Non-degenerate Perturbation Theory

Suppose one wants to solve the eigenvalue problem

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

and where $\hat{H}$ can be written as the sum of two terms,

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

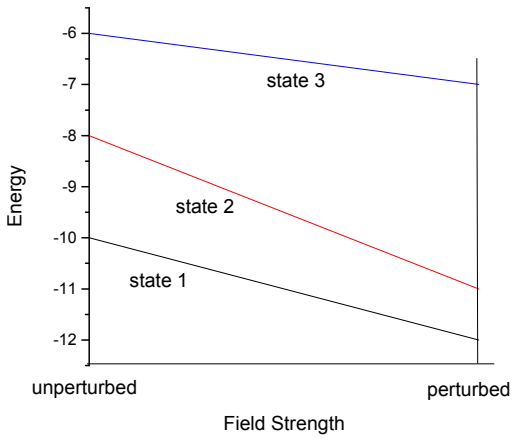
and where one knows the eigenfunctions and eigenvalues of $\hat{H}^0$

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

The difference between the two Hamiltonians, $\hat{V}$ 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 $\hat{H}^0$. The perturbation $\hat{V}$ could be the result of putting the original system in an electric or magnetic field.
For example a hydrogen atom in a constant electric field F along the z axis has the perturbation

$$\hat{V} = -ezF\cos(\theta)$$

where θ is the angle between the position vector to the electron an the electric field F.
In this instance the energy and eigenfunctions of the perturbed Hamiltonian depend parametrically on the electric field. As illustrated in the figure below, the energy and the wavefunction of the various unperturbed states varies with field strength.



Sometimes the form of the perturbation is subtle. For example we might be interested in the effect of the size of the nucleus on the energy of a one-electron atom. When we ignore the size of the nucleus we write the electrostatic potential experienced by the electron as

$\frac{-Ze^2}{4\pi\varepsilon_0 r}$ where $0 \le r < \infty$.

When we take the size of the nucleus into account the potential becomes

$$\frac{-Ze^2}{4\pi\varepsilon_0 R_0} \; for \; 0 \le r \le R_0 \; and \; \frac{-Ze^2}{4\pi\varepsilon_0 r} \; for \; R_0 \le r < \infty$$

where R_0 is the radius of the nucleus and the perturbation then becomes

$$\hat{V} = \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{1}{R_0}\right) for \; 0 \le r \le R_0 \; and \; 0 \; for \; R_0 \le r < \infty$$

In this instance there isn't an external parameter like an electric field.
Both types of perturbations may be dealt with using Rayleigh Schrodinger perturbation theory, which we will now develop. We begin by introducing the Hamiltonian

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

when the perturbation is due to an external field λ is the field strength. If there is no external field $\hat{H}(\lambda)$ is a fictitious Hamiltonian that 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. Lets suppose that we are interested in the effect of the perturbation on the Φ_0^0 state of the unperturbed system so the eigenvalue problem for $\hat{H}(\lambda)$ is

$$\hat{H}(\lambda)\Phi_0(\lambda) = E_0(\lambda)\Phi_0(\lambda)$$

where as $\lambda \to 0 \quad \Phi_0(\lambda) \;\&\; E_0(\lambda) \to \Phi_0^0 \;\&\; E_0^0$. We assume that both $\Phi_0(\lambda) \;\&\; E_0(\lambda)$ have a Maclaurin series expansion in λ and write

$$\Phi_0(\lambda) = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!}\left(\frac{d^N\Phi_0(\lambda)}{d\lambda^N}\right)_{\lambda=0} = \sum_{N=0}^{\infty} \lambda^N \Phi_0^{(N)}$$

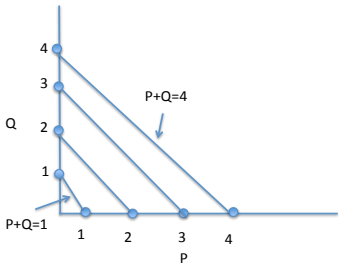
and

$$E_0(\lambda)=\sum_{N=0}^{\infty}\frac{\lambda^N}{N!}\left(\frac{d^N E_0(\lambda)}{d\lambda^N}\right)_{\lambda=0}=\sum_{N=0}^{\infty}\lambda^N E_0^{(N)}$$

Inserting these expansions into the Schrodinger equation gives

$$\left(\hat{H}^0+\lambda\hat{V}\right)\sum_{N=0}^{\infty}\lambda^N\Phi_0^{(N)}=\sum_{P=0}^{\infty}\sum_{Q=0}^{\infty}\lambda^{Q+P}E_0^{(P)}\Phi_0^{(Q)}$$

The sum $\sum_{P=0}^{\infty}\sum_{Q=0}^{\infty}\lambda^{Q+P}E_0^{(P)}\Phi_0^{(Q)}$ may be transformed to a more convenient form as follows.



If we let $N=P+Q$ then we can cover all points in the PQ plane by summing along the diagonals

$$\sum_{P=0}^{\infty}\sum_{Q=0}^{\infty}\lambda^{Q+P}E_0^{(P)}\Phi_0^{(Q)}=\sum_{N=0}^{\infty}\sum_{P=0}^{N}\lambda^N E_0^{(P)}\Phi_0^{(N-P)}=\sum_{N=0}^{\infty}\lambda^N\sum_{P=0}^{N}E_0^{(P)}\Phi_0^{(N-P)}$$

From which we obtain

$$\sum_{N=0}^{\infty}\lambda^N\left(\hat{H}^0\Phi_0^N+(1-\delta_{N0})\hat{V}\Phi_0^{N-1}-\sum_{P=1}^{N}E_0^P\Phi_0^{N-P}\right)=0$$

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.

$$\hat{H}^0\Phi_0^N+(1-\delta_{N0})\hat{V}\Phi_0^{N-1}-\sum_{P=1}^{N}E_0^P\Phi_0^{N-P}=0\text{ , for }N=0,1,2,\cdots,\infty$$

The first equation in this sequence is

$$\hat{H}^0\mathbf{\Phi}_0^0 = E_0^0\mathbf{\Phi}_0^0$$

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

$$\hat{H}^0\mathbf{\Phi}_0^{(1)} + \hat{V}\mathbf{\Phi}_0^0 = E_0^{(1)}\mathbf{\Phi}_0^0 + E_0^0\mathbf{\Phi}_0^{(1)}$$

or

$$\left(\hat{H}^0 - E_0^0\right)\mathbf{\Phi}_0^{(1)} + \left(\hat{V} - E_0^{(1)}\right)\mathbf{\Phi}_0^0 = 0$$

Keep in mind that the unknowns are the first order correction to the energy and wavefunction, $E_0^{(1)}$ & $\mathbf{\Phi}_0^{(1)}$. To find $E_0^{(1)}$ we multiply both sides of the above equation by the complex conjugate of the unperturbed solution, $\mathbf{\Phi}_0^0$ and integrate. This gives us

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{H}^0 - E_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle + \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} - E_0^1 \middle| \mathbf{\Phi}_0^0 \right\rangle = 0$$

and because $\hat{H}^0$ is Hermitian

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{H}^0 - E_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = 0$$

and the first order correction to the energy is simply the average of the perturbing potential over the unperturbed wavefunction.

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^0 \right\rangle = E_0^{(1)}$$

Note that this result depends on the eigenvalue E_0^0 being non-degenerate. If for example the unperturbed function Φ_1^0 (orthogonal to Φ_0^0) also has the eigenvalue E_0^0 and we formed

$$\left\langle \mathbf{\Phi}_1^0 \middle| \hat{H}^0 - E_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle + \left\langle \mathbf{\Phi}_1^0 \middle| \hat{V} - E_0^1 \middle| \mathbf{\Phi}_0^0 \right\rangle = 0$$

we now have

$$\left\langle \mathbf{\Phi}_1^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^0 \right\rangle = 0$$

which may not be true. This possibility is addressed in our discussion of degenerate perturbation theory and we will continue this discussion assuming the state we are considering is non-degenerate.

We will leave the determination of $\mathbf{\Phi}_0^{(1)}$ for the time being and consider the second order equation

$$\left(\hat{H}^0 - E_0^0\right)\mathbf{\Phi}_0^{(2)} + \left(\hat{V} - E_0^{(1)}\right)\mathbf{\Phi}_0^{(1)} = E_0^{(2)}\mathbf{\Phi}_0^0$$

To isolate $E_0^{(2)}$ we once again multiply both sides by the complex conjugate of the unperturbed solution and integrate. And because $\hat{H}^0$ is Hermitian this results in

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} - E_0^{(1)} \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = E_0^{(2)}$$

To deal with $\left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle$, the coefficient of $E_0^{(1)}$, we need to consider the normalization of the perturbed solution, $\mathbf{\Phi}_0(\lambda)$. Rather than selecting the conventional normalization

$$\left\langle \mathbf{\Phi}_0(\lambda) \middle| \mathbf{\Phi}_0(\lambda) \right\rangle = 1$$

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

$$\left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0(\lambda) \right\rangle = 1 = \left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^0 \right\rangle + \left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle \lambda + \left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(2)} \right\rangle \lambda^2 + \left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(3)} \right\rangle \lambda^3 + \cdots$$

Of course after we obtain $\mathbf{\Phi}_0(\lambda)$ we may renormalize it to 1. Intermediate normalization is convenient because it requires that all of the corrections $\mathbf{\Phi}_0^{(N)}$, are orthogonal to the unperturbed wavefunction $\mathbf{\Phi}_0^0$

$$\left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(N)} \right\rangle = \delta_{0N}$$

Returning to the second order equation we see that $\left\langle \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = 0$ and so the second order correction to the energy is

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = E_0^{(2)}$$

and as yet we do not know $\mathbf{\Phi}_0^{(1)}$. It is interesting that $E_0^{(2)}$ is always negative. We may show this as follows.

$$E_0^{(2)} = \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} - E_0^{(1)} \middle| \mathbf{\Phi}_0^{(1)} \right\rangle = \left\langle (\hat{V} - E_0^{(1)}) \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle$$

From the first order equation

$$\left(\hat{V} - E_0^{(1)}\right) \mathbf{\Phi}_0^0 = -\left(\hat{H}^0 - E_0^0\right) \mathbf{\Phi}_0^{(1)}$$

So

$$E_0^{(2)} = -\left\langle \mathbf{\Phi}_0^{(1)} \middle| \hat{H}^0 - E_0^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle$$

But from the variation principle

$$\left\langle \mathbf{\Phi}_0^{(1)} \middle| \hat{H}^0 \middle| \mathbf{\Phi}_0^{(1)} \right\rangle \geq E_0^0 \quad \text{, and } \therefore E_0^{(2)} \leq 0$$

Lets continue and determine $E_0^{(3)}$. Writing the third order equation

$$\left(\hat{H}^0 - E_0^0\right) \mathbf{\Phi}_0^{(3)} + \left(\hat{V} - E_0^{(1)}\right) \mathbf{\Phi}_0^{(2)} = E_0^{(3)} \mathbf{\Phi}_0^0 + E_0^{(2)} \mathbf{\Phi}_0^{(1)}$$

multiplying by the complex conjugate of $\mathbf{\Phi}_0^0$ and integrating we obtain

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} - E_0^{(1)} \middle| \mathbf{\Phi}_0^{(2)} \right\rangle = \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^{(2)} \right\rangle = E_0^{(3)}$$

We may write this in terms of $\mathbf{\Phi}_0^{(1)}$ as follows. As we have seen from the first order equation we have

$$(\hat{V} - E_0^{(1)}) \mathbf{\Phi}_0^0 = -(\hat{H}^0 - E_0^0) \mathbf{\Phi}_0^{(1)}$$

and since

$$\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} - E_0^{(1)} \middle| \mathbf{\Phi}_0^{(2)} \right\rangle = E_0^{(3)} = \left\langle (\hat{V} - E_0^{(1)}) \mathbf{\Phi}_0^0 \middle| \mathbf{\Phi}_0^{(2)} \right\rangle$$

we have

$$E_0^{(3)} = -\left\langle \Phi_0^{(1)} \middle| \hat{H}^0 - E_0^0 \middle| \Phi_0^{(2)} \right\rangle$$

Using the second order equation this becomes

$$E_0^{(3)} = \left\langle \Phi_0^{(1)} \middle| \hat{V} - E_0^{(1)} \middle| \Phi_0^{(1)} \right\rangle$$

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 corrections to the wavefunction through N^{th} order determines the corrections to the energy through $(2N+1)^{th}$ order. Let's now find $\Phi_0^{(1)}$, the first order correction to the wavefunction. Occasionally one can solve the differential equation directly for $\Phi_0^{(1)}$ 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 $\Phi_0^{(1)}$ can be expanded in the eigenfunctions of the unperturbed Hamiltonian, $\hat{H}^0$ so that

$$\Phi_0^{(1)} = \sum_{\nu \neq 0} \Phi_\nu^0 C_{\nu 0}$$

where we exclude the unperturbed state Φ_0^0 from the summation because $\left\langle \Phi_0^0 \middle| \Phi_0^{(1)} \right\rangle = 0$

To determine the coefficients $C_{\nu 0}$ 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

$$C_{\eta 0} = \frac{\left\langle \Phi_\eta^0 \middle| \hat{V} \middle| \Phi_0^0 \right\rangle}{E_0^0 - E_\eta^0}$$

and therefore

$$\Phi_0^{(1)} = \sum_{\nu \neq 0} \frac{\left\langle \Phi_\nu^0 \middle| \hat{V} \middle| \Phi_0^0 \right\rangle \Phi_\nu^0}{E_0^0 - E_\nu^0}$$

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

$$E_0^{(2)} = \sum_{\nu \neq 0} \frac{\left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_\nu^0 \right\rangle \left\langle \mathbf{\Phi}_\nu^0 \middle| \hat{V} \middle| \mathbf{\Phi}_0^0 \right\rangle}{E_0^0 - E_\nu^0} = \sum_{\nu \neq 0} \frac{\left| \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_\nu^0 \right\rangle \right|^2}{E_0^0 - E_\nu^0} = \sum_{\nu \neq 0} \frac{\left| V_{0\nu} \right|^2}{E_{0\nu}^0}$$

where

$$V_{0\nu} = \left\langle \mathbf{\Phi}_0^0 \middle| \hat{V} \middle| \mathbf{\Phi}_\nu^0 \right\rangle \;\; \& \;\; E_{0\nu}^0 = E_0^0 - E_\nu^0$$

and in a similar fashion

$$E_0^{(3)} = \sum_{\nu \neq 0} \sum_{\sigma \neq 0} \frac{V_{0\nu} V_{\nu\sigma} V_{\sigma 0}}{E_{0\nu}^0 E_{0\sigma}^0} - V_{00} \sum_{\nu \neq 0} \frac{\left| V_{0\nu} \right|^2}{\left| E_{0\nu}^0 \right|^2}$$