Stationary perturbation theory for degenerate states

As we established in the previous lecture the applicability of nondegenerate perturbation theory requires that the expansion coefficient of the first- and higher order wave function

$$\psi_n^{(1)} = \sum_i a_{ni} \psi_i^{(0)}$$

are small, i.e. $|a_{ni}| = \left|\frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}}\right| << 1$

or $|H'_{ni}| << |E_n^{(0)} - E_i^{(0)}|$

However, if there are degeneracies among the unperturbed energies the denominator in the expression above vanishes. Therefore, the formal theory must be reexamined to determine what modifications are needed in the degenerate case.

In simple terms what the degenerate perturbation theory aims to do is to construct a new basis (out of the degenerate states) so that H'_{in} matrix is diagonal in it. In other words it aims to kill H'_{in} matrix elements for all $i \neq n$. If $H'_{in} = 0$ then the coefficients a_{ni} will not blow up. Once such a basis is found one may proceed as in the nondegenerate case.

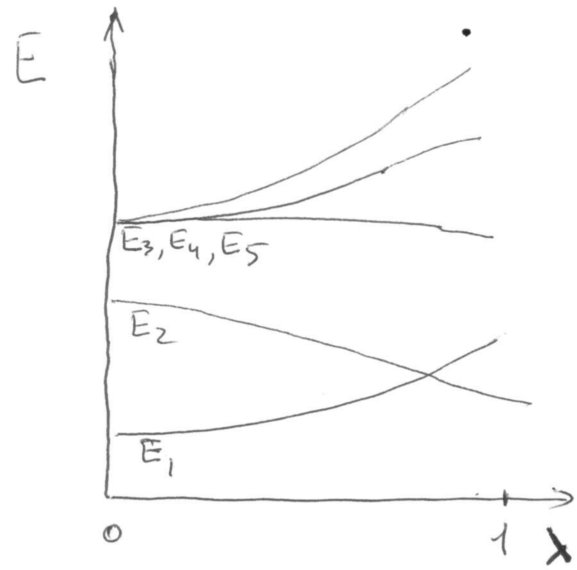
Let us first consider qualitatively what happens to the eigenvalues of the perturbed problem

$$H\psi_n = E_n \psi_n \qquad H = H^0 + \lambda H'$$

when λ is varied from 0 to, say, 1.

As $\lambda \to 0$ the eigenvalues of $H\psi_n = E\psi_n$ go to the eigenvalues of the unperturbed problem $H^0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

When $\lambda > 0$ the perturbation may (and often does) split the energy levels. The degeneracy stems from symmetries inherent to the system at hand. The perturbation may (and often does) destroys those symmetries, either partially or completely.



Suppose we deal with an energy level whose degree of degeneracy is q:

$$H^{\circ} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \qquad E_1^{(0)} = E_2^{(0)} = \dots = E_q^{(0)}$$

When λ is decreased and approaches 0 $\quad E_1 \dots E_q \to E_1^{(0)}$

Does this mean $\lim\limits_{\lambda \to 0} \psi_n = \psi_n^{(0)}$. Not necessarily. If $E_n^{(0)}$ is nondegenerate there is unique $\psi_n^{(0)}$ corresponding to eigenvalue $E_n^{(0)}$, and we can be sure $\lim\limits_{\lambda \to 0} \psi_n = \psi_n^{(0)}$

However, if $E_n^{(0)}$ is the eigenvalue of the q-fold degenerate level then any linear combination

$$c_{n1} \psi_1^{(0)} + c_{n2} \psi_2^{(0)} + \dots + c_{nq} \psi_q^{(0)}$$

is a solution of the unperturbed problem.

All we can say is that

$$\lim_{\lambda \to 0} \psi_n = \sum_{i=1}^{q} c_{ni} \psi_i^{(0)} \qquad 1 \le n \le q$$

Our task is to determine the right zeroth-order wave functions. (in which H' is diagonal). Let us denote

$$\phi_n^{(0)} = \lim_{\lambda \to 0} \psi_n = \sum_{i=1}^{q} c_{ni} \psi_i^{(0)} \qquad 1 \le n \le q$$

Coefficients c_{ni} depend on perturbation H'.

The treatment of the q-fold degenerate level just like the nondegenerate treatment in the previous lecture, except that insted of $\psi_n^{(0)}$ $(1 \le n \le q)$ we use $\phi_n^{(0)}$:

$$\psi_n = \phi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots \qquad n = 1, \ldots, q$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \qquad n = 1, \ldots q$$

Substitution into $H\psi_n = E_n \psi_n$ yields:

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

Equating the coefficients of the λ^1 terms we get

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

or

$$H^0 |\psi_n^{(1)}\rangle - E_n^{(0)} |\psi_n^{(1)}\rangle = E_n^{(1)} |\phi_n^{(0)}\rangle - H' |\phi_n^{(0)}\rangle \qquad n = 1, \ldots, q$$

Now if we multiply by $\langle \psi_m^{(0)}|$ $(1 \le m \le q)$ we get

$$\underbrace{\cancel{\langle \psi_m^{(0)} | H^0 | \psi_n^{(1)} \rangle}}_{E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle} - \cancel{E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle} = E_n^{(1)} \langle \psi_m^{(0)} | \phi_n^{(0)} \rangle - \langle \psi_m^{(0)} | H' | \phi_n^{(0)} \rangle$$

Then

$$\langle \psi_m^{(0)} | H' | \phi_n^{(0)} \rangle - E_n^{(1)} \langle \psi_m^{(0)} | \phi_n^{(0)} \rangle \qquad m = 1, \ldots, q$$

Recalling that $\phi_n^{(0)} = \sum_{i=1}^{q} c_{ni} \psi_i^{(0)}$ we can rewrite it as

$$\sum_{i=1}^{q} c_{ni} \langle \psi_m^{(0)} | H' | \psi_i^{(0)} \rangle - E_n^{(1)} \sum_{i=1}^{q} c_{ni} \underbrace{\langle \psi_m^{(0)} | \psi_i^{(0)} \rangle}_{\delta_{mi}} = 0$$

This is nothing but the eigenvalue problem:

$$W c = \varepsilon c \qquad (*)$$

where

$$W_{mi} = \langle \psi_m^{(0)} | H' | \psi_i^{(0)} \rangle = H'_{mi} \qquad m, i = 1 \ldots q$$

By solving the secular equation

$$\begin{vmatrix} H'_{11}-\varepsilon & H'_{12} & \cdots & H'_{1q} \\ H'_{21} & H'_{22}-\varepsilon & \cdots & \cdot \\ \vdots & & & \\ H'_{q1} & H'_{q2} & \cdots & H'_{qq}-\varepsilon \end{vmatrix} = 0$$

we obtain $\varepsilon = E_1^{(1)}, \dots E_q^{(1)}$ — the first order corrections to the energy.

If the roots are all different then the perturbation lifts the degeneracy completely.

Eigenvectors (coefficients c_{ni}) found by solving equation (*) can now be used to find the correct zero order wave functions

$$\phi_n^{(0)} = c_{n1}\psi_1^{(0)} + \dots + c_{nq}\psi_q^{(0)} \qquad n = 1 \dots q$$

assuming that $\sum_{i=1}^{q} |c_{ni}|^2 = 1$.

Obviously in $\phi_n^{(0)}$ basis H' is diagonal. Thus,

$$\langle \phi_n^{(0)} | H' | \phi_m^{(0)} \rangle = \delta_{nm} \langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle$$

When $n \neq m$ these matrix elements vanish.

With the new basis $\phi_1^{(0)}, \dots \phi_q^{(0)}, \psi_{q+1}^{(0)}, \psi_{q+2}^{(0)}, \dots$ we have removed the ambiguities due to the degeneracy of H_0. It can be used to compute higher order corrections (if necessary). Note that

$$E_n^{(1)} = \langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle \qquad n = 1 \dots q$$

$$E_i^{(1)} = \langle \psi_i^{(0)} | H' | \psi_i^{(0)} \rangle \qquad i > q \quad \text{(assuming } i \text{ is nondegenerate)}$$

the expressions are essentially the same as for the nondegenerate case, except the change of the basis.