Lecture 12

Time independent non degenerate
perturbation theory

\[ E_n = E_n^0 + E_n^1 + E_n^2 + \ldots \]

\[ E_n^1 = \langle \psi_n^0 | \sum V | \psi_n^0 \rangle \]

\[ E_n^2 = \sum_{m \neq n} \frac{K \langle \psi_n^0 | V | \psi_m^0 \rangle \langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n^0 - E_m^0} \]

These are the main useful formulas.

Example 1: Relativistic corrections to Hydrogen eigenvalues

Non relativistic

\[ H_0 = \frac{\vec{p}^2}{2m} - \frac{e^3}{r} \]

Relativistic

\[ H = \sqrt{mc^2 + \vec{p}^2 c^2} - \frac{e}{r} - mc^2 \]

\[ mc - mc^2 \] is designed so both Hamiltonians agree when \( \vec{p} = 0 \); we are looking for corrections in powers of \( \vec{p} \).
\[ \sqrt{1 + x} = 1 + \frac{1}{2} x - \frac{1}{8} x^2 + \cdots \]

\[ \sqrt{m^2 c^4 + p^2 c^2} - mc^2 = \]

\[ mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} - mc^2 = \]

\[ mc^2 \left( 1 + \frac{p^2}{2m^2 c^2} - \frac{(p^2)^2}{8m^4 c^4} + \cdots \right) - mc^2 = \]

\[ \frac{p^2}{2m} - \frac{(p^2)^2}{8m^3 c^2} + \cdots \]

A good check is to make sure both terms have the same dimension - not \( p^2/mc^2 \) is dimensionless.

Define

\[ H = \frac{p^2}{2m} - \frac{(p^2)^2}{8m^3 c^2} \]

\[ H_0 = \frac{p^2}{2m} - \frac{\xi^2}{\tilde{r}} \]

\[ V = -\frac{(p^2)^2}{8m^3 c^2} \]

We consider the correction to the hydrogen binding energy,

\[ E_1 = \langle 1001 \mid V \mid 1100 \rangle = \]

\[ -\frac{1}{8m^2 c^2} \langle 1001(p^2) \mid 1100 \rangle \]
To compute this we need an expression for the wave function

$$\langle \ell | 100 \rangle = Y_{\ell,0}(\theta, \phi) \frac{2}{(a_0)^{\ell/2}} e^{-\ell/a_0} ; \quad Y_{\ell,0} = \frac{1}{\sqrt{4\pi}}$$

where $a_0$ is the Bohr radius.

The correction is:

$$\langle 100 | \mathbf{V} | 100 \rangle =$$

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 dr \frac{1}{4\pi} \frac{2}{(a_0)^{\ell/2}} e^{-\ell/a_0} (\frac{\hbar^4}{8m^3c^4} \int_0^\infty r^2 dr \ p^2 (e^{-\ell/a_0}) \ p' (e^{-\ell/a_0}) - \frac{\hbar^4}{2a_0^6 m^3 c^4} \int_0^\infty r^2 \ e^{-2\ell/a_0} dr$$

$$- \frac{\hbar^4}{2a_0^7 m^3 c^4} \int_0^\infty r^2 \ e^{-2\ell/a_0} \ dr + \frac{\hbar^4}{2a_0^7 m^3 c^4} \int_0^\infty \frac{2r}{a_0} \ e^{-2\ell/a_0} \ dr$$

$$- \frac{\hbar^4}{4a_0^9 m^3 c^4} \int_0^\infty u^2 e^{-u} du$$

$$u = \frac{2r}{a_0}$$
\[
\sum_{m=1}^{n} e^{-u} du = \frac{d}{dn^2} \sum_{m=1}^{n} e^{-u} du =
\]
\[
\frac{d}{dn^2} \sum_{m=1}^{n} e^{-u} du = \frac{d}{dn^2} \frac{1}{m} \sum_{m=1}^{n} e^{-u} du
\]
\[
= \frac{d}{dn} \left( -\frac{1}{m^2} \right) = 2 \frac{1}{m^3} \bigg|_{m=1} = 2 (-e^{-u} + e^{u})
\]

Multiplying the expression on the last page by \(2\) gives:

\[
E' = -\frac{\hbar^4}{2a_o^4 m^3 c^2}
\]

Because we get a non-zero \(E'\), we do not have to worry about degeneracies in this case.

Example 2: Shifted Harmonic Oscillator - Here I use creation and annihilation operators.
\[ H_0 = \frac{\hbar \omega}{\sqrt{n}} \left( a^+ a + \frac{1}{2} \right) \]

\[ \langle n \mid 1 \rangle = \frac{1}{\sqrt{n}} (a^+)^n \mid 0 \rangle \]

\[ a \mid 0 \rangle = 0 \]

\[ \langle n \mid m \rangle = \delta_{nm} \]

\[ a \mid n \rangle = \sqrt{n} \mid n-1 \rangle \]

\[ a^+ \mid n \rangle = \sqrt{n+1} \mid n+1 \rangle \]

Let

\[ H = \frac{\hbar \omega}{\sqrt{n}} (a^+ a + \frac{1}{2}) + \Delta (a + a^+) \]

Note we add \( a + a^+ \) so \( H \) is Hermitian.

In this example, the first correction vanishes.

\[ \Delta \langle n \mid a^+ a \mid n \rangle = \]

\[ \Delta \langle n \mid n-1 \rangle \sqrt{n} + \Delta \langle n \mid n+1 \rangle \sqrt{n+1} \]

by equation (1)
In this case the first non zero correction is $E_2^2$.

$$E_2^2 = \sum_{m \neq n} \frac{\l<n1v1m\r>^2}{E_n - E_m}$$

$$E_n - E_m = \hbar \omega (n + \frac{1}{2} - m - \frac{1}{2}) = \hbar \omega (n - m)$$

$$\l<n1v1m\r> = \l<n\big|\Delta (a + a^\dagger)\big|m1\r> =$$

$$\Delta \sqrt{m} \l<n1m-1\r> + \Delta \sqrt{m+1} \l<n1m+1\r>$$

$$n + \frac{1}{2}, \quad m = n + \frac{1}{2}, \quad n, \quad m = n - \frac{1}{2}$$

In this case there are only 2 nonzero terms in the infinite sum.

$$E_2^2 = \frac{\l<n1v1n-1\r>^2}{E_n - E_{n-1}} + \frac{\l<n1v1n+1\r>^2}{E_n - E_{n+1}}$$

$$= \frac{\Delta^2 n}{\hbar \omega} - \frac{\Delta^2 (n+1)}{\hbar \omega}$$

$$= \frac{\Delta^2}{\hbar \omega}$$

$$= -\frac{\Delta^2}{\hbar \omega}$$
In this case it turns out that second order perturbation mean gives the exact result.

To see this note

\[ H = \hbar \omega (a^+a + \frac{n}{2}) + \Delta (a+a^+) \]

Let \( c \) be an arbitrary real constant \( \Delta \)

\[ H = \hbar \omega (a^+(a^+c+c) + \frac{1}{2}) + \Delta c^+c-a+a^+c-c \]

\[ = \hbar \omega \left[ (a^+c)(a^+c) + \frac{1}{2} - c (a+a) - c (a^+c) + c^2 \right] \]

\[ + \Delta (a+a) + \Delta (a^+c) - 2c\Delta \]

Let \( a' = a + c \)

\[ = \hbar \omega \left( a'^+a' + \frac{1}{2} \right) - \hbar \omega c (a'^+a'^+) + \hbar \omega c^2 \]

\[ + \Delta (a'^+a'^+) - 2c\Delta \]

We can cancel the \( a'^+a'^+ \) by choosing

\[ \Delta = \hbar \omega c \quad c = \frac{\Delta}{\hbar \omega} \]

\[ = \hbar \omega \left( a'^+a' + \frac{1}{2} \right) + \frac{\Delta^2}{\hbar \omega} - 2 \frac{\Delta^2}{\hbar \omega} \]

Note: \( \Gamma a'^+a' = \Gamma a+c \quad a^+c+c = \Gamma a^+c^+c = 1 \)

\[ = \hbar \omega (n+\frac{1}{2}) - \frac{\Delta^2}{\hbar \omega} (2-1) = \hbar \omega (n+\frac{1}{2}) - \frac{\Delta^2}{\hbar \omega} \]
In this case

1. We had to go to second order
2. Only a finite # of terms in the infinite sum are non-0
3. It gave the exact result

Example 3

\[ H = \begin{pmatrix} \lambda & \Delta \\ \Delta & \lambda \end{pmatrix}, \quad H_0 = \begin{pmatrix} \lambda & 0 \\ 0 & \lambda \end{pmatrix}, \quad V = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} \]

\[ \Psi = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Psi' = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E_1 = \lambda, \quad E_2 = \lambda \]

\[ \langle \Psi | V | \Psi' \rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \]

\[ \langle \Psi' | V | \Psi \rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 \]

Again we need to go to second order.

\[ E_1^2 = \frac{\langle \Psi | V | \Psi' \rangle^2}{\lambda - \lambda_2} = \frac{\langle 1 | 0 \rangle (0 \Delta) (1) \langle 0 | 1 \rangle}{\lambda - \lambda_2} = \frac{\Delta^2}{\lambda_2 - \lambda_1} \]

\[ E_2^2 = \frac{\langle \Psi' | V | \Psi \rangle^2}{\lambda - \lambda_1} = \frac{\langle 0 | 1 \rangle (\Delta 0) (1) \langle 1 | 0 \rangle}{\lambda - \lambda_1} = \frac{\Delta^2}{\lambda_2 - \lambda_1} \]
This can also be solved exactly.

The eigenvalue we roots of

\[ \det (E \mathbf{I} - \mathbf{H}) = \det \begin{pmatrix} E - \lambda_1 - \Delta & 1 \\ -1 & E - \lambda_2 \end{pmatrix} \]

\[ E^2 - (\lambda_1 + \lambda_2)E + \lambda_1 \lambda_2 - \Delta^2 = 0 \]

using the quadratic formula,

\[ E = \frac{1}{2} \left[ (\lambda_1 + \lambda_2) \pm \sqrt{(\lambda_1 + \lambda_2)^2 - 4(\lambda_1 \lambda_2 - \Delta^2)} \right] \]

\[ = \frac{1}{2} \left[ (\lambda_1 + \lambda_2) \pm \sqrt{(\lambda_1 - \lambda_2)^2 + 4\Delta^2} \right] \]

\[ = \frac{1}{2} \left[ (\lambda_1 + \lambda_2) \pm (\lambda_1 - \lambda_2) \sqrt{1 + \frac{4\Delta^2}{(\lambda_1 - \lambda_2)^2}} \right] \]

\[ = \frac{1}{2} \left[ (\lambda_1 + \lambda_2) \pm (\lambda_1 - \lambda_2) \left( 1 + \frac{\Delta^2}{\lambda_1 - \lambda_2} + \ldots \right) \right] \]

\[ E_1 = \lambda_1 + \frac{\Delta^2}{\lambda_1 - \lambda_2} \]

\[ E_2 = \lambda_2 - \frac{\Delta^2}{\lambda_1 - \lambda_2} \]

we see perturbation theory gives

agrees with the leading term

in the Taylor series for the

exact solution.
Degenerate case

Since $H_0$ is simple it usually has a lot of symmetries. In this case it is common to have a lot of symmetries.

If $H_0$ is invariant under rotations

$$U(R)H_0U(R) = H_0$$

$$[\mathbf{J}, H_0] = 0$$

$$H_0 |\psi_n\rangle = E_n |\psi_n\rangle$$

$$H_0 J_\pm |\psi_n\rangle = J_\pm H_0 |\psi_n\rangle = E_n J_\pm |\psi_n\rangle$$

This means that if $|\psi_n\rangle \neq J_\pm |\psi_n\rangle$ then they are both eigenvectors of $H_0$ with eigenvalue $E_n$.

To treat the degenerate case assume

$$H_0 |\psi_n\rangle = E_n |\psi_n\rangle$$

$$H = H_0 + V$$

as before. If a state is degenerate we can relabel the states.
(Assuming $N$ states with the same eigenvalue) so the first $N$ states have the same eigenvalue:

\[ H_0 \Psi_n = E_n \Psi_n \quad n = 1 \ldots N \]
\[ H_0 \Psi_n = E_n \Psi_n \quad n = N+1 \ldots \infty \quad E_n \neq E_1 \]

We still can assume

\[ \langle \Psi_n | \Psi_m \rangle = 8 \delta_{nm} \]

we cannot use non degenerate perturbation theory because except $\Delta(E_0)$ there are denominators

\[ \frac{1}{E_n - E_m} \]

which are not defined when

\[ E_n = E_m \]

To treat this we define 2 projection operators

\[ P = \sum_{n=1}^{N} | \Psi_n \rangle \langle \Psi_n | \]
\[ Q = \sum_{n=N+1}^{\infty} | \Psi_n \rangle \langle \Psi_n | \]
Mere satisfy

\[ P + Q = \sum_{n=1}^{\infty} \langle \psi_n^+ | \psi_n^- \rangle = I \]

\[ p^2 = p \quad Q^2 = Q \quad P \cdot Q = Q \cdot P = 0 \]

Next we write

\[ H = H_0 + V = (P + \omega)(H_0 + V)(P + \omega) = \]

\[ PH_0 P + QH_0 Q + PV + PVQ + QVP + QVQ \]

Note

\[ QH_0 P = E_0 P = 0 = PHQ \]

we express this as 2 terms

\[ H_0' = PH_0 P + PV + QH_0 Q \]

\[ V' = PVQ + QVP + QVQ \]

\[ H = H_0' + V' \]

we want to find eigenvalues and eigenvectors of \( H_0' \)
\[ \phi_n \quad n > N \]

\[ (P H_0 P + P V P + G H G) \psi_n^o > \]

\[ (\sigma + \sigma + E_\sigma) \psi_n^o > \]

so the original eigenvalues \( n > N \) are also eigenvalues of \( H'_o \) with the same eigenvalues \( E_n^o \)

For \( n \leq N \) we have to diagonalize \( P H_0 P + P V P \)

\[ \psi_n^o' = \sum_{k=1}^{N} C_n^k \psi_k^o > \]

\[ (P H_0 P + P V P) \psi_n^o > = E' \psi_n^o' > \]

\[ (E_1^o + P V P) \psi_n^o > = E' \psi_n^o' > \]

multiply by \( \psi_m^o > \)
\[
\langle \psi_m^0 | (E_i^0 + P V P) \sum_{k=1}^{N} c_k^* \psi_R^0 \rangle = \sum_{k=1}^{N} \langle \psi_m^0 | \psi_R^0 \rangle c_k E
\]

\[
\sum_{k=1}^{N} \left( E_i^0 S_{mk} + \langle \psi_m^0 | \psi_R^0 \rangle \right) c_k = \sum_{k=1}^{N} S_{mk} c_k E
\]

We can write this as a matrix eigenvalue problem:

\[
\sum_{k=1}^{N} \left( (E - E_i^0) S_{mk} + \langle \psi_m^0 | \psi_R^0 \rangle \right) c_k = 0
\]

This is an eigenvalue problem for an \( N \times N \) matrix, where the eigenvalues are the values of \( E \) that make

\[
\det \left( (E - E_i^0) I_{N \times N} + \langle \psi_m^0 | \psi_R^0 \rangle \right) = 0
\]

This means the matrix does not have an inverse, which implies there are non-zero solutions \( c_k \).
The determinant is degree $N$ polynomial in $E$. The matrix $M_{mn} = E_i \delta_{mn} + \langle \psi_n' | V | \psi_n' \rangle$ is Hermitian so

* There are $N$ real eigenvalues $E_n'$

and $N$ eigenfunctions that can be chosen to be orthonormal:

* $| \psi_n' \rangle = \sum_{k=1}^{N} C_k^* | \psi_k \rangle$

Note:

$P \mid \psi_n' \rangle = \mid \psi_n' \rangle$

$Q \mid \psi_n' \rangle = 0$.

The $N$ eigenvalues $E_n'$ are the solution to the problem.

They may or may not lift the degeneracy.
Note that either
\[ \{ |\psi_n^0 \rangle \}_{n=1}^N \text{ or } \{ |\psi_n^1 \rangle \}_{n=1}^N \]
are a basis for the subspace spanned by the degenerate eigenstates.

The \( E_n^0 \) are not necessarily degenerate because \( V \) may lift the degeneracy.

In many cases it is possible to guess \( |\psi_n \rangle \) that diagonalize the \( N \times N \) matrix \( P (H_0 + V) P \).

It is now possible to improve this using non-degenerate perturbation theory.
assume that a pair of
of the eigenstates \( |\psi_n'\rangle \)
are still degenerate

\[
E_n^1 = \langle \psi_n' | (PVG + QVP + QVQ) | \psi_n' \rangle
\]

\[
E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_n' | (PVG + QVP + QVQ) | \psi_m' \rangle|^2}{E_n^0 - E_m^0}
\]

\[
= \sum_{m > n} \frac{|\langle \psi_n' | (PVG) | \psi_m' \rangle|^2}{E_n^0 - E_m^0}
\]

since this only involves \( m > n \) the
denominators will be non 0, unless the eigenvalue \( E_n^0 \) happens

to be equal to one of the
\( E_m^0 = E_n^0 \) for \( m > n \).

examples