Light - atom interaction

1. Hamiltonian

Pure atomic system: $\hat{H}_0 = \frac{1}{2m}\hat{P}^2 + V_c(r) \rightarrow$ provides atomic structure

In the presence of the external fields

$$\hat{H} = \frac{1}{2m}[\hat{p} + e\hat{A}]^2 - e\varphi + V_c(r)$$

$\hat{A}$ — vector potential; φ — electrostatic potential

Coulumb (or radiation) gauge: $\nabla\cdot\vec{A} = 0$, $\varphi = 0$

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

$$\hat{H} = \frac{1}{2m}[p + eA]^2 + V(r) \approx \underbrace{\frac{1}{2m}\hat{P}^2 + V_c(r)}_{\text{atomic structure}} + \underbrace{\frac{e}{m}\vec{A}\cdot\vec{p}}_{\text{perturbation}} + \frac{e^2}{2m}A^2$$

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

$$\boxed{\hat{H} = \underbrace{\frac{1}{2m}\hat{P}^2 + V_c(r)}_{\hat{H}_0} + \underbrace{e\vec{r}\cdot\vec{E}}_{\hat{H}_I}}$$

$\hat{H}_I$ — interaction hamiltonian

2. Interaction of an atom with a classical field (perturbative approach)

We are going to treat the interaction with e-m field as perturbation. Thus, its effect will enable transitions b/w various states

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

time-dependent perturbation theory

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

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

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

The situation we are going to consider is that at some point of time our system is initialized → we know the exact initial stat $|i\rangle \Rightarrow C_i = 1,\ C_{f\neq i} = 0$

If no interaction, an atom would stay in this state forever (since it is the eigenstate of $\hat{H}_0$)

First order perturbation theory

$$C(t) = \underbrace{C^{(0)}(t)}_{\text{no interaction}} + \underbrace{C^{(1)}(t)}_{\sim H_i} + \ldots \quad \text{(we neglect)}$$

$$C_i^{(0)} = 1 \qquad C_{f\neq i}^{(0)} = 0$$

$$\dot{c}_i^{(1)} = -\frac{i}{\hbar} \langle i | \hat{H}_I | i \rangle$$

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

$$\hat{H}_I(t) = e\vec{r}\,\vec{E}_0 \cos\omega t = -\vec{d}\,\vec{E}_0 \cos\omega t$$

Transition dipole moment $\langle f | -\vec{d}\vec{E}_0 | i \rangle = \wp_{fi} E_0$
determines the selection rules
if $\wp_{fi} = 0$ transition is forbidden

Since $\vec{r}$ is parity-odd, the state 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 $|i\rangle$ $\dot{c}_i^{(1)} = 0$, $c_i^{(1)}(t) = 0$
Thus, in the first approximation the initial state is unperturbed.

$$c_f^{(1)} = -\frac{i}{\hbar} \int_0^t (\wp_{fi} \cdot E_0) \cos\omega t \, e^{i\omega_{fi} t} dt =$$

$$= -\frac{i}{2\hbar} (\wp_{fi} \cdot E_0) \int_0^t \left(e^{i(\omega+\omega_{fi})t} + e^{-i(\omega-\omega_{fi})t} \right) dt =$$

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

Rotating wave approximation $|\omega - \omega_{fi}| \ll \omega, \omega_{fi}$
$\rightarrow$ we can neglect the first term

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

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

$\Delta = \omega - \omega_{fi}$ - detuning of the laser from the atomic resonance

For $\Delta \neq 0$ (non-resonant conditions)

$$P_{fi} \leq \frac{|\wp_{fi} E_0|^2}{\hbar^2} \frac{1}{\Delta^2}$$

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

$$P_{fi}\Big|_{\Delta=0} = \frac{|\wp_{fi} E_0|^2}{4\hbar^2} t^2 \longleftarrow$$ not physical for large t, since $P \leq 1$

It is more accurate to define the transition probability rate $W_{fi} = dP_{fi}/dt$

We will use $\lim\limits_{t\to\infty} \frac{\sin^2(\frac{\Delta \cdot t}{2})}{\Delta^2} = \frac{\pi t}{2} \delta(\Delta)$

Thus we can present $P_{fi} = \frac{|\wp_{fi} E_0|^2}{\hbar^2} \frac{\pi t}{2} \delta(\Delta)$

and $W_{fi} = \frac{|\wp_{fi} E_0|^2}{\hbar^2} \frac{\pi}{2} \delta(\Delta)$

If there are many possible final states, then the total probability to leave the initial state $|i\rangle$ is

$$W_{i\to[f]} = \sum_f \frac{|\wp_{fi} E_0|^2}{\hbar^2} \frac{\pi}{2} \delta(\omega - \omega_{fi})$$

Fermi's golden rule