Summary of perturbation theory equations

Time independent perturbation expansion

Suppose we have a reference Hamiltonian $\mathcal{H}_0$ for which we know all of the eigenvalues and eigenfunctions:

$$\mathcal{H}_0 \Phi_n^0 = E_n^0 \Phi_n^0.$$  \hspace{1cm} (1)

Now we want to approximate the eigenvalues $E_n$ and eigenfunctions $\Phi_n$ of total Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, where the second term is small compared to the reference Hamiltonian term. If the $n^{\text{th}}$ zero-order eigenstate ($E_n^0$) is not degenerate, then we can make the following expansion. We will use the shorthand notation $\langle \Phi_k^0 | \mathcal{H}_1 | \Phi_m^0 \rangle \equiv V_{km}$.

$$E_n \approx E_n^0 + V_{nn} + \sum_{m \neq n} \frac{|V_{mn}|^2}{E_n^0 - E_m^0} + O(V^3).$$  \hspace{1cm} (2)

$$\Phi_n \approx \Phi_n^0 + \sum_{m \neq n} \Phi_m^0 \frac{V_{mn}}{E_n^0 - E_m^0} + O(V^2).$$  \hspace{1cm} (3)

If, on the other hand, the zero-order eigenstate ($E_n^0$) is degenerate with one or more other eigenstates, another method must be used. Suppose there are $N$ such degenerate states which we will label $\{\Phi_{n_i}^0\}$, where $i = 1, 2, \ldots, N$. We suppose that we can find $N$ new zero-order states $\{\Phi_{n_i}^\alpha\}$ from linear combinations of the original states, by diagonalizing the following $N \times N$ matrix:

$$
\begin{pmatrix}
E_{n_1}^0 + V_{n_1 n_1} & V_{n_1 n_2} & V_{n_1 n_3} & \cdots & V_{n_1 n_N} \\
V_{n_2 n_1} & E_{n_2}^0 + V_{n_2 n_2} & V_{n_2 n_3} & \cdots & V_{n_2 n_N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
V_{n_N n_1} & V_{n_N n_2} & V_{n_N n_3} & \cdots & E_{n_N}^0 + V_{n_N n_N}
\end{pmatrix}
\begin{pmatrix}
C_{n_1}^\alpha \\
C_{n_2}^\alpha \\
\vdots \\
C_{n_N}^\alpha
\end{pmatrix}
= E^\alpha
\begin{pmatrix}
C_{n_1}^\alpha \\
C_{n_2}^\alpha \\
\vdots \\
C_{n_N}^\alpha
\end{pmatrix}$$  \hspace{1cm} (4)

The energy eigenvalues $\{E^\alpha\}$ correspond to corrections up to first order in the perturbation for this system. Each eigenvalue $E^\alpha$ corresponds to a linear combination of the zero order eigenfunctions in terms of the coefficients $\{C_{n_i}^\alpha\}$:

$$\Phi^{\alpha} = \sum_{i=1}^{N} C_{n_i}^\alpha \Phi_{n_i}^0.$$  \hspace{1cm} (5)

If necessary, these new zero order eigenfunctions can now be corrected to first and higher order using the non-degenerate formalism.
Variational methods

It is a general property of a Hermitian operator, like the Hamiltonian $\mathcal{H}$, that the lowest eigenvalue $E_0$ satisfies an inequality of the form

$$E_0 \leq \frac{\langle \phi | \mathcal{H} | \phi \rangle}{\langle \phi | \phi \rangle}. \quad (6)$$

In this expression $\phi$ represents a trial wavefunction. The equality holds when $\phi = \psi_0$, the exact ground state wavefunction.

We can use the inequality of Eq. (6) to actively search for the minimum using variational techniques. This leads to a very powerful and well-used approximation scheme. To demonstrate how it works for a simple case, consider the Hamiltonian for a hydrogen atom:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi \varepsilon_0 r}. \quad (7)$$

We are interested in finding an approximation to the ground state wavefunction, which we can assume to be spherically symmetric. For example, suppose that we take a trial wavefunction of the form

$$\phi(r) = \frac{e^{-\alpha r^2}}{\sqrt{4\pi}}, \quad (8)$$

where $\alpha$ is the variational parameter to be determined. We need to carry out the following integrals:

$$\langle \phi | \phi \rangle = \int_0^\infty r^2 dr e^{-2\alpha r^2} = \frac{1}{16} \sqrt{\frac{2\pi}{\alpha^3}}. \quad (9)$$

$$\langle \phi | \nabla^2 | \phi \rangle = \langle \phi | \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} | \phi \rangle = -\frac{3\alpha}{16} \sqrt{\frac{2\pi}{\alpha^3}}. \quad (10)$$

$$\langle \phi | \frac{1}{r} | \phi \rangle = \frac{1}{4\alpha}. \quad (11)$$

Putting all of these results, together, we find

$$E(\alpha) \equiv \frac{\langle \phi | \mathcal{H} | \phi \rangle}{\langle \phi | \phi \rangle} = 3\alpha \frac{\hbar^2}{2m} - \frac{4\sqrt{\alpha}}{\sqrt{2\pi} 4\pi \varepsilon_0} \frac{Ze^2}{\mathcal{H}}. \quad (12)$$

In order to simplify the notation, we define the Bohr radius:

$$a_0 \equiv \frac{4\pi \varepsilon_0 \hbar^2}{me^2}. \quad (13)$$

In these terms,

$$E(\alpha) = \frac{e^2}{8\pi \varepsilon_0 a_0} \left( 3\alpha a_0^2 - \frac{8Z \sqrt{\alpha} a_0}{\sqrt{2\pi}} \right). \quad (14)$$
In order to find the minimum value of $E(\alpha)$, we evaluate

$$\frac{dE(\alpha)}{d\alpha}\bigg|_{\alpha_0} = 0,$$

to find

$$\alpha_0 = \frac{8Z^2}{9\pi a_0^3}.$$  \hspace{1cm} (16)

We can then evaluate the minimum energy:

$$E(\alpha_0) = -\frac{e^2}{8\pi \varepsilon_0 a_0} \frac{8Z^2}{3\pi}.$$ \hspace{1cm} (17)

This result is 15% higher energy the correct answer, since

$$\frac{E(\alpha_0) - E_0}{E_0} = -0.15.$$ \hspace{1cm} (18)

A plot of the exact and optimized trial wavefunctions are shown below.

![Wavefunction Plot](image)

Considering the incorrect shape of the optimized trial wavefunction, the accuracy of the energy estimate is remarkable.

**Summary of time dependent theory equations**

**Time dependent perturbation expansion**

Now suppose that the perturbation depends on time, $\mathcal{H}(\mathbf{r},t) = \mathcal{H}_0(\mathbf{r}) + \mathcal{H}_1(\mathbf{r},t)$. The
The differential equation we must solve is
\[ i\hbar \frac{\partial \Phi(r, t)}{\partial t} = \mathcal{H}(r, t)\Phi(r, t). \] (19)
We will again assume that we know all of the eigenvalues and eigenfunctions of the reference Hamiltonian
\[ \mathcal{H}_0 \phi_n^0 = E_n^0 \phi_n^0. \] (20)
In this case, the time dependence of the zero order eigenfunctions takes the form:
\[ \phi_n^0(r, t) = \phi_n^0(r)e^{-iE_n^0 t/\hbar}. \] (21)
The spatial functions \( \phi_n^0(r) \) form a complete orthonormal set of functions. The full solution is expected to take the form
\[ \Phi(r, t) = \sum_n a_n(t)\phi_n^0(r)e^{-iE_n^0 t/\hbar}, \] (22)
where the coefficients \( a_n(t) \) are to be determined from solution of the first order differential equation:
\[ \frac{da_n(t)}{dt} = \frac{1}{i\hbar} \sum_m a_m(t)e^{i(E_n^0 - E_m^0)t/\hbar} \langle \phi_n^0 | \mathcal{H}_1 | \phi_m^0 \rangle. \] (23)
At this point, we have not made any approximations. In order to proceed, we expand the coefficients as a sum of orders of approximation:
\[ a_n(t) = a_n^{(0)}(t) + a_n^{(1)}(t) + a_n^{(2)}(t) \ldots. \] (24)
In general we will assume that the system is initially in a well-defined state of the zero order Hamiltonian:
\[ a_m^{(0)}(t) = \delta_{nm}. \] (25)
The equation for the first order coefficient \( a_n^{(1)}(t) \) then takes the form:
\[ a_n^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} dt' e^{i(E_n^0 - E_m^0)t'/\hbar} \langle \phi_n^0 | \mathcal{H}_1 | \phi_m^0 \rangle(t'). \] (26)
Thus the first order coefficients can be determined from a knowledge of the matrix elements of the time-dependent perturbation \( \mathcal{H}_1(r, t) \). Higher order corrections can be determined from the lower order coefficients.

We will consider the first order coefficients for the case in which there is a harmonic time dependence which is “turned on” at time \( t = 0 \):
\[ \mathcal{H}_1(r, t) = V(r) \left( e^{i\omega t} + e^{-i\omega t} \right) \Theta(t), \] (27)
where \( \Theta(t) \) denotes the Heaviside step function. If the system is initially \( t < 0 \) in the zero order state \( \Phi_n^0 \), the effects of the perturbation to first order in \( V \) is given by
\[ \Phi_n(r, t) \approx \phi_n^0(r)e^{-iE_n^0 t/\hbar} + \sum_m a_m^{(1)}(t)\phi_m^0(r)e^{-iE_m^0 t/\hbar}, \] (28)
where
\[ a_m^{(1)}(t) = -\frac{V_{mn}}{i\hbar} \left[ e^{i(\omega_{mn} + \omega)t} - 1 - \frac{e^{i(\omega_{mn} - \omega)t} - 1}{\omega_{mn} + \omega - \omega_{mn} - \omega} \right]. \] (29)

In this expression, \( \omega_{mn} = \frac{E_m^0 - E_n^0}{\hbar} \). For large times \( t \), it can be shown that the squared modulus of the exitation coefficient \( a_m^{(1)}(t) \) determines the transition rate:
\[ R_{n \rightarrow m} = \frac{|a_m^{(1)}(t)|^2}{t} \approx \frac{2\pi}{\hbar^2} |V_{mn}|^2 \left( \delta(\omega_{mn} + \omega) + \delta(\omega_{mn} - \omega) \right), \] (30)
or
\[ R_{n \rightarrow m} \approx \frac{2\pi}{\hbar} |V_{mn}|^2 \left( \delta(E_m^0 - E_n^0 + \hbar \omega) + \delta(E_m^0 - E_n^0 - \hbar \omega) \right). \] (31)