On the side: Review of Perturbation Theory

When the task is to estimate properties of a system that cannot be solved easily but is similar to one of the systems that has known solutions, such as the harmonic oscillator, the method of choice is perturbation theory. The discussion here is limited to bound stationary states (i.e. the solutions to the time independent Schrödinger equation). Perturbation theory can also be applied to scattering states and gives the Born expansion.

Assume H_0 is a simple time independent Hamiltonian that can be solved and let $|u_k>$ denote the stationary states:

$$H_0|u_k>=E_k|u_k>$$

Let

$$H \equiv H_0 + H'$$

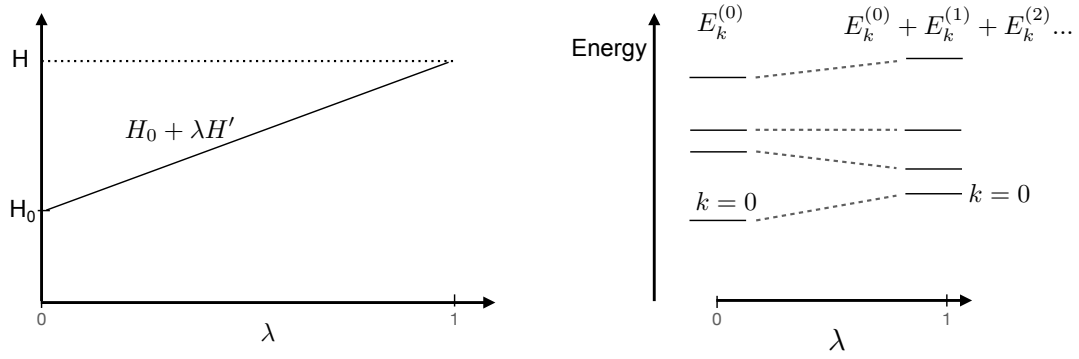
be the full time independent Hamiltonian where the H' term makes the problem too complicated to be solved exactly. Imagine turning H' on gradually:

$$H = H_0 + \lambda H'$$

where

$$\lambda \in [0,1].$$

In the end we will let $\lambda \to 1$.



Example: The vibration of a diatomic molecule is a good example for the use of perturbation theory. The zeroth order problem is the harmonic approximation and anharmonicity is then introduced as a perturbation.

Let the equilibrium separation between the atoms be r_0 and Taylor expand the potential about that distance:

$$\begin{aligned} v(r) &= v(r_0) + (r-r_0)v'(r_0) + \frac{(r-r_0)^2}{2}v''(r_0) + \frac{(r-r_0)^3}{3!}v'''(r_0) + ... \\ &= a\tilde{r}^2 + b\tilde{r}^3 + ... \end{aligned}$$

Here we have chosen $v(r_0) = 0$, used the fact that $v'(r_0) = 0$ (minimum at r_0) and defined $\tilde{r} \equiv r - r_0$. Only the first term is included in H_0

$$H_0 = -\frac{\hbar^2}{2\mu}\frac{d^2}{d\tilde{r}^2} + a\tilde{r}^2$$

which gives the harmonic oscillator Hamiltonian, and then the rest of the terms are treated as a perturbation:

$$H' = b\tilde{r}^3 + ...$$

One clear effect of the perturbation is that $\Delta n = \pm 2$ transitions become possible when the perturbation H' is turned on while they are not allowed for the pure harmonic oscillator.

We want to find the eigenstates $|\psi>$ and eigenvalues W such that

$$H|\psi> = W|\psi> .$$

Assume H' is small and expand both $|\psi>$ and W in a power series expansion:

$$|\psi> = |\psi_0> + \lambda|\psi_1> + \lambda^2|\psi_2> + \lambda^3|\psi_3> + ...$$

$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \lambda^3 W_3 + ...$$

These expansions do not always converge, but there are many cases where they converge so fast that we only need to include the first few terms. The trick is often to find a zeroth order Hamiltonian H_0 such that H' is sufficiently small. Substitute this into the Schrödinger equation:

$$\overbrace{(H_0 + \lambda H')}^{H}\ \overbrace{(\psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + ...)}^{\psi} = \overbrace{(W_0 + \lambda W_1 + \lambda^2 W_2 + ...)}^{W}\ \overbrace{(\psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + ...)}^{\psi}$$

This equation holds for any value of λ, so we can equate coefficients of equal powers of λ: To 0-th order:

$$H_0|\psi_0>=W_0|\psi_0> \quad \text{or} \quad (H_0-W_0)|\psi_0>=0.$$

To 1-st order:

$$\lambda(H_0|\psi_1>+H'|\psi_0>)=\lambda(W_1|\psi_0>+W_0|\psi_1>)$$

or

$$(H_0-W_0)|\psi_1>=(W_1-H')|\psi_0> .$$

To 2-nd order:

$$\lambda^2(H_0|\psi_2>+H'|\psi_1>)=\lambda^2(W_0|\psi_2>+W_1|\psi_1>+W_2|\psi_0>)$$

or

$$(H_0-W_0)|\psi_2>=(W_1-H')|\psi_1>+W_2|\psi_0> .$$

etc.

To zeroth Order: We just get the Schrödinger equation for the unperturbed problem. So we choose any one of the unperturbed eigenstates as the zeroth order approximation:

$$|\psi_0>=|u_m>$$

$$W_0=E_m$$

In order to obtain the corrections to the state m due to the perturbation, we must treat separately the case when the energy level E_m is not degenerate (case A) and the more complex case when the level is degenerate (case B).

Case A: (non-degenerate level)

We will assume for now that E_m is non-degenerate. Note that we can add any multiple of $|\psi_0>$ to any of the other terms $|\psi_s>$ and the equations remain unchanged because

$$(H_0-W_0)|\psi_0>=0.$$

For example, if $|\psi_1>$ is a solution to the first order equation then so is $(|\psi_1>+a|\psi_0>)$:

$$\begin{aligned}(H_0-W_0)(|\psi_1>+a|\psi_0>) &= (H_0-W_0)|\psi_1>+a(H_0-W_0)|\psi_0> \\ &= (H_0-W_0)|\psi_1> \\ &= (W_1-H')|\psi_0> \ .\end{aligned}$$

Therefore, we can choose $|\psi_s>$ such that $<\psi_0|\psi_s>=0$ when $s>0$.

Applying this general result to the equation for the 1st order correction (after left multiplying with $<\psi_0|$ gives:

$$\begin{aligned}0 &=<\psi_0|W_1-H'|\psi_0> \\ &= W_1<\psi_0|\psi_0>-<\psi_0|H'|\psi_0> \\ \text{So}: \quad W_1 &= \frac{<\psi_0|H'|\psi_0>}{<\psi_0|\psi_0>} \ .\end{aligned}$$

Applying this to the equation for the second order correction gives:

$$\begin{aligned} 0 &= < \psi_0|W_1 - H'|\psi_1 > + W_2 < \psi_0|\psi_0 > \\ &= 0 - < \psi_0|H'|\psi_1 > + W_2 < \psi_0|\psi_0 > \\ \text{So}: \quad W_2 &= \frac{< \psi_0|H'|\psi_1 >}{< \psi_0|\psi_0 >} \ . \end{aligned}$$

Generally, for any $s > 0$:

$$W_s = \frac{< \psi_0|H'|\psi_{s-1} >}{< \psi_0|\psi_0 >}.$$

Note that it is sufficient to know $|\psi >$ to order $s-1$ in order to finding W to order s.

Similarly, one can find the perturbation corrections to the wave function, i.e. the state vector. The first order correction, $|\psi_1 >$, is expanded in the set of orthonormal eigenstates of H_0

$$|\psi_1 >= \sum_n a_n |u_n > \ .$$

This can be done because the eigenstates of H_0 form a complete set for functions satisfying the same boundary conditions and therefore also the first order correction. The expression above assumes that all the eigenstates of H_0 are bound states, i.e. only discrete spectrum. (More generally, there could also be a continuous part of the spectrum and the expansion would then be of the form

$$|\psi_1 >= \sum_n a_n |u_n > + \int_0^\infty dk \ a_k |u_k > \ .$$

The $\sum_n$ includes the discrete spectrum of the eigenstates and the integral $\int_0^\infty$ includes the continuum spectrum).

We can now substitution the expansion of $|\psi_1 >$ into the first order equation

$$(H_0 - W_0)|\psi_1 >= (W_1 - H')|\psi_0 > \ .$$

Lets assume we are studying how much the E_m level changes when the perturbation H' is applied, so we take $W_0 = E_m$, $|\psi_0 >= |u_m >$

$$\sum_{n \neq m} a_n (E_n - E_m)|u_n >= (W_1 - H')|u_m >$$

The $n = m$ term is left out in the summation because we must have $a_m = 0$ since $< \psi_1|\psi_0 >= 0$, i.e., $< \psi_1|u_m >= 0$. Left multiplying with $< u_\ell|$ gives

$$\sum_{n \neq m} a_n (E_n - E_m) \underbrace{< u_\ell|u_n >}_{\delta_{\ell n}} = W_1 < u_\ell|u_m > - < u_\ell|H'|u_m >$$

$$a_\ell (E_\ell - E_m) = - < u_\ell|H'|u_m >$$

$$a_\ell = \frac{< u_\ell|H'|u_m >}{E_m - E_\ell} \qquad \ell \neq m$$

Having obtained an explicit expression for the first order correction to the state vector, it is now possible to write the second order correction to the eigenvalue only in terms of the solution to the known, zeroth order quantities. The second order equation, obtained from the λ^2 terms, is

$$(H_0 - W_0)|\psi_2 >= (W_1 - H')|\psi_1 > +W_2|\psi_0 >$$

To get the second order correction to the energy, we left multiply by $< \psi_0|$

$$0 =< \psi_0|H'|\psi_1 > +W_2 < \psi_0|\psi_0 >$$
$$W_2 = \frac{< \psi_0|H'|\psi_1 >}{< \psi_0|\psi_0 >}$$

The second order correction to the energy can now be written more explicitly in terms of the zeroth-order states. Using the solution for $|\psi_1 >$ and choosing $|\psi_0 >= |m >$,

$$|\psi_1 >= \sum_{n \neq m} a_n |n > \quad \text{with} \quad a_n = \frac{< n|H'|m >}{E_m - E_n} \ ,$$

gives

$$W_2 =< m|H'| \sum_{n \neq m} \frac{< n|H'|m >}{E_m - E_n} |n >$$
$$= \sum_{n \neq m} \frac{< m|H'|n >< n|H'|m >}{E_m - E_n} \ .$$

Using the fact that H' is Hermitian gives

$$W_2 = \sum_{n \neq m} \frac{| < n|H'|m > |^2}{E_m - E_n} \ .$$

The second order correction to the state vector is again obtained by expanding in the eigenstates of H_0

$$|\psi_2 >= \sum_{n \neq m} a_n^{(2)} |n >$$

and substituting into the λ^2 equation

$$\sum_{n \neq m} (E_n - E_m) a_n^{(2)} |n >= \sum_{\ell \neq m} a_\ell^{(1)} (W_1 - H')|\ell > +W_2|m > \ .$$

Left multiplying by $< k|$ gives

$$a_k^{(2)} = \sum_{n \neq m} \frac{< k|H'|n >< n|H'|m >}{(E_m - E_k)(E_m - E_n)} - \frac{< k|H'|m >< m|H'|n >}{(E_m - E_k)^2} \ .$$

Case B: (degenerate energy levels, skipped)