &= \frac{1}{\sqrt{N!}} \langle 0 | \psi(\vec{r}_N) \cdots \psi(\vec{r}_1) | n_{k_1}, n_{k_2}, \cdots n_{k_N} \rangle \\
&= \frac{1}{\sqrt{N!}} \sum_{i_1, \cdots i_N} \phi_{i_N}(\vec{r}_N) \cdots \phi_{i_1}(\vec{r}_1) \langle 0 | d_{i_N} \cdots d_{i_1} | n_{k_1}, n_{k_2}, \cdots n_{k_N} \rangle \\
&= \frac{1}{\sqrt{N!}} \sum_P (\pm)^P \phi_{k_{PN}}(\vec{r}_N) \cdots \phi_{k_{P1}}(\vec{r}_1) = \frac{1}{\sqrt{N!}} \det \phi_{k_i}(\vec{r}_j)
\end{aligned}$$

The normalization constants C_F and C_B are given

$$
\begin{aligned}
C_F &= \frac{1}{\sqrt{N!}} \\
C_B &= \frac{1}{\sqrt{N!\prod_k n_k!}}
\end{aligned}
$$

The normalization can be given by [145]

$$
\int d^3r_1 \cdots \vec{r}_N |\Phi_\Lambda(\vec{r}_1 \cdots \vec{r}_N)|^2 = 1
$$

For bosons:

$$
\begin{aligned}
\langle \vec{r}_1, \cdots, \vec{r}_N | \{n_k\} \rangle &= \frac{1}{\sqrt{N!}} \langle 0 | \psi(\vec{r}_N) \cdots \psi(\vec{r}_1) | n_{k_1}, n_{k_2}, \cdots \rangle \\
&= \frac{1}{\sqrt{N!}} \sum_{i_1, \cdots i_N} \phi_{i_N}(\vec{r}_N) \cdots \phi_{i_1}(\vec{r}_1) \langle 0 | d_{i_N} \cdots d_{i_1} | n_{k_1}, n_{k_2}, \cdots \rangle \\
&= \frac{1}{\sqrt{N!}} \sum_{i_1, \cdots i_N} \phi_{i_N}(\vec{r}_N) \cdots \phi_{i_1}(\vec{r}_1) \langle 0 | \cdots (d_{k_2})^{n_{k_2}} (d_{k_1})^{n_{k_1}} | n_{k_1}, n_{k_2}, \cdots \rangle \\
& \qquad \{i_1, \cdots i_N\} = \{ \overbrace{k_1, k_1 \cdots k_1}^{n_{k_1}}, \overbrace{k_2, k_2 \cdots k_2}^{n_{k_2}}, \cdots \}, \quad \text{as a set} \\
&= \frac{1}{\sqrt{N!}} \sum_{i_1, \cdots i_N} \phi_{i_N}(\vec{r}_N) \cdots \phi_{i_1}(\vec{r}_1) \sqrt{n_{k_1}! n_{k_2}! \cdots} \\
&= \frac{1}{\sqrt{N!}} \frac{1}{n_{k_1}! n_{k_2}! \cdots} \sum_P \phi_{i_{PN}}(\vec{r}_N) \cdots \phi_{i_{P1}}(\vec{r}_1) \sqrt{n_{k_1}! n_{k_2}!, \cdots}
\end{aligned}
$$

We cannot find the overlapped values by the substitution in the form of natural free sum. Thus,

$$
= 1 \frac{}{\sqrt{N! n_{k_1}! n_{k_2}! \cdots} \sum_P \phi_{i_{PN}}(\vec{r}_N) \cdots \phi_{i_{P1}}(\vec{r}_1), \qquad \{i_1, i_2, \cdots, i_N\} = \{ \overbrace{k_1, k_1 \cdots k_1}^{n_{k_1}}, \overbrace{k_2, k_2 \cdots k_2}^{n_{k_2}}, \cdots \}}
$$

[145]Consider the noemalization. For the fermions:

$$
\begin{aligned}
\int d^3r_1 \cdots \vec{r}_N |\Phi_{\{n_{k_i}\}}(\vec{r}_1 \cdots \vec{r}_N)|^2 &= \frac{1}{N!} \sum_{PQ} (-)^P (-)^Q \int d^3r_1 \cdots d^3r_N \, \phi^*_{k_{Q1}}(\vec{r}_1) \phi_{k_{P1}}(\vec{r}_1) \cdot \phi^*_{k_{Q2}}(\vec{r}_2) \phi_{k_{P2}}(\vec{r}_2) \cdots \\
&= \frac{1}{N!} \sum_P \int d^3r_1 \cdots d^3r_N \, \phi^*_{k_{P1}}(\vec{r}_1) \phi_{k_{P1}}(\vec{r}_1) \cdot \phi^*_{k_{P2}}(\vec{r}_2) \phi_{k_{P2}}(\vec{r}_2) \cdots = 1
\end{aligned}
$$

While for the bosons:

$$
\begin{aligned}
\int d^3r_1 \cdots \vec{r}_N |\Phi_{\{n_{k_i}\}}(\vec{r}_1 \cdots \vec{r}_N)|^2 &= \frac{1}{N! n_{k_1}! n_{k_2}! \cdots} \sum_{PQ} \int d^3r_1 \cdots d^3r_N \, \phi^*_{i_{Q1}}(\vec{r}_1) \phi_{i_{P1}}(\vec{r}_1) \cdot \phi^*_{i_{Q2}}(\vec{r}_2) \phi_{i_{P2}}(\vec{r}_2) \cdots \\
& \qquad \{i_1, \cdots i_N\} = \{ \overbrace{k_1, k_1 \cdots k_1}^{n_{k_1}}, \overbrace{k_2, k_2 \cdots k_2}^{n_{k_2}}, \cdots \}, \\
&= \frac{1}{n_{k_1}! n_{k_2}! \cdots} \sum_P \int d^3r_1 \cdots d^3r_N \, \phi^*_{i_1}(\vec{r}_1) \phi_{i_{P1}}(\vec{r}_1) \cdot \phi^*_{i_2}(\vec{r}_2) \phi_{i_{P2}}(\vec{r}_2) \cdots = 1
\end{aligned}
$$

Further, the orthonormal condition can be given by

$$\langle \vec{r}_1, \cdots, \vec{r}_N | \vec{r}_1{}', \cdots, \vec{r}_N{}' \rangle = \frac{1}{N!} \sum_P (\pm)^P \delta(\vec{r}_1 - \vec{r}_{P1}{}') \cdots \delta(\vec{r}_N - \vec{r}_{PN}{}')$$

6.7 Operator and the Interactoin in Second Quantization Formalism

Now we consider the second quantization approach and the form of operator that can be introduced to the given single-particle operator F and to the two-particle operator G, which we defined in first quantization earlier:

$$\begin{aligned} F &= \sum_{i=1}^{N} f(\vec{r}_i) \\ G &= \frac{1}{2} \sum_{i \neq j} g(\vec{r}_i, \vec{r}_j) \end{aligned}$$

[146]

First, we need to confirm the complete system I_N of N-particle systems: [147]

[146] In first quantization, the kinetic energy can be an example of the single-particle operator F:

$$F = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m}$$

For the two-particle operator G, the Coulomb interaction can be of the typical example:

$$G = \frac{1}{2} \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

[147] In the fermions cases:

$$\begin{aligned} \hat{I}_N &= \int d^3 r_1 \cdots d^3 r_N \, |\vec{r}_1, \cdots, \vec{r}_N\rangle\langle \vec{r}_1, \cdots, \vec{r}_N| \\ &= \frac{1}{N!} \sum_{i_1', \cdots, i_N'} \sum_{i_1, \cdots, i_N} d_{i_1'}^\dagger \cdots d_{i_N'}^\dagger |0\rangle\langle 0| d_{i_1} \cdots d_{i_N} \\ &\quad \times \int d^3 r_1 \cdots d^3 r_N \, \phi_{i_1'}^*(\vec{r}_1) \phi_{i_1}(\vec{r}_1) \cdots \phi_{i_N'}^*(\vec{r}_N) \phi_{i_N}(\vec{r}_N) \\ &= \frac{1}{N!} \sum_{i_1, \cdots, i_N} |n_{i_1} \cdots n_{i_N}\rangle\langle n_{i_1} \cdots n_{i_N}| \\ &= \sum_{i_1 \prec \cdots \prec i_N} |n_{i_1} \cdots n_{i_N}\rangle\langle n_{i_1} \cdots n_{i_N}| \quad \text{Note that there are only non-zeros.} \end{aligned}$$

148

$$
\begin{aligned}
|\vec{r}_1, \cdots, \vec{r}_N\rangle &= \frac{1}{\sqrt{N!}} \hat{\psi}^\dagger(\vec{r}_1) \cdots \hat{\psi}^\dagger(\vec{r}_N)|0\rangle = \frac{1}{\sqrt{N!}} \prod_{j=1}^{N} \hat{\psi}^\dagger(\vec{r}_j)|0\rangle \\
\hat{I}_N &= \int d^3r_1 \cdots d^3r_N \, |\vec{r}_1, \cdots, \vec{r}_N\rangle\langle\vec{r}_1, \cdots, \vec{r}_N| \\
&= \sum_{\alpha_1, \cdots, \alpha_N} \frac{\prod_{\alpha_i} n_{\alpha_i}!}{N!} |n_{\alpha_1} \cdots n_{\alpha_N}\rangle\langle n_{\alpha_1} \cdots n_{\alpha_N}| \\
&= \sum_{\alpha_1 \prec \alpha_2 \prec \cdots} |n_{\alpha_1} n_{\alpha_2} \cdots\rangle\langle n_{\alpha_1} n_{\alpha_2} \cdots|
\end{aligned}
$$

Calculate the matrix elements of the operator below for the arbitrary N-particle states $\alpha = \{n_{\alpha_1} \cdots, n_{\alpha_N}\}$ and $\beta = \{n_{\beta_1} \cdots, n_{\beta_N}\}$:

$$
\mathcal{F} = \int d^3r \hat{\psi}^\dagger(\vec{r}) f(\vec{r}) \hat{\psi}(\vec{r})
$$

$$
\begin{aligned}
\langle\alpha|\mathcal{F}|\beta\rangle &= \int d^3r \int d^3r_1 \cdots d^3r_{N-1} \, \langle\alpha|\hat{\psi}^\dagger(\vec{r})|\vec{r}_1, \cdots, \vec{r}_{N-1}\rangle f(\vec{r}) \langle\vec{r}_1, \cdots, \vec{r}_{N-1}|\hat{\psi}(\vec{r})|\beta\rangle \\
&= N \int d^3r_1 \cdots d^3r_{N-1} d^3r \, \langle\alpha|\vec{r}_1, \cdots, \vec{r}_{N-1}, \vec{r}\rangle f(\vec{r}) \langle\vec{r}_1, \cdots, \vec{r}_{N-1}, \vec{r}|\beta\rangle \\
&= \int d^3r_1 \cdots d^3r_N \, \sum_{i=1}^{N} \Phi_\alpha^*(\vec{r}_1, \cdots, \vec{r}_N) f(\vec{r}_i) \Phi_\beta(\vec{r}_1, \cdots, \vec{r}_N) \\
&= \int d^3r_1 \cdots d^3r_N \, \Phi_\alpha^*(\vec{r}_1, \cdots, \vec{r}_N) F \Phi_\beta(\vec{r}_1, \cdots, \vec{r}_N)
\end{aligned}
$$

---

148 For the bosons:

$$
\begin{aligned}
\hat{I}_N &= \int d^3r_1 \cdots d^3r_N \, |\vec{r}_1, \cdots, \vec{r}_N\rangle\langle\vec{r}_1, \cdots, \vec{r}_N| \\
&= \frac{1}{N!} \sum_{i'_1, \cdots, i'_N} \sum_{i_1, \cdots, i_N} d^\dagger_{i'_1} \cdots d^\dagger_{i'_N} |0\rangle\langle 0| d_{i_1} \cdots d_{i_N} \\
&\quad \times \int d^3r_1 \cdots d^3r_N \, \phi^*_{i'_1}(\vec{r}_1) \phi_{i_1}(\vec{r}_1) \cdots \phi^*_{i'_N}(\vec{r}_N) \phi_{i_N}(\vec{r}_N) \\
&= \sum_{k_1, k_2 \cdots} \frac{\prod_k n_k!}{N!} |n_{k_1}, n_{k_2}, \cdots\rangle\langle n_{k_1}, n_{k_2}, \cdots| \\
& \qquad \{i_1, \cdots, i_N\} = \{ \overbrace{k_1, k_1 \cdots k_1}^{n_{k_1}}, \overbrace{k_2, k_2 \cdots k_2}^{n_{k_2}}, \cdots \} \\
&= \sum_{k_1 \prec k_2 \cdots} |n_{k_1}, n_{k_2}, \cdots\rangle\langle n_{k_1}, n_{k_2}, \cdots|, \qquad \sum n_{k_i} = N
\end{aligned}
$$

The above indicates that we can use *calF* to correspond to the single-particle operator F. [149]

In the same way, we consider the two-particle operator:

$$\mathcal{G} = \frac{1}{2}\int d^3r d^3r\,'\hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}\,')g(\vec{r}_i,\vec{r}_j)\hat{\psi}(\vec{r}\,')\hat{\psi}(\vec{r}), \quad g(r_i,r_j) = g(r_j,r_i),\ (i \neq j)$$

Calculation for the matrix elements of the above yields

$$\begin{aligned}
\langle\alpha|\mathcal{G}|\beta\rangle &= \frac{1}{2}\int d^3r d^3r\,' \int d^3r_1 \cdots d^3r_{N-2} \\
&\quad \times\langle\alpha|\hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}\,')|\vec{r}_1,\cdots,\vec{r}_{N-2}\rangle g(\vec{r},\vec{r}\,')\langle\vec{r}_1,\cdots,\vec{r}_{N-2}|\hat{\psi}(\vec{r}\,')\hat{\psi}(\vec{r})|\beta\rangle \\
&= \frac{1}{2}N(N-1)\int d^3r_1\cdots d^3r_{N-2}d^3rd^3r\,' \\
&\quad \times\ \langle\alpha|\vec{r}_1,\cdots,\vec{r}_{N-2},\vec{r},\vec{r}\,'\rangle g(\vec{r},\vec{r}\,')\langle\vec{r}_1,\cdots,\vec{r}_{N-2},\vec{r},\vec{r}\,'|\beta\rangle \\
&= \int d^3r_1\cdots d^3r_N \\
&\quad \times\frac{1}{2}\sum_{i\neq j}^{N}\Phi^*_\alpha(\vec{r}_1,\cdots,\vec{r}_N)g(\vec{r}_i,\vec{r}_j)\Phi_\beta(\vec{r}_1,\cdots,\vec{r}_N) \\
&= \int d^3r_1\cdots d^3r_N\ \Phi^*_\alpha(\vec{r}_1,\cdots,\vec{r}_N)G\Phi_\beta(\vec{r}_1,\cdots,\vec{r}_N)
\end{aligned}$$

This indicates that we can use *calG* to correspond to the two-particle operator G. [150] We can summarize that in the form:

$$\begin{aligned} F &\Leftrightarrow \mathcal{F} \\ G &\Leftrightarrow \mathcal{G} \end{aligned}$$

Second Quantized Example

- Particle density operator

$$\sum_i \delta(\vec{r}-\vec{r}_i) \longrightarrow \hat{n}(\vec{r}) = \hat{\psi}^\dagger(\vec{r})\hat{\psi}(\vec{r})$$

---

[149] We put the complete system I_{N-1} of $N-1$ particle system into the equation:

$$\hat{\psi}^\dagger(\vec{r})|\vec{r}_1,\cdots,\vec{r}_{N-1}\rangle = (-1)^{N-1}\sqrt{N}|\vec{r}_1,\cdots,\vec{r}_{N-1},\vec{r}\rangle$$

and

$$\Phi^*_\alpha(\vec{r}_1,\cdots,\vec{r}_N)\Phi_\beta(\vec{r}_1,\cdots,\vec{r}_N)$$

Note that the commutation of arbitrary r_i and r_j is symmetric.

[150] In our typical case, we used $g(r_1,r_2) = g(r_2,r_1$ in the equation; however, in general cases, we will obtain $\mathcal{G} = \frac{1}{2}\int\int d^3r\,d^3r'\psi^\dagger(\vec{r})\psi^\dagger(\vec{r}\,')g^S(\vec{r},\vec{r}\,')\psi(\vec{r}\,')\psi(\vec{r})$ when we use $G = \frac{1}{2}\sum_{i,j}g(r_i,r_j) = \frac{1}{2}\sum_{i,j}g^S(r_i,r_j)$

- Total energy-momentum operator [151]

$$-\sum_i \frac{\hbar^2}{2m}\vec{\nabla}_i^2 \longrightarrow -\int d^3r\ \hat{\psi}^\dagger(\vec{r})\frac{\hbar^2}{2m}\vec{\nabla}^2\hat{\psi}(\vec{r}) = \int d^3r\ \frac{1}{2m}\left(\frac{\hbar}{i}\vec{\nabla}\hat{\psi}(\vec{r})\right)^\dagger\left(\frac{\hbar}{i}\vec{\nabla}\hat{\psi}(\vec{r})\right)$$

- Density-density correlation operator [152]

$$\hat{n}(\vec{r},\vec{r}') = \sum_{i\neq j}\delta(\vec{r}-\vec{r}_i)\delta(\vec{r}'-\vec{r}_j) \longrightarrow = \hat{n}(\vec{r})\hat{n}(\vec{r}') - \delta(\vec{r}-\vec{r}')\hat{n}(\vec{r})$$

---

[151] Use the integration by parts.

[152]

$$\begin{aligned}
\hat{n}(\vec{r},\vec{r}') &= \sum_{i\neq j}\delta(\vec{r}-\vec{r}_i)\delta(\vec{r}'-\vec{r}_j) \\
&\longrightarrow \hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}')\hat{\psi}(\vec{r}')\hat{\psi}(\vec{r}) = \pm\hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}')\hat{\psi}(\vec{r})\hat{\psi}(\vec{r}') \\
&= \hat{\psi}^\dagger(\vec{r})\big(\hat{\psi}^\dagger(\vec{r}')\hat{\psi}(\vec{r}) - \delta(\vec{r}-\vec{r}')\big)\hat{\psi}(\vec{r}') = \hat{n}(\vec{r})\hat{n}(\vec{r}') - \delta(\vec{r}-\vec{r}')\hat{n}(\vec{r})
\end{aligned}$$

7 Single-particle States and Mean-field Approximations in Fermion Systems

Generally speaking, to obtain the eigenstates of many-particle systems with interactions is considered much complicated. Among the different types of approximation methods performed effectively to solve the many-particle problems, we focus our discussion on the most fundamental and essential of which; the mean-field approximations and the single-particle approximations. We begin our discussion by considering the simplified spinless fermion systems. Following our discussion in the previous section, we let one-body of potential be $v(\vec{r})$ and let the inter-electronic interaction be $g(\vec{r}-\vec{r}\,')$. In such case, the Hamiltonian can be written as

$$\begin{aligned} H &= \int d^3r\, \psi^\dagger(\vec{r})\left(\frac{-\hbar^2\nabla^2}{2m}+v(\vec{r})\right)\psi(\vec{r}) \\ &\quad +\frac{1}{2}\int d^3r \int d^3r\,'\; \psi^\dagger(\vec{r})\psi^\dagger(\vec{r}\,')g(\vec{r}-\vec{r}\,')\psi(\vec{r}\,')\psi(\vec{r}) \end{aligned}$$

The Coulomb force can be written

$$g(\vec{r}-\vec{r}\,') = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}-\vec{r}\,'|}$$

.

Let us now consider a problem of determining the ground state $|G\rangle$ of the fixed number of particles N in the system:

$$\begin{aligned} N &= \langle G|\hat{N}|G\rangle \\ \hat{N} &= \int d^3r\, \hat{n}(\vec{r}), \quad \hat{n}(\vec{r}) = \psi^\dagger(\vec{r})\psi(\vec{r}) \end{aligned}$$

In fact, this is commonly known to be insoluble for N ¿ 2 (many-body problem). In our following subsections, we will consider the certain types of approximated solutions to solve the many-body problems.

7.1 Single-particle Orbit and Unitary Transformation of Fermi Operator

Let us consider the following trial function for the ground state in the many-particle system: [153]

$$|G\rangle = c_1^\dagger c_2^\dagger \cdots c_N^\dagger |0\rangle$$

[153] The wavefunction in such form is called the single-particle wavefunction.

Note that c_j can be transformed in applying the unitary transformation U_{ij} to the annihilation operator d_j of the fermions used in second quantization: (Vacuum $|0\rangle$ is the invariable)

$$\begin{aligned} d_i &= \sum_j U_{ij} c_j, \quad c_j = \sum_j d_k U^*_{kj} \\ U_{ij} &= \{\boldsymbol{U}\}_{ij}, \boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{U}\boldsymbol{U}^\dagger = \boldsymbol{I} \\ \sum_k U_{ik} U^*_{jk} &= \sum_k U_{ki} U^*_{kj} = \delta_{ij} \end{aligned}$$

The field operator can be written in correspond to the above transformation:

$$\begin{aligned} \hat{\psi}(\vec{r}) &= \sum_j \phi_j(\vec{r}) d_j = \sum_k \varphi_k(\vec{r}) c_k \\ \varphi_k(\vec{r}) &= \sum_j \phi_j(\vec{r}) U_{jk} \end{aligned}$$

Now we can demonstrate that $\varphi_j(\vec{r}),\ j = 1, 2, \cdots$ formulates the following orthonormalized complete system: [154]

$$\begin{aligned} \int d^3r\ \varphi^*_i(\vec{r}) \varphi_j(\vec{r}) &= \delta_{ij} \\ \sum_j \varphi^*_j(\vec{r}) \varphi_j(\vec{r}\,') &= \delta(\vec{r} - \vec{r}\,') \end{aligned}$$

While contrarily in the arbitrary orthonormalized complete system $\{\varphi_k(\vec{r})\}$, each function of this complete system can be expanded over the complete system $\{\phi_j(\vec{r})\}$:

$$\varphi_k(\vec{r}) = \sum_j \phi_j(\vec{r}) U_{jk}$$

The expansion coefficient in the above can formulate U_{ij}, by which the unitary

---

154

$$\begin{aligned} \int d^3r\, \varphi^*_i(\vec{r}) \varphi_j(\vec{r}) &= \int d^3r\, \phi^*_k(\vec{r}) U^*_{ki} \phi_l(\vec{r}) U_{lj} = U^*_{ki} U_{kj} = \delta_{ij} \\ \varphi_j(\vec{r}) \varphi^*_j(\vec{r}\,') &= \phi_k(\vec{r}) U_{kj} \phi^*_l(\vec{r}\,') U^*_{lj} = \phi_k(\vec{r}) \phi^*_k(\vec{r}\,') = \delta(\vec{r} - \vec{r}\,') \end{aligned}$$

matrix is formed. [155] Hence, the new operator $\{c_j\}$ defined by this unitary matrix also satisfies the anticommutation relation of fermion. [156] Based on which we write

$$\langle \vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N | G \rangle = C_F \det\{\varphi_i(\vec{r}_j)\}$$

This may give us a act that to consider $|G\rangle$ analogues to having $\varphi_k(\vec{r})$ for the single-particle orbit which takes oart in making the ground state. We use the variation principle for $\varphi_k(\vec{r})$

$$\langle G|H|G\rangle$$

In our following discussions, we will consider the mean-field approximation that takes the smallest value in the above. We will now demonstrate a step-by-step calculation of each term that makes up $\langle G|H|G\rangle$.

7.2 Total Energy of Single-particle States

The equation $\{\hat{\psi}(\vec{r}), c_j^\dagger\} = \varphi_j(\vec{r})$ gives $\hat{\psi}(\vec{r})c_j^\dagger = -c_j^\dagger \hat{\psi}(\vec{r}) + \varphi_j(\vec{r})$, which further giving:

$$\begin{aligned}\hat{\psi}(\vec{r})|G\rangle &= \{-c_1^\dagger \hat{\psi}(\vec{r}) + \varphi_1(\vec{r})\} c_2^\dagger \cdots c_N^\dagger |0\rangle \\ &= -\sum_{j=1}^{N} (-1)^j \varphi_j(\vec{r}) c_1^\dagger \cdots c_{j-1}^\dagger c_{j+1}^\dagger \cdots c_N^\dagger |0\rangle\end{aligned}$$

A one-body energy term can be written

$$\langle G| \int d^3r\, \hat{\psi}^\dagger(\vec{r}) \left(\frac{-\hbar^2\nabla^2}{2m} + v(\vec{r}) \right) \hat{\psi}(\vec{r}) |G\rangle = \sum_{j=1}^{N} I(j)$$

$$I(j) = \int d^3r\, \varphi_j^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r}) \right) \varphi_j(\vec{r})$$

155

$$\begin{aligned}\int d^3r\, \varphi_i^*(\vec{r})\varphi_j(\vec{r}) &= \int d^3r\, \phi_k^*(\vec{r}) U_{ki}^* \phi_l(\vec{r}) U_{lj} = U_{ki}^* U_{kj} = \delta_{ij} \\ U_{jk} &= \int d^3r\, \phi_j^*(\vec{r}) \varphi_k(\vec{r}) \\ U_{ik} U_{jk}^* &= \int d^3r'\, \phi_i^*(\vec{r}')\varphi_k(\vec{r}') \int d^3r\, \phi_j(\vec{r})\varphi_k^*(\vec{r}) = \int d^3r\, \phi_i^*(\vec{r})\phi_j(\vec{r}) = \delta_{ij}\end{aligned}$$

156

$$\{c_i, c_j^\dagger\} = \{d_k U_{ki}^*, d_l^\dagger U_{lj}\} = U_{ki}^* U_{kj} = \delta_{ij}$$

In the same way, we may write

$$
\begin{aligned}
\hat{\psi}(\vec{r}\,')\hat{\psi}(\vec{r})|G\rangle &= \hat{\psi}(\vec{r}\,')\{-c_1^\dagger\hat{\psi}(\vec{r}) + \varphi_1(\vec{r})\}c_2^\dagger\cdots c_N^\dagger|0\rangle \\
&= -\sum_{j=1}^{N}(-1)^j\varphi_j(\vec{r})\hat{\psi}(\vec{r}\,')c_1^\dagger\cdots c_{j-1}^\dagger c_{j+1}^\dagger\cdots c_N^\dagger|0\rangle \\
&= \sum_{k<j}(-1)^{j+k}\varphi_k(\vec{r}\,')\varphi_j(\vec{r})c_1^\dagger\cdots c_{k-1}^\dagger c_{k+1}^\dagger\cdots c_{j-1}^\dagger c_{j+1}^\dagger\cdots c_N^\dagger|0\rangle \\
&\quad+\sum_{j<k}(-1)^{j+k+1}\varphi_k(\vec{r}\,')\varphi_j(\vec{r})c_1^\dagger\cdots c_{j-1}^\dagger c_{j+1}^\dagger\cdots c_{k-1}^\dagger c_{k+1}^\dagger\cdots c_N^\dagger|0\rangle \\
&= \sum_{k<j}(-1)^{j+k}\{\varphi_k(\vec{r}\,')\varphi_j(\vec{r}) - \varphi_j(\vec{r}\,')\varphi_k(\vec{r})\} \\
&\qquad\times c_1^\dagger\cdots c_{k-1}^\dagger c_{k+1}^\dagger\cdots c_{j-1}^\dagger c_{j+1}^\dagger\cdots c_N^\dagger|0\rangle
\end{aligned}
$$

Thus,

$$
\begin{aligned}
&\langle G|\,\frac{1}{2}\int d^3r\int d^3r\,'\ \hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}\,')g(\vec{r}-\vec{r}\,')\hat{\psi}(\vec{r}\,')\hat{\psi}(\vec{r})|G\rangle \\
&= \frac{1}{2}\int d^3r\int d^3r\,'g(\vec{r}-\vec{r}\,')\sum_{k<j}|\varphi_k(\vec{r}\,')\varphi_j(\vec{r}) - \varphi_j(\vec{r}\,')\varphi_k(\vec{r})|^2 \\
&= \frac{1}{2}\int d^3r\int d^3r\,'g(\vec{r}-\vec{r}\,')\sum_{k\neq j}\{|\varphi_k(\vec{r}\,')|^2|\varphi_j(\vec{r})|^2 - \varphi_k^*(\vec{r}\,')\varphi_j(\vec{r}\,')\varphi_j^*(\vec{r})\varphi_k(\vec{r})\} \\
&= \sum_{k<j}(J(k,j) - K(k,j))
\end{aligned}
$$

$$
\begin{aligned}
J(k,j) &= \int d^3r\int d^3r\,'|\varphi_i(\vec{r})|^2\, g(\vec{r}-\vec{r}\,')\,|\varphi_j(\vec{r})|^2 \\
&= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{|\varphi_k(\vec{r}\,')|^2|\varphi_j(\vec{r})|^2}{|\vec{r}-\vec{r}\,'|} \\
K(k,j) &= \int d^3r\int d^3r\,'\varphi_k^*(\vec{r}\,')\varphi_j(\vec{r}\,')\,g(\vec{r}-\vec{r}\,')\,\varphi_j^*(\vec{r})\varphi_k(\vec{r}) \\
&= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{\varphi_k^*(\vec{r}\,')\varphi_j(\vec{r}\,')\varphi_j^*(\vec{r})\varphi_k(\vec{r})}{|\vec{r}-\vec{r}\,'|}
\end{aligned}
$$

The total energy E_T can be given [157]

$$
E_T = \sum_i I(i) + \sum_{i<j}\big(J(i,j) - K(i,j)\big)
$$

These J(k, j) and K(k, j) are respectively called the Coulomb integral and the exchange integral of both having positive quantities. The integrals satisfy the following relations:

[157] The $i = j$ terms are canceled by the Coulomb integral and the exchange integral

158 159 160

$$J(i,j) \geq K(i,j) \geq 0$$

Further, satisfy the following: [161]

$$J(i,i) + J(j,j) \geq 2J(i,j)$$

158

$$\begin{aligned} J(1,2) - K(1,2) &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \, \frac{1}{|\vec{r}-\vec{r}\,'|} \frac{1}{2}\Big(|\varphi_1(\vec{r}\,')|^2 |\varphi_2(\vec{r})|^2 + |\varphi_1(\vec{r})|^2 |\varphi_2(\vec{r}\,')|^2 \\ &\quad -\varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,')\varphi_2^*(\vec{r})\varphi_1(\vec{r}) - \varphi_1^*(\vec{r})\varphi_2(\vec{r})\varphi_2^*(\vec{r}\,')\varphi_1(\vec{r}\,') \Big) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \, \frac{1}{|\vec{r}-\vec{r}\,'|} \frac{1}{2}(|Z|^2|Y|^2 + |X|^2|U|^2 - X^*YZU* - Z^*UXY^*) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \, \frac{1}{|\vec{r}-\vec{r}\,'|} \frac{1}{2}|XU - YZ|^2 \geq 0 \\ & X = \varphi_1(\vec{r}\,'), \quad Y = \varphi_2(\vec{r}\,'), \quad Z = \varphi_2(\vec{r}), \quad U = \varphi_1(\vec{r}) \end{aligned}$$

159 Let us write

$$\frac{e^{-\mu r}}{r} = \frac{1}{2\pi^2} \int d^3k \, e^{i\vec{k}\cdot\vec{r}} \frac{1}{k^2+\mu^2} = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \frac{4\pi}{k^2+\mu^2}$$

Where we interpret as $\mu \to 0$ so that

$$\frac{1}{r} = \frac{1}{2\pi^2} \int d^3k \, e^{i\vec{k}\cdot\vec{r}} \frac{1}{k^2} = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \frac{4\pi}{k^2}$$

160

$$\begin{aligned} K(1,2) &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k \, \frac{1}{k^2} \int d^3r \int d^3r\,' \, e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \, \varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,')\varphi_2^*(\vec{r})\varphi_1(\vec{r}) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k \, \frac{1}{k^2} \int d^3r e^{i\vec{k}\cdot\vec{r}} \varphi_2^*(\vec{r})\varphi_1(\vec{r}) \int d^3r\,' e^{-i\vec{k}\cdot\vec{r}\,'} \, \varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,') \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k \, \frac{1}{k^2} \left| \int d^3r e^{i\vec{k}\cdot\vec{r}} \varphi_2^*(\vec{r})\varphi_1(\vec{r}) \right|^2 \geq 0 \end{aligned}$$

161

$$\begin{aligned} & J(i,i) + J(j,j) - J(i,j) - J(j,i) = \frac{e^2}{4\pi\epsilon_0} \int d\vec{r} \int d\vec{r}\,' \\ & \quad \times \frac{1}{|\vec{r}-\vec{r}\,'|} \big(|\varphi_i(\vec{r})|^2 |\varphi_i(\vec{r}\,')|^2 + |\varphi_j(\vec{r})|^2 |\varphi_j(\vec{r}\,')|^2 - |\varphi_i(\vec{r})|^2 |\varphi_j(\vec{r}\,')|^2 - |\varphi_j(\vec{r})|^2 |\varphi_i(\vec{r}\,')|^2 \big) \\ & = \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\vec{k}} \frac{4\pi}{k^2} \int d\vec{r} \int d\vec{r}\,' e^{i\vec{k}\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{r}\,'} \times \Big(|\varphi_i(\vec{r})|^2 - |\varphi_j(\vec{r})|^2 \Big) \Big(|\varphi_i(\vec{r}\,')|^2 - |\varphi_j(\vec{r}\,')|^2 \Big) \\ & = \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\vec{k}} \frac{4\pi}{k^2} \left| \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \Big(|\varphi_i(\vec{r})|^2 - |\varphi_j(\vec{r})|^2 \Big) \right|^2 \geq 0 \end{aligned}$$

Expectation Value of Free Fermion System

In contrast to the fermion systems, the simplest form of many-particle states where the single-particle states are packed to the fermi energy of E_F, is called a " Fermi sea ". In the second quantization representation, we can write

$$|F\rangle = \prod_{\epsilon_{\vec{k}} \le E_F} d^\dagger_{\vec{k}} |0\rangle$$
$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$$
$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{k}} \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

Let us now demonstrate the calculations for the expectation values of the second quantized operators in the Fermi sea.

- Particle density [162]

$$\langle F|\, \hat{n}(\vec{r}) \mid F\rangle = \frac{N}{V} = \frac{1}{6\pi} k_F^3$$

- Particle-particle correlation function [163]

$$\langle F|\hat{n}(\vec{r}, \vec{r}\,') \mid F\rangle = \left(\frac{N}{V}\right)^2 \left(1 - (f(k_F|\vec{r} - \vec{r}\,'|))^2\right)$$
$$f(k_F R) = 3\,\frac{\sin k_F R - k_F R \cos k_F R}{k_F^3 R^3}$$

The above equations show that the particles repel each other in the real space given by the Pauli 's exclusion principle; the effect is known as the Exchange hole.

---

[162]

$$\begin{aligned}\langle F|\hat{n}(\vec{r}) \mid F\rangle &= \langle F|\hat{\psi}^\dagger(\vec{r})\hat{\psi}(\vec{r})|F\rangle \\ &= \frac{1}{V}\sum_{\vec{k},\vec{k}\,'} e^{-i(\vec{k}-\vec{k}\,')\cdot\vec{r}} \langle F|d^\dagger_{\vec{k}} d_{\vec{k}\,'}|F\rangle \\ &= \frac{1}{V}\sum_{\vec{k},\epsilon_{\vec{k}}\le E_F} \langle F|d^\dagger_{\vec{k}} d_{\vec{k}}|F\rangle = \frac{N}{V}\end{aligned}$$

while

$$N = \sum_{\vec{k},\epsilon_{\vec{k}}\le E_F} 1 = \left(\frac{L}{2\pi}\right)^3 \int_{\epsilon_{\vec{k}}\le E_F} d\vec{k} = V\frac{1}{8\pi^3}\frac{4\pi^2}{3}k_F^3 = V\frac{1}{6\pi}k_F^3$$

[163] In calculating the interaction terms, we first write $g(\vec{r}-\vec{r}\,') = \delta(\vec{r}-\vec{R}_A)\delta(\vec{r}\,'-\vec{R}_B)$ to directly

7.3 Mean Field Equations: Hartree-Fock Equations

Now we consider obtaining the basis function $\varphi_i(\vec{r})$ that includes the lowest variational energy we evaluated in the last subsection. Since the basis function is known as the complex quantity, we write the variation of $\varphi_i^*(\vec{r})$ while knowing that we may take the variation of $\varphi_i^*(\vec{r})$ independently of $\varphi_i(\vec{r})$. Before we do so, we consider the binding condition by introducing the normalization condition $\int d^3r\ \varphi_i^*(\vec{r})\varphi_i(\vec{r}) = 1$ using a set of N Lagrangian uncertain multipliers $\epsilon_i,\ i = 1,\cdots,N$: (We will consider the orthogonal conditions later.)

$$\frac{\delta}{\delta\varphi_i^*(\vec{r})}\Big(E_T - \sum_i \epsilon_i \int d^3r\ \varphi_i^*(\vec{r})\varphi_i(\vec{r})\Big) = 0$$

$$= \Big(-\frac{\hbar^2\nabla^2}{2m} + v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\int d^3r\,'\frac{|\varphi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} - \epsilon_i\Big)\varphi_i(\vec{r})$$

$$-\frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\Big(\int d^3r\,'\frac{\varphi_j^*(\vec{r}\,')\varphi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\Big)\varphi_j(\vec{r})$$

---

obtain from $J - K$ as following:

$$\begin{aligned}
\langle F|\,\hat{n}(\vec{r},\vec{r}\,')\,|\,F\rangle &= \sum_{k\le k_F,k'\le k_F}\int d^3r\int d^3r\,'\delta(\vec{r}-\vec{R}_A)\delta(\vec{r}\,'-\vec{R}_B) \\
&\qquad \Big(|\psi_{\vec{k}}(\vec{r}\,')|^2|\psi_{\vec{k}\,'}(\vec{r})|^2 - \psi_{\vec{k}}^*(\vec{r}\,')\psi_{\vec{k}\,'}(\vec{r}\,')\psi_{\vec{k}\,'}^*(\vec{r})\psi_{\vec{k}}(\vec{r})\Big) \\
&= \sum_{k\le k_F,k'\le k_F}\Big(\frac{1}{V^2} - \frac{1}{V^2}e^{-i\vec{k}\cdot\vec{R}_B}e^{i\vec{k}\,'\cdot\vec{R}_B}e^{-i\vec{k}\,'\cdot\vec{R}_A}e^{i\vec{k}\cdot\vec{R}_A}\Big) \\
&= \frac{1}{V^2}\sum_{k\le k_F,k'\le k_F}\Big(1 - e^{i(\vec{k}-\vec{k}\,')\cdot(\vec{R}_A-\vec{R}_B)}\Big) \\
&= \frac{1}{V^2}\big(\sum_{k\le k_F}1\big)^2 - \frac{1}{V^2}\big|\sum_{k\le k_F}e^{i\vec{k}\cdot(\vec{R}_A-\vec{R}_B)}\big|^2 = \Big(\frac{N}{V}\Big)^2\big(1 - f(k_F|\vec{R}_A-\vec{R}_B|)\big)
\end{aligned}$$

Here we calculate below:

$$\begin{aligned}
\frac{N}{V}f(k_F|\vec{R}_A-\vec{R}_B|) &= \frac{1}{V}\sum_{k\le k_F}e^{i\vec{k}\cdot(\vec{R}_A-\vec{R}_B)} = \frac{1}{V}\frac{L^3}{(2\pi)^3}\int_{k\le k_F}d\vec{k}\,e^{ik|\vec{R}_A-\vec{R}_B|\cos\theta} \\
&= \frac{1}{(2\pi)^3}(2\pi)\int_0^{k_F}dk\,k^2\frac{e^{ikR_{AB}} - e^{-ikR_{AB}}}{ikR_{AB}} = \frac{1}{2\pi^2R_{AB}}\int_0^{k_F}\int_0^{k_F}dk\,k\sin kR_{AB} \\
&= k_F^3\frac{1}{2\pi^2}\frac{\sin k_FR_{AB} - R_{AB}\cos k_FR_{AB}}{k_FR_{AB}^3} \\
&= \frac{N}{V}3\,\frac{\sin k_FR_{AB} - R_{AB}\cos k_FR_{AB}}{k_F^3R_{AB}^3}
\end{aligned}$$

giving $\int_0^K dk\cos kR = \frac{1}{R}\sin KR$, note that we have $\int_0^K dkk\sin kR = \frac{1}{R^2}(\sin KR - KR\cos KR)$.

We rewrite the above:

$$H_F \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

The operator H_F can be defined as:

$$\begin{aligned} H_F \mathcal{O} &= \Big(-\frac{\hbar^2 \nabla^2}{2m} + v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^{N} \int d^3r\,' \frac{|\varphi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} \Big) \mathcal{O}(\vec{r}) \\ &\quad -\frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^{N} \Big(\int d^3r\,' \frac{\varphi_j^*(\vec{r}\,') \cdot \mathcal{O}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \Big) \varphi_j(\vec{r}) \end{aligned}$$

The non-linear operator H_F provided above can be applied to all i and therefore, the solution will be the orthogonal system. [164] This is called the Hartree-Fock equation. Here note that the equation itself depends on φ_i of the solution thereby, the solution must be determined self-consistently. Usually, this equation possesses more than one solution in the N-particle system:

$$\{\varphi_i(\vec{r})\}, \quad i = 1, \cdots, N$$

However, based on the variation principle, we know the solution that contributes to the lowest total energy can only become the ground state. We organize the N-functions that provide the ground states to the N-particle system:

$$\varphi_1^N(\vec{r}), \cdots, \varphi_N^N(\vec{r})$$

The eigenvalue ϵ_i^N and the total energy of the Hartree-Fock equation can be given by (we clarify the N-particles dependence in the form) [165]

$$\begin{aligned} \epsilon_i^N &= I^N(i) + \sum_{j=1}^{N} \big(J^N(i,j) - K^N(i,j) \big) \\ E_T^N &= \sum_{i=1}^{N} I^N(i) + \sum_{i<j}^{N} \big(J^N(i,j) - K^N(i,j) \big) \end{aligned}$$

[164] If we show a Hermitian of H_F while no degeneration being observed, we can understand that the eigenfunctions of different eigenvalues become orthogonal. The Hermitian we show is clear by leaving out the kinetic energy; the Hermitian of the kinetic energy is already known.

[165] The Hartree-Fock equation is integrated over all space after multiplied by $\varphi_i^*(\vec{r})$:

$$\epsilon_i^N = I^N(i) + \sum_j (J^N(i,j) - K^N(i,j))$$

[166] Now we consider taking away (to make travel a finite distance) one electron in $\varphi_\alpha(\vec{r})$. To be succinct, we consider the ionization of the orbit $\varphi_\alpha(\vec{r})$. In this way, the Hartree-Fock equation changes its form, which causing its solution to change in accordance. So far as the degree of change being negligible, the system $|G,\alpha\rangle$ in N ? 1 particles system can be obtained as described in the below. The system below comprises the electron configuration of excluding φ_α from $\varphi_1^N(\vec{r}),\cdots,\varphi_N^N(\vec{r})$ that attributes to the ground state in N-particle system:

$$|G,\alpha\rangle = c_1^\dagger \cdots c_{\alpha-1}^\dagger c_{\alpha+1}^\dagger \cdots |0\rangle$$

The total energy of the ionization of the system within this approximation can be written

$$\begin{aligned} E_T^{N-1}(\alpha) &= \langle G,\alpha|H|G,\alpha\rangle \\ &= \sum_{i\neq\alpha} I^N(i) + \sum_{i<j;i\neq\alpha,j\neq\alpha} \left(J^N(i,j) - K^N(i,j)\right) \end{aligned}$$

Let us define the ionization energy $\mathcal{I}(\alpha)$ (where there is no relaxation of the electrons system) as

$$\mathcal{I}(\alpha) \quad = \quad E_T^{N-1}(\alpha) - E_T^N$$

So, $-\epsilon_\alpha$ gives the ionization energy of the orbit: [167] [168]

$$\mathcal{I}(\alpha) \quad = \quad -\epsilon_\alpha^N \quad \text{(Koopman'sTheorem)}$$

Fermi Sea and Hartree-Fock Equations

Let us now identify that the solution of Hartree-Fock equation includes the Fermi sea. Here, we assume the system is in a uniform positive charge background to satisfy the condition of electric neutrality. One-body potential is therefore given

$$v(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0}\rho_+ \int d^3r\,' \frac{e^{-\mu|\vec{r}-\vec{r}\,'|}}{|\vec{r}-\vec{r}\,'|} = -4\pi\rho_+ \frac{e^2}{4\pi\epsilon_0}\frac{1}{\mu^2}, \quad \mu = +0$$

[166] Note that $i = j$ terms in Coulomb integral and the exchange integral cancel each other (cancel the self-interaction).

[167]

$$\begin{aligned} \mathcal{I}(\alpha) &= E_T^{N-1}(\alpha) - E_T^N \\ &= -I^N(\alpha) - \sum_{i=1}^{N}(J^N(\alpha,i) - K(\alpha,i)) \\ &= -\epsilon_\alpha^N \end{aligned}$$

[168] In general, a stable particle-system takes $\epsilon_i < 0$

Here, the electric neutrality condition gives the charge density of the uniform positive charge:

$$\rho_+ = \frac{N}{V}$$

In the following, we consider the Hartree-Fock equation of the orbital function $\varphi_k = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$. First, we write the Coulomb term of the operator as (given ($|\varphi_k|^2 = \frac{1}{V}$))

$$\frac{e^2}{4\pi\epsilon_0} \sum_{k' \le k_F} \int d^3r\,' \frac{1}{V} \frac{1}{|\vec{r} - \vec{r}\,'|} = \frac{e^2}{4\pi\epsilon_0} \int d^3r\,' \frac{N}{V} \frac{1}{|\vec{r} - \vec{r}\,'|} = -v(\vec{r})$$

This can be canceled by the potential term. While, for the commuting term we may write

$$\begin{aligned}
& -\frac{e^2}{4\pi\epsilon_0} \int d^3r\,' \sum_{k' \le k_F} \frac{1}{V^{3/2}} \frac{1}{|\vec{r} - \vec{r}\,'|} e^{-i\vec{k}\,'\cdot\vec{r}\,'} e^{i\vec{k}\cdot\vec{r}\,'} e^{i\vec{k}\,'\cdot\vec{r}} \\
= & \left(-\frac{e^2}{4\pi\epsilon_0} \int d^3r\,' \sum_{k' \le k_F} \frac{1}{V} \frac{1}{|\vec{r} - \vec{r}\,'|} e^{-i(\vec{k} - \vec{k},')\cdot(\vec{r} - \vec{r}\,')} \right) \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \\
= & \left(-\frac{e^2}{4\pi\epsilon_0} \int d^3r\,' \sum_{k' \le k_F} \frac{1}{V} \frac{e^{i(\vec{k} - \vec{k},')\cdot\vec{R}}}{R} \right) \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}
\end{aligned}$$

This indicates that the orbital function $\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$ becomes the eigenfunction of the Hartree-Fock equation such that the eigenvalue $\epsilon_{\vec{k}}$ can be obtained by [169] [170]

$$\begin{aligned}\epsilon_{\vec{k}} &= \frac{\hbar^2 k^2}{2m} - \epsilon_{\vec{k}}^{ex} \\ \epsilon_{\vec{k}}^{ex} &= \frac{e^2}{4\pi\epsilon_0}\int d^3r\,' \sum_{k'\le k_F}\frac{1}{V}\frac{e^{i(\vec{k}-\vec{k},')\cdot\vec{R}}}{R} \\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi}\left(k_F + \frac{k_F^2-k^2}{2k}\log\left|\frac{k_F+k}{k_F-k}\right|\right)\end{aligned}$$

169

$$\begin{aligned}\frac{e^2}{4\pi\epsilon_0}\int d^3r\,' \sum_{k'\le k_F}\frac{1}{V}\frac{e^{i(\vec{k}-\vec{k},')\cdot\vec{R}}}{R} &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{2\pi^2}\int d^3r\,'\int d\vec{K}\,\frac{e^{i\vec{K}\cdot\vec{R}}}{K^2}e^{i(\vec{k}-\vec{k},')\cdot\vec{R}} \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{k'\le k_F}\frac{1}{V}\frac{1}{2\pi^2}\int d\vec{K}(2\pi)^3\delta(\vec{k}-\vec{k},'+\vec{K})\frac{1}{K^2} \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{k'\le k_F}\frac{1}{V}(4\pi)\frac{1}{|\vec{k}-\vec{k}\,'|^2} \\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi^2}\int_{k'\le k_F} d\vec{k}\,'\frac{1}{|\vec{k}-\vec{k}\,'|^2} \\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi^2}2\pi\int_0^{k_F} dk' k'^2\int_1^{-1} d(\cos\theta)\frac{1}{k^2+k'^2-2kk'\cos\theta} \\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi^2}2\pi\int_0^{k_F} dk'\,k'^2\frac{1}{-2kk'}\log\left|k^2+k'^2-2kk't\right|\Big|_{t=-1}^{t=1} \\ &= \frac{e^2}{4\pi\epsilon_0}\pi k\int_0^{k_F} dk'\,k'\log\left|\frac{k'+k}{k'-k}\right| \\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi}\left(k_F+\frac{k_F^2-k^2}{2k}\log\left|\frac{k_F+k}{k_F-k}\right|\right)\end{aligned}$$

170

8 The Single-particle State and Mean Field Approximation in Electron Spin System

8.1 Hamiltonian of Many-particle System

Based on our discussion in the last section, we investigate the many-electron systems as the model of typical fermion systems with the spin. Note that the Coulomb force is independent of the spin in the Hamiltonian, which we may write as

$$
\begin{aligned}
H &= H_0 + H_{int} \\
H_0 &= \sum_{\sigma=1,2} \int d^3r \; \psi_\sigma^\dagger(\vec{r}) \left(\frac{-\hbar^2 \nabla^2}{2m} + v(\vec{r}) \right) \psi_\sigma(\vec{r}) \\
H_{int} &= \frac{1}{2} \sum_{\sigma,\sigma'=1,2} \int d^3r \int d^3r\,' \; \psi_\sigma^\dagger(\vec{r}) \psi_{\sigma'}^\dagger(\vec{r}\,') \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{r}'|} \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r})
\end{aligned}
$$

8.2 Spin-orbital Function

Except for the interaction, the term H_0 forms the simple sum of the spin variables in the Hamiltonian thus, has a single-particle state in the separation of variable form $|j\mu\rangle$. We can describe the fact in the form

$$
\begin{aligned}
H_0 |j\mu\rangle &= \epsilon_{j\mu} |j\mu\rangle \quad (\epsilon_{j\mu} = \epsilon_j) \\
|j\mu\rangle &= \varphi_j(\vec{r}) \chi_\mu(\sigma) c_{j\mu}^\dagger |0\rangle \\
\left(\frac{-\hbar^2 \nabla^2}{2m} + v(\vec{r}) \right) \varphi_j(\vec{r}) &= \epsilon_j \varphi_j(\vec{r})
\end{aligned}
$$

Here $c_{j\mu}$ is the annihilation operator of the fermions, which satisfies the anticommutation relation

$$
\{c_{j\mu}, c_{j'\mu'}^\dagger\} = \delta_{jj'} \delta_{\mu\mu'}, \; \{c_{j\mu}, c_{j'\mu'}\} = 0, \; \{c_{j\mu}^\dagger, c_{j'\mu'}^\dagger\} = 0
$$

While $\chi_\mu(\sigma)$ represents the orthonormalized spin function. Let us suppose $s_z = \frac{\hbar}{2}\sigma_z$ whose eigenstate $\mu = \uparrow\downarrow$ can be written as [171]

$$
s_z |\chi_\uparrow\rangle = \frac{\hbar}{2} |\chi_\uparrow\rangle \quad s_z |\chi_\downarrow\rangle = -\frac{\hbar}{2} |\chi_\downarrow\rangle
$$

171

$$
s_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad |\chi_\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\chi_\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
$$

In this way, we have $\chi_\uparrow(1) = 1$, $\chi_\uparrow(2) = 0$, $\chi_\downarrow(1) = 0$, $\chi_\downarrow(2) = 1$.

$$\chi_\uparrow(\sigma) = |\chi_\uparrow\rangle_\sigma, \quad \chi_\downarrow(\sigma) = |\chi_\downarrow\rangle_\sigma, \qquad \sigma = 1, 2$$

These spin functions satisfy both the orthonormality

$$\langle\chi_\mu|\chi_{\mu'}\rangle = \sum_\sigma \chi_\mu^*(\sigma)\chi_{\mu'}(\sigma) = \delta_{\mu\mu'}$$

and the condition for the completeness

$$\sum_\mu |\chi_\mu\rangle\langle\chi_\mu| = \boldsymbol{I}_2$$

$$\sum_\mu \chi_\mu(\sigma)\chi_\mu^*(\sigma') = \delta_{\sigma\sigma'}$$

The space coordinates $\vec{r}$ and the spin coordinates $\sigma = 1, 2$ are together regarded as $\tau = (\vec{r}, \sigma)$, the orbital function $\phi_{j\mu}(\tau)$ can be defined as

$$\phi_{j\mu}(\tau) = \varphi_j(\vec{r})\chi_\mu(\sigma), \quad \tau = (\vec{r}, \sigma)$$

Note that our discussion in previous section can be applied exactly the same way to the cases having the spin by considering the spin-orbital function.

8.3 The Total Energy of Single-particle States

We write the following single-particle wavefunction for the N-particle system:

$$|G\rangle = |j_1\mu_1, \cdots, j_N\mu_N\rangle = c^\dagger_{j_1\mu_1}\cdots c^\dagger_{j_N\mu_N}|0\rangle$$

The expectation value of H_0 under this state can be written according to the discussion in the previous section: [172]

$$\langle G|H_0|G\rangle = \sum_{n=1}^N I(j_n)$$

$$I(j_n) = \sum_{n=1}^N \int d^3r\ \varphi^*_{j_n}(\vec{r})\Big(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\Big)\varphi_{j_n}(\vec{r})$$

[172] We use the normalization of the spin function: $(\langle\mu|\mu\rangle = 1\ )$

The expectation value of interaction also follows our discussion in the previous section:

$$\begin{aligned}
\langle G|H_{int}|G\rangle &= \sum_{n<n'}(J(k_n\mu_n, j_{n'}\tau_{n'}) - K(k_n\mu_n, j_{n'}\tau_{n'})) \\
J(k\mu, j\nu) &= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{|\varphi_k(\vec{r}')|^2\langle\mu|\mu\rangle|\varphi_j(\vec{r})|^2\langle\nu|\nu\rangle}{|\vec{r}-\vec{r}'|} \\
&= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{|\varphi_k(\vec{r}')|^2|\varphi_j(\vec{r})|^2}{|\vec{r}-\vec{r}'|} = J(k,j) \\
K(k\mu, j\nu) &= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{\varphi_k^*(\vec{r}')\varphi_j(\vec{r}')\langle\mu|\nu\rangle\varphi_j^*(\vec{r})\langle\nu|\mu\rangle\varphi_k(\vec{r})}{|\vec{r}-\vec{r}'|} \\
&= \frac{e^2}{4\pi\epsilon_0}\int d^3r\int d^3r\,'\frac{\varphi_k^*(\vec{r}')\varphi_j(\vec{r}')\varphi_j^*(\vec{r})\varphi_k(\vec{r})}{|\vec{r}-\vec{r}'|}\delta_{\mu\nu} = \begin{cases} K(k,j) & \mu=\nu \\ 0 & \mu\neq\nu \end{cases}
\end{aligned}$$

Note that the exchange integrals here contribute only to the same spin functions. The total energy E_T is therefore written

$$E_T = \sum_n I(j_n) + \sum_{n<n'} J(j_n, j_{n'}) - \sum_{\substack{n<n' \\ \mu_n=\mu_{n'}}} K(j_n, j_{n'})$$

となる。

8.4 The Hartree-Fock Equation in Electron Systems

We discussed the one-body wavefunction in the last section:

$$|G\rangle = |j_1\mu_1, \cdots, j_N\mu_N\rangle = c_{j_1\mu_1}^\dagger \cdots c_{j_N\mu_N}^\dagger|0\rangle$$

Now we consider obtaining the orbital function $\varphi_i(\vec{r})$ which includes the total energy as “ stationary ” in variation terms. In here, we assume that the spin function is already given. We write the orbital function that possesses spin up ↑ electrons as $\varphi_i^\uparrow$ while we describe the orbital function that possesses the spin down ↓ electrons as $\varphi_i^\downarrow$, and introduce them by using normalization condition and N-undetermined multipliers. The result, which is in the form of the Hartree-Fock equation, can be easily obtained by recalling the spinless cases:

$$\begin{aligned}
H_F^\uparrow\varphi_i^\uparrow(\vec{r}) &= \epsilon_i^\uparrow\varphi_i^\uparrow(\vec{r}) \\
H_F^\downarrow\varphi_i^\downarrow(\vec{r}) &= \epsilon_i^\downarrow\varphi_i^\downarrow(\vec{r})
\end{aligned}$$

The operators $H_F^{\uparrow}$ and $H_F^{\downarrow}$ are defined respectively in the forms:

$$\begin{aligned}
H_F^{\uparrow}\mathcal{O} &= \Big(-\frac{\hbar^2\nabla^2}{2m} + v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0}\sum_{n=1}^{N}\int d^3r\,'\frac{|\varphi_{j_n}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\Big)\mathcal{O}(\vec{r}) \\
&- \frac{e^2}{4\pi\epsilon_0}\sum_{n,\mu_n=\uparrow}\Big(\int d^3r\,'\frac{\varphi_{j_n}^*(\vec{r}\,')\cdot\mathcal{O}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\Big)\varphi_{j_n}(\vec{r}) \\
H_F^{\downarrow}\mathcal{O} &= \Big(-\frac{\hbar^2\nabla^2}{2m} + v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0}\sum_{n=1}^{N}\int d^3r\,'\frac{|\varphi_{j_n}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\Big)\mathcal{O}(\vec{r}) \\
&- \frac{e^2}{4\pi\epsilon_0}\sum_{n,\mu_n=\downarrow}\Big(\int d^3r\,'\frac{\varphi_{j_n}^*(\vec{r}\,')\cdot\mathcal{O}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\Big)\varphi_{j_n}(\vec{r})
\end{aligned}$$

These nonlinear operators $H_F^{\uparrow}$ and $H_F^{\downarrow}$ are found in the equivalent forms in the equations for the orbital functions of respective spins thereby, the solutions of the equations can be naturally given in the orthogonal systems. One can understand the solution of the different spins by considering the spin functions; the orthogonal systems can be also given.

PartIV
Electronic Structure of Many-Electron Atoms

9 Periodic Table and One-electronic Level of Atoms

9.1 One-electronic Level Structure of a Hydrogen-like Atom

We begin with obtaining a single-particle structure of a hydrogen-like atom. The Schroedinger equation for the Hamiltonian in our case can be written

$$
\begin{aligned}
h &= \frac{p^2}{2m} - \frac{\alpha}{r} \\
h\psi &= E\psi \\
\alpha &= \frac{Ze^2}{4\pi\epsilon_0}
\end{aligned}
$$

The angular momentum operator:

$$
\begin{aligned}
\vec{L} &= \vec{r} \times \vec{p} \\
L_i &= \epsilon_{ijk} r_j p_k
\end{aligned}
$$

can give [173] [174]

$$[\vec{L}, h] = 0$$

Further (obeys the Pauli 's),

$$\vec{M} = \frac{1}{2m}(\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) - \frac{\alpha}{r}\vec{r}$$

[173] We can first write

$$[r_i, p_j]f = r_i p_j f - p_j r_i f = r_i p_j f - (p_j r_i) f - r_i p_j f = +i\hbar \partial_j r_i f = i\hbar \delta_{ij} f \longrightarrow [r_i, p_j] = i\hbar \delta_{ij}$$
$$[p_i, f]g = p_i f g - f p_i g = (p_i f)g + f p_i g - f p_i g = (p_i f)g = -i\hbar(\partial_i f)g \quad \longrightarrow [p_i, f] = -i\hbar(\partial_i f)$$

$$[p_i, r^{-n}] = -i\hbar \partial_i (r_j r_j)^{-n/2} = i\hbar(n/2)(r_j r_j)^{-n/2-1} 2r_i = i\hbar n r^{-n-2} r_i$$

[174]

$$[L_i, p_a] = \epsilon_{ijk}[r_j p_k, p_a] = \epsilon_{ijk}[r_j, p_a]p_k = i\hbar \epsilon_{iak} p_k$$
$$[L_i, p^2] = \epsilon_{iab}[r_a p_b, p_\ell p_\ell] = \epsilon_{iab}(p_\ell [r_a, p_\ell] + [r_a, p_\ell]p_\ell)p_b = 2i\hbar \epsilon_{i\ell b} p_\ell p_b = 0 \ [\vec{L}, \frac{p^2}{2m}] = 0$$

$$[L_i, r^{-1}] = \epsilon_{iab}[r_a p_b, r^{-1}] = \epsilon_{iab} r_a [p_b, r^{-1}] = \epsilon_{iab} r_a i\hbar r^{-3} r_i = 0$$
$$\textit{Likewise}, \quad [L_i, r^{-n}] = 0$$

Thus,

$$[\vec{L}, h] = 0$$

which gives [175]

$$[\vec{M}, h] = 0$$

So, $\vec{L}$ and $\vec{M}$ become the conserved quantities. Further, [176]

$$[M_a, M_b] = -i\hbar\frac{2}{m}h\epsilon_{abc}L_c$$

175

$$\begin{aligned}
[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i, p^2] &= \epsilon_{ijk}[p_jL_k - L_jp_k, p_\ell p_\ell] = \epsilon_{ijk}(p_j[L_k,p^2] - [L_j,p^2]p_k) = 0\\
[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i, r^{-1}] &= \epsilon_{ijk}[p_jL_k - L_jp_k, r^{-1}] = \epsilon_{ijk}([p_j,r^{-1}]L_k - L_j[p_k,r^{-1}]) = i\hbar r^{-3}\epsilon_{ijk}(r_jL_k - L_jr_k)\\
&= i\hbar r^{-3}\epsilon_{ijk}(r_j\epsilon_{kab}r_ap_b - \epsilon_{jab}r_ap_br_k)\\
&= i\hbar r^{-3}\{(\delta_{ia}\delta_{jb}-\delta_{ib}\delta_{ja})r_jr_ap_b + (\delta_{ia}\delta_{kb}-\delta_{ib}\delta_{ka})r_ap_br_k)\}\\
&= i\hbar r^{-3}\{(r_jr_ip_j - r_jr_jp_i + r_ip_kr_k - r_kp_ir_k)\\
&= i\hbar r^{-3}\{r_jr_ip_j - r^2p_i + r_ip_kr_k - r_k(r_kp_i + [p_i,r_k])\}\\
&= i\hbar r^{-3}(r_jr_ip_j - 2r^2p_i + r_ip_kr_k + i\hbar r_i)\\
[r^{-1}r_i, p^2] &= -[p^2, r^{-1}r_i] = -r^{-1}[p^2,r_i] - [p^2,r^{-1}]r_i = 2i\hbar r^{-1}p_i - [p^2,r^{-1}]r_i\\
&= 2i\hbar r^{-1}p_i - p_\ell[p_\ell,r^{-1}]r_i - [p_\ell,r^{-1}]p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar p_\ell r^{-3}r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar(r^{-3}p_\ell + [p_\ell,r^{-3}])r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar r^{-3}p_\ell r_\ell r_i - i\hbar[p_\ell,r^{-3}]r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= i\hbar r^{-3}(2r^2p_i - p_\ell r_\ell r_i - r_\ell p_\ell r_i) - 3(i\hbar)^2r^{-5}r_\ell r_\ell r_i\\
&= i\hbar r^{-3}(2r^2p_i - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 3i\hbar r_i)
\end{aligned}$$

Thus,

$$\begin{aligned}
[M_i, h] &= -\frac{\alpha}{2m}i\hbar r^{-3}(r_jr_ip_j + r_ip_kr_k - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_\ell r_ip_\ell + r_ip_\ell r_\ell - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_\ell[r_i,p_\ell] + [r_i,p_\ell r_\ell] - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_i[r_i,p_i] + [r_i,p_i]r_i - 2i\hbar r_i) = 0
\end{aligned}$$

176

$$\begin{aligned}
(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i &= \epsilon_{ijk}(p_jL_k - L_jp_k) = \epsilon_{ijk}(p_jL_k - p_kL_j - [L_j,p_k])\\
&= \epsilon_{ijk}(p_jL_k - p_kL_j - i\hbar\epsilon_{jkl}p_l) = \epsilon_{ijk}(p_jL_k - p_kL_j) - 2i\hbar\delta_{il}p_l\\
&= \epsilon_{ijk}(p_jL_k - p_kL_j) - 2i\hbar p_i\\
&= \epsilon_{ijk}(p_j\epsilon_{kab} - p_k\epsilon_{jab})r_ap_b - 2i\hbar p_i\\
&= \{(\delta_{ia}\delta_{jb}-\delta_{ib}\delta_{ja})p_j + (\delta_{ia}\delta_{kb}-\delta_{ib}\delta_{ka})p_k\}r_ap_b - 2i\hbar p_i\\
&= p_jr_ip_j - p_jr_jp_i + p_kr_ip_k - p_kr_kp_i - 2i\hbar p_i\\
&= 2p_jr_ip_j - 2p_jr_jp_i - 2i\hbar p_i\\
&= 2p_j(p_jr_i + i\hbar\delta_{ij}) - 2p_j(p_ir_j + i\hbar\delta_{ij}) - 2i\hbar p_i\\
&= 2p^2r_i - 2p_jp_ir_j - 2i\hbar p_i
\end{aligned}$$

In the bound states $E < 0$, we can write

$$\tilde{M}_a = \sqrt{-\frac{m}{2E}} M_a$$

Such that we can assume:

$$[\tilde{M}_a, \tilde{M}_b] = i\hbar\epsilon_{abc}L_c$$

$$
\begin{aligned}
&\frac{1}{4}[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a,(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b] \\
=&[p^2r_a - p_ip_ar_i - i\hbar p_a, p^2r_b - p_jp_br_j - i\hbar p_b] \\
=&[p^2r_a, p^2r_b - p_jp_br_j - i\hbar p_b] \\
&-[p_ip_ar_i, p^2r_b - p_jp_br_j - i\hbar p_b] \\
&-i\hbar[p_a, p^2r_b - p_jp_br_j - i\hbar p_b] \\
=&[p^2r_a, p^2r_b] - [p^2r_a, p_jp_br_j] - i\hbar[p^2r_a, p_b] \\
&-[p_ip_ar_i, p^2r_b] + [p_ip_ar_i, p_jp_br_j] + i\hbar[p_ip_ar_i, p_b] \\
&-i\hbar[p_a, p^2r_b] + i\hbar[p_a, p_jp_br_j] + (i\hbar)^2[p_a, p_b] \\
=&\{p^2[r_a, p^2]r_b + p^2[p^2, r_b]r_a\} - \{p^2[r_a, p_jp_b]r_j + p_jp_b[p^2, r_j]r_a\} - i\hbar p^2[r_a, p_b] \\
&-\{p_ip_a[r_i, p^2]r_b + p^2[p_ip_a, r_b]r_i\} + \{p_ip_a[r_i, p_jp_b]r_j + p_jp_b[p_ip_a, r_j]r_i\} + i\hbar p_ip_a[r_i, p_b] \\
&-i\hbar p^2[p_a, r_b] + i\hbar p_jp_b[p_a, r_j] \\
=&\{2i\hbar p^2p_ar_b - 2i\hbar p^2p_br_a\} - i\hbar\{p^2(\delta_{aj}p_b + \delta_{ab}p_j)r_j - 2p_jp_bp_jr_a\} - (i\hbar)^2p^2\delta_{ab} \\
&-\{2i\hbar p_ip_ap_ir_b - i\hbar p^2(\delta_{ib}p_a + \delta_{ab}p_i)r_i\} + i\hbar\{p_ip_a(\delta_{ij}p_b + \delta_{ib}p_j)r_j - p_jp_b(\delta_{ij}p_a + \delta_{aj}p_i)r_i\} + (i\hbar)^2p_ip_a\delta_{ib} \\
&+(i\hbar)^2p^2\delta_{ab} - (i\hbar)^2p_jp_b\delta_{aj} \\
=&\{\overbrace{2i\hbar p^2p_ar_b}^{4} - \overbrace{2i\hbar p^2p_br_a}^{5}\} - i\hbar\{p^2(p_br_a + \overbrace{\delta_{ab}p_jr_j}^{1}) - \overbrace{2p_jp_bp_jr_a}^{5}\} - \overbrace{(i\hbar)^2p^2\delta_{ab}}^{2} \\
&-\{\overbrace{2i\hbar p_ip_ap_ir_b}^{4} - i\hbar p^2(p_ar_b + \overbrace{\delta_{ab}p_ir_i}^{1})\} + i\hbar\{\overbrace{p_ip_ap_br_i}^{6} + \overbrace{p_bp_ap_jr_j}^{7} - \overbrace{p_ip_bp_ar_i}^{7} - \overbrace{p_ap_bp_ir_i}^{6}\} + \overbrace{(i\hbar)^2p_bp_a}^{3} \\
&+\overbrace{(i\hbar)^2p^2\delta_{ab}}^{2} - \overbrace{(i\hbar)^2p_ap_b}^{3} \\
=&i\hbar p^2(p_ar_b - p_br_a) = i\hbar p^2(r_bp_a - r_ap_b) = -i\hbar p^2(r_ap_b - r_bp_a)
\end{aligned}
$$

$$
\begin{aligned}
&\frac{1}{2}[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a, r^{-1}r_b] \\
=&[p^2 r_a - p_i p_a r_i - i\hbar p_a, r^{-1}r_b] = [p^2 r_a, r^{-1}r_b] - [p_i p_a r_i, r^{-1}r_b] - i\hbar[p_a, r^{-1}r_b] \\
=&p_i[p_i, r^{-1}r_b]r_a + [p_i, r^{-1}r_b]p_i r_a - p_i[p_a, r^{-1}r_b]r_i - [p_i, r^{-1}r_b]p_a r_i - i\hbar[p_a, r^{-1}r_b] \\
&\qquad([p_\alpha, r^{-1}r_\beta] = r^{-1}[p_\alpha, r_\beta] + [p_\alpha, r^{-1}]r_\beta = -i\hbar r^{-1}\delta_{\alpha\beta} + i\hbar r^{-3}r_\alpha r_\beta) \\
=&i\hbar p_i(-r^{-1}\delta_{ib} + r^{-3}r_i r_b)r_a + i\hbar(-r^{-1}\delta_{ib} + r^{-3}r_i r_b)p_i r_a - i\hbar p_i(-r^{-1}\delta_{ab} + r^{-3}r_a r_b)r_i \\
&- i\hbar(-r^{-1}\delta_{ib} + r^{-3}r_i r_b)p_a r_i - (i\hbar)^2(-r^{-1}\delta_{ab} + r^{-3}r_a r_b) \\
=&i\hbar\{-p_b r^{-1}r_a + \overbrace{p_i r^{-3}r_i r_b r_a}^{3} - \overbrace{r^{-1}p_b r_a}^{2} + \overbrace{r^{-3}r_i r_b p_i r_a}^{1} + \delta_{ab}p_i r^{-1}r_i - \overbrace{p_i r^{-3}r_a r_b r_i}^{3} \\
&+ \overbrace{r^{-1}p_a r_b}^{2} - \overbrace{r^{-3}r_i r_b p_a r_i}^{1} + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_a r_b\} \\
=&i\hbar\{-p_b r^{-1}r_a + \overbrace{r^{-1}(p_a r_b - p_b r_a)}^{2} + \overbrace{r^{-3}r_i r_b(p_i r_a - p_a r_i)}^{1} + \delta_{ab}p_i r^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_a r_b\} \\
=&i\hbar\{-p_b r^{-1}r_a + \overbrace{r^{-1}(r_b p_a - r_a p_b)}^{2} + \overbrace{r^{-3}r_i r_b(r_a p_i - r_i p_a)}^{1} + \delta_{ab}p_i r^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_a r_b\} \\
=&i\hbar\{-p_b r^{-1}r_a + r^{-1}(\overbrace{r_b p_a}^{1} - r_a p_b) + r^{-3}r_i r_b r_a p_i - \overbrace{r^{-1}r_b p_a}^{1} + \delta_{ab}p_i r^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_a r_b\} \\
=&i\hbar\{-p_b r^{-1}r_a - r^{-1}r_a p_b + r^{-3}r_i r_b r_a p_i + \delta_{ab}p_i r^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_a r_b\}
\end{aligned}
$$

This gives

$$
\begin{aligned}
&\frac{1}{2}\{[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a, r^{-1}r_b] + [r^{-1}r_a, (\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b]\} \\
&= i\hbar\{-p_b r^{-1}r_a + p_a r^{-1}r_b - r^{-1}(r_a p_b - r_b p_a)\} \\
&= i\hbar\{-r^{-1}p_b r_a - [p_b, r^{-1}]r_a + r^{-1}p_a r_b + [p_a, r^{-1}]r_b - r^{-1}(r_a p_b - r_b p_a)\} \\
&= i\hbar\{r^{-1}(-p_b r_a + p_a r_b) - r^{-1}(r_a p_b - r_b p_a)\} \\
&= i\hbar\{r^{-1}(-r_a p_b + r_b p_a) - r^{-1}(r_a p_b - r_b p_a)\} \\
&= -2i\hbar r^{-1}(r_a p_b - r_b p_a)
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[M_a, M_b] &= [\frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a - \alpha r^{-1}r_a, \frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b - \alpha r^{-1}r_b] \\
&= -\frac{1}{m^2}i\hbar p^2(r_a p_b - r_b p_a) + \frac{\alpha}{m}2i\hbar r^{-1}(r_a p_b - r_b p_a) \\
&= -i\hbar\frac{2}{m}\left(\frac{p^2}{2m} - \frac{\alpha}{r}\right)\epsilon_{abc}L_c = -i\hbar\frac{2}{m}h\epsilon_{abc}L_c \\
&\qquad \epsilon_{abc}L_c = \epsilon_{abc}\epsilon_{cij}r_i p_j = (\delta_{ai}\delta_{bj} - \delta_{aj}\delta_{bi})r_i p_j = r_a p_b - r_b p_a
\end{aligned}
$$

Now we write [177]

$$\vec{L}\cdot\vec{M} = \vec{M}\cdot\vec{L} = 0$$
$$\vec{L}\cdot\tilde{\vec{M}} = \tilde{\vec{M}}\cdot\vec{L} = 0$$

Further we can write [178]

$$[M_i, L_j] = \epsilon_{ijk} M_k$$
$$[\tilde{M}_i, L_j] = \epsilon_{ijk} \tilde{M}_k$$

177

$$\begin{aligned}
\vec{M}\cdot\vec{L} &= \frac{1}{2m}(\vec{p}\times\vec{L} - \vec{L}\times\vec{p})_i L_i - \alpha r^{-1} r_i L_i \\
&= \frac{1}{m}(p^2 r_i - p_j p_i r_j - i\hbar p_i)\epsilon_{iab} r_a p_b - \alpha r^{-1} r_i \epsilon_{iab} r_a p_b \\
&= -\frac{1}{m}\epsilon_{iab}(p_j p_i r_j r_a p_b + i\hbar p_i r_a p_b) \\
&= -\frac{1}{m}\epsilon_{iab}\{p_j p_i(p_b r_j r_a + [r_j r_a, p_b]) + i\hbar p_i(p_b r_a + [r_a, p_b])\} \\
&= -\frac{1}{m}\epsilon_{iab}\{p_j p_i [r_j r_a, p_b] + i\hbar p_i [r_a, p_b]\} \\
&= -\frac{1}{m}\epsilon_{iab}\{p_j p_i(\delta_{ja} p_b + \delta_{ab} r_a) + (i\hbar)^2 p_i \delta_{ab}\} = 0 \\
\vec{L}\cdot\vec{M} &= (\vec{M}\cdot\vec{L})^\dagger = 0
\end{aligned}$$

178

$$\begin{aligned}
[M_i, L_j] = &\frac{2}{m}\epsilon_{jab}[p^2 r_i - p_j p_i r_j - i\hbar p_i, r_a p_b] - \alpha\epsilon_{jab}[r^{-1} r_i, r_a p_b] \\
=&\frac{2}{m}\epsilon_{jab}\{[p^2, r_a] p_b r_i + p^2 r_a [r_i, p_b] \\
&- [p_j p_i, r_a] p_b r_j - p_j p_i r_a [r_j, p_b] \\
&- i\hbar [p_i, r_a] p_b\} \\
&- \alpha\epsilon_{jab} r_a \{r^{-1}[r_i, p_b] + [r^{-1}, p_b] r_i\} \\
=&\frac{2i\hbar}{m}\epsilon_{jab}\{-2 p_a p_b r_i + p^2 r_a \delta_{ib} \\
&+ (\delta_{ja} p_i + \delta_{ia} p_j) p_b r_j - p_j p_i r_a \delta_{jb} \\
&+ i\hbar \delta_{ia} p_b\} \\
&- \alpha\epsilon_{jab} r_a \{r^{-1}\delta_{ib} - r^{-3} r_b r_i\} \\
=&\frac{2i\hbar}{m}\{\epsilon_{jai} p^2 r_a \\
&+ \epsilon_{jib} p_j p_b r_j \\
&+ \epsilon_{jib} i\hbar p_b\} \\
&- \alpha\epsilon_{jai} r_a r^{-1} \\
=& i\hbar\epsilon_{ija}\{\frac{2}{m}(p^2 r_a - p_j p_a r_j - i\hbar p_a) - \alpha r^{-1} r_a\} = \epsilon_{ija} M_a
\end{aligned}$$

Calculate for M^2, we obtain [179]

[179]

$$
\begin{aligned}
M^2 =&\{\frac{1}{2m}\epsilon_{iab}(p_aL_b - L_ap_b) - \alpha r^{-1}r_i\}\{\frac{1}{2m}\epsilon_{icd}(p_cL_d - L_cp_d) - \alpha r^{-1}r_i\} \\
=&\frac{1}{4m^2}(\delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc})(p_aL_b - L_ap_b)(p_cL_d - L_cp_d) \\
&- \frac{\alpha}{2m}\epsilon_{iab}\{(p_aL_b - L_ap_b)r^{-1}r_i + r^{-1}r_i(p_aL_b - L_ap_b)\} + \alpha^2 \\
=&\frac{1}{4m^2}\{(p_aL_b - L_ap_b)(p_aL_b - L_ap_b) - (p_aL_b - L_ap_b)(p_bL_a - L_bp_a)\} \\
&- \frac{\alpha}{2m}\epsilon_{iab}\{(p_aL_b - L_ap_b)r^{-1}r_i + r^{-1}r_i(p_aL_b - L_ap_b)\} + \alpha^2
\end{aligned}
$$

First,

$$
\begin{aligned}
&(p_aL_b - L_ap_b)(p_aL_b - L_ap_b) - (p_aL_b - L_ap_b)(p_bL_a - L_bp_a) \\
=&(p_aL_b - L_ap_b)(p_aL_b - L_ap_b - p_bL_a + L_bp_a) \\
=&(p_aL_b - p_bL_a - [L_a, p_b])(p_aL_b - p_bL_a - [L_a, p_b] - p_bL_a + p_aL_b + [L_b, p_a]) \\
=&(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c)(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c - p_bL_a + p_aL_b + i\hbar\epsilon_{bac}p_c) \\
=&2(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c)(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d) \\
=&2\Big\{p_aL_b(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d) \\
&- p_bL_a(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d) \\
&- i\hbar\epsilon_{abc}p_c(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d)\Big\} \\
=&2\Big\{p_aL_bp_aL_b - p_aL_bp_bL_a - i\hbar\epsilon_{abd}p_aL_bp_d \\
&- p_bL_ap_aL_b + p_bL_ap_bL_a + i\hbar\epsilon_{abd}p_bL_ap_d \\
&- i\hbar\epsilon_{abc}p_cp_aL_b + i\hbar\epsilon_{abc}p_cp_bL_a - \hbar^2\epsilon_{abd}\epsilon_{abc}p_cp_d\Big\} \\
=&2\Big\{p_a(p_aL_b + [L_b, p_a])L_b - p_ap_bL_bL_a - i\hbar\epsilon_{abd}p_a(p_dL_b + [L_b, p_d]) \\
&- p_bp_aL_aL_b + p_b(p_bL_a + [L_a, p_b])L_a + i\hbar\epsilon_{abd}p_b(p_dL_a + [L_a, p_d]) \\
&- \hbar^2 2p^2\Big\} \\
=&2\Big\{p^2L^2 - p_ap_bL_bL_a + \hbar^2\epsilon_{abd}\epsilon_{bdc}p_ap_c \\
&+ p_bp_aL_aL_b + p^2L^2 - \hbar^2\epsilon_{abd}\epsilon_{adc}p_bp_c - 2\hbar^2p^2\Big\} \\
=&2\Big\{2p^2L^2 - p_ap_bL_bL_a + \hbar^2 2\delta_{ac}p_ap_c \\
&+ p_bp_aL_aL_b + \hbar^2 2\delta_{bc}p_bp_c - 2\hbar^2p^2\Big\} \\
=&4p^2L^2 + 4\hbar^2p^2 + 2p_ap_b(L_aL_b - L_bL_a) = 4p^2(L^2 + \hbar^2)
\end{aligned}
$$

$$M^2 = \frac{2}{m} h(L^2 + \hbar^2) + \alpha^2$$

In the next step:

$$\begin{aligned}
\epsilon_{iab}\{(p_a L_b - L_a p_b) r^{-1} r_i &= \epsilon_{iab}\{p_a r^{-1} L_b r_i - L_a(r^{-1} p_b + [p_b, r^{-1}]) r_i\} \\
=& \epsilon_{iab}\{(r^{-1} p_a + [p_a, r^{-1}]) L_b r_i - r^{-1} L_a p_b r_i - i\hbar L_a r^{-3} r_b r_i\} \\
=& \epsilon_{iab}\{(r^{-1} p_a + i\hbar r^{-3} r_a) L_b r_i - r^{-1} L_a p_b r_i\} \\
=& \epsilon_{iab}\{r^{-1} p_a L_b r_i + i\hbar r^{-3}(L_b r_a + i\hbar \epsilon_{baj} r_j) r_i - r^{-1} L_a p_b r_i\} \\
=& \epsilon_{iab}\{r^{-1} p_a L_b r_i + i\hbar r^{-3} i\hbar \epsilon_{baj} r_j r_i - r^{-1} L_a p_b r_i\} \\
& [r_i, L_j] = \epsilon_{jab}[r_i, r_a p_b] = \epsilon_{jab} r_a [r_i, p_b] = i\hbar \epsilon_{jab} r_a \delta_{ib} = i\hbar \epsilon_{ija} r_a \\
=& r^{-1} \epsilon_{iab}(p_a L_b - L_a p_b) r_i + 2\hbar^2 r^{-1}
\end{aligned}$$

By adding the two above, we obtain

$$\begin{aligned}
M^2 =& \frac{p^2}{m^2}(L^2 + \hbar^2) \\
& - \frac{\alpha}{2m} r^{-1}\{\epsilon_{iab}\Big(r_i(p_a L_b - L_a p_b) + (p_a L_b - L_a p_b) r_i\Big) + 2\hbar^2\} + \alpha^2
\end{aligned}$$

While we know

$$\begin{aligned}
\epsilon_{iab}\{r_i(p_a L_b - L_a p_b) + (p_a L_b - L_a p_b) r_i\} &= \epsilon_{iab}\{r_i p_a L_b - r_i L_a p_b + p_a L_b r_i - L_a p_b r_i\} \\
=& \epsilon_{iab}\{r_i p_a L_b - r_i(p_b L_a + [L_a, p_b]) + (L_b p_a + [p_a, L_b]) r_i - L_a p_b r_i\} \\
=& \epsilon_{iab}\{r_i p_a L_b - r_i p_b L_a - i\hbar r_i \epsilon_{abc} p_c + L_b p_a r_i + i\hbar \epsilon_{abc} p_c r_i - L_a p_b r_i\} \\
=& \epsilon_{iab}\{r_i p_a L_b - r_i p_b L_a + L_b p_a r_i - L_a p_b r_i\} \\
=& \epsilon_{iab}\{r_i p_a L_b - r_a p_i L_b + L_b p_a r_i - L_b p_i r_a\} \\
=& \epsilon_{iab}(r_i p_a - r_a p_i) L_b + L_b \epsilon_{iab}(p_a r_i - p_i r_a) \\
=& \epsilon_{iab}(r_i p_a - r_a p_i) L_b + L_b \epsilon_{iab}(r_i p_a - r_a p_i) = 2L^2
\end{aligned}$$

We can obtain

$$\begin{aligned}
M^2 =& \frac{p^2}{m^2}(L^2 + \hbar^2) - \frac{\alpha}{m}\frac{2}{r}(L^2 + \hbar^2) + \alpha^2 \\
=& \frac{2}{m} h(L^2 + \hbar^2) + \alpha^2
\end{aligned}$$

For the bound states energy $E < 0$, we can write [180]

$$0 = \frac{2E}{m}((L \pm \tilde{M})^2 + \hbar^2) + \alpha^2$$

At the same time, we know that

$$\begin{aligned} \vec{I} =& \frac{1}{2}(\vec{L} + \vec{\tilde{M}}) \\ \vec{J} =& \frac{1}{2}(\vec{L} - \vec{\tilde{M}}) \end{aligned}$$

and [181]

$$\begin{aligned} [I_i, I_j] =& i\hbar\epsilon_{ijk} I_k \\ [J_i, J_j] =& i\hbar\epsilon_{ijk} J_k \end{aligned}$$

satisfy the commutation relations for the angular momentum thereby, independent of each other: [182]

$$[I_i, J_j] = 0$$

180

$$\begin{aligned} -\frac{2E}{m}\tilde{M}^2 =& \frac{2E}{m}(L^2 + \hbar^2) + \alpha^2 \\ 0 =& \frac{2E}{m}(L^2 + \tilde{M}^2 + \hbar^2) + \alpha^2 \\ =& \frac{2E}{m}((L \pm \tilde{M})^2 + \hbar^2) + \alpha^2 \end{aligned}$$

181

$$\begin{aligned} [I_i, I_j] =& \frac{1}{4}\Big([\tilde{M}_i, \tilde{M}_j] + [\tilde{M}_i, L_j] + [L_i, \tilde{M}_j] + [L_i, L_j]\Big) \\ =& \frac{i\hbar}{4}\epsilon_{ijk}(\tilde{L}_k + \tilde{M}_k + \tilde{M}_k + L_k) = \epsilon_{ijk} I_k \end{aligned}$$

$$\begin{aligned} [J_i, J_j] =& \frac{1}{4}\Big([\tilde{M}_i, \tilde{M}_j] - [\tilde{M}_i, L_j] - [L_i, \tilde{M}_j] + [L_i, L_j]\Big) \\ =& \frac{i\hbar}{4}\epsilon_{ijk}(\tilde{L}_k - \tilde{M}_k - \tilde{M}_k + L_k) = \epsilon_{ijk} J_k \end{aligned}$$

182

$$\begin{aligned} [I_i, J_j] =& \frac{1}{4}[L_i + \tilde{M}_i, L_j - \tilde{M}_j] \\ =& \frac{1}{4}([L_i, L_j] - [L_i, \tilde{M}_j] + [\tilde{M}_i, L_j] - [\tilde{M}_i, \tilde{M}_j]) \\ =& i\hbar\epsilon_{ijk}(L_k - \tilde{M}_k + \tilde{M}_k - L_k) = 0 \end{aligned}$$

Using the half-odd integers i and j, we can express

$$
\begin{aligned}
I^2 =& \hbar^2 i(i+1) \\
J^2 =& \hbar^2 j(j+1)
\end{aligned}
$$

and given $\vec{L} \cdot \tilde{M} = 0$, we let n be the integers and further write [183]

$$
E = -\frac{m\alpha^2}{2\hbar^2}\frac{1}{n^2}
$$

Since the degeneration $\vec{I} = \vec{L} + \vec{\tilde{M}}$ is given, the possible L for $i = \frac{n-1}{2}$ can be found in

$$
0, 1, \cdots, \frac{n-1}{2}
$$

The total degeneration therefore can be expressed as

$$
\sum_{\ell=0}^{\frac{n-1}{2}} (2\ell + 1) = n^2
$$

183

$$
i = j = \frac{n-1}{2}
$$

Thus we write

$$
\begin{aligned}
0 =& \frac{2E}{m}(4I^2 + \hbar^2) + \alpha^2 \\
=& \frac{2E\hbar^2}{m}(4i(i+1) + 1) + \alpha^2 \\
=& \frac{2E\hbar^2}{m}((n-1)(n+1) + 1) + \alpha^2 = \frac{2E\hbar^2}{m} n^2 + \alpha^2 \\
E =& -\frac{m\alpha^2}{2\hbar^2}\frac{1}{n^2}
\end{aligned}
$$

9.2 The Hamiltonian in Many-electron Atoms

We consider the following second quantization formalism as the Hamiltonian in many-electron atoms of having the nucleus at the origin with the charge $+Ze$:

$$\begin{aligned}
H &= H_0 + H_{int} \\
H_0 &= \int d\tau\, \psi^\dagger(\tau) h(\tau) \psi^\dagger(\tau) \\
&= \sum_\sigma \int d\vec{r}\, \psi_\sigma^\dagger(\vec{r}) \Big(-\frac{\hbar^2 \vec{\nabla}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \Big) \psi_\sigma(\vec{r}) \\
H_{int} &= \frac{1}{2} \int d\tau \int d\tau' \psi^\dagger(\tau) \psi^\dagger(\tau') g(|\tau - \tau'|) \psi(\tau') \psi(\tau) \\
&= \frac{1}{4\pi\epsilon_0} \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \sum_\sigma \sum_{\sigma'} \psi_\sigma^\dagger(\vec{r}) \psi_{\sigma'}^\dagger(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_{\sigma'}(\vec{r}') \psi_\sigma(\vec{r}) \\
\int d\tau &= \int d^3 r \sum_\sigma
\end{aligned}$$

The second quantized operator:

$$\psi(\tau) = \psi_\sigma(\vec{r}), \quad \tau = (\vec{r}, \sigma)$$

which forms

$$\phi_{\alpha\mu}(\tau) = \phi_\alpha(\vec{r}) \chi_\mu(\sigma)$$

,a complete set of normalized spin-orbital function for the bound states in central force field, and which can be further defined as in the followings:

$$\begin{aligned}
\psi(\tau) &= \psi_\sigma(\vec{r}) = \sum_{\alpha,\mu} \phi_\alpha(\vec{r}) \chi_\mu(\sigma) c_{\alpha\mu} \\
\{c_{\alpha\mu}^\dagger, c_{\alpha'\mu'}\} &= \delta_{\alpha\alpha'} \delta_{\mu\mu'}, \{c_{\alpha,\mu}, c_{\alpha'\mu'}\} = 0, \\
\alpha : nlm &= \{1\mathrm{s},\ 2\mathrm{s},\ 2\mathrm{p}_{\mathrm{m}=1} \cdots\} \\
\Big(-\frac{\hbar^2 \vec{\nabla}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \Big) \phi_{nlm}(\vec{r}) &= \epsilon_{nlm} \phi_{nlm}(\vec{r}) \\
\vec{\ell}^{\,2} \phi_{nlm}(\vec{r}) &= \hbar^2 l(l+1) \phi_{nlm}(\vec{r}) \\
\ell_z \phi_{nlm}(\vec{r}) &= \hbar m \phi_{nlm}(\vec{r}) \\
\vec{\ell} &= \vec{r} \times \frac{\hbar}{i} \vec{\nabla} \\
s_z \chi_{\uparrow\downarrow}(\sigma) &= \pm \frac{1}{2} \hbar \chi_{\uparrow\downarrow}(\sigma) \\
\vec{s}^{\,2} \chi_{\uparrow\downarrow}(\sigma) &= \frac{1}{2} (\frac{1}{2} + 1) \hbar^2 \chi_{\uparrow\downarrow}(\sigma)
\end{aligned}$$

Now, by using the fact that both the angular momentum and the spin being conserved, we can express by spectroscopy notation:

$$s(l=0),\ p(l=1),\ d(l=2),\ f(l=3),\ g(l=4),\ h(l=5),\cdots$$

9.3 Periodic Law of the Elements and the Shielding Effect

If the interaction between electrons can be ignored while the electrons move independently then, the ground state of N-electron system can be obtained by packing the particles of up to two for each level of the eigenstate of H_0 in the lower to the higher energy order. Let us summarize the single-particle eigenenergy ϵ_{nlm} of H_0:

- Let n be the principal quantum number, be the orbital angular momentum quantum number, and m be the magnetic angular momentum quantum number.
- We define $n = 1, 2, 3, \cdots$, which can be also expressed as $\ell = 0, 1, 2, \cdots, n$ or $\ell = 0(s)$, $\ell = 1(p)$, $\ell = 2(d)$, and $\ell = 3(f)$.
- The energy degenerates for the magnetic angular momentum quantum number. (Spherical-symmetric potential)

$$\epsilon_{nlm} = \epsilon_{nlm'}$$

- The energy also degenerates for the orbital angular momentum quantum number. (Peculiarity of Coulomb force)

$$\epsilon_{nlm} = \epsilon_{nl'm}$$

- The smaller the principal quantum number n, the lower the energy becomes.

$$\begin{aligned}\epsilon_{nlm} &< \epsilon_{n'lm}, \quad n < n', \\ & (1s) < (2s) < (3s) < \cdots \\ & (2p) < (3p) < (4p) < \cdots \\ & (3d) < (4d) < \cdots\end{aligned}$$

In considering the interaction among electrons, the center of the nucleus is known to have relatively large electron density, and which gives a stronger shielding against the central force generated by the nucleus thereby, the interaction energy is considered to be low. There is a greater probability for the existence of interaction at periphery of atomic nucleus when there is smaller angular momentum. Such effects may in fact provide us a clue for solving the degeneration problem of the orbital angular momentum for a pure Coulomb force. Given these facts, it is clear that the ground states of the elements in the small to large electron number order are given by the electron configurations described in the following.

$$\begin{array}{rl}
H^1 & (1s)^1 \\
He^2 & (1s)^2 \\
Li^3 & (He)(2s)^1 \\
Be^4 & (He)(2s)^2 \\
B^5 & (He)(2s)^2(2p)^1 \\
C^6 & (He)(2s)^2(2p)^2 \\
N^7 & (He)(2s)^2(2p)^3 \\
O^8 & (He)(2s)^2(2p)^4 \\
F^9 & (He)(2s)^2(2p)^5 \\
Ne^{10} & (He)(2s)^2(2p)^6 \\
Na^{11} & (Ne)(3s) \\
Mg^{12} & (Ne)(3s)^2 \\
Al^{13} & (Ne)(3s)^2(3p)^1 \\
Si^{14} & (Ne)(3s)^2(3p)^2 \\
P^{15} & (Ne)(3s)^2(3p)^3 \\
S^{16} & (Ne)(3s)^2(3p)^4 \\
Cl^{17} & (Ne)(3s)^2(3p)^5 \\
Ar^{18} & (Ne)(3s)^2(3p)^6
\end{array}$$

Up until this point, we all understand the above with considering the Coulomb force. Now, we only consider the Coulomb force to just pack the electron in $3d$; however, now we should further consider the shielding effect we have discussed before, which makes $(4s)$ energetically lower than $3d$:

$$\begin{array}{rl}
K^{19} & (Ar)(4s)^1 \\
Ca^{20} & (Ar)(4s)^2
\end{array}$$

Therefore, the electron is filled first in $(4s)$. After for a while, the electrons go into $(3d)$, which are called the transition metals. The electron in such elements found at the farthest from the nucleus possesses some common properties that $(4s)^2$ has, hence the two shares the similar chemical properties.

$$
\begin{array}{rll}
Sc^{21} & (Ar)(3d)^1(4s)^2 & \\
Ti^{22} & (Ar)(3d)^2(4s)^2 & \\
V^{23} & (Ar)(3d)^3(4s)^2 & \\
Cr^{24} & (Ar)(3d)^5(4s)^1 & (\ exception) \\
Mn^{25} & (Ar)(3d)^5(4s)^2 & \\
Fe^{26} & (Ar)(3d)^6(4s)^2 & \\
Co^{27} & (Ar)(3d)^7(4s)^2 & \\
Ni^{28} & (Ar)(3d)^8(4s)^2 & \\
Cu^{29} & (Ar)(3d)^{10}(4s)^1 & (\ exception) \\
Zn^{30} & (Ar)(3d)^{10}(4s)^2 & \\
\vdots & &
\end{array}
$$

10 Electron Configurations and Multiplet Structures

10.1 Multiplet Terms and Perturbation Theory

In the previous section, we generalized to understand the effects of many-electron via the shielding effect. Now, we take a look at the Coulomb interaction with a perspective of the perturbation theory. Before we start, it is important to note that the Hamiltonian including the interaction takes the total orbital angular momentum as well as the total spin as the conserved quantity. We will study this in a second quantization form. Generally, in the second quantization, the total orbital angular momentum operator and the spin operator is given as

$$
\begin{aligned}
\vec{L} &= \int d^3r \sum_{\sigma} \psi_\sigma^\dagger(\vec{r})\ \vec{\ell}(\vec{r})\psi_\sigma(\vec{r}) \\
\vec{S} &= \int d^3r \sum_{\sigma,\sigma'} \psi_\sigma^\dagger(\vec{r})\vec{s}_{\sigma\sigma'}\psi_{\sigma'}(\vec{r})
\end{aligned}
$$

More precisely, the operators above can be expressed by using a specific representation:

$$
\begin{aligned}
\vec{\ell}(\vec{r}) &= -i\hbar\vec{r}\times\vec{\nabla} \\
\vec{s} &= \frac{\hbar}{2}[\vec{\sigma}]_{\sigma\sigma'}
\end{aligned}
$$

Here $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ can be understood as the matrix representations called Pauli matrices in the following: [184]

$$
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
$$

[184]

$$
\sigma_\alpha^2 = I,\ \sigma_\alpha\sigma_\beta = -\sigma_\beta\sigma_\alpha\ (\alpha \neq \beta),\ \sigma_x\sigma_y = i\sigma_z, \cdots
$$

The above satisfies the commutation relations for the angular momentum: [185]

$$
\begin{aligned}
[L_i, L_j] &= i\hbar\epsilon_{ijk}L_k \\
[S_i, S_j] &= i\hbar\epsilon_{ijk}S_k
\end{aligned}
$$

[185]For example,

$$
\begin{aligned}
L_x L_y &= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi_\sigma^\dagger(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x \psi_\sigma(\vec{r})\psi_\tau^\dagger(\vec{r}')_y(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})\psi_\tau(\vec{r}') \\
&= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi_\sigma^\dagger(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x \{-\psi_\tau^\dagger(\vec{r}')\psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}')\delta_{\sigma\tau}\}(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})_y\psi_\tau(\vec{r}') \\
&= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi_\sigma^\dagger(\vec{r})\psi_\tau^\dagger(\vec{r}')(-i\hbar\vec{r}\times\vec{\nabla}_r)_x(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})_y\psi_\tau(\vec{r}')\psi_\sigma(\vec{r}) \\
&\quad + \int d^3r \sum_\sigma \psi_\sigma^\dagger(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x(-i\hbar\vec{r}'\times\vec{\nabla}_r)_y\psi_\sigma(\vec{r})
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[L_x, L_y] &= \int d^3r \sum_\sigma \psi_\sigma^\dagger(\vec{r})[(-i\hbar\vec{r}\times\vec{\nabla}_r)_x, (-i\hbar\vec{r}'\times\vec{\nabla}_r)_y]\psi_\sigma(\vec{r}) \\
&= i\hbar\int d^3r \sum_\sigma \psi_\sigma^\dagger(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_z\psi_\sigma(\vec{r}) \\
&= i\hbar L_z
\end{aligned}
$$

To give an example for the spin operator:

$$
\begin{aligned}
S_x S_y &= \int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi_\sigma^\dagger(\vec{r})\frac{\hbar}{2}[\sigma^x]_{\sigma\sigma'}\psi_\sigma(\vec{r})\psi_\tau^\dagger(\vec{r}')_y\frac{\hbar}{2}[\sigma^y]_{\tau\tau'}\psi_\tau(\vec{r}') \\
&= \frac{\hbar^2}{4}\int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi_\sigma^\dagger(\vec{r})\frac{\hbar}{2}[\sigma^x]_{\sigma\sigma'}\{-\psi_\tau^\dagger(\vec{r}')\psi_{\sigma'}(\vec{r}) + \delta(\vec{r}-\vec{r}')\delta_{\sigma'\tau}\}[\sigma^y]_{\tau\tau'}\psi_{\tau'}(\vec{r}') \\
&= \frac{\hbar^2}{4}\int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi_\sigma^\dagger(\vec{r})\psi_\tau^\dagger(\vec{r}')[\sigma^x]_{\sigma\sigma'}[\sigma^y]_{\tau\tau'}\psi_{\tau'}(\vec{r}')\psi_{\sigma'}(\vec{r}) \\
&+ \frac{\hbar^2}{4}\int d^3r \sum_{\sigma\tau'} \psi_\sigma^\dagger(\vec{r})[\sigma^x\sigma^y]_{\sigma\tau'}\psi_{\tau'}(\vec{r})
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[S_x, S_y] &= i\hbar\int d^3r \sum_{\sigma\sigma'} \psi_\sigma^\dagger(\vec{r})\frac{\hbar}{2}[\sigma^z]_{\sigma\sigma'}\psi_{\sigma'}(\vec{r}) \\
&= i\hbar S_z
\end{aligned}
$$

$\vec{L}$ and $\vec{S}$ commute with Hamiltonians that include interaction. [186] [187] [188] [189] [190]

[186]For

$$[H_0, \vec{L}] = 0$$

, we understand from the following that it obeys:

$$
\begin{aligned}
H_0 L_\alpha &= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 (-\psi^\dagger_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) + \delta(\vec{r}\vec{r}\,')\delta_{\sigma\sigma'}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \\
&\quad -(\frac{\hbar^2}{2m}) \int d^3r \sum_\sigma \psi^\dagger_{\sigma'}(\vec{r}) \vec{\nabla}_r{}^2 \big[\ell^r_\alpha \psi_{\sigma'}(\vec{r})\big]
\end{aligned}
$$

$$
\begin{aligned}
L_\alpha H_0 &= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}\,') \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}\,') \ell^{r'}_\alpha (-\psi^\dagger_\sigma(\vec{r}) \psi_{\sigma'}(\vec{r}\,') + \delta(\vec{r}\vec{r}\,')\delta_{\sigma\sigma'}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r\,' \sum_\sigma \sum_{\sigma'} (-) \psi^\dagger_{\sigma'}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&\quad -(\frac{\hbar^2}{2m}) \int d^3r\,' \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}\,') \ell^{r'}_\alpha \vec{\nabla}_{r'}{}^2 \psi_\sigma(\vec{r}\,')
\end{aligned}
$$

[187]Next, we consider the interaction term. First we have

$$
\begin{aligned}
(\frac{e^2}{2})^{-1} H_{int} L_\alpha &= \int d^3r d^3r\,' d^3r\,'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma''}(\vec{r}\,'') \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}\,'') \\
&= \int d^3r d^3r\,' d^3r\,'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \Big(-\psi^\dagger_{\sigma''}(\vec{r}\,'') \psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}\,'')\delta_{\sigma\sigma''} \Big) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r} \\
&= \int d^3r d^3r\,' d^3r\,'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') (-) \psi_{\sigma'}(\vec{r}\,') \psi^\dagger_{\sigma''}(\vec{r}\,'') \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}\,'') \\
&\quad + \int d^3r d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \ell^r_\alpha \psi_\sigma(\vec{r}) \\
&= \int d^3r d^3r\,' d^3r\,'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \Big(\psi^\dagger_{\sigma''}(\vec{r}\,'') \psi_{\sigma'}(\vec{r}\,') - \delta(\vec{r}\,'-\vec{r}\,'')\delta_{\sigma'\sigma''} \Big) \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}\,' \\
&\quad + \int d^3r d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \ell^r_\alpha \psi_\sigma(\vec{r}) \\
&= \int d^3r d^3r\,' d^3r\,'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}\,'') \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}\,'') \\
&\quad - \int d^3r d^3r\,' \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}\,') \\
&\quad + \int d^3r d^3r\,' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') g(\vec{r}-\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \ell^r_\alpha \psi_\sigma(\vec{r})
\end{aligned}
$$

[188]While we can write

$$
\begin{aligned}
(\frac{e^2}{2})^{-1} L_\alpha H_{int} &= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\ell^{r''}_\alpha \psi_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\psi^\dagger_{\sigma'}(\vec r')g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\ell^{r''}_\alpha \Big(-\psi^\dagger_\sigma(\vec r)\psi_{\sigma''}(\vec r'')+\delta(\vec r-\vec r'')\delta_{\sigma\sigma''}\Big)\psi^\dagger_{\sigma'}(\vec r')g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')(-)\psi^\dagger_\sigma(\vec r)\ell^{r''}_\alpha \psi_{\sigma''}(\vec r'')\psi^\dagger_{\sigma'}(\vec r')g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\\
&\quad +\int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec r')g(\vec r''-\vec r')\psi_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')\Big)\\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')-\delta(\vec r'-\vec r'')\delta_{\sigma'\sigma''}\Big)g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\\
&\quad +\int d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec r')g(\vec r''-\vec r')\psi_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')\Big)\\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\psi^\dagger_{\sigma'}(\vec r')\ell^{r''}_\alpha \psi_{\sigma''}(\vec r'')g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\\
&\quad -\int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\ell^{r''}_\alpha \Big(g(\vec r-\vec r'')\psi_{\sigma'}(\vec r'')\psi_\sigma(\vec r)\Big)\\
&\quad +\int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec r')g(\vec r''-\vec r')\psi_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')\Big)\\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\psi^\dagger_{\sigma'}(\vec r')g(\vec r-\vec r')\psi_{\sigma'}(\vec r')\psi_\sigma(\vec r)\ell^{r''}_\alpha \psi_{\sigma''}(\vec r'')\\
&\quad +\int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)g(\vec r-\vec r'')\psi_\sigma(\vec r)\ell^{r''}_\alpha \psi_{\sigma'}(\vec r'')\\
&\qquad +\int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_\sigma(\vec r)\Big(\ell^{r''}_\alpha g(\vec r-\vec r'')\Big)\psi_\sigma(\vec r)\psi_{\sigma'}(\vec r'')\\
&\quad +\int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_{\sigma'}(\vec r')g(\vec r''-\vec r')\psi_{\sigma'}(\vec r')\ell^{r''}_\alpha \psi_{\sigma''}(\vec r'')\\
&\qquad +\int d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_{\sigma'}(\vec r')\Big(\ell^{r''}_\alpha g(\vec r''-\vec r')\Big)\psi_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
(\frac{e^2}{2})^{-1}[H_{int}, L_\alpha] &= \int d^3r\, d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec r'')\psi^\dagger_{\sigma'}(\vec r')\Big(\Big(\ell^{r'}_\alpha+\ell^{r''}_\alpha\Big)g(\vec r''-\vec r')\Big)\psi_{\sigma'}(\vec r')\psi_{\sigma''}(\vec r'')\\
&= 0
\end{aligned}
$$

We used the fact that the angular momentum is the first order differential operator. Physically, the interaction is the internal force of the two body force such that the angular momentum is conserved.

[189] As for the spin we can write

$$
\begin{aligned}
H_0 S_\alpha &= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \\
&= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) \Big(-\psi^\dagger_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}\,') \delta_{\sigma\sigma'} \Big) [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \\
&= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) h(r) [s_\alpha]_{\sigma'\sigma''} \psi_\sigma(\vec{r}) \psi_{\sigma''}(\vec{r}\,') \\
&\quad + \int d^3r \sum_{\sigma\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) [s_\alpha]_{\sigma\sigma''} \psi_{\sigma''}(\vec{r}) \\
S_\alpha H_0 &= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) h(r) \psi_\sigma(\vec{r}) \\
&= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \Big(-\psi^\dagger_\sigma(\vec{r}) \psi_{\sigma''}(\vec{r}\,') + \delta(\vec{r}-\vec{r}\,') \delta_{\sigma\sigma''} \Big) h(r) \psi_\sigma(\vec{r}) \\
&= \int d^3r\, d^3r\,' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} h(r) \psi_{\sigma''}(\vec{r}\,') \psi_\sigma(\vec{r}) \\
&\quad + \int d^3r\, d^3r\,' \sum_{\sigma\sigma'} \psi^\dagger_{\sigma'}(\vec{r}) [s_\alpha]_{\sigma'\sigma} h(r) \psi_\sigma(\vec{r})
\end{aligned}
$$

Thus,

$$[S_\alpha H_0] = 0$$

[190]

$$
\begin{aligned}
[H_{int}, S_\alpha] &= \frac{1}{2} \int d^3r\, d^3r'\, g(|\vec{r}-\vec{r}\,'|) \int d^3r'' \sum_{\sigma\sigma'\sigma''\sigma'''} [\psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}), \psi^\dagger_{\sigma''}(\vec{r}\,'') [s_\alpha]_{\sigma''\sigma'''} \psi_{\sigma'''}(\vec{r}\,'')] \\
&= \frac{1}{2} \int d(1) \int d(2) g(1,2) \int d(3) \int d(4) [\psi^\dagger(1)\psi^\dagger(2)\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)]
\end{aligned}
$$

Here we have

$$
\begin{aligned}
[\psi^\dagger(1)\psi^\dagger(2)\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)] &= \psi^\dagger(1)\psi^\dagger(2)[\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)] \\
&\quad + [\psi^\dagger(1)\psi^\dagger(2), \psi^\dagger(3)[s]_{34}\psi(4)]\psi(2)\psi(1) \\
&= \psi^\dagger(1)\psi^\dagger(2)[\psi(2)\psi(1), \psi^\dagger(3)][s]_{34}\psi(4) \\
&\quad + \psi^\dagger(3)[s]_{34}[\psi^\dagger(1)\psi^\dagger(2), \psi(4)]\psi(2)\psi(1)
\end{aligned}
$$

$$[\psi(2)\psi(1), \psi^\dagger(3)] = \psi(2)\psi(1)\psi^\dagger(3) - \psi^\dagger(3)\psi(2)\psi(1)$$
$$= \psi(2)(-\psi^\dagger(3)\psi(1) + \delta(31)) - \psi^\dagger(3)\psi(2)\psi(1)$$
$$= \delta(31)\psi(2) - \delta(32)\psi(1)$$
$$[\psi^\dagger(1)\psi^\dagger(2), \psi(3)] = -\delta(31)\psi^\dagger(2) + \delta(32)\psi^\dagger(1)$$
$$[\psi^\dagger(1)\psi^\dagger(2), \psi(4)] = -\delta(41)\psi^\dagger(2) + \delta(42)\psi^\dagger(1)$$

Thus,

$$[H_{int}, S_\alpha] = \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(4)\psi^\dagger(1)\psi^\dagger(2)(\psi(2)[s]_{14}\psi(4) - \psi(1)[s]_{24}\psi(4))$$
$$+ \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)(-\psi^\dagger(3)[s]_{31}\psi^\dagger(2)\psi(2)\psi(1) + \psi^\dagger(3)[s]_{32}\psi^\dagger(1)\psi(2)\psi(1))$$
$$= \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)\psi^\dagger(1)\psi^\dagger(2)(\psi(2)[s]_{13}\psi(3) - \psi(1)[s]_{23}\psi(3))$$
$$+ \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)(-\psi^\dagger(3)[s]_{31}\psi^\dagger(2)\psi(2)\psi(1) + \psi^\dagger(3)[s]_{32}\psi^\dagger(1)\psi(2)\psi(1))$$
$$= \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)$$
$$\times \{\psi^\dagger(2)\psi(2)\psi^\dagger(1)[s]_{13}\psi(3) + \psi^\dagger(1)\psi(1)\psi^\dagger(2)[s]_{23}\psi(3)$$
$$- \psi^\dagger(2)\psi(2)\psi^\dagger(3)[s]_{31}\psi(1) - \psi^\dagger(1)\psi(1)\psi^\dagger(3)[s]_{32}\psi(2)\} = 0$$

In this way, we may have

$$
\begin{aligned}
[H_{int}, L_\alpha] =& \frac{1}{2}\int d(1)d(2)d(3)[\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi^\dagger(3)\ell_\alpha(3)\psi(3)] \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)[\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi(3)] + [\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi^\dagger(3)]\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)[\psi^\dagger(1)\psi^\dagger(2), \psi(3)]g(12)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)g(12)[\psi(2)\psi(1), \psi^\dagger(3)]\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)(-\delta(31)\psi^\dagger(2) + \delta(32)\psi^\dagger(1))g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)(\delta(31)\psi(2) - \delta(32)\psi(1))\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2) \\
& \times \{\Big(-\psi^\dagger(1)\ell_\alpha(1)\psi^\dagger(2) + \psi^\dagger(2)\ell_\alpha(2)\psi^\dagger(1)\Big)g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)\Big(\psi(2)\ell_\alpha(1)\psi(1) - \psi(1)\ell_\alpha(2)\psi(2)\Big)\} \\
=& \frac{1}{2}\int d(1)d(2) \\
& \times \{-\psi^\dagger(1)\psi^\dagger(2)\ell_\alpha(1)g(12)\psi(2)\psi(1) - \psi^\dagger(1)\psi^\dagger(2)\ell_\alpha(2)g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)\ell_\alpha(1)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)g(12)\ell_\alpha(2)\psi(2)\psi(1)\} \\
=& -\frac{1}{2}\int d(1)d(2)\{\psi^\dagger(1)\psi^\dagger(2)\Big(\ell_\alpha(1)g(12)\Big)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)\Big(\ell_\alpha(2)g(12)\Big)\psi(2)\psi(1)\} \\
=& -\frac{1}{2}\int d(1)d(2)\{\psi^\dagger(1)\psi^\dagger(2)\Big((\ell_\alpha(1) + \ell_\alpha(2))g(12)\Big)\psi(2)\psi(1)\} = 0
\end{aligned}
$$

191

$$[H, \vec{L}] = 0, \quad [H, \vec{S}] = 0, \quad [\vec{L}, \vec{S}] = 0$$

Each energy eigenstate can be given as a set of simultaneous eigenstates of $\vec{S}^2$, S_z, $\vec{L}^2$, and $\vec{L}_z$. Among which, the degeneration of energy can be observed for those having different $S_z = M_S$ and $L_z = M_L$. While among the levels with different $\vec{S}^2 = S(S+1)$ and $\vec{L}^2 = L(L+1)$, there is no matrix element for the Hamiltonian thus, the energy can be considered separately. [192]

To be more specific, when electric configuration $\{(n\ell)^{n_\ell}\}$ $(1 \le n_\ell \le 2(2\ell+1)$ is

---

[191] Let us have

$$\mathcal{A} = \int d(1)\psi^\dagger(1)A(1)\psi(1), \quad \mathcal{B} = \int d(2)\psi^\dagger(2)B(2)\psi(2) \quad then,$$

$$\begin{aligned}
[\mathcal{A}, \mathcal{B}] &= \int d(1) \int d(2)[\psi^\dagger(1)A(1)\psi(1), \psi^\dagger(2)B(2)\psi(2)] \\
&= \int d(1) \int d(2)\Big(\psi^\dagger(1)A(1)[\psi(1), \psi^\dagger(2)B(2)\psi(2)] + [\psi^\dagger(1)A(1), \psi^\dagger(2)B(2)\psi(2)]\psi(1) \\
\psi^\dagger(1)A(1)[\psi(1), \psi^\dagger(2)B(2)\psi(2)] &= \psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2) - \psi^\dagger(2)B(2)\psi(2)\psi(1)\} \\
&= \psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2) + \psi^\dagger(2)B(2)\psi(1)\psi(2)\} \\
&= \psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2) + (-\psi(1)\psi^\dagger(2) + \delta(12))B(2)\psi(2)\} \\
&= \psi^\dagger(1)A(1)B(2)\psi(2)\delta(12) \\
[\psi^\dagger(1)A(1), \psi^\dagger(2)B(2)\psi(2)]\psi(1) &= \{\psi^\dagger(1)A(1)\psi^\dagger(2)B(2)\psi(2) - \psi^\dagger(2)B(2)\psi(2)\psi^\dagger(1)A(1)\}\psi(1) \\
&= \{\psi^\dagger(1)A(1)\psi^\dagger(2)B(2)\psi(2) - \psi^\dagger(2)B(2)(-\psi^\dagger(1)\psi(2) + \delta(12))A(1)\}\psi(1) \\
&= \psi^\dagger(1)\psi^\dagger(2)A(1)B(2)\psi(2)\psi(1) - \psi^\dagger(2)\psi^\dagger(1)B(2)A(1)\psi(1)\psi(2) - \psi^\dagger(2)B(2)A(1)\psi(\\
[\mathcal{A}, \mathcal{B}] &= \int d(1)\psi^\dagger(1)[A, B]\psi(1)
\end{aligned}$$

[192] When the Hermitian operator $\mathcal{O}$ is commutable with the conserved quantity; i.e., commutable with Hamiltonian, the matrix element of the Hamiltonian becomes zero among the states with different eigenvalues of $\mathcal{O}$:

$$\begin{aligned}
[H, \mathcal{O}] &= H\mathcal{O} - \mathcal{O}H = 0 \\
\mathcal{O}|1\rangle &= o_1|1\rangle \\
\mathcal{O}|2\rangle &= o_2|2\rangle \\
o_1 &\neq o_2
\end{aligned}$$

Here,

$$\begin{aligned}
0 &= \langle o_1[H, \mathcal{O}]|o_2\rangle \\
&= \langle o_1 H\mathcal{O} - \mathcal{O}H|o_2\rangle \\
&= (o_1 - o_2)\langle o_1|H|o_2\rangle
\end{aligned}$$

Given $o_1 \neq o_2$, we can write

$$\langle o_1|H|o_2\rangle = 0$$

given, the interaction terms are not made merely by the summation of the spins such that each spin can possibly hold different energies. Under no interaction, the levels which have been degenerating may begin splitting at each value of the total spin. These are called multiplet terms. We will investigate the multiplet with a few examples after some preparation steps in the followings.

10.2 Angular Momentum Operator, Spin-orbital Function, and Second Quantization

Let us first make some preparation before we demonstrate a concrete example of calculations. We use a particular spin-orbital function to rewrite the angular momentum operator and the spin operator. [193]

193

$$
\begin{aligned}
\ell_\pm \phi_{\ell m} &= \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}\phi_{\ell m \pm 1} \\
\ell_z \phi_{\ell m} &= \hbar m \phi_{\ell m} \\
s_+ |\downarrow\rangle &= \hbar |\uparrow\rangle \\
s_- |\uparrow\rangle &= \hbar |\downarrow\rangle \\
s_z |\uparrow\rangle &= \frac{1}{2}\hbar |\uparrow\rangle \\
s_z |\downarrow\rangle &= -\frac{1}{2}\hbar |\downarrow\rangle
\end{aligned}
$$

$$
\begin{aligned}
L_z &= \int d^3r \sum_\sigma \psi_\sigma(\vec{r}) \ell_z \psi_\sigma(\vec{r}) \\
&= \sum_{\mu\mu'} \chi^*_\mu(\sigma)\chi_{\mu'}(\sigma) \int d^3r \sum_{jj'} \phi^*_j(\vec{r}) \ell_z \phi_{j'}(\vec{r}) c^\dagger_{j\mu} c_{j'\mu'} \\
&= \sum_{nlm} \hbar m c^\dagger_{nlm\mu} c_{nlm\mu}
\end{aligned}
$$

and so on.

$$
\begin{aligned}
L_z &= \sum_{nlm\mu} \hbar m c^\dagger_{nlm\mu} c_{nlm\mu} \\
L_\pm &= L_x \pm i L_y \\
&= \sum_{nlm\mu} \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{nlm\pm1\mu} c_{nlm\mu} \\
S_z &= \sum_{nlm} \frac{1}{2} \hbar (c^\dagger_{nlm\uparrow} c_{nlm\uparrow} - c^\dagger_{nlm\downarrow} c_{nlm\downarrow}) \\
S_+ &= \sum_{nlm} \hbar c^\dagger_{nlm\uparrow} c_{nlm\downarrow} \\
S_- &= \sum_{nlm} \hbar c^\dagger_{nlm\downarrow} c_{nlm\uparrow}
\end{aligned}
$$

The operator is expressed as

$$
\psi_\sigma(\vec{r}) = \sum_{\alpha\mu} \phi_\alpha(\vec{r}) \chi_\mu(\sigma) c_{\alpha,\mu}, \quad \alpha = (nlm)
$$

While one body term of the Hamiltonian can be written as

$$
H_0 = \sum_{nlm,\mu} \epsilon_{nlm} c^\dagger_{nlm,\mu} c_{nlm,\mu}
$$

The interaction term can be written as [194]

$$H_{int} = \sum_{n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4} I(n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4) \sum_{\ell,m} \sum$$

$$\begin{matrix} m_1, m_2, m_3, m_4 \\ m_1 + m = m_4 \\ m_3 + m = m_2 \end{matrix} \quad \sum_{\mu_1,\mu_2} c^\ell(l_1 m_1, l_4 m_4) c^\ell(l_2 m_2, l_3 m_3)$$

$$\times c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1}$$

$$c^\ell(lm, l'm') = \sqrt{\tfrac{4\pi}{2\ell+1}} \int d\Omega\, Y^*_{lm}(\Omega) Y_{\ell,m-m'}(\Omega) Y_{l,m,}(\Omega) : real$$

194

$$\begin{aligned}
H_{int} &= \sum_{\sigma\sigma'} \int d\vec{r}\, d\vec{r}\,'\, \psi_\sigma(\vec{r})^\dagger \psi_{\sigma'}(\vec{r}\,')^\dagger \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) \\
&= \sum_{\sigma\sigma'} \int d\vec{r}\, d\vec{r}\,' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \phi^*_{\alpha_1}(\vec{r}) \phi^*_{\alpha_2}(\vec{r}\,') \phi_{\alpha_3}(\vec{r}\,') \phi_{\alpha_4}(\vec{r}) \\
&\qquad \times \sum_{\mu_1,\mu_2,\mu_3,\mu_4} \chi^*_{\mu_1}(\sigma) \chi^*_{\mu_2}(\sigma') \chi_{\mu_3}(\sigma') \chi_{\mu_4}(\sigma) c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_3} c_{\alpha_4,\mu_4} \\
&= \int d\vec{r}\, d\vec{r}\,' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \phi^*_{\alpha_1}(\vec{r}) \phi^*_{\alpha_2}(\vec{r}\,') \phi_{\alpha_3}(\vec{r}\,') \phi_{\alpha_4}(\vec{r}) \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
&= \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \int dr\, dr\,' \int d\Omega \int d\Omega' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} R^*_{n_1 l_1}(r) R^*_{n_2 l_2}(r\,') R_{n_3 l_3}(r\,') R_{n_4 l_4}(r) \\
&\qquad \times Y^*_{l_1 m_1}(\Omega) Y^*_{l_2 m_2}(\Omega\,') Y_{l_3 m_3}(\Omega\,') Y_{l_4 m_4}(\Omega) \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
&= \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \sum_{\ell m} \frac{4\pi}{2\ell+1} \int dr\, R^*_{n_1 l_1}(r) R_{n_4 l_4}(r) \int dr\,' R^*_{n_2 l_2}(r\,') R_{n_3 l_3}(r\,') \cdot \frac{r_<^\ell}{r_>^{\ell+1}} \\
&\qquad \times \int d\Omega Y^*_{l_1 m_1}(\Omega) Y^*_{\ell m}(\Omega) Y_{l_4 m_4}(\Omega) \int d\Omega'\, Y^*_{l_2 m_2}(\Omega\,') Y_{\ell m}(\Omega') Y_{l_3 m_3}(\Omega\,') \\
&\qquad \times \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1}
\end{aligned}$$

$$= \sum_{n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4} I(n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4) \sum_{\ell,m} \sum_{\substack{m_1,\, m_2,\, m_3,\, m_4 \\ m_1 + m = m_4 \\ m_3 + m = m_2}} \sum_{\mu_1,\mu_2} c^\ell(l_1 m_1, l_4 m_4) c^\ell(l_2 m_2, l_3 m_3)$$

$$\times c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1}$$

$$c^\ell(lm, l'm') = \sqrt{\frac{4\pi}{2\ell+1}} \int d\Omega\, Y^*_{lm}(\Omega) Y_{\ell,m-m'}(\Omega) Y_{l,m,}(\Omega) : real$$

10.3 Some Concrete Examples of Multiplet Terms and the Method of Trace

10.3.1 $(1s)(2s)$

In this case, there are possibly four different degeneration states for the non-perturbation:

$$
\begin{aligned}
|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= c^{\dagger}_{1s\uparrow}c^{\dagger}_{2s\uparrow}|0\rangle \\
|(1s)^{\uparrow}(2s)^{\downarrow}\rangle &= c^{\dagger}_{1s\uparrow}c^{\dagger}_{2s\downarrow}|0\rangle \\
|(1s)^{\downarrow}(2s)^{\uparrow}\rangle &= c^{\dagger}_{1s\downarrow}c^{\dagger}_{2s\uparrow}|0\rangle \\
|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= c^{\dagger}_{1s\downarrow}c^{\dagger}_{2s\downarrow}|0\rangle
\end{aligned}
$$

We use the above as basis for calculating the degenerate perturbation theory. To make diagonalization of 4×4 Hamiltonian matrices, the conservation of the spin and angular momentum, which we discussed in the last subsection, should be considered. Here, we use $\hbar = 1$ in the calculations. The linear combination of the four states above can give the eigenstate for the total spin. To demonstrate this, let us first confirm that $S_+|(1s)^{\uparrow}(2s)^{\uparrow}\rangle = 0$ and $S_z|(1s)^{\uparrow}(2s)^{\uparrow}\rangle = (\frac{1}{2} + \frac{1}{2})\ |(1s)^{\uparrow}(2s)^{\uparrow}\rangle$ [195]

are the eigenstates of $S = 1$ and $M_S = 1$:

$$
\begin{aligned}
\vec{S}^2|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= 1(1+1)|(1s)^{\uparrow}(2s)^{\uparrow}\rangle \\
S_z|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= 1 \cdot |(1s)^{\uparrow}(2s)^{\uparrow}\rangle
\end{aligned}
$$

In other form, the above can be written as

$$|S = 1, M_S = 1\rangle = |(1s)^{\uparrow}(2s)^{\uparrow}\rangle$$

Likewise, we can write

$$
\begin{aligned}
\vec{S}^2|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= 1(1+1)|(1s)^{\downarrow}(2s)^{\downarrow}\rangle \\
S_z|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= -1 \cdot |(1s)^{\downarrow}(2s)^{\downarrow}\rangle
\end{aligned}
$$

The above indicates that $|(1s)^{\downarrow}(2s)^{\downarrow}\rangle$ being the eigenstate of $S = 1$ and $M_S = -1$:

$$|S = 1, M_S = -1\rangle = |(1s)^{\downarrow}(2s)^{\downarrow}\rangle$$

The states for $M_S = 0$ can be obtained by linear combination of $|(1s)^{\uparrow}(2s)^{\downarrow}\rangle$ and $|(1s)^{\downarrow}(2s)^{\uparrow}\rangle$, and among which the state for $S = 1$ is proportional to [196]

[195] Demonstrate this.

[196] Demonstrate this.

$$
\begin{aligned}
S_-|(1s)^\uparrow(2s)^\uparrow\rangle &= (c^\dagger_{1s\downarrow}c_{1s\uparrow} + c^\dagger_{1s\downarrow}c_{1s\uparrow} + \cdots)|(1s)^\uparrow(2s)^\uparrow\rangle \\
&= |(1s)^\uparrow(2s)^\downarrow\rangle + |(1s)^\downarrow(2s)^\uparrow\rangle
\end{aligned}
$$

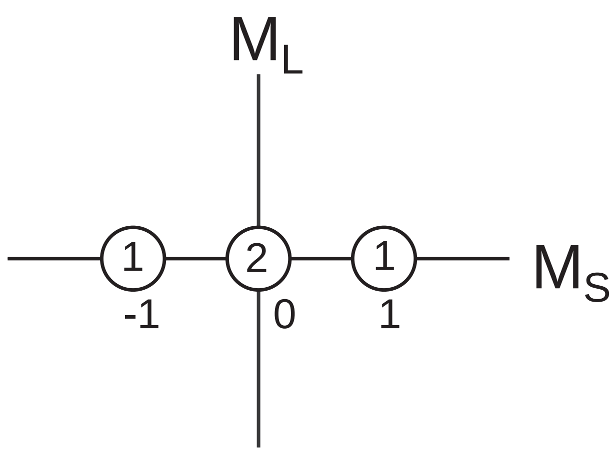
Consider the normalization we have

$$
\begin{aligned}
|S=1, M_S=0\rangle &= \frac{1}{\sqrt{2}}\big(|(1s)^\uparrow(2s)^\downarrow\rangle + |(1s)^\downarrow(2s)^\uparrow\rangle\big) \\
&= \frac{1}{\sqrt{2}}(c^\dagger_{1s\uparrow}c^\dagger_{2s\uparrow} + c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow})|0\rangle
\end{aligned}
$$

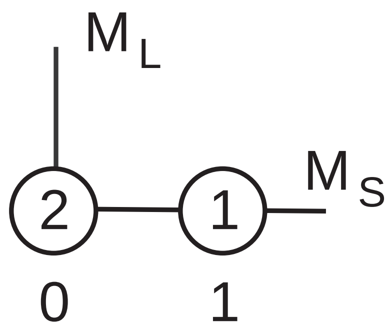
The rest of the states we know from general theory of angular momentum for $S=0$ can be written as an orthogonal form of the above:

$$
\begin{aligned}
|S=0, M_S=0\rangle &= \frac{1}{\sqrt{2}}\big(|(1s)^\uparrow(2s)^\downarrow\rangle - |(1s)^\downarrow(2s)^\uparrow\rangle\big) \\
&= \frac{1}{\sqrt{2}}(c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow} - c^\dagger_{1s\downarrow}c^\dagger_{2s\uparrow})|0\rangle
\end{aligned}
$$

We obtained the eigenstates without conducting diagonalization of the Hamiltonian matrices. This, in fact is one of the important features of the conserved quantity. We can easily understand how this may take place by the figures below that describe the dimension of the basis using the orbital angular momentum M_L and the spin angular momentum M_S:



Abbreviate the negative parts, we have



In general, the state for the total angular momentum L and the total spin S is expressed as ^{2S+1}L ($S(L=0)$, $P(L=1)$, $D(L=2)$, $F(L=3)$). The triplet degeneration state for $S=1$, for example, we have ^3S while for $S=0$ we have ^1S.

The energy for ^3S: [197]

$$\begin{aligned} E(^3S) &= \langle ^3S|H|^3S\rangle = \langle (1s)^\uparrow(2s)^\uparrow|H|(1s)^\uparrow(2s)^\uparrow\rangle \\ &= I(1s)+I(2s)+J(1s,2s)-K(1s,2s) \end{aligned}$$

While the energy for ^1S be [198]

$$\begin{aligned} E(^1S) &= \langle ^1S|H|^1S\rangle = I(1s)+I(2s)+J(1s,2s)+K(1s,2s) \\ |^1S\rangle &= \frac{1}{\sqrt{2}}(\ |(1s)^\uparrow(2s)^\downarrow\rangle - |(1s)^\downarrow(2s)^\uparrow\rangle\ ) \end{aligned}$$

In the above, we directly obtained the energy for ^1S. We now reconsider the above from different view. The Hamiltonian matrices are diagonalized by unitary transformation of the basis as we have demonstrated, and the traces of matrices are known to be invariables. The z-component of the angular momentum M is the conserved quantity so that the diagonalization procedures can be taken by each M since there is no matrix element found among the blocks that have different Ms. Hence, the trace is same for the before and after diagonalization. In our

[197] Using the degeneration, we have $|(1s)^\uparrow(2s)^\uparrow\rangle$ for ^3S.

[198]

$$\begin{aligned} \psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r})|(1s)^\uparrow(2s)^\downarrow\rangle &= (-1)\Big(\varphi_{1s}(\vec{r}')|\uparrow\rangle_{\sigma'}\varphi_{2s}(\vec{r})|\downarrow\rangle_\sigma - \varphi_{2s}(\vec{r}')|\downarrow\rangle_{\sigma'}\varphi_{1s}(\vec{r})|\uparrow\rangle_\sigma\Big)|0\rangle \\ \psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r})|(1s)^\downarrow(2s)^\uparrow\rangle &= (-1)\Big(\varphi_{1s}(\vec{r}')|\downarrow\rangle_{\sigma'}\varphi_{2s}(\vec{r})|\uparrow\rangle_\sigma - \varphi_{2s}(\vec{r}')|\uparrow\rangle_{\sigma'}\varphi_{1s}(\vec{r})|\downarrow\rangle_\sigma\Big)|0\rangle \end{aligned}$$

Thus,

$$\langle ^1S|H_{int}|^1S\rangle = \frac{1}{2}(2J(1s,2s)-2K(1s,2s)+4K(1s,2s)) = J(1s,2s)+K(1s,2s)$$

present case, for example, the block of $M = 0$ is the 2×2 matrix having the basis $(1s)^{\uparrow}(2s)^{\downarrow}$ and $(1s)^{\downarrow}(2s)^{\uparrow}$. After we make diagonalization for them, [consider the multiplet terms which will be given by this block] we have ${}^1S$ and ${}^3S$. So, we can write

$$\langle (1s)^{\uparrow}(2s)^{\downarrow}|H|(1s)^{\uparrow}(2s)^{\downarrow}\rangle + \langle (1s)^{\downarrow}(2s)^{\uparrow}|H|(1s)^{\downarrow}(2s)^{\uparrow}\rangle = \langle {}^1S|H|{}^1S\rangle + \langle {}^3S|H|{}^3S\rangle$$

Thus,

$$\begin{aligned} E({}^1S) + E({}^3S) &= E((1s)^{\uparrow}, (2s)^{\downarrow}) + E((1s)^{\downarrow}, (2s)^{\uparrow}) \\ &= 2(I(1s) + I(2s) + J(1s, 2s)) \end{aligned}$$

For the block of $M = 1$ we have

$$\begin{aligned} E({}^3S) &= E((1s)^{\uparrow}, (2s)^{\uparrow}) \\ &= I(1s) + I(2s) + J(1s, 2s) - K(1s, 2s) \end{aligned}$$

Hence, we obtain

$$E({}^1S) = I(1s) + I(2s) + J(1s, 2s) + K(1s, 2s)$$

We call the above,<u>the method of trace</u>. Further, we determine the wavefunction for the coordinates ’ representation:

$$\begin{aligned} \Psi_{{}^3S, M_S=1}(\vec{r}_1, \vec{r}_2) &= \langle r_1, r_2; \sigma_1, \sigma_2|{}^3S\rangle \\ &= \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_{1s}(\vec{r}_1)\chi_{\uparrow}(\sigma_1) & \varphi_{1s}(\vec{r}_2)\chi_{\uparrow}(\sigma_2) \\ \varphi_{2s}(\vec{r}_1)\chi_{\uparrow}(\sigma_1) & \varphi_{2s}(\vec{r}_2)\chi_{\uparrow}(\sigma_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(\vec{r}_1) & \varphi_{1s}(\vec{r}_2) \\ \varphi_{2s}(\vec{r}_1) & \varphi_{2s}(\vec{r}_2) \end{vmatrix} \chi_{\uparrow}(\sigma_1)\chi_{\uparrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}} \Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2) - \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2) \Big) \chi_{\uparrow}(\sigma_1)\chi_{\uparrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}} (\varphi_{1s}\varphi_{2s} - \varphi_{2s}\varphi_{1s}) \chi_{\uparrow}\chi_{\uparrow} \end{aligned}$$

In the same way we can write

$$\begin{aligned} \Psi_{{}^3S, M_S=-1}(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} \Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2) - \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2) \Big) \chi_{\downarrow}(\sigma_1)\chi_{\downarrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}} (\varphi_{1s}\varphi_{2s} - \varphi_{2s}\varphi_{1s}) \chi_{\downarrow}\chi_{\downarrow} \end{aligned}$$

The wavefunction for ^3S and $M_S = 0$ that are left out can be written as [199]

$$\begin{aligned}\Psi_{^3S,M_S=0}(\vec{r}_1,\vec{r}_2) &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2) - \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)+\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}} \\ &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}\varphi_{2s} - \varphi_{2s}\varphi_{1s}\Big)\frac{\chi_\uparrow\chi_\downarrow+\chi_\downarrow\chi_\uparrow}{\sqrt{2}}\end{aligned}$$

Apparently, the functions which belong to ^3S are antisymmetric to the switching of the particles $\vec{r}_1\sigma_1 \leftrightarrow \vec{r}_2\sigma_2$; however, we should note that the space component for the functions, the antisymmetric spin component, has symmetric property.

For ^1S, the function can be obtained as

$$\begin{aligned}\Psi_{^1S,M_S=0}(\vec{r}_1,\vec{r}_2) &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2) + \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)-\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}} \\ &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}\varphi_{2s} + \varphi_{2s}\varphi_{1s}\Big)\frac{\chi_\uparrow\chi_\downarrow-\chi_\downarrow\chi_\uparrow}{\sqrt{2}}\end{aligned}$$

The space component is symmetric while the spin component is antisymmetric for the above. The difference observed in the space components of the wavefunction creates the energy gap in physical terms.

10.3.2 $(1s)(1s)$

In this case, only one state is applicable to the non-perturbation state:

$$|(1s)^\uparrow(1s)^\downarrow\rangle = c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow}|0\rangle$$

where $M_S = 0$ is only valid. It is obvious that $S = 0$ therefore, ^1S is the only state we obtain.

10.3.3 $(1s)(2s)(3s)$

In this case, we can consider $2^3 = 8$ degenerate states for the non-perturbation. To make a list of the states in terms of M_S, we have:

[199]

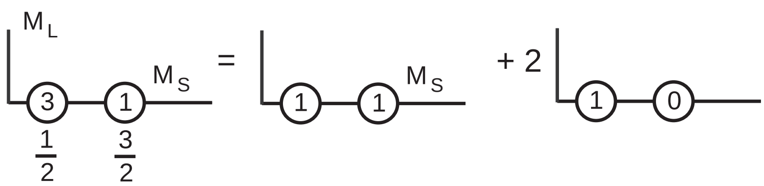
$$\begin{aligned}\langle r_1,r_2;\sigma_1,\sigma_2|(1s)^\uparrow(2s)^\downarrow\rangle &= \frac{1}{\sqrt{2!}}\begin{vmatrix}\varphi_{1s}(\vec{r}_1)\chi_\uparrow(\sigma_1) & \varphi_{1s}(\vec{r}_2)\chi_\uparrow(\sigma_2)\\ \varphi_{2s}(\vec{r}_1)\chi_\downarrow(\sigma_1) & \varphi_{2s}(\vec{r}_2)\chi_\downarrow(\sigma_2)\end{vmatrix} \\ &= \frac{1}{\sqrt{2}}\big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\big)\end{aligned}$$

$$\langle r_1,r_2;\sigma_1,\sigma_2|(1s)^\downarrow(2s)^\uparrow\rangle = \frac{1}{\sqrt{2}}\big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2) - \varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)\big)$$

m_{1s}	m_{2s}	m_{3s}	M_S
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

Therefore,

M_S	Number of states
$\frac{3}{2}$	1
$\frac{1}{2}$	3



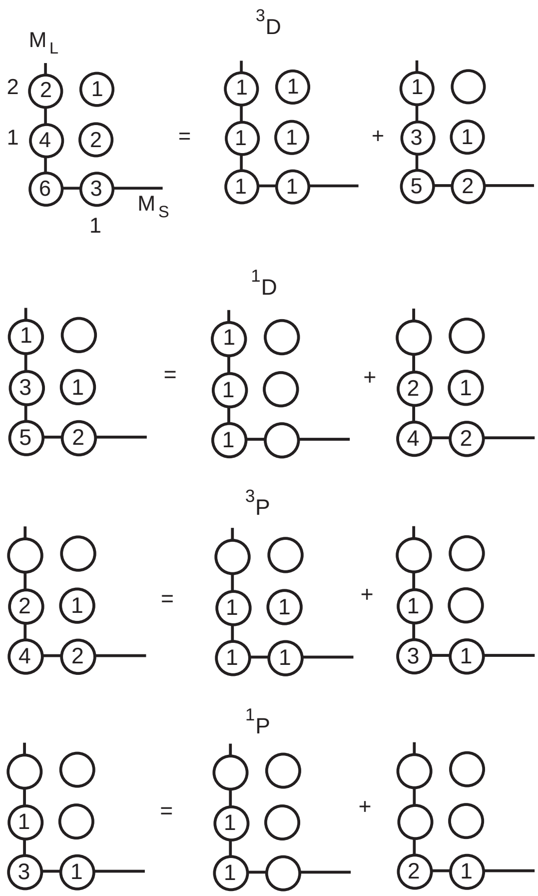
In short, we are having one ^4S and two ^2S.

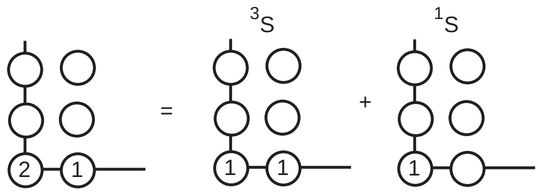
10.3.4 $(2p)(3p)$

In this case, we can think of $(2 \times 3)^2 = 36$ degenerate states for the non-perturbation. To make a list of the possible basis states using M_S and M_L, we have:

M_S	M_L	$(2p_{\ell_z})^{\uparrow,\downarrow}(3p_{\ell_z})^{\uparrow,\downarrow}$
1	2	$(2p_1)^\uparrow(3p_1)^\uparrow$
0	2	$(2p_1)^\uparrow(3p_1)^\downarrow$, $(2p_1)^\downarrow(3p_1)^\uparrow$
-1	2	$(2p_1)^\downarrow(3p_1)^\downarrow$
1	1	$(2p_1)^\uparrow(3p_0)^\uparrow$, $(2p_0)^\uparrow(3p_1)^\uparrow$
0	1	$(2p_1)^\uparrow(3p_0)^\downarrow$, $(2p_1)^\downarrow(3p_0)^\uparrow$, $(2p_0)^\uparrow(3p_1)^\downarrow$ $(2p_0)^\downarrow(3p_1)^\uparrow$
-1	1	$(2p_1)^\downarrow(3p_0)^\downarrow$, $(2p_0)^\downarrow(3p_1)^\downarrow$
1	0	$(2p_1)^\uparrow(3p_{-1})^\uparrow$, $(2p_0)^\uparrow(3p_0)^\uparrow$, $(2p_{-1})^\uparrow(3p_1)^\uparrow$
0	0	$(2p_1)^\uparrow(3p_{-1})^\downarrow$, $(2p_0)^\uparrow(3p_0)^\downarrow$, $(2p_{-1})^\uparrow(3p_1)^\downarrow$, $(2p_1)^\downarrow(3p_{-1})^\uparrow$, $(2p_0)^\downarrow(3p_0)^\uparrow$, $(2p_{-1})^\downarrow(3p_1)^\uparrow$
-1	0	$(2p_1)^\downarrow(3p_{-1})^\downarrow$, $(2p_0)^\downarrow(3p_0)^\downarrow$, $(2p_{-1})^\downarrow(3p_1)^\downarrow$
1	-1	$(2p_{-1})^\uparrow(3p_0)^\uparrow$, $(2p_0)^\uparrow(3p_{-1})^\uparrow$
0	-1	$(2p_{-1})^\uparrow(3p_0)^\downarrow$, $(2p_{-1})^\downarrow(3p_0)^\uparrow$, $(2p_0)^\uparrow(3p_{-1})^\downarrow$ $(2p_0)^\downarrow(3p_{-1})^\uparrow$
-1	-1	$(2p_{-1})^\downarrow(3p_0)^\downarrow$, $(2p_0)^\downarrow(3p_{-1})^\downarrow$
1	-2	$(2p_{-1})^\uparrow(3p_{-1})^\uparrow$
0	-2	$(2p_{-1})^\uparrow(3p_{-1})^\downarrow$, $(2p_{-1})^\downarrow(3p_{-1})^\uparrow$
-1	-2	$(2p_{-1})^\downarrow(3p_{-1})^\downarrow$

Therefore,





In other words ^3D, ^1D, ^3P, ^1P, ^3S, ^1S are given as multiplet terms.

According to the method of trace, the energy can be expressed as following forms as we are given $E(\alpha,\beta)=\langle\alpha|H|\beta\rangle$ and $^3D=E(^3D)$:

$$
\begin{aligned}
{}^3D=&\langle(2p_1)^\uparrow(3p_1)^\uparrow|H|(2p_1)^\uparrow(3p_1)^\uparrow\rangle=E((2p_1)^\uparrow(3p_1)^\uparrow)\quad(M_S=1,M_L=2)\\
=&I(2p_1)+I(3p_1)+J(2p_1,3p_1)-K(2p_1,3p_1)\\
{}^1D+{}^3D=&E((2p_1)^\uparrow(3p_1)^\downarrow)+E((2p_1)^\downarrow(3p_1)^\uparrow)\quad(M_S=0,M_L=2)\\
=&2I(2p_1)+2I(3p_1)+2J(2p_1,3p_1)\\
{}^3P\qquad+{}^3D=&E((2p_1)^\uparrow(3p_0)^\uparrow)+E((2p_0)^\uparrow(3p_1)^\uparrow)\quad(M_S=1,M_L=1)\\
=&I(2p_1)+I(3p_0)+I(2p_0)+I(3p_1)\\
&+J(2p_1,3p_0)-K(2p_1,3p_0)+J(2p_0,3p_1)-K(2p_0,3p_1)\\
{}^3S\qquad+{}^3P\qquad+{}^3D=&E((2p_1)^\uparrow(3p_{-1})^\uparrow)+E((2p_0)^\uparrow(3p_0)^\uparrow)+E((2p_{-1})^\uparrow(3p_1)^\uparrow)\quad(M_S=1,M_L=\\
=&I(2p_1)+I(3p_{-1})+I(2p_0)+I(3p_0)+I(2p_{-1})+I(3p_1)\\
&+J(2p_1,3p_{-1}))-K(2p_1,3p_{-1})+J(2p_0,3p_0)-K(2p_0,3p_0)\\
&+J(2p_{-1},3p_1)-K(2p_{-1},3p_1)\\
{}^1P+{}^3P+{}^1D+{}^3D=&E((2p_1)^\uparrow(3p_0)^\downarrow)+E((2p_1)^\downarrow(3p_0)^\uparrow)\\
&+E((2p_0)^\uparrow(3p_1)^\downarrow)+E((2p_0)^\downarrow(3p_1)^\uparrow)\quad(M_S=0,M_L=1)\\
=&I(2p_1)+I(3p_0)+I(2p_1)+I(3p_0)+I(2p_0)+I(3p_1)+I(2p_0)+I(3p_1)\\
&+J(2p_1,3p_0)+J(2p_1,3p_0)+J(2p_0,3p_1)+J(2p_0,3p_1)\\
{}^1S+{}^3S+{}^1P+{}^3P+{}^1D+{}^3D=&E((2p_1)^\uparrow(3p_{-1})^\downarrow)+E((2p_0)^\uparrow(3p_0)^\downarrow)+E((2p_{-1})^\uparrow(3p_1)^\downarrow)+E((2p_1)^\downarrow(3p_{-1})\\
&+E((2p_0)^\downarrow(3p_0)^\uparrow)+E((2p_{-1})^\downarrow(3p_1)^\uparrow)\quad(M_S=0,M_L=0)\\
&=2I(2p_1)+2I(3p_{-1})+2I(2p_0)+2I(3p_0)+2I(3p_1)+2I(2p_{-1})\\
&+J((2p_1,3p_{-1})+J(2p_0,3p_0))+J(2p_{-1},3p_1)+J(2p_1,3p_{-1})+\\
&+J(2p_0,3p_0)+J(2p_{-1},3p_1)
\end{aligned}
$$

Recast the above to have

$$
\begin{pmatrix}
1 & & & & & \\
1 & 1 & & & & \\
1 & & 1 & & & \\
1 & 1 & 1 & 1 & & \\
1 & & 1 & & 1 & \\
1 & 1 & 1 & 1 & 1 & 1
\end{pmatrix}
\begin{pmatrix}
{}^3D \\ {}^1D \\ {}^3P \\ {}^1P \\ {}^3S \\ {}^1S
\end{pmatrix}
=
\begin{pmatrix}
* \\ * \\ * \\ * \\ * \\ *
\end{pmatrix}
$$

The equation has a solution because the left side of the matrix has 1.

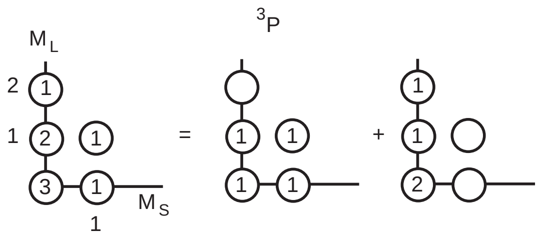
10.3.5 $(2p)^2$

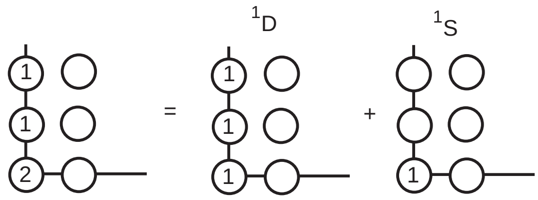
There are ${}_6C_2 = 15$ degenerate states for the non-perturbation. We make a list of possible states to be the basis by using M_S and M_L:

M_S	M_L	$(2p_{\ell_z})^{\uparrow,\downarrow}$
0	2	$(2p_1)^\uparrow(2p_1)^\downarrow$
1	1	$(2p_1)^\uparrow(2p_0)^\uparrow$
0	1	$(2p_1)^\uparrow(2p_0)^\downarrow$
1	0	$(2p_1)^\uparrow(2p_{-1})^\uparrow$
0	0	$(2p_1)^\uparrow(2p_{-1})^\downarrow$
0	1	$(2p_1)^\downarrow(2p_0)^\uparrow$
-1	1	$(2p_1)^\downarrow(2p_0)^\downarrow$
0	0	$(2p_1)^\downarrow(2p_{-1})^\uparrow$
-1	0	$(2p_1)^\downarrow(2p_{-1})^\downarrow$
0	0	$(2p_0)^\uparrow(2p_0)^\downarrow$
1	-1	$(2p_0)^\uparrow(2p_{-1})^\uparrow$
0	-1	$(2p_0)^\uparrow(2p_{-1})^\downarrow$
0	-1	$(2p_0)^\downarrow(2p_{-1})^\uparrow$
-1	-1	$(2p_0)^\downarrow(2p_{-1})^\downarrow$
0	-2	$(2p_{-1})^\uparrow(2p_{-1})^\downarrow$

M_S	M_L	状態数
0	2	1
0	1	2
0	0	3
0	-1	2
0	-2	1
1	1	1
1	0	1
1	-1	1
-1	1	1
-1	0	1
-1	-1	1

Therefore,





In other words, ^3P, ^1D, and ^1S are given as the multiplet terms.

In determining the energy by using the method of trace,

$$
\begin{aligned}
{}^1D \quad &= E((2p_1)^{\uparrow}(2p_1)^{\downarrow}) \quad (M_S = 0, M_L = 2) \\
&= 2I(2p_1) + J(2p_1, 2p_1) \\
{}^3P &= E(2p_1)^{\uparrow}, (2p_0)^{\uparrow}) \quad (M_S = 1, M_L = 1) \\
&= I(2p_1) + I(2p_0) + J(2p_1, 2p_0) - K(2p_1, 2p_0) \\
{}^1S + {}^1D + {}^3P &= E((2p_1)^{\uparrow}(2p_{-1})^{\downarrow}) + E((2p_1)^{\downarrow}(2p_{-1})^{\uparrow}) + E((2p_0)^{\uparrow}(2p_0)^{\downarrow}) \quad (M_S = 0, M_L = 0) \\
&= 2I(2p_1) + 2I(2p_0) + 2I(2p_{-1}) + 2J(2p_1, 2p_{-1}) + J(2p_0, 2p_0)
\end{aligned}
$$

can give the energy. To provide with other multiplet examples and their results,

10.3.6 *pd*

$$^3F,^3D,^3P,^1F,^1D,^1P$$

10.3.7 *pds*

$$^4F,^4D,^4P,2(^2F),2(^2D),2(^2P)$$

10.4 Electron-hole Transformation and the Multiplet $(nl)^x$

10.4.1 Multiplet $(nl)^x$

For the multiplets which fill the electrons of the particular orbits, we can obtain the following results:

- p^1 : ^2P
- p^2 : $^3P,^1D,^1S$
- p^3 : $^4S,^2D,^2P$
- p^4 : $^3P,^1D,^1S$
- p^5 : ^2P
- d^1 : ^2D
- d^2 : $^3F,^3P,^1G,^1D,^1S$
- d^3 : $^4F,^4P,^2H,^2G,^2F,2(^2D),^2P$
- d^4 : $^5D,^3H,^3G,2(^3F),^3D,2(^3P),^1I,2(^1G),^1F,2(^1D),2(^1S)$
- d^5 : $^6S,^4G,^4F,^4D,^4P,^2I,^2H,2(^2G),2(^2F),3(^2D),^2P,^2S$
- d^6 : $^5D,^3H,^3G,2(^3F),^3D,2(^3P),^1I,2(^1G),^1F,2(^1D),2(^1S)$
- d^7 : $^4F,^4P,^2H,^2G,^2F,2(^2D),^2P$
- d^8 : $^3F,^3P,^1G,^1D,^1S$
- d^9 : ^2D

The above indicates that $(nl)^x$ and $(nl)^{2(2l+1)-x}$ are given by the same multiplet term due to the electron-hole symmetry. In the following, we will investigate this characteristic.

10.4.2 Electron-hole Transformation

When we limit the electron configuration to the particular (nl), the angular momentum and the spin operator can be

$$
\begin{aligned}
L_z &= \sum_m \sum_\mu \hbar m c^\dagger_{m\mu} c_{m\mu} \\
L_\pm &= \sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{m\pm 1\mu} c_{m\mu} \\
S_z &= \frac{1}{2}\hbar \sum_m (c^\dagger_{m\uparrow} c_{m\uparrow} - c^\dagger_{m\downarrow} c_{m\downarrow}) \\
S_+ &= \hbar \sum_m c^\dagger_{m\uparrow} c_{m\downarrow} \\
S_- &= \hbar \sum_m c^\dagger_{m\downarrow} c_{m\uparrow}
\end{aligned}
$$

Let us define

$$
U = \prod_m \prod_\mu (c_{m\mu} + c^\dagger_{m\mu})
$$

then U and

$$
U^\dagger U = U U^\dagger = 1
$$

are the unitary operator. [200] Now we write

$$
\begin{aligned}
\vec{L}' &= U \vec{L} U^\dagger, \\
\vec{S}' &= U \vec{S} U^\dagger
\end{aligned}
$$

which giving

$$
\begin{aligned}
L'_z &= -L_z, \quad L'_\pm = -L_\mp \\
S'_z &= -S_z, \quad S'_\pm = -S_\mp
\end{aligned}
$$

therefore, [201]

$$
\begin{aligned}
\vec{L}'^2 &= \frac{1}{2}(L'_+ L'_- + L'_- L'_+) + L'^2_z = \vec{L}^2 \\
\vec{S}'^2 &= \vec{S}^2
\end{aligned}
$$

200

$$
(c + c^\dagger)(c^\dagger + c) = c c^\dagger + c^\dagger c = 1
$$

201

$$
\begin{aligned}
(c + c^\dagger) c (c + c^\dagger) &= c^\dagger c c^\dagger = c^\dagger \\
(c + c^\dagger) c^\dagger (c + c^\dagger) &= c
\end{aligned}
$$

So, for the arbitrary multiplet $|G\rangle$, we can write

$$\vec{L}^2|G\rangle = \hbar L(L+1)|G\rangle$$
$$\vec{S}^2|G\rangle = \hbar S(S+1)|G\rangle$$

This gives

$$Uc_{m\mu}U^\dagger = c^\dagger_{m\mu}$$
$$Uc^\dagger_{m\mu}U^\dagger = c_{m\mu}$$

Thus,

$$\begin{aligned}
L'_z &= \sum_m \sum_\mu \hbar m c_{m\mu} c^\dagger_{m\mu} \\
&= \sum_m \sum_\mu \hbar m (1 - c^\dagger_{m\mu} c_{m\mu}) = -L_z \\
L'_\pm &= \sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c_{m\pm 1\mu} c^\dagger_{m\mu} \\
&= -\sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{m\mu} c_{m\pm 1\mu} \\
L'_+ &= -\sum_m \sum_\mu \hbar \sqrt{(l - m)(l + m + 1)} c^\dagger_{m\mu} c_{m+1\mu} \\
&= -\sum_{m'} \sum_\mu \hbar \sqrt{(l - m' + 1)(l + m')} c^\dagger_{m'-1\mu} c_{m'\mu}, \quad m' = m+1 \\
&= -L_- \\
L'_- &= -\sum_m \sum_\mu \hbar \sqrt{(l + m)(l - m + 1)} c^\dagger_{m\mu} c_{m-1\mu} \\
&= -\sum_{m'} \sum_\mu \hbar \sqrt{(l + m' + 1)(l - m')} c^\dagger_{m'+1\mu} c_{m'\mu}, \quad m' = m-1 \\
&= -L_+ \\
S'_z &= \frac{1}{2}\hbar \sum_m (c_{m\uparrow} c^\dagger_{m\uparrow} - c_{m\downarrow} c^\dagger_{m\downarrow}) = -S_z \\
S'_+ &= \hbar \sum_m c_{m\downarrow} c^\dagger_{m\uparrow} = -S_- \\
S'_- &= \hbar \sum_m c_{m\uparrow} c^\dagger_{m\downarrow} = -S_+
\end{aligned}$$

So that we can write in the form: [202]

$$\vec{L'}^2|G'\rangle = \hbar L(L+1)|G'\rangle$$
$$\vec{S'}^2|G'\rangle = \hbar S(S+1)|G'\rangle$$
$$|G'\rangle = U|G'\rangle$$

As we can readily confirm: [203]

$$|G\rangle \in (nl)^x \leftrightarrow |G'\rangle \in (nl)^{2(2l+1)-x}$$

Therefore, generally speaking, $(nl)^x$ and $(nl)^{2(2l+1)-x}$ may give the same multiplet term.

10.5 Hund 's Rule

Although we can determine the multiplets that are given in the way described in the last few subsections, further calculations (integrations) are required to determine the energy states for such multiplets. In considering the states which contributes to the lowest energy level, an experiential rule called the Hund 's rule can be applied.

> *Hund 's Rule:* Among all multiplets that are given by an electron configuration, the spin with the greatest level may possess the lowest energy. When there are more than one maximum multiplicity spins then, the one with the greatest orbital angular momentum among them has the lowest energy level. In the case where there are more than one maximum multiplicities of the greatest orbital angular momentum then, the spin which has the greatest orbital angular momentum L has the lowest energy level.

---

[202]

$$U\vec{L}^2U^\dagger U|G\rangle = \hbar L(L+1)U|G\rangle$$
$$U\vec{S}^2U^\dagger U|G\rangle = \hbar S(S+1)U|G\rangle$$

[203] In the case for d^x, if we have

$$|t\rangle = c^\dagger_{1\uparrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}|0\rangle$$

then we can write

$$|t'\rangle = U|t\rangle = c^\dagger_{-2\uparrow}c^\dagger_{-2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{0\downarrow}c^\dagger_{2\uparrow}|0\rangle$$

Yet it is considered as an experiential rule, the Hund 's rule has been widely accepted. As we have discussed earlier, in the physical terms, the spin function indeed holds symmetric property in electron replacement for the spins with maximum multiplicity while the space part of the wavefunction is antisymmetric based on the Pauli 's principle. In other words, the wavefunction becomes zero when arbitrary two electron coordinates are the same, and from which we may assume that the Coulomb interaction energy among electrons can be obtained. For the orbital angular momenta of the same spin, the greater the momentum, the less chances are for the electrons to come close to each other since they move at farther distance away because of the centrifugal force. For the last part of the rule that relates to L, there is a small Coulomb repulsion and the low probability for the electrons of greater m value to come close to each other in filling out the parallel spin.

10.6 Spin-orbit Interaction

In considering the electrons in an atom with large atomic number, the relativistic correction will be required. The most important term can be the spin-orbit interaction. By following the procedures we demonstrated in our earlier discussions, the term written below can be added after the second quantization: [204]

---

[204]

$$
\begin{aligned}
H_{SO} &= C\int d^3r \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r})\frac{1}{r}\frac{\partial V}{\partial r}\vec{s}_{\sigma\sigma'}\cdot\vec{\ell}\,\psi_{\sigma'}(\vec{r}), \quad C=\frac{\hbar}{4m^2c^2} \\
&= C\sum_{nl}\sum_{n'l'}\int dr\, r^2\phi^*_{nl}(r)\frac{1}{r}\frac{\partial V}{\partial r}\phi_{n'l'}(r) \longrightarrow \xi(nl,n'l') \\
&\times \sum_{\sigma\sigma'}\sum_{\mu\mu'}\chi^*_\mu(\sigma)\vec{s}_{\sigma\sigma'}\chi_{\mu'}(\sigma)\cdot\int d\Omega Y^*_{lm}(\Omega)\,\vec{\ell}\,Y_{l'm'}(\Omega)c^\dagger_{nlm\mu}c_{n'l'm'\mu'} \\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m \\
&\times\Bigg[\frac{1}{2}\Bigg\{\langle\chi_\uparrow|s_+|\chi_\downarrow\rangle\int d\Omega Y^*_{lm-1}(\Omega)\,\ell_-\,Y_{lm}(\Omega)c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow} \\
&\qquad + \langle\chi_\downarrow|s_-|\chi_\uparrow\rangle\int d\Omega Y^*_{lm+1}(\Omega)\,\ell_-\,Y_{lm}(\Omega)c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow}\Bigg\} \\
&\qquad + \sum_\mu\langle\chi_\mu|s_z|\chi_\mu\rangle\int d\Omega Y^*_{lm}(\Omega)\,\ell_z\,Y_{lm}(\Omega)c^\dagger_{nlm\mu}c_{n'lm\mu}\Bigg] \\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m\frac{\hbar^2}{2}\Bigg\{\sqrt{(l+m)(l-m+1)}c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow}+\sqrt{(l-m)(l+m+1)}c^\dagger_{nlm+1\uparrow}c_{n'lm\downarrow} \\
&\qquad + m(c^\dagger_{nlm\uparrow}c_{n'lm\uparrow}-c^\dagger_{nlm\downarrow}c_{n'lm\downarrow})\Bigg\}
\end{aligned}
$$

$$
\begin{aligned}
H_{SO} &= C\int d^3r \sum_{\sigma\sigma'} \psi_\sigma^\dagger(\vec{r})\frac{1}{r}\frac{\partial V}{\partial r}\vec{s}_{\sigma\sigma'}\cdot\vec{\ell}\,\psi_{\sigma'}(\vec{r}), \quad C=\frac{\hbar}{4m^2c^2} \\
&= C\sum_{nl}\sum_{n'l'}\int dr\, r^2\phi_{nl}^*(r)\frac{1}{r}\frac{\partial V}{\partial r}\phi_{n'l'}(r) \longrightarrow \xi(nl,n'l') \\
&\times \sum_{\sigma\sigma'}\sum_{\mu\mu'}\chi_\mu^*(\sigma)\vec{s}_{\sigma\sigma'}\chi_{\mu'}(\sigma)\cdot\int d\Omega Y_{lm}^*(\Omega)\,\vec{\ell}\,Y_{l'm'}(\Omega)c_{nlm\mu}^\dagger c_{n'l'm'\mu'} \\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m\sum_{\mu\mu'}\langle Y_{lm}\chi_\mu|\,(\vec{s}\cdot\vec{\ell})\,|Y_{lm'}\chi_{\mu'}\rangle\, c_{nlm\mu}^\dagger c_{n'lm'\mu'}
\end{aligned}
$$

As far as the effect of the term described above is concerned with only to the discussion of the multiplet; i.e., the eigenstate of L and S, an effective addition of the term to the Hamiltonian is known to be able to bring such discussion:

$$H_{SO}^{eff} = A\vec{S}\cdot\vec{L}$$

Having confirmed with the fact above, we can easily understand that the application of the term no longer allows to conserve the spin and the orbital angular momentum; however,

$$
\begin{aligned}
H_{SO}^{eff} &= A\frac{1}{2}(\vec{J}^2-\vec{S}^2-\vec{L}^2) \\
\vec{J} &= \vec{S}+\vec{L}
\end{aligned}
$$

which indicates that the composition of the spin and the orbital angular momentum $\vec{J}$ is in fact the conserved quantity:

$$
\begin{aligned}
\vec{J}^2 &= J(J+1) \\
J &= |L-S|, |L-S|+1, \cdots, L+S
\end{aligned}
$$

Therefore, the degenerating levels other than ^1S in the multiplet, which we discussed in the last subsection, are considered to further split due to the spin-orbit interaction. The structure of further splitting of the multiplet is called the *fine structure*. This fine structure can be given by

$$E_{SO}^J = A\frac{1}{2}\big[J(J+1)-L(L+1)-S(S+1)\big]$$

The interval among the levels,

$$\Delta E_{SO}^J = E_{SO}^J - E_{SO}^{J-1} = AJ$$

is proportional to J within one multiplet term. This is known as the *Lande* **'***s interval rule.* [205]

Equivalence of H_{SO} and H_{SO}^{eff}

Let us first define:

$$H_{am} = \int d\tau\, \psi^\dagger(\tau)\xi(r)s_a\ell_m\psi(\tau), \quad a, m = x, y, z$$
$$H_{SO} = H_{xx} + H_{yy} + H_{zz}$$

According to $[s_a, s_b] = i\hbar\epsilon_{abc}s_c$, we can write

$$[S_a, H_{bm}] = \int d\tau\, \psi^\dagger(\tau)\xi(r)[s_a, s_b]\ell_m\psi(\tau) = i\hbar\epsilon_{abc}H_{cm}$$

for $\vec{S} = \int d\tau\psi(\tau)\vec{s}\psi(\tau)$

This yields $H_{\pm m} = H_{xm} \pm iH_{ym}$ so that

$$(H_{xm}, H_{ym}, H_{zm})$$

becomes the irreducible vector operator for S. In the same manner,

$$(H_{ax}, H_{ay}, H_{az})$$

becomes the irreducible vector operator for L.

Now, suppose

$$(T_x, T_y, T_z)$$

satisfies

$$[J_\alpha, T_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}T_\gamma$$

for an angular momentum operator $\vec{J}$. In such case,

$$(T_x, T_y, T_z)$$

[205] We first considered the multiplet splitting caused by the Coulomb interaction before we consider the fine structures given by the spin-orbit interaction. This we call the R-S coupling. Intrinsically, for the atoms with larger atomic numbers, only the J becomes the conserved quantity. The direct treatment of the levels organized by J is called the J-J coupling.

is regarded as irreducible vector operator of J. [206]

The commutation relations for non-zero can be:

$$[J_z, T_\pm] = \pm\hbar T_\pm$$
$$[J_+, T_-] = 2\hbar T_z$$
$$[J_-, T_+] = -2\hbar T_z$$

For the eigenfunction $|jm\rangle$ of J^2 and J_z, it is written as

$$\begin{aligned}\langle jm|[J_z, T_\pm]|jm'\rangle =& \pm\,\hbar\langle jm|T_\pm|jm'\rangle \\ =&\hbar(m-m')\langle jm|T_\pm|jm'\rangle\end{aligned}$$

So that we can write

$$\langle jm|T_\pm|jm'\rangle \neq 0, \qquad m-m'=\pm 1$$

Moreover,

$$\begin{aligned}J_+|jm\rangle =& \hbar\sqrt{(j-m)(j+m+1)}|jm+1\rangle \\ J_-|jm\rangle =& \hbar\sqrt{(j+m)(j-m+1)}|jm-1\rangle\end{aligned}$$

gives

$$0 = \langle jm|[J_-, T_-]|jm'\rangle$$
$$= \hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|T_-|jm'\rangle - \hbar\sqrt{(j+m')(j-m'+1)}\langle jm|T_-|jm'-1\rangle$$

On the one hand, we have $m' = m+2$ so, we can write in the form:

$$\sqrt{(j-m)(j+m+1)}\langle jm+1|T_-|jm+2\rangle = \sqrt{(j+m+2)(j-m-1)}\langle jm|T_-|jm+1\rangle$$
$$\frac{\langle jm+1|T_-|jm+2\rangle}{\sqrt{(j+m+2)(j-m-1)}} = \frac{\langle jm|T_-|jm+1\rangle}{\sqrt{(j+m+1)(j-m)}} = independentof\text{m}$$

206

$$\begin{aligned}[J_a, T_a] =& 0 \\ [J_z, T_x] =& i\hbar T_y \\ [J_z, T_y] =& -i\hbar T_x \text{より}\end{aligned}$$
$$\begin{aligned}[J_z, T_\pm] &= \pm\hbar T_\pm \\ [J_+, T_+] &= (i[J_x, T_y] + i[J_y, T_x]) = 0 \\ [J_+, T_-] &= (-i[J_x, T_y] + i[J_y, T_x]) = 2\hbar T_z \\ [J_-, T_+] &= (i[J_x, T_y] - i[J_y, T_x]) = -2\hbar T_z \\ [J_-, T_-] &= (-i[J_x, T_y] - i[J_y, T_x]) = 0\end{aligned}$$

Now,

$$\langle jm|J_-|jm+1\rangle = \sqrt{(j-m)(j+m+1)}\hbar$$

gives

$$\langle jm|T_-|jm+1\rangle = c_-\langle jm|J_-|jm+1\rangle$$

Thus, we can write as

$$0 = \langle jm|[J_+, T_+]|jm'\rangle$$
$$= \hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|T_+|jm'\rangle - \hbar\sqrt{(j-m')(j+m'+1)}\langle jm|T_+|jm'+1\rangle$$

For $m' = m-2$, on the other hand, we can write as

$$\sqrt{(j+m)(j-m+1)}\langle jm-1|T_+|jm-2\rangle = \sqrt{(j-m+2)(j+m-1)}\langle jm|T_+|jm-1\rangle$$
$$\frac{\langle jm-1|T_+|jm-2\rangle}{\sqrt{(j-m+2)(j+m-1)}} = \frac{\langle jm|T_+|jm-1\rangle}{\sqrt{(j+m)(j-m+1)}} = independentofm$$

Now,

$$\langle jm|J_+|jm-1\rangle = \sqrt{(j-m+1)(j+m)}\hbar$$

gives

$$\langle jm|T_+|jm-1\rangle = c_+\langle jm|J_+|jm-1\rangle$$

and gives

$$0 = \langle jm|[J_z, T_z]|jm'\rangle = \hbar(m-m')\langle jm|T_z|jm'\rangle$$
$$\langle jm|T_z|jm'\rangle \neq 0, \quad m = m'$$

Further, we can write

$$\begin{aligned}
0 =& \langle jm|[J_+, T_-]|jm\rangle = 2\hbar\langle jm|T_z|jm\rangle \\
=& \hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|T_-|jm\rangle - \hbar\sqrt{(j-m)(j+m+1)}\langle jm|T_-|jm+1\rangle \\
=& c_-\hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|J_-|jm\rangle - \hbar\sqrt{(j-m)(j+m+1)}\langle jm|J_-|jm+1\rangle \\
=& c_- 2\hbar\langle jm|J_z|jm\rangle
\end{aligned}$$

This gives

$$\langle jm|T_z|jm\rangle = c_-\langle jm|J_z|jm\rangle$$

Finally,

$$
\begin{aligned}
0 =&\langle jm|[J_-, T_+]|jm\rangle = -2\hbar\langle jm|T_z|jm\rangle \\
=&\hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|T_+|jm\rangle - \hbar\sqrt{(j+m)(j-m+1)}\langle jm|T_+|jm-1\rangle \\
=&c_+\hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|J_+|jm\rangle - \hbar\sqrt{(j+m)(j-m+1)}\langle jm|J_+|jm-1\rangle \\
=&c_+ 2\hbar\langle jm|J_z|jm\rangle
\end{aligned}
$$

which is yielding

$$
\langle jm|T_z|jm\rangle = c_+\langle jm|J_z|jm\rangle
$$

That is

$$
c_- = c_+
$$

Thus, we can define the reduction of the matrix element $\langle j||T||j\rangle$ which does not depend on m or

$$
\begin{aligned}
\langle jm|\vec{T}|jm'\rangle =& c\langle jm|\vec{J}|jm'\rangle \\
c \equiv& \frac{\langle j||T||j\rangle}{\sqrt{j(j+1)(2j+1)}}
\end{aligned}
$$

We can rewrite the above as

$$
\begin{aligned}
\langle LSM_LM_S|H_{SO}|LSM_LM_S\rangle =& c\langle LSM_LM_S|\vec{L}\cdot\vec{S}|LSM_LM_S\rangle \\
c =& \frac{\langle LS||H_{SO}||LS\rangle}{\sqrt{L(L+1)(2L+1)S(S+1)(2S+1)}}
\end{aligned}
$$

To provide a concrete example of the above, let us suppose d^n where $(n \le 5)$, the ground state should have the maximum multiplicity spin according to the Hund ’ s rule:

$$
{}^SL, \quad S = \frac{n}{2}
$$

This also gives the greatest value for the orbital angular momentum:

$$
L = 3n - (1 + 2 + \cdots + n) = 3n - \frac{n(n+1)}{2} = \frac{5n - n^2}{2} = \frac{(5-n)n}{2}
$$

The states for $M_S = S$ and $M_L = L$:

$$
|M_S = S, M_L = L\rangle = c^\dagger_{3-1\uparrow}c^\dagger_{3-2\uparrow}\cdots c^\dagger_{3-n\uparrow}|0\rangle
$$

The above is used to calculate both sides of the equation:

$$\zeta_d \hbar^2 \frac{1}{2} L = cSL$$
$$c = \hbar^2 \frac{\zeta_d}{2S}$$
$$\zeta_d = \int dr\, r^2 |\phi_{nl=2}(r)|^2 > 0$$

Under $n \geq 6$, we may write

$$S = \frac{10-n}{2}$$
$$L = -\{3(10-n) - (1+2+\cdots+(10-n)\}$$
$$= -3(10-n) + \frac{(10-n)(11-n)}{2} = \frac{(10-n)(n-5)}{2}$$

The state can be determined as

$$|M_S = S, M_L = L\rangle = c^\dagger_{2\uparrow} c^\dagger_{1\uparrow} c^\dagger_{0\uparrow} c^\dagger_{-1\uparrow} c^\dagger_{-2\uparrow} c^\dagger_{3-1\downarrow} c^\dagger_{3-2\downarrow} \cdots c^\dagger_{3-(n-5)\downarrow} |0\rangle$$

with which we calculate the both sides of the equation:

$$\zeta_d \hbar^2 (-) \frac{1}{2} (2+1+\cdots+(3-(n-5))) = \zeta_d \hbar^2 (-) \frac{(10-n)(n-5)}{2} = cSLThus,$$
$$c = -\hbar^2 \frac{\zeta_d}{2S}$$

Where $c > 0$, $d^{1,2,3,4,5}$ is considered to be in the normal position while $d^{6,7,8,9}$ is considered to be in the inverse position under $c < 0$. We have $c = 0$ for d^0 and d^{10}.

PartV

Interaction of Light and Matter

11 Classical Electromagnetic Field

In this section, we discuss the classical electromagnetic field that obeys the Maxwell 's equation to help us understand the quantum phenomena associated with light.

11.1 Maxwell 's Equation

To begin, let us consider a case with a particle in vacuum, which carries an electric charge e_i, and can be found in the coordinates $\vec{r}_i$. The Maxwell 's model for $i = 1, \cdots, N$ becomes

$$\begin{aligned} \mathrm{rot}\,\vec{E} + \frac{\partial \vec{B}}{\partial \vec{t}} &= 0 \\ \mathrm{rot}\,\vec{H} - \frac{\partial \vec{D}}{\partial t} &= \vec{j} \\ \mathrm{div}\,\vec{D} &= \rho \\ \mathrm{div}\,\vec{B} &= 0 \end{aligned}$$

The vacuum permittivity and permeability are used to write in the form:

$$\begin{aligned} \vec{D} &= \epsilon_0 \vec{E} \\ \vec{H} &= \frac{1}{\mu_0} \vec{B} \end{aligned}$$

For the charge density and the current density, the coordinates of the particle is used and they are written as:

$$\begin{aligned} \rho(\vec{r}) &= \sum_{i=1}^{N} e_i \delta(\vec{r} - \vec{r}_i) \\ \vec{j}(\vec{r}) &= \sum_{i=1}^{N} e_i \dot{\vec{r}}_i \delta(\vec{r} - \vec{r}_i) \end{aligned}$$

Note that the equations satisfy the conservation of electric charge: [207]

$$\frac{\partial\rho}{\partial t} + \operatorname{div}\vec{j} = 0$$

As for another fundamental equation to this system, we consider an equation of motion for a particle in $\vec{r}_i$ that obeys the Lorentz force. Here, we let m_i be the particle mass:

$$m_i\ddot{\vec{r}}_i = e_i\vec{E}(\vec{r}_i) + e_i\dot{\vec{r}}_i \times \vec{B}(\vec{r}_i)$$

The time resolution for the particle 's kinetic energy T is expressed by [208]

$$\dot{T} = \int dV \vec{E}\cdot\vec{j}$$

Here we assume V to be an arbitrary region that includes $\vec{r}_i$. The Maxwell 's

---

207

$$\begin{aligned}\frac{\partial\rho}{\partial t} &= \sum_i e_i \frac{\partial}{\partial t}\delta(\vec{r}-\vec{r}_i(t)) \\ &= \sum_i e_i\dot{\vec{r}}_i\cdot\vec{\nabla}_{r_i}\delta(\vec{r}-\vec{r}_i(t)) \\ &= \sum_i e_i\dot{\vec{r}}_i\cdot(-1)\vec{\nabla}_r\delta(\vec{r}-\vec{r}_i(t))\end{aligned}$$

Further,

$$\operatorname{div}\vec{j} = \sum_i e_i\dot{\vec{r}}_i\cdot\vec{\nabla}_r\delta(\vec{r}-\vec{r}_i(t))$$

208

$$\begin{aligned}\frac{d}{dt}\sum_i\frac{1}{2}m_i\dot{\vec{r}}_i^2 &= \sum_i m_i\dot{\vec{r}}_i\cdot\ddot{\vec{r}}_i = \sum_i e_i\dot{\vec{r}}_i\cdot(\vec{E}_i + \dot{\vec{r}}_i\times\vec{B}_i) \\ &= \sum_i e_i\dot{\vec{r}}_i\cdot\vec{E}_i = \int dV\vec{E}\cdot\vec{j} \\ & \quad E_i = E(\vec{r}_i), \quad B_i = B(\vec{r}_i)\end{aligned}$$

equation provides [209]

$$\begin{aligned}\vec{P} &= \vec{E}\times\vec{H}\\ E_{em} &= \int dV\mathcal{E}_{em}\\ \mathcal{E}_{em} &= \frac{1}{2}(\epsilon_0\vec{E}^2+\mu_0\vec{H}^2)\end{aligned}$$

Hence,

$$\frac{d}{dt}(T+E_{em})+\int_{\partial V}d\vec{S}\cdot\vec{P}=0$$

We understand that P denotes the momentum of the electromagnetic field while E_{em} denotes the energy of the electromagnetic field. (P is known as the Poynting vector.)

11.2 The Vector Potential and Scalar Potential

First, note $\mathrm{div}\,\vec{B}=0$ can give
[210]

[209]Maxwell 's equation can give

$$\begin{aligned}\vec{H}\cdot\mathrm{rot}\,\vec{E}+\mu_0\vec{H}\cdot\dot{\vec{H}} &= 0\\ \vec{E}\cdot\mathrm{rot}\,\vec{H}-\epsilon_0\vec{E}\cdot\dot{\vec{E}} &= \vec{E}\cdot\vec{j}\end{aligned}$$

We take the difference between the equations above:

$$-\mathrm{div}\,(\vec{E}\times\vec{H})-\frac{1}{2}\frac{d}{dt}(\epsilon_0\vec{E}^2+\mu_0\vec{H}^2)=\vec{E}\cdot\vec{j}$$

$$\mathrm{div}\,\vec{P}+\frac{d\mathcal{H}_{em}}{dt}+\vec{E}\cdot\vec{j}=0$$

Thus,

$$\begin{aligned}\mathrm{div}\,(\vec{A}\times\vec{B}) &= \partial_i\epsilon_{ijk}A_jB_k\\ &= \epsilon_{ijk}(\partial_iA_j)B_k+\epsilon_{ijk}A_j(\partial_i)B_k\\ &= \epsilon_{kij}(\partial_iA_j)B_k-\epsilon_{jik}A_j(\partial_i)B_k\\ &= \mathrm{rot}\,\vec{A}\cdot\vec{B}-\vec{A}\cdot\mathrm{rot}\,\vec{B}\end{aligned}$$

[210]An arbitrary vector field $\vec{X}$ can be expressed by

$$\begin{aligned}\vec{X}=\vec{X}_T+\vec{X}_L\\ \mathrm{div}\,\vec{X}_T=0\\ \mathrm{rot}\,\vec{X}_L=0\end{aligned}$$

Note that $\vec{X}_L$ and $\vec{X}_T$ are respectively called the longitudinal and transverse components. When the vector field described above is definable in all region of space, we may express the field by the potential:

$$\begin{aligned}\vec{X}_T &= \operatorname{rot}\vec{A} \\ \vec{X}_L &= \operatorname{grad}\phi\end{aligned}$$

[211] [212]

$$\vec{B} = \mathrm{rot}\,\vec{A}$$

[211]The Fourier expansion for the arbitrary field is written as

$$\vec{X}(\vec{r}) = \sum_{\vec{k}} X_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

which yields

$$\begin{aligned} \mathrm{div}\,X &= \sum_{\vec{k}} i\vec{k}\cdot\vec{X}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \\ \mathrm{rot}\,X &= \sum_{\vec{k}} i\vec{k}\times\vec{X}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \end{aligned}$$

Now, let us write down the orthonormalization of the right-handed system for

$$\vec{e}_{\vec{k}\sigma=0} = \frac{\vec{k}}{k}, \quad \vec{e}_{\vec{k}\sigma=1}, \quad \vec{e}_{\vec{k}\sigma=2}$$

we obtain

$$\begin{aligned} \vec{X}_L &= \sum_{\vec{k}} (\vec{X}_{\vec{k}}\cdot\vec{e}_{\vec{k},0})\vec{e}_{\vec{k},0} e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}} \frac{(\vec{X}_{\vec{k}}\cdot\vec{k})\vec{k}}{k^2} e^{i\vec{k}\cdot\vec{r}} \\ (\vec{X}_L)_\alpha &= \sum_{\vec{k}} \frac{k_\alpha k_\beta}{k^2} X_\beta e^{i\vec{k}\cdot\vec{r}} \\ \vec{X}_T &= \sum_{\vec{k}} \sum_{\sigma=1,2} (\vec{X}_{\vec{k}}\cdot\vec{e}_{\vec{k}\sigma})\vec{e}_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}} \left(\vec{X}_{\vec{k}} - \frac{(\vec{X}_{\vec{k}}\cdot\vec{k})\vec{k}}{k^2}\right) e^{i\vec{k}\cdot\vec{r}} \\ (\vec{X}_T)_\alpha &= \sum_{\vec{k}} (\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}) X_\beta e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}} (\sum_{\sigma=1,2} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta) X_\beta e^{i\vec{k}\cdot\vec{r}} \end{aligned}$$

Conditions for the complete system give

$$\sum_{\sigma} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta = \frac{k_\alpha k_\beta}{k^2} + \sum_{\sigma=1,2} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta = \delta_{\alpha\beta}$$

such that we write

$$\sum_{\sigma=1,2} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta = \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}$$

This is valid since

$$\begin{aligned} \vec{v} &= (\vec{v}\cdot\vec{e}_\sigma)\vec{e}_\sigma \\ v_\alpha &= v_\beta (\vec{e}_\sigma)_\beta (\vec{e}_\sigma)_\alpha \end{aligned}$$

is written for the arbitrary vector $\vec{v}$. We can further write the above as

$$(\vec{e}_\sigma)_\beta (\vec{e}_\sigma)_\alpha = \delta_{\alpha\beta}$$

A similar formula to the expansion of the function is given as

$$\sum_j \psi_j^*(x)\psi_j(x') = \delta(x - x')$$

Thus,

$$\mathrm{rot}\left(\vec{E}+\frac{\partial\vec{A}}{\partial t}\right)=0$$

Rewrite the equation above of the physical quantity:

$$\vec{E}=-\frac{\partial\vec{A}}{\partial t}-\vec{\nabla}\phi$$

---

[212]Let us summarize the relationship between differential-form and the vector calculus formulas:

$$\begin{aligned}
\Omega_0 &= f \\
d\Omega_0 &= \partial_i f\ dx_i \quad :\mathrm{grad}\, f \\
d^2\Omega_0 &= \partial_j\partial_i f\ dx_j\wedge dx_i=0 \quad :\mathrm{rot}\,\mathrm{grad}\, f=0 \\
\Omega_1 &= A_i dx_i \quad :\vec{A} \\
d\Omega_1 &= \partial_j A_i\ dx_j\wedge dx_i \quad :\mathrm{rot}\,\vec{A} \\
d^2\Omega_1 &= \partial_k\partial_j A_i\ dx_k\wedge dx_j\wedge dx_i=0 \quad :\mathrm{div}\,\mathrm{rot}\,\vec{A}=0 \\
\Omega_2 &= A_i * dx_i=\epsilon_{ijk}A_i dx_j\wedge dx_k \quad :\vec{A} \\
d\Omega_2 &= \partial_\ell A_i dx_\ell * dx_i=\partial_i A_i\ dx_1\wedge dx_2\wedge dx_3 \quad :\mathrm{div}\,\vec{A} \\
d^2\Omega_2 &= 0
\end{aligned}$$

Here we define

$$\begin{aligned}
*1 &= dx_1\wedge dx_2\wedge dx_3 \\
*dx_1 &= dx_2\wedge dx_3,\ *dx_2=dx_3\wedge dx_1,\ *dx_3=dx_1\wedge dx_2, \\
*(dx_1\wedge dx_2) &= dx_3,\quad *(dx_2\wedge dx_3)=dx_1,\quad *(dx_3\wedge dx_1)=dx_2, \\
*(dx_1\wedge dx_2\wedge dx_3) &= 1
\end{aligned}$$

giving

$$\begin{aligned}
A &= A_i dx_i \\
*dA &= \mathrm{rot}\, A=(\mathrm{rot}\, A)_i dx_i \\
*d*A &= \mathrm{div}\, A \\
d\phi &= \mathrm{grad}\,\phi=\nabla\phi \\
*d*d\phi &= \Delta\phi
\end{aligned}$$

$$\begin{aligned}
\mathrm{div}\,\mathrm{rot}\,\vec{A} &= *d*(*dA)=d(dA)=0 \\
\mathrm{rot}\,\mathrm{grad}\, f &= *d(df)=0
\end{aligned}$$

For the integral formula, we can write

$$\begin{aligned}
\int_V d\Omega_2 &= \int_{\partial V}\Omega_2 \quad : \quad \int_V \mathrm{div}\,\vec{A}\, dV=\int_{\partial V}\vec{A}\cdot d\vec{S} \\
\int_S d\Omega_1 &= \int_{\partial S}\Omega_1 \quad : \quad \int_S \mathrm{rot}\,\vec{A}\cdot d\vec{S}=\int_{\partial S}\vec{A}\cdot d\vec{r} \\
\int_L d\Omega_0 &= \int_{\partial L}\Omega_0 \quad : \quad \int_L \mathrm{grad}\, f\cdot d\vec{r}=f(\vec{r})\Big|_{\vec{r}=\vec{r}_{ini}}^{\vec{r}=\vec{r}_{fin}}
\end{aligned}$$

by using the vector potential $\vec{A}$ and the scalar potential ϕ.

Note that the physical quantities $\vec{E}$ and $\vec{B}$ stay constant even though the gauge transformation is conducted under the arbitrary space-time equation $\chi(\vec{r}, t)$:

$$\begin{aligned} \vec{A} &\rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\chi \\ \phi &\rightarrow \phi' = \phi - \frac{\partial \chi}{\partial t} \end{aligned}$$

$$\vec{E}' = \vec{E}, \quad \vec{B}' = \vec{B}$$

We must note that there are certain degrees of freedom left in the potential expression. The Maxwell 's equation is rewritten by using such potential. rot $\vec{H} - \dot{\vec{D}} = \vec{j}$ gives [213]

$$\begin{aligned} -\Box \vec{A} &\equiv \frac{1}{c^2}\ddot{\vec{A}} - \Delta \vec{A} = -\vec{\nabla}(\mathrm{div}\, \vec{A} + \frac{1}{c^2}\dot{\phi}) + \mu_0 \vec{j} \\ c^2 &= \frac{1}{\epsilon_0 \mu_0} \end{aligned}$$

While div $\vec{D} = \rho$ gives

$$-\Delta\phi = \mathrm{div}\, \dot{\vec{A}} + \frac{1}{\epsilon_0}\rho$$

Let us have a particular Coulomb gauge

$$\mathrm{div}\, \vec{A} = 0$$

and by which we obtain two relational expressions of the Maxwell 's equation:

$$\begin{aligned} -\Box \vec{A} &= = \mu_0 \vec{J} \\ -\Delta\phi &= \frac{1}{\epsilon_0}\rho \end{aligned}$$

Note that the equation for the scalar potential

$$\vec{J} = \vec{j} - \epsilon_0 \vec{\nabla}\dot{\phi}$$

can be easily integrated: [214]

$$\phi(\vec{r}) = \frac{1}{4\pi\epsilon_0}\sum_i \frac{e_i}{|\vec{r} - \vec{r}_i|}$$

[213]The equation $\frac{1}{\mu_0}\mathrm{rot}\,\mathrm{rot}\,\vec{A} - \epsilon_0(-\ddot{\vec{A}} - \vec{\nabla}\dot{\phi}) = \vec{j}$ gives $\vec{\nabla}\mathrm{div}\,\vec{A} - \Delta\vec{A} + \frac{1}{c^2}\left(\ddot{\vec{A}} + \nabla\dot{\phi}\right) = \mu_0\vec{j}$

[214]The solution for

$$-\Delta f(\vec{r}) = \delta(\vec{r})$$

is

$$f(\vec{r}) = \frac{1}{4\pi r}$$

Hence, we can further rewrite the first equation into the form:

$$\vec{J} = \sum_i \left(-\frac{\partial}{\partial t} \vec{\nabla} \frac{e_i}{4\pi|\vec{r} - \vec{r}_i|} + e_i \dot{\vec{r}}_i \delta(\vec{r} - \vec{r}_i) \right)$$

Note that [215]

$$\operatorname{div} \vec{J} = 0$$

Let us now suppose that the system is in a box with the volume V and the edge length of L. We conduct the Fourier transformation of A under the periodic boundary condition:

[216]

$$\begin{aligned} \vec{A} &= \frac{1}{\sqrt{V}} \sum_{\vec{k}} \vec{A}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \\ \vec{k} &= \frac{2\pi}{L}(n_x, n_y, n_z), \quad n_i = \cdots, -2, -1, 0, 1, 2, \cdots \end{aligned}$$

The vector potential can be written in the following form by using $\vec{k} \cdot \vec{A}_{\vec{k}} = 0$ which is given by $\operatorname{div} \vec{A} = 0$:

[217]

$$\hat{k} \cdot \vec{e}_{k\sigma=1} = 0, \hat{k} \cdot \vec{e}_{k\sigma=2} = 0, \quad \vec{e}_{k1} \cdot \vec{e}_{k2} = 0$$

giving

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}} \sum_{\sigma=1,2} \vec{e}_{\vec{k}\sigma} q_{\vec{k}\sigma}(t) e^{i\vec{k}\cdot\vec{r}}$$

We can use the fact that A is being real to express $\vec{e}_{-\vec{k}\sigma} = \vec{e}_{\vec{k}\sigma}$. This allows us to use $\vec{A}_{-\vec{k}} = \vec{A}^*_{\vec{k}}$. Therefore,

$$q^*_{\vec{k}\sigma}(t) = q_{-\vec{k}\sigma}(t)$$

In the same way, we can write

$$\phi(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \phi_{\vec{k}}(t) e^{i\vec{k}\cdot\vec{r}}$$

215

$$\operatorname{div} \vec{J} = -\frac{\partial}{\partial t} \epsilon_0 \Delta\phi + \operatorname{div} \vec{j} = \frac{\partial}{\partial t} \rho + \operatorname{div} \vec{j} = 0$$

216

$$A_{\vec{k}} = \frac{1}{\sqrt{V}} \int dV \vec{A}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}}$$

217

$$\vec{A}_{\vec{k}} = \frac{1}{\sqrt{\epsilon_0}} \sum_{\sigma=1,2} \vec{e}_{\vec{k}\sigma} q_{\vec{k}\sigma}(t)$$

$$\vec{j}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \vec{j}_{\vec{k}}(t) e^{i\vec{k}\cdot\vec{r}}$$

Given the information above, we now move on to discuss $\Box \vec{A} = \mu_0 \vec{J}$. The longitudinal components (components in $\vec{k}$ direction) can be expressed by using div $\vec{A} = 0$:

$$\epsilon_0 i k^2 \dot{\phi}_{\vec{k}} \quad - \quad \vec{k} \cdot \vec{j}_{\vec{k}} = 0$$

By time-differentiating the Poisson 's equation, and further using the continuity equation, we write:

$$\epsilon_0 \Delta \dot{\phi} = -\dot{\rho} = \nabla_r \cdot \vec{j}$$

And from which, the Fourier components are written as $-k^2 \dot{\phi}_k = i\vec{k} \cdot \vec{j}_{\vec{k}}$ and therefore, the relational expression for the longitudinal components is automatically satisfied. Now, for the transverse components:
[218]

$$\begin{aligned} \ddot{q}_{\vec{k}\sigma} + \omega_{\vec{k}}^2 q_{\vec{k}\sigma} &= \frac{1}{\sqrt{\epsilon_0 V}} \vec{e}_{\vec{k}\sigma} \cdot \int dV \vec{j}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} \\ &= \frac{1}{\sqrt{\epsilon_0 V}} \sum_i e_i \, (\vec{e}_{\vec{k}\sigma} \cdot \dot{\vec{r}}_i) e^{-i\vec{k}\cdot\vec{r}_i} \qquad (\omega = ck) \end{aligned}$$

This is the equation the vector potential must satisfy, and which is in fact equivalent to the Maxwell 's equation. The equation describes the forced oscillation for each polarized light $\vec{e}_{\vec{k}\sigma}$.

---

[218]

$$\begin{aligned} \vec{e}_{\vec{k}\sigma} \cdot \Big(-\Box \vec{A}(\vec{r}) \Big) &= \vec{e}_{\vec{k}\sigma} \cdot \frac{1}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}} \sum_{\sigma=1,2} \vec{e}_{\vec{k}\sigma} \big(\frac{1}{c^2} \ddot{q}_{\vec{k}\sigma} + k^2 q_{\vec{k}\sigma} \big) e^{i\vec{k}\cdot\vec{r}} = \frac{1}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}} \big(\frac{1}{c^2} \ddot{q}_{\vec{k}\sigma} + k^2 q_{\vec{k}\sigma} \big) e^{i\vec{k}\cdot\vec{r}} \\ \vec{e}_{\vec{k}\sigma} \cdot \mu_0 \vec{J}(\vec{r}) &= \vec{e}_{\vec{k}\sigma} \cdot \vec{j}(\vec{r}) = \mu_0 \frac{1}{\sqrt{V}} \, \vec{e}_{\vec{k}\sigma} \cdot \sum_{\vec{k}} \vec{j}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \end{aligned}$$

Thus,

$$\frac{1}{c^2} \ddot{q}_{\vec{k}\sigma} + k^2 q_{\vec{k}\sigma} \quad = \quad \mu_0 \sqrt{\epsilon_0} \vec{e}_{\vec{k}\sigma} \vec{j}_{\vec{k}} = \frac{\mu_0 \sqrt{\epsilon_0}}{\sqrt{V}} \int dV \vec{e}_{\vec{k}\sigma} \vec{j}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}}$$

11.3 Classical Field Equations

First, we consider the energy of the electromagnetic field by dividing it into two parts: [219] [220]

$$
\begin{aligned}
E_{em} &= \frac{1}{2}\int dV\left(\epsilon_0(\dot{\vec{A}}+\vec{\nabla}\phi)^2+\frac{1}{\mu_0}(\mathrm{rot}\,\vec{A})^2\right) \\
&= E_{rad}+E_{coulomb} \\
E_{rad} &= \frac{1}{2}\int dV\left(\epsilon_0\dot{\vec{A}}^2+\frac{1}{\mu_0}(\mathrm{rot}\,\vec{A})^2\right) \\
E_{coulomb} &= \epsilon_0\frac{1}{2}\int dV\left(2\dot{\vec{A}}\vec{\nabla}\phi+\vec{\nabla}\phi\cdot\vec{\nabla}\phi\right) \\
&= -\epsilon_0\frac{1}{2}\int dV\left(2\phi\ \mathrm{div}\,\dot{\vec{A}}+\phi\Delta\phi\right) \\
&= \frac{1}{2}\int dV\ \rho\phi \\
&= \frac{1}{2}\sum_{ij}\frac{e_ie_j}{4\pi\epsilon_0|\vec{r}_i-\vec{r}_j|} \\
&= \sum_{i<j}\frac{e_ie_j}{4\pi\epsilon_0|\vec{r}_i-\vec{r}_j|}+(expansiontermsoftheself-interaction)
\end{aligned}
$$

Note that $E_{coulomb}$ is the Coulomb interaction (we do not consider the expansion terms of self-interaction here) while E_{rad} is the energy of radiation field. If we have

$$p_{\vec{k}\sigma}(t)=\dot{q}_{-\vec{k}\sigma}(t)$$

219

$$\int dV\mathrm{div}\,(f\vec{\nabla}g)=\int dV\vec{\nabla}f\cdot\vec{\nabla}g+\int dV f\Delta g=\int_{\partial V}d\vec{S}\cdot f\vec{\nabla}g$$

The boundary terms are cancelled due to the periodic boundary condition thus,

$$\int dV\vec{\nabla}f\cdot\vec{\nabla}g=-\int dV f\Delta g=-\int dV(\Delta f)g$$

220

$$\int \mathrm{div}\,(\phi\dot{\vec{A}})=\int_{\partial V}d\vec{S}\cdot\phi\dot{\vec{A}}=0$$

Thus,

$$\int dV\phi\mathrm{div}\,\dot{\vec{A}}=-\int dV\dot{\vec{A}}\cdot\vec{\nabla}\phi$$

then we can write

$$\vec{A}(\vec{r},t) = \frac{1}{\sqrt{\epsilon_0 V}}\sum_{\vec{k}}\sum_{\sigma=1,2}\vec{e}_{\vec{k}\sigma}q_{\vec{k}\sigma}(t)e^{i\vec{k}\cdot\vec{r}}$$
$$\dot{\vec{A}}(\vec{r},t) = \frac{1}{\sqrt{\epsilon_0 V}}\sum_{\vec{k}}\sum_{\sigma=1,2}\vec{e}_{\vec{k}\sigma}p_{\vec{k}\sigma}(t)e^{-i\vec{k}\cdot\vec{r}}$$

We substitute the above into E_{rad}: [221]

$$E_{rad} = \frac{1}{2}\sum_{\vec{k}}\sum_{\sigma=1,2}\left(p_{\vec{k}\sigma}p_{-\vec{k}\sigma} + c^2k^2 q_{\vec{k}\sigma}q_{-\vec{k}\sigma}\right)$$

By adding the kinetic energy $T = \frac{1}{2}\sum_i \ddot{\vec{r}}^2$, the classical energy is expressed in the form:

$$H = T + E_{rad} + E_{coulomb}$$

We let $q_{\vec{k}\sigma}, p_{\vec{k}\sigma}$, of radiation field and $\vec{r}_i$ of the particle system be the canonical variables, while we let whose conjugate momenta be

$$\vec{P}_i = m_i\dot{\vec{r}}_i + e_i\vec{A}(\vec{r}_i) = m_i\dot{\vec{r}}_i + e_i\vec{A}_i$$

The Hamiltonian is therefore given by:

$$\begin{aligned}
H &= H_{part} + H_{rad} + H_{coulomb}\\
H_{part} &= \sum_i \frac{1}{2m_i}(\vec{P}_i - e_i\vec{A}(\vec{r}_i))^2\\
&= \sum_i \frac{1}{2m_i}\left(\vec{P}_i - e_i\frac{1}{\sqrt{\epsilon_0 V}}\sum_{\vec{k}\sigma}\vec{e}_{\vec{k}\sigma}q_{\vec{k}\sigma}e^{i\vec{k}\cdot\vec{r}_i}\right)^2\\
H_{rad} &= +\frac{1}{2}\sum_{\vec{k}}\sum_{\sigma=1,2}\left(p_{\vec{k}\sigma}p_{-\vec{k}\sigma} + c^2k^2 q_{\vec{k}\sigma}q_{-\vec{k}\sigma}\right)\\
H_{coulomb} &= \sum_{i<j}\frac{e_ie_j}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}
\end{aligned}$$

---

[221] For the energy of a magnetic field:

$$\begin{aligned}
\mathrm{div}\,(\vec{A}\times\mathrm{rot}\,\vec{A}) &= \mathrm{rot}\,\vec{A}\cdot\mathrm{rot}\,\vec{A} - \vec{A}\cdot\mathrm{rot}\,\mathrm{rot}\,\vec{A}, \quad (\vec{\nabla}\cdot(\vec{A}\times\vec{B}) = \vec{\nabla}\times\vec{A}\cdot\vec{B} - \vec{A}\cdot\vec{\nabla}\times\vec{B})\\
&= \mathrm{rot}\,\vec{A}\cdot\mathrm{rot}\,\vec{A} - \vec{A}\cdot\mathrm{grad}\,\mathrm{div}\,A + \vec{A}\cdot\Delta\vec{A}
\end{aligned}$$

which cancels the surface terms thus using $\mathrm{div}\,\vec{A} = 0$, we can write

$$\int dV\,\mathrm{rot}\,\vec{A}\cdot\mathrm{rot}\,\vec{A} = -\int dV\,\vec{A}\cdot\Delta\vec{A}$$

The canonical equations are given by:

$$
\begin{aligned}
\frac{\partial H}{\partial q_{\vec{k}\sigma}} &= -\dot{p}_{\vec{k}\sigma} \\
\frac{\partial H}{\partial p_{\vec{k}\sigma}} &= \dot{q}_{\vec{k}\sigma} \\
\frac{\partial H}{\partial r^{\alpha}_{\vec{k}\sigma}} &= -\dot{P}^{\alpha}_{\vec{k}\sigma} \\
\frac{\partial H}{\partial P^{\alpha}_{\vec{k}\sigma}} &= \dot{r}^{\alpha}_{\vec{k}\sigma}
\end{aligned}
$$

Therefore, the equation of motion for the particles is written as [222]

$$m_i\ddot{\vec{r}}_i = e_i(\vec{E}(\vec{r}_i) + \dot{\vec{r}}_i \times B(\vec{r}_i))$$

The Maxwell 's equation is also written as

[222]For the particle system we can write

$$\begin{aligned}
\dot{r}_i^\alpha &= \frac{\partial H}{\partial P_i^\alpha} \\
&= \frac{1}{m_i}(P_i^\alpha - e_i A^\alpha(\vec{r}_i)) \\
-\dot{P}_i^\alpha &= \frac{\partial H}{\partial r_i^\alpha} \\
&= \frac{1}{m_i}(\vec{P}_i - e_i\vec{A}(\vec{r}_i)) \cdot (-e_i)\partial_\alpha \vec{A}(\vec{r}_i) + e_i\partial_\alpha\phi(\vec{r}_i) \\
&= -e_i\dot{r}_i^\beta\partial_\alpha A^\beta(\vec{r}_i) + e_i\partial_\alpha\phi(\vec{r}_i)
\end{aligned}$$

Here note:

$$\begin{aligned}
\frac{\partial}{\partial r_i^\alpha}H_{coulomb} &= \frac{\partial}{\partial r_i^\alpha}\frac{1}{4\pi\epsilon_0}\sum_{a<b}\frac{1}{|\vec{r}_a - \vec{r}_b|} \\
&= \frac{\partial}{\partial r_i^\alpha}\frac{1}{4\pi\epsilon_0}\sum_{j(\neq i)}\frac{1}{|\vec{r}_a - \vec{r}_b|} \\
&= \partial_\alpha e_i\phi(\vec{r}_i) = \partial_\alpha e_i\phi_i
\end{aligned}$$

$$\begin{aligned}
\vec{A}_i &= \vec{A}(\vec{r}_i) \\
\frac{d}{dt}\vec{A}_i &= \left.\frac{d\vec{A}(\vec{r})}{dt}\right|_{\vec{r}=\vec{r}_i} + \dot{\vec{r}_i}\cdot\vec{\nabla}_{\vec{r}_i}\vec{A}_i
\end{aligned}$$

Hence,

$$\begin{aligned}
m_i\ddot{r}_i^\alpha &= \dot{P}_i^\alpha - e_i\dot{A}_i^\alpha(\vec{r}_i) - e_i\,\dot{\vec{r}_i}\cdot\vec{\nabla}_i A_i^\alpha(\vec{r}_i) \\
&= e_i\dot{r}_i^\beta\partial_\alpha A^\beta(\vec{r}_i) - e_i\partial_\alpha\phi(\vec{r}_i) \\
&\quad -e_i\dot{A}_i^\alpha(\vec{r}_i) - e_i\dot{r}_i^\beta\partial_\beta A_i^\alpha(\vec{r}_i) \\
&= e_i\big(-\partial_\alpha\phi(\vec{r}_i) - \dot{A}_i^\alpha(\vec{r}_i) + \dot{r}_i^\beta\partial_\alpha A^\beta(\vec{r}_i) - \dot{r}_i^\beta\partial_\beta A_i^\alpha(\vec{r}_i)\big)
\end{aligned}$$

Further,

$$\begin{aligned}
(\dot{\vec{r}} \times \mathrm{rot}\,\vec{A})_\alpha &= \epsilon_{\alpha\beta\gamma}\dot{r}^\beta\epsilon_{\gamma\eta\xi}\partial_\eta A^\xi \\
&= (\delta_{\alpha\eta}\delta_{\beta\xi} - \delta_{\alpha\xi}\delta_{\beta\eta})\dot{r}^\beta\partial_\eta A^x i \\
&= \dot{r}^\beta\partial_\alpha A^\beta - \dot{r}^\beta\partial_\beta A^\alpha
\end{aligned}$$

Thus,

$$m_i\ddot{\vec{r}}_i = e_i(\vec{E}(\vec{r}_i) + \dot{\vec{r}}_i \times B(\vec{r}_i))$$

[223]

$$\ddot{q}_{-\vec{k}\sigma} + c^2k^2 q_{-\vec{k}\sigma} = \frac{1}{\sqrt{\epsilon_0 V}} \sum_i e_i(\dot{\vec{r}}_i \cdot \vec{e}_{\vec{k}\sigma}) e^{i\vec{k}\cdot\vec{r}_i}$$

Therefore, we must note that the velocity for a gauge invariant particle is

$$\dot{\vec{r}}_i = \frac{1}{m_i}\big(P_i - e_i\vec{A}(\vec{r}_i)\big)$$

Finally, we write the quantity by using the canonical variables:

$$\begin{aligned}
\vec{E} =& -\dot{\vec{A}} - \vec{\nabla}\phi \\
=& -\frac{1}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}\sigma} \vec{e}_{\vec{k}\sigma} p_{\vec{k}\sigma} e^{-i\vec{k}\cdot\vec{r}} - \vec{\nabla}\phi \\
\vec{B} =& \text{rot}\,\vec{A} \\
=& \frac{i}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}\sigma} \vec{k}\times\vec{e}_{\vec{k}\sigma} q_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}} b
\end{aligned}$$

11.4 Field Momentum

The momentum of the electromagnetic field $\vec{G}_{em}$ is calculated with the Poynting vectors as described in the followings:

[223] For the radiation field:

$$\begin{aligned}
-\dot{p}_{\vec{k}\sigma} &= \frac{\partial H}{\partial q_{\vec{k}\sigma}} \\
&= c^2k^2 q_{-\vec{k}\sigma} + \sum_i \frac{1}{m_i}\left(\vec{P}_i - e_i \frac{1}{\sqrt{\epsilon_0 V}} \sum_{\vec{k}\sigma} \vec{e}_{\vec{k}\sigma} q_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}_i}\right)\cdot\big(-e_i \frac{1}{\sqrt{\epsilon_0 V}} \vec{e}_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}_i}\big) \\
&= c^2k^2 q_{-\vec{k}\sigma} + \sum_i \frac{1}{m_i}(\vec{P}_i - e_i\vec{A}_i)\cdot\big(-e_i \frac{1}{\sqrt{\epsilon_0 V}} \vec{e}_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}_i}\big) \\
&= c^2k^2 q_{-\vec{k}\sigma} - \frac{1}{\sqrt{\epsilon_0 V}} \sum_i e_i(\dot{\vec{r}}_i \cdot \vec{e}_{\vec{k}\sigma}) e^{i\vec{k}\cdot\vec{r}_i} \\
\dot{q}_{\vec{k}\sigma} &= \frac{\partial H}{\partial p_{\vec{k}\sigma}} = p_{-\vec{k}\sigma} \\
\ddot{q}_{-\vec{k}\sigma} &= \dot{p}_{-\vec{k}\sigma} \\
&= -c^2k^2 q_{-\vec{k}\sigma} + \frac{1}{\sqrt{\epsilon_0 V}} \sum_i e_i(\dot{\vec{r}}_i \cdot \vec{e}_{\vec{k}\sigma}) e^{i\vec{k}\cdot\vec{r}_i}
\end{aligned}$$

$$
\begin{aligned}
\vec{G} &= \frac{1}{c^2}\int dV\vec{P} = \frac{1}{c^2}\int dV\vec{E}\times\vec{H} \\
&= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\big(\dot{\vec{A}}+\vec{\nabla}\phi\big)\times \mathrm{rot}\,\vec{A} \\
&= \vec{G}^0_{em}+\vec{G}'_{em} \\
\vec{G}^0_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,\dot{\vec{A}}\times \mathrm{rot}\,\vec{A} \\
\vec{G}'_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,\vec{\nabla}\phi\times \mathrm{rot}\,\vec{A}
\end{aligned}
$$

The momentum of the pure radiation field $\vec{G}^0_{em}$ can be described using canonical variables: [224]

$$
\vec{G}^0_{em} = -i\sum_{\vec{k}\sigma}\vec{k}\,p_{\vec{k}\sigma}q_{\vec{k}\sigma}
$$

We further rewrite the terms that are given due to the existing particles. (Note that the boundary terms are cancelled due to the integration by parts and the periodic boundary condition. Note also the Coulomb gauge conditions.):

$$
\begin{aligned}
\vec{G}'_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,\vec{\nabla}\times(\phi\,\mathrm{rot}\,\vec{A})-\phi\,\mathrm{rot}\,\mathrm{rot}\,\vec{A} \\
&= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,\phi\,\Delta\vec{A} = -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,(\Delta\phi)\,\vec{A} \\
&= \frac{1}{c^2}\frac{1}{\epsilon_0\mu_0}\int dV\,\rho\vec{A} = \sum_j e_j\vec{A}_j
\end{aligned}
$$

224

$$
\begin{aligned}
\vec{G}^0_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\,\dot{\vec{A}}\times \mathrm{rot}\,\vec{A} \\
&= -\frac{1}{c^2}\frac{1}{\mu_0}\frac{1}{\sqrt{\epsilon_0}}\sum_{\vec{k}}\sum_{\sigma}\frac{1}{\sqrt{\epsilon_0}}\vec{e}_{\vec{k}\sigma}p_{\vec{k}\sigma}\times(i\vec{k}\times\sum_{\sigma'}\vec{e}_{\vec{k}\sigma'}q_{\vec{k}\sigma'}) \\
&= -i\sum_{\vec{k}}\sum_{\sigma\sigma'}p_{\vec{k}\sigma}q_{\vec{k}\sigma'}\,\vec{e}_{\vec{k}\sigma}\times(\vec{k}\times\vec{e}_{\vec{k}\sigma'}) \\
&= -i\sum_{\vec{k}\sigma}\vec{k}\,p_{\vec{k}\sigma}q_{\vec{k}\sigma}
\end{aligned}
$$

$$
\vec{e}\times(\vec{k}\times\vec{e}) = \vec{k},\quad (|\vec{e}|=1)
$$

Therefore, the total momentum $\vec{G}_T$ is given by the sum of the momentum of the particle system and the momentum of the radiation field:

$$\begin{aligned}\vec{G}_T &= \sum_j m_j \dot{\vec{r}}_j + \vec{G}_{em} \\ &= \sum_j \vec{P}_j + \vec{G}^0_{em}\end{aligned}$$

11.5 Angular Momentum of the Field

Let us calculate for the angular momentum $\vec{J}_{em}$ of the electromagnetic field:

$$\begin{aligned}\vec{J}_{em} &= \frac{1}{c^2}\int dV \vec{r} \times \vec{P} = \frac{1}{c^2}\int dV \vec{r} \times (\vec{E}\times\vec{H}) \\ &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV \vec{r} \times \left(\dot{\vec{A}} + \vec{\nabla}\phi\right) \times \mathrm{rot}\,\vec{A} \\ &= \vec{J}^0_{em} + J'_{em} \\ \vec{J}^0_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\, \vec{r} \times (\dot{\vec{A}} \times \mathrm{rot}\,\vec{A}) \\ \vec{J}'_{em} &= -\frac{1}{c^2}\frac{1}{\mu_0}\int dV\, \vec{r} \times (\vec{\nabla}\phi \times \mathrm{rot}\,\vec{A})\end{aligned}$$

We divide the angular momentum $\vec{J}^0_{em}$ of the pure radiation field into the following two parts: [225]

---

[225]

$$\begin{aligned}(\dot{A} \times \mathrm{rot}\,\vec{A})_i =& \epsilon_{ijk}\dot{A}_j \epsilon_{klm}\partial_l A_m = (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})\dot{A}_j\partial_l A_m \\ =& \dot{A}_j\partial_i A_j - \dot{A}_j\partial_j A_i = \dot{A}_j\partial_i A_j - \partial_j(\dot{A}_j A_i) + \frac{\partial}{\partial t}(\partial_j A_j)A_i \\ =& \dot{A}_j\partial_i A_j - \partial_j(\dot{A}_j A_i) \\ (\vec{r} \times (\dot{A} \times \mathrm{rot}\,\vec{A}))_a =& \epsilon_{abc}r_b\dot{A}_j\partial_c A_j - \epsilon_{abc}r_b\partial_j(\dot{A}_j A_i) \\ =& \epsilon_{abc}r_b\dot{A}_j\partial_c A_j - \partial_j(\epsilon_{abc}r_b\dot{A}_j A_i) + \epsilon_{abc}\partial_j(r_b)\partial_j(\dot{A}_j A_c) \\ =& \epsilon_{abc}r_b\dot{A}_j\partial_c A_j - \partial_j(\epsilon_{abc}r_b\dot{A}_j A_c) + \epsilon_{abc}\dot{A}_b A_c \\ =& \dot{A}_j(\vec{\ell}A_j)_a - \partial_j(\epsilon_{abc}r_b\dot{A}_j A_c) + \epsilon_{abc}\dot{A}_b A_c\end{aligned}$$

Leave out the boundary terms to obtain

$$\int_V d^3r\, \vec{r} \times (\dot{A} \times \mathrm{rot}\,\vec{A}) = \int_V d^3r\, \dot{A}_j \vec{\ell} A_j + \int_V d^3r\, \dot{\vec{A}} \times \vec{A}$$

$$
\begin{aligned}
\vec{J}_{em} &= \vec{J}^{\ell}_{em} + J^{s}_{em} \\
\vec{J}^{\ell}_{em} &= -\frac{1}{\mu_0 c^2}\int_V d^3r\, \dot{A}_j \vec{\ell} A_j \\
\vec{J}^{s}_{em} &= -\frac{1}{\mu_0 c^2}\int_V d^3r\, \dot{\vec{A}} \times \vec{A} \\
&= -\sum_{k,\sigma\sigma'} (\vec{e}_{k\sigma} \times \vec{e}_{k\sigma'}) p_{k\sigma} q_{k\sigma'}
\end{aligned}
$$

If we conduct the integrations by parts to the terms which arisen from the existence of the particles for a number of times then, we can rewrite the angular momentum into [226]

$$
\vec{J}'_{em} = -\epsilon_0 \int dV \Delta\phi\, \vec{r} \times \vec{A} = \int dV\, \rho \vec{r} \times \vec{A} = \sum_j \vec{r}_j \times (e_j \vec{A}_j)
$$

The angular momentum $\vec{J}_T$ is therefore given by the sum of the angular momentum of the particle system and that of radiation field:

$$
\begin{aligned}
\vec{J}_T &= \sum_j \vec{r}_j \times (m_j \dot{\vec{r}})_j + \vec{J}_{em} = \sum_j \vec{L}_j + \vec{J}^{0}_{em} \\
\vec{L}_j =& \vec{r}_j \times (m\dot{\vec{r}}_j + e_j A_j) = \vec{r}_j \times \vec{P}_j
\end{aligned}
$$

226

$$
\vec{\nabla}\phi \times \mathrm{rot}\,\vec{A} = \vec{\nabla} \times (\phi \mathrm{rot}\,\vec{A}) - \phi \mathrm{rot}\,\mathrm{rot}\,\vec{A} = \vec{\nabla} \times (\phi \mathrm{rot}\,\vec{A}) + \phi \Delta \vec{A}
$$

$$
\begin{aligned}
\vec{r} \times (\vec{\nabla}\phi \times \mathrm{rot}\,\vec{A}) =& \vec{r} \times (\vec{\nabla} \times (\phi \mathrm{rot}\,\vec{A})) + \vec{r} \times \phi \Delta \vec{A} \\
[\vec{r} \times (\vec{\nabla} \times (\phi \mathrm{rot}\,\vec{A}))]_i =& \epsilon_{ijk} r_j \epsilon_{klm} \partial_l (\phi \mathrm{rot}\,\vec{A})_m = (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}) r_j \partial_l (\phi \mathrm{rot}\,\vec{A})_m \\
=& r_j \partial_i (\phi \mathrm{rot}\,\vec{A})_j - r_j \partial_j (\phi \mathrm{rot}\,\vec{A})_i \\
=& \partial_i (r_j \phi (\mathrm{rot}\,\vec{A})_j) - \phi (\mathrm{rot}\,\vec{A})_i - \partial_j (r_j \phi (\mathrm{rot}\,\vec{A})_i) + 3\phi (\mathrm{rot}\,\vec{A})_i \\
=& \partial_i (r_j \phi (\mathrm{rot}\,\vec{A})_j) - \partial_j (r_j \phi (\mathrm{rot}\,\vec{A})_i) + 2\phi (\mathrm{rot}\,\vec{A})_i
\end{aligned}
$$

$$
\begin{aligned}
[\vec{r} \times \phi \Delta \vec{A}]_i =& \epsilon_{ijk} r_j \phi \partial_l \partial_l A_k \\
=& \partial_l (\epsilon_{ijk} r_j \phi \partial_l A_k) - \epsilon_{ijk} \phi \partial_j A_k - \epsilon_{ijk} r_j (\partial_l \phi) \partial_l A_k \\
=& \partial_l (\epsilon_{ijk} r_j \phi \partial_l A_k) - \epsilon_{ijk} \phi \partial_j A_k - \partial_l \big(\epsilon_{ijk} r_j (\partial_l \phi) A_k\big) + \epsilon_{ijk} (\partial_j \phi) A_k + \epsilon_{ijk} r_j (\partial_l \partial_l \phi) A_k \\
=& \partial_l (\epsilon_{ijk} r_j \phi \partial_l A_k) - \epsilon_{ijk} \phi \partial_j A_k - \partial_l \big(\epsilon_{ijk} r_j (\partial_l \phi) A_k\big) + \partial_j (\epsilon_{ijk} \phi A_k) - \epsilon_{ijk} \phi (\partial_j A_k) + \epsilon_{ijk} r_j (\partial_l \partial_l \phi) \\
=& \partial_l (\epsilon_{ijk} r_j \phi \partial_l A_k) - \partial_l \big(\epsilon_{ijk} r_j (\partial_l \phi) A_k\big) + \partial_j (\epsilon_{ijk} \phi A_k) - 2\phi (\mathrm{rot}\,\vec{A})_i + (\Delta\phi)(\vec{r} \times \vec{A})_i
\end{aligned}
$$

$$
\vec{J}'_{em} = -\epsilon_0 \int dV \Delta\phi\, \vec{r} \times \vec{A} = \int dV\, \rho \vec{r} \times \vec{A} = \sum_j \vec{r}_j (e_j \times A_j)
$$

12 The Interacting Particle System and Electromagnetic Field as Field Quantity

12.1 Lagrangian Density and Equation of Motion

According to our discussions from the last section, the Maxwell 's equation is

$$\Box \vec{A} = \vec{\nabla}(\mathrm{div}\,\vec{A} + \frac{1}{c^2}\dot{\phi}) - \mu_0 \vec{j}$$
$$\frac{1}{c}\Delta\phi = -\frac{1}{c}\frac{\partial}{\partial t}\mathrm{div}\,\vec{A} - \mu_0 c\rho$$

[227] The Maxwell 's equation can be written in the covariant form to the Lorentz transformation:

$$\partial_\mu(\partial^\mu A^\nu - \partial^\nu A^\mu) = \mu_0 j^\nu$$
$$\partial_\mu f^{\mu\nu} = \mu_0 j^\nu$$

227

$$\Box \vec{A} = \vec{\nabla}(\mathrm{div}\,\vec{A} + \frac{1}{c^2}\dot{\phi}) - \mu_0 \vec{j}$$
$$\frac{1}{c}\Delta\phi = -\frac{1}{c}\frac{\partial}{\partial t}\mathrm{div}\,\vec{A} - \mu_0 c\rho$$

Note:

$$\mathrm{div}\,\vec{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t} = \partial_\mu A^\mu$$

the first equation is then rewritten as

$$-\partial_\mu\partial^\mu A^i = -\partial^i\partial_\mu A^\mu - \mu_0 j^i$$

While the second equation is rewritten by

$$\Box\frac{1}{c}\phi + \frac{1}{c^3}\frac{\partial\phi}{\partial t} = -\frac{1}{c}\frac{\partial}{\partial t}\left(\partial_\mu A^\mu - \frac{1}{c^2}\frac{\partial}{\partial t}\phi\right) - \mu_0 c\rho$$
$$-\partial_\mu\partial^\mu A^0 = -\partial^0\partial_\mu A^\mu - \mu_0 j^0$$

By organizing the above, the Maxwell 's equation can be written as

$$\partial_\mu(\partial^\mu A^\nu - \partial^\nu A^\mu) = \mu_0 j^\nu$$
$$\partial_\mu f^{\mu\nu} = \mu_0 j^\nu$$

Recall our earlier discussions:

$$
\begin{aligned}
A_0 &= \frac{1}{c}\phi \\
A_1 &= -A^1 = -A_x \\
A_2 &= -A^2 = -A_y \\
A_3 &= -A^3 = -A_z \\
f^{\mu\nu} &= \partial^\mu A^\nu - \partial^\nu A^\mu \\
j^0 &= c\rho \\
j^i &= (\vec{j})_i
\end{aligned}
$$

The actions derived from the least-action principle, including the actions caused by the particle systems, can be given by the followings. ($\tau_{(i)}$ denotes the eigentime of the ith particle. ($d\tau_{(i)} = dt\sqrt{1-\frac{v_i^2}{c^2}}$):

$$
\begin{aligned}
S_{em} &= S_0 + S_{rad} + S_{el} = \int d^4x \,\big(\mathcal{L}_0(x) + \mathcal{L}_{rad}(x) + \mathcal{L}_{el}(x)\big) \\
&\quad (d^4x = dx^0dx^1dx^2dx^3 = cdtd^3r) \\
\mathcal{L}_0(x) &= -\sum_i m_i c \int d\tau_{(i)} \sqrt{g_{\mu\nu}\frac{dx^\mu_{(i)}}{d\tau_{(i)}}\frac{dx^\nu_{(i)}}{d\tau_{(i)}}}\,\delta^4(x - x_{(i)}) \\
S_0 &= -\sum_i m_i c \int d\tau_{(i)} \sqrt{g_{\mu\nu}\frac{dx^\mu_{(i)}}{d\tau_{(i)}}\frac{dx^\nu_{(i)}}{d\tau_{(i)}}} = -\sum_i m_i c \int dt\,\sqrt{g_{\mu\nu}\dot{x}^\mu_{(i)}\dot{x}^\nu_{(i)}} \\
\mathcal{L}_{rad}(x) &= -\frac{1}{4\mu_0 c} f_{\mu\nu}f^{\mu\nu} \\
S_{rad} &= -\frac{1}{4\mu_0}\int dtd^3r\, f_{\mu\nu}f^{\mu\nu} \\
\mathcal{L}_{el}(x) &= -j^\mu(x)A_\mu(x) \\
S_{el} &= \int d^4x\,\mathcal{L}_{el}(x) = -\sum_i \int dt\, e_i A_\mu(x_{(i)})\dot{x}^\mu_{(i)} = \sum_i \int dt\, e_i\big(-\phi(\vec{r}_i,t) + \dot{\vec{r}}_i\cdot\vec{A}(\vec{r}_i,t)\big) \\
j^\mu(x) &= \sum_i ce_i \int d\tau_{(i)}\,\delta^4(x - x_{(i)})x'^\mu_{(i)} = (c\sum_i e_i\delta^3(\vec{r}-\vec{r}_i), e_i\dot{\vec{r}}_i\delta^3(\vec{r}-\vec{r}_i))
\end{aligned}
$$

The equation of motion for the radiation field is:

$$
\begin{aligned}
\frac{\delta\mathcal{L}_{rad}}{\delta A_\mu(x)} &= \frac{1}{4\mu_0}\partial_\nu\frac{\partial}{\partial\partial_\nu A_\mu}(\partial_\kappa A_\rho - \partial_\rho A_\kappa)(\partial^\kappa A^\rho - \partial^\rho A^\kappa) \\
&= \frac{1}{\mu_0}\partial_\nu f^{\nu\mu} \\
\frac{\delta\mathcal{L}_{el}}{\delta A_\mu(x)} &= -j^\mu
\end{aligned}
$$

We have already discussed the equation for the particle system.

12.2 Energy-momentum Tensor and the Conservation Law

If we multiply the Maxwell 's equation (field equation) $\partial_\mu f^{\mu\nu} = \mu_0 j^\nu$ by $f_{\lambda\nu}$ along with a further calculation, we obtain: [228]

$$\begin{aligned}\partial_\mu T^\mu{}_\lambda &= f_{\lambda\nu} j^\nu \\ T^\mu{}_\lambda &= \frac{1}{\mu_0}\left(f^{\kappa\mu} f_{\kappa\lambda} - \frac{1}{4}\delta^\mu{}_\lambda f^{\kappa\nu} f_{\kappa\nu}\right)\end{aligned}$$

$T^\mu{}_\lambda$ is called the energy-momentum tensor of electromagnetic field. Specifically, it is $T^{\mu\nu} = g^{\lambda\nu} T^\mu{}_\lambda$:

$$\begin{aligned}T^{\mu\nu} &= \frac{1}{\mu_0}\left(g^{\lambda\nu} g_{\kappa\alpha} g_{\lambda\beta} f^{\kappa\mu} f^{\alpha\beta} - \frac{1}{4} g^{\lambda\nu}\delta^\mu{}_\lambda f^{\kappa\nu} f_{\kappa\nu}\right) \\ &= \frac{1}{\mu_0}\left(g_{\kappa\alpha} f^{\kappa\mu} f^{\alpha\nu} - \frac{1}{4} g^{\mu\nu} f^{\kappa\nu} f_{\kappa\nu}\right)\end{aligned}$$

What we described in the above is symmetric to $T^{\mu\nu} = T^{\nu\mu}$ and therefore the

---

[228]

$$\begin{aligned}f_{\lambda\nu}\partial_\mu f^{\mu\nu} &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - f^{\mu\nu}\partial_\mu f_{\lambda\nu} \\ &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - \frac{1}{2} f^{\mu\nu}(\partial_\mu f_{\lambda\nu} - \partial_\nu f_{\lambda\mu}), \quad f^{\mu\nu} = -f^{\nu\mu} \\ &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - \frac{1}{2} f^{\mu\nu}(\partial_\mu f_{\lambda\nu} + \partial_\nu f_{\mu\lambda} + \partial_\lambda f_{\nu\mu}) + \frac{1}{2} f^{\mu\nu}\partial_\lambda f_{\nu\mu} \\ &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) + \frac{1}{2} f^{\mu\nu}\partial_\lambda f_{\nu\mu} \\ &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - \frac{1}{4}\partial_\lambda (f^{\mu\nu} f_{\mu\nu}) = \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - \frac{1}{4}\partial_\lambda (f^{\kappa\nu} f_{\kappa\nu}) \\ &= \partial_\mu (f_{\lambda\nu} f^{\mu\nu}) - \frac{1}{4}\delta^\mu{}_\lambda \partial_\mu (f^{\kappa\nu} f_{\kappa\nu}) \\ &= \partial_\mu \left(f^{\kappa\mu} f_{\kappa\lambda} - \frac{1}{4}\delta^\mu{}_\lambda f^{\kappa\nu} f_{\kappa\nu}\right)\end{aligned}$$

Thus,

$$\partial_\mu f_{\lambda\nu} + \partial_\nu f_{\mu\lambda} + \partial_\lambda f_{\nu\mu} = \partial_\mu(\partial_\lambda A_\nu - \partial_\nu A_\lambda) + \partial_\nu(\partial_\mu A_\lambda - \partial_\lambda A_\mu) + \partial_\lambda(\partial_\nu A_\mu - \partial_\mu A_\nu) = 0$$

energy-momentum tensor is expressed in the form: [229]

$$
\begin{aligned}
T^{00} &= -\frac{1}{2}(\epsilon_0\vec{E}^2 + \mu_0\vec{H}^2) = -\mathcal{H}_{em} \\
T^{k0} &= -\frac{1}{c}(\vec{P})_k, \quad \vec{P} = \vec{E}\times\vec{H} \\
T^{kl} &= \epsilon_0 E_k E_l + \mu_0 H_k H_l - \delta_{kl}\frac{1}{2}(\epsilon_0\vec{E}^2 - \mu_0\vec{H}^2))
\end{aligned}
$$

Note also:

$$\partial_\mu T^{\mu\kappa} = f^{\kappa\nu} j_\nu$$

If the equation of motion for ith particle is written by $\frac{d\pi^\mu_{(i)}}{dt} = e_i \dot{x_{\kappa(i)}} f^{\mu\kappa}$, then we can write:

$$\int_V d^3r\, j_(x) = \sum_i e_i \dot{x_{\kappa(i)}} f^{\mu\kappa}$$

---

[229]

$$
f_{\mu\nu} = \begin{pmatrix} 0 & \frac{E_x}{c} & \frac{E_y}{c} & \frac{E_z}{c} \\ -\frac{E_x}{c} & 0 & -B_z & B_y \\ -\frac{E_y}{c} & B_z & 0 & -B_x \\ -\frac{E_z}{c} & 0 & B_x & 0 \end{pmatrix}_{\mu\nu}
$$

$$
\begin{aligned}
f^{\alpha\beta} &= g^{\alpha\mu} g^{nu\beta} f_{\mu\nu} \\
&= \left\{ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & \frac{E_x}{c} & \frac{E_y}{c} & \frac{E_z}{c} \\ -\frac{E_x}{c} & 0 & -B_z & B_y \\ -\frac{E_y}{c} & B_z & 0 & -B_x \\ -\frac{E_z}{c} & 0 & B_x & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \right\}_{\alpha\beta} \\
&= \begin{pmatrix} 0 & -\frac{E_x}{c} & -\frac{E_y}{c} & -\frac{E_z}{c} \\ \frac{E_x}{c} & 0 & -B_z & B_y \\ \frac{E_y}{c} & B_z & 0 & -B_x \\ \frac{E_z}{c} & -B_y & B_x & 0 \end{pmatrix}_{\alpha\beta}
\end{aligned}
$$

which gives

$$f^{\alpha\beta} f_{\alpha\beta} = -\frac{2}{c^2}\vec{E}^2 + 2\vec{B}^2$$

$\mathrm{T}^{k0} = -\frac{1}{c}\vec{P}_k, \quad \vec{P} = \vec{E}\times\vec{H}$
$Further, \quad T^{kl} = \frac{1}{\mu_0}(\frac{1}{c^2}E_kE_l + B_kB_l + \delta_{kl}\frac{1}{2}(-\frac{1}{c^2}\vec{E}^2 + \vec{B}^2))$
$= \epsilon_0 E_k E_l + \mu_0 H_k H_l - \delta_{kl}\frac{1}{2}(\epsilon_0\vec{E}^2 - \mu_0\vec{H}^2))$

Having mentioned the above: [230]

$$\frac{d}{dt}\sum_i \pi^{\mu}_{(i)} = \frac{1}{c}\frac{\partial}{\partial t}\int_V d^3r\, T^{0\mu}$$

The expressions in each component:

$$\sum_i M_i c^2 + \int_V d^3r\, \mathcal{H}_{em}(\vec{r}) = const.$$
$$\sum_i M_i \vec{v}_i + \int_V d^3r\, \vec{P}(\vec{r}) = const.$$

which represent the conservation of momentum and energy.

13 Quantization of Electromagnetic Field and the Charged Particles

We conduct quantization of the system as we follow the classic canonical equation we obtained in the previous section. For the operators, we have the canonical variables in the radiation field $q_{\vec{k}\sigma}$ and $p_{\vec{k}\sigma}$, and the canonical variable of the particle system $\vec{r}_i$ and its conjugate momentum $\vec{P}_i = m_i\dot{\vec{r}}_i + e_i\vec{A}$. The commutation relation is imposed between the operators:

$$\begin{aligned}[q_{\vec{k}\sigma}, p_{\vec{k}'\sigma'}] &= i\hbar\delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'} \\ [r_i^{\alpha}, P_j^{\beta}] &= i\hbar\delta_{ij}\delta_{\alpha\beta}\end{aligned}$$

To clarify more, we use a differential representation for the particle system:

$$\vec{P}_i = -i\hbar\vec{\nabla}_i$$

230

$$\begin{aligned}\frac{d}{dt}\sum_i \pi^{\mu}_{(i)} &= \int_V d^3r\, \partial_\nu T^{\nu\mu} \\ &= \frac{1}{c}\frac{\partial}{\partial t}\int_V d^3r\, T^{0\mu} + \int_V \partial_i T^{i\mu} \\ &= \frac{1}{c}\frac{\partial}{\partial t}\int_V d^3r\, T^{0\mu} + \int_S dS_i T^{i\mu} = \frac{1}{c}\frac{\partial}{\partial t}\int_V d^3r\, T^{0\mu}\end{aligned}$$

For the radiation field, we express in boson representation:

$$
\begin{aligned}
q_{\vec{k}\sigma} &= \sqrt{\frac{\hbar}{2\omega_k}}(a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma}) \\
p_{\vec{k}\sigma} &= i\sqrt{\frac{\hbar\omega_k}{2}}(a^\dagger_{\vec{k}\sigma} - a_{-\vec{k}\sigma}) \\
[a_{\vec{k}\sigma}, a^\dagger_{\vec{k}'\sigma'}] &= \delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'} \\
[a_{\vec{k}\sigma}, a_{-\vec{k}'\sigma'}] &= 0 \\
[a^\dagger_{\vec{k}\sigma}, a^\dagger_{-\vec{k}'\sigma'}] &= 0
\end{aligned}
$$

The vector potential can be written by using the representations above: [231]

$$
\vec{A}(\vec{r}) = \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} \vec{e}_{\vec{k}\sigma}(a^\dagger_{\vec{k}\sigma} e^{-i\vec{k}\cdot\vec{r}} + a_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}})
$$

231

$$
\begin{aligned}
\vec{A}(\vec{r}) &= \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \vec{e}_{\vec{k}\sigma} q_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}} \\
&= \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} \vec{e}_{\vec{k}\sigma}(a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma}) e^{i\vec{k}\cdot\vec{r}} \\
&= \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} \vec{e}_{\vec{k}\sigma}(a^\dagger_{\vec{k}\sigma} e^{-i\vec{k}\cdot\vec{r}} + a_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}})
\end{aligned}
$$

Commutation Relation of a Field Quantity

Here, we calculate for the commutation relations of the field quantity: [232]

$$
\begin{aligned}
[A_\alpha(\vec{r}), A_\beta(\vec{r}\,')] =& 0 \\
[E_\alpha(\vec{r}), E_\beta(\vec{r}\,')] =& 0 \\
[B_\alpha(\vec{r}), B_\beta(\vec{r}\,')] =& 0 \\
[E_\alpha(\vec{r}), A_\kappa(\vec{r}\,')] =& i\hbar \frac{1}{\epsilon_0 V} \epsilon_{\alpha\beta\gamma} \partial'_\gamma \delta(\vec{r} - \vec{r}\,')
\end{aligned}
$$

13.1 Hamiltonian

The Hamiltonian of the classical system therefore can be rewritten by the operators we have defined: [233]

232

$$
\begin{aligned}
[A_\alpha(\vec{r}), A_\beta(\vec{r}\,')] =& 0 \\
[E_\alpha(\vec{r}), E_\beta(\vec{r}\,')] =& 0 \\
[B_\alpha(\vec{r}), B_\beta(\vec{r}\,')] =& 0 \\
[E_\alpha(\vec{r}), A_\beta(\vec{r}\,')] =& -\frac{1}{\epsilon_0 V} \sum_{\vec{k}\sigma} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta [p_{\vec{k}\sigma}, q_{\vec{k}\sigma}] e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\
=& \frac{i\hbar}{\epsilon_0 V} \sum_{\vec{k}\sigma} (\vec{e}_{\vec{k}\sigma})_\alpha (\vec{e}_{\vec{k}\sigma})_\beta e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\
=& \frac{i\hbar}{\epsilon_0 V} \sum_{\vec{k}} (\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}) e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\
[E_\alpha(\vec{r}), B_\beta(\vec{r}\,')] =& \epsilon_{\beta\gamma\kappa} \partial'_\gamma [E_\alpha(\vec{r}), A_\kappa(\vec{r}\,')] \\
=& -\frac{\hbar}{\epsilon_0 V} \sum_{\vec{k}} (\delta_{\alpha\kappa} - \frac{k_\alpha k_\kappa}{k^2}) \epsilon_{\beta\gamma\kappa} k_\gamma e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\
=& -\frac{\hbar}{\epsilon_0 V} \sum_{\vec{k}} \epsilon_{\beta\gamma\alpha} k_\gamma e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\
=& i \frac{\hbar}{\epsilon_0 V} \epsilon_{\alpha\beta\gamma} \partial'_\gamma \delta(\vec{r} - \vec{r}\,')
\end{aligned}
$$

233

$$
\begin{aligned}
\frac{1}{2} \sum_k \left(p_{\vec{k}\sigma} p_{-\vec{k}\sigma} + \omega_k^2 q_{\vec{k}\sigma} q_{-\vec{k}\sigma} \right) &= \sum_k \frac{\hbar\omega_k}{4} \left(-(a^\dagger_{\vec{k}\sigma} - a_{-\vec{k}\sigma})(a^\dagger_{-\vec{k}\sigma} - a_{\vec{k}\sigma}) + (a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma})(a^\dagger_{\vec{k}\sigma} + a_{-\vec{k}\sigma}) \right) \\
&= \sum_k \hbar\omega_k \frac{1}{4} (a_{-\vec{k}\sigma} a^\dagger_{-\vec{k}\sigma} + a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma}) + a^\dagger_{-\vec{k}\sigma} a_{-\vec{k}\sigma}) + a_{\vec{k}\sigma} a^\dagger_{\vec{k}\sigma}) \\
&= \sum_k \hbar\omega_k \frac{1}{2} (a_{\vec{k}\sigma} a^\dagger_{\vec{k}\sigma} + a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma}) \\
&= \sum_k \hbar\omega_k (a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} + \frac{1}{2})
\end{aligned}
$$

234

$$
\begin{aligned}
H &= H_{part} + H_{rad} + H_{coulomb} \\
H_{part} &= \sum_i \frac{1}{2m_i}(-i\hbar\vec{\nabla}_i - e_i\vec{A}(\vec{r}_i))^2 \\
\vec{A}(\vec{r}_i) &= \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} \vec{e}_{\vec{k}\sigma}(a^\dagger_{\vec{k}\sigma} e^{-i\vec{k}\cdot\vec{r}_i} + a_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}_i}) \\
H_{rad} &= \sum_{\vec{k}} \sum_{\sigma=1,2} \hbar\omega_k (n_{\vec{k}\sigma} + \frac{1}{2}) \\
n_{\vec{k}\sigma} &= a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma'} \\
H_{coulomb} &= \sum_i \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|}
\end{aligned}
$$

13.2 Momentum

Here, the field momentum is written as [235]

$$
\vec{G}^0_{em} = \sum_{\vec{k}\sigma} \hbar\vec{k}\; n_{\vec{k}\sigma}
$$

234

$$
\vec{A}(\vec{r}_i) = \frac{1}{\sqrt{\epsilon_o V}} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} \vec{e}_{\vec{k}\sigma}(a^\dagger_{\vec{k}\sigma} e^{-i\vec{k}\cdot\vec{r}_i} + a_{\vec{k}\sigma} e^{i\vec{k}\cdot\vec{r}_i})
$$

235

$$
\begin{aligned}
G^0_{em} &= -i \sum_{\vec{k}\sigma} \vec{k}\; p_{\vec{k}\sigma} q_{\vec{k}\sigma} \\
&= \frac{1}{2} \sum_{\vec{k}\sigma} \hbar\vec{k}(a^\dagger_{\vec{k}\sigma} - a_{-\vec{k}\sigma})(a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma}) \\
&= \frac{1}{2} \sum_{\vec{k}\sigma} \hbar\vec{k}(a^\dagger_{\vec{k}\sigma} a^\dagger_{-\vec{k}\sigma} - a_{-\vec{k}\sigma} a_{\vec{k}\sigma} + a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} - a_{-\vec{k}\sigma} a^\dagger_{-\vec{k}\sigma}) \\
&= \sum_{\vec{k}\sigma} \hbar\vec{k}\; a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} \quad (\vec{k} \leftrightarrow -\vec{k})
\end{aligned}
$$

Note that we have $(\vec{k} \leftrightarrow -\vec{k})$ in the last form above.

The momentum of the particle is added to the equation above, and we further write

$$\begin{aligned}\vec{G}_T &= \vec{G}_p + \vec{G}^0_{em}\\ &= \sum_i \frac{\hbar}{i}\vec{\nabla}_i + \sum_{\vec{k}\sigma} \hbar\vec{k}\, n_{\vec{k}\sigma}\\ \vec{G}_p &= \sum_i \frac{\hbar}{i}\vec{\nabla}_i\end{aligned}$$

We can also show that the commutators of the momentum and the Hamiltonian to be defined as [236]

$$[H, \vec{G}_T] = 0$$

14 Interaction of Electromagnetic Field with Matter

We now consider the terms A and A^2 as the perturbation Hamiltonian since the absence of the terms causes the particle system and the radiation field to be separated from one another. In our following discussions, we apply the perturbation theory in considering the issue here. The two terms are in the Coulomb gauge: [237]

$$\vec{P}_i \cdot \vec{A}(\vec{r}_i) = \vec{A}(\vec{r}_i) \cdot \vec{P}_i$$

236

$$\begin{aligned}[e^{i\vec{k}\cdot\vec{r}_j}, \vec{\nabla}_j] &= -i\vec{k}e^{i\vec{k}\cdot\vec{r}_j}\\ [a, a^\dagger a] &= a\\ [a^\dagger, a^\dagger a] &= -a^\dagger\\ [(\vec{A}(\vec{r}_i))_\alpha, \vec{G}_T] &= \frac{1}{\sqrt{\epsilon_0 V}}\sum_{\vec{k}\sigma}\sqrt{\frac{\hbar}{2\omega_k}}(\vec{e}_{\vec{k}\sigma})_\alpha\Big([a^\dagger_{\vec{k}\sigma}e^{-i\vec{k}\cdot\vec{r}_i}, \frac{\hbar}{i}\vec{\nabla}_i + \hbar\vec{k}n_{\vec{k}\sigma}]\\ &\quad +[a_{\vec{k}\sigma}e^{i\vec{k}\cdot\vec{r}_i}, \frac{\hbar}{i}\vec{\nabla}_i + \hbar\vec{k}n_{\vec{k}\sigma}]\Big) = 0\\ [H_{part}, \vec{G}_T] &= 0\\ [H, \vec{G}_T] &= [H_{part} + H_{rad} + H_{coulomb}, \vec{G}_p + \vec{G}^0_{em}]\\ &= [H_{rad} + H_{coulomb}, \vec{G}_p + \vec{G}^0_{em}]\\ &= [H_{coulomb}, \vec{G}_p + \vec{G}^0_{em}]\\ &= [H_{coulomb}, \vec{G}_p] = 0\end{aligned}$$

237

$$[\vec{P}_i, \vec{A}(\vec{r}_i)]* = \vec{A}_i \cdot \vec{P}_i(*) + (\vec{P}_i \cdot \vec{A}_i) * - \vec{A}_i(\cdot \vec{P}_i *) = -i\hbar \mathrm{div}\, \vec{A}(\vec{r}_i) = 0$$

Having aware of the fact above, separate the Hamiltonian in the system:

$$H = H_0 + H_{int}$$

Here H_0 is the Hamiltonian described in the following with the particle system and the radiation field being separated:

$$\begin{aligned} H_0 &= H_p + H_{rad} \\ H_p &= -\sum_i \frac{\hbar^2}{2m_i}\Delta_i + \sum_i \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \\ H_{rad} &= \sum_{\vec{k}} \sum_{\sigma=1,2} \hbar\omega_k (n_{\vec{k}\sigma} + \frac{1}{2}) \end{aligned}$$

While H_{int} denotes the interaction between particle system and the radiation field due to the vector potential:

$$\begin{aligned} H_{int} &= H^{(1)} + H^{(2)} \\ H^{(1)} &= \sum_i \frac{i\hbar e_i}{m_i} \vec{A}(\vec{r}_i) \cdot \vec{\nabla}_i \\ &= \frac{1}{\sqrt{\epsilon_o V}} \sum_i \frac{i\hbar e_i}{m_i} \sum_{\vec{k}\sigma} \sqrt{\frac{\hbar}{2\omega_k}} (a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma}) e^{i\vec{k}\cdot\vec{r}_i} \, (\vec{e}_{\vec{k}\sigma} \cdot \vec{\nabla}_i) \\ H^{(2)} &= \sum_i \frac{\hbar (e_i)^2}{2m_i} \vec{A}(\vec{r}_i)^2 \\ &= \sum_i \frac{\hbar (e_i)^2}{2m_i} \frac{1}{\epsilon_o V} \sum_{\vec{k}\vec{k}'\sigma\sigma'} \frac{\hbar(\vec{e}_{\vec{k}\sigma} \cdot \vec{e}_{\vec{k}'\sigma'})}{2\sqrt{\omega_k \omega_{k'}}} (a^\dagger_{-\vec{k}\sigma} + a_{\vec{k}\sigma})(a^\dagger_{-\vec{k}'\sigma'} + a_{\vec{k}'\sigma'}) e^{i(\vec{k}\cdot\vec{r}_i + \vec{k}'\cdot\vec{r}_i')} \end{aligned}$$

The non-perturbation basis set can be written by the eigenstate $\Psi_m(\{\vec{r}_i\})$ and eigenenergy E_m of the particle system, as well as by the state vector $|\{n_{\vec{k}\sigma}\}\rangle$ of the radiation field. (We exclude the zero-point energy in this case.):

$$\begin{aligned} H_0 |m; \{n_{\vec{k}\sigma}\}\rangle &= (E_m + \sum_{\vec{k}\sigma} n_{\vec{k}} \hbar\omega_{\vec{k}})) |m; \{n_{\vec{k}\sigma}\}\rangle \\ |m; \{n_{\vec{k}\sigma}\}\rangle &= |\{n_{\vec{k}\sigma}\}\rangle \Psi_m(\{\vec{r}_i\}) \\ H_p \Psi_m(\{\vec{r}_i\} &= E_m \Psi_m(\{\vec{r}_i\}) \\ H_{rad} |\{n_{\vec{k}\sigma}\}\rangle &= \sum_{\vec{k}\sigma} n_{\vec{k}} \hbar\omega_{\vec{k}} |\{n_{\vec{k}\sigma}\}\rangle \end{aligned}$$

Note that $H^{(1)}$ denotes the photon absorption and emission while $H^{(2)}$ denotes the process involving the two photons. So far, we have ignored the relativity effects on the particle system but since we recognize the lowest order relativity correction

$$-\frac{e\hbar}{2m} \vec{\sigma} \cdot \mathrm{rot}\, \vec{A}$$

the following term then be added to the perturbation Hamiltonian:

$$H^{(s)} = -\sum_i \frac{e_i\hbar}{2m_i}\vec{\sigma}\cdot \mathrm{rot}_i\,\vec{A}_i = -\sum_i \frac{e_i\hbar}{2m_i}\vec{\sigma}\cdot\vec{\nabla}_i\times\vec{A}_i$$
$$= -\frac{1}{\sqrt{\epsilon_0 V}}\sum_i\sum_{k,\sigma}\frac{ie_i\hbar}{2m_i}\sqrt{\frac{\hbar}{2\omega_k}}(a^\dagger_{-\vec{k}\sigma}+a_{\vec{k}\sigma})e^{i\vec{k}\cdot\vec{r}_i}\vec{\sigma}\cdot(\vec{e}_{\vec{k}\sigma}\times\vec{k})$$

14.1 Fermi 's Golden Rule

Let us review the Fermi 's golden rule that relates to the transition probability of the states calculated by the perturbation theory. We consider the non-perturbation system and its state:

$$H_0|n\rangle = E_n|n\rangle$$

Then, we suppose all system to be governed by (time independent) Hamiltonian:

$$H = H_0 + H_{int}$$

We determine the probability of transition per unit time from the time zero of non-perturbation state a to the non-perturbation state b. We assume in this case that the perturbation is small enough while having sufficient observation time.

- Interaction representation

  Schroedinger equation:

$$i\hbar\partial_t\Psi = (H_0 + H_{int})\Psi$$

  From the equation above, we let [238]

$$\Psi = e^{-iH_0t/\hbar}\Psi^{\mathrm{I}}$$

  giving

$$i\hbar\partial_t\Psi^{\mathrm{I}} = H^{\mathrm{I}}_{int}\Psi^{\mathrm{I}}$$
$$H^{\mathrm{I}}_{int} = e^{iH_0t/\hbar}H_{int}e^{-iH_0t/\hbar}$$

  This is known as the interaction representation. Now, we write

$$\Psi^{\mathrm{I}}(t) = \sum_n c_n(t)|n\rangle$$

[238] Make substitution.

and which gives:

$$\begin{aligned} i\hbar\dot{c}_n &= \sum_m \langle n|H^{\mathrm{I}}_{int}|m\rangle c_m \\ &= \sum_m \langle n|H_{int}|m\rangle e^{i(E_n-E_m)t/\hbar} c_m \end{aligned}$$

Thus, we can simply derive the conservation of probability (self-evident?):

$$\frac{d}{dt}\sum_n |c_n(t)|^2 = 0$$

Now, go back to our initial discussion where

$$c_a(t=0) = 1, \quad c_n(t=0) = 0, \ (n \neq a)$$

and we suppose only a very little time has elapsed from the initial condition. The successive approximate solution can be obtained by [239]

$$c_b(t) = \langle b|H_{int}|a\rangle \frac{e^{i(E_b-E_a)t/\hbar} - 1}{E_b - E_a}$$

which gives

$$|c_b(t)|^2 = |\langle b|H_{int}|a\rangle|^2 2\frac{\cos(E_b-E_a)t/\hbar}{(E_b-E_a)^2}$$

Here, if we use [240] [241]

$$\delta(x) = \lim_{\alpha\to\infty}\frac{1-\cos\alpha x}{\pi\alpha x^2}$$

the probability of transition $w_{a\to b}$ from a to b per unit time can be given by the following: [242]

$$w_{a\to b} = \frac{1}{t}|c_b(t)|^2 \longrightarrow \frac{2\pi}{\hbar}|\langle b|H_{int}|a\rangle|^2\delta(E_b-E_a)$$

239

$$i\hbar\dot{c}_b(t) = \langle b|H_{int}|a\rangle e^{i(E_b-E_a)t/\hbar}c_a$$

240 The effective range of the successive approximation will be

$$|\langle b|H_{int}|a\rangle| << |E_b - E_a|$$

We also know that this is time independent.

241

$$\int_{-\infty}^{\infty} dy \frac{1-\cos\alpha x}{y^2} = \pi$$

242 The validity of the substitution in the delta function can be proven by

$$\frac{|E_a-E_b|t}{\hbar} >> 1$$

In other words, the transition occurs between the different states with the same energy. If the final state b, for example, belongs to the continuous spectrum with the density of states $\rho(E_b)$ at energy interval dE_b, there will be $\rho(E_b)dE_b$ states, thereby the transition probability can be

$$\int w_{a\to b}\rho(E_b)dE_b = \frac{2\pi}{\hbar}|\langle b|H_{int}|a\rangle|^2\rho(E_b)$$

This is known as the Fermi 's golden rule. [243]

14.2 Transition Matrix Elements and Dipole Transition

We now discuss the absorption and emission of light exclusively to during the first order where we can apply the Fermi 's golden rule. To do so, we must calculate the following matrix elements: [244]

$$\begin{aligned}\langle m_b;\{n_{\vec{k}\sigma}\}_b|H^{(1)}||m_a;\{n_{\vec{k}\sigma}\}_a\rangle &= \sum_{\vec{k}\sigma} M^p_{ba}(\vec{k},\sigma)M^{rad}_{ba}(\vec{k},\sigma) \\ M^p_{ba}(\vec{k},\sigma) &= = \int\prod d\vec{r}_i\Psi^*_b(\{\vec{r}_i\})\Big(\sum_i \frac{i\hbar e_i}{m_i}e^{i\vec{k}\cdot\vec{r}_i}(\vec{e}_{\vec{k}\sigma}\cdot\vec{\nabla}_i)\Big)\Psi_a(\{\vec{r}_i\}) \\ M^{rad}_{ba}(\vec{k},\sigma) &= \frac{1}{\sqrt{\epsilon_o V}}\sqrt{\frac{\hbar}{2\omega_k}}\langle\{n_{\vec{k}\sigma}\}_b|(a^\dagger_{-\vec{k}\sigma}+a_{\vec{k}\sigma})|\{n_{\vec{k}\sigma}\}_a\rangle\end{aligned}$$

We use the following evaluation for the radiation field:

$$\begin{aligned}\sqrt{\frac{\hbar}{2\omega}}\langle n-1|a|n\rangle &= \sqrt{\frac{\hbar}{2\omega}}\sqrt{n} \\ \sqrt{\frac{\hbar}{2\omega}}\langle n+1|a^\dagger|n\rangle &= \sqrt{\frac{\hbar}{2\omega}}\sqrt{n+1}\end{aligned}$$

Now consider the matrix element $M^p_{ba}(\vec{k}\sigma)$ given by the wavefunction $\Psi_m(\{\vec{r}_i\})$ of the particle system $(m = a, b)$. We let the radius of an atom be a to estimate the energy difference E for before and after the transition, thereby supposing the bound energy of the atom as

$$E = \hbar\omega \approx \frac{e^2}{4\pi\epsilon_0 a}$$

which gives the wave number k of the related light:

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{c} = \frac{E}{\hbar c} \approx \frac{1}{a}\frac{e^2}{4\pi\epsilon_0\hbar c} = \alpha\frac{1}{a}$$

[243] The approximation.

[244] Consider the fermion system. For the boson system, normalization must be considered.

Thus,

$$k \approx \frac{\alpha}{a} << \frac{1}{a}, \quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137},$$

Note that α is the non-dimensional physical constant called the fine-structure constant. In the region where the wavefunction of the particle system possesses the finite values, we can only consider the wave number of the light and

$$\vec{k} = 0$$

Further, we write the following for the Hamiltonian H_p of the particle system: [245]

$$[H_p, \vec{r}_i] = -\frac{\hbar^2}{m}\vec{\nabla}_i$$
$$[H_p, r_{i,\alpha}] = -\frac{\hbar^2}{m}\partial_{i,\alpha}$$

Since the states are the eigenstates of the Hamiltonian:

$$\begin{aligned}
M_{ba}^p &\approx M_{ba}^{p,e-dipole} \\
M_{ba}^{p,e-dipole} &= (E_b - E_a)\int \prod d\vec{r}_i \Psi_b^*(\{\vec{r}_i\})\left(\sum_i (\vec{e}_{\vec{k}=0,\sigma}\cdot\vec{r}_i)\frac{ie_i}{\hbar}\right)\Psi_a(\{\vec{r}_i\}) \\
&= (E_b - E_a)\langle b|\sum_i (\vec{e}_{\vec{k}=0,\sigma}\cdot\vec{r}_i)\frac{ie_i}{\hbar}|a\rangle \\
&= -i\omega_{ba}\mu_{\sigma,ba}^T \\
\mu_{\sigma,ba}^T &= \sum_i \langle b|\mu_\sigma^i|a\rangle, \qquad \hbar\omega_{ba} = E_b - E_a \\
&\langle b|\cdots|a\rangle \equiv \int \prod d\vec{r}_i \Psi_b^*(\{\vec{r}_i\})(\cdots)\Psi_a(\{\vec{r}_i\}), \\
\mu_\sigma^i &= \vec{e}_{\vec{k},\sigma}\cdot\vec{\mu}_i, \quad \vec{\mu}_i = e_i\vec{r}_i \ \ (electricdipole)
\end{aligned}$$

The approximation at $e^{i\vec{k}\cdot r_i} \to 1$ is called the electric dipole. Commonly, the oscillator strength f_{ba} is defined so as to express the magnitude of the transition for $b \to a$:

$$f_{ab} = \frac{2m}{e^2\hbar\omega_{ba}}|M_{ba}^p|^2$$

245

$$[\frac{p^2}{2m}, r] = \frac{p}{2m}2[p,r] = \frac{p}{2m}2(-)i\hbar = -ip\frac{\hbar}{m}$$

The total sum rule is satisfied by the oscillator strength of the electric dipole transition: [246]

$$\sum_b f_{ba} = N$$

Some transitions particularly provide essential contributions, and those contributions are considered as $\mathcal{O}(1)$.

If there is a zero contribution from the electric dipole approximation due to the symmetry, the degree of order described in the following must be considered. Here, assume $e^{i\vec{k}\cdot r_i} \to 1 + i\vec{k}\cdot\vec{r}_i$,

$$M^p_{ba} \approx M^{p,e-d}_{ba} + \int \prod d\vec{r}_i \Psi^*_b(\{\vec{r}_i\}) \left(\frac{i\hbar e_i}{m_i} \sum_i i\vec{k}\cdot\vec{r}_i(\vec{e}_{\vec{k},\sigma}\cdot\vec{\nabla}_i) \right) \Psi_a(\{\vec{r}_i\})$$

[246] First, confirm the double commutator in the following:

$$\begin{aligned}
[\sum_i^N r_{i,\alpha}, [H_p, \sum_j^N r_{j,\beta}]] =& \frac{1}{2m}[\sum_i^N r_{i,\alpha}, [\sum_k^N \vec{p}_k^2, \sum_j^N r_{j,\beta}]] \\
=& -2i\hbar\frac{1}{2m}[\sum_i^N r_{i,\alpha}, \sum_j^N p_{j,\beta}] \\
=& (-2i\hbar)(i\hbar)\frac{1}{2m}N\delta_{\alpha\beta} = \frac{\hbar^2}{m}N\delta_{\alpha\beta} \\
[\sum_i^N(\vec{e}_\sigma\cdot\vec{r}_i), [H_p, \sum_j^N(\vec{e}_\sigma\cdot\vec{r}_j)]] =& (\vec{e}_\sigma)_\alpha(\vec{e}_\sigma)_\alpha\frac{\hbar^2}{m}N = \frac{\hbar^2}{m}N
\end{aligned}$$

$[x,[H,x]] = [x, Hx - xH] = xHx - x^2H - Hx^2 + xHx = 2xHx - x^2H - Hx^2$ gives

$$\begin{aligned}
\langle a|[x,[H,x]]|a\rangle =& 2\langle a|xHx|a\rangle - \langle a|x^2H|a\rangle - \langle a|Hx^2|a\rangle \\
=& 2\langle a|xHx|a\rangle - E_a\langle a|x^2|a\rangle - E_a\langle a|x^2|a\rangle \\
=& 2\sum_b\langle a|x|b\rangle\langle b|Hx|a\rangle - 2E_a\sum_b\langle a|x|b\rangle\langle b|x|a\rangle \\
=& 2\sum_b(E_b - E_a)|\langle b|x|a\rangle|^2
\end{aligned}$$

Thus, given $x = \sum_i \vec{e}_\sigma\cdot\vec{r}_i$, we use $\langle a|a\rangle = 1$ and the completeness of the intermediate state:

$$\sum_b f_{ba} = \sum_b \frac{2m}{e^2\hbar}\omega_{ba}|\mu^T_{\sigma,ba}|^2 = \sum_b \frac{2}{e^2m\hbar^2}(E_b - E_a)|\mu^T_{\sigma,ba}|^2 = N$$

Now, [247]

$$(\vec{k}\cdot\vec{r})(\vec{e}\cdot\vec{\nabla}) = \frac{1}{2}(\vec{k}\times\vec{e})\cdot\vec{\ell} + \frac{1}{2}[H_p, (\vec{k}\cdot\vec{r})(\vec{e}\cdot\vec{r})]$$

which provides

$$\begin{aligned}
M_{ba}^{p} &\approx M_{ba}^{p,e-d} + M_{ba}^{p,e-q} + M_{ba}^{p,m-d_2}\\
M_{ba}^{p,e-q} &= (E_b - E_a)\int \prod d\vec{r}_i \Psi_b^*(\{\vec{r}_i\})\left(\sum_i (\vec{k}\cdot\vec{r}_i)(\vec{e}_{\vec{k},\sigma}\cdot\vec{r}_i)\frac{ie_i}{2\hbar}\right)\Psi_a(\{\vec{r}_i\})\\
M_{ba}^{p,m-d_1} &= \int \prod d\vec{r}_i \Psi_b^*(\{\vec{r}_i\})\left(\sum_i \frac{i\hbar e_i}{m_i}\left(\frac{1}{2}(\vec{k}\times\vec{e}_{\vec{k}\sigma})\cdot\vec{\ell}\right)\Psi_a(\{\vec{r}_i\})\right.
\end{aligned}$$

This $M_{ba}^{p,e-q}$ is called the matrix element of the double-dipole transition. The contribution of $M_{ba}^{p,m-d_1}$ together with the contribution of (261) is called the matrix element of the magnetic dipole transition in the following. The contribution of $M_{ba}^{p,m-d_2}$ is used for handling the first-oerder contribution of $H^{(s)}$ via $e^{i\vec{k}\cdot\vec{r}} = 1$ and the dipole approximation:

$$\begin{aligned}
M_{ba}^{p,m-d} &= \int \prod d\vec{r}_i \Psi_b^*(\{\vec{r}_i\})\left(\sum_i \frac{i\hbar e_i}{2m_i}(\vec{e}_{\vec{k}\sigma}\times\vec{k})\cdot\vec{M}\right)\Psi_a(\{\vec{r}_i\})\\
\vec{M} &= \vec{\ell} + \vec{\sigma} = \vec{\ell} + 2\vec{s}
\end{aligned}$$

Before we move on to demonstrate a much more simple calculation for the electric dipole approximation, let us take care of the calculation for the density of states in the radiation field. Suppose the system is in a box having side length L, the number of existing states $\rho(E)dE$ found at energy $[E, E+dE]$ then be disintegrated into the solid angle $d\Omega$ and the wave number $[k, k+dk]$:

[247] Confirm the following relation:

$$\begin{aligned}
(\vec{k}\times\vec{e})(\vec{r}\times\vec{\nabla}) &= \epsilon_{ijk}k_j e_k \epsilon_{iab} r_a \partial_b = (\delta_{ja}\delta_{kb} - \delta_{jb}\delta_{ka})k_j e_k r_a \partial_b\\
&= k_j e_k r_j \partial_k - k_j e_k r_k \partial_j\\
[H_p, r_i r_j] &= r_i[H_p, r_j] + [H_p, r_i]r_j = -\frac{\hbar^2}{m}(r_i\partial_j + \partial_j r_i)
\end{aligned}$$

And thus,

$$\begin{aligned}
(\vec{k}\cdot\vec{r})(\vec{e}\cdot\vec{\nabla}) &= k_i r_i e_j \partial_j = \frac{1}{2}k_i e_j(r_i\partial_j - r_j\partial_i) + \frac{1}{2}k_i e_j(r_i\partial_j + r_j\partial_i)\\
&= \frac{1}{2}(\vec{k}\times\vec{e})\cdot(\vec{r}\times\vec{\nabla}) + \frac{1}{2}[H_p, (\vec{k}\cdot\vec{r})(\vec{e}\cdot\vec{r})]
\end{aligned}$$

248

$$\rho(E) = V\frac{1}{(2\pi)^3}\frac{\omega^2}{\hbar c^3}d\Omega$$

14.3 Light Emission

We consider the following transition based on our discussion in the last subsection:

	States of atomic system	Energy of atomic system	Radiation field
Initial state	a	E_a	$\{n_i\}$
Final state	b	E_b	$^{\exists}\nu\ n_\nu + 1$

The energy of the emitted light can be expressed by the conservation of energy (delta function of the Fermi 's golden rule):

$$\hbar\omega = E_a - E_b$$

The emission probability of the light $wd\Omega$ into the solid angle $d\Omega$ as the polarized light σ per unit time is determined via the Fermi 's golden rule:

$$wd\Omega = \frac{2\pi}{\hbar} \times \frac{1}{\epsilon_0 V}\omega^2|\mu_\sigma^{\mathrm{T}}|^2 \times \frac{\hbar}{2\omega}(\bar{n}_{k\sigma}+1) \times \rho(E)$$

For the number of photons detected in the radiation field, $\bar{n}_{k\sigma}$ is used in the above as the average value of the wave number k and the polarized light σ. By organizing the above, we obtain:

$$\begin{aligned} w &= w_{sp} + w_{ind} = \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3}|\mu_\sigma^{\mathrm{T}}|^2(\bar{n}_{k\sigma}+1) \\ w_{sp} &= \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3}|\mu_\sigma^{\mathrm{T}}|^2\bar{n}_{k\sigma} \\ w_{ind} &= \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3}|\mu_\sigma^{\mathrm{T}}|^2 \end{aligned}$$

In the above equations, w_{ind} is proportional to $\bar{n}_{k\sigma}$, and which is known as the induced emission while the rest of the terms are known as the spontaneous emission.

248

$$\begin{aligned} \rho dE &= \frac{dkk^2d\Omega}{(\frac{2\pi}{L})^3} = V\frac{k^2dkd\Omega}{(2\pi)^3} \\ E &= \hbar ck \\ \rho(E) &= V\frac{1}{(2\pi)^3}\frac{E^2}{(\hbar c)^3}d\Omega = V\frac{1}{(2\pi)^3}\frac{\omega^2}{\hbar c^3}d\Omega \end{aligned}$$

14.4 Light Absorption

The transition occurred by the light absorption can be considered in the same way we did for the emission of the light so that we can write down the following expression by use of $n_{\vec{k}\sigma} + 1 \rightarrow n_{\vec{k}\sigma}$

$$w_a = \frac{\omega^3}{8\pi^2\epsilon_0\hbar c^3}|\mu_\sigma^{\mathrm{T}}|^2\bar{n}_{k\sigma}$$

Note that this representation above can be also written in another way by letting the strength of incident light $I(\omega)d\omega$ be [249]

$$I(\omega)d\omega = c\frac{\hbar\omega n}{V}\rho_\omega d\omega = (velocity)(energydensity)\rho_\omega d\omega$$

thus,

$$w_a = \frac{\pi}{\epsilon_0\hbar^2 c}|\mu_\sigma^{\mathrm{T}}|^2 I(\omega)$$

If the two-level system a and b is thermal equilibrium through the radiation field ($E_b - E_a = \hbar\omega$), we let the atomic numbers of respective level be N_a and N_b to define the transition matrix elements for the particles system as $A_{a\rightarrow b} = A_{b\rightarrow a}$ therefore, we obtain:

$$N_b A_{b\rightarrow a}(n+1) = N_a A_{a\rightarrow b} n$$

We assume the Boltzmann distribution for the particles system:

$$\frac{N_b}{N_a} = e^{-(E_b - E_a)/k_B T} = e^{-hbar\omega/k_B T}$$

which gives the Planck 's radiation formula:

$$n = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

[249]

$$\rho(E)dE = \tilde{\rho}(\omega)d\omega$$

which gives

$$\tilde{\rho}(\omega) = \rho(E)\hbar$$

$$I(\omega) = \frac{\hbar^2\omega c n}{V}\rho(E)$$

PartVI
Appendix

A Separation of Variables for Hel,holtz Equation in Polar Coordinates

Consider the Helmholtz equation:

$$\Delta u + k^2 u = 0$$

We let the polar coordinates be

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad x = r\cos\theta$$

from which we express

$$\begin{aligned}
\Delta_{3D} &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\
&= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \\
\Delta_{2D} &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \\
&= \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}
\end{aligned}$$

In the three-dimension:

$$u(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Rewrite the Helmholtz equation, we obtain

$$\begin{aligned}
\Delta u + k^2 u &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\
&= \frac{1}{r^2}\frac{\partial R}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\Theta\Phi + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} + k^2 R\Theta\Phi = 0
\end{aligned}$$

$$\sin^2\theta\left(\frac{\frac{d}{dr}\big(r^2\frac{dR}{dr}\big)}{R} + k^2r^2\right) + \sin\theta\frac{\frac{d}{d\theta}\big(\sin\theta\frac{d\Theta}{d\theta}\big)}{\Theta} \quad = \quad -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

Consider the independent variables, we write:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\mu^2 = (constant)$$

$$\frac{\frac{d}{dr}\big(r^2\frac{dR}{dr}\big)}{R} + k^2r^2 = -\frac{1}{\sin\theta}\frac{\frac{d}{d\theta}\big(\sin\theta\frac{d\Theta}{d\theta}\big)}{\Theta} + \frac{\mu^2}{\sin^2\theta}$$

Let both sides of the equation be the constant λ:

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}\big(r^2\frac{dR}{dr}\big) + \big(k^2 - \frac{\lambda}{r^2}\big)R &= 0\\ \frac{1}{\sin\theta}\frac{d}{d\theta}\big(\sin\theta\frac{d\Theta}{d\theta}\big) + \big(\lambda - \frac{\mu^2}{\sin^2\theta}\big)\Theta &= 0\end{aligned}$$

Where Φ is $\Phi(\phi) = e^{i\mu\phi}$, its single-valuedness is ensured by $\mu = m = scalar$:

$$\Phi(\phi) = e^{i\mu\phi}, \quad m = \cdots, -2, -1, 0, 1, 2, \cdots$$

Where Θ is $x = \cos\theta$ such that

$$\frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -\sin\theta\frac{d}{dx}$$

, giving

$$\begin{aligned}\frac{1}{\sin\theta}\frac{d}{d\theta}\big(\sin\theta\frac{d\Theta}{d\theta}\big) &= \frac{d}{dx}\left(\sin^2\theta\frac{d\Theta}{dx}\right)\\ &= \frac{d}{dx}\left((1-x^2)\frac{d\Theta}{dx}\right)\end{aligned}$$

Thus,

$$\frac{d}{dx}\left((1-x^2)\frac{d\Theta}{dx}\right) + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0$$

This is known as the associated Legendre differential equation, and which is in the form of the Sturm-Liouville equation:

$$\frac{d}{dx}\big(p(x)\frac{du}{dx}\big) + (\lambda\rho(x) - q(x))u = 0$$

In the case of

$$\lambda = \ell(\ell+1), \quad \ell = 0, 1, 2, \cdots$$

there is bounded solutions at $x = \pm 1$, which is expressed by $P_\ell^m(x)$ and known as the associated Legendre function of the first kind.

B Spherical Function

B.1 Legendre Differential Equation

$$\begin{aligned}\frac{d}{dx}\left[(1-x^2)\frac{dP_\ell}{dx}\right] + \lambda P_\ell &= \frac{d}{dx}\left[(1-x^2)\frac{dP_\ell}{dx}\right] + \ell(\ell+1)P_\ell\\ &= (1-x^2)P_\ell'' - 2xP_\ell' + \ell(\ell+1)P_\ell = 0\end{aligned}$$

This is called the Legendre differential equation. On the closed interval $[-1, 1]$ the bounded solutions exist at $\ell = 0, 1, 2, 3, \cdots$. The solutions to the equation are the polynomials, and they are known as the Legendre polynomials. The characteristics of the polynomials are described in the followings:

$$\begin{aligned}
P_\ell(x) &= \sum_{n=0}^{\ell} C_n x^n, \ \left(C_n = \prod_{j=0}^{n-1} \frac{\ell(\ell+1) - j(j+1)}{2(j+1)^2}\right) \\
&= \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell}(x^2-1)^\ell \\
P_0(x) &= 1 \\
P_1(x) &= x \\
P_2(x) &= \frac{3}{2}x^2 - \frac{1}{2} \\
&\vdots \\
\int_{-1}^{1} dx P_{\ell'}(x) P_\ell(x) &= \delta_{\ell\ell'} \frac{2}{2\ell+1}
\end{aligned}$$

An expansion of the generating function is also valid:

$$\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{\ell=0}^{\infty} P_\ell(\cos\theta) \frac{1}{r_>} \left(\frac{r_<}{r_>}\right)^\ell$$

B.2 Associated Legendre Differential Equation

$$\{(1-x^2)\frac{dP_\ell^m}{dx}\} + \big(\ell(\ell+1) - \frac{m^2}{1-x^2}\big)P_\ell^m = 0$$

This is known as the associated Legendre differential equation. The solutions to the equation are obtained through the solutions $P_\ell(x)$ of the Legendre differential equation:

$$P_\ell^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_\ell(x)$$

which satisfies the orthogonal relation:

$$\int_{-1}^{1} dx P_\ell^m(x) P_{\ell'}^m(x) = \delta_{\ell\ell'} \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!}$$

B.3 Spherical Function

Here, we define the spherical function $Y_{\ell m}$ as

$$Y_{\ell m}(\theta, \phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} P_l^m(\cos\theta) e^{im\phi}$$

There are some relations the above spherical function satisfies:

- Orthonormality

$$\langle Y_{\ell' m'} | Y_{\ell m} \rangle \equiv \int d\Omega Y^*_{\ell' m'}(\theta, \phi) Y_{\ell m}(\theta, \phi) = \delta_{\ell, \ell'} \delta_{mm'}$$

- The action of ladder operator

$$L_{\pm} Y_{\ell m} = \hbar \sqrt{(\ell \mp m)(\ell \pm +1)} Y_{\ell m \pm 1}$$

- Addition theorem

$$Y_{\ell m=0}(\cos 0) Y_{\ell m=0}(\omega) = \sum_{m=-\ell}^{\ell} Y^*_{\ell m}(\theta', \phi') Y_{\ell m}(\theta, \phi)$$

  where ω is the angle formed by (θ, ϕ) direction and (θ', ϕ') direction such that

$$\cos \omega = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - phi')$$

To rewrite the above, we have

$$\begin{aligned} P_\ell(\cos \omega) &= P_\ell(\cos \theta) P_\ell(\cos \theta') + 2 \sum_{m=1}^{\ell} \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(\cos \theta) P_\ell^m(\cos \theta') \cos m(\phi - \phi') \\ &= \frac{4\pi}{2\ell + 1} \sum_m Y^*_{\ell m}(\theta', \phi') Y_{\ell m}(\theta, \phi) \end{aligned}$$

C Spherical Bessel Function

C.1 Spherical Bessel Function

Spherical Bessel equation:

$$\left\{ \left(\frac{d^2}{dx^2} + \frac{2}{x} \frac{d}{dx} \right) + 1 - \frac{\ell(\ell+1)}{x^2} \right\} R(x) = 0$$

has two independent solutions, which include a canonical solution at origin (spherical Bessel function) $j_\ell(x)$ and a non-canonical solution (spherical Neumann function) $n_\ell(x)$. The two solutions can be further expressed as

$$\begin{aligned} j_\ell(x) &= (-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \left(\frac{\sin x}{x} \right) \xrightarrow{x \to 0} \frac{x^\ell}{(2\ell+1)!!} \\ n_\ell(x) &= -(-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \left(\frac{\cos x}{x} \right) \xrightarrow{x \to 0} -\frac{(2\ell-1)!!}{x^{\ell+1}} \end{aligned}$$

In some cases, the Hankel function of the first and the second kinds are defined by

$$\begin{aligned} h_\ell^{(1)}(x) &= j_\ell(x) + i n_\ell(x) \\ h_\ell^{(2)}(x) &= j_\ell(x) - i n_\ell(x) \end{aligned}$$

in which two linearly independent solutions exist. The asymptotic forms for large arguments especially, one obtains:

$$\begin{aligned} j_\ell(x) &\xrightarrow{x\to\infty} \frac{1}{x}\sin\left(x - \frac{\ell\pi}{2}\right) \\ n_\ell(x) &\xrightarrow{x\to\infty} -\frac{1}{x}\cos\left(x - \frac{\ell\pi}{2}\right) \\ h_\ell^{(1)}(x) &\xrightarrow{x\to\infty} (-i)^{\ell+1}\frac{e^{ix}}{x} \\ h_\ell^{(2)}(x) &\xrightarrow{x\to\infty} (i)^{\ell+1}\frac{e^{-ix}}{x} \end{aligned}$$

The two important formulas obtained by the above are

$$e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty}(2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos\theta)$$

$$\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} = ik\sum_{\ell=0}^{\infty}(2\ell+1)j_\ell(kr_<)h_\ell^{(1)}(kr_>)P_\ell(\hat{r}\cdot\hat{r}')$$