P4410 LECTURE 29

Administrivia: Last problem on previous set will not be graded — assigned prematurely, and similar problem on current set. ← If you see something weird like that please let me know!

Correction from Friday: Spin-orbit energy correction.

$$E^{(1)}_{nlj} = \langle n l j m_j | \hat{H}' | n l j m_j \rangle = \frac{(Z\alpha)^4}{2} \frac{mc^2}{n^3 l(l+\frac{1}{2})(l+1)} \frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

Time-dependent perturbation theory:

When $\hat{H}$ is not time-dependent, use pert. theory to find approximations to the exact energy eigenstates/values, starting from the exact solutions for the zeroth-order Hamiltonian.

Now if $\hat{H}$ is time-dependent, these eigenstates & eigenvalues are not very useful: $\langle E \rangle$ is not a constant, and even the exact eigenstates of $\hat{H}(t)$ don't give the time dependence of the state in a straightforward way. To get time dependence, need to solve Schrödinger eqn:

$$i\hbar \frac{d|\psi(t)\rangle}{dt} = \hat{H}(t)|\psi(t)\rangle .$$

Often this is not solvable analytically (a nice exception is the NMR problem). Often only numerical solutions are practical. But, for some situations we can treat $\hat{H}$ as a large, solvable, time-independent part with a time-dependent perturbation. Application: transitions between states in a field.

So $\hat{H} = \hat{H}_0 + \hat{H}'(t)$, $\frac{\partial \hat{H}_0}{\partial t} = 0$.

Apply perturbation theory:

Write $\hat{H}_0$ solutions as before: $\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$, $\langle m^{(0)}|n^{(0)}\rangle = \delta_{mn}$

We don't have to worry about degeneracy in $\hat{H}_0$ since we're ~~not~~ out to find eigenstates of $\hat{H}'(t)$.

Again, introduce a bookkeeping constant λ to keep track of the order of the approximation. Difference is that we're trying to solve the time-dependent Schr. eqn. for $\hat{H}_0 + \hat{H}'(t)$, not the $\hat{H}|\psi\rangle = E|\psi\rangle$ eigenvalue eqn. We need to exploit the fact that with $\lambda\hat{H}' \to 0$, solution is just to expand $|\psi(t=0)\rangle$ in $\hat{H}_0$ basis and apply $e^{-\frac{iE_n^{(0)}t}{\hbar}}$ to each term.

So write exact vector as a sum:

$$|\psi(t)\rangle = \sum_n C_n(t)\, e^{\frac{-iE_n^{(0)}t}{\hbar}} |n^{(0)}\rangle, \quad C_n(0) = \langle n^{(0)}|\psi(0)\rangle$$

(This is not an approximation, since $|n^{(0)}\rangle$ form a complete basis.)
(For $\lambda\hat{H}' \to 0$, $C_n(t) = C_n(0)$)

Now plug solution into Schröd. eqn:

$$\left(i\hbar\frac{d}{dt} - \hat{H}_0 - \lambda\hat{H}'(t)\right) \sum_m C_m(t)\, e^{-\frac{iE_m^{(0)}t}{\hbar}} |m^{(0)}\rangle = 0$$

Take the $\frac{d}{dt}$ and the $\hat{H}_0$ and each pulls an E_m out of the $|m^{(0)}\rangle$.
OK – but we want equation for each C_m separately.

So, project both sides with $\langle n^{(0)}| e^{iE_n^{(0)}t/\hbar}$

$$(*) \quad i\hbar \frac{dC_n}{dt} = \lambda \sum_m C_m(t) \exp\left[i\left(E_n^{(0)} - E_m^{(0)}\right)t/\hbar\right] \langle n^{(0)}|\hat{H}'(t)|m^{(0)}\rangle$$

Still exact! To integrate it, need initial conditions: Start in an eigenstate of $\hat{H}_0$: $|\psi(0)\rangle = |k^{(0)}\rangle \Rightarrow C_n(0) = \delta_{nk}$.

(Note – since Schr. eqn. is linear, can start in a superposition of states but solve each component this way.)

Now comes the approximation. Look for a series solution of $C_n(t)$ in powers of λ:

$$C_n(t) = C_n(0) + \lambda C_n^{(1)}(t) + \lambda^2 C_n^{(2)}(t) + \cdots$$

where want to determine the $C_n^{(1)}(t)$, etc. Since we're only interested in these, not perturbed energies, this is easier than T.I.P.T. Substitute series into $(*)$, treat result as a fn. of λ; collect terms of order λ and equate them. Zeroth order is trivial; that's just initial condition.

First order: $i\hbar \dfrac{dC_n^{(1)}}{dt} = \exp\left[i\left(E_n^{(0)} - E_k^{(0)}\right)t/\hbar\right] \langle n^{(0)}|\hat{H}'(t)|k^{(0)}\rangle$

integrate:

$$C_f^{(1)}(t) = \frac{-i}{\hbar} \int_0^t dt' \exp\left[i(E_f - E_i)t'/\hbar\right] H'_{fi}(t') \quad \text{where } H'_{fi}(t) = \langle f|H'(t)|i\rangle$$

with a slight notation change: drop superscripts on energies, states (since we aren't interested in time-independent state corrections), take $|k^{(0)}\rangle \to |i\rangle$, $|n^{(0)}\rangle \to |f\rangle$ → i.e. initial and final, both eigenstates of $\hat{H}_0$.

Now we can define a transition probability:

$$P_{fi}(t) \equiv \left| \langle f | \psi(t) \rangle \right|^2 = \left| C_f^{(1)}(t) \right|^2$$

Things to note:

$P_{fi}(t)$ is an order λ^2 expression.

$C_f^{(1)}(t)$ is a fourier transform in time of the (time-dependent) matrix element of $\hat{H}'$ between i and f, evaluated at the angular frequency $\frac{\Delta E}{\hbar}$ (Bohr frequency) associated with the energy change under consideration.