Lecture 15

Degenerate perturbation theory

Normally if $H = H_0 + V$ and H_0 is easy to solve it will often be because there are some simplifying symmetries

If $SH = HS$

and $H|\psi\rangle = E|\psi\rangle$

then $HS|\psi\rangle = SH|\psi\rangle = ES|\psi\rangle$

which means $S|\psi\rangle$ is also an eigenstate of H with the same eigenvalue,

In this case non degenerate perturbation theory is not applicable.

Assume that H_0 has N eigenstates with the same eigenvalue. Relabel states for $|\psi_1^0\rangle \cdots |\psi_N^0\rangle$ all have eigenvalue E^0 and $E_n^0 \neq E^0$ for all $n > N$.

Without loss of generality we can choose $|\psi_k\rangle$ $1 \leq k \leq N$ satisfying

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad n,m \leq N$$

Let P_N be the orthogonal projection operator on the subspace of the Hilbert space spanned by the N eigenstates with eigenvalue E^0

$$P_N = \sum_{n=1}^{N} |\psi_n^0\rangle\langle\psi_n^0|$$

note that

$$P_N = P_N^\dagger = P_N^2 \qquad P_N H_0 = E^0 P_N$$

Define

$$Q_N = I - P_N$$

It follows that

$$Q_N = Q_N^\dagger = Q_N^2$$

$$Q_N P_N = P_N Q_N = 0$$

$$P_N + Q_N = I$$

$$Q_N = \sum_{n=N+1}^{\infty} |\psi_n^0\rangle\langle\psi_n^0|$$

using these relations

$$H = H_0 + V =$$

$$(P_N + Q_N)(H_0 + V)(P_N + Q_N)$$

$$E^0 P_N + P_N V P_N + Q_N H_0 Q_N +$$

$$Q_N V P_N + P_N V Q_N + Q_N V Q_N$$

note that

$$P_N H_0 Q_N = Q_N H_0 P_N = E^0 P_N Q_N = 0$$

The strategy is to replace H_0 and V by

$$H_0' = P_N H P_N + Q_N H_0 Q_N$$

$$V' = P_N V Q_N + Q_N V P_N + Q_N V Q_N$$

Then from the decomposition on the last page

$$H = H_0 + V = H_0' + V'$$

To use perturbation theory we need to diagonalize H_0' -

The $Q_N H_0 Q_N$ part is already diagonal

$$H_0' |\psi_n\rangle = E_n^0 |\psi_n\rangle \qquad n > N$$

for $n \leq N$

$$\langle \psi_m^0 | H_0' | \psi_n^0 \rangle = E^0 \delta_{mn} + \langle \psi_m^0 | V | \psi_n^0 \rangle$$

This is an $N \times N$ Hermitian matrix, H'_{mn}, that can be diagonalized

eigenvalues:

$$\det(E' \delta_{mn} - H'_{mn}) = 0$$

has N roots E_n' $n = 1 \cdots N$

$$\Pi_n = \frac{\prod_{E_m' \neq E_n'} (H' - E_m')}{\prod_{E_m' \neq E_n'} (E_n' - E_m')}$$

project on eigenstate of H' with eigenvalue E_n' $1 \leq n \leq N$

since each $|\psi_n^0\rangle$ is a linear combination of the $|\psi_n^0\rangle$ for $n \leq N$

$$\langle \psi_n^{\circ\circ} | \psi_m^{\circ\circ} \rangle = 0 \qquad n \leq N \quad m > N$$

normally it is enough to stop after H_0' has been diagonalized. Because it is not diagonal in the original basis, the new eigenstates will not generally have the same eigenvalue - even when two of them have the same eigenvalue

$$\langle \psi_n^{\circ\prime} | V' | \psi_m^{\circ\prime} \rangle = 0 \qquad n, m \leq N$$

because V' has a Q_N on the right or left and

$$Q_N | \psi_n^{\circ\prime} \rangle = 0 \qquad n \leq N$$

so there are <u>never</u> any terms where one is dividing by $1/(E_n^{\circ\prime} - E_m^{\circ\prime})$

diagonalizing H_0^1 is the same problem and diagonalizing V

When the eigenvalues are all the same there are many possible choices of $|\psi_n^i\rangle$

A lot of work can be saved if they are chosen so

$$V|\psi_n^i\rangle = v_n|\psi_n^i\rangle$$

* The problem is to diagonalize $P_N + P_N$. The resulting solution has terms of $N-1$ powers of the potential

Example: Hydrogen atom with spin $|\psi_n\rangle = |n\ell m_\ell s\rangle$ (1)

or $|\psi_n'\rangle = |n\ell m_\ell s m_s\rangle$ (2)

These are 2 possible bases for an electron interacting with a proton with a Coulomb interaction. There are small corrections - for example the electron sees a proton moving in a circle - This creates a magnetic field that couples to the electron's magnetic moment. This results in a V of the form

$$V = \frac{e^2}{2m_e^2}\frac{1}{r^3}\vec{L}\cdot\vec{S} = V_{LS}(r)\,\vec{L}\cdot\vec{S}$$

In the absence of this spin orbit interaction eigenstates with different m, m_ℓ, m_s all have the same eigenvalues provided n, ℓ are the same

since $\bar{J}^2 = (\bar{L}+\bar{S})^2 = L^2 + S^2 + 2\bar{L}\cdot\bar{S}$

we have

$$\bar{L}\cdot\bar{S} = \frac{1}{2}\left(\bar{J}^2 - L^2 - S^2\right)$$

this means that

$$\langle n\, j\, m\, \ell\, s \,|\, V_{so}\, \bar{L}\cdot\bar{S} \,|\, n\, j'\, m'\, \ell\, s\rangle =$$

$$\langle n\ell | V_{so} | n\ell\rangle \delta_{mm'} \times \frac{1}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)$$

note:

* this choice of basis diagonalizes V
* there is still a $2j+1$ fold degeneracy

state with different l_is will have their eigenvalues shifted

* If we use the basis $|n\, l\, m_l\, s\, m_s\rangle$ we would get a non diagonal matrix in m_l, m_s.

The problem could still be done but it would be necessary to diagonalize a matrix. Clearly the matrix that does this is $C^{jm}_{m_l m_s}$.

If the atom is put in a magnetic field then

the energy is shifted by

$$V = -\bar{\mu}_s \cdot \bar{B} = -\frac{eh}{m_e c}\bar{S}\cdot\bar{B}$$

If we choose coordinates so $\bar{B}$ is in the z direction then

$$V = -\frac{eh}{m_e c} S_z B$$

unlike the spin orbit interaction, this is diagonal in the basis $|n\ell m_s m_s\rangle$, but not in the basis $|n\ell j m_j\rangle$.

When both interactions appear then the choice of basis normally depends on which V is larger, however in both cases the full interaction matrix is not diagonal.

Next we consider the case when $H = H_0 + V(t)$. where here the perturbing interaction may depend explicitly on time.

This can be an explicitly time dependent interaction or a time independent interaction that is turned on at a given time.

To treat this situation we use the "interaction picture" which is "between" the Schrodinger and Heisenberg pictures

Recall

Schrodinger Picture

$$|\psi(t)\rangle = e^{-iHt}|\psi(0)\rangle$$

$$\langle O(t)\rangle = \langle \psi(t)|O|\psi(t)\rangle$$

$$= \langle \psi(0)|e^{iHt} O e^{-iHt}|\psi(0)\rangle$$

Heisenberg picture

$$O(t) = e^{iHt} O e^{-iHt}$$

$$|\psi\rangle = |\psi(0)\rangle$$

$$\langle O(t)\rangle = \langle \psi|O(t)|\psi\rangle$$

$$= \langle \psi(0)|e^{iHt} O e^{-iHt}|\psi(0)\rangle$$

Both pictures give identical observables. For the interaction picture

$$H = H_0 + V(t)$$

$$|\psi_I(t)\rangle = e^{iH_0 t}\,|\psi_S(t)\rangle$$

$$O_I(t) = e^{iH_0 t}\,O(0)\,e^{-iH_0 t}$$

In this case

$$\langle O(t)\rangle = \langle \psi_I(t)|O_I(t)|\psi_I(t)\rangle =$$

$$\langle \psi_S(t)|\underbrace{e^{-iH_0 t}\,e^{iH_0 t}}_{I}\,O(0)\,\underbrace{e^{-iH_0 t}\,e^{iH_0 t}}_{I}\,|\psi_S(t)\rangle$$

$$\langle \psi_S(t)|O_S|\psi_S(t)\rangle = \langle \psi_H|O_H(t)|\psi_H\rangle$$

all three pictures give the same probabilities, expectation values and ensemble averages

$$\frac{d}{dt}|\psi_I(t)\rangle = iH_0\,e^{iH_0 t}|\psi_S(t)\rangle + e^{iH_0 t}(-iH)|\psi_S(t)\rangle$$

$$= e^{iH_0 t}(-iH + iH_0)e^{-iH_0 t}\,e^{iH_0 t}\,|\psi_S(t)\rangle$$

$$= -iV_I(t)|\psi_I(t)\rangle$$

This gives

$$\frac{d|\Psi_I(t)\rangle}{dt} = -i V_I(t) |\Psi_I(t)\rangle$$

with initial condition

$$|\Psi_I(0)\rangle = |\Psi_S(0)\rangle = |\Psi_H\rangle$$

The differential equation and initial condition can be expressed as an integral equation

$$|\Psi_I(t)\rangle = |\Psi_I(0)\rangle - i \int_0^t V_I(t') |\Psi_I(t')\rangle dt'$$

This can be formally solved by iteration —

$$|\Psi_I(t)\rangle = \lim_{n \to \infty} |\Psi_I^{(n)}(t)\rangle$$

$$|\Psi_I^{(0)}(t)\rangle = |\Psi_S(0)\rangle$$

$$|\Psi_I^{(n)}(t)\rangle = |\Psi_I^{0}(t)\rangle - i\int_0^{t'} V_I(t')\,|\Psi_I^{(n-1)}(t')\,dt'$$

In order to discuss the convergence first consider the second order term

$$|\Psi_I^{(2)}(t)\rangle = |\Psi_I^{0}(t)\rangle - i\int_0^{t'} V_I(t')\,|\Psi_I^{0}(t')\rangle\,dt'$$

$$(-i)^2\int_0^{t} V_I(t'')\int_0^{t''} V_I(t')\,|\Psi_I^{0}(t')\rangle\,dt\,dt''$$

remarks

(1) since $[H_0, V_S] \neq$ in general

$[V_I(t'), V_I(t'')] \neq 0$ -

ie. the interactions at different times do not generally commute

(2) $t \geq t'' \geq t'$ has

$V_I(t'')\,V_I(t')$

with $V_I(t')$ to the right of $V_I(t'')$

If we consider $0 \le t', t'' < t$ there are 2 possible orderings $t' > t''$ and $t'' > t'$

$$\int_0^t dt' \int_0^{t'} dt'' \; V_I(t') V_I(t'') = \quad (t' > t'')$$

$$\int_0^t dt'' \int_0^{t''} dt' \; V_I(t'') V_I(t') \quad (t'' > t')$$

$$= \frac{1}{2} \int_0^t dt' \int_0^t dt'' \left(\theta(t'' - t') \, V_I(t'') V_I(t') + \theta(t' - t'') \, V_I(t') V_I(t'') \right)$$

In general if there are N times $0 \le t_i \le t$ there are $N!$ possible orderings

$$T\left(V_I(t_1) \; V_I(t_2) \right) =$$

$$\theta(t_1 - t_2) \, \theta(t_2 - t_3) \cdots \theta(t_{N-1} - t_N) \, V_I(t_1) V_I(t_2) \cdots V_I(t_N) +$$

similar contributions from each ordering

This gives the following expression for $|\psi_I(t)\rangle$

$$|\psi_I(t)\rangle = |\psi_S(0)\rangle + \sum_{n=1}^{\infty} \frac{1}{n!} \int_0^t dt_1 \cdots dt_n \, T\left(V_I(t_1) \cdots V_I(t_n)\right) |\psi_S(0)\rangle$$

This is called the Dyson expansion. The advantage of writing things this way is that there are not variables in the limits of integration. If V_S is bounded

$$\| T(V_I(t_1) \cdots V_I(t_n)) \| =$$

$$\| V_I(t_{\sigma(1)}) \cdots V_I(t_{\sigma(n)}) \| \qquad \sigma(t_1) > \sigma(t_2) > \cdots$$

$$\| e^{iH_0 t_{\sigma(1)}} V e^{-iH_0(t_{\sigma(1)} - t_{\sigma(2)})} V \cdots V e^{-iH_0 t_n} \|$$

$$\leq \|V\|^n$$

It follows that

$$\left\| \sum_{n=1}^{\infty} \frac{1}{n!} \int_0^t dt_1 \cdots dt_n \, T(V_I(t_1) \cdots V_I(t_n)) \, |\Psi_S(0)\rangle \right\|$$

$$\leq \sum_{n=1}^{\infty} \frac{1}{n!} t^n \, |||V_S|||^n = e^{t |||V_S|||} < \infty$$

this means that if $\forall t$, $|||V_S||| < \infty$ that the series converges strongly