VII. Radiative Transitions

A. Einstein Coefficients

- Introduced by Einstein to derive Planck's Law for blackbody radiation
- Consider 2 energy levels $E_m > E_n$ in a system with many levels
  - ◇ In the transition $m \to n$ a photon is emitted with frequency

$$\omega = \frac{(\,E_m - E_n\,)}{\hbar}$$

  - ◇ This photon will have a polarization (usually circular) which we will label α
- Spontaneous emission
  - ◇ Probability per unit time of the $m \to n$ transition into solid angle $d\Omega$ with polarization α

$$dT_S = A_{mn\alpha} d\Omega \tag{1}$$

  - ◇ Occurs even in the absence of a radiation field
- Absorption
  - ◇ Probability per unit time of the $n \to m$ transition in the presence of a radiation field with energy density $u_\alpha(\omega, \theta)$

$$dT_a = B_{nm\alpha} u_\alpha(\omega, \theta) d\Omega \tag{2}$$

  - ◇ Because the energy spectrum is not infinitely sharp, one should consider a 'line profile' of frequencies $\phi(\nu)$
- Induced (stimulated) emission
  - ◇ Probability per unit time of the $m \to n$ transition in the presence of a radiation field

$$dT_i = B_{nm\alpha} u_\alpha(\omega, \theta) d\Omega \tag{3}$$

- Detailed balance
  - ◇ In equilibrium, the number of atoms in state m, n designated (N_m, N_n) must follow

$$N_m\,[\,A_{mn\alpha} + u_\alpha(\omega, \theta) B_{mn\alpha}\,] = N_n B_{nm\alpha} u_\alpha(\omega, \theta) \tag{4}$$

  - ◇ This relation applies for every pair m, n and all polarizations
- Thermal Equilibrium

- Occupation of each state is proportional to the degeneracy of the state g_n and Boltzman's factor

$$N_n \propto \; g_n \exp\left(-E_n/kT \right) \tag{5}$$

- Our detailed balance equation becomes

$$B_{nm\alpha} u_\alpha(\omega,\theta) = \frac{g_m}{g_n} \left[A_{mn\alpha} + u_\alpha(\omega,\theta) B_{mn\alpha} \right] \; e^{(E_m - E_n)/kT} \tag{6}$$

- Consider $T \to \infty \; \Rightarrow \; u_\alpha(\omega,\theta) \to \infty$

$$g_n B_{nm\alpha} = g_m B_{mn\alpha} \tag{7}$$

- Solving for u_α using the above relation

$$u_\alpha(\omega,\theta,T) = \frac{A_{mn\alpha}}{B_{mn\alpha}} \frac{1}{e^{\hbar\omega/kT} - 1}$$

- Matching Planck's Law (or even R-J spectra at low ω)

$$\frac{A_{mn\alpha}}{B_{mn\alpha}} = \frac{\hbar \omega^3}{8\pi^3 c^3} \tag{8}$$

- Substituting for all of the coefficients and integrating over $d\Omega$
  - We recover Planck's Law

$$u(\omega,T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \tag{9}$$

  - Photon density: Relating $u d\omega = \varepsilon d\varepsilon$

$$n(\varepsilon,T) = \frac{\varepsilon^2}{\pi^2 (\hbar c)^3} \left(e^{\varepsilon/kT} - 1 \right)^{-1} \tag{10}$$

B. Semi-Classical Theory

- Treat the atom with quantum mechanics
- <u>But</u>, radiation is treated classically
  - Will predict the correct induced radiation process
  - Fails for spontaneous emission!
  - So, we derive the spontaneous rate by using our relations for the Einstein coefficients
- Justification

- ◇ Classical limit → # photons per state is large

$$n_{ph} \gg 1/\lambda_c^3 \approx 1/(\alpha a_0)^3 \tag{11}$$

- ◇ In this case, induced emission dominates spontaneous emission
- ◇ QM → Extrapolate to low photon density because of the linearity of the process

- Hamiltonian

$$H = \frac{p^2}{2m} - \frac{e}{2mc}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) + \frac{e^2A^2}{2mc^2} + e\phi \tag{12}$$

- ◇ Coulomb gauge: $\vec{\nabla}\cdot\vec{A} = 0$

$$\begin{aligned}\vec{p}\cdot\vec{A}\chi = \vec{\nabla}\cdot(\vec{A}\chi) &= (\vec{\nabla}\cdot\vec{A})\chi + \vec{A}\cdot\nabla\chi \\ &= (\vec{A}\cdot\vec{p})\chi\end{aligned}$$

- ◇ Therefore

$$H = \frac{p^2}{2m} - \frac{e}{mc}\left(\vec{A}\cdot\vec{p}\right) + \frac{e^2A^2}{2mc^2} + e\phi \tag{13}$$

- First vs. second order perturbation theories
  - ◇ Note $\vec{A}\cdot\vec{p}$ corresponds to single photon processes
  - ◇ A^2 leads to two-photon processes
  - ◇ When can we ignore the A^2 term?

$$\eta \equiv \frac{epA/mc}{e^2A^2/2mc^2} = \frac{2ev/c}{\alpha^2 a_0 A} \gg 1 \tag{14}$$

  - ◇ Taking $v/c \sim \alpha$ and $A \sim \lambda E$

$$\eta^2 \sim \frac{4\hbar\omega}{2\pi\alpha a_0^2 \lambda E^2}$$

  - ◇ Finally, $\lambda \sim a_0/\alpha$ and $n_{ph} \sim E^2/\hbar\omega$

$$\eta^2 \sim \left(n_{ph}a_0^3\right)^{-1}$$

  - ◇ Demanding first order

$$n_{ph}a_0^3 \ll 1 \tag{15}$$

    - ▲ i.e. # photons in the Bohr radius is small
    - ▲ Ignore A^2 term ⇒ single photon emission
  - ◇ Constraint on photon flux

$$\begin{array}{lll} F \ll 10^{21} & \mathrm{erg/cm^2 \cdot s} & \text{optical} \\ F \ll 10^{24} & \mathrm{erg/cm^2 \cdot s} & \mathrm{x-ray} \end{array}$$

▲ Astrophysical systems

$$\begin{array}{lll} F \approx 10^{11} & \mathrm{erg/cm^2 \cdot s} & \text{Sun} \\ F \approx 10^{16} & \mathrm{erg/cm^2 \cdot s} & \text{one lt-day from a QSO} \end{array}$$

C. Absorption and Induced Emission

- Assume there is an external radiation field with sufficient photon density to ignore A^2 terms
  - ◇ First order

$$V^{(1)} = -\frac{e}{mc}\vec{p} \cdot \vec{A} = \frac{ie\hbar}{mc}\vec{A} \cdot \vec{\nabla} \tag{16}$$

  - ◇ Assume $\vec{A} = 0$ for $t < 0$ and $t > \mathcal{T} \gg$ oscillation (period of the wave)
  - ◇ Express the wave vector as

$$\vec{A} = \vec{A}(t)\mathrm{e}^{i\vec{k}\cdot\vec{r}} \tag{17}$$

- Apply Fermi's Golden Rule
  - ◇ Calculate the Fourier transform of $V^{(1)}$

$$V_{fi}(\omega_{fi}) = \frac{ie\hbar}{2mc}\int_{-\infty}^{\infty} dt\ \mathrm{e}^{i\omega_{fi}t}\ \vec{A}(t) \cdot <\phi_f|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\vec{\nabla}|\phi_i>$$

  - ◇ Transition probability

$$P_{fi} = \frac{4\pi^2 e^2}{m^2c^2}\left|\vec{A}(\omega_{fi})\right|^2\left|<\phi_f|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\,\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i>\right|^2$$

    - ▲ $\hat{\varepsilon}$ = unit vector parallel to $\vec{A}$
    - ▲ Specifies the polarization
- Consider a plane-wave solution for $\vec{A}$

$$\vec{A} = \frac{1}{2}\int d\omega\left[\vec{A}_0(\omega)\mathrm{e}^{i(\vec{k}\cdot\vec{r}-\omega t)} + \vec{A}_0^*(\omega)\mathrm{e}^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] \tag{18}$$

  - ◇ With this definition, $\vec{A}$ is real
  - ◇ For $|\omega_{fi}| \gg \mathcal{T}^{-1}$ and $\omega_{fi} > 0$

$$\vec{A}(\omega_{fi}) = \frac{1}{2}A_0(\omega_{fi})\mathrm{e}^{i\vec{k}_{fi}\cdot\vec{r}}$$

  - ◇ Altogether

$$P_{fi} = \frac{\pi^2 e^2}{m^2c^2}|A_0(\omega_{fi})|^2|<\phi_f|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i>|^2$$

- Relating $A_0(\omega_{fi})$ to the intensity of the incoming wave
  - ◇ E+M Review
  - ◇ Intensity

$$I = < \vec{S}\cdot\hat{n} > = \frac{e}{4\pi\mathcal{T}}\int dt|\vec{E}|^2 = \frac{c}{\mathcal{T}}\int d\omega|\vec{E}(\omega)|^2$$

    - ▲ $\vec{S}$ is the Poynting vector
    - ▲ $\hat{n}$ is the propagation direction of the radiation
  - ◇ Intensity per unit frequency

$$I(\omega) \equiv \frac{dI}{d\omega} = \frac{c|\vec{E}(\omega)|^2}{\mathcal{T}}$$

  - ◇ Electric field

$$\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} \Rightarrow \vec{E}(\omega) = -\frac{i}{2c}\omega\vec{A}_0(\omega)\ \mathrm{e}^{i\vec{k}\cdot\vec{r}}$$

  - ◇ Finally

$$|\vec{A}_0(\omega)|^2 = \frac{4c^2}{\omega^2}|\vec{E}(\omega)|^2 = \frac{c\mathcal{T}}{\omega^2}I(\omega)$$

  - ◇ Substituting

$$P_{fi} = \frac{4\pi^2e^2}{m^2c}\mathcal{T}\frac{I(\omega_{fi})}{\omega_{fi}^2}\Big|<\phi_f|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i>\Big|^2$$

  - ◇ Transition probability per unit time

$$\mathrm{w}_{fi} = \frac{P_{fi}}{\mathcal{T}} = \frac{4\pi^2e^2}{m^2c}\frac{I(\omega_{fi})}{\omega_{fi}^2}\Big|<\phi_f|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i>\Big|^2 \tag{19}$$

  - ◇ Stimulated emission

$$\begin{aligned}
\mathrm{w}_{if} &= \frac{4\pi^2e^2}{m^2c}\frac{I(\omega_{fi})}{\omega_{fi}^2}\Big|<\phi_i|\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_f>\Big|^2 \\
&= \int d^3\vec{r}\ \phi_i^*\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}\phi_f \\
&= \int d^3\vec{r}\ \phi_f\mathrm{e}^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}\phi_i \\
&= <\phi_f|\mathrm{e}^{-i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i>^* \\
&= \mathrm{w}_{fi}
\end{aligned}$$

    - ▲ Last expression was achieved by integrating by parts
    - ▲ Noting $\nabla\mathrm{e}^{i\vec{k}\cdot\vec{r}} = i\mathrm{e}^{i\vec{k}\cdot\vec{r}}\vec{k}$

▲ and $\vec{k} \cdot \hat{\varepsilon} = 0$

◇ Restatement of detailed balance

D. Spontaneous Emission

- Absorption: We defined the prob/sec of absorbing a photon with energy $\hbar\omega_{fi} = E_f - E_i$ with polarization α propagating in $d\Omega$:

$$dT_a = B_{if\alpha} I_\alpha(\omega, \Omega) d\Omega / c$$

- For a plane-wave propagating in a specific direction, express

$$I_\alpha(\omega, \Omega) = I_\alpha(\omega)\delta(\Omega)$$

- Transition probability per unit time (integrating over $d\Omega$)

$$\mathrm{w}_a = \int dT_a = \frac{1}{c} B_{if\alpha} I_\alpha(\omega_{if}) \tag{20}$$

- Solving for Einstein's coefficient, taking $\mathrm{w}_a = \mathrm{w}_{fi}$

$$B_{if\alpha} = \frac{4\pi^2 e^2}{m^2} \frac{1}{\omega_{if}^2} \left| <\phi_f| \mathrm{e}^{i\vec{k}\cdot\vec{r}} \hat{\varepsilon} \cdot \vec{\nabla} |\phi_i> \right|^2 \tag{21}$$

- For non-degenerate states, relate A_{fi} to B_{if}

$$A_{fi\alpha} = \frac{\hbar\omega_{fi}^3}{8\pi^3 c^3} B_{if\alpha} \tag{22}$$

$$= \frac{e^2 \hbar\omega_{fi}}{2\pi m^2 c^3} \left| <\phi_f| \mathrm{e}^{i\vec{k}\cdot\vec{r}} \hat{\varepsilon} \cdot \vec{\nabla} |\phi_i> \right|^2 \tag{23}$$

- Probability/sec of spontaneously emitting a photon with $\hbar\omega_{if} = E_f - E_i$ into solid angle $d\Omega$ with polarization α is

$$dT_S = A_{fi\alpha} d\Omega$$

E. Dipole Approximation

- Transition rates require the evaluation of terms of the form

$$<\phi_f| \mathrm{e}^{i\vec{k}\cdot\vec{r}} \hat{\varepsilon} \cdot \vec{\nabla} |\phi_i>$$

- Dipole approximation

$$\mathrm{e}^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} + \cdots \approx 1 \tag{24}$$

◇ Require $\vec{k} \cdot \vec{r} \ll 1$

◇ This condition implies

$$\vec{k}\cdot\vec{r} \sim ka \sim \frac{\omega}{c}a \sim a\frac{\Delta E}{\hbar c} \sim \frac{a}{\hbar c}Z^2\alpha^2 mc^2$$
$$\sim Z^2\alpha \ll 1$$

- Result

$$<\phi_f|e^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\phi_i> \approx \frac{i}{\hbar}\left(\hat{\varepsilon}\cdot\vec{P}\right)_{fi} = \frac{i}{\hbar}\left(\hat{\varepsilon}\cdot\vec{p}\right)_{fi} \tag{25}$$

- Recall, the time evolution of an operator is given by

$$\frac{dX}{dt} = \frac{\partial X}{\partial t} + \frac{i}{\hbar}[H, X]$$

◇ Here, we consider $\vec{p} = m\dot{\vec{r}}$

$$\dot{\vec{r}} = \frac{d}{dt}\vec{r} = \frac{\partial\vec{r}}{\partial t} + \frac{i}{\hbar}[H, \vec{r}] \tag{26}$$

◇ Because our matrix element only includes $\vec{\nabla}|\phi_i>$, we can discard $\vec{A}$ altogether: ($H \to H_0$ in the evolution of $\vec{r}$)

$$\vec{p} = \frac{im}{\hbar}[H_0, \vec{r}] \tag{27}$$

- Rewriting the matrix element

$$\begin{aligned}\frac{i}{\hbar}\left(\hat{\varepsilon}\cdot\vec{p}\right)_{fi} &= -\frac{m}{\hbar^2}\left([H_0, \hat{\varepsilon}\cdot\vec{r}]\right)_{fi}\\ &= \frac{m}{\hbar^2}\left[<\phi_f|\hat{\varepsilon}\cdot\vec{r}\,H_0|\phi_i> - <\phi_f|H_0\,\hat{\varepsilon}\cdot\vec{r}|\phi_i>\right]\\ &= \frac{m}{\hbar^2}(E_i - E_f)\left(\hat{\varepsilon}\cdot\vec{r}\right)_{fi}\\ &= \frac{m}{\hbar}\omega_{fi}\left(\hat{\varepsilon}\cdot\vec{r}\right)_{fi}\end{aligned}$$

- Finally, the transition probability/time is

$$d\mathrm{w_{fi}} = \frac{d\Omega}{2\pi}\frac{e^2}{\hbar c}\frac{\omega_{fi}^3}{c^2}\left|\left(\hat{\varepsilon}\cdot\vec{r}\right)_{fi}\right|^2 \tag{28}$$

- Radiated power per unit solid angle is

$$\frac{dP}{d\Omega} = \hbar\omega_{if}\frac{d\mathrm{w}}{d\Omega} = \frac{e^2}{2\pi c^3}\omega_{fi}^4\left|\left(\hat{\varepsilon}\cdot\vec{r}\right)_{fi}\right|^2 \tag{29}$$

◇ Consider the polarization $\hat{\varepsilon}$ which must be perpendicular to the propagation direction $\hat{n}$

- ◇ Consider two linear polarizations

$$\hat{\varepsilon}_1 \perp \hat{n}\ ,\ \hat{\varepsilon}_1 \perp \vec{r} \ \rightarrow\ \text{no emission}\,(\,\hat{\varepsilon}\cdot\vec{r}\,)_{fi} = 0$$
$$\hat{\varepsilon}_2 \perp \hat{n}\ ,\ \hat{\varepsilon}_2 \perp \hat{\varepsilon}_1 \ \rightarrow\ \text{All of the emission!}$$

- ◇ Let β be the angle between $\vec{r}$ and $\hat{n}$
- ◇ Fig

- Total power per unit solid angle (summed over polarization)

$$\frac{dP}{d\Omega} = \frac{e^2}{2\pi c^3}\omega_{fi}^4 \sin^2\beta \left|<\phi_f|\vec{r}|\phi_i>\right|^2 \tag{30}$$

- Total power (integrating over $d\Omega = 2\pi\ d\cos\beta$)

$$P_{fi} = \frac{4}{3}\frac{e^2\omega_{fi}^4}{c^3}\left|<\phi_f|\vec{r}|\phi_i>\right|^2 \tag{31}$$

  - ◇ This power looks a lot like the classical Larmar radiation formula (corresponding to dipole radiation) of E+M
  - ◇ For an oscillating dipole (recall the SHO), we simply replace the time average of the moment by the matrix element of the same quantity

$$|\vec{r}|^2 = 2 < |\vec{r}|^2 > \rightarrow 2|(\vec{r})_{fi}|^2$$

  - ◇ This is an example of the correspondence principle between classical and quantum properties

- Transition probability/time (divide power by $\hbar\omega_{fi}$)

$$A_{fi} = \frac{4}{3}\alpha c\left(\frac{\omega_{fi}}{c}\right)^3 |r_{fi}|^2 \tag{32}$$

  - ◇ Recall

$$E = \frac{1}{2}\frac{e^2}{a_0} = \frac{hc}{\lambda}\ \Rightarrow\ |r_{fi}|^2 \sim a_0^2 \sim (\alpha\lambda)^2$$

  - ◇ Expect

$$A_{fi} \sim \alpha^3\omega_{fi} \tag{33}$$

- ◇ Total probability/time A_i of an electron in state i radiating a photon (via dipole radiation) is obtained by summing over all states f with $E_f < E_i$

$$A_i \equiv \sum_{E_f<E_i} A_{fi} \tag{34}$$

- ◇ Radiation lifetime

$$\mathcal{T}_i \equiv \frac{1}{A_i} \sim \frac{1}{\alpha^3 \omega_{max}} \tag{35}$$

- Oscillator strength

$$f_{fi} \equiv f(i \to f) \equiv \frac{2m}{\hbar}\omega_{fi}\left|<\phi_f|\vec{r}|\phi_i>\right|^2 \tag{36}$$

- ◇ Typically, we expect (for allowed dipole transitions)

$$f_{fi} \approx \frac{2m}{\hbar}\omega\alpha^2\lambda^2 \sim \frac{2mc\lambda_c}{\hbar} \sim 1$$

- ◇ Therefore

$$A_{fi} = \frac{2}{3}\alpha\frac{\hbar\omega_{fi}}{mc^2}\omega_{fi}f_{fi} = 2.9 \times 10^9 \left(\frac{\nu}{\nu_{Lyc}}\right)^2 f_{fi}\ \mathrm{s}^{-1} \tag{37}$$

- ◇ And

$$P_{fi} = \frac{2}{3}\alpha\frac{(\hbar\omega_{fi})^2}{mc^2}\omega_{fi}f_{fi} = 0.058 \left(\frac{\nu}{\nu_{Lyc}}\right)^2 f_{fi}\ \mathrm{erg/s} \tag{38}$$

F. Selection Rules for One Electron Spectra

- (Aside on Parity)
  - ◇ Parity operator $\mathcal{P}$

$$\mathcal{P}\Psi(\vec{r},t) = \Psi(-\vec{r},t) \tag{39}$$

  - ◇ Eigenstates of $\mathcal{P}$
    - ▲ Even functions → eigenvalue = +1
    - ▲ Odd functions → eigenvalue = −1
  - ◇ Expand any Ψ

$$\Psi = \Psi_{even} + \Psi_{odd}$$

  - ◇ Commutation relations

▲ Consider

$$\begin{aligned}\mathcal{P}\vec{r}\,\Psi &= \mathcal{P}\vec{r}\,\Psi_{even} + \mathcal{P}\vec{r}\,\Psi_{odd}\\ &= -\vec{r}\,\Psi_{even} + \vec{r}\,\Psi_{odd}\\ &= -\vec{r}\mathcal{P}\Psi_{even} - \vec{r}\mathcal{P}\Psi_{odd}\\ &= -\vec{r}\mathcal{P}\,\Psi\end{aligned}$$

▲ Therefore

$$\{\mathcal{P}, \vec{r}\} = 0 \tag{40}$$

$$[\mathcal{P}, \vec{r}] = -\vec{r}\mathcal{P} \tag{41}$$

- Laporte's Rule: Transitions between states of the same parity are forbidden
  - ◇ For an H-like ion (or any particle in a central potential with orbital and magnetic quantum numbers m, ℓ)

    $$\text{Parity eigenvalue} = (-1)^{\ell}$$

  - ◇ Only transitions between even and odd values of ℓ are permitted

    $$<f|\vec{r}|i> = 0 \text{ if } |i> \text{ and } |f> \text{ have the same parity}$$

- Light polarized $||\ \hat{z}$ (one electron)
  - ◇ $\vec{r} \rightarrow z \ \ \Rightarrow \ \ T_0^{(1)}\sqrt{\frac{4\pi}{3}}$
  - ◇ m-values: $\Delta m = 0$
  - ◇ ℓ-values: $\Delta\ell = \pm 1$
    - ▲ Wigner says $\Delta\ell = \pm 1, 0$
    - ▲ Parity says $\Delta\ell \neq 0$
- Circular polarization
  - ◇ $\vec{r} \rightarrow x + iy \ \ \Rightarrow \ \ T_{\pm 1}^{(1)}$
  - ◇ m-values: $\Delta m = \pm 1$
  - ◇ ℓ-values
    - ▲ Wigner $\rightarrow \Delta\ell = \pm 1, 0$
    - ▲ Parity $\rightarrow \Delta\ell \neq 0$
- Summary (dipole approximation)
  - (a) Parity eigenvalue $\mathcal{P}$ must change in the transition
  - (b) The total orbital angular momentum changes at most by unit: $\Delta\ell = 0, \pm 1$
    - i. For one electron atoms, $\Delta\ell \neq 0$
    - ii. Transitions between two states with $\ell = 0$ are forbidden
  - (c) The magnetic quantum number m changes according to
    - ◇ $\Delta m = 0 \rightarrow$ polarization parallel to $\hat{z}$

- $\diamond$ $\Delta m = \pm 1 \rightarrow$ polarization $\perp \hat{z}$

(d) The total spin S remains unchanged $\Delta S = 0$. This is because $[\vec{r}, \vec{S}] = 0$. For helium, this means transitions between an ortho and para state are forbidden.

G. Summary of Sum Rules

- Key: Useful for checking consistency of calculations, understanding constraints and estimating f values
- Thomas-Reiche-Kuhn Sum Rule
  - $\diamond$ For <u>any atom</u>, with or without external fields, for any polarization, and any coupling (LS,JJ,RS) and for Z electrons

$$\sum_f f_{fi} = Z \tag{42}$$

    - ▲ Where i is any initial state (e.g. $|n\ell m m_s\rangle$)
    - ▲ Sum is over all final states such that $|f\rangle$ is a complete set of eigenvalues
  - $\diamond$ Proof:
    - ▲ First note that for any two operators A, B

$$\begin{aligned}(AB)_{fi} &= \langle f|AB|i\rangle \\ &= \langle f|A\sum_k |k\rangle\langle k|B|i\rangle \\ &= \sum_k \langle f|A|k\rangle\langle k|B|i\rangle \\ &= \sum_k A_{fk}B_{ki}\end{aligned}$$

    - ▲ Recall

$$\begin{aligned}i(\vec{p})_{fi} &= m\omega_{fi}(\vec{r})_{fi} \\ f_{fi} &= \frac{2m}{\hbar}\omega_{fi}|(\vec{r})_{fi}|^2\end{aligned}$$

    - ▲ For polarization in the $\hat{x}$ direction, we have

$$\begin{aligned}f_{fi} &= \frac{2i}{\hbar}(x)_{fi}(p_x)_{fi} \\ &= -\frac{2i}{\hbar}(x)_{if}(p_x)_{fi}\end{aligned}$$

    - ▲ Taking half the sum of both expressions along with the AB relation

$$\begin{aligned}\sum_f f_{fi} &= \frac{i}{\hbar}\sum_f [\,(x)_{fi}(p_x)_{if} - (p_x)_{fi}(x)_{if}\,] \\ &= \frac{i}{\hbar}[p_x, x]_{ii}\end{aligned}$$

- ▲ Treat p_x and x as the sum of the operators for each electron

$$\sum_f f_{fi} = \sum_{n=1}^{Z} = Z \tag{43}$$

- Wigner-Kirkwood Sum Rule
  - ◇ Consider the 'average' oscillator strength
  - ◇ Averaged over initial state + summed over final state

$$\begin{aligned}\bar{f}_{n'\ell',n\ell} &\equiv \frac{1}{2\ell+1}\sum_{m'=-\ell}^{\ell}\sum_{m=-\ell}^{\ell} f_{n'\ell'm',n\ell m} \\ &= \frac{2m}{3\hbar e^2}\frac{\omega_{nn'}}{2\ell+1}\sum_{m'}\sum_{m} |<f|er|i>|^2\end{aligned}$$

  - ◇ Implies

$$\bar{f}_{n\ell,n'\ell'} = -\frac{g_{n\ell}}{g_{n'\ell'}}\bar{f}_{n'\ell',n\ell} \tag{44}$$

  - ◇ Without derivation

$$\sum_{m'} \bar{f}_{n'\ell\pm1,n\ell} = \pm\frac{1}{3}\frac{(\ell+\frac{1}{2}\pm\frac{1}{2})(2\ell+1\pm2)}{(2\ell+1)} \tag{45}$$

  - ◇ Implications → Change of n and ℓ in the same sense is more probable than the opposite sense
    - ▲ e.g. $2p \to 3s$ is more probable than $2p \leftarrow 3s$
    - ▲ Tables of A values let you calculate branching ratios
    - ▲ Lyman series in Hydrogen

$$A_{10,n1} = \frac{8\times10^9\ 2^8\ n(n-1)^{2n-2}}{9(n+1)^{2n+2}}\ \mathrm{s}^{-1} \tag{46}$$

H. Line Broadening

- Atomic levels are <u>not</u> infinitely sharp
  - ◇ Number of physical mechanisms determine the line shape $\phi(\nu)$
  - ◇ Should be included in our discussion of the Einstein coefficients, etc.
- Doppler Broadening
  - ◇ Each atom in a gas has its own motion ⇒ different frequency of emission and absorption
  - ◇ Spreads the line out without changing the total strength

- ◇ To lowest order in v/c

$$\nu - \nu_0 = \nu_0 \frac{v}{c} \tag{47}$$

- ◇ Adopting a Maxwellian distribution

$$f(v)dv \propto \exp\left(-\frac{m_A v^2}{2kT}\right) dv$$

- ◇ Profile function

$$\phi_D(\nu) = \frac{1}{\Delta\nu_D\sqrt{\pi}} \exp\left[-\frac{(\nu-\nu_0)^2}{\Delta\nu_D^2}\right] \quad \text{with } \Delta\nu_D \equiv \frac{\nu_0}{c}\sqrt{\frac{2kT}{m_A}} \tag{48}$$

- ◇ Line-center ($\nu = \nu_0$ cross-section for each atom (neglecting stimulated emission)

$$\begin{aligned} \sigma_{\nu_0} &= B_{12}\frac{h\nu_0}{4\pi}\phi(\nu_0) \\ &= \frac{\pi e^2}{mc} f_{12} \frac{1}{\Delta\nu_D\sqrt{\pi}} \end{aligned}$$

- ◇ Turbulent velocities (macroscopic velocity fields)

$$\Delta\nu_D = \frac{\nu_0}{c}\left(\frac{2kT}{m_A} + \xi^2\right)^{1/2} \tag{49}$$

- ◇ Velocity expressions (taking $\xi = 0$)

$$\begin{aligned} &\Delta\nu_D \to b \equiv \sqrt{\frac{2kT}{m_A}} \\ &\text{Doppler parameter: } b = \sigma\sqrt{2} \\ &\text{Velocity dispersion: } \sigma \\ &\phi_D(v) = \frac{1}{b\sqrt{\pi}} \exp\left[-\frac{v^2}{b^2}\right] \end{aligned}$$

- Natural Broadening
  - ◇ Uncertainty principle: Product of the lifetime of a state and its spread in energy $\sim \hbar$
  - ◇ Spontaneous decay: Rate

$$\gamma \equiv \frac{1}{\mathcal{T}} = \sum_m A_{nm} \tag{50}$$

  - ▲ Sum over all states $E_m < E_n$
  - ▲ Perturbation theory (without deviation)

$$|c_n(t)|^2 = \exp(-\gamma_n t) \tag{51}$$

◇ Lorentzian profile

$$\phi_{NB}(\nu) = \frac{\gamma/4\pi^2}{(\nu-\nu_0)^2 + (\gamma/4\pi)^2} \tag{52}$$

◇ Voigt profile

- ▲ Generally have Natural and Doppler broadening
  - ○ Doppler broadening dominates the inner profile of the line
  - ○ Lorentzian dominates the wings

$$\phi(\nu) \propto \frac{1}{(\nu-\nu_0)^2 + \gamma^2} \text{ vs. } \exp(-\nu^2/\nu_D^2)$$

- ▲ Profile is an average of the velocity states of the atom

$$\phi_V(\nu) = \frac{\gamma}{4\pi} \int\limits_{-\infty}^{\infty} \frac{\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{mv^2}{2kT}\right)}{(\nu-\nu_0-\nu_0 v/c)^2 + (\gamma/4\pi)^2} dv \tag{53}$$

- ▲ Introduce the Voigt function

$$H(a,u) = \frac{a}{\pi} \int\limits_{-\infty}^{\infty} \frac{\mathrm{e}^{-y^2} dy}{a^2 + (u-y)^2} \tag{54}$$

- ▲ Identify

$$a \equiv \frac{\gamma}{4\pi\Delta\nu_D} \tag{55}$$

$$u \equiv \frac{\nu-\nu_0}{\Delta\nu_D} \tag{56}$$

- ▲ Voigt profile

$$\phi_V(\nu) = (\Delta\nu_D)^{-1}\pi^{-\frac{1}{2}} H(a,u) \tag{57}$$