

# 3 Time-independent Perturbation Theory I

## 3.1 Small perturbations of a quantum system

Consider Hamiltonian

$$H_0 + \hat{V}, \quad (1)$$

where  $H_0$  and  $\hat{V}$  both time-ind., and  $\hat{V}$  represents small perturbation to Hamiltonian  $H_0$ , whose eigenfctns and eigenvals.  $|n\rangle$  and  $E_n$  are known,

$$H_0|n\rangle = E_n|n\rangle. \quad (2)$$

### Nondegenerate perturbation theory

★★ Suppose for now  $|n\rangle$  nondegenerate. ★★ Reasonable to assume if  $\hat{V}$  is small, perturbations to  $|n\rangle$  and  $E_n$  should be small. So we have a small dimensionless param. in which to expand, replace  $\hat{V}$  by  $\epsilon\hat{V}$ , take  $\epsilon \ll 1$ . Assume soln to  $H|\psi\rangle = E|\psi\rangle$  can be expanded

$$E = E_n + \epsilon\delta E_{(1)} + \epsilon^2\delta E_{(2)} + \dots \quad (3)$$

$$|\psi\rangle = |n\rangle + \epsilon|\psi_{(1)}\rangle + \epsilon^2|\psi_{(2)}\rangle \dots \quad (4)$$

Since  $|n\rangle$  form complete set, the states  $|\psi_{(1)}\rangle$  and  $|\psi_{(2)}\rangle$  may be expanded

$$|\psi\rangle = |n\rangle + \epsilon \sum_m C_m |m\rangle + \epsilon^2 \sum_m D_m |m\rangle + \dots \quad (5)$$

Now substitute (1-5) into  $H\psi = E\psi$ ,

$$\begin{aligned} & (H_0 + \epsilon\hat{V})(|n\rangle + \epsilon \sum_m C_m |m\rangle + \dots) \\ & = (E_n + \epsilon\delta E_{(1)} + \dots)(|n\rangle + \epsilon \sum_m C_m |m\rangle + \dots), \end{aligned} \quad (6)$$

or, using (2),

$$\epsilon \left( \hat{V}|n\rangle + \sum_m C_m E_m |m\rangle \right) + \epsilon^2 \left( \sum_m C_m \hat{V}|m\rangle + \sum_m D_m E_m |m\rangle \right) + \dots$$

$$= \epsilon \left( \delta E_{(1)} |n\rangle + E_n \sum_m C_m |m\rangle \right) \quad (7)$$

$$+ \epsilon^2 \left( \delta E_{(2)} |n\rangle + \delta E_{(1)} \sum_m C_m |m\rangle + E_n \sum_m D_m |m\rangle \right).$$

Now equate powers of  $\epsilon$  to find ( $\mathcal{O}(1)$ ):

$$\hat{V}|n\rangle + \sum_m C_m E_m |m\rangle = \delta E_{(1)} |n\rangle + E_n \sum_m C_m |m\rangle. \quad (8)$$

Now take inner product with  $\langle n|$ , use  $\langle n|m\rangle = \delta_{nm}$ :

$$\boxed{\delta E_{(1)} = \langle n|\hat{V}|n\rangle} \quad (9)$$

so 1st-order shift in energy level for state  $|n\rangle$  is just expectation value of  $\hat{V}$  in that state. Now take inner product with  $\langle m|$ , find

$$\boxed{C_m = \frac{\langle m|\hat{V}|n\rangle}{E_n - E_m}, \quad m \neq n} \quad (10)$$

so energy eigenstate is, to 1st order,

$$|\psi\rangle = |n\rangle + \epsilon \left( C_n |n\rangle + \sum_{m \neq n} \frac{|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} \right) + \mathcal{O}(\epsilon^2). \quad (11)$$

What is the coefficient  $C_n$ ? Actually we can't determine it! Note we could write instead of (9),

$$|\psi\rangle = (1 + \epsilon C_n) \left( |n\rangle + \epsilon \sum_{m \neq n} \frac{|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} \right) + \mathcal{O}(\epsilon^2) \quad (12)$$

the same up to corrections of  $\mathcal{O}(\epsilon^2)$ . Here see that  $C_n$  just is part of overall normalization factor; can't determine since S.-eqn. is linear. Same applies to  $D_n$ , etc. Go back and expand to 2nd order, using (9) and (10). Find:

$$\delta E_{(2)} = \sum_{m \neq n} \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m}, \quad \text{so} \quad (13)$$

$$\boxed{E = E_n + \epsilon \langle n|\hat{V}|n\rangle + \epsilon^2 \sum_{m \neq n} \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} + \mathcal{O}(\epsilon^3)} \quad (14)$$

Note when we actually do calculations we will set  $\epsilon = 1$  at end—we just put it in to help classify the terms in powers of  $\hat{V}$  formally!

### 3.2 DC Stark effect

(Shift of energy levels of atom placed in static homogeneous electric field). Consider atom in constant  $\mathbf{E}$  field. Potential energy of each charge in atom just work done to move charge from origin in presence of field. So

$$\hat{V} = -\mathbf{E} \cdot \sum_i q_i \mathbf{r}_i \quad (15)$$

$$= -\mathbf{E} \cdot \mathbf{d} \quad (16)$$

where  $q_i$  is charge on  $i$ th particle,  $\mathbf{r}_i$  is position of  $i$ th particle in atom, and  $\mathbf{d}$  is the dipole moment operator.

★ Temporarily let's write energies as  $\mathcal{E}$  to avoid confusion with  $E$ -field.

Continue to assume eigenstates of  $H_0$  nondegenerate—first order energy shift (from (9)):

$$\delta\mathcal{E}_{(1)} = -\mathbf{E} \cdot \sum_i q_i \langle n | \mathbf{r}_i | n \rangle = 0 \quad (17)$$

That this vanishes follows from  $\langle n | \mathbf{r}_i | n \rangle = \int d^3r_i \mathbf{r}_i |\psi_n(\mathbf{r}_i)|^2 = 0$ , since  $|n\rangle$  are eigenstates of parity  $\hat{\Pi}$ , but  $\mathbf{r}$  is odd under parity. So we have to go to 2nd order (Eq. (14)):

$$\delta\mathcal{E}_{(2)} = \sum_{m \neq n} \frac{\langle n | \hat{V} | m \rangle \langle m | \hat{V} | n \rangle}{E_n - E_m} \quad (18)$$

$$= \sum_{\alpha\beta} E_\alpha E_\beta \sum_{m \neq n} \frac{\langle n | d_\alpha | m \rangle \langle m | d_\beta | n \rangle}{E_n - E_m} \quad (19)$$

$$\equiv -\frac{1}{2} \sum_{\alpha\beta} \alpha^{\alpha\beta} E_\alpha E_\beta \quad (20)$$

where we made analogy with classical E & M in last step above— $\alpha^{\alpha\beta}$  is *polarizability tensor*. For atom without permanent dipole moment,  $\mathbf{d}$

itself  $\propto$  applied field  $\mathbf{E}$ ,  $\mathbf{d} = \underline{\alpha}\mathbf{E}$ . Work done on atomic “springs” by  $E$ -field is

$$\delta W = \sum_i q_i \mathbf{E} \cdot \delta \mathbf{r}_i = \mathbf{E} \cdot \delta \mathbf{d} = \sum_{\alpha\beta} E_\alpha \alpha^{\alpha\beta} \delta E_\beta \quad (21)$$

So total work involved in increasing field from 0 to  $\mathbf{E}$  is

$$W = \int \sum_{\alpha\beta} E_\alpha \alpha^{\alpha\beta} \delta E_\beta \quad (22)$$

$$= \frac{1}{2} \sum_{\alpha\beta} \alpha^{\alpha\beta} E_\alpha E_\beta \quad (23)$$

This is work stored in atomic “springs”, but we must add to this the decrease in system’s energy due to changed positions of particles in  $\mathbf{E}$ :

$$U = -\mathbf{E} \cdot \mathbf{d} = -\sum_{\alpha\beta} \alpha^{\alpha\beta} E_\beta E_\alpha \quad (24)$$

Total energy shift must be *negative*:

$$\delta \mathcal{E} = W + U = -\frac{1}{2} \alpha^{\alpha\beta} E_\alpha E_\beta \quad (25)$$

so our quantum result (20) actually in accord with classical intuition here, as it should be since we are treating  $E$ -field classically. Check to make sure you see why  $\alpha$  defined in (20) is always positive if  $n = 0$ , ground state!

Note to get final answer to (2) need to know matrix elements of dipole operator, can calculate later.

### 3.3 Degenerate perturbation theory

Note that we start with a state labelled by  $|n\rangle$  and perturb around it. Energy shift (18) well-defined if states nondegenerate, but what if there is an  $|m\rangle$  for which  $E_n = E_m$  in (18). Theory breaks down. Need to go back and redo things for the degenerate case. Call e’s states of  $H$   $|n, \alpha\rangle$  where  $n$  labels energy level and  $\alpha$  labels different energy e’s states with same energy e’value,

$$H_0|n, \alpha\rangle = E_n|n, \alpha\rangle \quad (26)$$

$$\langle n, \alpha|m, \beta\rangle = \delta_{mn}\delta_{\alpha\beta} . \quad (27)$$

Let's again expand energy and wave fctn.,

$$E = E_n + \delta E_{(1)} + \delta E_{(2)} \quad (28)$$

$$|\psi\rangle = |n, \alpha\rangle + \sum_{m\beta} C_{m\beta}|m, \beta\rangle + \dots \quad (29)$$

where I suppressed the  $\epsilon$ 's for compactness. Completeness says

$$\hat{V}|n, \alpha\rangle = \sum_{m,\beta} |m, \beta\rangle \langle m, \beta|\hat{V}|n, \alpha\rangle, \quad (30)$$

so generalization of (7) to  $\mathcal{O}(\epsilon)$  is

$$\begin{aligned} \hat{V}|n, \alpha\rangle + \sum_{m,\beta} C_{m\beta} E_m |m, \beta\rangle \\ &= \sum_{m,\beta} |m, \beta\rangle \left( \langle m, \beta|\hat{V}|n, \alpha\rangle + C_{m\beta} E_m \right) \\ &= \delta E_{(1)} |n, \alpha\rangle + E_n \sum_{m\beta} C_{m\beta} |m, \beta\rangle. \end{aligned} \quad (31)$$

Coefficient of  $|m, \beta\rangle$  on both sides of (31) must agree, so

$$\langle m, \beta|\hat{V}|n, \alpha\rangle + C_{m\beta} E_m = E_n C_{m\beta} + \delta E_{(1)} \delta_{nm} \delta_{\alpha\beta}. \quad (32)$$

Two cases again:

$m \neq n$

$$C_{m\beta} = \frac{\langle m\beta|\hat{V}|n\alpha\rangle}{E_n - E_m} \quad (33)$$

$m=n$

$$\delta E_{(1)} \delta_{\alpha\beta} = \langle n\beta|\hat{V}|n\alpha\rangle \quad (34)$$

If  $\langle n\beta|\hat{V}|n\alpha\rangle = 0$  when  $\alpha \neq \beta$ , the equation (34) makes sense, and we get

$$\delta E_{(1)} = \langle n\alpha|\hat{V}|n\alpha\rangle \quad (35)$$

Note this means possibly a different splitting for each of the initially degenerate states  $|n\alpha\rangle$ , but is otherwise more or less same as nondegenerate case. *But* if  $\langle n\beta|\hat{V}|n\alpha\rangle \neq 0$  when  $\alpha \neq \beta$ , Eq. (34) doesn't have a solution, we get some kind of contradiction. What's going on?

★★ Recall what we said about eigenvectors corresponding to distinct eigenvalues being orthogonal. If eigenvalues are degenerate, various eigenvectors need not be orthogonal—**however** if they aren't, we can construct a new set corresponding to same e'value which are! ★★.

Can pull similar trick here: construct  $N$  linearly independent combinations ( $N$  is the degeneracy of  $E_n$ , e'value in question) of form

$$N \text{ eigenstates } \begin{cases} |A\rangle = \sum_{\alpha} A_{\alpha} |n\alpha\rangle \\ |B\rangle = \sum_{\alpha} B_{\alpha} |n\alpha\rangle \\ |C\rangle = \sum_{\alpha} C_{\alpha} |n\alpha\rangle \\ \vdots \end{cases} \quad (36)$$

Now choose  $\{A_{\alpha}, B_{\alpha}, \dots\}$  such that

$$\langle A|\hat{V}|B\rangle = 0, \text{ etc.} \quad (37)$$

Redo previous calc. leading to (32), find now no inconsistency, rather

$$\begin{aligned} \delta E_{(1)} &= \langle A|\hat{V}|A\rangle && \text{if } |A\rangle \text{ is unperturbed state,} \\ &= \langle B|\hat{V}|B\rangle && \text{if } |B\rangle \text{ is unperturbed state,} \\ &\vdots \end{aligned} \quad (38)$$

If (37) holds, means  $\hat{V}$  is diagonal on subspace of degenerate eigenvectors, so can write  $\hat{V}|A\rangle = V_A|A\rangle$ , etc. In terms of the original basis this is

$$\sum_{\alpha} A_{\alpha} \hat{V}|n, \alpha\rangle = V_A \sum_{\alpha} A_{\alpha} |n, \alpha\rangle, \quad (39)$$

and inner product with  $\langle n, \beta|$  is

$$\sum_{\alpha} \langle n, \beta|\hat{V}|n, \alpha\rangle A_{\alpha} = V_A A_{\beta}, \quad (40)$$

or, in suggestive matrix form,

$$\underline{V} \vec{A} = V_A \vec{A}, \text{ etc.} \quad (41)$$

So we have reduced the degenerate state perturbation problem to the problem of diagonalizing  $\hat{V}$  and finding its eigenvalues and eigenvectors. Once found, the  $N$  eigenvalues  $V_A, V_B, \text{ etc.}$  give the energy perturbations,  $E = E_n + V_A, E_n + V_B, \dots$

## Summary

I know this is confusing. Here's what you have to do in practice. If you have  $N$  degenerate states  $|\alpha\rangle$  corresponding to one eigenvalue  $E$ , construct the matrix  $\langle\alpha|V|\alpha'\rangle$ . If it happens to be diagonal, you've got it easy: for each  $\alpha$ , read off the 1st order energy shifts,  $\delta E_\alpha = \langle\alpha|V|\alpha\rangle$ . The wave function will have no 1st order shift arising from the  $\langle\alpha|V|\alpha'\rangle$ , but beware it can still have corrections coming from the  $\langle\alpha|V|m\rangle$ , where the  $|m\rangle$  are the states outside the degenerate manifold you're looking at. If  $\langle\alpha|V|\alpha'\rangle$  isn't diagonal, you need to find a new basis  $|\alpha'\rangle$  in which it is, i.e. diagonalize it! You get eigenvalues  $V_A, V_B, \dots$  (the new energy shifts) and eigenvectors  $|A\rangle, |B\rangle, \dots$ , which are linear combinations of the old  $|\alpha\rangle$ . If you calculate the 1st order correction to the wavefunction with the new basis, the terms containing  $\langle A|V|B\rangle$  will again vanish for  $A \neq B$ , but don't forget you will still have terms like  $\langle m|V|A\rangle$  which are nonzero.

## Linear Stark effect

Note for nondegenerate case 1st order Stark shift vanished, i.e.  $\delta E \sim E^2$ . If two or more atomic states degenerate, need to go back & compute matrix elements

$$\langle n, \alpha | \hat{V} | n, \beta \rangle \quad (42)$$

and diagonalize. While diagonal elements in original basis will still vanish due to parity (recall  $\hat{V} \propto E\mathbf{r}$ ), off-diagonal ones needn't. Thus when  $\hat{V}$  is nondiagonal there will in general be linear shift  $\propto E$ . Linear dependence on applied field therefore  $\implies$  degenerate states. Equivalent in classical case to atom with *permanent dipole moment*, i.e. in a field dipole moment

has a zeroth-order piece:  $\mathbf{d} = \mathbf{d}(E = 0) + \delta\mathbf{d}(E)$ . Energy  $\mathcal{E} \simeq -\mathbf{d} \cdot \mathbf{E} \propto E$  unlike (23).

Hydrogen atom  $n=2$  states

Take  $\mathbf{B} \parallel \hat{z}$ , so  $\hat{V} = -Eez$ . 4 degenerate  $n = 2$  states of H:

$$\psi_{200} = \frac{1}{2a_0^{3/2}} 2 \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00} \quad (43)$$

$$\psi_{21m} = \frac{1}{2a_0^{3/2}} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{1m}, \quad m = 1, 0, -1 \quad (44)$$

Note

1.  $\ell = 0$  state has even parity,  $\ell = 1$  states odd parity, whereas  $\hat{V}$  has odd parity, so only states with different  $\ell$  couple (only  $\langle 200|\hat{V}|21m\rangle$  and  $\langle 21m|\hat{V}|200\rangle$  are nonzero in degenerate subspace).
2.  $\hat{V}$  commutes with  $\hat{L}_z$ , so only connects states with same  $m$  value! Therefore only  $\langle 200|\hat{V}|210\rangle$  is nonvanishing.

Therefore matrix  $\underline{V}$  in original basis is just  $2 \times 2$ :

$$\underline{V} = \begin{bmatrix} \langle 200|z|200\rangle = 0 & \langle 200|z|210\rangle \\ \langle 210|z|200\rangle & \langle 210|z|210\rangle = 0 \end{bmatrix} \quad (45)$$

Calculate:

$$\begin{aligned} \langle 200|\hat{V}|210\rangle &= \int_0^\infty r^2 dr (2a_0)^{-3} e^{-r/a_0} \frac{2r}{\sqrt{3}a_0} \left(1 - \frac{r}{2a_0}\right) r \\ &\times \int d\Omega Y_{00}^* \cos\theta Y_{10} \\ &= -3a_0 \end{aligned} \quad (46)$$

Now find eigenvalues  $\delta E_{(1)}$  (i.e., diagonalize):

$$\det \begin{bmatrix} -\delta E_{(1)} & -3eEa_0 \\ -3eEa_0 & -\delta E_{(1)} \end{bmatrix} = 0 \quad (47)$$

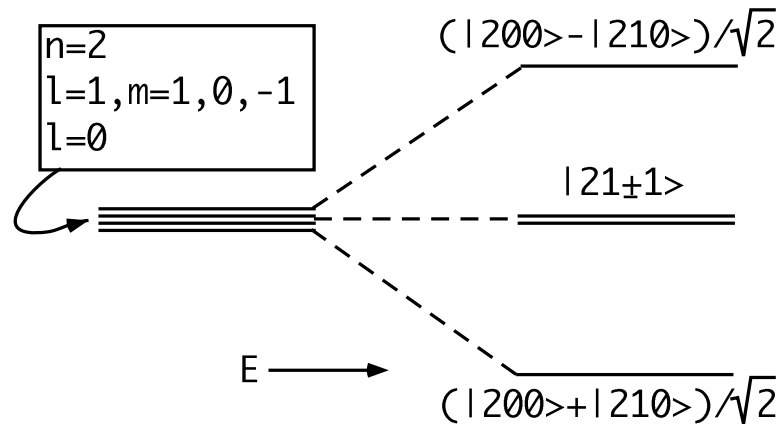


Figure 1: Stark splittings of hydrogenic energy levels.

or  $\delta E_{(1)} = \pm 3eEa_0$ . Eigenvectors in subspace are (note (45) is proportional to  $\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ .)

$$|\psi_1\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \equiv \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle)$$

and

$$|\psi_2\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \equiv \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle) \quad (48)$$

Note

1. that the new states are not eigenstates of  $\hat{L}^2$ , since  $\hat{L}^2$  doesn't commute with  $H$ .
2. that for the case of degenerate states Stark splitting *linear* in E-field!