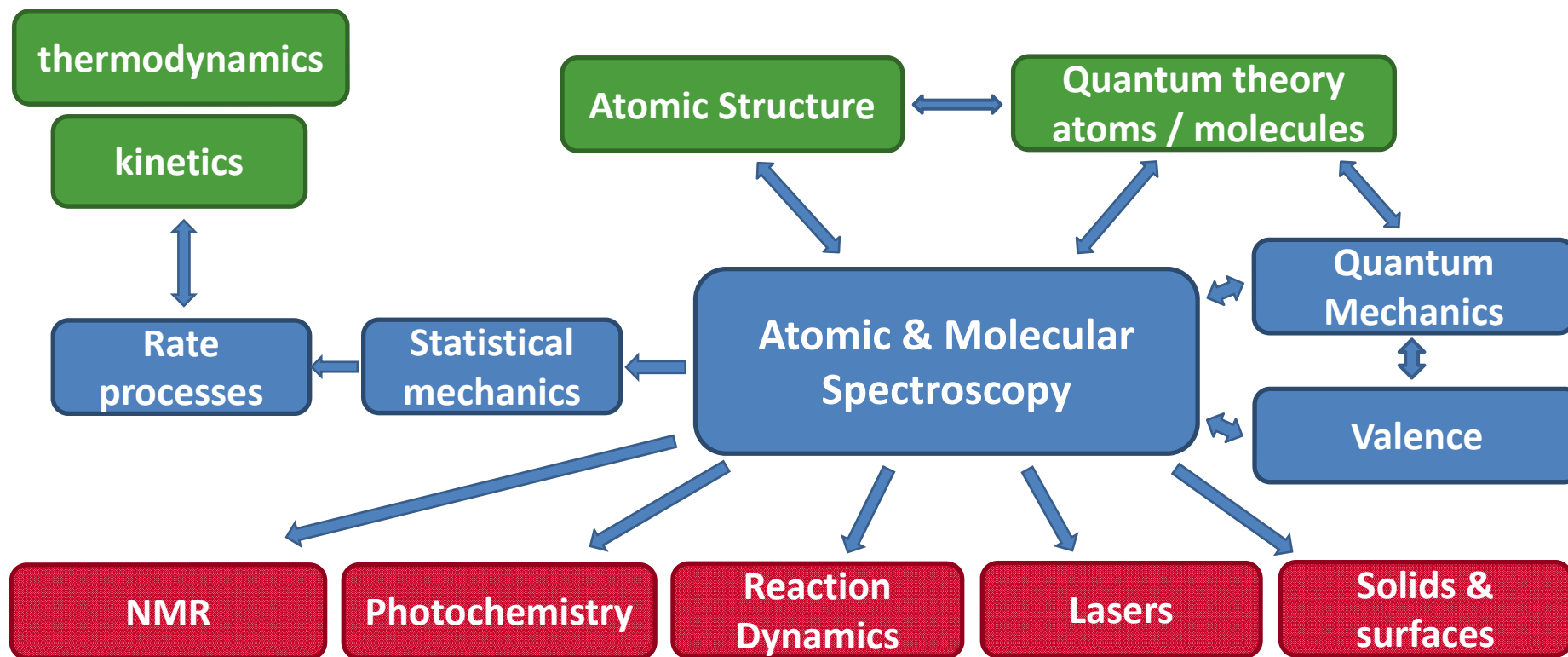




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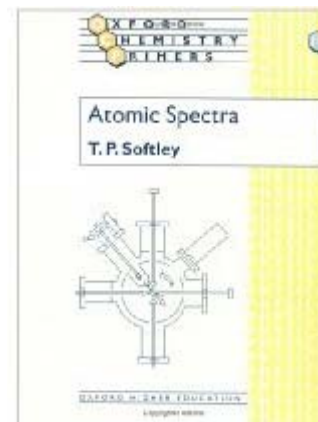
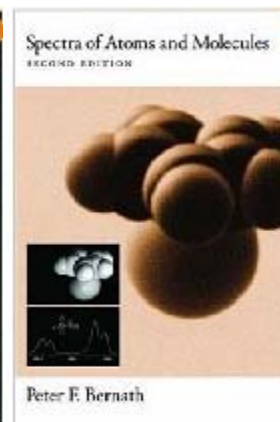
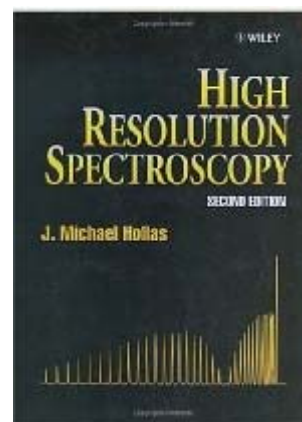
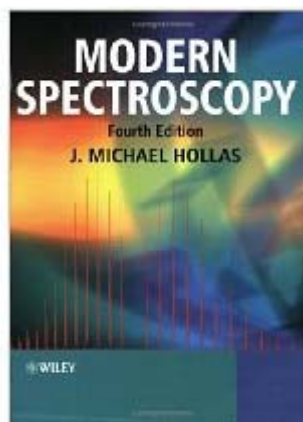
Atomic and Molecular Spectroscopy

Dr Stuart Mackenzie



Resources

- Handouts (colour online)
- Tutorials
- Books:



- *Modern Spectroscopy* (4th ed. 2004) JM Hollas
- *High Resolution Spectroscopy* (2nd ed., 1998) JM Hollas
- *Molecular Spectroscopy* (OUP Primer) JM Brown
- *Spectra of Atoms and Molecules* (2nd ed. 2005) Bernath
- *Fundamentals of Molecular Spectroscopy* (4th ed. 1994) Banwell & McCash
- *Atomic Spectra* (OUP Primer) TP Softley
- *Molecular Quantum Mechanics* (4th ed.) Atkins and Friedman
- *Electronic and Photoelectron Spectroscopy*, Ellis, Feher and Wright
- Practicals:
 - II-03 HCl, DCl spectra II-04 Fluorescence and quenching
 - II-05 I₂ visible spectrum II-08 Flame atomic absorption
 - II-10 Na/Na⁺ atomic spec II-17 Computational Raman
 - II-18 N₂⁺ spectrum

Lecture 1: General Aspects of Spectroscopy

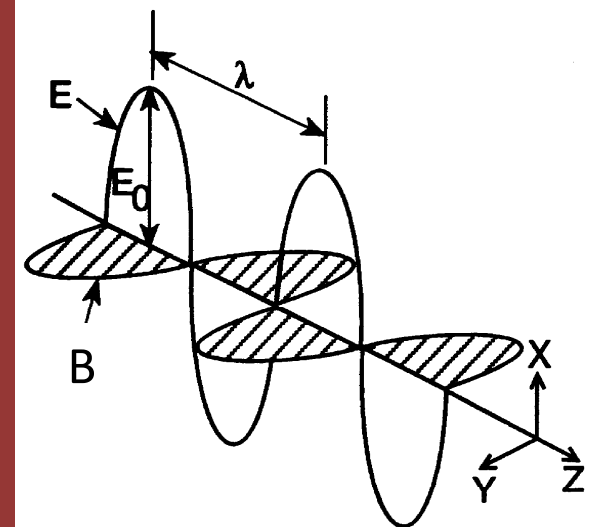
1.1 Electromagnetic radiation

- Transverse wave of perpendicular, sinusoidally oscillating electric and magnetic fields

$$E = E_0 \sin(kx - \omega t + \phi)$$

with wavevector, $k = 2\pi/\lambda$
and angular frequency, $\omega = 2\pi\nu$

- Characterised by:
 - **wavelength, λ** (in m) or
 - **frequency, ν** (in Hz)
- Speed *in vacuo* **defined** as $c_{vac} = 299\,792\,458\text{ ms}^{-1}$
- $c = \nu\lambda = \omega/k$
- c_{vac} is related to the permittivity (electric constant) and permeability (magnetic constant) of free space:
(proof comes from Maxwell's Equations)



A plane electromagnetic wave propagating in the z-direction

$$c^2 = \frac{1}{\mu_0 \epsilon_0}$$

1.2 Quantised Light: Photons

It will usually be convenient to consider light as a stream of zero rest mass particles or packages of radiation called **photons** with the following properties:

- **Energy, $E = h\nu$**

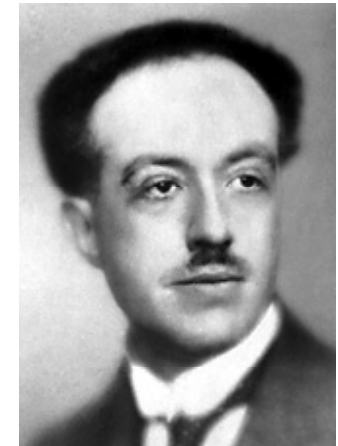
in which h is **Planck's constant, $h = 6.626 \times 10^{-34}$ Js**



Max Planck
(1855-1947)

- **Linear momentum, $p = E/c = h\nu/c = h/\lambda$ (de Broglie)**

Louis de Broglie
(1892-1987)



- **(spin) Angular momentum** equivalent to a quantum number of 1:

$$j_{ph} = 1 \quad i.e., \quad |\underline{j}_{ph}| = \sqrt{2}\hbar$$

n.b., 1) photons are Bosons (*i.e.*, obey Bose-Einstein statistics)

2) photons have *helicity* (projection of angular momentum on the direction of travel) of ± 1 only (*i.e.*, not 0)

1.3 Quantities and Units

Wavelength, λ : SI unit = m [or μm , nm or Angström, $1 \text{ \AA} = 10^{-10} \text{ m}$]

λ is *dependent* on the (refractive index of the) medium in which the wave travels

Frequency, ν : SI unit = Hz (i.e., cycles s^{-1}) [or MHz = 10^6 Hz, GHz = 10^9 Hz]

frequency is *independent* of the medium

Energy, E: SI unit = J,

BUT : It is hard to measure energy directly. Spectra are recorded as line intensities as a function of **frequency** or **wavelength**.

The conversion to energy *appears* simple: **$E = h\nu = hc/\lambda$**

But h is only known to 8 significant figures. Hence, it is convenient to introduce

Wavenumber, a *property* defined as reciprocal of the vacuum wavelength:
and whose units are universally quoted as **cm^{-1}** (*n.b.* not m^{-1})

$$\bar{\nu} = \frac{1}{\lambda_{vac}}$$

Wavenumber is directly proportional to **energy**, **$E = hc\bar{\nu}$** and thus we commonly quote “energies” in units of cm^{-1} .

1.4 Energy levels: The Born Oppenheimer Approximation

The total energy of a molecular system comprises:

- The translation of the whole molecule, T_{trans} (*n.b. we'll neglect this as trivial*)
- Kinetic energy, T_e and T_n of electrons and nuclei, respectively
- Potential energy, V_{ee} and V_{nn} of electrons and nuclei, respectively
- Potential energy between nuclei and electrons, V_{ne}

$$\hat{H}_{tot} = \hat{H}_e + \hat{H}_n = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} + \hat{T}_n + \hat{V}_{nn}$$

The Born Oppenheimer Approximation (*Annal. Phys.*, **84**, 457 (1927))

Due to the difference in mass between the electron and nuclei, the motion of the two may be separated and the total molecular wavefunction, Ψ_{tot} , may, to a good approximation, be written

$$\Psi_{tot} = \Psi_{el}(q, Q) \Psi_n(Q)$$

electron coordinates *nuclear coordinates*

and the resulting total energy is a simple sum

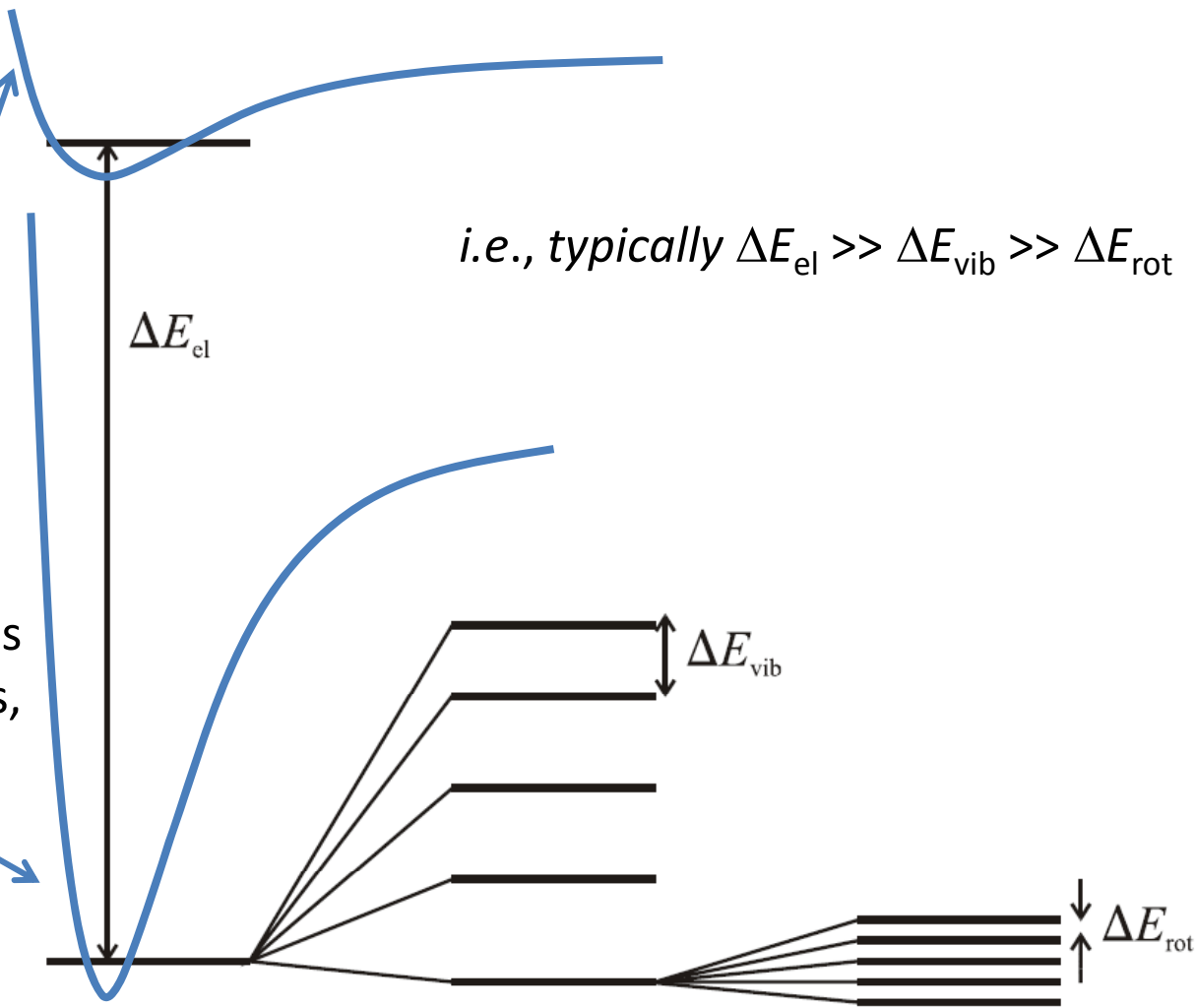
$$E_{tot} = E_{el} + E_{nuc}$$

It will be convenient, though less rigorous, to further factorise Ψ_n further into vibrational and rotational parts so $\Psi_{tot} = \Psi_{el} \Psi_{vib} \Psi_{rot}$ and $E_{tot} = E_{el} + E_{vib} + E_{rot}$

Molecular Energy Levels

Different electronic states (electronic arrangements, configurations or terms)

i.e., typically $\Delta E_{el} \gg \Delta E_{vib} \gg \Delta E_{rot}$



Electronic

Vibrational

Rotational

$\Delta E \approx 2 \times 10^4 - 10^5 \text{ cm}^{-1}$

$10^2 - 5 \times 10^3 \text{ cm}^{-1}$

3 – 300 GHz
(0.1 – 10 cm^{-1})

Transitions at $\lambda \approx$

500 – 100 nm

100 μm – 2 μm

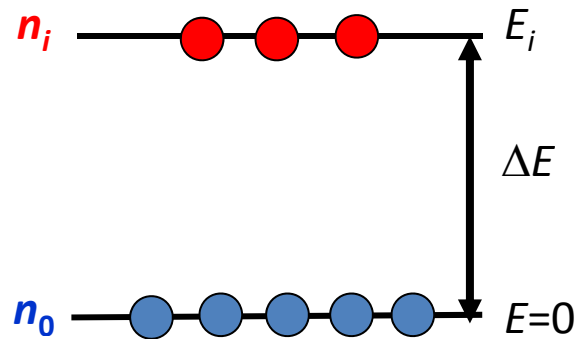
10 cm – 1 mm

Vis – UV

infrared

microwave

1.5 The Population of Energy levels



The Boltzmann Law

At thermal equilibrium, the population of the i th energy level is given by:

$$n_i = \frac{N}{q} g_i \exp\left(-\frac{E_i}{kT}\right)$$

$$q = \sum_{\text{levels } i} g_i \exp\left(-\frac{E_i}{kT}\right)$$

Where:

q is the **molecular partition function** (see HT Stat. Mech. notes)

g_i is the **degeneracy** of the i th level (the *no.* states with same energy)

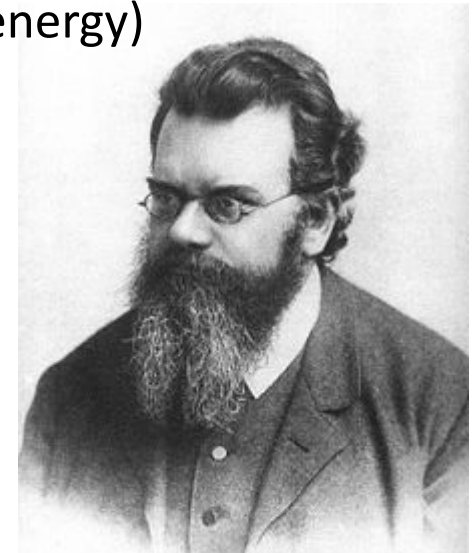
E_i is the **energy** of the i th level

k is the **Boltzmann constant** ($= R/N_A = 1.381 \times 10^{-23} \text{ J K}^{-1}$)

T is the **Kelvin temperature**

Hence, relative to n_0 :

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} \exp\left(\frac{-\Delta E}{kT}\right)$$

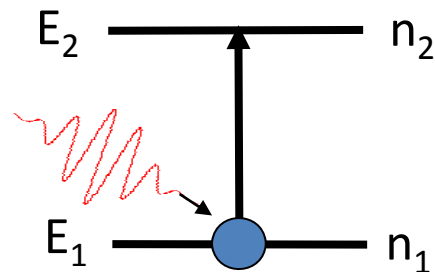


Ludwig Boltzmann 1844-1906

1.6 The Interaction of Light and Matter I: A simple classical picture

Consider the ways in which a single photon might interact with a system of two energy levels E_1 and E_2 , with populations n_1 and n_2 , respectively:

A. Stimulated absorption, $M + h\nu \rightarrow M^*$



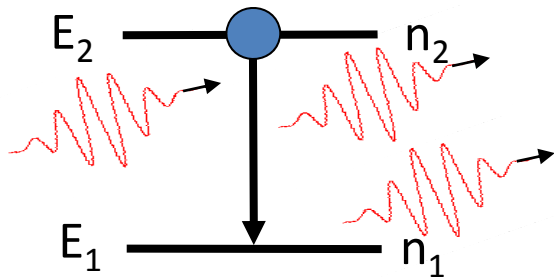
- The photon is lost
- The system absorbs energy $E = h\nu = E_2 - E_1$

$$\text{rate of absorption} = \frac{dn_1}{dt} \propto \rho(E_{21})n_1 \Rightarrow \frac{dn_1}{dt} = -B_{12}\rho(E_{21})n_1$$

In which B_{12} is the Einstein Coefficient of Absorption and $\rho(E_{21})$ is the radiation energy density (energy of radiation field m^{-3}) at energy E_{21} , which, for a black-body at temperature T , is given by **Planck's Law**

$$\text{radiation density, } \rho(E) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{E}{kT}\right) - 1}$$

B. Stimulated emission $M^* + h\nu \rightarrow M + 2h\nu$



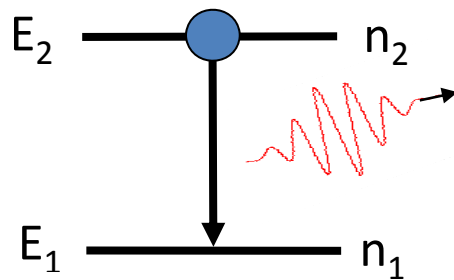
- Additional photon created with same frequency, polarization, direction and phase as the original
- The system relaxes, *i.e.*, emits energy

$$\text{rate of stimulated emission} = \frac{dn_2}{dt} \propto \rho(E_{21})n_2 \Rightarrow \frac{dn_2}{dt} = -B_{21}\rho(E_{21})n_2$$

in which B_{21} is the Einstein coefficient of stimulated emission.

Einstein showed that for a system to reach equilibrium a 3rd process must occur:

C. Spontaneous emission $M^* \rightarrow M + h\nu$



- A photon is created with $E = E_2 - E_1 = h\nu$
- The system relaxes, *i.e.*, emits energy

$$\text{rate of spontaneous emission} = \frac{dn_2}{dt} \propto n_2 \Rightarrow \frac{dn_2}{dt} = -An_2$$

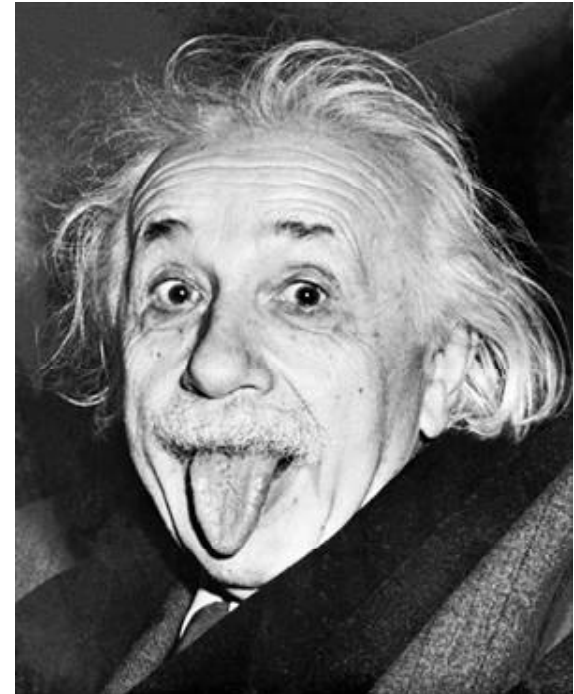
1.7 The Einstein Coefficients [A. Einstein, *Z. Phys.*, **18**, 121 (1917)]

At equilibrium: $\frac{dn_1}{dt} = 0$, *i.e.*, $B_{12} \overset{\text{abs}^n}{\rho(E_{21})} n_1 = A_{21} \overset{\text{spont. emission}}{n_2} + B_{21} \overset{\text{stim. emission}}{\rho(E_{21})} n_2$

Rearranging, $\rho(E_{21}) = \frac{A_{21} n_2}{B_{12} n_1 - B_{21} n_2} = \frac{A_{21}}{B_{12} \left\{ \frac{g_1}{g_2} \exp\left(\frac{E_{21}}{kT}\right) \right\} - B_{21}}$

c.f. Planck's Law $\rho(E_{21}) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{E_{21}}{kT}\right) - 1}$

Yielding: $g_1 B_{12} = g_2 B_{21}$ and $A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}$

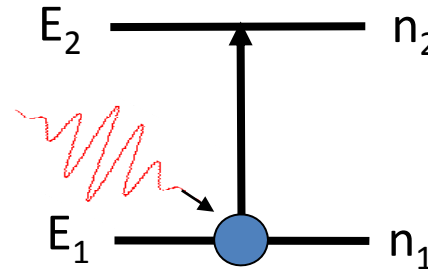


There is only one independent Einstein coefficient

What are the implications of the fact that the A-coefficient, $A \propto \nu^3$?

1.8 Interactions of Light and Matter II: A time-dependent treatment

We will often use pictures like



to consider transitions.

Indeed our approach will be

- i) to determine the eigenstates (*stationary states*) of a system
- and then ii) consider allowed transitions between these states

i.e., the photon doesn't explicitly figure

An aside

The total wavefunction, Ψ_{tot} , satisfies the *time-dependent* Schrödinger equation:

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{where} \quad \hat{H} = \hat{H}_0 + V(t) \quad \text{and} \quad V(t) = -\mu E_0 \cos \omega t$$

dipole interaction with oscillating \underline{E} field.

Eigenstates are the solutions of the t -independent Schrödinger eqⁿ: $\hat{H}_0 \phi_n = E_n^0 \phi_n$

stationary states

and the full (t -dep) wavefunction is $\phi_n \exp\{-iE_n^0 t / \hbar\}$

Ψ_{tot} is a linear combination of stationary states $\psi = \sum_n c_n(t) \phi_n \exp\{-iE_n^0 t / \hbar\}$

Time-dependent coefficients

end

After some manipulation (see MQM, Ch 6), we arrive at **the rate of transition to state m from a well-defined, *i.e.*, pure, initial state, j , to be:**

$$\frac{dc_m(t)}{dt} = \underbrace{\frac{E_0}{2i\hbar}}_1 \left\{ \underbrace{\exp\frac{i(E_m^0 - E_j^0 + \hbar\omega)t}{\hbar} + \exp\frac{i(E_m^0 - E_j^0 - \hbar\omega)t}{\hbar}}_2 \right\} \underbrace{\int \phi_m^* \hat{\mu} \phi_j d\tau}_3$$

Thus, for non-zero transition probability (*i.e.*, allowed transitions):

1. $E_0 \neq 0$ there must be non-zero radiation intensity, **and**
2. $E_m^0 - E_j^0 = \pm \hbar\omega$ *i.e.*, energy must be conserved, **and**
3. $\int \phi_m^* \hat{\mu} \phi_j d\tau \neq 0$ The "**transition dipole moment**" must be non-zero

1.9 The Transition Dipole Moment, R_{21}

The **transition dipole moment, TDM**, is defined as $R_{21} = \int \psi_2^* \hat{\mu} \psi_1 d\tau = \langle \psi_2 | \hat{\mu} | \psi_1 \rangle$

where the **dipole moment operator**, $\hat{\mu} = \sum_i q_i \hat{r}_i$ ← *Position vector of i th particle*
↑ *Charge on i th particle*

$\hat{\mu}$ operates upon our initial wavefunction ψ_1 producing a new state $\psi = \hat{\mu} | \psi_1 \rangle$

TDM, R_{21} , thus represents the transition *amplitude* of ending up in our particular state, ψ_2 , determined by the overlap integral of ψ_2 with ψ : $\langle \psi_2 | \psi \rangle = \langle \psi_2 | \hat{\mu} | \psi_1 \rangle$

The rate of transition (or intensity) is the square of this amplitude:

$$i.e., \text{ transition intensity } \propto R_{21}^2 = \left(\int \psi_2^* \hat{\mu} \psi_1 d\tau \right)^2 = \langle \psi_2 | \hat{\mu} | \psi_1 \rangle^2$$

The **TDM** is, unsurprisingly, closely related to the **Einstein B coefficient** (after all they both describe the same thing):

$$B_{21} = \frac{8\pi^3}{(4\pi\epsilon_0)3h^2} R_{21}^2 = \frac{1}{6\epsilon_0\hbar^2} R_{21}^2$$

1.10 The Transition Dipole Moment and spectroscopic selection rules

$$Int \propto R_{21}^2 = \left(\int \psi_2^* \hat{\mu} \psi_1 d\tau \right)^2 = \langle \psi_2 | \hat{\mu} | \psi_1 \rangle^2$$

The **TDM** is thus the ultimate source of *spectroscopic selection rules* for “dipole allowed transitions”.

i.e., of all the conceivable energetically allowed transitions it determines which actually occur and encompasses symmetry and angular momentum constraints.

Forbidden transitions have $R_{21} = 0$

Allowed transitions have $R_{21} \neq 0$