PERTURBATION METHODS

Perturbation methods are useful when we cannot solve the Schrödinger equation for the system of interest, but we know the solutions for a similar system. These solutions can be used to obtain approximate solutions for the original system.

An example of such a system is a one-electron atom in an electric field $\mathcal{E}$. Taking the z coordinate in the direction of $\mathcal{E}$, the Hamiltonian is $H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + ez\mathcal{E}$, where e is the electron charge, Z the atomic number, and z the value of the coordinate of the electron (fixing the origin at the nucleus). This Hamiltonian cannot be partitioned into one-coordinate terms, and therefore cannot be solved analytically. We do know the solutions of the operator including the first two terms, which is the hydrogenic H, and the last term is small relative to the electron-nucleus interaction (this statement applies to ordinary electric field, but not to strong laser fields).

The basic approach of perturbation methods is to partition H into the unperturbed $H^{(0)}$ and the perturbation $H^{(1)}$. The latter is usually written as $\lambda H'$, where H' is the perturbation operator, which depends on the type of perturbation, and λ is the parameter, which gives the perturbation strength. In the example given,

$$H^{(0)} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}, \quad H' = ez, \quad \lambda = \mathcal{E}.$$

The application of perturbation treatment requires:

- All the solutions of $H^{(0)}$ are known,

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

- The effect of $H^{(1)}$ is relatively small.

When $\lambda \to 0$, $\psi_n \to \psi_n^{(0)}$ and $E_n \to E_n^{(0)}$. We can therefore write the expansions in λ

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

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

Substitution in the Schrödinger equation gives

$$H^{(0)}\psi_n^{(0)} + \lambda\left[H^{(0)}\psi_n^{(1)} + H'\psi_n^{(0)}\right] + \lambda^2\left[H^{(0)}\psi_n^{(2)} + H'\psi_n^{(1)}\right] + \cdots =$$

$$= E_n^{(0)}\psi_n^{(0)} + \lambda\left[E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}\right]$$

$$+\lambda^2\left[E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}\right] + \cdots .$$

For the two series to be equal, the coefficients of the same power of λ must be equal.

The zero order terms (λ independent) give $H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, which is just the unperturbed equation.

The first-order equation is

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

from which we shall find $\psi_n^{(1)}$ and $E_n^{(1)}$, and the 2nd order equation is

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

which will give the second-order corrections $\psi_n^{(2)}$ and $E_n^{(2)}$.

First order corrections

The eigenfunctions $\{\psi_m^{(0)}\}$ of H_0 provide a basis, and $\psi_n^{(1)}$ is expanded

$$\psi_n^{(1)} = \sum_m a_{nm}\psi_m^{(0)}.$$

Substituting this expansion in the first-order equation gives

$$H^{(0)}\sum_m a_{nm}\psi_m^{(0)} + H'\psi_n^{(0)} = E_n^{(0)}\sum_m a_{nm}\psi_m^{(0)} + E_n^{(1)}\psi_n^{(0)}.$$

Using the fact that $\psi_m^{(0)}$ is an eigenfunction of $H^{(0)}$, we get

$$\sum_m a_{nm}E_m^{(0)}\psi_m^{(0)} + H'\psi_n^{(0)} = E_n^{(0)}\sum_m a_{nm}\psi_m^{(0)} + E_n^{(1)}\psi_n^{(0)}.$$

A scalar product of $\langle\psi_k^{(0)}|$ and the last equation (or, using a different language, multiplying by $\psi_k^{(1)^*}$ and integrating) gives

$$a_{nk}E_k^{(0)} + \langle\psi_k^{(0)}|H'|\psi_n^{(0)}\rangle = a_{nk}E_n^{(0)} + E_n^{(1)}\delta_{kn}.$$

This is a large set of equations, one for each value of k. For $k = n$ the equation gives

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

so that the energy is given to first order by

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

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

All other equations, for which $k \neq n$, give

$$a_{nk} = \frac{\langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}, \quad \text{and}$$

$$\psi_n \approx \psi_n^{(0)} + \lambda \sum_{k \neq n}^{\infty} \frac{\langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} = \psi_n^{(0)} + \sum_{k \neq n}^{\infty} \frac{\langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)}.$$

What is a_{nn}? It should have been obtained from the equation with $k = n$, but it cancels out. The equations to be satisfied do not depend on the value of a_{nn}, which is therefore arbitrary. It is usually chosen as zero.

What happens if there is degeneracy, i.e. some $m \neq n$ with $E_m^{(0)} = E_n^{(0)}$? If in such cases $\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle = 0$, the relevant a_{nm} drops from the equations and may be assigned arbitrary values, usually zero. If the integral does not vanish, the equations here are not applicable. This problem will be discussed later.

Second order corrections

The equation is

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

To be determined: $\psi_n^{(2)}$ and $E_n^{(2)}$. Expand as before,

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

Substitute in the equation,

$$H^{(0)}\sum_m b_{nm}\psi_m^{(0)} + H'\sum_m a_{nm}\psi_m^{(0)} =$$

$$= E_n^{(0)}\sum_m b_{nm}\psi_n^{(0)} + E_n^{(1)}\sum_m a_{nm}\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)}.$$

The first term can be replaced by $\sum_m b_{nm}E_n^{(0)}\psi_m^{(0)}$. Taking a scalar product by $\langle\psi_k^{(0)}|$:

$$b_{nk}E_k^{(0)} + \sum_m a_{nm}\langle\psi_k^{(0)}|H'|\psi_m^{(0)}\rangle = E_n^{(0)}b_{nk} + E_n^{(1)}a_{nk} + E_n^{(2)}\delta_{nk}.$$

For $k = n$

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

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

To second order

$$E_n \approx E_n^{(0)} + \langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle + \sum_{m\neq n}^{\infty} \frac{|\langle\psi_m^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}.$$

For $k \neq n$,

$$b_{nk}\left(E_n^{(0)} - E_k^{(0)}\right) = \sum_m a_{nm}\langle\psi_n^{(0)}|H'|\psi_m^{(0)}\rangle - E_n^{(1)}a_{nk} =$$

$$= \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|H'|\psi_n^{(0)}\rangle\langle\psi_k^{(0)}|H'|\psi_m^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} - \frac{\langle\psi_n^{(0)}|H'|\psi_n^{(0)}\rangle\langle\psi_k^{(0)}|H'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}.$$

To second order,

$$\psi_n \approx \psi_n^{(0)} + \sum_{k\neq n} \frac{\langle\psi_k^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}\psi_k^{(0)} +$$

$$+ \sum_{k\neq n}\left\{\sum_{m\neq n} \frac{\langle\psi_m^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle\langle\psi_k^{(0)}|H^{(1)}|\psi_m^{(0)}\rangle}{\left[E_n^{(0)} - E_m^{(0)}\right]\left[E_n^{(0)} - E_k^{(0)}\right]}\right.$$

$$\left. - \frac{\langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle\langle\psi_k^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle}{\left[E_n^{(0)} - E_k^{(0)}\right]^2}\right\}\psi_k^{(0)}.$$

In general, the energy correction of order n will have terms with n integrals of the form $\langle\psi^{(0)}|H^{(1)}|\psi^{(0)}\rangle$ in the numerator and $n-1$ differences of $E^{(0)}$ in the denominator. The expression for the function will include n integrals and n energy differences.