Physics 531 - Lecture 8 - Interaction with E&M fields

We learn most about the structure of atoms and molecules through their interaction with electromagnetic fields. Resonances in the absorption and emission of electromagnetic waves reveal the energy-level structure.

Fundamental Hamiltonian

Given a collection of charged particles with charges $\{q_i\}$ masses $\{m_i\}$, the classical Hamiltonian which describes their interaction with the electromagnetic field is typically expressed in terms of the potentials $(\vec{A}, \phi)$

$$\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial}{\partial t}\vec{A}$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\Rightarrow H = \sum_i \frac{1}{2m_i}\left(\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{x}_i, t)\right)^2 - \sum_i q_i \phi(\vec{x}_i, t) + \underbrace{V(\vec{x}_i)}_{\text{interaction between charges}}$$

Quantum mechanically $\vec{p} = \frac{\hbar}{i}\vec{\nabla}$ for each particle

The physics is invariant under a change of gauge.

$$\vec{A} \to \vec{A} + \vec{\nabla}\chi$$

$$\phi \to \phi - \frac{1}{c}\frac{\partial \chi}{\partial t}$$

Quantum mechanically, the different gauges represent different unitary ~~rep~~ representations

Let $\hat{U} = \exp\left\{\frac{-i}{\hbar}\sum_i \frac{q_i}{mc}\chi(\vec{x}_i, t)\right\}$

$$\Rightarrow \hat{U}^\dagger \hat{p}_i \hat{U} = \vec{p}_i - \frac{q_i}{c}\vec{\nabla}\chi$$

Let $|\tilde{\psi}\rangle = U|\psi\rangle$

If $\frac{\partial}{\partial t}|\psi\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle$

$$\frac{\partial}{\partial t}|\tilde{\psi}\rangle = -\frac{i}{\hbar}\tilde{H}|\psi\rangle$$

where $\vec{A} \to \vec{A} + \vec{\nabla}\chi$

$$\phi \to \phi - \frac{1}{c}\frac{\partial \chi}{\partial t}$$

Note: A unitary transformation does not change observed quantities (measured results, probabilities of outcomes)

Special Choices

"Coulomb Gauge": $\vec{\nabla}\cdot\vec{A} = 0$ (always possible)

$\Rightarrow \phi(\vec{x},t)$ = Coulomb potential due to external source

Electromagnetic wave in free space

$$\phi(\vec{x},t) = 0$$

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

Plane wave solution $\vec{A}(\vec{x},t) = Re\left(\underbrace{\hat{\epsilon}}_{\text{polarization}} A_0 e^{i(\vec{k}\cdot\vec{x} - \omega t)}\right)$

$$\vec{E} = Re\left(\hat{\epsilon}\, E_0\, e^{i(\vec{k}\cdot\vec{x} - \omega t)}\right)$$

$$\vec{B} = Re\left[(\hat{k}\times\hat{\epsilon})\, B_0\, e^{i(\vec{k}\cdot\vec{x} - \omega t)}\right]$$

$$E_0 = B_0 = +i\frac{\omega}{c}A_0 \quad **$$

In this Gauge the Hamiltonian becomes

$$H = \underbrace{\sum_i \frac{\vec{p}_i^2}{2m_i} + V(\vec{x}_1, \ldots \vec{x}_n)}_{\text{"Atomic Hamiltonian"}} \rightarrow \sum_i \Big(\frac{q_i}{m_i c} \vec{p}_i \cdot \vec{A}(\vec{x}_i, t) - \frac{q_i^2}{2m_i c^2} \vec{A}^2(\vec{x}_i, t) \Big)$$

Perturbation (time dependent)

Note: For weak fields (weaker than internal fields) we typically neglect the $\vec{A}^2$ term

One electron case: Put nucleus @ origin, infinitely massive

$$\hat{H}_{int} = \frac{e}{mc} \vec{p} \cdot \vec{A}(\vec{x}, t)$$

$\vec{x}, \vec{p}$ are position and momentum of electron relative to nucleus

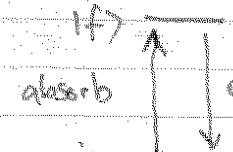
Electromagnetic wave

$$\hat{H}_{int} = \frac{eA_0}{mc} \vec{\epsilon} \cdot \vec{p}\, e^{i\vec{k}\cdot\vec{x}}\, e^{-i\omega t} + \underbrace{h.c.}_{\text{Hermitian conjugation}}$$

This is a time-dependent perturbation of the form

$$\hat{H}_{int} = \underbrace{\hat{H}^{(+)} e^{-i\omega t}}_{\text{"positive frequency component"}} + \underbrace{\hat{H}^{(-)} e^{+i\omega t}}_{\text{"negative freq. component"}}$$

According to Fermi's Golden Rule, Given initial and final states



$$W_{i \leftarrow f} = \frac{2\pi}{\hbar^2} |\langle f | \hat{H}^{(+)} | i \rangle|^2 \underbrace{D(\omega)}_{\text{Density of states}}$$

The key quantity that depends on the atomic structure is the transition matrix element

$$\boxed{\langle f|\hat{H}^{(+)}|i\rangle = \frac{eA_0}{mc}\,\vec{\epsilon}\cdot\langle f|\hat{\vec{p}}\,e^{i\vec{k}\cdot\hat{\vec{x}}}|i\rangle}$$

Multipole expansion

We the wavelength of the radiation $\lambda = \frac{2\pi}{k}$ is much longer than the size of the charge distribution the radiation couples with different strengths to multipoles of the distribution.

We see this through the expansion for $|\vec{x}| \ll \frac{1}{|\vec{k}|}$

$$\Rightarrow e^{i\vec{k}\cdot\vec{x}} \approx 1 + i\vec{k}\cdot\vec{x} + (\vec{k}\cdot\vec{x})^2 + \dots$$

To lowest order $e^{i\vec{k}\cdot\vec{x}} \approx 1$

$$\Rightarrow \langle f|\hat{H}^{(+)}|i\rangle = \frac{eA_0}{mc}\,\vec{\epsilon}\cdot\langle f|\hat{\vec{p}}|i\rangle$$

Aside: $[\hat{\vec{x}}, \hat{H}_0] = [\hat{\vec{x}}, \frac{\hat{\vec{p}}^2}{2m}] = i\hbar\frac{\hat{\vec{p}}}{m}$

$$\Rightarrow \langle f|\hat{H}^{(+)}|i\rangle = \frac{eA_0}{c}\,\vec{\epsilon}\cdot\underbrace{\langle f|[\hat{\vec{x}}, \hat{H}_0]|i\rangle}_{(E_i - E_f)\langle f|\hat{\vec{x}}|i\rangle}$$

$$\Rightarrow \langle f|\hat{H}^{(+)}|i\rangle = +e\left(\frac{i\omega_{fi}A_0}{c}\right)\vec{\epsilon}\cdot\langle f|\vec{x}|i\rangle$$

$$= \langle f|(-\vec{d}\cdot\vec{E}_0)|i\rangle$$

where $\vec{d} = -e\vec{x}$

The dominant effect is thus electric dipole

$$\boxed{\hat{H}_{int} = -\hat{\vec{d}} \cdot \vec{E}_0}$$

where $\vec{E}_0 = E_0 \vec{\epsilon}$ is the electric field complex amplitude at the position of the atom (center of mass).

- the Göppert-Mayer transformation

We can see the electric dipole interaction (and then generalizations to higher multipole moments) through a Gauge transformation

Define Gauge function: $\chi(\vec{x},t) = \vec{x} \cdot \vec{A}(0,t)$

$\vec{A} \Rightarrow \vec{A}(\vec{x},t) - \vec{A}(0,t)$ $\quad \left(\hat{U} = e^{\frac{i}{\hbar} \vec{d} \cdot \vec{A}(0,t)} \right)$

$$\phi \Rightarrow \vec{x} \cdot \left(\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right) = -\vec{x} \cdot \vec{E}(0,t)$$

In the lowest approximation we evaluate all fields at the origin (center of mass)

$\Rightarrow \vec{A} = 0$ in new gauge

$$\therefore \hat{H} = \frac{\hat{p}^2}{2m} + V - e\phi = \frac{\hat{p}^2}{2m} + V \underbrace{- \hat{\vec{d}} \cdot \vec{E}(0,t)}_{\text{Dipole perturbation}}$$

More generally $\hat{U} = \exp\left\{ -\frac{i}{\hbar} \int d^3x \, \hat{\vec{P}}(\vec{x}) \cdot \vec{E}(\vec{x},t) \right\}$

$\hat{\vec{P}}$: Electric dipole density

$$\Rightarrow \boxed{\hat{H} = \hat{H}_{atom} + \int d^3x \, \underbrace{\hat{\vec{P}} \cdot \vec{E}}_{\text{polarization}} + \int d^3x \, \underbrace{\hat{\vec{M}} \cdot \vec{B}}_{\text{magnetization}}}$$

The dominant effect is the electric dipole

$$\hat{H}_{int}^{(+)} = -\hat{d}\cdot\vec{E}_0$$

where $\vec{E}_0 = E_0\hat{\epsilon}$ is the electric field complex amplitude at the position (center mass) of the atom

Absorption rate:

$$W_{e\leftarrow g} = \frac{2\pi}{\hbar^2}|\langle e|\hat{H}^{(+)}|g\rangle|^2\,\delta(\omega)$$

$$= 2\pi|E_0|^2\frac{e^2}{\hbar^2}|\hat{\epsilon}\cdot\langle e|\vec{x}|g\rangle|^2\,\delta(\omega)$$

[Aside: The intensity of the field $I_0 = \frac{c}{2\pi}|E_0|^2$]

$$\Rightarrow W_{e\leftarrow g} = 4\pi^2 I_0\left(\frac{e^2}{\hbar^2 c^2}\right)|\hat{\epsilon}\cdot\langle e|\vec{x}|g\rangle|^2\,\delta(\omega)$$

Aside: For unpolarized light on $\frac{1}{3}$ along any direction in space

$$|\hat{\epsilon}\cdot\langle e|\vec{x}|g\rangle|^2 \Rightarrow \frac{1}{3}|\langle e|\vec{x}|g\rangle|^2$$

Photon flux: $\Phi_0 = \frac{I_0}{\hbar\omega} = \frac{\text{Rate of incident photons}}{(\text{Area})}$

Define absorption cross-section

$$W_{e\leftarrow g} = \Phi\,\sigma_{eg}^{abs}$$

$$\Rightarrow \boxed{\sigma_{eg}^{abs}(\omega) = \frac{4\pi^2}{3}\alpha|\langle e|\vec{x}|g\rangle|^2\,\delta(\omega)\,\omega}$$

Unpolarized light

(Stimulated) Emission

The incident electromagnetic field can also drive (stimulated) transitions from excited to a lower lying state

In the Fermi Golden rule regime

$$W^{Stim}_{g\leftarrow e} = \frac{2\pi}{\hbar^2} |\langle g| \hat{H}^{(-)} |e\rangle|^2 \mathcal{D}(\omega)$$

$$= \frac{2\pi}{\hbar^2} |\langle e| \hat{H}^{(+)} |g\rangle|^2 \mathcal{D}(\omega)$$

$$= W^{abs}_{e\leftarrow g}$$

(Spontaneous) Emission

Even in the absence of an incident field, an atom can spontaneously emit. Fundamentally, this arises from vacuum fluctuations which induce a radiating dipole. This is due to one "vacuum photon" per mode.

$$W_{emission} = \frac{4\pi^2}{3} \frac{e^2}{\hbar^2} |\langle e| \vec{x} |g\rangle|^2 \mathcal{U}(\omega)$$

Where I have written $|E_0|^2 \mathcal{D}(\omega) = 2\pi \mathcal{U}(\omega)$

$\mathcal{U}(\omega)$ = Energy density / frequency interval

For a single photon $\mathcal{U}(\omega) = \left(\frac{\hbar\omega}{V}\right)\left(\frac{V}{\pi^2}\frac{\omega^2}{c^3}\right)$

($\frac{\hbar\omega}{V}$: energy density; $\frac{V}{\pi^2}\frac{\omega^2}{c^3}$: Density of modes in a volume V)

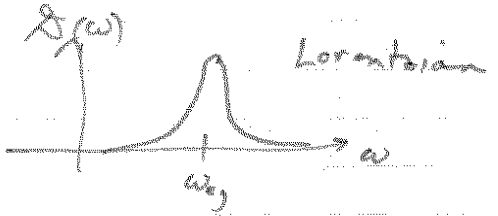
$$\Rightarrow \boxed{W_{emission} = \frac{4}{3}\alpha |\langle e| \vec{x} |g\rangle|^2 \frac{\omega^3}{c^2} = \frac{4}{3} \frac{|\langle e| \vec{d} |g\rangle|^2 k^3}{\hbar}}$$

$$= \Gamma \quad \text{(spontaneous emission rate)}$$

Line Shape

In the absence of any other "broading" mechanism the spontaneous emission leads to a finite linewidth known as the natural linewidth of absorption.

$$\Rightarrow \mathcal{D}_{eg}(\omega) = \frac{\frac{\Gamma}{2\pi}}{(\omega-\omega_{eg})^2 + \frac{\Gamma^2}{4}}$$



On resonance $\mathcal{D}_{eg}(\omega_{eg}) = \frac{2}{\pi}\frac{1}{\Gamma}$

$\Rightarrow$ On resonance absorption cross-section (unpolarized)

$$\sigma_{abs}(\omega_{eg}) = \frac{8\pi}{3}\alpha\,|\langle e|\vec{r}|g\rangle|^2\,\frac{\omega_{eg}}{\Gamma}$$

$$= 2\pi\lambda^2 \qquad \lambda = \frac{\lambda}{2\pi}$$

$$\boxed{\sigma_{abs}^{(res)} = \frac{\lambda^2}{2\pi}} \quad \text{unpolarized}$$

Independent of matrix element

Oscillator Strength

The "strength" of absorption depends on the matrix element $|\langle e|\vec{r}|g\rangle|^2$. A characteristic strength is ~~the linewidth / but converging this to~~

$$f_{eg} = \frac{2}{3}\left(\frac{m\omega_{eg}}{\hbar}\right)|\langle e|\vec{r}|g\rangle|^2 \quad \left(\begin{array}{c}\text{Oscillator}\\ \text{strength}\end{array}\right)$$

We can interpret this as the ratio $\frac{\frac{1}{3}|\langle e|\vec{r}|g\rangle|^2}{\left(\frac{m\omega_{eg}}{\hbar}\right)}$

simple $\longrightarrow$ harmonic oscillator width

The oscillator strength arises naturally when comparing the absorption cross-section with calculated quantum mechanically (as we did) with a classical analysis based on simple harmonic motion.

An important result is the sum-rule

$$\boxed{\sum_e f_{eg} = 1}$$

Proof: $\sum_e f_{eg} = \sum_e \left(f_{eg}^x + f_{eg}^y + f_{eg}^z \right)$

$$f_{eg}^x = \frac{2m\omega_{eg}}{3\hbar} |\langle e|\hat{x}|g\rangle|^2 = \frac{2m\omega_{eg}}{\hbar} \langle g|\hat{x}|e\rangle\langle e|\hat{x}|g\rangle$$

Aside: $\langle e|\hat{x}|g\rangle = \frac{-i}{m\omega_{eg}} \langle e|\hat{p}_x|g\rangle$ (as we saw earlier)

$$\Rightarrow f_{eg}^x = \frac{2m\omega_{eg}}{3\hbar} \left[\langle g|\hat{x}|e\rangle \left(\frac{-i}{m\omega_{eg}} \langle e|\hat{p}_x|g\rangle \right) + \left(\frac{i}{m\omega_{eg}} \langle g|\hat{p}_x|e\rangle \right) \langle e|\hat{x}|g\rangle \right]$$

$$\therefore \sum_e f_{eg}^x = \frac{-i}{3\hbar} \sum_e \left(\langle g|\hat{x}|e\rangle\langle e|\hat{p}_x|g\rangle - \langle g|\hat{p}_x|e\rangle\langle e|\hat{x}|g\rangle \right)$$

$$= \frac{-i}{3\hbar} \langle g|\underbrace{(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})}_{=i\hbar}|g\rangle = \frac{1}{3}$$

$$\therefore \boxed{\sum_e f_{eg} = 1}$$

For hydrogenic atoms the oscillator strength falls off with principal quantum number n.

The vast majority of the osc. strength in $1s \to 2p$