Recitation notes

Perturbation theory

One of the main concepts that help understand the interaction of matter with electromagnetic field and with any other kind of weak (compared to bonding) external stimulus is perturbation theory. In QM books it is usually presented as a powerful way of calculating non-hydrogen-like atoms, in reality most of the real like calculations are done with variational theory while perturbation theory is used to understand the physical aspect of matter/wave interaction.

Let us consider a system whose Hamiltonian can be expressed as a known unperturbed Hamiltonian \( \hat{H}_0 \) plus a secondary operator whose magnitude is small compared to the unperturbed one \( \hat{W} \):

\[
\hat{H} = \hat{H}_0 + \hat{W}
\]

A common practice, introduced mainly to check and understand the magnitude of the effect of the “perturbation” \( \hat{W} \) is to express it as

\[
\hat{W} = \lambda \hat{W} \rightarrow \lambda \ll 1.
\]

Let us now assume that we know the solution to the eigenvalue problem for the unperturbed Hamiltonian and the solution is quantized and non degenerate with \( p \) being an integer that represents the quantum index.

\[
\hat{H}_0 \left| \phi_p \right> = E_p \left| \phi_p \right>
\]

The new Hamiltonian can be written as a function of \( \lambda \) and consequently the new eigenvalue problem can be rewritten as a function of \( \lambda \) (\( \lambda \) actually is a parameter for the problem not a variable)

\[
\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{W}
\]

\[
\hat{H}(\lambda) \left| \phi_p(\lambda) \right> = E_p(\lambda) \left| \phi_p(\lambda) \right>
\]

We can physically assume that both the eigenvalue and the eigenfunctions that solve this problem can be expressed as polynomial expansion in \( \lambda \), the expression would look as follows, for the sake of clarity we will concentrate just on second order polynomial, the result can be easily extrapolated to higher orders.

\[
E(\lambda) = \sum \lambda^q \varepsilon_q = \varepsilon_0 + \lambda \varepsilon_1 + \lambda^2 \varepsilon_2 + O(\lambda^3)
\]

\[
\left| \psi(\lambda) \right> = \sum \lambda^q |q> = |0> + \lambda |1> + \lambda^2 |2> + O(\lambda^3)
\]

Using this expansions we can rewrite the eigenvalue problem:
\[
\left( \hat{H}_0 + \lambda \hat{W} \right) \left( \sum \lambda^q |q\rangle \right) = \left( \sum \lambda^q \varepsilon_q \right) \left( \sum \lambda^q |q\rangle \right)
\]
\[
\hat{H}_0 |0\rangle + \sum \lambda^q \varepsilon_q |q\rangle + O(\lambda^4) = |0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + O(\lambda^4)
\]
\[
\hat{H}_0 |0\rangle + \hat{H}_0 |1\rangle + \hat{H}_0 |2\rangle + \lambda \hat{W} |0\rangle + \lambda^2 \hat{W} |1\rangle + \lambda^3 \hat{W} |2\rangle = |0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + \lambda^3 |3\rangle
\]
\[
= \varepsilon_0 |0\rangle + \lambda \varepsilon_1 |1\rangle + \lambda^2 \varepsilon_2 |2\rangle + \lambda^3 \varepsilon_3 |3\rangle
\]
\[
\begin{align*}
\hat{H}_0 |0\rangle + \hat{H}_0 |1\rangle + \hat{H}_0 |2\rangle + \lambda \hat{W} |0\rangle + \lambda^2 \hat{W} |1\rangle + \lambda^3 \hat{W} |2\rangle &= |0\rangle + \varepsilon_0 |1\rangle + \lambda \varepsilon_1 |2\rangle + \lambda^2 \varepsilon_2 |3\rangle \\
&\quad + \lambda^3 \varepsilon_3 |4\rangle
\end{align*}
\]
(0, 0) = 1.
Now because \( E_n \equiv E(\lambda = 0) = \varepsilon_0 \) it is trivial to see that within a phase: \( |0\rangle = |\varphi_n\rangle \)

For the zero order:
\[
\hat{H}_0 |0\rangle = \varepsilon_0 |0\rangle
\]
For the each of these equation we will impose the eigenvalue \( \psi(\lambda) \) to be normalized in this case this condition (\( \psi(\lambda = 0) \)) is easily met if: \( \langle 0|0\rangle = 1 \).

Now because \( E_n \equiv E(\lambda = 0) = \varepsilon_0 \) it is trivial to see that within a phase: \( |0\rangle = |\varphi_n\rangle \)

For the first order:
\[
\left( (\hat{H}_0 - \varepsilon_0 I) + (\hat{W} - \varepsilon_1 I) \right) |0\rangle = 0
\]
Normalizing the eigenfunction |0⟩ + λ |1⟩ we get: \( \langle 0|1\rangle = \langle 1|0\rangle = 0 \)

Projecting everything on \( |0\rangle \) and remembering that \( |0\rangle = |\varphi_n\rangle \) we get:
\[
\langle \varphi_n | (\hat{H}_0 - \varepsilon_0 I) + (\hat{W} - \varepsilon_1 I) |0\rangle = 0
\]
\[
\langle \varphi_n | \hat{H}_0 |1\rangle - \varepsilon_0 \langle \varphi_n | 1\rangle + \langle \varphi_n | \hat{W} |0\rangle - \varepsilon_1 \langle \varphi_n | 1\rangle = 0
\]
\[
\langle \varphi_n | \hat{W} |\varphi_n\rangle = \varepsilon_1
\]

So the first energy correction is simply \( E_n(\lambda) = E_0 + \lambda \langle \varphi_n | \hat{W} |\varphi_n\rangle \)

Let us now project the same equation on all of the other eigenfunctions:
\[
\langle \varphi_p | (\hat{H}_0 - \varepsilon_0 I) + (\hat{W} - \varepsilon_1 I) |0\rangle = 0
\]
\( p \neq n \)
\[
E_p - E_n \langle \varphi_p | 1\rangle + \langle \varphi_p | \hat{W} |\varphi_n\rangle = 0
\]
\[
|1\rangle = \sum_p \frac{\langle \varphi_p | \hat{W} |\varphi_n\rangle}{(E_n - E_p)} |\varphi_p\rangle
\]
\[
|\psi(\lambda)\rangle = |\varphi_n\rangle + \lambda \sum_p \frac{\langle \varphi_p | \hat{W} |\varphi_n\rangle}{(E_n - E_p)} |\varphi_p\rangle
\]

This result is really important because it testifies that any perturbation mixes the original state with a combination of all the other states with coefficients that are inversely
proportional to the energy distances between the states and directly proportional to the projection of those states on the unperturbed state via the perturbation operator. (If you express the operator in term of a matrix the projection coefficient are the non-diagonal terms).

A perfectly similar calculation leads to find the second order terms. We will mention here just the second order energy perturbation result:

$$\varepsilon_2 = \sum_p \frac{|\langle \phi_p | \hat{W} | \phi_n \rangle |^2}{(E_n - E_p)}$$

Let’s now calculate the solution of an anharmonic oscillator with the following potential energy:

$$V(x) = \frac{1}{2} m \omega^2 x^2 + a \omega \hbar x^3 + b \omega \hbar x^4$$

It is easy to see that the $W = ax^3 + bx^4$

So the first order correction to the energy are:

$$\varepsilon_1 = \langle \phi_n | \hat{W} | \phi_n \rangle = a \omega \hbar \langle \phi_n | x^3 | \phi_n \rangle + b \langle \phi_n | x^4 | \phi_n \rangle$$

The first term is always zero, because is always an odd function integrated over all space while the second term can be calculated (with Mathematica or just copied from books):

$$\langle \phi_n | x^4 | \phi_n \rangle = \left( \frac{3}{4} \frac{\hbar}{m \omega} \right)^2 (2n^2 + 2n + 1)$$

To calculate the effect of the cubic term we have to go and calculate the second order effects, the calculation involve the recognition that the only non vanishing terms are the ones for $n \pm 1$ and $n \pm 3$ and it yields the following result:

$$\varepsilon_2 = \sum_p \frac{|\langle \phi_p | a^2 \hbar \omega | \phi_n \rangle |^2}{(E_n - E_p)} = \left[ \frac{15}{4} \left( n + \frac{1}{2} \right)^2 - \frac{7}{16} \right] a^2 \hbar \omega$$

Thus the energy eigenvalues for this problem can be rewritten as:

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega + \left[ \frac{15}{4} \left( n + \frac{1}{2} \right)^2 - \frac{7}{16} \right] a^2 \hbar \omega + \frac{3}{4} \left( \frac{\hbar}{m \omega} \right)^2 (2n^2 + 2n + 1) \hbar \omega$$

Now if we assume $b=0$ we can calculate that calculate that:

$$E_n - E_{n-4} = \left( 1 - \frac{15}{2} a^2 n \right) \hbar \omega$$

and more importantly we can recalculate the eigenstates of the problems:

$$|\psi(\lambda)\rangle = |\phi_n \rangle + 3 a \left( \frac{n + 1}{2} \right)^{\frac{3}{2}} |\phi_{n+1} \rangle + 3 a \left( \frac{n}{2} \right)^{\frac{3}{2}} |\phi_{n-1} \rangle + a \left( \frac{3 (n + 3)(n + 2)(n + 1)}{8} \right)^{\frac{1}{2}} \left( \frac{n + 3}{2} \right)^{\frac{1}{2}} |\phi_{n+3} \rangle + a \left( \frac{3 (n - 2)(n - 1)n}{8} \right)^{\frac{1}{2}} \left( \frac{n - 1}{2} \right)^{\frac{1}{2}} |\phi_{n-3} \rangle$$