

Chapter 14

Radiating Dipoles in Quantum Mechanics

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Electric dipole moment vector operator

Electric dipole moment vector operator for collection of charges is

$$\vec{\hat{\mu}} = \sum_{k=1}^N q_k \vec{\hat{r}}$$

Single charged quantum particle bound in some potential well, e.g., a negatively charged electron bound to a positively charged nucleus, would be

$$\vec{\hat{\mu}} = -q_e \vec{\hat{r}} = -q_e [\hat{x}\vec{e}_x + \hat{y}\vec{e}_y + \hat{z}\vec{e}_z]$$

Expectation value for electric dipole moment vector in $\Psi(\vec{r}, t)$ state is

$$\langle \vec{\mu}(t) \rangle = \int_V \Psi^*(\vec{r}, t) \vec{\hat{\mu}} \Psi(\vec{r}, t) d\tau = \int_V \Psi^*(\vec{r}, t) (-q_e \vec{\hat{r}}) \Psi(\vec{r}, t) d\tau$$

Here, $d\tau = dx dy dz$

Time dependence of electric dipole moment

Energy Eigenstate

Starting with

$$\langle \vec{\mu}(t) \rangle = \int_V \Psi^*(\vec{r}, t) \left(-q_e \vec{r} \right) \Psi(\vec{r}, t) d\tau$$

For a system in eigenstate of Hamiltonian, where wave function has the form,

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r}) e^{-iE_n t / \hbar}$$

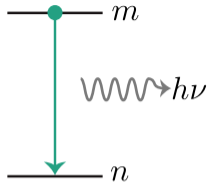
Electric dipole moment expectation value is

$$\langle \vec{\mu}(t) \rangle = \int_V \psi_n^*(\vec{r}) e^{iE_n t / \hbar} \left(-q_e \vec{r} \right) \psi_n(\vec{r}) e^{-iE_n t / \hbar} d\tau$$

Time dependent exponential terms cancel out leaving us with

$$\langle \vec{\mu}(t) \rangle = \int_V \psi_n^*(\vec{r}) \left(-q_e \vec{r} \right) \psi_n(\vec{r}) d\tau \quad \text{No time dependence!!}$$

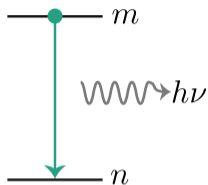
No bound charged quantum particle in energy eigenstate can radiate away energy as light or at least it appears that way – Good news for Rutherford's atomic model.



But then how does a bound charged quantum particle in an excited energy eigenstate radiate light and fall to lower energy eigenstate?



Time dependence of electric dipole moment - A Transition



During transition wave function must change from Ψ_m to Ψ_n

During transition wave function must be linear combination of Ψ_m and Ψ_n

$$\Psi(\vec{r}, t) = a_m(t)\Psi_m(\vec{r}, t) + a_n(t)\Psi_n(\vec{r}, t)$$

Before transition we have $a_m(0) = 1$ and $a_n(0) = 0$

After transition $a_m(\infty) = 0$ and $a_n(\infty) = 1$

Time dependence of electric dipole moment - A Transition

To maintain normalization during transition we require

$$|a_m(t)|^2 + |a_n(t)|^2 = 1.$$

Electric dipole moment expectation value for $\Psi(\vec{r}, t)$ is

$$\begin{aligned}\langle \vec{\mu}(t) \rangle &= \int_V \Psi^*(\vec{r}, t) \vec{\mu} \Psi(\vec{r}, t) d\tau \\ &= \int_V [a_m^*(t) \Psi_m^*(\vec{r}, t) + a_n^*(t) \Psi_n^*(\vec{r}, t)] \vec{\mu} [a_m(t) \Psi_m(\vec{r}, t) + a_n(t) \Psi_n(\vec{r}, t)] d\tau\end{aligned}$$

$$\begin{aligned}\langle \vec{\mu}(t) \rangle &= a_m^*(t) a_m(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_m(\vec{r}, t) d\tau + a_m^*(t) a_n(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau \\ &+ a_n^*(t) a_m(t) \int_V \Psi_n^*(\vec{r}, t) \vec{\mu} \Psi_m(\vec{r}, t) d\tau + a_n^*(t) a_n(t) \int_V \Psi_n^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau\end{aligned}$$

Time dependence of electric dipole moment - A Transition

$$\begin{aligned}\langle \vec{\mu}(t) \rangle &= a_m^*(t)a_m(t) \underbrace{\int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_m(\vec{r}, t) d\tau}_{\text{Time Independent}} + a_m^*(t)a_n(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau \\ &+ a_n^*(t)a_m(t) \int_V \Psi_n^*(\vec{r}, t) \vec{\mu} \Psi_m(\vec{r}, t) d\tau + a_n^*(t)a_n(t) \underbrace{\int_V \Psi_n^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau}_{\text{Time Independent}}\end{aligned}$$

1st and 4th terms still have slower time dependence due to $a_n(t)$ and $a_m(t)$ but this electric dipole variation will not lead to appreciable energy radiation.

Drop these terms and focus on faster oscillating 2nd and 3rd terms

$$\langle \vec{\mu}(t) \rangle = a_m^*(t)a_n(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau + a_n^*(t)a_m(t) \int_V \Psi_n^*(\vec{r}, t) \vec{\mu} \Psi_m(\vec{r}, t) d\tau$$

Two integrals are complex conjugates of each other.

Since $\langle \vec{\mu}(t) \rangle$ must be real we simplify to

$$\langle \vec{\mu}(t) \rangle = \Re \left\{ a_m^*(t)a_n(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau \right\}$$

Time dependence of electric dipole moment - A Transition

$$\langle \vec{\mu}(t) \rangle = \Re \left\{ a_m^*(t) a_n(t) \int_V \Psi_m^*(\vec{r}, t) \vec{\mu} \Psi_n(\vec{r}, t) d\tau \right\}$$

Inserting stationary state wave function, $\Psi_n(\vec{r}, t) = \psi_n(\vec{r}) e^{-iE_n t/\hbar}$, gives

$$\langle \vec{\mu}(t) \rangle = \Re \left\{ a_m^*(t) a_n(t) \underbrace{\left[\int_V \psi_m^*(\vec{r}) \vec{\mu} \psi_n(\vec{r}) d\tau \right]}_{\langle \vec{\mu} \rangle_{mn}} e^{i(E_m - E_n)t/\hbar} \right\}$$

$\omega_{mn} = (E_m - E_n)/\hbar$ is angular frequency of emitted light and
 $\langle \vec{\mu} \rangle_{mn}$ is *transition dipole moment*—peak magnitude of dipole oscillation

$$\langle \vec{\mu} \rangle_{mn} = \int_V \psi_m^*(\vec{r}) \vec{\mu} \psi_n(\vec{r}) d\tau$$

Finally, write oscillating electric dipole moment vector as

$$\langle \vec{\mu}(t) \rangle = \Re \left\{ a_m^*(t) a_n(t) \langle \vec{\mu} \rangle_{mn} e^{i\omega_{mn}t} \right\}$$

Transition dipole moment

In summary, the superposition state

$$\Psi(\vec{r}, t) = a_m(t)\Psi_m(\vec{r}, t) + a_n(t)\Psi_n(\vec{r}, t)$$

has oscillating electric dipole moment vector

$$\langle \vec{\mu}(t) \rangle = \Re \left\{ a_m^*(t) a_n(t) \langle \vec{\mu} \rangle_{mn} e^{i\omega_{mn}t} \right\}$$

where

$$\langle \vec{\mu} \rangle_{mn} = \int_V \psi_m^*(\vec{r}) \vec{\hat{\mu}} \psi_n(\vec{r}) d\tau$$

Integrals give *transition selection rules* for various spectroscopies

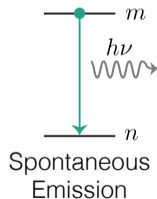
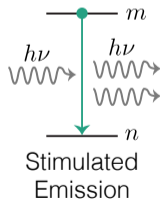
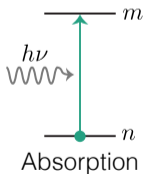
$$(\mu_x)_{mn} = \int_V \psi_m^* \hat{\mu}_x \psi_n d\tau, \quad (\mu_y)_{mn} = \int_V \psi_m^* \hat{\mu}_y \psi_n d\tau, \quad (\mu_z)_{mn} = \int_V \psi_m^* \hat{\mu}_z \psi_n d\tau$$

$$\text{where } \mu_{mn}^2 = |(\mu_x)_{mn}|^2 + |(\mu_y)_{mn}|^2 + |(\mu_z)_{mn}|^2$$

- $\omega_{mn} = (E_m - E_n)/\hbar$ is angular frequency of emitted light
- $a_m^*(t)a_n(t)$ gives time scale of transition.
- $\langle \vec{\mu} \rangle_{mn}$ is *transition dipole moment*—amplitude of dipole oscillation

Okay, so...

- Wave function in superposition of energy eigenstates can have oscillating electric dipole moment which will emit light until system is entirely in lower energy state.
- But how does atom in higher energy eigenstate get into this superposition of initial and final eigenstates in first place? 🤔
- One way to shine light onto the atom. The interaction of the atom and light leads to absorption and stimulated emission of light.



Rate of Light Absorption and Stimulated Emission

Potential energy of $\vec{\mu}$ of quantum system interacting with a time dependent electric field, $\vec{\mathcal{E}}(\vec{r}, t)$ is

$$\hat{V}(t) = -\vec{\mu} \cdot \vec{\mathcal{E}}(\vec{r}, t) = -\vec{\mu} \cdot \vec{\mathcal{E}}_0(\vec{r}) \cos \omega t$$

and Hamiltonian becomes $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$.

- If light wavelength is long compared to system size (atom or molecule) we can ignore \vec{r} dependence of $\vec{\mathcal{E}}$ and assume system is in spatially uniform $\vec{\mathcal{E}}(t)$ oscillating in time. Holds for atoms and molecules until x-ray wavelengths and shorter.
- When time dependent perturbation is present old stationary states of \hat{H}_0 (before light was turned on) are no longer stationary states.

Rate of Light Absorption and Stimulated Emission

To describe time dependence of electric dipole moment write wave function as linear combination of stationary state eigenfunction of \hat{H}_0 , i.e., when $\hat{V}(t)$ is absent.

$$\Psi(\vec{r}, t) = \sum_{m=1}^n a_m(t) \Psi_m(\vec{r}, t)$$

Need to determine time dependence of $a_m(t)$ coefficients.

As initial condition take $|a_n(0)|^2 = 1$ and $|a_{m \neq n}(0)|^2 = 0$.

Putting $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ and $\Psi(\vec{r}, t)$ into time dependent Schrödinger Equation

$$\hat{H}(t)\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

and skipping many steps we eventually get

$$\frac{da_m(t)}{dt} \approx -\frac{i}{\hbar} \int_V \Psi_m^*(\vec{r}, t) \hat{V}(t) \Psi_n(\vec{r}, t) d\tau$$

Rate of Light Absorption and Stimulated Emission

Using our expression for $\hat{V}(t) = -\vec{\hat{\mu}} \cdot \vec{\mathcal{E}}_0(\vec{r}) \cos \omega t$ and $\Psi_n = \psi_n e^{-iE_n t/\hbar}$ we get

$$\frac{da_m(t)}{dt} \approx -\frac{i}{\hbar} \int_V \Psi_m^*(\vec{r}, t) \hat{V}(t) \Psi_n(\vec{r}, t) d\tau = -\frac{i}{\hbar} \underbrace{\left[\int_V \psi_m^* \vec{\hat{\mu}} \psi_n d\tau \right]}_{\text{transition moment integral}} e^{i\omega_{mn}t} \cdot \vec{\mathcal{E}}_0 \cos \omega t$$

Setting $|a_n(0)|^2 = 1$ and $|a_m(0)|^2 = 0$ for $n \neq m$ (after many steps) we find

$$|a_m(t)|^2 = \frac{\langle \mu_{mn} \rangle^2 t}{6\epsilon_0 \hbar^2} u(\nu_{mn})$$

$u(\nu_{mn})$ is radiation density at $\nu_{mn} = \omega_{mn}/2\pi$.

Rate at which $n \rightarrow m$ transition from absorption of light energy occurs is

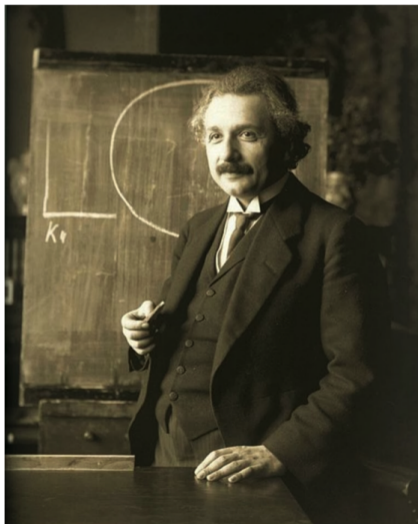
$$R_{n \rightarrow m} = \frac{d|a_m(t)|^2}{dt} = \frac{\langle \mu_{mn} \rangle^2}{6\epsilon_0 \hbar^2} u(\nu_{mn})$$

Okay, but what about spontaneous emission?

An atom or molecule in an excited energy eigenstate can spontaneously emit light and return to its ground state in the absence of any electromagnetic radiation, i.e., $\hat{V}(t) = 0$

- How does spontaneous emission happen? 🤔
- In this lecture's derivations we treat light as classical E&M wave. No mention of photons.
- Treating light classically gives no explanation for how superposition gets formed.
- To explain *spontaneous emission* we need quantum field theory, which for light is called quantum electrodynamics (QED).
- Beyond scope of course to give QED treatment.
- Instead, we examine Einstein's approach to absorption and stimulated emission of light and see what he learned about spontaneous emission.

Light Absorption and Emission (Meanwhile, back in 1916)



Zur Quantentheorie der Strahlung.

Von A. Einstein¹⁾

Die formale Ähnlichkeit der Kurve der chromatischen Verteilung der Temperaturstrahlung mit Maxwell'schen Geschwindigkeits-Verteilungsgesetz ist zu frappant, als daß sie lange hätte verborgen bleiben können. In der Tat wurde bereits W. Wien in der wichtigen theoretischen Arbeit, in welcher er sein Verschiebungsgesetz

$$\rho = \nu^3 f\left(\frac{\nu}{T}\right) \quad (1)$$

ableitete, durch diese Ähnlichkeit auf eine weitergehende Bestimmung der Strahlungsformel geführt. Er fand hierbei bekanntlich die Formel

$$\rho = \alpha \nu^3 e^{-\frac{h\nu}{kT}} \quad (2)$$

welche als Grenzgesetz für große Werte von $\frac{\nu}{T}$ auch heute als richtig anerkannt wird (Wien-

¹⁾ Zuerst abgedruckt in den Mitteilungen der Physikalischen Gesellschaft Zürich. Nr. 18, 1916.

Light Absorption and Emission (Meanwhile, back in 1916)

Before any of this quantum theory was worked out. At this time Einstein used Planck's distribution

$$u(\nu) = \frac{8\pi\nu^2}{c_0^3} \left(\frac{h\nu}{e^{h\nu/k_B T} - 1} \right)$$

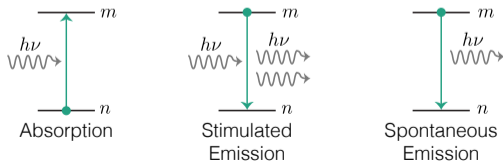
to examine how atom interacts with light inside cavity full of radiation.

- For **Light Absorption** he said atom's light absorption rate, $R_{n \rightarrow m}$, depends on light frequency, ν_{mn} , that excites N_n atoms from level n to m , and is proportional to light intensity shining on atom

$$R_{n \rightarrow m} = N_n B_{nm} u(\nu_{mn})$$

B_{nm} is Einstein's proportionality constant for light absorption.

- For **Light Emission**, when atom drops from m to n level, he proposed 2 processes: **Spontaneous Emission** and **Stimulated Emission**



Light Absorption and Emission (Meanwhile, back in 1916)

- **Spontaneous Emission:** When no light is in cavity, atom spontaneously radiates away energy at rate proportional only to number of atoms in m th level,

$$R_{m \rightarrow n}^{\text{spont}} = N_m A_{mn}$$

- ▶ A_{mn} is Einstein's proportional constant for spontaneous emission.
 - ▶ Einstein knew oscillating dipoles radiate and he assumed the same for atoms.
 - ▶ Remember, in 1916, he wouldn't know about stationary states and Schrödinger Eq. incorrectly predicting atoms do not spontaneously radiate.
- **Stimulated Emission:** From E&M Einstein guessed that emission was also generated by external oscillating electric fields—light in cavity—and that stimulated emission rate is proportional to light intensity and number of atoms in m th level.

$$R_{m \rightarrow n}^{\text{stimul}} = N_m B_{mn} u(\nu_{mn})$$

B_{mn} is Einstein's proportional constant for stimulated emission.

Light Absorption and Emission (Meanwhile, back in 1916)

Taking 3 processes together and assuming that absorption and emission rates are equal at equilibrium

$$R_{n \rightarrow m} = R_{m \rightarrow n}^{\text{spont}} + R_{m \rightarrow n}^{\text{stimul}}$$

we obtain

$$N_n B_{nm} u(\nu_{mn}) = N_m [A_{mn} + B_{mn} u(\nu_{mn})]$$

Einstein knew from Boltzmann's statistical mechanics that n and m populations at equilibrium depends on temperature

$$\frac{N_m}{N_n} = e^{-(E_m - E_n)/k_B T} = e^{-\hbar\omega/k_B T}$$

We can rearrange the rate expression and substitute for N_m/N_n to get

$$A_{mn} + B_{mn} u(\nu_{mn}) = \frac{N_n}{N_m} B_{mn} u(\nu_{mn}) = e^{\hbar\omega/k_B T} B_{nm} u(\nu_{mn})$$

and then get

$$u(\nu_{mn}) = \frac{A_{mn}}{B_{nm} e^{\hbar\omega/k_B T} - B_{mn}}$$

Light Absorption and Emission (Meanwhile, back in 1916)

Einstein compared his expression to Planck's

$$u(\nu_{mn}) = \underbrace{\frac{A_{mn}}{B_{nm}e^{\hbar\omega/k_B T} - B_{mn}}}_{\text{Einstein}} = \underbrace{\frac{8\pi\nu_{mn}^2}{c_0^3} \left(\frac{h\nu_{mn}}{e^{h\nu/k_B T} - 1} \right)}_{\text{Planck}}$$

- $B_{nm} = B_{mn}$, i.e., stimulated emission and absorption rates must be equal to agree with Planck.

$$u(\nu_{mn}) = \underbrace{\frac{A_{mn}}{B_{nm}} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right)}_{\text{Einstein}} = \underbrace{\frac{8\pi\nu_{mn}^2}{c_0^3} \left(\frac{h\nu_{mn}}{e^{h\nu/k_B T} - 1} \right)}_{\text{Planck}}$$

- **Relationship between spontaneous and stimulated emission rates:**

$$\boxed{\frac{A_{mn}}{B_{nm}} = \frac{8\pi\nu_{mn}^2}{c_0^3} h\nu_{mn} = \frac{8\pi h\nu_{mn}^3}{c_0^3}}$$

Amazing Einstein got this far without full quantum theory.

Light Absorption and Emission

Fast forward to Schrödinger's discovery of quantum wave equation, which gives light absorption rate as

$$R_{n \rightarrow m} = \frac{\langle \mu_{mn} \rangle^2}{6\epsilon_0 \hbar^2} u(\nu_{mn}) = B_{mn} u(\nu_{mn})$$

setting this equal to Einstein's rate for absorption gives

$$B_{mn} = \frac{\langle \mu_{mn} \rangle^2}{6\epsilon_0 \hbar^2}$$

from which we can calculate the spontaneous emission rate

$$A_{mn} = \frac{8\pi h \nu_{mn}^3}{c_0^3} \frac{\langle \mu_{mn} \rangle^2}{6\epsilon_0 \hbar^2}$$

- For H atom, spontaneous emission rate from 1st excited state to ground state is $\sim 10^8/\text{s}$ in agreement with what A_{mn} expression above would give.
- QED tells us that quantized electromagnetic field has zero point energy.
- It is these “vacuum fluctuations” that “stimulate” charge oscillations that lead to spontaneous emission process.

Selection Rules for Transitions

Transition Selection Rules

- In all spectroscopies you find that transition rate between certain levels will be nearly zero.
- This is because corresponding transition moment integral is zero.
- For electric dipole transitions we found that transition rate depends on

$$\langle \vec{\mu} \rangle_{mn} = \int_V \psi_m^*(\vec{r}) \vec{\mu} \psi_n(\vec{r}) d\tau$$

ψ_m and ψ_n are stationary states in absence of electric field.

Harmonic Oscillator Selection Rules

Consider quantum harmonic oscillator transitions.

- Imagine vibration of diatomic molecule with electric dipole moment.
- This is 1D problem so we write electric dipole moment operator of harmonic oscillator in series expansion about its value at equilibrium

$$\mu(\hat{r}) = \mu(r_e) + \frac{d\mu(r_e)}{dr}(\hat{r} - r_e) + \frac{1}{2} \frac{d^2\mu(r_e)}{dr^2}(\hat{r} - r_e)^2 + \dots$$

- 1st term in expansion, $\mu(r_e)$, is permanent electric dipole moment of harmonic oscillator associated with oscillator at rest.
- 2nd term describes linear variation in electric dipole moment with changing r .
- We will ignore 3rd and higher-order terms in expansion.

Harmonic Oscillator

Plug 1st two terms of expansion into transition moment integral

$$\begin{aligned}\langle \mu_{nm} \rangle &= \int_{-\infty}^{\infty} \psi_m^*(r) \left(\mu(r_e) + \frac{d\mu(r_e)}{dr} (\hat{r} - r_e) \right) \psi_n(r) dr, \\ &= \cancel{\mu(r_e) \int_{-\infty}^{\infty} \psi_m^*(r) \psi_n(r) dr} + \left(\frac{d\mu(r_e)}{dr} \right) \int_{-\infty}^{\infty} \psi_m^*(r) (\hat{r} - r_e) \psi_n(r) dr\end{aligned}$$

Since $m \neq n$ we know that 1st integral is zero as stationary state wave functions are orthogonal leaving us with

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) \int_{-\infty}^{\infty} \psi_m^*(r) (\hat{r} - r_e) \psi_n(r) dr$$

In quantum harmonic oscillator it is convenient to transform into coordinate ξ using $x = r - r_e$ and $\xi = \alpha x$ to obtain

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) \int_{-\infty}^{\infty} \chi_m^*(\xi) \hat{\xi} \chi_n(\xi) d\xi$$

Harmonic Oscillator

With harmonic oscillator wave function, $\chi_n(\xi)$, we obtain

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) A_m A_n \int_{-\infty}^{\infty} H_m \xi H_n e^{-\xi^2} d\xi$$

Using recursive relation, $\xi H_n = \frac{1}{2} H_{n+1} + n H_{n-1}$, we obtain

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) A_m A_n \left[\frac{1}{2} \int_{-\infty}^{\infty} H_m H_{n+1} e^{-\xi^2} d\xi + n \int_{-\infty}^{\infty} H_m H_{n-1} e^{-\xi^2} d\xi \right]$$

To simplify expression we rearrange

$$A_m A_n \int_{-\infty}^{\infty} H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi = \delta_{m,n} \quad \text{to} \quad \int_{-\infty}^{\infty} H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi = \frac{\delta_{m,n}}{A_m A_n}$$

Substitute into expression for $\langle \mu_{nm} \rangle$ gives

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) \left[\frac{1}{2} \frac{A_n}{A_{n+1}} \delta_{m,n+1} + n \frac{A_n}{A_{n-1}} \delta_{m,n-1} \right]$$

Harmonic Oscillator

Recalling

$$A_n \equiv \frac{1}{\sqrt{2^n n! \pi^{1/2}}}$$

we finally obtain transition dipole moment for harmonic oscillator

$$\langle \mu_{nm} \rangle = \left(\frac{d\mu(r_e)}{dr} \right) \left[\sqrt{\frac{n+1}{2}} \delta_{m,n+1} + \sqrt{\frac{n}{2}} \delta_{m,n-1} \right]$$

- For absorption, $m = n + 1$, transition is $n \rightarrow n + 1$ and $\langle \mu_{mn} \rangle^2$ gives

$$R_{n \rightarrow n+1} = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \langle \mu_{mn} \rangle^2 = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \left(\frac{d\mu(r_e)}{dr} \right)^2 \frac{n+1}{2}$$

- For emission, $m = n - 1$, transition is $n \rightarrow n - 1$ and $\langle \mu_{mn} \rangle^2$ gives

$$R_{n \rightarrow n-1} = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \langle \mu_{mn} \rangle^2 = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \left(\frac{d\mu(r_e)}{dr} \right)^2 \frac{n}{2}$$

Harmonic Oscillator

$$R_{n \rightarrow n+1} = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \left(\frac{d\mu(r_e)}{dr} \right)^2 \frac{n+1}{2} \quad \text{and} \quad R_{n \rightarrow n-1} = \frac{u(\nu_{mn})}{6\epsilon_0 \hbar^2} \left(\frac{d\mu(r_e)}{dr} \right)^2 \frac{n}{2}$$

- Selection rule for harmonic oscillator is $\Delta n = \pm 1$.
- Also, for allowed transitions $(d\mu(r_e)/dr)$ must be non-zero.

For allowed transition it is not important whether a molecule has permanent dipole moment but rather that dipole moment of molecule varies as molecule vibrates.

- In later lectures we will examine transition selection rules for other types of quantized motion, such as quantized rigid rotor and orbital motion of electrons in atoms and molecules.

- Quantum transitions in one dimension