Lecture 7

Degenerate perturbation theory

Rayleigh Schrödinger perturbation theory breaks down when two or more of the unperturbed states have the same energy eigenvalue. Unfortunately, this is a common situation.

To treat this consider

\[ H = H_0 + \Delta V \]

\[ H_0 \left| \psi_n^0 \right> = E_n^0 \left| \psi_n^0 \right> \]

Assume \( E_1^0 = E_2^0 = \cdots = E_N^0 \) so the ground state has an \( N \)-fold degeneracy.

Define

\[ P = \sum_{n=1}^{N} \left| \psi_n^0 \right>< \psi_n^0 \right| \]

Obviously \( P^2 = P = P^* \) so \( P \) is an orthogonal projector. We also define

\[ Q = I - P = \sum_{n=N+1}^{\infty} \left| \psi_n^0 \right>< \psi_n^0 \right| \]

So

\[ I = P + Q \]

\[ P \cdot Q = Q \cdot P = 0 \]
we write

\[ H = H_0 + \lambda V = I (H_0 + \lambda V) I = \]
\[ = (P + \Omega) (H_0 + \lambda V) (P + \Omega) \]
\[ = PHP + \Omega H_0 \Omega + \lambda (\Omega V P + P V \Omega + \Omega V \Omega) \]

note that

\[ \Omega H_0 P = H_0 \Omega P = 0 \quad \text{and} \quad PH_0 \Omega = (\Omega H_0 P)^\dagger = 0 \]

here PHP is essentially an N x N matrix. It can be diagonalized by computer

\[ PHP 14 > = E 14 > \]

\[ \sum_{n=1}^{\infty} \psi_n > \langle \psi_n | H | \psi_m > \langle \psi_m | 14 > = \sum_{n=1}^{\infty} E \psi_n > \langle \psi_n | 14 > \]

multiply by \( \langle \varphi_1 | \)

\[ \sum_{m=1}^{\infty} \langle \varphi_k | H | \psi_m > = \sum_{m=1}^{\infty} (E \delta_{km}) \langle \psi_m | 14 > = 0 \]

solving this eigenvalue problem gives \( N \) eigenvalues and \( N \) orthogonal vectors \( | \varphi_1 > \ldots | \varphi_N > \).
\( |\psi_e\rangle = \sum_{m=1}^{N} |\psi_m\rangle \langle \psi_m | \psi_e\rangle \)

\[ \text{PHP} |\psi_e\rangle = E_e |\psi_e\rangle \quad l=1\ldots N \]

\[ \langle \psi_e | \psi_m \rangle = 0 \quad m > N \]

Next we note

\( \alpha \epsilon_1 \ldots \epsilon_p \) are not necessarily degenerate - however since

\( \lambda \) was treated exactly - they

have a complex \( \lambda \) dependence.

\[ |\psi_1\rangle \ldots |\psi_N\rangle \quad |\psi_{N+1}\rangle \ldots |\psi_{\infty}\rangle \]

Is an orthonormal basis and

the Hamiltonian

\[ H_0 = \text{PHP} + \text{OH}_0 \text{A} \]

is diagonal in this basis i.e.

\[ H_0 |\psi_k\rangle = E_k |\psi_k\rangle \quad k \leq N \]

\[ H_0 |\psi_m\rangle = E_m |\psi_m\rangle \quad m > N+1 \]

Or

\[ H_0 |\psi_m\rangle = E_m \]

\( |\psi_1\rangle \ldots |\psi_N\rangle \quad |\psi_{N+1}\rangle \ldots |\psi_{\infty}\rangle \)

\[ E_k = \left\{ \begin{array}{ll}
E_k & k < N \\
E_m & m > N+1
\end{array} \right. \]
The exact problem is replaced by

\((\mathcal{H}_0' + \lambda V') |\Psi\rangle = E |\Psi\rangle\)

where \(V'\) is

\[ V' = \mathcal{Q}V\mathcal{P} + \mathcal{P}V\mathcal{Q} + \mathcal{Q}V\mathcal{Q} \]

in this case we can apply the methods of non degenerate perturbation theory.

For the first \(n\) states

\[ \langle \Psi_n | V' | \Psi_n \rangle = 0 \]

because \(\langle \Psi_n | \mathcal{Q} \rangle = \langle \Psi_n | \mathcal{P} \rangle = 0\) so there is no first order correction to these states.

For the second order correction

\[ \sum_m \frac{\langle \Psi_n | V' | \Psi_m \rangle \langle \Psi_m | V' | \Psi_n \rangle}{E_n^m - E_n^o} \]

in this case for \(n > N\) the \(V'\) can only give something non zero when \(m > N\).
so even if the unperturbed p\text{rim} states are degenerate, there are NO zero denominators.

The second order correction can be non-zero, but it is not exactly second order.

This explains why the calculation of the splitting of the spin states in the weak magnetic field worked—it is because the interaction was already diagonal in the magnetic quantum number.

Had we used a different basis or would have had to use degenerate perturbation theory.

Example—consider

\[ H = -\frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r} + \frac{e^2}{2me} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S} \]

The \( \mathbf{L} \cdot \mathbf{S} \) term is a small correction due to the electron's spin interacting with the magnetic field generated by the orbiting electron.
It can be derived from the Dirac equation (relativistic treatment of an electron in a Coulomb field) by making a non-relativistic reduction.

In this case the basis functions have the form

\[ |\Psi > \sim |nl el_z \frac{1}{2} s_z > \]

which are products of radial and spin wave functions.

\[ V \sim \frac{e^3}{2m_0} \frac{1}{r^3} \bar{L} \cdot \bar{S} \]

states with different \( l_z \) and \( s_z \) are degenerate in the absence of the interaction. The problem is to diagonalize

\[ \langle nl el_z \frac{1}{2} s_z | (H + V) | nl el_z \frac{1}{2} s_z \rangle \]

for fixed \( n, l, e \)
Thus for each value of \( \ell \) we have to diagonalize a \((2\ell+1) \times 2 \times (2\ell+1) \times 2\) matrix by inspection \((E_S) = \frac{1}{2}(L^2 - L_z^2 - S^2)\) so if we use Clebsch-Gordan coefficients

\[
\langle \ell m | n \ell \ell m_s \ell m_s \rangle
\]

these are matrix elements of the unitary transformation that diagonalizes this matrix. The eigenvalues are

\[
E = E_0 + \frac{e^2}{2me} \frac{1}{2} (\ell(\ell+1) - 2(L^2) - \frac{1}{2}L_z^2) \langle n \ell m | \frac{1}{r_3} | n \ell m \rangle
\]

the factor \( \frac{1}{r_3} \) looks singular - but

(i) the volume element has a factor of \( r^2 \)

(ii) for \( \ell = 0 \) the correction vanishes - for \( \ell > 0 \) the square of the wave function \( \propto r^{2\ell} \) so the singularity never causes a problem

(iii) check Schwingen to calculate \( \langle \frac{1}{r_3} \rangle \) using the Hellmann Feynman theorem
This problem still has a degeneracy in the magnetic quantum number $m$ - but this causes no problems because the finite matrix is diagonal and the states are orthogonal to the $|m\rangle$ states.

Time dependent perturbation theory.

Sometimes we have a situation where we understand the time evolution of a system and we want to see what happens if we turn on an interaction - like an electric or magnetic field. We want to allow for the possibility that the field might be time dependent.
we start by introducing the interaction picture which is between the Schrodinger and Heisenberg picture

\[ \langle \Psi | A(t) | \Psi(0) \rangle = e^{iH_0 t} \langle \Psi(0) | A(0) | \Psi(0) \rangle \]

\[ A(t) = A(0) e^{iH_0 t} \]

Clearly both give the same expectation values as a function of time.

For the interaction picture

\[ \langle \Psi_\uparrow(t) | A(t) | \Psi_\uparrow(0) \rangle = e^{iH_0 t} \langle \Psi_\uparrow(0) | A(0) | \Psi_\uparrow(0) \rangle \]

\[ A_\uparrow(t) = e^{iH_0 t / \hbar} A(0) e^{-iH_0 t / \hbar} \]

with these definitions \[ \langle \Psi | A(t) | \Psi \rangle \]

is unchanged.
we consider the structure of the equations of motion.

The time evolution operator is

\[ U(t', t) = e^{iH(t' - t)} e^{-iHt} \]

This clearly gives

\[ U(t', t) |\Psi_s(t)\rangle = e^{iH(t' - t)} e^{-iHt} |\Psi_s(t)\rangle \]

In the absence of interactions, \( |\Psi_s(t)\rangle = |\Psi_s(t')\rangle \) and we recover the Heisenberg picture for the non-interacting system.

\[
\frac{i\hbar}{dt} |\Psi_{s'}(t)\rangle = \\
\frac{i\hbar}{dt} e^{iH_{\text{tot}}/\hbar} |\Psi_s(t)\rangle = \\
e^{iH_{\text{tot}}/\hbar} \left( i\hbar \frac{iH_{\text{tot}}/\hbar + H}{\hbar} \right) |\Psi_s(t)\rangle = \\
e^{iH_{\text{tot}}/\hbar} V |\Psi_s(t)\rangle = \\
\]
\( (e^{\frac{i\hat{H}t}{\hbar}} v e^{-\frac{i\hat{H}t}{\hbar}}) (e^{\frac{i\hat{H}t}{\hbar}} |\Psi_\tau(t)\rangle) = V(t) |\Psi_\tau(t)\rangle \)

where

\[ V_\tau(t) = e^{-\frac{i\hat{H}_\tau t}{\hbar}} V(t) e^{\frac{i\hat{H}_\tau t}{\hbar}} \]

which is the interaction picture Hamiltonian

\[ i\hbar \frac{d}{dt} |\Psi_\tau(t)\rangle = V_\tau(t) |\Psi_\tau(t)\rangle \]

If we integrate this we get

\[ |\Psi_\tau(t)\rangle = |\Psi_\tau(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^{t} V_\tau(t') |\Psi_\tau(t')\rangle \]

If \( V = 0 \) this shows that \( |\Psi(t)\rangle = |\Psi(t_0)\rangle \)

which is what you expect for a Heisenberg picture wave function \( \hat{H} = \hat{H}_0 \).
It is possible to develop a perturbation series in $\mathbf{V}(t)$ by iterating the equation

$$\left| \psi_{\pm}^{(n)}(t) \right> = \left| \psi_{\pm}(t_0) \right> - \frac{i}{\hbar} \int_{t_0}^{t} V_{\pm}(t') \left| \psi_{\pm}(t_0) \right> dt'$$

Thus

$$\left| \psi_{\pm}^{(n)}(t) \right> = \left| \psi_{\pm}(t_0) \right> - \frac{i}{\hbar} \int_{t_0}^{t} V_{\pm}(t') \left| \psi_{\pm}(t_0) \right> dt'$$

$$+ \left( -\frac{i}{\hbar} \right)^2 \int_{t_0}^{t} V_{\pm}(t') \int_{t_0}^{t'} V_{\pm}(t'') \left| \psi_{\pm}(t_0) \right> dt'' dt'$$

We can express the full solution as

$$\left| \psi_{\pm}(t) \right> = \left| \psi_{\pm}(t_0) \right>$$

$$+ \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n V_{\pm}(t_1) \cdots V_{\pm}(t_n) \left| \psi_{\pm}(t_0) \right>$$

Note that for $(t-t_0)$ finite on

$$\text{III} \text{VIII} = \sup \frac{||\mathbf{V}(t)||}{||\psi||} = C < \infty$$

This series converges.
To show this consider the second term
\[ \int_{t_0}^{t'} \int_{t_0}^{t''} V_1(t') V_2(t'') \]

in this integral \( t' > t'' \)

\[ \int_{t_0}^{t'} \int_{t_0}^{t''} V_1(t') V_2(t'') = t' > t'' \]

\[ \int_{t_0}^{t} \int_{t}^{t'} dt'' dt' \]

we can write the total integral as
\[
\frac{1}{2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \Theta(t-t'') V_1(t') V_2(t'') + \]
\[
\frac{1}{2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \Theta(t''-t') V_1(t'') V_2(t')
\]

we define
\[
T(V_1(t_1) V_2(t_2)) = V_1(t_1) V_2(t_2) \Theta(t_1-t_2) + V_1(t_2) V_2(t_1) \Theta(t_2-t_1)
\]

called the time order product.
\[
\int_{t_0}^{t_1} \int_{t_0}^{t} = \int_{t_0}^{t}
\]
so we can write the second order term as
\[
\frac{1}{2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' T (V_t(t') V_t(t''))
\]
for the \( n \) norm term there are \( n! \) possible time orderings so we can replace the single nested integral by
\[
\frac{1}{n!} \int_{t_0}^{t} dt_1 \ldots dt_n T (V_t(t_1) \ldots V_t(t_n))
\]
using this in the series expression:
\[
|\Psi(t)\rangle = |\Psi(t_0)\rangle + \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_1 \ldots dt_n T (V_t(t_1) V_t(t_n)) |\Psi(t)\rangle
\]
The norm of the \( n \) term in this series is bounded by
\[
\left| \frac{t-t_0}{\hbar} \right|^n \|V(t)\|^n
\]
so the series is bounded by \( e^{-c} \)
Where \( \|V\|_t = \sup_{t, t' \leq t} \|V(t')\| \)

The convergence breaks down when
the interaction is unbounded or the
intervar is infinite.

The series on the last page is
called the Dyson series.