Phys 487 Discussion 14 – Selection Rules

Given • $H(t) = H^{(0)} + H'(t)$, • $\left\{ E_n^{(0)}, \left|n^{(0)}\right\rangle \right\}$ = the eigen-* of $H^{(0)}$ • initial state $\left|\psi(t=0)\right\rangle = \left|i^{(0)}\right\rangle$

then $\boxed{\left|\psi(t)\right\rangle = \sum_n c_n(t)\, e^{-i\omega_n t}\left|n^{(0)}\right\rangle}$ with $\boxed{i\hbar\,\dot{c}_f(t) = \sum_n H'_{fn}\, e^{i\omega_{fn}t} c_n(t)}$ • $\omega_{fn} \equiv \left(E_f^{(0)} - E_n^{(0)}\right)/\hbar$ • $H'_{fn} \equiv \left\langle f^{(0)}\middle|H'\middle|n^{(0)}\right\rangle$

& to 1st order in $H' \ll H^{(0)}$, $\boxed{c_f(t) \approx \delta_{fi} + \frac{1}{i\hbar}\int_0^t H'_{fi}(t')e^{i\omega_{fi}t'}dt'}$ $\rightarrow$ $\boxed{P_{i\to f} = \left|c_f(t)\right|^2}$

• Fermi's Golden Rule : $\boxed{R_{i\to f} \equiv \frac{P_{i\to f}}{t} = \frac{2\pi}{\hbar}\left|V_{fi}\right|^2 \rho\left(E_f\right)}$

Problem 1 : E1 Transitions

As we saw in class, the time-dependent perturbation $H'(\vec{r},t)$ that is produced by an

EM wave at lowest order in the small parameter $\vec{k}\cdot\vec{r} \approx r/\lambda << 1$ (typical situation in atomic physics) is the "**E1**" or "Electric Dipole" term, which comes from approximating the EM wave's electric field as constant over space, i.e. $\vec{E}(\vec{r}) \approx \vec{E}_0$. This is clearly reasonable when the E-field's wavelength is enormous compared to the tiny size of the atom! For such a constant field, using the Hermitian perturbation form

$$H'(\vec{r},t) = V(\vec{r})e^{i\omega t} + V^*(\vec{r})\, e^{-i\omega t}$$

that we used to derive Fermi's Golden Rule, we obtained

$$V^{\mathrm{E1}}(\vec{r}) = -q\frac{\vec{E}_0}{2}\cdot\vec{r} = -\frac{q}{2}\left(E_{0x}x + E_{0y}y + E_{0z}z\right).$$

Our study of time-dependent perturbation theory has taught us that a transition between atomic states i and f can only occur if $V_{fi} = \left\langle n_f\, l_f\, m_f \middle| V(\vec{r}) \middle| n_i\, l_i\, m_i \right\rangle$ is not zero. For an **E1 transition** to be **allowed**, this transition matrix element must be non-zero for $V(\vec{r}) \sim x$ and/or y and/or z (corresponding to the 3 possible linear-polarization directions from which any EM wave can be built).

(a) As we said in class, we would *really* like to avoid integrating $V_{fi} = \left\langle n_f\, l_f\, m_f \middle| V(\vec{r}) \middle| n_i\, l_i\, m_i \right\rangle$ … which we can do by expressing x, y, and z in terms of different operators, specifically those for which the $\left|nlm\right\rangle$ states are *eigenstates*. Those operators are L^2, L_z, and the atom's Hamiltonian. These fabulous commutators will save us :

$$\left[L_z, x\right] = i\hbar y\,, \quad \left[L_z, x\right] = -i\hbar x\,, \quad \left[L_z, x\right] = 0\,.$$

These are not the usual commutators for angular momentum! You have to go back to the definition $\vec{L} = \vec{r}\times\vec{p}$ and evaluate L_z in cartesian coordinates. First, prove this:

$$[AB, C] = A[B,C] + \left[A,C\right]B \qquad \text{☺ USEFUL! ☺}$$

(It is incredibly useful, but not worth memorizing since it takes 1 line to derive!) Then prove the three commutation relations above.

(b) Using one of those commutators to replace z, show that for $\vec{E}_0 \parallel \hat{z}$, $V_{fi} \sim \langle n_f\, l_f\, m_f | z | n_i\, l_i\, m_i \rangle = 0$ — i.e. no E1 transition is possible from $i \rightarrow f$ — unless $m_f - m_i \equiv$ **$\Delta m = 0$**. This is our first E1 selection rule!

IMPORTANT: Remember that $x, y, z, p_x, p_y, p_z, L_x, L_y, L_z, \ldots$ are all **Hermitian operators**, which basically allows them to "act to the left" as long as you watch out for *complex conjugates*. We did a partial selection-rule calculation in class, the steps we completed may help you. If this is unclear, great time to review Hermitian operators → ask your instructor!

(c) Repeat this exercise for $\vec{E}_0 \parallel \hat{x}$ and $\vec{E}_0 \parallel \hat{y}$. Combine your results to show that waves with such polarizations can only produce E1 transitions between states with **$\Delta m = \pm 1$**. That's our second selection rule. NOTE: This is the one we started deriving in class but didn't finish, you might find our partial work helpful.

(d) Finally, what about the l quantum number? Take this rather extraordinary commutator as given :

$$\left[L^2, \left[L^2, \vec{r}\,\right]\right] = 2\hbar^2\left(\vec{r}\,L^2 + L^2\vec{r}\,\right)$$

(I"m sure you can derive it, but not now!) Evaluate the transition matrix element

$$\langle n'\,l'\,m' | \left[L^2, \left[L^2, \vec{r}\,\right]\right] | n\,l\,m \rangle$$

and deduce that allowed E1 transitions — i.e., those with $\langle n'l'm' | \vec{r} | n\,l\,m \rangle \neq 0$ — require

$$2\left[l(l+1) + l'(l'+1)\right] = \left[l'(l'+1) - l(l+1)\right]^2.$$

Finally, show that E1 transitions require **$\Delta l = \pm 1$**. This is our best evidence so far that **photons have spin 1**.

Problem 2 : Higher Order Transitions

(a) Starting with the electric field of a plane wave, $\vec{E}(\vec{r},t) = E_0 \cos\left(\vec{k}\cdot\vec{r} - \omega t\right)$, make the atomic-scale approximation $\vec{k}\cdot\vec{r} \ll 1$ to <u>one more order than before</u>, so that $\vec{E}(\vec{r})$ is not purely constant. The answer is in the footnote[1] as a check.

(b) Construct the corresponding time-dependent perturbation $H'(\vec{r},t) = V(\vec{r})e^{i\omega t} + V^*(\vec{r})\,e^{-i\omega t}$ for this new order of position-dependence, and show that transitions of this order (**E2 = Electric Quadrupole**) require

$$V_{fi}^{\mathrm{E2}} \sim \langle n_f\, l_f\, m_f | \left(\hat{k}\cdot\vec{r}\right)\left(\hat{E}_0\cdot\vec{r}\right) | n_i\, l_i\, m_i \rangle \neq 0$$

i.e. we need $\langle n_f\, l_f\, m_f | \, x_a x_b \, | n_i\, l_i\, m_i \rangle \neq 0$ for at least one choice of components x_a and x_b.

FYI: Do you remember the form of the **quadrupole moment** of a charge distribution from E&M? It is a tensor with exactly such terms $x_a x_b$ as weighting factors : $Q_{ab} = \int dq\, \left(3x_a x_b - r^2\delta_{ab}\right)$ where $r^2 = x_1^2 + x_2^2 + x_3^2$.

---

[1] $\vec{E}(\vec{r},t) \approx \vec{E}_0\left[\cos(\omega t) + \left(\vec{k}\cdot\vec{r}\right)\sin(\omega t)\right]$