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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:

$$\mathcal{H}_0 \Phi_n^0 = E_n^0 \Phi_n^0. \tag{1}$$

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

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

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

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 $\{\Phi^{0\alpha}\}$ from linear combinations of the original states, by diagonalizing the following $N \times N$ matrix:

$$\begin{pmatrix} E_{n_1}^0 + V_{n_1 n_1} & V_{n_1 n_2} & V_{n_1 n_3} & \ldots & V_{n_1 n_N} \\ V_{n_2 n_1} & E_{n_2}^0 + V_{n_2 n_2} & V_{n_2 n_3} & \ldots & V_{n_3 n_N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ V_{n_N n_1} & V_{n_N n_3} & V_{n_N n_3} & \ldots & E_{n_N}^0 + V_{n_N n_N} \end{pmatrix} \begin{pmatrix} C_{n_1}^\alpha \\ C_{n_2}^\alpha \\ \vdots \\ C_{n_N}^\alpha \end{pmatrix} = E^\alpha \begin{pmatrix} C_{n_1}^\alpha \\ C_{n_2}^\alpha \\ \vdots \\ C_{n_N}^\alpha \end{pmatrix} \tag{4}$$

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

$$\Phi^{0\alpha} = \sum_{i=1}^{N} C_{n_i}^\alpha \Phi_{n_i}^0. \tag{5}$$

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

$$E_0 \leq \frac{\langle\phi|\mathcal{H}|\phi\rangle}{\langle\phi||\phi\rangle}. \tag{6}$$

In this expression ϕ 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:

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}. \tag{7}$$

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

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

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

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

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

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

Putting all of these results, to gether, we find

$$E(\alpha) \equiv \frac{\langle\phi|\mathcal{H}|\phi\rangle}{\langle\phi||\phi\rangle} = 3\alpha\frac{\hbar^2}{2m} - \frac{4\sqrt{\alpha}}{\sqrt{2\pi}}\frac{Ze^2}{4\pi\epsilon_0}. \tag{12}$$

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

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}. \tag{13}$$

In these terms,

$$E(\alpha) = \frac{e^2}{8\pi\epsilon_0 a_0}\left(3\alpha a_0^2 - \frac{8Z\sqrt{\alpha}a_0}{\sqrt{2\pi}}\right). \tag{14}$$

In order to find the minimum value of $E(\alpha)$, we evaluate

$$\left.\frac{dE(\alpha)}{d\alpha}\right|_{\alpha_0} = 0, \tag{15}$$

to find

$$\alpha_0 = \frac{8Z^2}{9\pi a_0^2}. \tag{16}$$

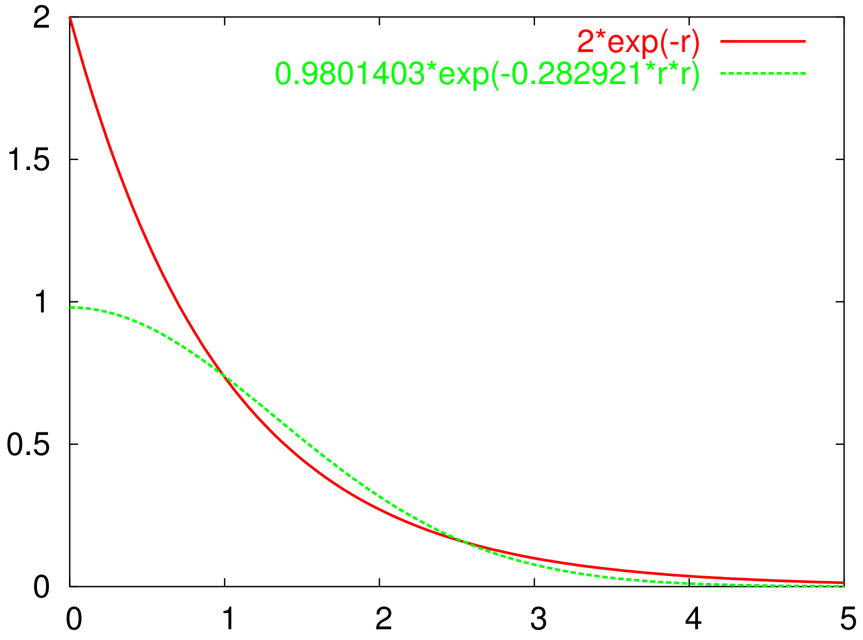
We can then evaluate the minimum energy:

$$E(\alpha_0) = -\frac{e^2}{8\pi\epsilon_0 a_0}\frac{8Z^2}{3\pi}. \tag{17}$$

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

$$\frac{E(\alpha_0) - E_0}{E_0} = -0.15. \tag{18}$$

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



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 differential equation we must solve is

$$i\hbar \frac{\partial \Phi(\mathbf{r},t)}{\partial t} = \mathcal{H}(\mathbf{r},t)\Phi(\mathbf{r},t). \tag{19}$$

We will again assume that we know all of the eigenvalues and eigenfunctions of the reference Hamiltonian

$$\mathcal{H}_0 \Phi_n^0 = E_n^0 \Phi_n^0. \tag{20}$$

In this case, the time dependence of the zero order eigenfunctions takes the form:

$$\Phi_n^0(\mathbf{r},t) = \phi_n^0(\mathbf{r}) \mathrm{e}^{-iE_n^0 t/\hbar}. \tag{21}$$

The spatial functions $\phi_n^0(\mathbf{r})$ form a complete orthonormal set of functions. The full solution is expected to take the form

$$\Phi(\mathbf{r},t) = \sum_n a_n(t) \phi_n^0(\mathbf{r}) \mathrm{e}^{-iE_n^0 t/\hbar}, \tag{22}$$

where the coefficients $a_n(t)$ are to be determined from solution of the first order differential equation:

$$\frac{da_n(t)}{dt} = \frac{1}{i\hbar} \sum_m a_m(t) \mathrm{e}^{i(E_n^0 - E_m^0)t/\hbar} \langle \phi_n^0 | \mathcal{H}_1 | \phi_m^0 \rangle. \tag{23}$$

At this point, we have not made any approximations. In order to proceed, we expand the coefficients as a sum of orders of approximation:

$$a_n(t) = a_n^{(0)}(t) + a_n^{(1)}(t) + a_n^{(2)}(t) \ldots. \tag{24}$$

In general we will assume that the system is initially in a well-defined state of the zero order Hamiltonian:

$$a_m^{(0)}(t) = \delta_{nm}. \tag{25}$$

The equation for the first order coefficient then takes the form:

$$a_n^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} dt' \mathrm{e}^{i(E_n^0 - E_m^0)t'/\hbar} \langle \phi_n^0 | \mathcal{H}_1 | \phi_m^0 \rangle (t'). \tag{26}$$

Thus the first order coefficients can be determined from a knowledge of the matrix elements of the time-dependent perturbation $\mathcal{H}_1(\mathbf{r},t)$. 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 $t = 0$:

$$\mathcal{H}_1(\mathbf{r},t) = V(\mathbf{r}) \left(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t} \right) \Theta(t), \tag{27}$$

where $\Theta(t)$ denotes the Heaviside step function. If the system is initially $(t < 0)$ in the zero order state Φ_n^0, the effects of the perturbation to first order in V is given by

$$\Phi_n(\mathbf{r},t) \approx \phi_n^0(\mathbf{r}) \mathrm{e}^{-iE_n^0 t/\hbar} + \sum_m a_m^{(1)}(t) \phi_m^0(\mathbf{r}) \mathrm{e}^{-iE_m^0 t/\hbar}, \tag{28}$$

where

$$a_m^{(1)}(t) = -\frac{V_{mn}}{i\hbar}\left[\frac{\mathrm{e}^{i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega} - \frac{\mathrm{e}^{i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega}\right]. \tag{29}$$

In this expression, $\omega_{mn} \equiv \frac{E_m^0 - E_n^0}{\hbar}$. For large times t, it can be shown that the squared modulus of the exitation coefficient $a_m^{(1)}(t)$ determines the transition rate:

$$R_{n\to m} = \frac{|a_m^{(1)}(t)|^2}{t} \approx \frac{2\pi}{\hbar^2}|V_{mn}|^2\left(\delta(\omega_{mn}+\omega) + \delta(\omega_{mn}-\omega)\right), \tag{30}$$

or

$$R_{n\to m} \approx \frac{2\pi}{\hbar}|V_{mn}|^2\left(\delta(E_m^0 - E_n^0 + \hbar\omega) + \delta(E_m^0 - E_n^0 - \hbar\omega)\right). \tag{31}$$