Time-independent perturbation theory for nondegenerate states

Apart from a few special cases, obtaining the exact analytical solution to the Schrödinger equation is essentially an impossible task. However, in many problems of practical interest the Hamiltonian can be broken up into the sum of two terms:

$$H = H^0 + \lambda H'$$

where the solutions to H^0 are known and $\lambda H'$ can be considered small in some sense. In this case there is a systematic procedure for obtaining approximate solutions to the problem with Hamiltonian H. It is called the perturbation theory. In the above expression, Hamiltonian H^0 is called the unperturbed Hamiltonian, while $\lambda H'$ is called the perturbation Hamiltonian (or just perturbation). The criterion that establishes the smallness of $\lambda H'$ will emerge in the course of the derivations. But we can controll the smallnes assuming λ to be small.

Suppose the solutions to the unperturbed SE are

$$H^0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad \text{and} \quad \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}$$

We will seek the solutions of the perturbed problem as series in terms of powers of λ:

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

Here the superscript (i) denotes the order of corrections. For example, $\lambda E_n^{(1)}$ is the first-order correction to the energy.

If we substitute the expansions in terms of powers of λ into the Schrödinger equation (with Hamiltonian H) we get:

$$(H^0 + \lambda H')(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots) \cdot (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots)$$

If we now multiply everything and collect like powers of λ (i.e. terms of roughly the same order of smallness) we obtain:

$$H^0 \psi_n^{(0)} + \lambda (H^0 \psi_n^{(1)} + H' \psi_n^{(0)}) + \lambda^2 (H^0 \psi_n^{(2)} + H' \psi_n^{(1)}) + \ldots =$$

$$= E_n^{(0)} \psi_n^{(0)} + \lambda (E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}) + \lambda^2 (E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}) + \ldots$$

At the lowest order (λ^0) we have

$$H^0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

At the first order of λ we get

$$H^0 \psi_n^{(1)} + H' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \qquad (*)$$

At the second order of λ it becomes

$$H^0 \psi_n^{(2)} + H' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)} \qquad (**)$$

We can continue as long as we wish or as long as calculations remain feasible.

The above equation for λ^0 gives nothing new as we know the solutions for H^0. Let us consider equation $(*)$ for λ^1: We can multiply it by $\langle \psi_n^{(0)} |$:

$$\underbrace{\langle \psi_n^{(0)} | H^0 | \psi_n^{(1)} \rangle}_{E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle} + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

With that we obtain

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

Thus the lowest correction to the energy is the expectation value of the perturbation computed with the zero-order (unperturbed) wave function.

Equations (*), (**) and those for higher orders of λ can be rearranged as follows

$$\left(H^{0} - E_n^{(0)}\right)\psi_n^{(1)} = \left(E_n^{(1)} - H'\right)\psi_n^{(0)} \qquad (a)$$

$$\left(H^{0} - E_n^{(0)}\right)\psi_n^{(2)} = \left(E_n^{(1)} - H'\right)\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \qquad (b)$$

$$\vdots$$

These equations have an interesting property. The left-hand side remains unchanged under the replacement

$\psi_n^{(s)} \to \psi_n^{(s)} + \alpha\psi_n^{(0)}$ $(s>0)$ where α is an arbitrary constant.

Therefore, if $\psi_n^{(s)}$ is a solution so is $\psi_n^{(s)} + \alpha\psi_n^{(0)}$. We need an extra constraint to remove this ambiguity. There are two popular choices. First is to construct $\psi_n^{(i)}$ so that it is normalized. The second is to keep all corrections orthogonal to $\psi_n^{(0)}$:

$$\langle \psi_n^{(s)} | \psi_n^{(0)} \rangle = 0 \qquad s>0$$

Any of the choices yields the same correction to the energy, $E_n^{(s)}$, while the wave functions that emerge may differ by a phase factor.

Now let us take eq. (a). Let us note that $\psi_n^{(1)}$, like any other function can be expanded in terms of $\psi_n^{(0)}$:

$$|\psi_n^{(1)}\rangle = \sum_m c_{nm} |\psi_m^{(0)}\rangle$$

With that eq. (a) becomes

$$\left(H^0 - E_n^{(0)}\right) \sum_m c_{nm} |\psi_m^{(0)}\rangle = \left(E_n^{(1)} - H'\right) |\psi_n^{(0)}\rangle$$

after multiplying by $\langle \psi_j^{(0)}|$ we get

$$\left(E_j^{(0)} - E_n^{(0)}\right) c_{nj} + H'_{jn} = E_n^{(1)} \delta_{jn} \qquad H'_{jn} = \langle \psi_j^{(0)} | H' | \psi_n^{(0)} \rangle$$

When $j = n$ we obtain the first-order correction to the energy $E_n^{(1)} = H'_{nn}$ as we did above.

When $j \neq n$ we can find ~~the~~ the coefficients c_{nj}

$$c_{nm} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

When we now substitute this back to $|\psi_n^{(1)}\rangle = \sum_m c_{nm} |\psi_m^{(0)}\rangle$ we get

$$\psi_n^{(1)} = {\sum_{m \neq n}}' \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} + c_{nn} \psi_n^{(0)}$$

The coefficient c_{nn} is determined using the constraint, which we mentioned earlier: $\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0$

With this choice of the constraint

$$c_{nn} = 0$$

Up to the first order in λ our solution is

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \frac{\lambda H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \qquad E_n = E_n^{(0)} + \lambda H'_{nn}$$

In order for the expansion in terms of powers of λ to make sense the coefficients the expansion should be less than 1:

$$|\lambda H'_{mn}| \ll |E_n^{(0)} - E_m^{(0)}|$$

In other words, matrix elements of the perturbation should be small compared to the difference between the unperturbed energy levels.

Let us now turn to the second order correction. We will again expand $\psi_n^{(2)}$ in terms of the eigenstates of H^0:

$$\psi_n^{(2)} = \sum_m d_{nm} \psi_m^{(0)}$$

Substitution into eq. (6) yields:

$$\sum_m E_m^{(0)} d_{nm} |\psi_m^{(0)}\rangle + H'|\psi_n^{(1)}\rangle = E_n^{(0)} \sum_m d_{nm} |\psi_m^{(0)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle$$

After multiplying by $\langle\psi_j^{(0)}|$ it gives

$$(E_j^{(0)} - E_n^{(0)}) d_{nj} + \langle\psi_j^{(0)}|H'|\psi_n^{(1)}\rangle = E_n^{(2)}\delta_{jn} + E_n^{(1)}\langle\psi_j^{(0)}|\psi_n^{(1)}\rangle$$

When $j = n$ we obtain $E_n^{(2)}$:

$$E_n^{(2)} = \langle\psi_n^{(0)}|H'|\psi_n^{(1)}\rangle = \sum_{m\neq n} \langle\psi_n^{(0)}| \frac{H' H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle = \sum_{m\neq n}' \frac{H'_{nm} H'_{mn}}{E_n^{(0)} - E_m^{(0)}} =$$

$$= \sum_{m\neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

When $j \neq n$ the equation above becomes

$$(E_n^{(0)} - E_j^{(0)}) d_{nj} = \langle\psi_j^{(0)}|H' \sum_{k\neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle - H'_{nn} \underbrace{\langle\psi_j^{(0)}| \sum_{k\neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle}_{\text{only } \frac{H'_{jn}}{E_n^{(0)} - E_j^{(0)}} \text{ survives}}$$

or

$$d_{nj} = \frac{1}{E_n^{(0)} - E_j^{(0)}} \left(\sum_{k\neq n}' \frac{H'_{jk} H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \right) - \frac{H'_{nn} H'_{jn}}{(E_n^{(0)} - E_j^{(0)})^2}$$

and again we find that $d_{nn} = 0$

One thing to note in the above formula for $E_n^{(2)}$ is that the second order shift to the ground state energy is negative (or at least nonpositive)