QM atomic transitions

We'll take an approach to understanding transitions from the quantum perspective

- An isolated atom in a pure energy eigenstate is in a *stationary* state:

$$\psi_n(\mathbf{r},t) = u_n(\mathbf{r})e^{-iE_n t/\hbar}$$

  - There is time dependence to the phase, but the amplitude remains constant. So, no transitions.

- An applied EM field of the right frequency can induce a mixture of two states:

$$\psi_1(\mathbf{r},t) = u_1(\mathbf{r})e^{-iE_1 t/\hbar} \qquad \psi_2(\mathbf{r},t) = u_2(\mathbf{r})e^{-iE_2 t/\hbar}$$

  - Superposition:

$$\psi(\mathbf{r},t) = a_1(t)\psi_1(\mathbf{r},t) + a_2(t)\psi_2(\mathbf{r},t)$$

  - w/ normalization: $\left|a_1(t)\right|^2 + \left|a_2(t)\right|^2 = 1$

QM charge distribution

- The electron is not localized in QM.
- The *charge* density can be calculated from ψ:

  $$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2$$

- For a stationary state:

  $$\rho(\mathbf{r},t) = -e\left|\psi_n(\mathbf{r},t)\right|^2 = -e\left|u_n(\mathbf{r})e^{-E_n t/\hbar}\right|^2 = -e\left|u_n(\mathbf{r})\right|^2$$

  – No time dependence, charge is not moving!
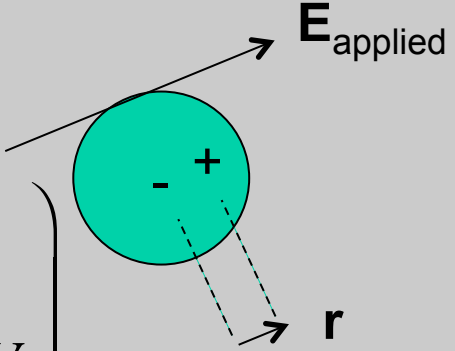
- For a superposition state:

  $$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2 = -e\left|a_1\psi_1 + a_2\psi_2\right|^2$$

  $$= -e\left(\left|a_1\psi_1\right|^2 + \left|a_2\psi_2\right|^2 + a_1 a_2^{*}\psi_1\psi_2^{*} + a_1^{*} a_2\psi_1^{*}\psi_2\right)$$

  – Cross terms will lead to oscillation in the charge distribution. This oscillation can lead to EM radiation.

QM dipole moment calculation

- The nucleus is localized, but the electron charge is distributed.

- The effective position is calculated like the center of mass, so dipole moment is:

$$\mu(t) = -e \int \mathbf{r} \left| \psi(\mathbf{r},t) \right|^2 dV \qquad \mathbf{p} = q\mathbf{r}$$

$$\mu(t) = -e \left(\int \mathbf{r} \left| a_1 \psi_1 \right|^2 dV + \int \mathbf{r} \left| a_2 \psi_2 \right|^2 dV \right. \\ \left. + \int a_1 a_2^* \mathbf{r} \psi_1 \psi_2^* \, dV + \int a_1^* a_2 \mathbf{r} \psi_1^* \psi_2 \, dV \right)$$

  - Terms in red go to zero

- Probability density is 'even', r is 'odd': parity forces them to zero

Time dependent dipole moment

- The cross terms (which are like interference terms in optics), lead to time dependent oscillation:

$$\mu_{osc}(t) = -e\left(a_1 a_2^* \int \mathbf{r}\, \psi_1 \psi_2^* \, dV + a_1^* a_2 \int \mathbf{r}\, \psi_1^* \psi_2 \, dV \right)$$

$$= -e\left(a_1 a_2^* \int \mathbf{r}\, u_1(\mathbf{r}) u_2^*(\mathbf{r}) e^{+i(E_2-E_1)t/\hbar} \, dV + a_1^* a_2 \int u_1(\mathbf{r}) u_2^*(\mathbf{r}) e^{-i(E_2-E_1)t/\hbar} \, dV \right)$$

- Oscillation frequency: $\omega_{21} = (E_2 - E_1)/\hbar$

$$\mu_{osc}(t) = -e\,\mathrm{Re}\left[2 a_1 a_2^* \mu_{21} e^{i\omega_{21}t} \right]$$

$$\mu_{21} = \int u_1(\mathbf{r})(-e\mathbf{r}) u_2^*(\mathbf{r}) \, dV \qquad \text{Dipole "matrix element"}$$

- μ_{21} is the part that depends on the atomic structure, independent of the populations.
- This is a vector, but the direction of r corresponds to the E-field direction, relative to the atom or molecule.

QM dipole radiation: lifetime

- Estimate the radiated power from this oscillating dipole.

$$P_{rad} = \frac{1}{4\pi\varepsilon_0} \frac{2}{3} \frac{e^2 \ddot{x}^2(t)}{c^3} = \frac{1}{4\pi\varepsilon_0} \frac{2}{3} \frac{\ddot{\mu}^2(t)}{c^3}$$

Note: μ = p

$$\mu_{osc}(t) = -e \operatorname{Re}\left[2a_1 a_2^* \mu_{21} e^{i\omega_{21}t} \right]$$

$$\left(z + z^* \right)^2 = |z|^2$$

$$P_{rad} = \frac{1}{4\pi\varepsilon_0} \frac{2}{3} \frac{4e^2 \omega_{21}^4 \mu_{21}^2}{c^3} |a_1|^2 |a_2|^2 \cos[\omega_{21}t]$$

Time average over fast oscillation:

$$\overline{P}_{rad} = P'_{rad} |a_1|^2 |a_2|^2, \quad P'_{rad} = \frac{e^2 \omega_{21}^4 \mu_{21}^2}{3\pi\varepsilon_0 c^3} \equiv \frac{\hbar\omega_{21}}{\tau_{sp}}$$

$$\tau_{sp} = \frac{1}{A_{21}} = \frac{3\pi\hbar\varepsilon_0 c^3}{e^2 \omega_{21}^3 \mu_{21}^2}$$

Estimate of spontaneous lifetime

Spontaneous decay

- If we assume that the excitation probability of the upper level is small, then $|a_1|^2 = 1 - |a_2|^2 \approx 1$

- We can then deduce the change in upper level population:

$$\frac{dE}{dt} = -\bar{P}_{rad} = \hbar\omega_{21}\frac{d}{dt}|a_2(t)|^2$$

$$\frac{d}{dt}|a_2(t)|^2 \approx -\frac{1}{\tau_{sp}}|a_2(t)|^2 \rightarrow |a_2(t)|^2 \approx |a_2(0)|^2 \exp\left[-t/\tau_{sp}\right]$$

- This connects the spontaneous emission rate to a quantum calculation of the dipole moment.