Perturbation Theory 1

1 Expansion of Complete System

Let's take a look of an expansion for the function $\psi(\boldsymbol{r})$ in terms of the complete system $\{\phi_n(\boldsymbol{r})\}$:

$$\psi(\boldsymbol{r}) = \sum_{n=1}^{\infty} \phi_n(\boldsymbol{r}) c_n \tag{1}$$

In general, this expansion is possible for any complete set $\{\phi_n\}$.

2 Time-independent Perturbation Theory

2.1 Generalization

To begin with, we take the Hamiltonian of the system H. The solution for Schrodinger's equation is not necessarily obtained in an analytical form. In this case, we can write the wavefunction $\psi(\boldsymbol{r})$ as linear combination of orthonormal wavefunction (1) to obtain the coefficient c_n.

$$H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \Rightarrow H\sum_{n=1}^{\infty} \phi_n(\boldsymbol{r}) c_n = E\sum_{n=1}^{\infty} \phi_n(\boldsymbol{r}) c_n \tag{2}$$

Integrate the equation by multiplying $\phi_m^*(\boldsymbol{r})$ from the left side:

$$\sum_{n=1}^{\infty} \langle \phi_m | H | \phi_n \rangle c_n = E\sum_{n=1}^{\infty} \langle \phi_m | \phi_n \rangle c_n = Ec_m \tag{3}$$

We used orthonormality of the wavefunction.

The equation (3) is a simultaneous linear equation; we can define the components of matrix H as:

$$H_{mn} = \langle \phi_m | H | \phi_n \rangle \tag{4}$$

Then we can rewrite as following:

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} & \cdots & H_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \cdots \\ c_n \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \cdots \\ c_n \end{pmatrix} \tag{5}$$

We obtain the eigenvalue of (5) $E^{(j)}\,(j = 1, 2, \cdots, n)$ and its corresponding eigenvectors as:

$$\begin{pmatrix} c_1^{(j)} \\ c_2^{(j)} \\ \cdots \\ c_n^{(j)} \end{pmatrix} \tag{6}$$

Then the eigenstate (eigenenergy $E^{(j)}$) for Hamiltonian H may be written as:

$$\psi^{(j)}(\boldsymbol{r}) = \sum_{k=1}^{\infty} \phi_k(\boldsymbol{r}) c_k^{(j)} \tag{7}$$

2.2 Application of Perturbation

We begin with a case where there is an external field in addition to a simple potential. Hamiltonian for the simple potential can be expressed as H_0, and the Hamiltonian that expresses the interaction of the electrons with the external force such as electromagnetic field, we can write it as H'. The total Hamiltonian H is:

$$H = H_0 + H' \tag{8}$$

For Hamiltonian H_0, the eigenenergy $E_j^{(0)}$ that corresponds to the eigenstate $\{\phi_j(\boldsymbol{r})\}$ is already determined, and we call H_0 an unperturbed Hamiltonian, and H' a perturbed Hamiltonian.

$$H_0|\phi_j\rangle = E_j^{(0)}|\phi_j\rangle \tag{9}$$

The eigenstate we attempt to obtain, can be expressed with linear combination of ϕ_j:

$$|\psi_n\rangle = \sum_j |\phi_j\rangle c_{jn} \tag{10}$$

The following is the equation to be solved:

$$H|\psi_n\rangle = E_n|\psi_n\rangle \tag{11}$$

Multiply by $\langle\phi_k|$ from the left side:

$$(E_k^{(0)} - E_n)c_{kn} + \sum_j H'_{kj} c_{jn} = 0 \tag{12}$$

Now we define $H'_{kj} = \langle\phi_k|H'|\phi_j\rangle$.

We can conduct an expansion to the coefficients c_{jn} and to the energy E_n by the degrees of perturbation Hamiltonian:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots \tag{13}$$

$$c_{kn} = c_{kn}^{(0)} + c_{kn}^{(1)} + c_{kn}^{(2)} + \cdots \tag{14}$$

The perturbation theory is the procedure to determine the solutions through the power series. Hamiltonian is written as following in order to specify the order of perturbation:

$$H = H_0 + \lambda H' \tag{15}$$

Equations (13~14) are corrected to be:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{16}$$

$$c_{kn} = c_{kn}^{(0)} + \lambda c_{kn}^{(1)} + \lambda^2 c_{kn}^{(2)} + \cdots \tag{17}$$

At the final stage of the procedure, we set $\lambda = 1$

Substitute the equations (16~17) into (12) to organize each term of the equation in the order of λ, and then we achieve the following equation:

$$\begin{aligned} & \{(E_k^{(0)} - E_n^{(0)})c_{kn}^{(0)}\} \\ + & \lambda\{(E_k^{(0)} - E_n^{(0)})c_{kn}^{(1)} - E_n^{(1)}c_{kn}^{(0)} + \sum_j H'_{kj}c_{jn}^{(0)}\} \\ + & \lambda^2\{(E_k^{(0)} - E_n^{(0)})c_{kn}^{(2)} - E_n^{(1)}c_{kn}^{(1)} - E_n^{(2)}c_{kn}^{(0)} + \sum_j H'_{kj}c_{jn}^{(1)}\} \\ + & \cdots\cdots = 0 \end{aligned} \tag{18}$$

The equation above (18) can be solved also, by fixing the orders of λ ,

$$(E_k^{(0)} - E_n^{(0)})c_{kn}^{(0)} = 0 \tag{19}$$

$$(E_k^{(0)} - E_n^{(0)})c_{kn}^{(1)} - E_n^{(1)}c_{kn}^{(0)} + \sum_j H'_{kj}c_{jn}^{(0)} = 0 \tag{20}$$

$$(E_k^{(0)} - E_n^{(0)})c_{kn}^{(2)} - E_n^{(1)}c_{kn}^{(1)} - E_n^{(2)}c_{kn}^{(0)} + \sum_j H'_{kj}c_{jn}^{(1)} = 0 \tag{21}$$

2.3 Nondegenerate

Zero order perturbation: the zero degree term of H' or λ corresponds to the situation where there is no perturbation.

From the equation (19):

$$c_{nn}^{(0)} = 1 \,, \quad c_{kn}^{(0)} = 0 \ (k \neq n) \tag{22}$$

We designated ${c_{nn}}^{(0)} = 1$, however it may not be normalized with the degrees greater than 1, hence we must re-normalize it in the calculation in later on.

First-order perturbation: Take (20) into consideration, the term $k = n$ is:

$$-E_n^{(1)}c_{nn}^{(0)} + \sum_j H'_{nj}c_{jn}^{(0)} = 0 \quad (c_{jn}^{(0)} = \delta_{jn}) \tag{23}$$

Then we can obtain:

$$E_n^{(1)} = H'_{nn} \tag{24}$$

Moreover, when we consider the term for $k \neq n$, $c_{nn}^{(1)}$ can be determined. For the term $k \neq n$, the equation (20) may be reformed as:

$$(E_k^{(0)} - E_n^{(0)})c_{kn}^{(1)} + H'_{kn}c_{nn}^{(0)} = 0 \tag{25}$$

Accordingly,

$$c_{kn}^{(1)} = \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \qquad (k \neq n) \tag{26}$$

$c_{nn}^{(1)}$ cannot be determined by (25) but it is determined by the normalization condition $\langle \psi_n | \psi \rangle = 1$. Characteristically, the following indicates the normalization condition:

$$\langle \psi_n | \psi_n \rangle = \sum_{j,k} \langle \psi_j | \psi_k \rangle c_{jn}^* c_{kn} = \sum_k c_{kn}^* c_{kn} = \sum_k \{ |c_{kn}^{(0)}|^2 + \lambda (c_{kn}^{(0)*} c_{kn}^{(1)} + c_{kn}^{(1)*} c_{kn}^{(0)}) + \cdots \} = 1 \tag{27}$$

Here we use (22) to write:

$$c_{nn}^{(1)} + c_{nn}^{(1)^*} = 0 \tag{28}$$

In other words, the real part of $c_{nn}^{(1)}$ takes 0, and the imaginary part is arbitrary, but in this case we take:

$$c_{nn}^{(1)} = 0 \tag{29}$$

Second-order perturbation: We begin with solving for (21). Where $k = n$, we obtain:

$$E_n^{(2)} = \sum_{k(\neq n)} \frac{|H'_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{30}$$

Where $k \neq n$, with application of (24)(26), we obtain:

$$c_{kn}^{(2)} = \sum_{p(\neq n)} \frac{H'_{kp} H'_{pn}}{(E_n^{(0)} - E_p^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{H'_{nn} H'_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} \qquad (k \neq n) \tag{31}$$

With the condition for normalization $\langle \psi_n | \psi_n \rangle = 1$,

$$c_{nn}^{(2)} + c_{nn}^{(2)*} + \sum_{p(\neq n)} \frac{|H'_{pn}|^2}{(E_n^{(0)} - E_p^{(0)})^2} = 0$$

Consequently, the real part of $c_{nn}^{(2)}$ can be determined but the imaginary part cannot be determined. In other words, the imaginary part of $c_{nn}^{(2)}$ takes arbitrary values, but for now, we take the imaginary part of the function as 0. Hence, we determine the following:

$$c_{nn}^{(2)} = -\frac{1}{2}\sum_{p(\neq n)} \frac{|H'_{pn}|^2}{(E_n^{(0)} - E_p^{(0)})^2} \tag{32}$$

2.4 Degenerate states

Suppose the states $n_\alpha,\ n_\beta, \cdots$ are degenerate in energy. In this situation, the equation (26) cannot be applied because the denominator will take 0. Going back to the equation (20), we can rewrite it as:

$$\sum_\beta [-E_j^{(1)}\delta_{\alpha\beta} + H'_{n_\alpha n_\beta}]c_{n_\beta j}^{(0)} = 0 \tag{33}$$

j represents a new eigenstate of $H = H_0 + H'$. Accordingly, we can solve the simultaneous linear equations (33) for the degeneracies.

There is a situation in which $H'_{n_\alpha n_\beta} = 0$ while the energy degenerates. j represents the number of levels made by recombination of degenerating $n_\alpha,\ n_\beta \cdots$.

$$E_j = E_n^{(10)} + \lambda^2 E_j^{(2)} \quad (E_j^{(1)} = 0) \tag{34}$$

$$c_{n_\alpha j} = c_{n_\alpha j}^{(0)} + \lambda c_{n_\alpha j}^{(1)} \tag{35}$$

$$c_{mj} = \lambda c_{mj}^{(1)} \quad (m \neq n_\alpha) \tag{36}$$

In the equation (21) when $k = n_\alpha$:

$$E_j^{(2)} c_{n\alpha j}^{(0)} = \sum_m H'_{n_\alpha m} c_{mj}^{(1)} \tag{37}$$

Where $m \neq n_\alpha$, with the equation (20):

$$(E_m^{(0)} - E_n^{(0)})c_{mj}^{(1)} + \sum_{n_\alpha} H'_{mn_\alpha} c_{n_\alpha j}^{(0)} = 0 \tag{38}$$

Accordingly, the following equation is obtained from (37)(38) by erasing $c_{mj}^{(1)}$:

$$-E_j^{(2)} c_{n_\alpha j}^{(0)} + \sum_{n_\beta} \sum_{m(\neq n_1 \cdots n_s)} \frac{H'_{n_\alpha m} H'_{mn_\beta}}{E_n^{(0)} - E_m^{(0)}} c_{n_\beta j}^{(0)} = 0 \tag{39}$$

Therefore, we can solve the simultaneous linear equation above.