Lecture 29 - Perturbation theory

What's important:
· time-independent perturbation theory
Text: Gasiorowicz, Chap. 16

Most of the Hamiltonians that we are faced with in atomic and molecular physics cannot be solved exactly. However, the terms in the Hamiltonian can frequently be arranged in a numerical hierarchy, with some terms having larger numerical values than others. We saw this in the helium atom, where the effect of repulsion between electrons is weaker than the attraction between an electron and a nucleus. There, we solved the problem by discarding the electron repulsion term in favour of an effective charge on the nucleus. In this lecture, we'll do a little better, but still using the idea that we can determine a set of wavefunctions for the most important interaction in the Hamiltonian, then *perturb* those states by introducing a weaker interaction. We will do this only for time-independent perturbations, and non-degenerate states.

Non-degenerate bound states

Let's start off with an "unperturbed" Hamiltonian H_o whose eigenvalues can be solved analytically. To make the equations less opaque, the Dirac notation is used, where a wavefunction is represented by

$$| E >,$$

and the Schrödinger equation is written

$$H_o |E_i^o> = E_i^o |E_i^o>. \quad (1)$$

To this Hamiltonian is added a perturbing interaction

$$\lambda V$$

where λ is a dimensionless parameter, assumed to be small. The complete Hamiltonian obeys

$$H |E_i> = (H_o + \lambda V) |E_i> = E_i |E_i>. \quad (2)$$

Now, we assume that

$$|E_i> \rightarrow |E_i^o> \quad \text{as } \lambda \rightarrow 0.$$

Although this looks completely plausible, it is not without problems when there is more than one state at a given E_i^o, *i.e.*, when $|E_i^o>$ is degenerate. So, we make the further restriction that $|E_i^o>$ is non-degenerate.

Next, expand both the eigenvalues E_i and the eigenfunctions $|E_i>$ as a power series in λ

$$|E_i> = |E_i^o> + \lambda |E_i^{(1)}> + \lambda^2 |E_i^{(2)}> + ... \quad (3a)$$

$$E_i = E_i^o + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ... \quad (3b)$$

With the series (3), Eq. (2) becomes

$$(H_o + \lambda V)\{|E_i^o\rangle + \lambda |E_i^{(1)}\rangle + \lambda^2 |E_i^{(2)}\rangle + ...\}$$
$$= \{E_i^o + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ...\} \bullet \{|E_i^o\rangle + \lambda |E_i^{(1)}\rangle + \lambda^2 |E_i^{(2)}\rangle + ...\}.$$

Collecting terms in λ,

$$[H_o |E_i^o\rangle - E_i^o |E_i^o\rangle]$$
$$+ \lambda [H_o |E_i^{(1)}\rangle + V |E_i^o\rangle - E_i^o |E_i^{(1)}\rangle - E_i^{(1)} |E_i^0\rangle]$$
$$- \lambda^2 [H_o |E_i^{(2)}\rangle + V |E_i^{(1)}\rangle - E_i^{(1)} |E_i^{(1)}\rangle - E_i^o |E_i^{(2)}\rangle - E_i^{(2)} |E_i^0\rangle]$$
$$+ \lambda^3 ...$$
$$= 0$$

Now, this expression should vanish for any arbitrary value of λ, meaning that each term in square brackets must vanish separately. Term by term:

$H_o |E_i^o\rangle = E_i^o |E_i^o\rangle$ nothing new here, just a restatement of (1)

$H_o |E_i^{(1)}\rangle + V |E_i^o\rangle = E_i^o |E_i^{(1)}\rangle + E_i^{(1)} |E_i^0\rangle$ from λ term, first order (4)

$H_o |E_i^{(2)}\rangle + V |E_i^{(1)}\rangle = E_i^{(1)} |E_i^{(1)}\rangle + E_i^o |E_i^{(2)}\rangle + E_i^{(2)} |E_i^0\rangle$ from λ^2 term, second order

We can use these terms to construct *first order perturbation theory* (from λ term) or *second order perturbation theory* (from λ^2 term).

To determine the first order energies $E_i^{(1)}$ and states $|E_i^{(1)}\rangle$, we make use of the fact that the unperturbed wavefunctions $|E_i^o\rangle$ form a complete set of orthonormal states. This allows us to expand

$$|E_i^{(1)}\rangle = \sum_{j=1}^{\infty} a_{ij}^{(1)} |E_j^o\rangle, \quad (5)$$

where $a_{ij}^{(1)}$ are a set of coefficients to be determined. It's not as bad as it might seem. Just substitute (5) into (4) for the first order states $|E_i^{(1)}\rangle$ to obtain:

$$H_o \sum_j a_{ij}^{(1)} |E_j^o\rangle + V |E_i^o\rangle = E_i^o \sum_j a_{ij}^{(1)} |E_j^o\rangle + E_i^{(1)} |E_i^0\rangle$$

from which

$$\sum_j a_{ij}^{(1)} (E_j^o - E_i^o) |E_j^o\rangle = (E_i^{(1)} - V) |E_i^0\rangle.$$

Close this equation with

$$\langle E_k^o|$$

and use the orthogonality condition

$$\langle E_k^o|E_i^0\rangle = \int \psi^o(E_k^o)^* \psi^o(E_i^o)\, dx = \delta_{ik}$$

to give

$$\sum_j a_{ij}^{(1)} (E_j^o - E_i^o) \delta_{jk} = \delta_{ik} E_i^{(1)} - \langle E_k^o| V |E_i^0\rangle. \quad (6)$$

First, let $k = i$ in Eq. (6) to determine the shifted energies. This selects

$$0 = E_i^{(1)} - V_{ii} \qquad \text{where } V_{ii} = \langle E_i^o | V | E_i^0 \rangle$$

or

$$E_i^{(1)} = V_{ii}. \tag{7}$$

In other words, Eq. (7) establishes that

$$E_i = E_i^o + \lambda V_{ii}.$$

To obtain the perturbed wavefunctions, we take $k \neq i$ in (6) and perform the sum over j

$$a_{ik}^{(1)} (E_k^o - E_i^o) = - \langle E_k^o | V | E_i^0 \rangle$$

or

$$a_{ik}^{(1)} = V_{ki} / (E_i^o - E_k^o) \qquad \text{where } V_{ki} = \langle E_k^o | V | E_i^0 \rangle.$$

Now, this gives us $a_{ik}^{(1)}$ but not $a_{ii}^{(1)}$: clearly $k = i$ will give us grief from the denominator on the RHS. To obtain the latter, we have to use the normalization condition on the wavefunction. So far, we have established (after substitutions) that the complete wavefunction reads:

$$|E_i\rangle = |E_i^0\rangle + \lambda a_{ii}^{(1)} |E_i^0\rangle + \lambda \sum_{j \neq i} \{V_{ji} / (E_i^o - E_j^o)\} |E_j^0\rangle$$

or

$$|E_i\rangle = (1+\lambda a_{ii}^{(1)}) |E_i^0\rangle + \lambda \sum_{j \neq i} \{V_{ji} / (E_i^o - E_j^o)\} |E_j^0\rangle.$$

To do the normalization, close this with $\langle E_i|$, yielding

$$1 = \{(1+\lambda a_{ii}^{(1)*}) \langle E_i^0| + \lambda \sum_{j \neq i} \{V_{ji}^* / (E_i^o - E_j^o)\} \langle E_j^0|\}$$
$$\bullet \{(1+\lambda a_{ii}^{(1)}) |E_i^0\rangle + \lambda \sum_{j \neq i} \{V_{ji} / (E_i^o - E_j^o)\} |E_j^0\rangle\}$$

or

$$1 = |1+\lambda a_{ii}^{(1)}|^2 + \text{terms of order } \lambda^2. \tag{8}$$

The summation terms first order in λ have disappeared because the summation is over $j \neq i$, which vanishes because of orthogonality $\langle E_i^o | E_j^0 \rangle = 0$. Carry on with Eq. (8):

$$1 = 1+\lambda(a_{ii}^{(1)*} + a_{ii}^{(1)}) + \text{another term of order } \lambda^2$$
$$1 + 2\lambda \, \mathrm{Re} a_{ii}^{(1)}.$$

Thus, to a consistent first order approximation in λ,

$$\mathrm{Re} a_{ii}^{(1)} = 0.$$

Further, $\mathrm{Im} a_{ii}^{(1)}$ doesn't appear to this order of λ, so

$$a_{ii}^{(1)} = 0. \tag{9}$$

Collecting these results and changing back to our conventional notation:

$$E_i = E_i^o + \lambda V_{ii}$$
$$\psi_i = \psi_i^o + \lambda \sum_{j \neq i} \{V_{ji} / (E_i^o - E_j^o)\} \psi_j^o$$

where

$$V_{ij} = \int \psi_j^{o*} V \psi_i^o d\,\mathbf{r}.$$

This is the complete expansion to first order in λ. Second order perturbation theory is covered in most texts, and fourth year quantum courses.

Example

Just as a simple example of how to set up a perturbation problem, consider the harmonic oscillator problem with a potential λx^4 added as a perturbation.

$$H = p^2/2m + m\omega^2 x^2/2 + \lambda x^4 \qquad \text{(anharmonic oscillator)}$$

Here, the unperturbed solution is

$$\psi_n^o = [(\alpha/\pi)^{1/2} / (2^n n!)]^{1/2} \exp(-\alpha x^2/2)\, H_n(\sqrt{\alpha}\, x) \qquad \alpha = m\omega/\hbar$$

$$E_n^o = (n + 1/2)\, \omega\hbar.$$

What we have to do is evaluate

$$V_{ij} = \int \psi_j^{o*} x^4 \psi_i^o d\,\mathbf{r}$$

for the relevant states.