Set 7:

Classical & Semi-Classical Oscillators

Dipole Approximation

- Radiation field

$$\mathbf{E}_{\mathrm{rad}} = \frac{q}{c}\left[\frac{\hat{\mathbf{n}}}{\kappa^3 R} \times ((\hat{\mathbf{n}} - \beta) \times \dot{\beta})\right]$$
$$\mathbf{B}_{\mathrm{rad}} = \hat{\mathbf{n}} \times \mathbf{E}_{\mathrm{rad}}$$

- A collection of particles

$$\mathbf{E}_{\mathrm{rad}} = \sum_i \frac{q_i}{c}\left[\frac{\hat{\mathbf{n}}_i}{\kappa_i^3 R_i} \times ((\hat{\mathbf{n}}_i - \beta_i) \times \dot{\beta}_i)\right]$$

- Take the limit of coherent emission of particles such that the wavelength $\lambda \gg L$, the dimension of the emission region.
- Approximation equivalent to non-relativistic velocities u since the scale of the oribits $l < L$

$$\frac{L}{c} \ll \tau \sim \frac{l}{u} < \frac{L}{u} \quad \rightarrow u \ll c$$

Dipole Approximation

- The light travel time across $L \ll$ time scale of change in charged particle orbits

$$\tau \sim \frac{1}{\nu} \sim \frac{\lambda}{c} \gg \frac{L}{c}$$

- So $\kappa_i \approx 1$, $\hat{\mathbf{n}}_i = \hat{\mathbf{n}}$ and $R_i \approx R_0$ the mean distance

$$\mathbf{E}_{\rm rad} = \sum_i \frac{q_i}{c} \left[\frac{\hat{\mathbf{n}}}{R_0} \times (\hat{\mathbf{n}} \times \dot{\beta}_i) \right]$$

- Defining the electric dipole moment

$$\mathbf{d} = \sum_i q_i \mathbf{r}_i$$

$$\mathbf{E}_{\rm rad} = \frac{1}{c^2 R_0} [\hat{\mathbf{n}} \times (\hat{\mathbf{n}} \times \ddot{\mathbf{d}})]$$

Dipole Approximation

- Larmor formula

$$\frac{dP}{d\Omega} = \frac{\ddot{d}^2}{4\pi c^3}\sin^2\Theta \qquad P = \frac{2\ddot{d}^2}{3c^3}$$

- Frequency structure reflects $d(t)$

$$d(t) = \int_{-\infty}^{\infty} e^{-i\omega t} d(\omega) d\omega$$

$$\ddot{d}(t) = -\int_{-\infty}^{\infty} \omega^2 d(\omega) e^{-i\omega t} d\omega$$

in the electric field

$$E(\omega) = -\frac{1}{c^2 R_0}\omega^2 d(\omega)\sin\Theta$$

Dipole Approximation

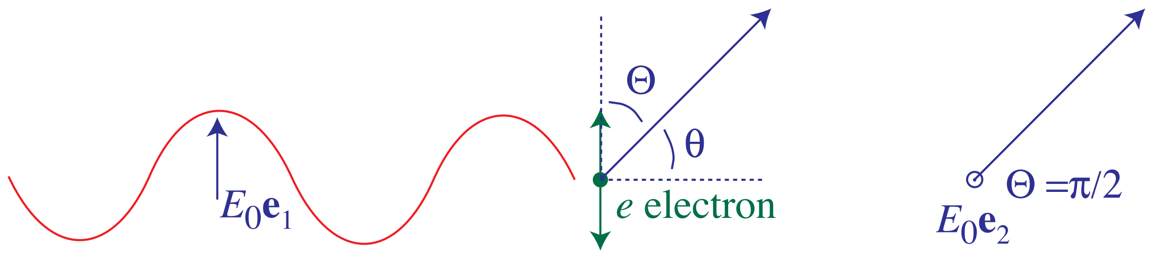
- Energy spectrum $dA = R_0^2 d\Omega$

$$\frac{dW}{d\omega d\Omega} = c|E(\omega)|^2 R_0^2 = \frac{1}{c^3}\omega^4 |d(\omega)|^2 \sin^2\Theta$$
$$\frac{dW}{d\omega} = \frac{8\pi\omega^4}{3c^3}|d(\omega)|^2$$

- Dipole radiation frequencies reflect frequencies in the dipole moment. Generalize to higher order in the expansion of L/λ or $k\Delta R_i$

Thomson Scattering

- Simplest example: single free electron system



- Incoming wave of frequency ω_0 provides oscillatory force for acceleration. For non-relativistic velocities the Lorentz force is dominated by the electric field

$$\mathbf{F} = e\mathbf{E} = eE_0 \sin\omega_0 t\,\hat{\mathbf{e}} = m\mathbf{a}$$

$$\mathbf{a} = \frac{eE_0}{m} \sin\omega_0 t\,\hat{\mathbf{e}}$$

Thomson Scattering

- Dipole formula

$$\mathbf{d} = e\mathbf{r}\,, \quad \ddot{\mathbf{d}} = e\mathbf{a} = \frac{e^2 E_0}{m} \sin\omega_0 t\, \hat{\mathbf{e}}$$

$$\frac{dP}{d\Omega} = \frac{\ddot{d}^2}{4\pi c^3} \sin^2\Theta = \frac{e^4 E_0^2}{m^2} \frac{1}{4\pi c^3} \sin^2\Theta \langle \sin^2\omega_0 t \rangle$$

$$= \frac{e^4 E_0^2}{8\pi m^2 c^3} \sin^2\Theta \qquad \to P = \frac{e^4 E_0^2}{3 m^2 c^3}$$

- Power is independent of frequency
- Differential Cross Section: $P = \langle S \rangle \sigma_T$

$$\frac{d\sigma_T}{d\Omega} = \frac{\frac{dP}{d\Omega}}{\langle S \rangle} = \frac{\text{outgoing power}}{\text{incoming flux}}$$

$$= \frac{\frac{e^4}{8\pi m^2 c^3} E_0^2 \sin^2\Theta}{\frac{c}{8\pi} E_0^2} = \frac{e^4}{m^2 c^4} \sin^2\Theta$$

Thomson Scattering

- Cross section decreases with mass (so electrons not protons dominate), defines a classical size for a point particle $r_0 = e^2/mc^2$. Total cross section

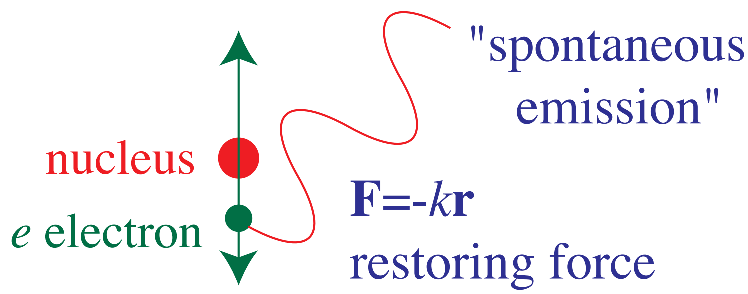
$$\sigma_T = \int \frac{d\sigma_T}{d\Omega} d\Omega = \frac{8\pi}{3} r_0^2$$

- Θ is angle between $\hat{\mathbf{e}}$ and $\hat{\mathbf{n}}$. Relate to scattering angle θ and polarization
- For $\hat{\mathbf{e}} \perp \hat{\mathbf{n}}$ (polarization out of scattering plane) then $\sin\Theta = 1$. For polarization in the scattering plane $\Theta = \pi/2 - \theta$
- Average over the two incoming polarization states

$$\frac{d\sigma_T}{d\Omega} = \frac{1}{2} r_0^2 [1 + \sin^2(\frac{\pi}{2} - \theta)] = \frac{1}{2} r_0^2 (1 + \cos^2\theta)$$

Classical Line Emission

- An electron bound in a central force provides a classical model for spontaneous emission in an atomic line



- Given a restoring force $\mathbf{F} = -k\mathbf{r}$ there is a natural frequency of oscillation. Neglecting radiation

$$ma = -kr \rightarrow \ddot{x} + \frac{k}{m}x = 0 \rightarrow \ddot{x} + \omega_0^2 x = 0$$

where $\omega_0 = \sqrt{(k/m)}$

Radiation Reaction

- But an accelerating electron will radiate causing the oscillator to lose energy as a damped oscillator

$$\ddot{x} + \Gamma \dot{x} + \omega_0^2 x = 0$$

  where Γ is the damping rate due to radiation losses

- Larmor's formula gives power radiated or energy lost to radiation per unit time

$$P = \frac{2e^2 \ddot{x}^2}{3c^3}$$

Radiation Reaction

- If one assumes that losses are small across one period of the oscillation then (like the Rosseland approximation) one can iterate the solution

$$\ddot{x} \approx -\omega_0^2 x \quad \rightarrow \quad x \approx A\cos(\omega_0 t + \delta)$$

$$P = \frac{2e^2}{3c^3}(-\omega_0^2 x)^2 = \frac{2e^2}{3c^3}\omega_0^4 x^2$$

- Set equal to mechanical work / time? by radiation reaction

$$\frac{2e^2}{3c^3}\omega_0^4 x^2 = -F_{\rm rad}\dot{x}$$

- Problem: since $x \propto \cos(\omega_0 t + \delta)$ and $\dot{x} \propto \sin(\omega_0 t + \delta)$ this formula cannot be satisfied instantaneously representing a breakdown of the classical treatment

Radiation Reaction

- Try average over an oscillation period $T = 2\pi/\omega_0$ and match integral of $\cos^2$ with $\sin^2$

$$\int_0^{\frac{2\pi}{\omega_0}} dt \frac{2e^2}{3c^3}\omega_0^4 A^2 \cos^2(\omega_0 t + \delta) = -\int_0^{\frac{2\pi}{\omega_0}} dt F_{\rm rad}[-A\omega_0 \sin(\omega_0 t + \delta)]$$

$$\frac{2e^2}{3c^3}\omega_0^4 A^2 \frac{1}{2} = \frac{F_{\rm rad}}{\sin(\omega_0 t + \delta)} A\omega_0 \frac{1}{2}$$

- Solve for the reaction force

$$F_{\rm rad} = \frac{2e^2\omega_0^3}{3c^3} A \sin(\omega_0 t + \delta)$$

$$= -\frac{2e^2\omega_0^2}{3c^3}\dot{x}$$

Radiation Reaction

- So the oscillator equation of motion becomes

$$\ddot{x} + \omega_0^2 x = F_{\rm rad}/m = -\frac{2e^2\omega_0^2}{3c^3 m}\dot{x}$$

$$\Gamma = \frac{2}{3}\frac{e^2\omega_0^2}{mc^3}$$

which quantifies the rate at which the orbit decays due to radiation losses - in a quantum description of the line this is related the Einstein coefficient for spontaneous emission

$$\ddot{x} + \Gamma\dot{x} + \omega_0^2 x = 0 \qquad x = e^{\alpha t}$$

$$\alpha^2 + \Gamma\alpha + \omega_0^2 = 0$$

$$\alpha = \frac{1}{2}(-\Gamma \pm \sqrt{\Gamma^2 - 4\omega_0^2})$$

Lorentz Line Profile

- Since $\Gamma \ll \omega_0$ one can expand

$$\alpha = \pm i\omega_0 \sqrt{1 - \frac{\Gamma^2}{4\omega_0^2}} - \Gamma/2 \approx \pm i\omega_0 - \Gamma/2$$

$$x(t) = x(0)e^{-\Gamma t/2}\cos(\omega_0 t + \delta)$$

- Get frequency content (define zero of time so that $\delta = 0$)

$$x(t) = x(0)e^{-\Gamma t/2}\frac{1}{2}\left[e^{i\omega_0 t} + e^{-i\omega_0 t}\right]$$

$$x(\omega) = \frac{1}{2\pi}\int x(t)e^{i\omega t}dt$$

$$= \frac{x(0)}{4\pi}\left[\frac{1}{\Gamma/2 - i(\omega + \omega_0)} + \frac{1}{\Gamma/2 - i(\omega - \omega_0)}\right]$$

Lorentz Line Profile

- Frequency content dominated by region around $\omega = \omega_0$, i.e. the second term

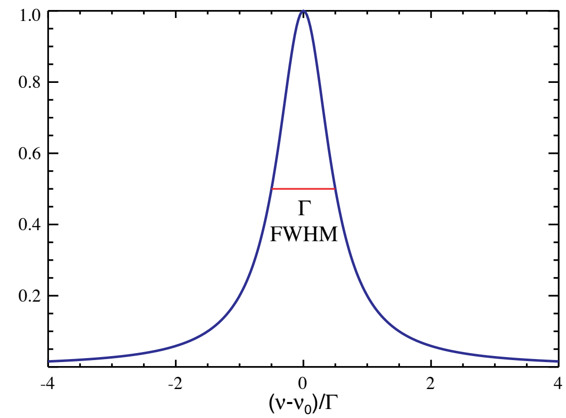
$$
\begin{aligned}
x(\omega) &\approx \frac{x(0)}{4\pi} \frac{1}{\Gamma/2 - i(\omega - \omega_0)} \\
|x(\omega)|^2 &\approx \frac{x^2(0)}{(4\pi)^2} \frac{1}{(\omega - \omega_0)^2 + (\Gamma/2)^2} \\
\frac{dW}{d\omega} &= \frac{8\pi\omega^4}{3c^3} e^2 |x(\omega)|^2 \\
&= \frac{8\pi\omega^4}{3c^3} \frac{e^2 x^2(0)}{(4\pi)^2} \frac{1}{(\omega - \omega_0)^2 + (\Gamma/2)^2}
\end{aligned}
$$

- Interpret the amplitude in terms of initial energy in the oscillator

$$
E_i = \frac{1}{2} k x^2(0) = \frac{1}{2} m \omega_0^2 x^2(0)
$$

Lorentz Line Profile

- All of the initial energy is emitted as radiation



$$\frac{dW}{d\omega} = \frac{8\pi\omega^4}{3c^3}\frac{e^2}{(4\pi)^2}\frac{2E_i}{m\omega_0^2}\frac{1}{(\omega-\omega_0)^2+(\Gamma/2)^2}$$

$$\frac{dW}{d\omega} = \frac{\omega^4}{\omega_0^2}\frac{e^2E_i}{3\pi mc^3}\frac{1}{(\omega-\omega_0)^2+(\Gamma/2)^2}$$

$$\left[\Gamma = \frac{2}{3}\frac{e^2\omega_0^2}{mc^3}\right]$$

$$\frac{dW}{d\omega} = E_i\frac{\Gamma/2\pi}{(\omega-\omega_0)^2+(\Gamma/2)^2}$$

Lorentz Line Profile

- Lorentz profile: FWHM = Λ with normalization

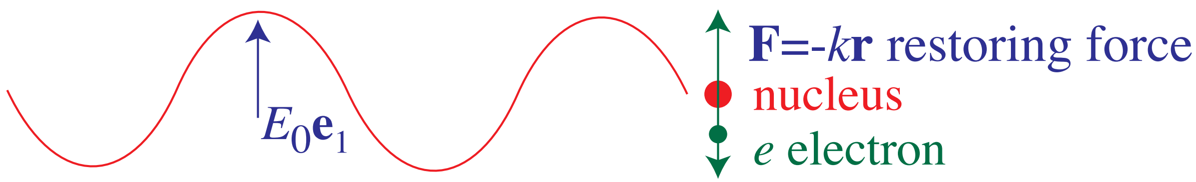
$$\left[\int d\omega \frac{\Gamma/2\pi}{(\omega-\omega_0)^2+(\Gamma/2)^2}=1\right]$$

- So that the decay rate is related to the frequency spread of the line $\Delta\omega = \Gamma$

$$\Delta\lambda = 2\pi c\frac{\Delta\omega}{\omega_0^2} = \frac{4\pi e^2}{3mc^2} \approx 1.2\times 10^{-12}\mathrm{cm}$$

Absorption

- Γ must be related to A_{21} the Einstein spontaneous emission coefficient. However a direct association is impeded in that an atomic state is classically unstable. Establish the relation by considering the absorption coefficient



- Driven oscillator: combination of the Thomson and line calculations with incident radiation at frequency ω

$$\ddot{x} + \Gamma\dot{x} + \omega_0^2 x = \frac{eE_0}{m} e^{i\omega t}$$

Absorption

- After transients from the initial conditions are gone due to damping

$$x = x_0 e^{i\omega t}$$

$$(-\omega^2 + \Gamma i\omega + \omega_0^2) x_0 e^{i\omega t} = \frac{eE_0}{m} e^{i\omega t}$$

- Solution

$$x_0 = \frac{eE_0}{m} \frac{1}{\omega_0^2 - \omega^2 + i\omega\Gamma}$$

$$\omega^2 - \omega_0^2 + i\omega\Gamma \equiv |A| e^{-i\delta} = |A|(\cos\delta - i\sin\delta)$$

$$|A|\cos\delta = \omega_0^2 - \omega^2\,, \qquad |A|\sin\delta = -\Gamma\omega$$

$$\tan\delta = \frac{\Gamma\omega}{\omega^2 - \omega_0^2}$$

$$x_0 = \left| \frac{eE_0}{m} \frac{-1}{\omega^2 - \omega_0^2 - i\omega\Gamma} \right| e^{i\delta}$$

Absorption

- Reradiated power

$$P = \frac{e^2\omega^4}{3c^3}|x_0|^2 = \frac{e^4\omega^4}{3c^3}\frac{E_0^2}{m^2}\frac{1}{(\omega^2-\omega_0^2)^2+(\Gamma\omega)^2}$$

- Interaction cross section

$$\sigma(\omega) = \frac{P}{\langle S\rangle} = \frac{P}{\frac{c}{8\pi}E_0^2} = \frac{8\pi}{3c^4}\frac{e^4\omega^4}{m^2}\frac{1}{(\omega^2-\omega_0^2)^2+(\Gamma\omega)^2}$$

$$= \sigma_T\frac{\omega^4}{(\omega^2-\omega_0^2)^2+(\Gamma\omega)^2} \qquad \left[\sigma_T = \frac{8\pi}{3}\left(\frac{e^2}{mc^2}\right)^2\right]$$

- If $\omega \gg \omega_0$ then $\sigma(\omega) \to \sigma_T$ and the electron behaves as a free particle

Rayleigh Scattering

- If $\omega \ll \omega_0$ then

$$\sigma(\omega) \to \sigma_T \left(\frac{\omega}{\omega_0}\right)^4$$

  and the steep frequency dependence is the reason the sky is blue and sunsets are red - is the limit where e.o.m is $\omega_0^2 x = (eE_0/m)e^{i\omega t}$

- If $\omega \approx \omega_0$ then line absorption and resonance

$$(\omega^2 - \omega_0^2) = (\omega - \omega_0)(\omega + \omega_0) \approx 2\omega_0(\omega - \omega_0)$$

$$\sigma(\omega) = \sigma_T \frac{\omega_0^4}{4\omega_0^2(\omega - \omega_0)^2 + (\Gamma\omega_0)^2}$$

$$\sigma(\omega) = \frac{\sigma_T}{4} \frac{\omega_0^2}{(\omega - \omega_0)^2 + (\Gamma/2)^2}$$

Absorption coefficient

- Relate to Lorentz profile

$$\sigma(\omega) = \frac{\sigma_T}{4}\frac{2\pi\omega_0^2}{\Gamma}\frac{\Gamma/2\pi}{(\omega-\omega_0)^2+(\Gamma/2)^2} \qquad \left[\Gamma = \frac{2}{3}\frac{e^2\omega_0^2}{mc^3}\right]$$

$$= 2\pi^2\frac{e^2}{mc}\frac{\Gamma/2\pi}{(\omega-\omega_0)^2+(\Gamma/2)^2} \qquad \left[\sigma_T = \frac{8\pi}{3}\left(\frac{e^2}{mc^2}\right)^2\right]$$

- Absorption coefficient, Einstein coefficient

$$\alpha_\nu = n\sigma(\omega) = \frac{h\nu_0}{4\pi}nB_{12}\phi(\nu)$$

$$\sigma(\omega) = \frac{h\nu_0}{4\pi}B_{12}\phi(\nu)$$

$$\int d\nu\sigma(\omega) = \int\frac{d\omega}{2\pi}\sigma(\omega) = \frac{2\pi^2}{2\pi}\frac{e^2}{mc} = \frac{h\nu_0}{4\pi}B_{12} \rightarrow B_{12} = \frac{4\pi^2e^2}{h\nu_0 mc}$$

Absorption coefficient

- Quantum results are stated against this classical result as an oscillator strength f_{12}

$$B_{12} = \frac{4\pi^2 e^2}{h\nu_0 mc} f_{12}$$

- The Einstein A_{21} spontaneous emission coefficient is then

$$A_{21} = \frac{2h}{c^2}\nu_0^3 \frac{g_1}{g_2} B_{12} = \frac{8\pi^2\nu_0^2 e^2}{mc^3}\frac{g_1}{g_2} f_{12} = 3\Gamma \frac{g_1}{g_2} f_{12}$$

  so that the rate Γ defines A_{21}

- We shall see that the relation is corrected in the semiclassical oscillator and $A_{21} = \Gamma(g_1/g_2) f_{12}$

Quantum Oscillator

- Schrodinger equation in the absence of radiation field

$$H\psi = i\hbar \frac{\partial \psi}{\partial t}$$

- The Hamiltonian including the radiation field is in Coulomb gauge $[\nabla \cdot A = 0$ and $\nabla^2 \phi = -4\pi\rho$ (=0 for radiation)]

$$H_{\text{relativistic}} = [(c\mathbf{q} - e\mathbf{A})^2 + m^2c^2]^{1/2} + e\phi$$

$$H \approx \frac{q^2}{2m} + e\phi - \frac{e}{mc}\mathbf{A} \cdot \mathbf{q} \quad H = H^0 + H^I$$

- Radiative transitions are approximated through an interaction Hamiltonian in time dependent perturbation theory

$$H^I = -\frac{e}{mc}\mathbf{A} \cdot \mathbf{q} = \frac{ie\hbar}{mc}\mathbf{A} \cdot \nabla$$

which connects the initial and final state

Quantum Oscillator

- Original eigenstates $|n\rangle$ such that $H^0|n\rangle = E_n|n\rangle$
- Expand the wave function in the original eigenfunctions

$$|\psi\rangle = \sum c_n |n\rangle e^{-iE_n t/\hbar}$$

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \left[H^0 + H^I\right]|\psi\rangle$$

$$i\hbar\frac{dc_m}{dt} = \sum_n \langle m|H^I|n\rangle c_n(t) e^{i(E_m - E_n)t/\hbar}$$

- Initially the atom is in the initial state $c_i = 1$ and $c_{n\neq i} = 0$ and the perturbation induces a transition to a final state $m = f$ with strength given by the matrix element $H^I_{fi}(t) = \langle f|H^I|i\rangle$. A short time T later

$$c_f(T) = -\frac{i}{\hbar}\int_0^T dt H^I_{fi}(t) e^{i(E_f - E_i)t/\hbar} \equiv -\frac{i}{\hbar}2\pi H^I_{fi}(\omega_{fi})$$

Quantum Oscillator

- The integral is a Fourier transform that picks out frequency $\omega_{fi} = (E_f - E_i)/\hbar$ in H^I with some width determined by how long (T) one waits before accumulating significant probability.
- Transition rate is the probability per unit time for the transition

$$w_{fi} = \frac{4\pi^2}{\hbar^2 T} |H^I_{fi}(\omega_{fi})|^2$$

- Field carries time dependence $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(t)e^{i\mathbf{k}\cdot\mathbf{r}}$ and integral picks out ω_{fi} component of field

$$H^I_{fi}(\omega_{fi}) = \mathbf{A}(\omega_{fi}) \frac{ie\hbar}{mc} \langle f|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla|i\rangle$$

$$\langle f|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla|i\rangle = \int d^3x \psi_f^* e^{i\mathbf{k}\cdot\mathbf{r}} \nabla\psi_i$$

in dipole approx $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ across region ψ has support

Einstein Coefficient

- Time reversal symmetry gives $w_{if} = w_{fi}$, is the quantum origin of the relationship between B_{12} and B_{21} the absorption and stimulated emission coefficient
- For absorption

$$w_{12} = B_{12} J_\nu$$

and what remains is to relate the A embedded in the interaction Hamiltonian with the specific intensity

$$\frac{dW}{dA d\omega dt} = \frac{c|E(\omega)|^2}{T}$$

$$\frac{dW}{dA d\nu dt} = \frac{2\pi c|E(\omega)|^2}{T}$$

Einstein Coefficient

- Given $\mathbf{B} = \nabla \times \mathbf{B}$ and $E_0 = B_0$, in Fourier space field and potential related by

$$|E(\omega)|^2 = \frac{\omega^2}{c^2}|A(\omega)|^2$$

- A plane wave is a delta function in angle so that $J_\nu = \frac{1}{4\pi}\int d\Omega I_\nu$ simply divides the result by 4π or

$$J_\nu = \frac{1}{2}\frac{\omega^2}{cT}|\mathbf{A}(\omega)|^2$$

Einstein Coefficient

- Eliminate in favor of J_ν

$$w_{fi} = \frac{2c}{\omega_{fi}^2} 4\pi^2 \frac{|H_{fi}^I(\omega_{fi})|^2}{|\mathbf{A}(\omega)|^2} J_\nu$$

$$= \frac{8\pi^2}{\omega_{fi}^2} \frac{e^2}{m^2 c} \left| \langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \nabla | i \rangle \right|^2 J_\nu$$

- Determines Einstein coefficient

$$B_{12} = \frac{8\pi^2}{\omega_{fi}^2} \frac{e^2}{m^2 c} \left| \langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \nabla | i \rangle \right|^2$$

Einstein Coefficient

- Determines the oscillator strength f_{12}, typically less than unity

$$
\begin{aligned}
B_{12} &= \frac{8\pi^2}{\omega_{fi}^2}\frac{e^2}{m^2 c}\left|\langle f|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla|i\rangle\right|^2 \\
&= \frac{4\pi^2 e^2}{\hbar\omega_{fi} mc} f_{12} \\
f_{12} &= \frac{2\hbar}{\omega_{fi} m}\left|\langle f|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla|i\rangle\right|^2
\end{aligned}
$$

- Stimulated emission can be similarly handled, the difference being for degenerate levels the result is averaged over initial states and summed over final states – hence the g_1, g_2 factors

Einstein Coefficient

- Spontaneous emission formally requires second (field) quantization but can be derived semiclassically by the Einstein relation. Key of the quantum derivation is the field behaves as a quantized oscillator and the states are normalized as

$$a^\dagger |n\rangle \propto (n+1)^{1/2} |n+1\rangle$$

  where the $n \gg 1$ returns the semiclassical stimulated emission coefficient B_{21} and the $n = 0$ returns the spontaneous emission A_{21}

- When the coefficients cannot be calculated A_{21} is measured and the others inferred

Line Profile

- The natural linewidth is determined by $A_{21} = \Gamma$ exactly as in the semiclassical theory (but without the relationship $\Gamma = 2e^2\omega_0^2/3mc^3$) , yielding a Lorentzian profile
- Linewidth is broadened by thermal motion. Frequency shifted according to the Doppler shift from the line of sight velocity $v_\parallel$

$$\nu - \nu_0 = \nu_0 \frac{v_\parallel}{c}$$

- The velocity distribution is Maxwellian given the atomic mass m_a

$$\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m_a v_\parallel^2/2kT} dv_\parallel$$

- The net result is a Voigt profile

$$\phi(\nu) = \frac{\Gamma}{4\pi^2} \int_{-\infty}^{\infty} dv_\parallel \frac{1}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m_a v_\parallel^2/2kT} dv_\parallel$$

Line Profile

- Finally, collisions can also broaden the profile. They introduce a random phase in the electric field. As shown in RL Problem 10.7, collisions of a frequency $\nu_{\rm col}$ cause $\langle |E(t)|^2 \rangle \propto e^{-\nu_{\rm col} t}$ (a Poisson process) and comparing this to the $e^{-\Gamma t/2}$ natural decay implies that the total Lorentzian width of the line

$$\Gamma \to \Gamma + 2\nu_{\rm col}$$

Electronic, Vibrational, Rotational Lines

- Electronic lines tend to have an energy given by the physical scale of the orbital (atom) and tends to be in the few eV energy scale

$$E_{\mathrm{elect}} \sim \frac{1}{2}\frac{p^2}{m_e} \sim \frac{1}{2}\frac{\hbar^2}{a^2 m_e} \qquad p \sim \frac{\hbar}{a}$$

- Molecules can have vibrations. For vibrations, the atoms execute simple harmonic motion around their equilibrium position with the restoring force associated with the electronic binding energy - so that a displacement of order a must given the electronic energy

$$E_{\mathrm{elect}} = \frac{1}{2}\frac{\hbar^2}{a^2 m_e} = \frac{1}{2}ka^2 = \frac{1}{2}m_a \omega_{\mathrm{vib}}^2 a^2$$

$$E_{\mathrm{vib}} = \hbar\omega_{\mathrm{vib}} = \frac{\hbar^2}{a^2 m_e^{1/2} m_a^{1/2}} \sim \left(\frac{m_e}{m_a}\right)^{1/2} E_{\mathrm{elect}}$$

Electronic, Vibrational, Rotational Lines

- Vibrational energies are lower by of order a percent of the electronic energies, i.e. $10^{-2} - 10^{-1}$ eV or infrared
- Rotational energy is associated with the moment of inertial $I \sim m_a a^2$

$$E_{\rm rot} \approx \frac{\hbar^2 \ell(\ell+1)}{2I} \sim \frac{\hbar^2}{2a^2 m_a} \approx \frac{m_e}{m_a} E_{\rm elect}$$

or 10^{-3} eV in the far infrared and radio

- Ratio of energies

$$E_{\rm elect} : E_{\rm vib} : E_{\rm rot} = 1 : \left(\frac{m_e}{m_a}\right)^{1/2} : \frac{m_e}{m_a}$$