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

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

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

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

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

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

$$(H_0 + \epsilon \hat{V})(|n\rangle + \epsilon \sum_m C_m |m\rangle + \cdots)$$

$$= (E_n + \epsilon \delta E_{(1)} + \cdots)(|n\rangle + \epsilon \sum_m C_m |m\rangle + \cdots), \quad (6)$$

or, using (2),

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

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

Now equate powers of \(\epsilon\) to find \(\mathcal{O}(1)\): \[
\hat{V}|n\rangle + \sum_m C_mE_m |m\rangle = \delta E_{(1)}|n\rangle + E_n \sum_m C_m |m\rangle.
\]

Now take inner product with \(\langle n|\), use \(\langle n|m\rangle = \delta_{nm}\): \[
\delta E_{(1)} = \langle n|\hat{V}|n\rangle
\]
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 \[
C_m = \frac{\langle m|\hat{V}|n\rangle}{E_n - E_m}, \quad m \neq n
\]
so energy eigenstate is, to 1st order, \[
|\psi\rangle = |n\rangle + \epsilon \left( C_n|n\rangle + \sum_{m \neq n} \frac{|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} \right) + \mathcal{O}(\epsilon^2).
\]

What is the coefficient \(C_n\)? Actually we can’t determine it! Note we could write instead of (9), \[
|\psi\rangle = (1 + \epsilon C_n) \left( |n\rangle + \epsilon \sum_{m \neq n} \frac{|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} \right) + \mathcal{O}(\epsilon^2)
\]
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:\[
\delta E_{(2)} = \sum_{m \neq n} \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m}, \quad \text{so}
\]
\[
E = E_n + \epsilon \langle n|\hat{V}|n\rangle + \epsilon^2 \sum_{m \neq n} \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|n\rangle}{E_n - E_m} + \mathcal{O}(\epsilon^3)
\]
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 $E$ field. Potential energy of each charge in atom just work done to move charge from origin in presence of field. So

$$\hat{V} = -\mathbf{E} \cdot \sum_i q_i \mathbf{r}_i$$

$$= -\mathbf{E} \cdot \mathbf{d}$$  \hspace{1cm} (15)

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.

$\star$ 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)):

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

That this vanishes follows from $\langle n|\mathbf{r}_i|n \rangle = \int d^3 r_i \mathbf{r}_i |\psi_n(\mathbf{r}_i)|^2 = 0$, 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):

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

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

$$\equiv -\frac{1}{2} \sum_{\alpha \beta} \alpha^{\alpha \beta} E_{\alpha} E_{\beta}$$  \hspace{1cm} (19)

where we made analogy with classical E & M in last step above—$\alpha^{\alpha \beta}$ is \textit{polarizability tensor}. For atom without permanent dipole moment, $\mathbf{d}$
itself $\propto$ applied field $\mathbf{E}$, $\mathbf{d} = \alpha \mathbf{E}$. Work done on atomic “springs” by $\mathbf{E}$-field is

$$\delta W = \sum_i q_i \mathbf{E} \cdot \delta \mathbf{r}_i = \mathbf{E} \cdot \delta \mathbf{d} = \sum_{\alpha\beta} E_\alpha \alpha^\beta \delta E_\beta$$  \hspace{1cm} (21)

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

$$W = \int \sum_{\alpha\beta} E_\alpha \alpha^\beta \delta E_\beta$$  \hspace{1cm} (22)

$$= \frac{1}{2} \sum_{\alpha\beta} \alpha^\beta E_\alpha E_\beta$$  \hspace{1cm} (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 $\mathbf{E}$:

$$U = -\mathbf{E} \cdot \mathbf{d} = -\sum_{\alpha\beta} \alpha^\beta E_\beta E_\alpha$$  \hspace{1cm} (24)

Total energy shift must be negative:

$$\delta \mathcal{E} = W + U = -\frac{1}{2} \alpha^\beta E_\alpha E_\beta$$  \hspace{1cm} (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’states of $\mathbf{H} |n, \alpha\rangle$ where $n$ labels energy level and $\alpha$ labels different energy e’states with same energy e’value,
\[ H_0 |n, \alpha \rangle = E_n |n, \alpha \rangle \]  
\[ \langle n, \alpha | m, \beta \rangle = \delta_{mn} \delta_{\alpha \beta} . \]  

Let’s again expand energy and wave fctn.,

\[ E = E_n + \delta E_{(1)} + \delta E_{(2)} \]  
\[ |\psi\rangle = |n, \alpha\rangle + \sum_{m, \beta} C_{m\beta} |m, \beta\rangle + \cdots \]

where I supressed the $\epsilon$’s for compactness. Completeness says

\[ \hat{V} |n, \alpha\rangle = \sum_{m, \beta} |m, \beta\rangle \langle m, \beta | \hat{V} |n, \alpha\rangle, \]  

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

\[ \hat{V} |n, \alpha\rangle + \sum_{m, \beta} C_{m\beta} E_m |m, \beta\rangle \]  
\[ = \sum_{m, \beta} |m, \beta\rangle \left( \langle m, \beta | \hat{V} |n, \alpha\rangle + C_{m\beta} E_m \right) \]  
\[ = \delta E_{(1)} |n, \alpha\rangle + E_n \sum_{m, \beta} C_{m\beta} |m, \beta\rangle. \]  

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

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

Two cases again:

\( m \neq n \)  
\[ C_{m\beta} = \frac{\langle m\beta | \hat{V} |n\alpha\rangle}{E_n - E_m} \]  

\( m=n \)  
\[ \delta E_{(1)} \delta_{\alpha \beta} = \langle n\beta | \hat{V} |n\alpha\rangle \]  

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

\[ \delta E_{(1)} = \langle n\alpha | \hat{V} |n\alpha\rangle \]
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

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

(36)

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

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

(37)

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

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

(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

$$
\sum_{\alpha} A_{\alpha} \hat{V}|n, \alpha\rangle = V_A \sum_{\alpha} A_{\alpha} |n, \alpha\rangle, 
$$

(39)

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

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

(40)

or, in suggestive matrix form,
\[ V \hat{A} = V_A \hat{A}, \text{ etc.} \quad (41) \]

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, \( E = E_n + V_A, E_n + V_B, \ldots \).

**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 \( V_A, V_B, \ldots \) (the new energy shifts) and eigenvectors \( |A\rangle, |B\rangle \ldots \), 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 \( \hat{V} \propto Er \)), 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 \( \mathbf{H} \):

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

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

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 \( \mathbf{V} \) in original basis is just \( 2 \times 2 \):

\[
\mathbf{V} = \begin{bmatrix}
\langle 200|z|200 \rangle & \langle 200|z|210 \rangle \\
\langle 210|z|200 \rangle & \langle 210|z|210 \rangle
\end{bmatrix}
\]

Calculate:

\[
\langle 200|\hat{V}|210 \rangle = \int_0^\infty r^2 dr (2a_0)^{-3} e^{-r/2a_0} \frac{2r}{\sqrt{3}a_0} \left( 1 - \frac{r}{2a_0} \right) r
\]

\[
\times \int d\Omega \ Y_{00}^* \cos \theta Y_{10}
\]

\[
= -3a_0
\]

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

\[
det \begin{bmatrix}
-\delta E_{(1)} & -3eEa_0 \\
-3eEa_0 & -\delta E_{(1)}
\end{bmatrix} = 0
\]
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

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

(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 \textit{linear} in E-field!