January 25, 2003

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:

$$\left(\begin{array}{lllll} E_{n_1}^0 + V_{n_1 n_1} & V_{n_1 n_2} & V_{n_1 n_3} & \ldots & V_{n_1 n_N} \\ V_{n_2 n_1} & E_{n_2}^0 + V_{n_2 n_2} & V_{n_2 n_3} & \ldots & V_{n_3 n_N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ V_{n_N n_1} & V_{n_N n_3} & V_{n_N n_3} & \ldots & E_{n_N}^0 + V_{n_N n_N} \end{array} \right) \left(\begin{array}{c} C_{n_1}^\alpha \\ C_{n_2}^\alpha \\ \vdots \\ C_{n_N}^\alpha \end{array} \right) = E^\alpha \left(\begin{array}{c} C_{n_1}^\alpha \\ C_{n_2}^\alpha \\ \vdots \\ C_{n_N}^\alpha \end{array} \right) \tag{4}$$

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

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

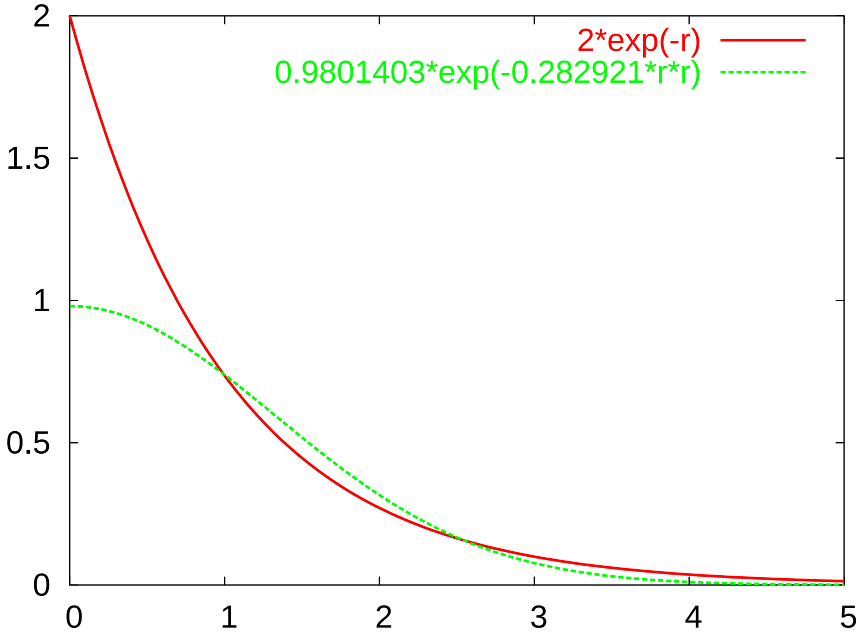
We can then evaluate the minimum energy:

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

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.