1 Perturbation Theory - Stationary

An exact solution of the Schrödinger equation exists only for a few idealized problems. Normally, one has to solve the problem using some approximate method. Perturbation Theory is applicable only to those cases in which the real system can be described by a small change in an easily solvable, idealized system. The Hamiltonian of the system can then be written as

perturbation

$$H = H_0 + \lambda V \tag{1}$$

Hamiltonian of the unperturbed system

where H and H_0 do not differ much. The parameter λ is called the SMALLNESS (or perturbation) parameter.

With this approach, we can describe a number of problems, for example in nuclear physics. There, the nucleus provides the strong central potential for the electrons; further interactions of less strength are described as perturbation. Examples are

- magnetic interactions (spin - orbit coupling)
- electrostatic repulsion of the electrons
- influence of external fields

Stationary perturbation theory $\Rightarrow V$ is not a function of time

The basic assumption is that the eigenfunctions and the eigenvalues of the unperturbed system are known, i.e.,

$$H_0|n\rangle_0 = E_n^{(0)}|n\rangle_0 \tag{2}$$

or

$$H_0\psi_n^0 = E_n^{(0)}\psi_n^{(0)} \tag{3}$$

We are then seeking the eigenvalues and the eigenfunctions of the total Hamiltonian H, i.e.,

$$(H_0 + \lambda V)\psi_n = E\psi_n \tag{4}$$

or

$$(H_0 + \lambda V)|n\rangle = E|n\rangle \tag{5}$$

$\uparrow$

perturbed wavefunction

If the deviation of the actual basis functions and eigenvalues from these zero-order ones is small, we can write

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \tag{6}$$

Second-order correction

$$|n\rangle = |n\rangle_0 + \lambda|n\rangle_1 + \lambda^2|n\rangle_2 + \cdots \tag{7}$$

unperturbed

first order correction

Inserting these two series into the SWE, we get

$$\begin{aligned} &(H_0 + \lambda V)\left(|n\rangle_0 + \lambda|n\rangle_1 + \lambda^2|n\rangle_2 + \cdots\right) = \\ &= \left[E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right]\left[|n\rangle_0 + \lambda|n\rangle_1 + \lambda^2|n\rangle_2 + \cdots\right] \end{aligned} \tag{8}$$

Now we group all the terms with the same coefficients λ^n to get

$$\lambda^0 \Rightarrow H_0|n\rangle_0 = E_n^{(0)}|n\rangle_0 \tag{9}$$

$$\lambda^1 \Rightarrow H_0|n\rangle_1 + V|n\rangle_0 = E_n^{(0)}|n\rangle_1 + E_n^{(1)}|n\rangle_0 \tag{10}$$

$$\lambda^2 \Rightarrow H_0|n\rangle_2 + V|n\rangle_1 = E_n^{(2)}|n\rangle_0 + E_n^{(1)}|n\rangle_1 + E_n^{(0)}|n\rangle_2 \tag{11}$$

0^{th} Approximation

If we set $\lambda = 0$, then there is no perturbation, and the above gives

$$(H_0 - E_n^{(0)})|n\rangle_0 = 0 \tag{12}$$

or

$$\left[E_n^{(0)} - E^{(0)}\right]|n\rangle_0 = 0 \tag{13}$$

This means that

$$E^{(0)} = E_n^{(0)} \tag{14}$$

i.e., we get the energy eigenstates of the unperturbed system.

1^{st} Approximation

The first-order approximation, i.e., corrections to the eigenvalues and eigenfunctions are found by solving $\lambda^1 \Rightarrow H_0|n\rangle_1 + V|n\rangle_0 = E_n^{(0)}|n\rangle_1 + E_n^{(1)}|n\rangle_0$, in which we assume that the first order correction $|n\rangle_1$, only slightly deviates from the unperturbed, so that one can write this deviation in terms of the unperturbed functions

$$|n\rangle_1 = \sum_j a_j |j\rangle_0 \tag{15}$$

Substitute this into

$$\left[H_0 - E_n^{(0)}\right] |n\rangle_1 = \left[E_n^{(1)} - V\right] |n\rangle_0 \tag{16}$$

leads to

$$\left(H_0 - E_n^{(0)}\right) \sum_j a_j |j\rangle_0 = \left[E_n^{(1)} - V\right] |n\rangle_0 \tag{17}$$

or

$$\sum_j a_j \left[E_j^{(0)} - E_n^{(0)}\right] |j\rangle_0 = \left[E_n^{(1)} - V\right] |n\rangle_0 \tag{18}$$

Multiplication by $\psi_m^{(0)*}$ (i.e., ${}_0\langle m|$) and subsequent integration gives

$$\sum_j a_j \left[E_j^{(0)} - E_n^{(0)}\right] {}_0\langle m|j\rangle_0 = E_n^{(1)}\, {}_0\langle m|n\rangle_0 - {}_0\langle m|V|n\rangle_0 \tag{19}$$

Now we use the fact that the eigenfunctions are orthonormal, i.e.,

$${}_0\langle m|k\rangle_0 = \delta_{mk} \tag{20}$$

and for the matrix element appearing on the rhs use the following notation

$$V_{mn} = {}_0\langle m|V|n\rangle_0 \tag{21}$$

$$= \int_{-\infty}^{\infty} dx \left(\psi_m^{(0)}\right)^* V(x) \psi_n^{(0)} \tag{22}$$

Introducing the above gives

$$\boxed{\left[E_m^{(0)} - E_n^{(0)}\right] a_m = E_n^{(1)} \delta_{nm} - V_{mn}} \tag{23}$$

(a) For $m = n$, the lhs is identically zero and we get

$$E_n^{(1)} - V_{nn} = 0 \tag{24}$$

$$\Rightarrow \boxed{E_n^{(1)} = V_{nn}} \tag{25}$$

(b) For $m \neq n$, we can find the admixture amplitudes of the other states, i.e., the coefficients a_m

$$\left[E_m^{(0)} - E_n^{(0)}\right] a_m = -V_{mn} \tag{26}$$

$$a_m = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \tag{27}$$

In the case $m = n$, we obviously cannot obtain a condition for $a_{m=n}$. That means that we need to determine a_n in a different manner. If we write the total wavefunction as

$$\begin{aligned} |n\rangle &= |n\rangle_0 + \lambda |n\rangle_1 && (28) \\ &= |n\rangle_0 + \lambda \sum_j a_j |j\rangle_0 && (29) \end{aligned}$$

from the requirement that $|n\rangle$ must be normalized to 1, we get

$$\begin{aligned} 1 = \langle n|n\rangle &= \left[{}_0\langle n| + \lambda \sum_j a_j^* \, {}_0\langle j| \right] \left[|n\rangle_0 + \lambda \sum_k a_k |k\rangle_0 \right] && (30) \\ &= {}_0\langle n|n\rangle_0 + \lambda \sum_j a_j^* \, {}_0\langle j|n\rangle_0 + \lambda \sum_k a_k \, {}_0\langle n|k\rangle_0 + \lambda^2 \sum_j \sum_k a_j^* a_k \, {}_0\langle j|k\rangle_0 && (31) \end{aligned}$$

Neglecting the term proportional to λ^2 (because we are calculating up to first order), we get

$$\begin{aligned} 1 &= 1 + \lambda \sum_j a_j^* \delta_{jn} + \lambda \sum_k a_k \delta_{kn} && (32) \\ &\Rightarrow \lambda (a_n^* + a_n) = 0 && (33) \end{aligned}$$

Now, as the wavefunction is determined up to a phase factor, we can choose a_n to be real, in which case

$$\begin{aligned} a_n^* &= a_n && (34) \\ &\Rightarrow \lambda 2 a_n = 0 && (35) \\ &\text{or} \quad a_n = 0 && (36) \end{aligned}$$

To summarize, the first order corrections are

$$\boxed{\begin{aligned} E_n^{(1)} &= V_{nn} \\ |n\rangle_1 &= \sum_{j \neq n} a_j |j\rangle_0, \qquad \text{where} \qquad a_j = \frac{V_{jn}}{E_n^{(0)} - E_j^{(0)}} \end{aligned}} \tag{37}$$

2^{nd} Approximation

Let us consider the second-order corrections to the eigenvalues, for which we need to consider

$$\lambda^2 \Rightarrow H_0|n\rangle_2 + V|n\rangle_1 = E_n^{(2)}|n\rangle_0 + E_n^{(1)}|n\rangle_1 + E_n^{(0)}|n\rangle_2 \tag{38}$$

Substituting the first-order result for $E_n^{(1)}$ gives

$$\left(H_0 - E_n^{(0)}\right)|n\rangle_2 = (V_{nn} - V)\,|n\rangle_1 + E_n^{(2)}|n\rangle_0 \tag{39}$$

Following the procedure outlined in the previous section (1st order approximation), but in this case expanding the second-order correction to the wavefunctions in terms of wavefunctions of the unperturbed system

$$|n\rangle_2 = \sum_s b_s|s\rangle_0 \tag{40}$$

gives

$$\left(H_0 - E_n^{(0)}\right)\sum_s b_s|s\rangle_0 = (V_{nn} - V)\sum_{j\neq n}\frac{V_{jn}}{E_n^{(0)} - E_j^{(0)}}|j\rangle_0 + E_n^{(2)}|n\rangle_0 \tag{41}$$

Now, multiplication with ${}_0\langle i|$ and subsequent integration gives

$$\sum_s b_s\left[E_s^{(0)} - E_n^{(0)}\right]\underbrace{{}_0\langle i|s\rangle_0}_{\delta_{is}} = \sum_{j\neq n}\frac{V_{jn}V_{nn}\,{}_0\langle i|j\rangle_0 - V_{jn}\,{}_0\langle i|V|j\rangle}{E_n^{(0)} - E_j^{(0)}} + E_n^{(2)}\,{}_0\langle i|n\rangle_0 \tag{42}$$

or

$$b_i\left[E_i^{(0)} - E_n^{(0)}\right] = \sum_{j\neq n}\frac{V_{jn}V_{nn}\delta_{ij} - V_{jn}V_{ij}}{E_n^{(0)} - E_j^{(0)}} + E_n^{(2)}\delta_{in} \tag{43}$$

(a) for $i = n$, again the lhs goes to zero which leads to

$$E_n^{(2)} = -\sum_{j\neq n}\frac{V_{jn}V_{nn}\overset{\nearrow 0}{\delta_{nj}} - V_{jn}V_{nj}}{E_n^{(0)} - E_j^{(0)}} \tag{44}$$

$$= \sum_{j\neq n}\frac{V_{jn}V_{nj}}{E_n^{(0)} - E_j^{(0)}} \tag{45}$$

(b) for $i \neq n$, we then get

$$
\begin{aligned}
b_i &= \sum_{j\neq n} \frac{V_{jn}V_{nn}\delta_{ij} - V_{jn}V_{ij}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_n^{(0)}\right)} && (46)\\
&= \sum_{\substack{j\neq n\\ i\neq n}} \frac{V_{jn}\left(V_{ij} - V_{nn}\delta_{ij}\right)}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_i^{(0)}\right)} && (47)
\end{aligned}
$$

The coefficient b_i goes to zero when $i = n$. The proof is the same as the one used for a_n.

To summarize, the second order corrections are

$$
\boxed{
\begin{aligned}
E_n^{(n)} &= \sum_{j\neq n} \frac{V_{jn}V_{nj}}{E_n^{(0)} - E_j^{(0)}}\\
|n\rangle_2 &= \sum_{i\neq n} b_i |i\rangle_0, \qquad \text{where } b_i = \sum_{\substack{j\neq n\\ i\neq n}} \frac{V_{jn}\left(V_{ij} - V_{nn}\delta_{ij}\right)}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_i^{(0)}\right)}
\end{aligned}
}
\tag{48}
$$

or, up to a second order we have

$$
\begin{aligned}
E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} && (49)\\
&= E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{j\neq n} \frac{V_{jn}V_{nj}}{E_n^{(0)} - E_j^{(0)}} && (50)
\end{aligned}
$$

$$
|n\rangle = |n\rangle_0 + \lambda \sum_{i\neq n} a_i |i\rangle_0 + \lambda^2 \sum_{i\neq n} b_i |i\rangle_0 \tag{51}
$$

The above expressions contain an interesting result, i.e., in in first order, the correction to the energy is simply the expectation value of the perturbation V, which is quite reasonable. If n denotes the ground state of the system, then always $E_n^{(0)} < E_j^{(0)}$, and the effect of the second order approximation is always negative regardless of the perturbation because

$$
V_{jn}V_{nj} = |V_{jn}|^2 \tag{52}
$$

For the application of perturbation theory, we assumed the perturbation to be small, i.e., the energy levels and their differences are not changed significantly. This can be expressed as

$$
\left| \frac{\lambda V_{mn}}{E_m^{(0)} - E_n^{(0)}} \right| \ll 1 \qquad \text{for } m \neq n \tag{53}
$$

Degenerate States

in the following, we will describe the application of the perturbation theory to a spectrum with degenerate states.

non - degenerate states	$\Rightarrow$	For any energy $E_n^{(0)}$, we have assumed that only one definite state $\|n\rangle_0$ exists
degenerate system	$\Rightarrow$	For a given level of energy $E_n^{(0)}$, a series of eigenfunctions $\|n_\beta\rangle_0$ exists, $\beta = 1, 2, \cdots s$ Such a level is called s-fold degenerate

(54)

To consider degenerate system, the approach that was previously outlined needs to be modified to "lift" the degeneracies prior to the application of the perturbation series. This can be achieved by writing the wave function in the zeroth-order approximation as a linear combination of the eigenfunctions $|n\rangle_0$. To illustrate the method, let us suppose that there are two degenerate energy levels for which the unperturbed eigenfunctions are $|1\rangle_0$ and $|2\rangle_0$, and for which the common energy is E^0. We now go back into our earlier result

$$\sum_j a_j \left[E_j^{(0)} - E_n^{(0)}\right] |j\rangle_0 = \left[E_n^{(1)} - V\right] |n\rangle_0 \tag{55}$$

and consider only those terms involving $|1\rangle_0$ and $|2\rangle_0$, temporarily neglecting all other terms. Since $E_j^{(0)} = E_n^{(0)} = E^{(0)}$, the lhs is identically zero and we have

$$\left[E_n^{(1)} - V\right] |n\rangle_0 = 0 \tag{56}$$

Now, as we said earlier, we expand $|n\rangle_0$ in terms of $|1\rangle_0$ and $|2\rangle_0$ to get

$$|n\rangle_0 = C_1|1\rangle_0 + C_2|2\rangle_0 \tag{57}$$

Substituting into the above equation gives

$$\left[E_n^{(1)} - V\right] [C_1|1\rangle_0 + C_2|2\rangle_0] = 0 \tag{58}$$

or

$$C_1 E_n^{(1)}|1\rangle_0 - C_1 V|1\rangle_0 + C_2 E_n^{(1)}|2\rangle_0 - C_2 V|2\rangle_0 = 0 \tag{59}$$

Multiplying by ${}_0\langle 1|$ and ${}_0\langle 2|$ (i.e., ψ_1^{0*} and ψ_2^{0*}) and integrating over the internal variables gives

$${}_0\langle 1| : \qquad C_1 E_n^{(1)} - C_1 \underbrace{{}_0\langle 1|V|1\rangle_0}_{V_{11}} + 0 - C_2 \underbrace{{}_0\langle 1|V|2\rangle_0}_{V_{12}} = 0 \tag{60}$$

$$ {}_0\langle 2| : \qquad 0 - C_1 \underbrace{{}_0\langle 2|V|1\rangle_0}_{V_{21}} + C_2 E_n^{(1)} - C_2 \underbrace{{}_0\langle 2|V|2\rangle_0}_{V_{22}} = 0 \tag{61} $$

Thus

$$ \left\{ \begin{array}{rcl} C_1 \left[E_n^{(1)} - V_{11} \right] - C_2 V_{12} & = & 0 \\ & & \\ -C_1 V_{21} + C_2 \left[E_n^{(1)} - V_{22} \right] & = & 0 \end{array} \right\} \tag{62} $$

We have arrived at two homogeneous equations with two unknowns. In order that there exits a solution, the determinant of the coefficients of the c's must vanish, i.e.,

$$ \left[\begin{array}{ll} E_n^{(1)} - V_{11} & -V_{12} \\ -V_{21} & E_n^{(2)} - V_{22} \end{array} \right] \left[\begin{array}{c} C_1 \\ C_2 \end{array} \right] = 0 \Rightarrow \underbrace{\left| \begin{array}{ll} E_n^{(1)} - V_{11} & -V_{12} \\ -V_{21} & E_n^{(2)} - V_{22} \end{array} \right| = 0}_{\Uparrow \ \text{secular equation}} \tag{63} $$

We then obtain

$$ \left. \begin{array}{rcl} \left(E_n^{(1)} - V_{11} \right) \left(E_n^{(2)} - V_{22} \right) - V_{12} V_{21} & = & 0 \\ \left(E_n^{(1)} \right)^2 - \left(V_{11} + V_{22} \right) E_n^{(1)} + V_{11} V_{22} - V_{12} V_{21} & = & 0 \end{array} \right\} \tag{64} $$

The above equation is quadratic for $E_n^{(1)}$; there are two solutions

$$ E_n^{(1)} = \frac{1}{2} \left(V_{11} + V_{22} \right) \pm \frac{1}{2} \sqrt{ \left(V_{11} + V_{22} \right)^2 - 4 \left(V_{11} V_{22} - V_{12} V_{21} \right) } \tag{65} $$

To simplify the further discussion, let us suppose that $V_{11} = V_{22}$. By noting that $V_{21} = V_{21}^*$, we then have

$$ \begin{aligned} E_n^{(1)} &= V_{11} \pm \frac{1}{2} \sqrt{ 4V_{11}^2 - 4V_{11}^2 + 4 \left| V_{12} \right|^2 } && (66) \\ &= V_{11} \pm \left| V_{12} \right| && (67) \end{aligned} $$

Hence

$$ \boxed{ \begin{array}{rcl} E_n & = & E_n^{(0)} + \lambda E_n^{(1)} \\ & = & E^{(0)} + \lambda \left(V_{11} \pm |V_{12}| \right) \\ & = & E^0 + \lambda V_{11} \pm \lambda |V_{12}| \end{array} } \tag{68} $$

The degeneracy of the level $|n\rangle$ is lifted under the influence of the perturbation and the s-fold degenerate state splits up energetically into s close-lying states.

Using

$$H_0|n\rangle_0 = E_n^{(0)}|n\rangle_0 \tag{69}$$

we can also calculate the zeroth-order approximation for the wavefunction. Dividing the two equations gives ($V_{11} = V_{22}$)

$$C_1\left[E_n^{(1)} - V_{11}\right] = C_2 V_{12} \tag{70}$$

$$C_2\left[E_n^{(1)} - V_{11}\right] = C_1 V_{21} \tag{71}$$

$$\Rightarrow \frac{C_1}{C_2} = \frac{C_2}{C_1}\frac{V_{12}}{V_{21}} \tag{72}$$

$$\Rightarrow \left(\frac{C_1}{C_2}\right)^2 = \frac{V_{12}}{V_{21}} \tag{73}$$

Now

$$V_{12} = |V_{12}|e^{-i\phi} \tag{74}$$

and

$$V_{21} = V_{12}^* \tag{75}$$

$$= |V_{12}|e^{i\phi} \tag{76}$$

$$\Rightarrow \left(\frac{C_1}{C_2}\right)^2 = \frac{|V_{12}|e^{-i\phi}}{|V_{12}|e^{i\phi}} \tag{77}$$

$$\frac{C_1}{C_2} = \pm e^{-i\phi} \tag{78}$$

or

$$C_2 = \pm C_1 e^{i\phi} \tag{79}$$

Substituting this into

$$|n\rangle_0 = C_1|1\rangle_0 + C_2|2\rangle_0 \tag{80}$$

gives

$$|n\rangle_0 = C_1\left[|1\rangle_0 \pm e^{i\phi}|2\rangle\right] \tag{81}$$

Normalizing $|n\rangle_0$ gives

$$
\begin{aligned}
{}_0\langle n|n\rangle_0 &= 1 && (82)\\
&= C_1^* \left[{}_0\langle 1| \pm e^{-i\phi}\, {}_0\langle 2| \right] \left[|1\rangle_0| \pm e^{i\phi}\, |2\rangle_0| \right] C_1 && (83)\\
&= |C_1|^2 \left[1 \pm e^{-i\phi}\, {}_0\langle 2|1\rangle_0 \pm e^{i\phi}\, {}_0\langle 1|2\rangle_0 + {}_0\langle 2|2\rangle_0 \right] && (84)\\
&= |C_1|^2 \cdot 2 && (85)\\
&\Rightarrow \quad C_1 = \frac{1}{\sqrt{2}} && (86)
\end{aligned}
$$

Hence, the zeroth approximation wavefunction is given by

$$
|n\rangle_0 = \frac{1}{\sqrt{2}} \left[|1\rangle_0 \pm e^{i\phi} |2\rangle_0 \right] \tag{87}
$$