Physics 531 - Lecture 8 - Interaction with EM fields

We learn most about the structure of atoms and molecules through their interactions 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 \( (\mathbf{A}, \phi) \)

\[
E = -\nabla \phi - \frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}^2
\]

\[
\mathbf{B} = \nabla \times \mathbf{A}
\]

\[
\mathbf{H} = \sum_i \frac{1}{2m_i} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{x}_i, t))^2 - \sum_i q_i \phi(\mathbf{x}_i, t) + V(\mathbf{x}_i)
\]

Quantum mechanically, \( \mathbf{p} = \hbar \nabla \) for each particle.

The physics is invariant under a change of gauge:

\[
\mathbf{A} \to \mathbf{A} + \nabla \chi
\]

\[
\phi \to \phi + \frac{1}{\epsilon} \frac{\partial \chi}{\partial t}
\]

Quantum mechanically, the different gauges represent different unitary representations.

Let \( \hat{U} = \exp \left\{ -\frac{i}{\hbar} \sum_i q_i \mathbf{A}(\mathbf{x}_i, t) \right\} \)

\[
\Rightarrow \hat{U} a_i \hat{U}^\dagger = \hat{p}_i - \frac{q_i}{\epsilon} \nabla \chi
\]
Let \(|\psi\rangle = 0\mid \psi\rangle\)

\[i \frac{\partial}{\partial t} \mid \psi\rangle = -\frac{i}{\hbar} \hat{H} \mid \psi\rangle\]

\[\frac{\partial}{\partial t} \mid \psi\rangle = -\frac{i}{\hbar} \hat{H} \mid \psi\rangle\]

where \(\hat{A} \rightarrow \hat{A} + \nabla \phi\)

\(\phi \rightarrow \phi = -\frac{1}{\epsilon} \frac{\partial \phi}{\partial t}\)

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

**Special Choices**

Coulomb gauge: \(\nabla \cdot \vec{A} = 0\)

(Always possible)

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

**Electromagnetic wave in free space**

\(\phi(x,t) = 0\)

\(\nabla^2 \vec{A} - \frac{1}{\epsilon} \frac{\partial^2 \vec{A}}{\partial t^2} = 0\)

Planar wave solution \(\vec{A}(x,t) = \text{Re}(\epsilon \vec{A}_0 e^{i(kx - \omega t)})\)

\(\vec{E} = \text{Re}(\epsilon \vec{E}_0 e^{i(kx - \omega t)})\)

\(\vec{B} = \text{Re}[(\vec{A} \times \vec{E}) \cdot \vec{B}_0 e^{i(kx - \omega t)}]\)

\(\vec{E}_0 = \vec{B}_0 = +i\epsilon \frac{\partial}{\partial t} \vec{A}_0\)
In this gauge, the Hamiltonian becomes

\[ H = \sum_i \frac{\vec{p}_i^2}{2m_i} + V(x_i, \ldots, x_e) + \sum_i \left( \frac{\hbar c}{m_i} \vec{p}_i \cdot \vec{A}(x_i, t) \right) \]

"Atomic Hamiltonian"

\[-\frac{\hbar^2 c}{2m_e c^2} \nabla^2 (\vec{A}(x_i, t)) \]

Perturbation (time dependent)

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

One electron case: Put nucleus at origin, infinitely massive

\[ \hat{H}_{\text{int}} = \frac{\hbar}{mc} \vec{p} \cdot \vec{A}(x, t) \]

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

Electromagnetic wave

\[ \hat{H}_{\text{int}} = \frac{\hbar c}{m_e} \vec{e} \cdot \vec{p} e^{i\vec{k} \cdot \vec{x} - i\omega t} + \text{h.c.} \]

Hamilton conjugate

This is a time-dependent perturbation of the form

\[ \hat{H}_{\text{int}} = \hat{H}^{(+)} e^{-i\omega t} + \hat{H}^{(-)} e^{i\omega t} \]

"positive frequency component"  "negative frequency component"

According to Fermi's Golden Rule,

Given initial and final states

\[ W_{i\rightarrow f} = \frac{2\pi}{\hbar^2} \left| \langle f | \hat{A}^{(+)} | i \rangle \right|^2 \rho_i(\omega) \]

\( \rho_i(\omega) \) Density of states
The key quantity that depends on the atomic structure is the transition matrix element

\[
\langle f | \hat{H}^{(\gamma)} | i \rangle = \frac{eA_0}{mc} \vec{e} \cdot \langle f | \vec{p} e^{ik \cdot \vec{r}} | i \rangle
\]

**Multipole expansion**

We see 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 \( |\vec{x}| \ll \frac{1}{|k|} \)

\[
\Rightarrow e^{ik \cdot \vec{x}} \approx 1 + ik \cdot \vec{x} + (k \cdot \vec{x})^2 + \ldots
\]

To lowest order \( e^{ik \cdot \vec{x}} \approx 1 \)

\[
\Rightarrow \langle f | \hat{H}^{(\gamma)} | i \rangle = \frac{eA_0}{mc} \vec{e} \cdot \langle f | \vec{p} | i \rangle
\]

Aside: \( [\hat{L}^2, \hat{A}_0] = \hat{L}^2, \frac{e^2}{mc} \hat{A}_0 \) = \( \frac{e^2}{m} \hat{A}_0 \)

\[
\Rightarrow \langle f | \hat{A}^{(\gamma)} | i \rangle = \frac{eA_0}{mc} \vec{e} \cdot \langle f | [\hat{L}^2, \hat{A}_0] | i \rangle
\]

\[
= \frac{eA_0}{mc} \vec{e} \cdot \langle f | \hat{L}^2 | i \rangle
\]

\[
= \frac{eA_0}{mc} \vec{e} \cdot \langle f | \hat{L}^2 | i \rangle
\]

\[
= \langle f | \hat{L}^2 | i \rangle
\]

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

where \( \vec{d} = -e \vec{x} \)
The dominant effect is thus electric dipole

$$\hat{A}_{\text{int}} = -\hat{J} \cdot \vec{E}_0$$

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

- the Göppert–Mayer transformations

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

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

$$\vec{A} = \vec{A}(x, t) - \vec{A}(0, t) \quad \left( V = e \frac{1}{m} \frac{\partial}{\partial t} \vec{A}(0, t) \right)$$

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

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

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

$$\hat{H} = \frac{\vec{p}^2}{2m} + V - e\phi = \frac{\vec{p}^2}{2m} + V - \frac{1}{c} \vec{d} \cdot \vec{E}(0, t)$$

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

Electric dipole density

$$\Rightarrow \hat{A} = \hat{A}_{\text{atom}} + \int d^3x \vec{P} \cdot \vec{E} + \int d^3x \vec{M} \cdot \vec{B}$$

Relativistic magnetoelation
The dominant effect is thus electric dipole

\[ \hat{\mathbf{A}}_\text{int} = -\mathbf{d} \cdot \mathbf{E}_0 \]

where \( \mathbf{E}_0 = E_0 \hat{z} \) is the electric field

complex amplitude at the position (center mass) of the atom.

Absorption rate:

\[ W_{\text{eq}} = \frac{2\pi}{\lambda^2} \left| \langle \mathbf{e}_L \hat{\mathbf{A}}_{\text{out}} \mathbf{g} \rangle \right|^2 \Delta(\omega) \]

\[ = 2\pi |E_0|^2 \frac{e^2}{\hbar^2} |\mathbf{e}_L \cdot \langle \mathbf{e}_L \mathbf{g} \rangle|^2 \Delta(\omega) \]

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

\[ \Rightarrow W_{\text{eq}} = 4\pi^2 I_0 \left( \frac{e^2}{\hbar^2} \right) |\mathbf{e}_L \cdot \langle \mathbf{e}_L \mathbf{g} \rangle|^2 \Delta(\omega) \]

\[ \left[ \text{Aside: For unpolarized light on } \frac{1}{2} \text{ along any direction in space} \right] 

\[ |\mathbf{e}_L \cdot \langle \mathbf{e}_L \mathbf{g} \rangle|^2 = \frac{1}{2} |\langle \mathbf{e}_L \mathbf{g} \rangle|^2 \]

\[ \text{Photon flux: } \Phi = \frac{I_0}{\Delta(\omega)} = \text{Rate of incident photons} \left( \frac{\text{area}}{\text{time}} \right) \]

Define absorption cross-section

\[ W_{\text{eq}} = \Phi \sigma_{\text{abs}} \]

\[ \Rightarrow \sigma_{\text{abs}}(\omega) = 4\pi^2 \alpha |\langle \mathbf{e} \mathbf{L} | \mathbf{g} \rangle|^2 \Delta(\omega) \omega \]

\[ \left[ \text{Unpolarized light} \right] \]
(Stimulated) Emission

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

\[ W_{g\rightarrow e}^{\text{stim}} = \frac{2\pi}{\hbar^2} |<g| A^{(-)}|e>|^2 \delta(w) \]

\[ = \frac{2\pi}{\hbar^2} |<e| A^{(+)}|g>|^2 \delta(w) \]

\[ = W_{\text{abs}} \]

(W_{e\rightarrow 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.

\[ W_{\text{emission}} = \frac{4\pi^2}{3} \frac{e^2}{\hbar^2} |<e| x |g>|^2 U(w) \]

Where I have written \( |E|^2 \delta(w) = 2\pi U(w) \)

\[ U(w) = \text{Energy density / frequency interval} \]

For a single photon \( U(w) = \left( \frac{k}{V} \right) \left( \frac{V}{\pi^2} \frac{\omega^2}{C^3} \right) \)

\[ W_{\text{emission}} = \frac{4}{3} \alpha \frac{1}{C^2} |<e| x |g>|^2 \frac{C^3}{\omega^2} = \frac{4}{3} \frac{|<e| x |g>|^2}{k^3} \]

\[ = \Gamma \] (spontaneous emission rate)
Line Shape

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

\[ \tilde{\sigma}(\omega) = \frac{1}{\pi} \frac{A^2}{(\omega - \omega_g)^2 + \frac{A^2}{4}} \]

On resonance: \[ \tilde{\sigma}_{\text{eq}}(\omega_g) = \frac{2}{\pi} \frac{1}{11} \]

\[ \Rightarrow \text{On resonance absorption cross-section (unpolarized)} \]

\[ \sigma_{\text{abs, unpolarized}}(\omega_g) = \frac{8\pi}{3} \langle |\langle 1 | x_1 | g \rangle|^2 \frac{\omega_g}{\hbar} \]

\[ = 2\pi \frac{\chi^2}{\hbar} \quad \chi = \frac{2}{2\pi} \]

\[ \sigma_{\text{abs, unpolarized}}(\text{res}) = \frac{\chi^2}{2\pi} \]

Independent of matrix element.

Oscillator Strength

The "strength" of absorption depends on the matrix element \( |\langle e | x_1 | g \rangle|^2 \). A characteristic strength is

\[ f_{\text{eq}} = \frac{2}{3} \left( \frac{m \omega_g}{\hbar} \right) |\langle e | x_1 | g \rangle|^2 \]

\( \frac{1}{3} |\langle e | x_1 | g \rangle|^2 \) (Oscillator strength)

We can interpret this as the ratio \( \frac{1}{3} |\langle e | x_1 | g \rangle|^2 \)

Simple \( \rightarrow \frac{m \omega_g}{\hbar} \)

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:

$$\sum \frac{f_{eg}}{e} = 1$$

Proof:

$$\sum \frac{f_{eg}}{e} = -\sum \frac{m_{eg}}{e} \left( f_{eg}^x + f_{eg}^y + f_{eg}^z \right)$$

$$f_{eg}^x = \frac{2m_{eg} \langle e l \chi l g \rangle^2}{3\hbar^2} = \frac{2m_{eg}}{\hbar} \langle g l \chi l e \rangle \langle e l \chi l g \rangle$$

Aside: \( \langle e l \chi l g \rangle = -\frac{i}{m_{eg}} \langle e l \beta g \rangle \) (as we saw earlier)

$$\Rightarrow f_{eg}^x = \frac{2m_{eg}}{3\hbar} \left[ \langle g l \chi l e \rangle \left( \frac{-i}{m_{eg}} \langle e l \beta g \rangle \right) + \frac{i}{m_{eg}} \langle g l \beta k \rangle \langle e l \chi g \rangle \right]$$

$$\sum_{e} f_{eg}^x = -\frac{i}{3\hbar} \sum_{e} \langle g l \chi l e \rangle \langle e l \beta g \rangle - \langle g l \beta k \langle e l \chi g \rangle$$

$$= -\frac{i}{3\hbar} \langle g | (\beta | x - x' | g ) \rangle = \frac{1}{3}$$

$$= \frac{i}{\hbar}$$

$$\sum_{e} f_{eg} = 1$$

For hydrogenic atoms, the oscillator strength falls off with principal quantum number \( n \).

The vast majority of the osc. strength in 1s \( \rightarrow 2p \).