Perturbation Theory

Frequently one wants to solve the eigenvalue problem

$$\hat{H}\Phi_\mu = E_\mu \Phi_\mu \text{ where } \mu = 0,1,2,\cdots,\infty$$

and $\hat{H}$ is the sum of two terms,

$$\hat{H} = \hat{H}^0 + (\hat{H} - \hat{H}^0) = \hat{H}^0 + \hat{V}$$

where one knows the eigenfunctions and eigenvalues of $\hat{H}^0$

$$\hat{H}^0 \Phi_\mu^0 = E_\mu^0 \Phi_\mu^0$$

$\hat{V}$ is called the perturbation and to the extent that $\hat{V}$ is (in some sense) small relative to $\hat{H}^0$ we expect the eigenfunctions and eigenvalues of $\hat{H}$ to be similar to those of $\hat{H}^0$. A powerful approach to the solution of the original eigenvalue problem is to use Rayleigh Schrodinger perturbation theory, which we will now develop. We begin by introducing the fictious Hamiltonian

$$\hat{H}(\lambda) = \hat{H}^0 + \lambda\hat{V}$$

which is equal to the Hamiltonian of interest , $\hat{H}$ when $\lambda = 1$ and to the Hamiltonian $\hat{H}^0$ whose eigenvalues and eigenfunctions we know, when $\lambda = 0$. λ is often called the ordering parameter.

The eigenvalue problem for $\hat{H}(\lambda)$ is

$$\hat{H}(\lambda)\Phi_\mu(\lambda) = E_\mu(\lambda)\Phi_\mu(\lambda)$$

where we note that $\Phi_\mu(\lambda)$ & $E_\mu(\lambda)$ are functions of λ .We assume that both Φ_μ & E_μ have a Maclaurin series expansion in λ and write

$$\Phi_\mu(\lambda) = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!}\left(\frac{d^N\Phi_\mu(\lambda)}{d\lambda^N}\right)_{\lambda=0} = \sum_{N=0}^{\infty}\lambda^N \Phi_\mu^{(N)}$$

and

$$E_\mu(\lambda) = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!}\left(\frac{d^N E_\mu(\lambda)}{d\lambda^N}\right)_{\lambda=0} = \sum_{N=0}^{\infty}\lambda^N E_\mu^{(N)}$$

Inserting these expansions into the Schrodinger equation gives

$$\left(\hat{H}+\lambda\hat{V}\right)\sum_{N=0}^{\infty}\lambda^N\Phi_\mu^{(N)}=\sum_{P=0}^{\infty}\lambda^P E_\mu^{(P)}\sum_{Q=0}^{\infty}\lambda^Q\Phi_\mu^{(Q)}$$

The right hand side may be rewritten as

$$\sum_{P=0}^{\infty}\lambda^P E_\mu^{(P)}\sum_{Q=0}^{\infty}\lambda^Q\Phi_\mu^{(Q)}=\sum_{N=0}^{\infty}\lambda^N\sum_{P=1}^{N}E_\mu^{(P)}\Phi_\mu^{(N-P)}$$

From which we obtain

$$\sum_{N=0}^{\infty}\lambda^N\left(\hat{H}\Phi_\mu^N+(1-\delta_{N0})\hat{V}\Phi_\mu^{N-1}-\sum_{P=1}^{N}E_\mu^P\Phi_\mu^{N-P}\right)=0$$

and since we want this to be true for arbitrary λ we set the coefficient of λ^N equal to zero and obtain the Rayleigh-Schrodinger equations.

$$\hat{H}\Phi_\mu^N+(1-\delta_{N0})\hat{V}\Phi_\mu^{N-1}-\sum_{P=1}^{N}E_\mu^P\Phi_\mu^{N-P}=0\text{, for } N=0,1,2,\cdots,\infty \text{ and } \mu=0,1,2,\cdots,\infty$$

The first equation in this sequence is

$$\hat{H}\Phi_\mu^0=E_\mu^0\Phi_\mu^0$$

and is recognized as the unperturbed problem for which we know all of the eigenvalues and eigenfunctions. The next, or first order equation, is

$$\hat{H}\Phi_\mu^{(1)}+\hat{V}\Phi_\mu^0=E_\mu^{(1)}\Phi_\mu^0+E_\mu^0\Phi_\mu^{(1)}$$

Keep in mind that the unknowns are the first order correction to the energy and wavefunction, $E_\mu^{(1)}$ & $\Phi_\mu^{(1)}$. To find $E_\mu^{(1)}$ we multiply both sides of the above equation by the complex conjugate of the unperturbed solution, Φ_μ^0 and integrate. This gives us

$$\left\langle\Phi_\mu^0\middle|\hat{H}\middle|\Phi_\mu^{(1)}\right\rangle+\left\langle\Phi_\mu^0\middle|\hat{V}\middle|\Phi_\mu^0\right\rangle=E_\mu^{(1)}\left\langle\Phi_\mu^0\middle|\Phi_\mu^0\right\rangle+E_\mu^0\left\langle\Phi_\mu^0\middle|\Phi_\mu^{(1)}\right\rangle$$

and because $\hat{H}$ is Hermetian we find that the first order correction to the energy is simply the average of the perturbing potential over the unperturbed wavefunction.

$$\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\mu^0 \right\rangle = E_\mu^{(1)}$$

We will leave the determination of $\Phi_\mu^{(1)}$ for the time being and consider the second order equation

$$\hat{H}\Phi_\mu^{(2)} + \hat{V}\Phi_\mu^{(1)} = E_\mu^{(2)}\Phi_\mu^0 + E_\mu^{(1)}\Phi_\mu^{(1)} + E_\mu^0\Phi_\mu^{(2)}$$

To isolate $E_\mu^{(2)}$ we once again multiply both sides by the complex conjugate of the unperturbed solution and integrate. This results in

$$\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\mu^{(1)} \right\rangle = E_\mu^{(2)} + E_\mu^{(1)} \left\langle \Phi_\mu^0 \middle| \Phi_\mu^{(1)} \right\rangle$$

To deal with $\left\langle \Phi_\mu^0 \middle| \Phi_\mu^{(1)} \right\rangle$, the coefficent of $E_\mu^{(1)}$, we need to consider the normalization of the perturbed solution, $\Phi_\mu(\lambda)$. Rather than selecting the conventional normalization

$$\left\langle \Phi_\mu(\lambda) \middle| \Phi_\mu(\lambda) \right\rangle = 1$$

we will choose the more convenient *intermediate* normalization in which the overlap between the perturbed and unperturbed wavefunctions is taken to be 1, i.e.,

$$\left\langle \Phi_\mu(\lambda) \middle| \Phi_\mu^0 \right\rangle = 1$$

Of course after we obtain $\Phi_\mu(\lambda)$ we may renormalize it to 1. Intermediate normalization is convenient because it requires that the unperturbed wavefunction Φ_μ^0 is orthogonal to all of the corrections $\Phi_\mu^{(N)}$,

$$\left\langle \Phi_\mu^0 \middle| \Phi_\mu^{(N)} \right\rangle = \delta_{0N}$$

Returning to the second order equation we see that $\left\langle \Phi_\mu^0 \middle| \Phi_\mu^{(1)} \right\rangle = 0$ and so the second order correction to the energy is

$$\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\mu^{(1)} \right\rangle = E_\mu^{(2)}$$

where as yet we do not know $\Phi_\mu^{(1)}$. Lets determine $E_\mu^{(3)}$ before find $\Phi_\mu^{(1)}$. Writing the third order equation

$$\hat{H}\Phi_\mu^{(3)} + \hat{V}\Phi_\mu^{(2)} = E_\mu^{(3)}\Phi_\mu^0 + E_\mu^{(2)}\Phi_\mu^{(1)} + E_\mu^{(1)}\Phi_\mu^{(2)} + E_\mu^0\Phi_\mu^{(3)}$$

multiplying by the complex conjugate of Φ_μ^0 and integrating we obtain

$$\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\mu^{(2)} \right\rangle = E_\mu^{(3)}$$

We may write this in terms of $\Phi_\mu^{(1)}$ as follows. From the first order equation we have

$$\hat{V}\Phi_\mu^0 = -\hat{H}\Phi_\mu^{(1)} + E_\mu^{(1)}\Phi_\mu^0 + E_\mu^0\Phi_\mu^{(1)}$$

and since

$$\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\mu^{(2)} \right\rangle = E_\mu^{(3)} = \left\langle \hat{V}\Phi_\mu^0 \middle| \Phi_\mu^{(2)} \right\rangle$$

we have

$$E_\mu^{(3)} = -\left\langle \Phi_\mu^{(1)} \middle| \hat{H} \middle| \Phi_\mu^{(2)} \right\rangle$$

Using the second order equation this becomes

$$E_\mu^{(3)} = \left\langle \Phi_\mu^{(1)} \middle| \hat{V} \middle| \Phi_\mu^{(1)} \right\rangle$$

and the third order correction to the energy is determined by the first order correction to the wavefunction. This is an example of the $2N+1$ rule, which states that the corrections to the wavefunction through N^{th} order determines the corrections to the energy through $(2N+1)^{th}$ order. Lets know find $\Phi_\mu^{(1)}$, the first order correction to the wavefunction. Occasionally one can solve the differential equation directly for $\Phi_\mu^{(1)}$ and we illustrate this approach in the examples. Most of the time however this is not possible and a more general approach is called for.

We will assume that the function $\Phi_\mu^{(1)}$ can be expanded in the eigenfunctions of the unperturbed hamitonian, $\hat{H}$ so that

$$\Phi_\mu^{(1)} = \sum_{\nu \neq \mu} \Phi_\nu^0 C_{\nu\mu}$$

where we exclude the unperturbed state Φ_μ^0 from the summation because $\left\langle \Phi_\mu^0 \middle| \Phi_\mu^{(1)} \right\rangle = 0$

To determine the coefficients $C_{\nu\mu}$ we insert the expansion into the first order equation , multiply through by the complex conjugate of one of the unperturbed eigenfunctions, say Φ_η^0 and integrate. This results in

$$C_{\eta\mu} = \frac{\left\langle \Phi_\eta^0 \middle| \hat{V} \middle| \Phi_\mu^0 \right\rangle}{E_\mu^0 - E_\eta^0}$$

and therefore

$$\Phi_\mu^{(1)} = \sum_{\nu\neq\mu} \frac{\left\langle \Phi_\nu^0 \middle| \hat{V} \middle| \Phi_\mu^0 \right\rangle \Phi_\nu^0}{E_\mu^0 - E_\nu^0}$$

Using this expression the second and third order corrections to the energy become

$$E_\mu^{(2)} = \sum_{\nu\neq\mu} \frac{\left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\nu^0 \right\rangle \left\langle \Phi_\nu^0 \middle| \hat{V} \middle| \Phi_\mu^0 \right\rangle}{E_\mu^0 - E_\nu^0} = \sum_{\nu\neq\mu} \frac{\left| \left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\nu^0 \right\rangle \right|^2}{E_\mu^0 - E_\nu^0} = \sum_{\nu\neq\mu} \frac{\left| V_{\mu\nu} \right|^2}{E_{\mu\nu}^0}$$

where

$$V_{\mu\nu} = \left\langle \Phi_\mu^0 \middle| \hat{V} \middle| \Phi_\nu^0 \right\rangle \;\;\&\;\; E_{\mu\nu}^0 = E_\mu^0 - E_\nu^0$$

and

$$E_\mu^{(3)} = \sum_{\nu\neq\mu} \sum_{\sigma\neq\mu} \frac{V_{\mu\nu} V_{\nu\sigma} V_{\sigma\mu}}{E_{\mu\nu}^0 E_{\mu\sigma}^0}$$