Perturbation Theory from Finite Basis Set Expansion

Terry P. Orlando
February 9, 2004

Consider the Hamiltonian

$$\hat{H} = \hat{H}_o + \hat{V}(\mathbf{r}) \tag{1}$$

and we wish to solve the Schrödinger Equation:

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{2}$$

Assume a finite linear basis set expansion of 2 states:

$$\Phi(\mathbf{r}) = c_1\phi_1^0(\mathbf{r}) + c_2\phi_2^0(\mathbf{r}))$$

where

$$\hat{H}_0\phi_i^0(\mathbf{r}) = E_i^0\phi_i^0(\mathbf{r})$$

The best estimate for the energy is

$$\begin{pmatrix} E_1^0 + V_{11} & V_{12} \\ V_{21} & E_2^0 + V_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Therefore:

$$\begin{vmatrix} E_1^0 + V_{11} - E & V_{12} \\ V_{21} & E_2^0 + V_{22} - E \end{vmatrix} = 0$$

And the Energy is

$$E_{1,2} = \frac{E_2^0 + V_{22} + E_1^0 + V_{11}}{2} \mp \sqrt{\left(\frac{E_2^0 + V_{22} - E_1^0 - V_{11}}{2}\right)^2 + |V_{12}|^2}$$

If $E_2^0 + V_{22} - E_1^0 - V_{11} \gg |V_{12}|$, then to 2nd order in $|V_{12}|$,

$$E_1 \approx E_1^0 + V_{11} + \frac{|V_{12}|^2}{E_1^0 + V_{11} - E_2^0 - V_{22}}$$

and

$$E_2 \approx E_2^0 + V_{22} + \frac{|V_{12}|^2}{E_2^0 + V_{22} - E_1^0 - V_{11}}$$

Likewise, the corresponding wave functions for these energies to first order in $|V_{12}|$ are,

$$\begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{V_{12}}{E_1^0+V_{11}-E_2^0-V_{22}} \end{pmatrix}$$

and

$$\begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{V_{21}}{E_2^0+V_{22}-E_1^0-V_{11}} \end{pmatrix}$$

If all the V's are small compared to the energies, then

(a) to **first order** in V,

$$E_1^{(1)} = E_1^0 + V_{11}$$

and

$$E_2^{(1)} = E_2^0 + V_{22}$$

and the corresponding wave functions are

$$\Phi_1(x) \approx \phi_1(x)$$

and

$$\Phi_2(x) \approx \phi_2(x)$$

(b) and to **second order** in V,

$$E_1^{(2)} = E_1^0 + V_{11} + \frac{|V_{12}|^2}{E_1^0 - E_2^0}$$

and

$$E_2^{(2)} = E_2^0 + V_{22} + \frac{|V_{12}|^2}{E_2^0 - E_1^0}$$

with wave functions

$$\Phi_1(x) \approx \phi_1(x) + \frac{V_{12}}{E_1^0 - E_2^0}\phi_2(x)$$

and

$$\Phi_2(x) \approx \phi_2(x) + \frac{V_{21}}{E_2^0 - E_1^0}\phi_1(x)$$

Note these expansions assume that $E_2^0 \neq E_1^0$.

What if $E_2^0 = E_1^0$? or What if $E_2^0 \approx E_1^0$?

Now Assume a finite linear basis set expansion of with **3 states**:

$$\Phi(\mathbf{r}) = c_1\phi_1^0(\mathbf{r}) + c_2\phi_2^0(\mathbf{r}) + c_3\phi_3^0(\mathbf{r})$$

where

$$\hat{H}_0\phi_i^0(\mathbf{r}) = E_i^0\phi_i^0(\mathbf{r})$$

The best estimate for the energy is

$$\begin{pmatrix} E_1^0 + V_{11} & V_{12} & V_{13} \\ V_{21} & E_2^0 + V_{22} & V_{23} \\ V_{31} & V_{32} & E_3^0 + V_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

Therefore:

$$\begin{vmatrix} E_1^0 + V_{11} - E & V_{12} & V_{13} \\ V_{21} & E_2^0 + V_{22} - E & V_{23} \\ V_{31} & V_{32} & E_3^0 + V_{33} - E \end{vmatrix} = 0$$

Expanding the determinant, we have

$$\begin{aligned} 0 = & \quad (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E) \\ - & \quad (E_1 + V_{11} - E)V_{23}V_{32} \\ - & \quad (E_2 + V_{22} - E)V_{31}V_{13} \\ - & \quad (E_3 + V_{33} - E)V_{21}V_{12} \\ + & \quad V_{12}V_{23}V_{31} + V_{13}V_{32}V_{12} \end{aligned}$$

To first order in V, need only the first line so that

$$0 \approx (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E)$$

and we find

$$E_1^{(1)} \approx E_1^0 + V_{11}$$

and

$$E_2^{(1)} \approx E_2^0 + V_{22}$$

and

$$E_3^{(1)} \approx E_3^0 + V_{33}$$

To second order in V one needs the first 4 lines so that

$$
\begin{aligned}
0 \approx \quad & (E_1 + V_{11} - E)(E_2 + V_{22} - E)(E_3 + V_{33} - E) \\
- \quad & (E_1 + V_{11} - E) V_{23} V_{32} \\
- \quad & (E_2 + V_{22} - E) V_{31} V_{13} \\
- \quad & (E_3 + V_{33} - E) V_{21} V_{12}
\end{aligned}
$$

so that

$$E_1^{(2)} \approx E_1^0 + V_{11} + \frac{|V_{12}|^2}{E_1^0 - E_2^0} + \frac{|V_{13}|^2}{E_1^0 - E_3^0}$$

and

$$E_2^{(2)} \approx E_2^0 + V_{22} + \frac{|V_{12}|^2}{E_2^0 - E_1^0} + \frac{|V_{23}|^2}{E_2^0 - E_3^0}$$

and

$$E_3^{(2)} \approx E_3^0 + V_{33} + \frac{|V_{13}|^2}{E_3^0 - E_1^0} + \frac{|V_{23}|^2}{E_3^0 - E_2^0}$$

In general,

$$E_n^{(2)} \approx E_n^0 + V_{nn} + \sum_{p \neq n} \frac{|V_{np}|^2}{E_n^0 - E_p^0} \qquad \text{provided} \qquad E_n^0 \neq E_p^0$$

and

$$|\Phi_n\rangle \approx |\phi_n\rangle + \sum_{p \neq n} \frac{V_{pn}}{E_n^0 - E_p^0} |\phi_p\rangle \qquad \text{provided} \qquad E_n^0 \neq E_p^0$$

This is known as **non-degenerate perturbation theory**.