PH 585 AMO

Lecture # 2

Interaction of a one-electron atom with EM fields

QM description of an atom;

$$H \Psi_{n\ell m} = E_n \Psi_{n\ell m} \;; \quad \Psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad E_n = -\frac{E_I Z^2}{n^2} \leftarrow n^2\text{-degenerate (excluding spin)}$$

How to describe EM field and where does it fit into the Hamiltonian? ⟹

Try classical description of the EM wave ⟹

$$\vec{\mathcal{E}}(\vec r,t) = \mathcal{E}_0(\omega)\,\hat{\vec\varepsilon}\,\sin(\vec k\cdot\vec r - \omega t + \delta_\omega)$$

$\hat{\vec\varepsilon}$ ← unit polarization vector (here linear polariz.) — generally comb. of $\hat{\vec\varepsilon}_1, \hat{\vec\varepsilon}_2 \perp \vec k$

$$\vec B(\vec r,t) = \frac{\mathcal{E}_0(\omega)}{\omega}(\vec k\times\hat{\vec\varepsilon})\sin(\vec k\cdot\vec r - \omega t + \delta_\omega)$$

$$|B| = \frac{|\mathcal{E}|}{c}, \quad \vec B \perp \vec{\mathcal{E}}, \quad \vec B, \vec{\mathcal{E}} \perp \vec k$$

$$\omega = kc$$

$\vec{\mathcal{E}}$ and $\vec{B}$ can be generated from scalar and vector potentials (φ and $\vec{A}$) by

$$\vec{\mathcal{E}}(\vec{r},t) = -\vec{\nabla}\varphi(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t)$$

$$\vec{B}_{(\vec{r},t)} = \vec{\nabla}\times\vec{A}(\vec{r},t)$$

Since $\vec{\mathcal{E}}$ & $\vec{B}$ are invariant under gauge transform

$\vec{A} \to \vec{A} + \vec{\nabla}\chi$, $\varphi \to \varphi - \frac{\partial \chi}{\partial t}$ (χ is any real differentiable func.)

$\Downarrow$

need to choose gauge (one more condition) $\Rightarrow$

choose Coulomb gauge $\Rightarrow \vec{\nabla}\cdot\vec{A} = 0$, $\varphi = 0$ $\Rightarrow$

convenient when there are no sources

$$\vec{\nabla}^2\vec{A} - \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = 0 \Rightarrow \vec{A}(\vec{r},t) = A_0(\omega)\hat{\vec{\mathcal{E}}}\cos(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)$$

How would we include $\vec{A}$ into the Hamiltonian $\Rightarrow$

see pp. 1016 – 1017 of B & J

In a nutshell: $H = \sum_{i=1}^{3} p_i \dot{q}_i - L$ ← generalized coord and momentum

H: Classical Mechanics; L: Lagrangian

Eqs. of motion (Hamiltonian mechanics)

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \; ; \; \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

Charged particle in EM field $\Rightarrow$ $m\ddot{\vec{r}} = \vec{F}$ ← Newton's law

$$\vec{F} = q(\vec{\mathcal{E}} + \vec{v}\times\vec{B}) = q\left(-\vec{\nabla}\varphi - \frac{\partial\vec{A}}{\partial t} + \vec{v}\times(\vec{\nabla}\times\vec{A})\right)$$

$q_{1,2,3} = (x, y, z)$

But $\vec{p} = m\vec{v} + q\vec{A}$

since EM field is not conservative

Need to find L ← Lagrangian $= \frac{mv^2}{2} - q\varphi + q\vec{v}\cdot\vec{A}$, so that $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$ ← Lagrange's equations of motion

reduces to $m\ddot{\vec{r}} = \vec{F}$

and then, using p_i, $\dot{q}_i$ & L $\Rightarrow$ find $\mathcal{H}$ $\Rightarrow$

$$\mathcal{H} = \frac{1}{2m}\left(\vec{P} - q\vec{A}\right)^2 + q\varphi$$

$\Rightarrow$ similar in QM $\Rightarrow$

↖ CM Hamiltonian of a spinless charged particle in EM field

$$\Rightarrow \frac{1}{2m}\left(\vec{P}^2 - q(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) + q^2\vec{A}^2\right) + q\varphi = H$$

← QM

↑ symmetrization (don't know whether $[\vec{P}, \vec{A}] = $

In the coordinate (position) representation,

$\vec{p} = -i\hbar\vec{\nabla} \Rightarrow$

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + i\hbar\frac{q}{2m}\left(\vec{A}\cdot\vec{\nabla} + \vec{\nabla}\cdot\vec{A}\right) + \frac{q^2}{2m}\vec{A}^2 + q\varphi$$

Need to solve $i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$

Note: Coulomb gauge $\Rightarrow \varphi = 0$, $\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow$

$$\vec{\nabla}\cdot(\vec{A}\Psi) = \vec{A}(\vec{\nabla}\Psi) + \underbrace{(\vec{\nabla}\cdot\vec{A})}_{=0}\Psi = \vec{A}\cdot(\vec{\nabla}\Psi)$$

So, $$H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + i\hbar\frac{q}{m}\vec{A}\cdot\vec{\nabla} + \frac{q^2}{2m}\vec{A}^2$$

Back to hydrogenic atoms $\Rightarrow$

$$\underset{q=-e}{H} = \underbrace{-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon r}}_{H_0} \underbrace{- i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2}_{H_{int}(t)}$$

weak, unless EM wave is from a high power laser

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \left[H_0 + H_{int}(t)\right]\Psi(\vec{r},t)$$

$$H_{int} = H'(t) = \frac{e}{m}\vec{A}\cdot\underbrace{\vec{p}}_{-i\hbar\vec{\nabla}}$$ ← treat as small perturbation

Review of time-dependent perturbation theory

$$i\hbar\frac{\partial\Psi}{\partial t} = [H_0 + \overset{(\lambda)}{H'}(t)]\Psi$$

We know $H_0\Psi_k = E_k\Psi_k$ ← energy levels and wave functions of unperturbed atom

Then, $\Psi(\vec{r},t) = \sum_k C_k(t)\Psi_k(\vec{r})e^{-iE_kt/\hbar}$

$P_{i\to f} = |\langle f|\Psi(\vec{r},t)\rangle|^2 = |c_f|^2$

⇕ solution of

$$\dot{C}_b(t) = \frac{1}{i\hbar}\sum_k \overset{(\lambda)}{H'_{bk}}(t)C_k(t)e^{i\omega_{bk}t}$$

$H'_{bk} = \langle\Psi_b|H'(t)|\Psi_k\rangle$

$C_b = C_b^{(0)} + \lambda C_b^{(1)} + \lambda^2 C_b^{(2)} + \dots$

parameters to keep track of order of the perturbation

$$\omega_{bk} = \frac{E_b - E_k}{\hbar}$$

$\dot{C}_b^{(0)} = 0$; $\dot{C}_b^{(1)} = \frac{1}{i\hbar}\sum_k H'_{bk}(t)\,C_k^{(0)}e^{i\omega_{bk}t}$ ← from initial cond.

$\vdots$

$$C_b^{(n)} = \frac{1}{i\hbar}\sum_k H'_{bk}(t)C_k^{(n-1)}e^{i\omega_{bk}t}$$

Let's say that our atom is in some stationary state Ψ_a with energy E_a at $t \le 0$ and the pulse of radiation is turned on at $t=0$. Then, the initial condition $\Rightarrow C_k^{(0)} = \delta_{ka}$ 6

First-order perturbation $\Rightarrow \dot{C}_b^{(1)} = \frac{1}{i\hbar} H'_{ba} e^{i\omega_{ba}t} \Rightarrow$

$$C_b^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \underbrace{H'_{ba}(t')}_{\substack{\parallel \\ -i\hbar\frac{e}{m}\langle\Psi_b|\vec{A}\cdot\vec{\nabla}|\Psi_a\rangle}} e^{i\omega_{ba}t'}dt' =$$

from p. 4

$$\langle\Psi_b|\vec{A}\cdot\vec{\nabla}|\Psi_a\rangle = \int \Psi_b^*(\vec{r})\,\vec{A}\cdot\vec{\nabla}\,\Psi_a(\vec{r})\,d\vec{r}$$

$\vec{A} = \frac{1}{2}A_0(\omega)\hat{\vec{\varepsilon}}\left(e^{i(\vec{k}\cdot\vec{r}-\omega t)} + c.c.\right)$

$$= -\frac{e}{2m}\Big\{A_0(\omega)\Big[e^{i\delta_\omega}\langle\Psi_b|e^{i\vec{k}\cdot\vec{r}}\hat{\vec{\varepsilon}}\cdot\vec{\nabla}|\Psi_a\rangle \cdot \underbrace{\int_0^t dt'\, e^{i(\omega_{ba}-\omega)t'}}_{①} + e^{-i\delta_\omega}\langle\Psi_b|e^{-i\vec{k}\cdot\vec{r}}\hat{\vec{\varepsilon}}\cdot\vec{\nabla}|\Psi_a\rangle \cdot \underbrace{\int_0^t dt'\, e^{i(\omega_{ba}+\omega)t'}}_{②}\Big]$$

; ①: 0, unless $\omega_{ba} = \omega$
② : 0, unless $\omega_{ba} = -\omega$

If EM is non-monochromatic $\Rightarrow$ need to integrate also with respect to ω

① : absorption ② : emission (stimulated)