1 Rayleigh-Schrödinger Perturbation Theory

The exact Hamiltonian is partitioned into a 0^{th} order component (unperturbed system) and a perturbation:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \tag{1}$$

where λ is the order parameter. The n^{th} exact wavefunction Ψ_n is an eigenfunction to the Hamiltonian:

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle \tag{2}$$

and the unperturbed system is already solved:

$$\hat{H}_0|\Psi_n^{(0)}\rangle = E_n^{(0)}|\Psi_n^{(0)}\rangle \tag{3}$$

Ψ_n and E_n could be expanded as:

$$|\Psi_n\rangle = |\Psi_n^{(0)}\rangle + \lambda|\Psi_n^{(1)}\rangle + \lambda^2|\Psi_n^{(2)}\rangle + \dots = \sum_{i=0} \lambda^i|\Psi_n^{(i)}\rangle \tag{4}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots = \sum_{i=0} \lambda^i E_n^{(i)} \tag{5}$$

Substitute these expansions into the Schrödinger equation:

$$\begin{aligned}
0 =& (\hat{H} - E_n)|\Psi_n\rangle \\
0 =& (\hat{H} - \sum_{j=0} \lambda^j E_n^{(j)}) \sum_{i=0} \lambda^i |\Psi_n^{(i)}\rangle \\
0 =& (\hat{H}_0 - E_n^{(0)} + \lambda\hat{V} - \lambda E_n^{(1)} - \lambda^2 E_n^{(2)} + \dots)(|\Psi_n^{(0)}\rangle + \lambda|\Psi_n^{(1)}\rangle + \lambda^2|\Psi_n^{(2)}\rangle + \dots)
\end{aligned} \tag{6}$$

By collecting the terms with matching orders of λ, we can obtain one equation for each order:

$$\lambda^0 : 0 = (\hat{H}_0 - E_n^{(0)})|\Psi_n^{(0)}\rangle \tag{7}$$

$$\lambda^1 : 0 = (\hat{H}_0 - E_n^{(0)})|\Psi_n^{(1)}\rangle + (\hat{V} - E_n^{(1)})|\Psi_n^{(0)}\rangle \tag{8}$$

$$\lambda^2 : 0 = (\hat{H}_0 - E_n^{(0)})|\Psi_n^{(2)}\rangle + (\hat{V} - E_n^{(1)})|\Psi_n^{(1)}\rangle - E_n^{(2)}|\Psi_n^{(0)}\rangle \tag{9}$$

$$\dots$$

$$\lambda^m : 0 = (\hat{H}_0 - E_n^{(0)})|\Psi_n^{(m)}\rangle + (\hat{V} - E_n^{(1)})|\Psi_n^{(m-1)}\rangle - \sum_{l=0}^{m-2} E_n^{(m-l)}|\Psi_n^{(l)}\rangle \tag{10}$$

The general m^{th} equation could be re-written as:

$$\hat{H}_0|\Psi_n^{(m)}\rangle + \hat{V}|\Psi_n^{(m-1)}\rangle = \sum_{l=0}^{m} E_n^{(m-l)}|\Psi_n^{(l)}\rangle \tag{11}$$

1.1 Energy Correction

The energy correction of each order could be obtained by projecting $\langle\Psi_n^{(0)}|$ onto corresponding equation (and denoting $\Psi_n^{(0)}$ as Φ_n):

$$\langle\Phi_n|\hat{H}_0|\Psi_n^{(m)}\rangle + \langle\Phi_n|\hat{V}|\Psi_n^{(m-1)}\rangle = \sum_{l=0}^{m} E_n^{(m-l)}\langle\Phi_n|\Psi_n^{(l)}\rangle \tag{12}$$

$$\langle\hat{H}_0\Phi_n|\Psi_n^{(m)}\rangle + \langle\Phi_n|\hat{V}|\Psi_n^{(m-1)}\rangle = \sum_{l=0}^{m} E_n^{(m-l)}\delta_{0l}$$

$$E_n^{(0)}\delta_{0m} + \langle\Phi_n|\hat{V}|\Psi_n^{(m-1)}\rangle = E_n^{(m)}$$

where we employed the intermediate normalisation condition:

$$\langle\Phi_n|\Psi_n^{(m)}\rangle = \delta_{m0} \tag{13}$$

Therefore, we can obtain the m^{th} order energy correction ($m > 0$) as:

$$E_n^{(m)} = \langle\Phi_n|\hat{V}|\Psi_n^{(m-1)}\rangle \tag{14}$$

1.2 Wavefunction Expansion

The perturbed wavefunctions could be expanded in a set of 0^{th} order wavefunction $\{\Phi_i\}$:

$$|\Psi_n^{(m)}\rangle = \sum_k a_{kn}^{(m)}|\Phi_k\rangle \tag{15}$$

By inserting the resolution of identity:

$$|\Psi_n^{(m)}\rangle = \sum_k |\Phi_k\rangle\langle\Phi_k|\Psi_n^{(m)}\rangle \tag{16}$$

we find that:

$$a_{kn}^{(m)} = \langle\Phi_k|\Psi_n^{(m)}\rangle \tag{17}$$

By the property of Hermitian operator:

$$a_{kn}^{(0)} = \langle\Phi_k|\Phi_n\rangle = \delta_{kn} \tag{18}$$

Also, by the intermediate normalisation condition we have defined:

$$a_{nn}^{(m)} = \langle\Phi_n|\Psi_n^{(m)}\rangle = \delta_{0m} \tag{19}$$

Since we do not need to expand the 0^{th} order wavefunction, we can safely say that $a_{nn}^{(m)} = 0$.

1.3 Wavefunction and Energy Expression

To obtain the exact form of the coefficients thus the wavefunction, we project $\langle\Phi_k|$ onto equations of corresponding order of λ. For example, to obtain $a_{kn}^{(1)}$, we project onto λ^1 equation:

$$\begin{aligned}
0 &= \langle\Phi_k|(\hat{H}_0 - E_n^{(0)})|\Psi_n^{(1)}\rangle + \langle\Phi_k|\hat{V} - E_n^{(1)}|\Phi_n\rangle \\
&= E_k^{(0)}\langle\Phi_k|\Psi_n^{(1)}\rangle - E_n^{(0)}\langle\Phi_k|\Psi_n^{(1)}\rangle + \langle\Phi_k|\hat{V}|\Phi_n\rangle - E_n^{(1)}\langle\Phi_k|\Phi_n\rangle \\
&= E_k^{(0)}a_{kn}^{(1)} - E_n^{(0)}a_{kn}^{(1)} + \langle\Phi_k|\hat{V}|\Phi_n\rangle - E_n^{(1)}\delta_{nk}
\end{aligned} \tag{20}$$

For $k \neq n$, we have:

$$a_{kn}^{(1)} = \frac{\langle\Phi_k|\hat{V}|\Phi_n\rangle}{E_n^{(0)} - E_k^{(0)}} = \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \tag{21}$$

Since $a_{nn}^{(1)} = \langle\Phi_n|\Psi_n^{(1)}\rangle = 0$, it is safe to exclude $n = k$ term in summations of $a_{kn}^{(1)}$. Now we have the expression for 1^{st} order wavefunction:

$$|\Psi_n^{(1)}\rangle = {\sum_k}' a_{kn}^{(1)}|\Phi_k\rangle$$

$$
\begin{aligned}
&= \sum_k{}' \frac{\langle \Phi_k | \hat{V} | \Phi_n \rangle}{E_n^{(0)} - E_k^{(0)}} | \Phi_k \rangle \\
&= \sum_k{}' \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} | \Phi_k \rangle
\end{aligned} \tag{22}
$$

where $\sum_k{}'$ denotes summation without $n = k$. And the 2^{nd} order energy correction follows as:

$$
\begin{aligned}
E_n^{(2)} &= \langle \Phi_n | \hat{V} | \Psi_n^{(1)} \rangle \\
&= \sum_k{}' \langle \Phi_n | \hat{V} | \Phi_k \rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \\
&= \sum_k{}' \frac{V_{nk} V_{kn}}{E_n^{(0)} - E_k^{(0)}} \\
&= \sum_k{}' \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}
\end{aligned} \tag{23}
$$