Chapter 4, Approximate methods

I. Time-independent perturbation method

Non-degenerate cases:

Suppose a real system is close to a simple system, the difference can be treated as a perturbation:

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

where $\hat{H}_0 \left| \phi_n^0 \right\rangle = E_n^0 \left| \phi_n^0 \right\rangle$ is known and the eigenfunctions are non-degenerate.

We assume the solution of $\hat{H} \left| \psi_n \right\rangle = E_n \left| \psi_n \right\rangle$ can be approximated as

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}', \qquad \text{where } 0 \le \lambda \le 1 \text{ is an arbitrary number}$$

$$\left| \psi_n \right\rangle = \left| \phi_n^0 \right\rangle + \lambda \left| \phi_n^{(1)} \right\rangle + \lambda^2 \left| \phi_n^{(2)} \right\rangle + \ldots$$

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

Substituting back, we have

$$\hat{H}_0(\left|\phi_n^0\right\rangle + \lambda\left|\phi_n^{(1)}\right\rangle + \lambda^2\left|\phi_n^{(2)}\right\rangle + \ldots)$$
$$+ \lambda\hat{H}'(\left|\phi_n^0\right\rangle + \lambda\left|\phi_n^{(1)}\right\rangle + \lambda^2\left|\phi_n^{(2)}\right\rangle + \ldots)$$
$$= (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\left|\phi_n^0\right\rangle + \lambda\left|\phi_n^{(1)}\right\rangle + \lambda^2\left|\phi_n^{(2)}\right\rangle + \ldots)$$

Counting the factors with the same power of λ:

0^{th} order (λ^0):

$$\hat{H}_0\left|\phi_n^0\right\rangle = E_n^0\left|\phi_n^0\right\rangle$$

1^{st} order (λ^1):

$$\hat{H}'\left|\phi_n^0\right\rangle + \hat{H}_0\left|\phi_n^{(1)}\right\rangle = E_n^{(1)}\left|\phi_n^0\right\rangle + E_n^0\left|\phi_n^{(1)}\right\rangle$$

2^{nd} order (λ^2):

$$\hat{H}'\left|\phi_n^{(1)}\right\rangle + \hat{H}_0\left|\phi_n^{(2)}\right\rangle = E_n^{(2)}\left|\phi_n^0\right\rangle + E_n^{(1)}\left|\phi_n^{(1)}\right\rangle + E_n^0\left|\phi_n^{(2)}\right\rangle$$

…

For 1^{st} order corrections, expand

$$\left|\phi_n^{(1)}\right\rangle = \sum_k c_{nk}^{(1)}\left|\phi_k^0\right\rangle$$

and then substitute back to 1st order eq.

$$\hat{H}'\left|\phi_n^0\right\rangle + \hat{H}_0\sum_k c_{nk}^{(1)}\left|\phi_k^0\right\rangle = E_n^{(1)}\left|\phi_n^0\right\rangle + E_n^0\sum_k c_{nk}^{(1)}\left|\phi_k^0\right\rangle$$

Multiply $\left\langle\phi_n^0\right|$ on the left and integrate

$$\left\langle\phi_n^0\middle|\hat{H}'\middle|\phi_n^0\right\rangle + \sum_k c_{nk}^{(1)}\left\langle\phi_n^0\middle|\hat{H}_0\middle|\phi_k^0\right\rangle = E_n^{(1)}\left\langle\phi_n^0\middle|\phi_n^0\right\rangle + E_n^0\sum_k c_{nk}^{(1)}\left\langle\phi_n^0\middle|\phi_k^0\right\rangle$$

Noting orthonormality $\left\langle\phi_n^0\middle|\phi_k^0\right\rangle = \delta_{nk}$, we have

$$\left\langle\phi_n^0\middle|\hat{H}'\middle|\phi_n^0\right\rangle + \sum_k c_{nk}^{(1)}E_k^0\delta_{nk} = E_n^{(1)} + E_n^0\sum_k c_{nk}^{(1)}\delta_{nk}$$

so

$$E_n^{(1)} = \left\langle\phi_n^0\middle|\hat{H}'\middle|\phi_n^0\right\rangle$$

Now multiply $\left\langle\phi_m^0\right|, m \neq n$, on the left and integrate

$$\left\langle\phi_m^0\middle|\hat{H}'\middle|\phi_n^0\right\rangle + \sum_k c_{nk}^{(1)}\left\langle\phi_m^0\middle|\hat{H}_0\middle|\phi_k^0\right\rangle = E_n^{(1)}\left\langle\phi_m^0\middle|\phi_n^0\right\rangle + E_n^0\sum_k c_{nk}^{(1)}\left\langle\phi_m^0\middle|\phi_k^0\right\rangle$$

Noting orthonormality again, we have

$$\left\langle\phi_m^0\middle|\hat{H}'\middle|\phi_n^0\right\rangle + \sum_k c_{nk}^{(1)}E_k^0\delta_{mk} = E_n^0\sum_k c_{nk}^{(1)}\delta_{mk}$$

so

$$c_{nm}^{(1)} = \frac{\left\langle \phi_m^0 \middle| \hat{H}' \middle| \phi_n^0 \right\rangle}{E_n^0 - E_m^0}, \qquad n \neq m$$

namely

$$\left| \psi_n \right\rangle \approx \left| \phi_n^0 \right\rangle + \sum_{m \neq n} \frac{\left\langle \phi_m^0 \middle| \hat{H}' \middle| \phi_n^0 \right\rangle}{E_n^0 - E_m^0} \left| \phi_m^{(0)} \right\rangle$$

1st order corrections to wavefunction include other 0th states (virtual excitation).

2nd order correction to energy:

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left\langle \phi_n^0 \middle| \hat{H}' \middle| \phi_m^0 \right\rangle \left\langle \phi_m^0 \middle| \hat{H}' \middle| \phi_n^0 \right\rangle}{E_n^0 - E_m^0}$$

Higher order corrections exist, but much more complicated.

Example: Harmonic oscillator in an external field

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 - \mathcal{E} q x$$

0th order solution→ harmonic oscillator:

$$E_n^0 = \left(\frac{1}{2} + n \right) \hbar \omega, \qquad \left| \phi_n^0 \right\rangle = \left| n \right\rangle$$

Express perturbation in ladder operators:

$$\hat{H}' = -\mathcal{E}qx = -\mathcal{E}q\sqrt{\frac{\hbar}{2\mu\omega}}\left(\hat{b} + \hat{b}^{+}\right)$$

1st order correction:

$$\begin{aligned} E_n^{(1)} &= \left\langle \phi_n^0 \middle| \hat{H}' \middle| \phi_n^0 \right\rangle \\ &= -\mathcal{E}q\sqrt{\frac{\hbar}{2\mu\omega}}\left\langle n \middle| \hat{b} + \hat{b}^{+} \middle| n \right\rangle \\ &= -\mathcal{E}q\sqrt{\frac{\hbar}{2\mu\omega}}\left[\sqrt{n}\langle n | n-1\rangle + \sqrt{n+1}\langle n | n+1\rangle\right] = 0 \end{aligned}$$

No contribution.

2nd order correction:

$$\begin{aligned} E_n^{(2)} &= \sum_{m\neq n}\frac{\left\langle \phi_n^0 \middle| \hat{H}' \middle| \phi_m^0 \right\rangle \left\langle \phi_m^0 \middle| \hat{H}' \middle| \phi_n^0 \right\rangle}{E_n^0 - E_m^0} \\ &= \frac{(\mathcal{E}q)^2}{\hbar\omega}\frac{\hbar}{2\mu\omega}\sum_{m\neq n}\frac{\left|\left\langle n \middle| \hat{b} + \hat{b}^{+} \middle| m \right\rangle\right|^2}{n-m} \\ &= \frac{(\mathcal{E}q)^2}{2\mu\omega^2}\sum_{m\neq n}\left[\frac{\left|\sqrt{m}\langle n | m-1\rangle + \sqrt{m+1}\langle n | m+1\rangle\right|^2}{n-m}\right] \\ &= \frac{(\mathcal{E}q)^2}{2\mu\omega^2}\left[\left(\frac{n+1}{-1}\right) + \left(\frac{n}{+1}\right)\right] = -\frac{(\mathcal{E}q)^2}{2\mu\omega^2} \end{aligned}$$

$$E_n \approx \left(\frac{1}{2}+n\right)\hbar\omega - \frac{(\mathcal{E}q)^2}{2m\omega^2}$$

Exact solution:

$$V = \frac{k}{2}\left(x^2 - \frac{2\mathcal{E}q}{k}x\right) = \frac{k}{2}\left(x - \frac{\mathcal{E}q}{k}\right)^2 - \frac{k}{2}\left(\frac{\mathcal{E}q}{k}\right)^2$$

$$E_n = \left(\frac{1}{2}+n\right)\hbar\omega - \frac{(\mathcal{E}q)^2}{2\mu\omega^2}$$

Perturbation involving degenerate states

Degeneracy could cause problems with the denominator in above expressions.

Suppose the *n*th states are *L*-fold degenerate for

$$\hat{H}_0\left|\phi_{n,l}^0\right\rangle = E_n^0\left|\phi_{n,l}^0\right\rangle \qquad l=1,2,\ldots, L$$

One can always recombine the degenerate states to form a new set of eigenfunctions:

$$\left|\chi_i^0\right\rangle = \sum_{l=1}^{L} c_{il}\left|\phi_{n,l}^0\right\rangle$$

such that they become non-degenerate with the perturbation.

How to determine c_{il}? We start by doing the same perturbative expansions:

$$\left|\psi_i\right\rangle = \left|\chi_i^0\right\rangle + \lambda\left|\chi_i^{(1)}\right\rangle + \lambda^2\left|\chi_i^{(2)}\right\rangle + ...$$

$$E_i = E_n^0 + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ...$$

Following the same procedure, we have

0^{th} order:

$$\hat{H}_0\left|\chi_i^0\right\rangle = E_n^0\left|\chi_i^0\right\rangle \qquad i=1,2,\ldots, L$$

1^{st} order:

$$(\hat{H}_0 - E_n^0)\left|\chi_i^{(1)}\right\rangle = (E_i^{(1)} - \hat{H}')\left|\chi_i^0\right\rangle$$

…

Expand the 1^{st} order wavefunction in terms of the 0^{th} order ones

$$\left|\chi_i^{(1)}\right\rangle = \sum_{l=1}^{L} a_{il}\left|\phi_{n,l}^0\right\rangle + \sum_k b_{ik}\left|\phi_k^0\right\rangle$$

where $\left|\phi_k^0\right\rangle$ are all the non-degenerate states of $\hat{H}_0$.

Substitute it back to the 1st order equation, we have

$$\sum_{l=1}^{L} a_{il}(E_n^0 - E_n^0)\left|\phi_{n,l}^0\right\rangle + \sum_{k} b_{ik}(E_k^0 - E_n^0)\left|\phi_k^0\right\rangle = \sum_{l=1}^{L} c_{il}(E_i^{(1)} - \hat{H}')\left|\phi_{n,l}^0\right\rangle$$

Multiplying on the left with $\left\langle\phi_{n,l'}^0\right|$ and integrate

$$\sum_{l=1}^{L} c_{il}\left(E_i^{(1)}\left\langle\phi_{n,l'}^0\middle|\phi_{n,l}^0\right\rangle - \left\langle\phi_{n,l'}^0\middle|\hat{H}'\middle|\phi_{n,l}^0\right\rangle\right) = 0$$

noting orthogonality $\left\langle\phi_{n,l}^0\middle|\phi_k^0\right\rangle = 0$.

Finally, we have the <u>secular equations</u>:

$$\sum_{l=1}^{L} c_{il}\left(E_i^{(1)} S_{l'l} - H'_{l'l}\right) = 0$$

where *S* and *H'* are the overlap and Hamiltonian matrices.

In order for the above simultaneous linear equation to have non-trivial solutions, the corresponding determinant has to be zero:

$$\det\left|H'_{l'l} - E_i^{(1)} S_{l'l}\right| = 0 \qquad \text{(\underline{secular determinant})}$$

In other words, the coefficients (c_{il}) and the 1st order energy correction ($E_i^{(1)}$) can be obtained at the same time.

II. Variation theory

The expectation value of an operator cannot be less than the lowest eigenvalue:

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

$|\psi\rangle$: trial wave function.

Proof:

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle$$

where $|\phi_n\rangle$ are eigenstates of $\hat{H}$.

$$\begin{aligned}\langle \psi | \hat{H} | \psi \rangle &= \sum_n \sum_m c_n^* c_m \langle \phi_n | \hat{H} | \phi_m \rangle \\ &= \sum_n \sum_m c_n^* c_m E_m \delta_{nm} \\ &= \sum_n |c_n|^2 E_n\end{aligned}$$

Assuming normalization, $\langle \psi | \psi \rangle = \sum |c_n|^2 = 1$, we have

$$\langle \psi | \hat{H} | \psi \rangle - E_0 = \sum_n |c_n|^2 (E_n - E_0) \geq 0$$

If trial wave function depends on an adjustable parameter, $\psi(c)$, one can vary c to achieve best results:

$$\frac{\partial\langle E\rangle}{\partial c} = 0$$

Example: ground state wavefunction of a harmonic oscillator.

Trial wave function: $\psi = e^{-cx^2}$

$$\langle\psi|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} e^{-cx^2}\frac{d^2}{dx^2}e^{-cx^2}\,dx + \frac{k}{2}\int_{-\infty}^{\infty} e^{-cx^2}x^2 e^{-cx^2}\,dx$$

$$= \frac{\hbar^2}{m}\left(\frac{\pi}{8}\right)^{1/2} c^{1/2} + \frac{k}{4}\left(\frac{\pi}{8}\right)^{1/2} c^{-3/2}$$

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} e^{-2cx^2}\,dx = \left(\frac{\pi}{2}\right)^{1/2} c^{-1/2}$$

so

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\hbar^2}{2m}c + \frac{k}{8}c^{-1}$$

$$\frac{\partial\langle E\rangle}{\partial c} = \frac{\hbar^2}{2m} - \frac{k}{8}c^{-2} = 0$$

solution:

$$c = \frac{\sqrt{km}}{2\hbar}$$

Substituting back to $\langle E \rangle$

$$\langle E \rangle = \frac{\hbar^2}{2m}\frac{\sqrt{km}}{2\hbar} + \frac{k}{8}\frac{2\hbar}{\sqrt{km}} = \frac{\hbar}{4}\sqrt{\frac{k}{m}} + \frac{\hbar}{4}\sqrt{\frac{k}{m}} = \frac{1}{2}\hbar\omega = E_0$$

Linear variation:

$$|\psi\rangle = \sum_i c_i |\varphi_i\rangle \qquad \text{with } |\varphi_i\rangle \text{ as arbitrary basis}$$

Substituting back to $\langle E \rangle$

$$E = \frac{\sum_i \sum_j c_i c_j \langle \varphi_i | \hat{H} | \varphi_j \rangle}{\sum_i \sum_j c_i c_j \langle \varphi_i | \varphi_j \rangle} = \frac{\sum_i \sum_j c_i c_j H_{ij}}{\sum_i \sum_j c_i c_j S_{ij}}$$

It can be proven to lead to the <u>secular equations</u>:

$$\sum_i c_i (H_{ik} - ES_{ik}) = 0$$

In matrix form:

$$\mathbf{Hc} = \mathbf{ScE} \qquad \text{(generalized eigenequation)}$$

Hamiltonian matrix:

$$H_{ij} = \langle \varphi_i | \hat{H} | \varphi_j \rangle$$

Overlap matrix:

$$S_{ij} = \langle \varphi_i | \varphi_j \rangle$$

Solution can be obtained from the secular determinant:

$$\det |H_{ik} - ES_{ik}| = 0$$

If basis functions are orthonormal, $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$, the secular equation becomes simply an eigenequation:

$$\mathbf{Hc} = \mathbf{cE}$$

in which **E** is a diagonal matrix containing all the eigenvalues and **c** are the corresponding eigenvectors.

Pros and cons of two approximation methods:

- Perturbation methods are good for small deviations from simple systems, not good for high-order corrections.
- Variation methods have lower limits, need no reference systems, but numerically more involved.