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

\[ \hat{H} = \hat{H}_0 + \lambda \hat{H}', \quad \text{where } 0 \leq \lambda \leq 1 \text{ is an arbitrary number} \]

\[ \left| \psi_n \right\rangle = \left| \phi_n^0 \right\rangle + \lambda \left| \phi_n^{(1)} \right\rangle + \lambda^2 \left| \phi_n^{(2)} \right\rangle + ... \]

\[ E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \]

Substituting back, we have
\[
\hat{H}_0 \left( |\phi_n^0\rangle + \lambda |\phi_n^{(1)}\rangle + \lambda^2 |\phi_n^{(2)}\rangle + \ldots \right)
+ \lambda \hat{H}' \left( |\phi_n^0\rangle + \lambda |\phi_n^{(1)}\rangle + \lambda^2 |\phi_n^{(2)}\rangle + \ldots \right)
= (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots) \left( |\phi_n^0\rangle + \lambda |\phi_n^{(1)}\rangle + \lambda^2 |\phi_n^{(2)}\rangle + \ldots \right)
\]

Counting the factors with the same power of \( \lambda \):

0\textsuperscript{th} order (\( \lambda^0 \)):

\[
\hat{H}_0 |\phi_n^0\rangle = E_n^0 |\phi_n^0\rangle
\]

1\textsuperscript{st} order (\( \lambda^1 \)):

\[
\hat{H}' |\phi_n^0\rangle + \hat{H}_0 |\phi_n^{(1)}\rangle = E_n^{(1)} |\phi_n^0\rangle + E_n^0 |\phi_n^{(1)}\rangle
\]

2\textsuperscript{nd} order (\( \lambda^2 \)):

\[
\hat{H}' |\phi_n^{(1)}\rangle + \hat{H}_0 |\phi_n^{(2)}\rangle = E_n^{(2)} |\phi_n^0\rangle + E_n^{(1)} |\phi_n^{(1)}\rangle + E_n^0 |\phi_n^{(2)}\rangle
\]

\[
\ldots
\]

For 1\textsuperscript{st} order corrections, expand

\[
|\phi_n^{(1)}\rangle = \sum_k c_{nk}^{(1)} |\phi_k^0\rangle
\]
and then substitute back to 1\(^{st}\) order eq.

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

Multiply \(\langle \phi_n^0 |\) on the left and integrate

\[
\langle \phi_n^0 |\hat{H}'|\phi_n^0\rangle + \sum_k c_{nk}^{(1)} \langle \phi_n^0 |\hat{H}_0|\phi_k^0\rangle = E_n^{(1)} \langle \phi_n^0 |\phi_n^0\rangle + E_n^0 \sum_k c_{nk}^{(1)} \langle \phi_n^0 |\phi_k^0\rangle
\]

Noting orthonormality \(\langle \phi_n^0 |\phi_k^0\rangle = \delta_{nk}\), we have

\[
\langle \phi_n^0 |\hat{H}'|\phi_n^0\rangle + \sum_k c_{nk}^{(1)} E_k^0 \delta_{nk} = E_n^{(1)} + E_n^0 \sum_k c_{nk}^{(1)} \delta_{nk}
\]

so

\[
E_n^{(1)} = \langle \phi_n^0 |\hat{H}'|\phi_n^0\rangle
\]

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

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

Noting orthonormality again, we have

\[
\langle \phi_m^0 |\hat{H}'|\phi_n^0\rangle + \sum_k c_{nk}^{(1)} E_k^0 \delta_{mk} = E_n^0 \sum_k c_{nk}^{(1)} \delta_{mk}
\]
so

\[ c_{nm}^{(1)} = \frac{\langle \phi_m^0 | \hat{H}' | \phi_n^0 \rangle}{E_n^0 - E_m^0}, \quad n \neq m \]

namely

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

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

2\textsuperscript{nd} order correction to energy:

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

Higher order corrections exist, but much more complicated.

Example: Harmonic oscillator in an external field

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 - E q x \]

0\textsuperscript{th} order solution→ harmonic oscillator:

\[ E_n^0 = \left( n + \frac{1}{2} \right) \hbar \omega, \quad |\phi_n^0 \rangle = |n \rangle \]
Express perturbation in ladder operators:

\[ \hat{H}' = -\mathcal{E}_q x = -\mathcal{E}_q \sqrt{\frac{\hbar}{2\mu\omega}} (\hat{b} + \hat{b}^+) \]

1st order correction:

\[ E_n^{(1)} = \langle \phi_n^0 | \hat{H}' | \phi_n^0 \rangle \]

\[ = -\mathcal{E}_q \sqrt{\frac{\hbar}{2\mu\omega}} \langle n| \hat{b} + \hat{b}^+ | n \rangle \]

\[ = -\mathcal{E}_q \sqrt{\frac{\hbar}{2\mu\omega}} \left[ \sqrt{n-n+1} \right] = 0 

No contribution.

2nd order correction:

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

\[ = \frac{(\mathcal{E}_q)^2}{\hbar \omega} \frac{\hbar}{2\mu\omega} \sum_{m \neq n} \frac{\langle n| \hat{b} + \hat{b}^+ | m \rangle^2}{n - m} \]

\[ = \frac{(\mathcal{E}_q)^2}{2\mu\omega^2} \sum_{m \neq n} \left[ \frac{\sqrt{n-m-1} + \sqrt{n+m+1} } {n - m} \right]^2 \]

\[ = \frac{(\mathcal{E}_q)^2}{2\mu\omega^2} \left[ \left( \frac{n+1}{-1} \right) + \left( \frac{n}{+1} \right) \right] = -\frac{(\mathcal{E}_q)^2}{2\mu\omega^2} \]
\[ E_n \approx \left( \frac{1}{2} + n \right) \hbar \omega - \frac{(\mathcal{E}q)^2}{2m\omega^2} \]

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

\[ \hat{H}_0 \phi^{0}_{n,l} = E^{0}_{n} \phi^{0}_{n,l} \]

\( l=1,2,\ldots, L \)

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

\[ \left| \chi^{0}_{i} \right> = \sum_{l=1}^{L} c_{il} \left| \phi^{0}_{n,l} \right> \]

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\textsuperscript{th} order:

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

1\textsuperscript{st} order:

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

... Expand the 1\textsuperscript{st} order wavefunction in terms of the 0\textsuperscript{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 1\text{st} order equation, we have

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

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

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

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

Finally, we have the secular equations:

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

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:

\[ \det \begin{vmatrix} H'_{ll} - E_i^{(1)} S_{ll} \end{vmatrix} = 0 \quad \text{(secular determinant)} \]

In other words, the coefficients ($c_{il}$) and the 1\text{st} 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 $\hat{H}$.

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{n} \sum_{m} c_n^* c_m \langle \phi_n | \hat{H} | \phi_m \rangle$$

$$= \sum_{n} \sum_{m} c_n^* c_m E_m \delta_{nm}$$

$$= \sum_{n} |c_n|^2 E_n$$

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 \( \langle E \rangle \)

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

Linear variation:

\[ |\psi\rangle = \sum_i c_i |\varphi_i\rangle \quad \text{with} \ |\varphi_i\rangle \text{ as arbitrary basis} \]

Substituting back to \( \langle E \rangle \)

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

It can be proven to lead to the secular equations:

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

In matrix form:

\[ Hc = ScE \quad \text{(generalized eigenequation)} \]
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:

\[ \det |H_{ik} - E S_{ik}| = 0 \]

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

\[ H\mathbf{c} = \mathbf{c}E \]

in which \( E \) is a diagonal matrix containing all the eigenvalues and \( \mathbf{c} \) 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.