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

$$The expectation value = (\psi(t),\mathcal{O}\psi(t))$$

[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

$$\int d^3r\, \phi_k(\vec{r})\phi_k^*(\vec{r}') = \delta(\vec{r}-\vec{r}')$$

Example of Free Space

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

$$\begin{aligned} O_R\{H(x)\phi(x)\} &= O_R\psi(x) = \psi(R^{-1}x) = H(R^{-1}x)\phi(R^{-1}x) \\ O_R\{H(x)\phi(x)\} &= O_R\{H(x)O_R^{-1}O_R\phi(x)\} = O_RH(x)O_R^{-1}\phi(R^{-1}x) \end{aligned}$$

Thus, the transformation for $H(x)$ as the operator acting upon the function can be given

$$H(R^{-1}x) = O_RH(x)O_R^{-1}$$

This indicates if $H(x)$ is invariable under the symmetry operation R, expressed in the form

$$\begin{aligned} H(R^{-1}x) &= H(x) \\ H &= O_RHO_R^{-1} \\ [H, O_R] &= HO_R - O_RH = 0 \end{aligned}$$

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} $(i, j = 1, \cdots, N)$:

$$\left[H, P_{ij}\right] = 0, \quad P_{ij}HP_{ij}^{-1} = H$$

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

$$\begin{aligned}\Phi^{\mathrm{B}}_{\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\\ \text{[Boson]} &\quad +\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+\cdots\\ &= \sum_{\substack{\text{All possible exchange of}\\ k_1,\cdots,k_N}} \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\end{aligned}$$

$$\begin{aligned}\Phi^{\mathrm{F}}_{\{k_1,k_2,\cdots,k_N\}}(\vec{r}_1,\cdots,\vec{r}_N) &= \phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\\ \text{[Fermion]} &\quad -\phi_{\underline{k_2}}(\vec{r}_1)\phi_{\underline{k_1}}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)+-\cdots\\ &= \sum_{\substack{\text{All possible exchange}\\ P \text{ of } k_1,\cdots,k_N}} (-1)^{\mathrm{P}}\phi_{k_1}(\vec{r}_1)\phi_{k_2}(\vec{r}_2)\cdots\phi_{k_N}(\vec{r}_N)\end{aligned}$$

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:

$$\begin{aligned} \Phi_\Lambda^B(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= +\Phi_\Lambda^B(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \ \text{(Boson)} \\ \Phi_\Lambda^F(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) &= -\Phi_\Lambda^F(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots) \ \text{(Fermion)} \end{aligned}$$

[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:

$$\begin{aligned} H_N &\rightarrow \mathcal{H} = \sum_k \epsilon_k \hat{n}_k, \quad \hat{n}_k = d_k^\dagger d_k \\ \Phi^{B,F}_{\{n_k\}}(\vec{r}_1, \cdots, \vec{r}_N) &\rightarrow |\{n_k\}\rangle = \prod_k |n_k\rangle \equiv \prod_k \frac{1}{\sqrt{n_k!}} (d_k{}^\dagger)^{n_k} |0\rangle \end{aligned}$$

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 $\mathcal{H}$:

$$\begin{aligned} \mathcal{H}|\{n_k\}\rangle &= E_{\{n_k\}} |\{n_k\}\rangle \\ E_{\{n_k\}} &= \sum_k \epsilon_k n_k \end{aligned}$$

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,

$$= 1 \Big/ \sqrt{N! n_{k_1}! n_{k_2}! \cdots} \sum_P \phi_{i_{PN}}(\vec{r}_N) \cdots \phi_{i_{P1}}(\vec{r}_1), \qquad \{i_1, i_2, \cdots, i_N\} = \{ \overbrace{k_1, k_1 \cdots k_1}^{n_{k_1}}, \overbrace{k_2, k_2 \cdots k_2}^{n_{k_2}}, \cdots \}$$

[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:

$$\begin{aligned} F &= \sum_{i=1}^{N} f(\vec{r}_i) \\ G &= \frac{1}{2} \sum_{i \neq j} g(\vec{r}_i, \vec{r}_j) \end{aligned}$$

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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:

$$\begin{aligned} \hat{I}_N &= \int d^3 r_1 \cdots d^3 r_N \, |\vec{r}_1, \cdots, \vec{r}_N\rangle\langle \vec{r}_1, \cdots, \vec{r}_N| \\ &= \frac{1}{N!} \sum_{i'_1, \cdots, i'_N} \sum_{i_1, \cdots, i_N} d^\dagger_{i'_1} \cdots d^\dagger_{i'_N} |0\rangle\langle 0| d_{i_1} \cdots d_{i_N} \\ &\qquad \times \int d^3 r_1 \cdots d^3 r_N \, \phi^*_{i'_1}(\vec{r}_1) \phi_{i_1}(\vec{r}_1) \cdots \phi^*_{i'_N}(\vec{r}_N) \phi_{i_N}(\vec{r}_N) \\ &= \frac{1}{N!} \sum_{i_1, \cdots, i_N} |n_{i_1} \cdots n_{i_N}\rangle\langle n_{i_1} \cdots n_{i_N}| \\ &= \sum_{i_1 \prec \cdots \prec i_N} |n_{i_1} \cdots n_{i_N}\rangle\langle n_{i_1} \cdots n_{i_N}| \quad \text{Note that there are only non-zeros.} \end{aligned}$$

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$$
\begin{aligned}
|\vec{r}_1,\cdots,\vec{r}_N\rangle &= \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\vec{r}_1)\cdots\hat{\psi}^\dagger(\vec{r}_N)|0\rangle = \frac{1}{\sqrt{N!}}\prod_{j=1}^{N}\hat{\psi}^\dagger(\vec{r}_j)|0\rangle \\
\hat{I}_N &= \int d^3r_1\cdots d^3r_N\ |\vec{r}_1,\cdots,\vec{r}_N\rangle\langle\vec{r}_1,\cdots,\vec{r}_N| \\
&= \sum_{\alpha_1,\cdots,\alpha_N}\frac{\prod_{\alpha_i} n_{\alpha_i}!}{N!}\,|n_{\alpha_1}\cdots n_{\alpha_N}\rangle\langle n_{\alpha_1}\cdots n_{\alpha_N}| \\
&= \sum_{\alpha_1\prec\alpha_2\prec\cdots}|n_{\alpha_1}n_{\alpha_2}\cdots\rangle\langle n_{\alpha_1}n_{\alpha_2}\cdots|
\end{aligned}
$$

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:

$$
\begin{aligned}
\hat{I}_N &= \int d^3r_1\cdots d^3r_N\ |\vec{r}_1,\cdots,\vec{r}_N\rangle\langle\vec{r}_1,\cdots,\vec{r}_N| \\
&= \frac{1}{N!}\sum_{i'_1,\cdots,i'_N}\sum_{i_1,\cdots,i_N} d^\dagger_{i'_1}\cdots d^\dagger_{i'_N}|0\rangle\langle 0|d_{i_1}\cdots d_{i_N} \\
&\qquad\times\int d^3r_1\cdots d^3r_N\ \phi^*_{i'_1}(\vec{r}_1)\phi_{i_1}(\vec{r}_1)\cdots\phi^*_{i'_N}(\vec{r}_N)\phi_{i_N}(\vec{r}_N) \\
&= \sum_{k_1,k_2\cdots}\frac{\prod_k n_k!}{N!}|n_{k_1},n_{k_2},\cdots\rangle\langle n_{k_1},n_{k_2},\cdots| \\
&\qquad\qquad \{i_1,\cdots,i_N\}=\{\overbrace{k_1,k_1\cdots k_1}^{n_{k_1}},\overbrace{k_2,k_2\cdots k_2}^{n_{k_2}},\cdots\} \\
&= \sum_{k_1\prec k_2\cdots}|n_{k_1},n_{k_2},\cdots\rangle\langle n_{k_1},n_{k_2},\cdots|, \qquad \sum n_{k_i}=N
\end{aligned}
$$

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

$$\begin{aligned}
\langle\alpha|\mathcal{G}|\beta\rangle &= \frac{1}{2}\int d^3rd^3r' \int d^3r_1\cdots d^3r_{N-2} \\
&\qquad \times\langle\alpha|\hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}')|\vec{r}_1,\cdots,\vec{r}_{N-2}\rangle g(\vec{r},\vec{r}')\langle\vec{r}_1,\cdots,\vec{r}_{N-2}|\hat{\psi}(\vec{r}')\hat{\psi}(\vec{r})|\beta\rangle \\
&= \frac{1}{2}N(N-1)\int d^3r_1\cdots d^3r_{N-2}d^3rd^3r' \\
&\qquad \times\ \langle\alpha|\vec{r}_1,\cdots,\vec{r}_{N-2},\vec{r},\vec{r}'\rangle g(\vec{r},\vec{r}')\langle\vec{r}_1,\cdots,\vec{r}_{N-2},\vec{r},\vec{r}'|\beta\rangle \\
&= \int d^3r_1\cdots d^3r_N \\
&\qquad \times\frac{1}{2}\sum_{i\neq j}^{N}\Phi^*_\alpha(\vec{r}_1,\cdots,\vec{r}_N)g(\vec{r}_i,\vec{r}_j)\Phi_\beta(\vec{r}_1,\cdots,\vec{r}_N) \\
&= \int d^3r_1\cdots d^3r_N\ \Phi^*_\alpha(\vec{r}_1,\cdots,\vec{r}_N)G\Phi_\beta(\vec{r}_1,\cdots,\vec{r}_N)
\end{aligned}$$

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

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$$\begin{aligned} \int d^3r\, \varphi^*_i(\vec{r}) \varphi_j(\vec{r}) &= \int d^3r\, \phi^*_k(\vec{r}) U^*_{ki} \phi_l(\vec{r}) U_{lj} = U^*_{ki} U_{kj} = \delta_{ij} \\ \varphi_j(\vec{r}) \varphi^*_j(\vec{r}\,') &= \phi_k(\vec{r}) U_{kj} \phi^*_l(\vec{r}\,') U^*_{lj} = \phi_k(\vec{r}) \phi^*_k(\vec{r}\,') = \delta(\vec{r} - \vec{r}\,') \end{aligned}$$

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

$$\langle G|\int d^3r\;\hat{\psi}^\dagger(\vec{r})\left(\frac{-\hbar^2\nabla^2}{2m} + v(\vec{r})\right)\hat{\psi}(\vec{r})|G\rangle = \sum_{j=1}^{N} I(j)$$

$$I(j) = \int d^3r\;\varphi_j^*(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right)\varphi_j(\vec{r})$$

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$$\begin{aligned}\int d^3r\,\varphi_i^*(\vec{r})\varphi_j(\vec{r}) &= \int d^3r\,\phi_k^*(\vec{r})U_{ki}^*\phi_l(\vec{r})U_{lj} = U_{ki}^*U_{kj} = \delta_{ij} \\ U_{jk} &= \int d^3r\,\phi_j^*(\vec{r})\varphi_k(\vec{r}) \\ U_{ik}U_{jk}^* &= \int d^3r'\,\phi_i^*(\vec{r}')\varphi_k(\vec{r}')\int d^3r\,\phi_j(\vec{r})\varphi_k^*(\vec{r}) = \int d^3r\,\phi_i^*(\vec{r})\phi_j(\vec{r}) = \delta_{ij}\end{aligned}$$

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$$\{c_i, c_j^\dagger\} \;=\; \{d_kU_{ki}^*, d_l^\dagger U_{lj}\} = U_{ki}^*U_{kj} = \delta_{ij}$$

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

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$$J(i,j) \geq K(i,j) \geq 0$$

Further, satisfy the following: [161]

$$J(i,i) + J(j,j) \geq 2J(i,j)$$

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$$\begin{aligned} J(1,2) - K(1,2) &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \frac{1}{|\vec{r} - \vec{r}\,'|} \frac{1}{2} \Big(|\varphi_1(\vec{r}\,')|^2 |\varphi_2(\vec{r})|^2 + |\varphi_1(\vec{r})|^2 |\varphi_2(\vec{r}\,')|^2 \\ &\qquad - \varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,')\varphi_2^*(\vec{r})\varphi_1(\vec{r}) - \varphi_1^*(\vec{r})\varphi_2(\vec{r})\varphi_2^*(\vec{r}\,')\varphi_1(\vec{r}\,') \Big) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \frac{1}{|\vec{r} - \vec{r}\,'|} \frac{1}{2} (|Z|^2|Y|^2 + |X|^2|U|^2 - X^*YZU* - Z^*UXY^*) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r\,' \frac{1}{|\vec{r} - \vec{r}\,'|} \frac{1}{2} |XU - YZ|^2 \geq 0 \\ &\quad X = \varphi_1(\vec{r}\,'), \quad Y = \varphi_2(\vec{r}\,'), \quad Z = \varphi_2(\vec{r}), \quad U = \varphi_1(\vec{r}) \end{aligned}$$

[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

$$\frac{1}{r} = \frac{1}{2\pi^2} \int d^3k\, e^{i\vec{k}\cdot\vec{r}} \frac{1}{k^2} = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \frac{4\pi}{k^2}$$

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$$\begin{aligned} K(1,2) &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k\, \frac{1}{k^2} \int d^3r \int d^3r\,' e^{i\vec{k}\cdot(\vec{r} - \vec{r}\,')} \varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,')\varphi_2^*(\vec{r})\varphi_1(\vec{r}) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k\, \frac{1}{k^2} \int d^3r e^{i\vec{k}\cdot\vec{r}} \varphi_2^*(\vec{r})\varphi_1(\vec{r}) \int d^3r\,' e^{-i\vec{k}\cdot\vec{r}\,'} \varphi_1^*(\vec{r}\,')\varphi_2(\vec{r}\,') \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2\pi^2} \int d^3k\, \frac{1}{k^2} \left| \int d^3r e^{i\vec{k}\cdot\vec{r}} \varphi_2^*(\vec{r})\varphi_1(\vec{r}) \right|^2 \geq 0 \end{aligned}$$

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$$\begin{aligned} J(i,i) + J(j,j) - J(i,j) - J(j,i) &= \frac{e^2}{4\pi\epsilon_0} \int d\vec{r} \int d\vec{r}\,' \\ &\quad \times \frac{1}{|\vec{r} - \vec{r}\,'|} \left(|\varphi_i(\vec{r})|^2 |\varphi_i(\vec{r}\,')|^2 + |\varphi_j(\vec{r})|^2 |\varphi_j(\vec{r}\,')|^2 - |\varphi_i(\vec{r})|^2 |\varphi_j(\vec{r}\,')|^2 - |\varphi_j(\vec{r})|^2 |\varphi_i(\vec{r}\,')|^2 \right) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\vec{k}} \frac{4\pi}{k^2} \int d\vec{r} \int d\vec{r}\,' e^{i\vec{k}\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{r}\,'} \times \Big(|\varphi_i(\vec{r})|^2 - |\varphi_j(\vec{r})|^2 \Big) \Big(|\varphi_i(\vec{r}\,')|^2 - |\varphi_j(\vec{r}\,')|^2 \Big) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\vec{k}} \frac{4\pi}{k^2} \left| \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \Big(|\varphi_i(\vec{r})|^2 - |\varphi_j(\vec{r})|^2 \Big) \right|^2 \geq 0 \end{aligned}$$

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

$$\begin{aligned} |F\rangle &= \prod_{\epsilon_{\vec{k}} \le E_F} d^\dagger_{\vec{k}} |0\rangle \\ \epsilon_{\vec{k}} &= \frac{\hbar^2 k^2}{2m} \\ \psi_{\vec{k}}(\vec{r}) &= \sum_{\vec{k}} \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \end{aligned}$$

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]

$$\begin{aligned} \langle F|\hat{n}(\vec{r},\vec{r}\,') \mid F\rangle &= \left(\frac{N}{V}\right)^2 \left(1 - (f(k_F|\vec{r}-\vec{r}\,'|))^2\right) \\ f(k_F R) &= 3\,\frac{\sin k_F R - k_F R \cos k_F R}{k_F^3 R^3} \end{aligned}$$

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.)

$$
\begin{aligned}
&\frac{\delta}{\delta\varphi_i^*(\vec{r})}\left(E_T - \sum_i \epsilon_i \int d^3r\ \varphi_i^*(\vec{r})\varphi_i(\vec{r})\right) = 0 \\
&= \left(-\frac{\hbar^2\nabla^2}{2m} + v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\int d^3r\,'\frac{|\varphi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} - \epsilon_i\right)\varphi_i(\vec{r}) \\
&\quad -\frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\left(\int d^3r\,'\frac{\varphi_j^*(\vec{r}\,')\varphi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_j(\vec{r})
\end{aligned}
$$

---

obtain from $J - K$ as following:

$$
\begin{aligned}
\langle F|\,\hat{n}(\vec{r},\vec{r}\,')\mid F\rangle &= \sum_{k\le k_F,k'\le k_F}\int d^3r\int d^3r\,'\delta(\vec{r}-\vec{R}_A)\delta(\vec{r}\,'-\vec{R}_B) \\
&\qquad \left(|\psi_{\vec{k}}(\vec{r}\,')|^2|\psi_{\vec{k}\,'}(\vec{r})|^2 - \psi_{\vec{k}}^*(\vec{r}\,')\psi_{\vec{k}\,'}(\vec{r}\,')\psi_{\vec{k}\,'}^*(\vec{r})\psi_{\vec{k}}(\vec{r})\right) \\
&= \sum_{k\le k_F,k'\le k_F}\left(\frac{1}{V^2} - \frac{1}{V^2}e^{-i\vec{k}\cdot\vec{R}_B}e^{i\vec{k}\,'\cdot\vec{R}_B}e^{-i\vec{k}\,'\cdot\vec{R}_A}e^{i\vec{k}\cdot\vec{R}_A}\right) \\
&= \frac{1}{V^2}\sum_{k\le k_F,k'\le k_F}\left(1 - e^{i(\vec{k}-\vec{k}\,')\cdot(\vec{R}_A-\vec{R}_B)}\right) \\
&= \frac{1}{V^2}\Big(\sum_{k\le k_F}1\Big)^2 - \frac{1}{V^2}\Big|\sum_{k\le k_F}e^{i\vec{k}\cdot(\vec{R}_A-\vec{R}_B)}\Big|^2 = \left(\frac{N}{V}\right)^2\big(1 - f(k_F|\vec{R}_A-\vec{R}_B|)\big)
\end{aligned}
$$

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

$$\begin{aligned} E_T^{N-1}(\alpha) &= \langle G,\alpha|H|G,\alpha\rangle \\ &= \sum_{i\neq\alpha} I^N(i) + \sum_{i<j;i\neq\alpha,j\neq\alpha}\big(J^N(i,j)-K^N(i,j)\big) \end{aligned}$$

Let us define the ionization energy $\mathcal{I}(\alpha)$ (where there is no relaxation of the electrons system) as

$$\mathcal{I}(\alpha) = E_T^{N-1}(\alpha) - E_T^N$$

So, $-\epsilon_\alpha$ gives the ionization energy of the orbit: [167] [168]

$$\mathcal{I}(\alpha) = -\epsilon_\alpha^N \quad (\text{Koopman}'\text{sTheorem})$$

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]

$$
\begin{aligned}
\epsilon_{\vec{k}} &= \frac{\hbar^2 k^2}{2m} - \epsilon^{ex}_{\vec{k}} \\
\epsilon^{ex}_{\vec{k}} &= \frac{e^2}{4\pi\epsilon_0}\int d^3r' \sum_{k'\le k_F}\frac{1}{V}\frac{e^{i(\vec{k}-\vec{k},')\cdot\vec{R}}}{R} \\
&= \frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi}\left(k_F + \frac{k_F^2-k^2}{2k}\log\left|\frac{k_F+k}{k_F-k}\right|\right)
\end{aligned}
$$

---

[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]

$$\begin{aligned}\langle G|H_0|G\rangle &= \sum_{n=1}^N I(j_n) \\ I(j_n) &= \sum_{n=1}^N \int d^3r\ \varphi^*_{j_n}(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right)\varphi_{j_n}(\vec{r})\end{aligned}$$

[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:

$$|G\rangle = |j_1\mu_1, \cdots, j_N\mu_N\rangle = c^\dagger_{j_1\mu_1}\cdots c^\dagger_{j_N\mu_N}|0\rangle$$

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 $\uparrow$ electrons as $\varphi_i^\uparrow$ while we describe the orbital function that possesses the spin down $\downarrow$ 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.