

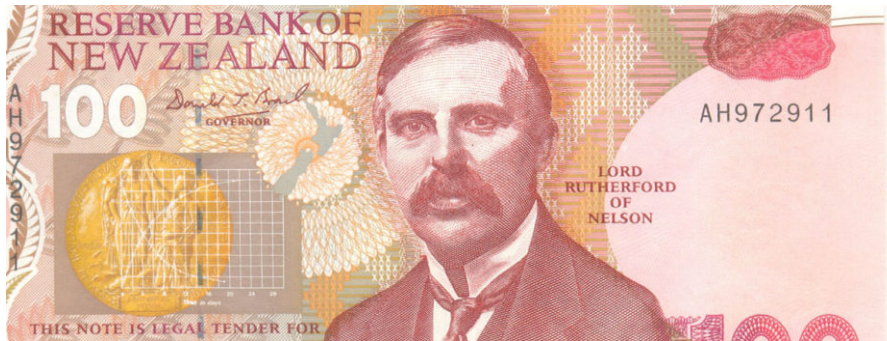
Radiating Dipoles in Quantum Mechanics

Chapter 14

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Electric dipole moment vector operator

Electric dipole moment vector operator for collection of charges is

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

Expectation value for electric dipole moment vector is

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

Let's focus on single bound charged QM particle.

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

with time dependent energy eigenstates given by

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

Time dependence of electric dipole moment

Energy Eigenstate

Starting with

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

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

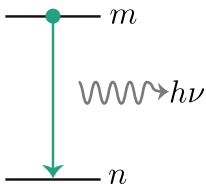
$$\langle \vec{\mu}(t) \rangle = \int_V \psi_n^*(\vec{r}) e^{iE_n t/\hbar} \left(-q_e \vec{r} \right) \psi_n(\vec{r}) e^{-iE_n t/\hbar} d\tau$$

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

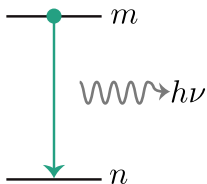
or at least it appears that way – Good news for Rutherford's atomic model.



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 $a_m(t = 0) = 1$ and $a_n(t = 0) = 0$

After transition $a_m(t = 0) = 0$ and $a_n(t = 0) = 1$

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

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

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

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, $\Psi_n(\vec{r}, t) = \psi_n(\vec{r})e^{-E_n t/\hbar}$, 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 an oscillating electric dipole moment vector given by

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

where

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

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

These integrals give *transition selection rules* for various spectroscopies

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

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

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? 🤔
- Problem is that we've been talking about light as both classical E&M wave and as photons, but in equations we treat light as classical E&M wave.
- And as we just saw, 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 a full QED treatment.
- Instead, examine Einstein's approach to absorption and stimulated emission of light and see what he teaches us about spontaneous emission.

Light Absorption and Emission

Potential energy of $\vec{\mu}$ of quantum system interacting with $\vec{\mathcal{E}}(\vec{r})$ is

$$\hat{V} = -\vec{\mu} \cdot \vec{\mathcal{E}}(\vec{r})$$

Shining light on system subjects it to time dependent $\vec{\mathcal{E}}(\vec{r}, t)$

$$\vec{\mathcal{E}}(\vec{r}, t) = \vec{\mathcal{E}}_0(\vec{r}) \cos \omega t$$

and adds a new term to the system's potential energy

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

- When time dependent perturbation is present old stationary states (before the light was turned on) are no longer stationary states.
- Effect of electric field on a molecule or atom with no permanent electric dipole moment is to induce an electric dipole moment.
- If electric field is oscillating we expect induced electric dipole to oscillate.
- 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.

Light Absorption and Emission

To describe time dependence of electric dipole moment write wave function as linear combination of stationary state eigenfunction 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 Eq

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

and skipping many steps we eventually get

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

Transition moment integrals

Using our expression for $\hat{V}(t)$ and $\Psi_n = \psi_n e^{-iE_n t/\hbar}$ we get

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

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

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

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

Rate at which $n \rightarrow m$ transition occurs is

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

In Rücksicht auf die nur unvollkommene Gestalt der Meridiankurven sowie auf die Richtung der Enden, welche zweifellos die Theorie zugrunde liegende Achsensymmetrie am ZZ beeinträchtigt, kann man die Berechnungen der berechneten und gefundenen Leistungen an der 6 kg- und 12 kg-Röhrenreihe als zulässig hinnehmen, zumal sie entgegengesetzte Vorzeichen besitzen. Bei der 1 kg Feder dagegen reicht dies zur Erklärung einer 4,8fachen Aufbiegung jedenfalls nicht aus, so daß man hierfür auf die angenommene Formel (18) zurückgreifen müßte. Wahrscheinlich ist es nicht unwahrscheinlich, daß in diesem Falle die Doppelsymmetrie bei der Umänderung verloren gegangen ist, ein Umstand, dem man in Gl. (8) näherungsweise durch Hinzufügung eines oder mehrerer Terme mit geraden Vielfachen von q genügen kann.

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(Eingegangen 26. Februar 1917.)

Über Quantentheorie der Strahlung.

Von A. Einstein¹⁾.

Die formale Ähnlichkeit der Kurve der chromatischen Verteilung der Temperaturstrahlung mit der Maxwellschen Geschwindigkeits-Verteilungskurve ist so frappant, als daß sie lange hätte übersehen werden können. In der Tat wurde schon W. Wien in der wichtigen theoretischen Arbeit, in welcher er sein Verschiebungsgesetz

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

ableitete, durch diese Ähnlichkeit auf eine weitere genaue Bestimmung der Strahlungsformel gedrungen. Er fand hierbei bekanntlich die Formel

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

welche als Grenzesetz für große Werte von ν heute bereits als richtig anerkannt wird (Wien-

sche Strahlungsformel). Heute wissen wir, daß keine Betrachtung, welche auf die klassische Mechanik und Elektrodynamik aufgebaut ist, eine brauchbare Strahlungsformel liefern kann, sondern daß die klassische Theorie notwendig auf die Rayleighsche Formel

$$Q = \frac{ka}{h} \nu^2 T \quad (3)$$

führt. Als dann Planck in seiner grundlegenden Untersuchung seine Strahlungsformel

$$Q = c \nu^3 \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad (4)$$

auf die Voraussetzung von diskreten Energie-Elementen gegründet hatte, aus welcher sich in rascher Folge die Quantentheorie entwickelte, geriet jene Wiensche Überlegung, welche zur Gleichung (2) geführt hatte, naturgemäß wieder in Vergessenheit.

Vor kurzem nun fand ich eine der ursprünglichen Wienschen Betrachtung¹⁾ verwandte, auf die Grundvoraussetzung der Quantentheorie sich stützende Ableitung der Planckschen Strahlungsformel, in welcher die Beziehung der Maxwellschen Kurve zu der chromatischen Verteilungskurve zur Geltung kommt. Diese Ableitung verdient nicht nur wegen ihrer Einfachheit Beachtung, sondern besonders deshalb, weil sie über den für uns noch so dunklen Vorgang der Emission und Absorption der Strahlung durch die Materie einige Klarheit zu bringen scheint. Indem ich einige vom Standpunkte der Quantentheorie naheliegende Hypothesen über die Strahlungs-Emission und -Absorption von Molekülen zugrunde legte, zeigte ich, daß Moleküle mit im Sinne der Quantentheorie bei Temperaturgleichgewicht verteilten Zuständen, im dynamischen Gleichgewicht mit Planckscher Strahlung stehen; es ergab sich auf diesem Wege die Plancksche Formel (4) in verblüffend einfacher und allgemeiner Weise. Sie ergab sich aus der Bedingung, daß die von der Quantentheorie geforderte Zustandsverteilung der inneren Energie der Moleküle allein durch Absorption

¹⁾ Verh. d. Deutschen physikal. Gesellschaft Nr. 12, 1894.

Light Absorption and Emission

In 1916, before quantum theory, Einstein used Planck's distribution

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

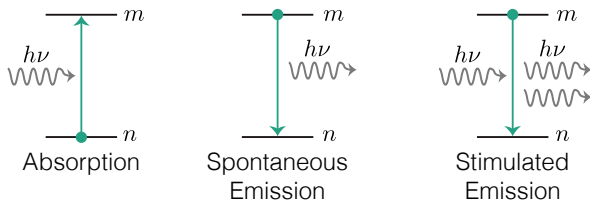
to examine how atom interacts with light inside cavity full of radiation.

For **Light Absorption** he reasoned that atom's rate of light absorption, $R_{n \rightarrow m}$, 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

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

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

For **Light Emission**, when atom drops from the m to n level, Einstein proposed two processes: **Spontaneous Emission** and **Stimulated Emission**



Light Emission - Spontaneous and Stimulated

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 Einsteins proportional constant for spontaneous emission.
- Einstein knew oscillating dipoles radiate and he assumed same for atom.
- Remember, in 1916 he didn'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.

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

B_{mn} is Einsteins proportional constant for stimulated emission.

Light Absorption and Emission

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

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

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

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

and then get

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

Light Absorption and Emission

When Einstein compared

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

to Planck's distribution

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

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

This leads to

$$\rho(\nu_{mn}) = \frac{A_{mn}}{B_{nm}} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right)$$

He found **relationship between spontaneous and stimulated emission rates**

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

Amazing Einstein got this far without full quantum theory and QED.

Light Absorption and Emission

Earlier we found that the stimulated emission rate was

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

setting this equal to Einstein's rate for stimulated emission gives

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

from which we can calculate the spontaneous emission rate

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

- 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.
- 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.

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 transitions of quantum harmonic oscillator.

- Imagine oscillating dipole moment of charged particle in harmonic oscillator potential or 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

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

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

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

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

In quantum harmonic oscillator it is convenient to transform into

Harmonic Oscillator

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

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

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

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

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 $\langle \mu \rangle_{nm}$ gives

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

Harmonic Oscillator

Recalling

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

we finally obtain transition dipole moment for harmonic oscillator

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

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

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

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

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

Harmonic Oscillator

- 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.