Light-atom interaction: semiclassical model

Quantum mechanical description of an atom

Isolated atomic system: $\hat{H}_0 = \frac{1}{2m}\hat{p}^2 + V_c(\vec{r})$

Coulumb interaction

Such Hamiltonian determines atomic structure.
Interaction with e-m field is a weak perturbation

In the presence of e-m field

$$\hat{H} = \frac{1}{2m}[\hat{\vec{p}} + e\hat{\vec{A}}]^2 - e\varphi + V_c(\vec{r}) \qquad \left\{ \begin{array}{l} \vec{B} = \nabla \times \vec{A} \\ \vec{E} = \nabla\varphi - \partial\vec{A}/\partial t \end{array} \right.$$

vector potential — electrostatic potential

Coulumb (or radiation) gauge: $\nabla \cdot \vec{A} = 0$, $\varphi = 0$
in this gauge $\vec{A}$ obeys a wave equation, if $\vec{E}$ and $\vec{B}$ obey it

$$\nabla^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0$$

$$\hat{H} = \frac{1}{2m}[\hat{\vec{p}} + e\vec{A}]^2 + V_c(\vec{r}) \approx \frac{\hat{p}^2}{2m} + V_c(\vec{r}) + \underbrace{\frac{e}{m}\vec{A}\cdot\vec{p}}_{1^{st}\ \text{order perturbation}} + \underbrace{\frac{e^2}{2m}A^2}_{2^{nd}\ \text{order perturbation}}$$

Dipole approximation: $\lambda \gg a$ (extend of the electron's wave function)

In this approximation $\vec{A}\cdot\vec{p} \approx \vec{E}\cdot\vec{d}$
(see discussion in Scully and Zubairy)

$$\hat{H} = \hat{H}_0 + \underbrace{e\vec{r}\cdot\vec{E}}_{\hat{H}_i}$$

$\hat{H}_i$ – interaction Hamiltonian

For this course, we will always assume that the light-atom interaction is weak enough not ~~to~~ affect the atomic energy level structure; we will be looking for small shifts in energyes of atomic levels, as well as for induces transitions b/w existing levels.

Time-dependent perturbation theory

$$|\psi(t)\rangle = \sum_k c_k(t)\, e^{-iE_k t/\hbar}\, |k\rangle$$

where $\hat{H}_0 |k\rangle = E_k |k\rangle$ — energy spectrum of the unaffected atoms

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = (\hat{H}_0 + \hat{H}_I)\,|\psi(t)\rangle$$

$$i\hbar \sum_k \left(\dot{c}_k e^{-iE_k t/\hbar} |k\rangle - \cancel{\frac{iE_k}{\hbar} c_k e^{-iE_k t/\hbar} |k\rangle} \right) =$$

$$= \cancel{\hat{H}_0 \sum_k c_k(t)\, e^{-iE_k t/\hbar} |k\rangle} + \hat{H}_i \sum_{k'} c_{k'}(t)\, e^{-iE_{k'} t/\hbar} |k'\rangle$$

$$i\hbar \sum_k \dot{c}_k e^{-iE_k t/\hbar} |k\rangle = \hat{H}_i \sum_{k'} c_{k'}(t)\, e^{-iE_{k'} t/\hbar} |k'\rangle$$

$\langle \ell | \times$ $$i\hbar \dot{c}_\ell(t) = \sum_{k'} c_{k'}(t)\, e^{-i(E_{k'} - E_\ell)t/\hbar} \langle \ell | \hat{H}_i | \hat{k}' \rangle$$

(drop "'" $k' \to k$)

$$\dot{c}_\ell(t) = -\frac{i}{\hbar} \sum_k c_k(t)\, e^{i\omega_{\ell k} t} \langle \ell | \hat{H}_i | k \rangle$$

$$\omega_{\ell k} = \frac{E_\ell - E_k}{\hbar}$$ transition frequency

Case I: ~~very~~ weak off-resonant interaction
or short-time interaction

We assume that at $t=0$ the system is in a well-defined state $|i\rangle$

$$c_i(t=0) = 1 \qquad c_{f\neq i}(t=0) = 0$$

If no interaction occures, an atom will remain in the same state (since it is the eigenstate of H_0)

Assuming that the transition probability is small

$$c_x(t) = c_x^{(0)}(t) + \underbrace{c_x^{(1)}(t)}_{\sim H_I} + \underbrace{c_x^{(2)}(t) + \ldots}_{\sim H_I^2}$$

neglect for the first-order perturbation theory

$$c_i^{(0)} = 1 \qquad c_f^{(0)} = 0 \text{ for } f \neq i$$

$$\dot{c}_\ell^{(1)}(t) = -\frac{i}{\hbar} \sum_k c_k^{(0)}(t) \langle \ell|\hat{H}_i|k\rangle e^{i\omega_{\ell k} t}$$

$$\dot{c}_i^{(1)}(t) = -\frac{i}{\hbar} \langle i|H_I|i\rangle \qquad \dot{c}_f^{(1)}(t) = -\frac{i}{\hbar} \langle f|\hat{H}_i|i\rangle e^{i\omega_{fi} t}$$

$$\hat{H}_I = -e\vec{r}\vec{E}_0 \cos\omega t = -\vec{d}\vec{E}_0 \cos\omega t = -\vec{d}\,\underbrace{\hat{e}_p}_{\text{polarization}} E_0 \cos\omega t$$

$$\langle f|H_I|i\rangle = \langle f|\vec{d}|i\rangle \vec{E}_0 \cos\omega t = \rho_{fi} E_0 \cos\omega t$$

where

$$\rho_{fi} = \langle f|\vec{d}\cdot\vec{e}_p|i\rangle$$

transition dipole moment

Does not depend on the magnitude of e-m field, but depends on its polarization

Determines selection rules

if $\rho_{if} = 0$ the transition is forbidden

Since $\vec{r}$ is parity-odd, the states f and i must have opposite parity to make possible electro-dipole transition. It also means $\langle i | \hat{H}_i | i \rangle = 0$ for any $|i\rangle$, and $c_i^{(1)} = 0$
Thus, in the first order, the initial state is unperterbed

Hydrogen atom $|k\rangle = |n, \ell, m\rangle$

$$\psi_{n\ell m} = A_{n\ell m} R_{n\ell}(\varkappa r) L_\ell^m(\cos\theta) e^{im\varphi}$$

$$\langle f | -e\vec{r}\,\vec{e}_p | i \rangle = (-e)\langle f | \cancel{x} \overset{\sin\theta\cos\varphi}{\cancel{\cos\theta\cos\varphi}} + \cancel{y}\sin\theta \cancel{\sin}\sin\varphi + \cancel{z}\cos\theta | i \rangle$$

if $\vec{E} \parallel \vec{z}$

$$\rho_{fi} = \langle f | \cancel{z} \cos\theta | i \rangle = \{ \cancel{spa}\text{ radial part} \} \cdot \int L_{\ell_f}^{*m_f}(\cos\theta) \cdot \cos\theta \, L_{\ell_i}^{m_i}(\cos\theta) d\theta$$

$$\times \int_0^{2\pi} e^{-i(m_f - m_i)\varphi} d\varphi \neq 0 \text{ only if } \boxed{\begin{array}{l} m_f = m_i \\ |\ell_f - \ell_i| = 1 \end{array}}$$

if $\vec{E}$ is in x-y plane

$$\rho_{fi} = \langle f | r \sin\theta \underset{\sin\varphi}{\cos\varphi} | i \rangle \neq 0 \quad \text{only if } \boxed{\begin{array}{l} |m_f - m_i| = \pm 1 \\ |\ell_f - \ell_i| = 1 \end{array}}$$

For any polarization $\Delta\ell = \pm 1$

$\Delta m = 0, \pm 1$

Back to our equation

$$\dot{c}_f^{(1)} = -\frac{i}{\hbar} \rho_{fi} E_0 \cos\omega t \, e^{i\omega_{fi} t}$$

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \rho_{fi} E_0 \cos\omega t' e^{i\omega_{ff} t'} dt' =$$

$$= -\frac{i}{2\hbar} \rho_{fi} E_0 \int_0^t \left(e^{i(\omega+\omega_{fi})t'} + e^{-i(\omega-\omega_{fi})t'} \right) dt' =$$

$$= + \frac{\rho_{fi} E_0}{2\hbar} \left(\frac{1 - e^{i(\omega+\omega_{fi})t}}{\omega + \omega_{fi}} - \frac{1 - e^{-i(\omega-\omega_{fi})t}}{\omega - \omega_{fi}} \right)$$

Strongest effect comes from the term closer to resonance $|\omega - \omega_{fi}| \ll \omega, \omega_{fi}$ → can neglect the first term

$$c_f^{(1)} \simeq \frac{\rho_{fi} E_0}{2\hbar} \frac{e^{-i(\omega-\omega_{fi})t} - 1}{\omega - \omega_{fi}}$$

Probability of the transition

$$P_{fi} = |c_{fi}^{(1)}|^2 = \frac{|\rho_{fi} E_0|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega-\omega_{fi}}{2} t\right)}{(\omega - \omega_{fi})^2} = \frac{|\rho_{fi} E_0|^2}{\hbar^2} \frac{\sin^2 \Delta\omega t/2}{\Delta\omega^2}$$

Detuning of the laser freq. from the resonance frequency $\Delta\omega = \omega - \omega_{fi}$

For $\Delta\omega \neq 0$ $\quad P_{fi} \leq \frac{|\rho_{fi} E_0|^2}{\hbar^2} \frac{1}{\Delta\omega^2}$

For $\Delta\omega \to 0$ $\quad \sin\frac{\Delta\omega \cdot t}{2} \approx \frac{\Delta\omega \cdot t}{2}$

$$P_{fi} \approx \frac{|\rho_{fi} E_0|^2}{4\hbar^2} t^2$$

~~only~~ $P_{fi} \ll 1$ is only valid for short times