

Astrophysics

Lecture 12

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[Faraday Rotation - Propagation along a Magnetic Field]

- Now we extend the discussion of plasma propagation effects by considering the effect of an external, fixed magnetic field \mathbf{B}_0 .

The properties of the waves will then depend on the direction of propagation relative to the magnetic field direction. For this reason the plasma is called ***anisotropic***.

Because of the magnetic field, a new frequency enters the problem, namely, the cyclotron frequency.

$$\text{cyclotron frequency} \quad \omega_B = \frac{eB_0}{m_e c} = 1.67 \times 10^7 \ (B_0/\text{G}) \ \text{s}^{-1}$$

$$\hbar\omega_B = 1.16 \times 10^{-8} \ (B_0/\text{G}) \ \text{eV}$$

If the fixed magnetic field \mathbf{B}_0 is much stronger than the field strengths of the propagating wave, then the equation of motion of an electron is approximately

$$m_e \frac{d\mathbf{v}}{dt} = -e\mathbf{E} - \frac{e}{c}\mathbf{v} \times \mathbf{B}_0$$

For simplicity, assume that **the wave propagates along the fixed field** $\mathbf{B}_0 = B_0\hat{\mathbf{z}}$, and assume that **the wave is circularly polarized and sinusoidal**.

$$\mathbf{E}_{\pm}(t) = E e^{-i\omega t} (\hat{\mathbf{x}} \pm i\hat{\mathbf{y}})$$

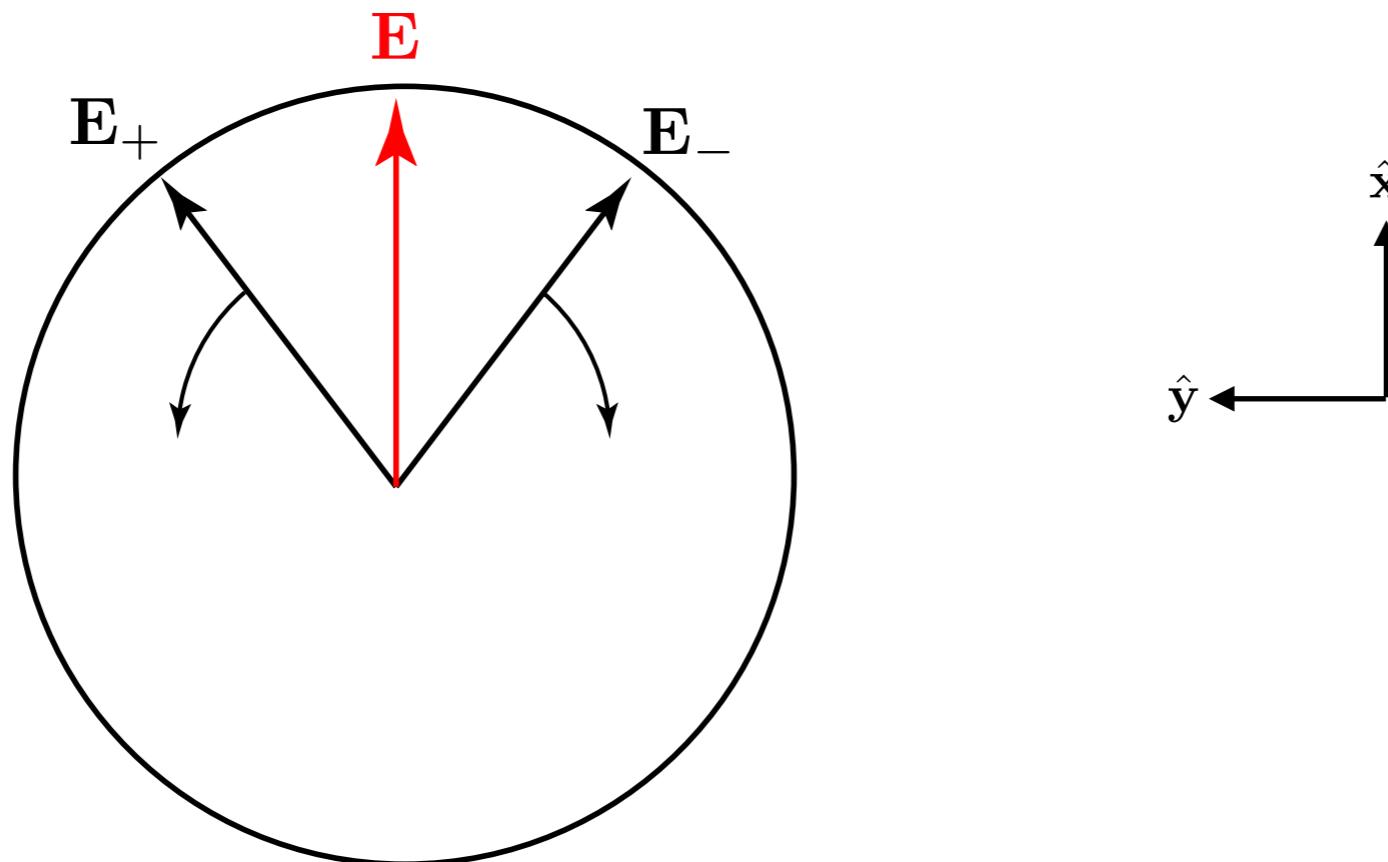
Here, \pm denotes right and left circular polarization.

Note that Rybiki & Lightman define oppositely the RCP and LCP.

Bases vectors for circularly rotating electric field

The bases vectors \mathbf{E}_\pm rotates counterclockwise (+) or clockwise (-) when viewed from the tip of the wave vector.

$$\begin{aligned}
 \text{Re}(\mathbf{E}_\pm) &= \text{Re}((\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) E e^{-i\omega t}) \\
 &= \text{Re}((\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) E (\cos \omega t - i \sin \omega t)) \\
 &\propto (\cos \omega t) \hat{\mathbf{x}} \pm (\sin \omega t) \hat{\mathbf{y}} \\
 &\propto \cos(\pm \omega t) \hat{\mathbf{x}} + \sin(\pm \omega t) \hat{\mathbf{y}}
 \end{aligned}$$



Now, we solve the equation of motion for an electron and obtain the dielectric constant.

$$m_e \frac{d\mathbf{v}}{dt} = -e\mathbf{E} - \frac{e}{c}\mathbf{v} \times \mathbf{B}_0$$

$\mathbf{E} \perp \mathbf{B}_0 \rightarrow \frac{d\mathbf{v}_{\parallel}}{dt} = 0 \quad \mathbf{v}_{\parallel} = \text{constant}$
 $\mathbf{v}_{\perp} = v_x \hat{\mathbf{x}} + v_y \hat{\mathbf{y}}$

$$(-i\omega)e^{-i\omega t}(v_x \hat{\mathbf{x}} + v_y \hat{\mathbf{y}}) = -\frac{e}{m_e} E e^{-i\omega t}(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) - \frac{e}{m_e c} e^{-i\omega t}(v_y B_0 \hat{\mathbf{x}} - v_x B_0 \hat{\mathbf{y}})$$

$$\rightarrow v_x = -\frac{ie}{m_e \omega} E - \frac{ieB_0}{m_e c \omega} v_y, \quad v_y = \pm \frac{e}{m_e \omega} E + \frac{ieB_0}{m_e c \omega} v_x$$

$$(1) \quad v_x = -\frac{ie}{m_e \omega} E - \frac{ieB_0}{m_e c \omega} \left(\pm \frac{e}{m_e \omega} E + \frac{ieB_0}{m_e c \omega} v_x \right)$$

$$\rightarrow \left(1 - \frac{e^2 B_0^2}{m_e^2 c^2 \omega^2} \right) v_x = -\frac{ie}{m_e \omega} E \left(1 \pm \frac{eB_0}{m_e c \omega} \right)$$

$$\rightarrow (\omega^2 - \omega_B^2) v_x = -\frac{ie}{m_e} E (\omega \pm \omega_B)$$

$$\rightarrow v_x = -\frac{ie}{m_e} E \frac{1}{\omega \mp \omega_B}$$

$$(2) \quad v_y = \pm \frac{e}{m_e \omega} E + \frac{ieB_0}{m_e c \omega} \left(-\frac{ie}{m_e \omega} E - \frac{ieB_0}{m_e c \omega} v_y \right)$$

$$\rightarrow \left(1 - \frac{e^2 B_0^2}{m_e^2 c^2 \omega^2} \right) v_y = \pm \frac{e}{m_e \omega} E \left(1 \pm \frac{eB_0}{m_e c \omega} \right)$$

$$\rightarrow (\omega^2 - \omega_B^2) v_y = \pm \frac{e}{m_e} E (\omega \pm \omega_B)$$

$$\rightarrow v_y = \pm \frac{e}{m_e} E \frac{1}{\omega \mp \omega_B}$$

Finally, the current density and conductivity are obtained to be

$\therefore \mathbf{v} = \frac{-ie}{m_e (\omega \mp \omega_B)} \mathbf{E}(t)$

$\mathbf{j} \equiv -nev = \sigma \mathbf{E}$

$\text{where } \sigma_{R,L} \equiv \frac{ine^2}{m_e (\omega \mp \omega_B)}$

Dielectric constant

$$\epsilon \equiv 1 - \frac{4\pi\sigma}{i\omega} = 1 - \frac{4\pi n e^2}{m_e \omega (\omega \mp \omega_B)}$$

$$\epsilon_{R,L} = 1 - \frac{\omega_p^2}{\omega (\omega \mp \omega_B)}$$

Dispersion relation

$$\omega^2 = k^2 c^2 + \frac{\omega_p^2 \omega}{\omega \mp \omega_B}$$

Phase velocity

$$v_p \equiv \frac{\omega}{k} = \frac{c}{n_r}$$

$$n_r = \sqrt{1 - \frac{\omega_p^2}{\omega (\omega \mp \omega_B)}}$$

Right (+) and left (-) circularly polarized waves travel with different speeds.

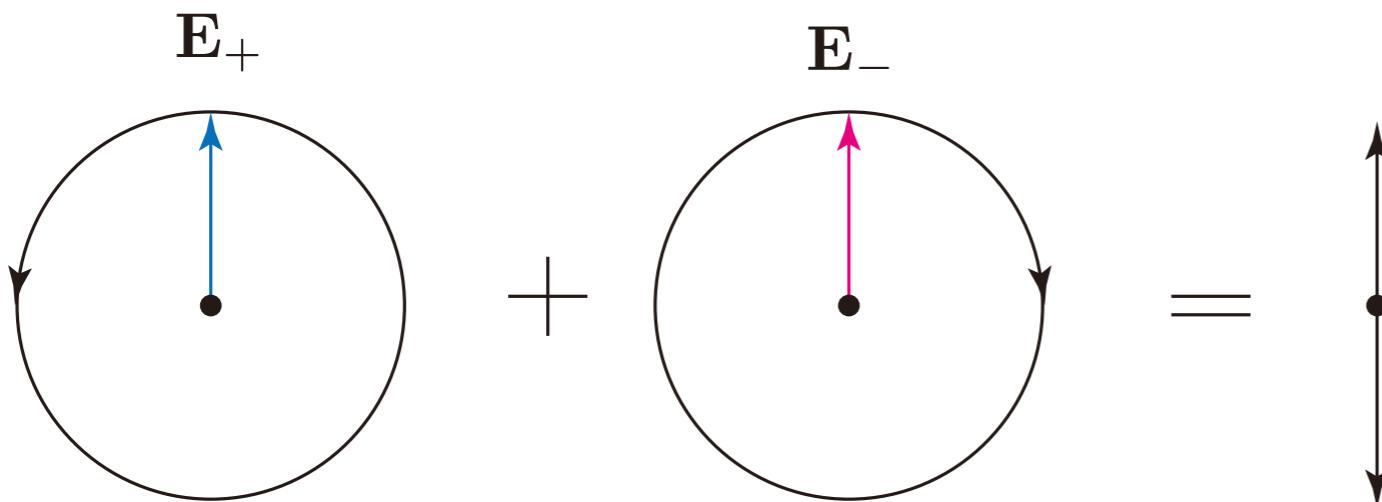
Speed difference sense is $v_R > v_L$.

These waves travel with different velocities. Therefore, a plane polarized wave, which is a linear superposition of a right-hand and a left-hand polarized wave, will not keep a constant plane of polarization, but **this plane will rotate as it propagates**. This effect is called **Faraday rotation**.

- **Faraday Rotation**

If the incident radiation is ***circularly polarized*** (either R or L), then the radiation will encounter different dispersion than unmagnetized case. But, the radiation will still remain circularly polarized.

If the incident radiation is ***linearly polarized***, i.e., a linear superposition of a right-hand and a left-hand polarized wave, then ***the line of polarization will rotate as it propagates***. This effect is called Faraday rotation.



$$\begin{aligned}
 \mathbf{E}(t) &= E e^{-i\omega t} \hat{\mathbf{x}} \\
 &= \frac{1}{2} [(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) + (\hat{\mathbf{x}} - i\hat{\mathbf{y}})] E e^{-i\omega t} \\
 &= \frac{1}{2} (\epsilon_+ + \epsilon_-) E e^{-i\omega t}
 \end{aligned}$$

Decomposition of linear polarization into components of right and left circular polarization

-
- The phase angle ϕ after traveling a distance d is, in general, if the wave number is not constant along the path, is given by

$$\phi_{R,L} = \int_0^d k_{R,L} ds$$

Assume that $\omega \gg \omega_p$ and $\omega \gg \omega_B$

$$\begin{aligned} k_{R,L} &= \frac{\omega}{c} \sqrt{\epsilon_{R,L}} = \frac{\omega}{c} \left[1 - \frac{\omega_p^2}{\omega^2 (1 \mp \omega_B/\omega)} \right]^{1/2} \approx \frac{\omega}{c} \left[1 - \frac{\omega_p^2}{2\omega^2} \left(1 \pm \frac{\omega_B}{\omega} \right) \right] \\ &= \frac{\omega}{c} - \frac{\omega_p^2}{2c\omega} \mp \frac{\omega_p^2 \omega_B}{2c\omega^2} = k_0 \mp \frac{1}{2} \Delta k \quad \left(\Delta k \equiv k_L - k_R = \frac{\omega_p^2 \omega_B}{c\omega^2} \right) \end{aligned}$$

Consider an electromagnetic wave that starts off linearly polarized in the x -direction at the source.

$$\mathbf{E}(t) = E e^{-i\omega t} \hat{\mathbf{x}} = \frac{1}{2} [(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) + (\hat{\mathbf{x}} - i\hat{\mathbf{y}})] E e^{-i\omega t}$$

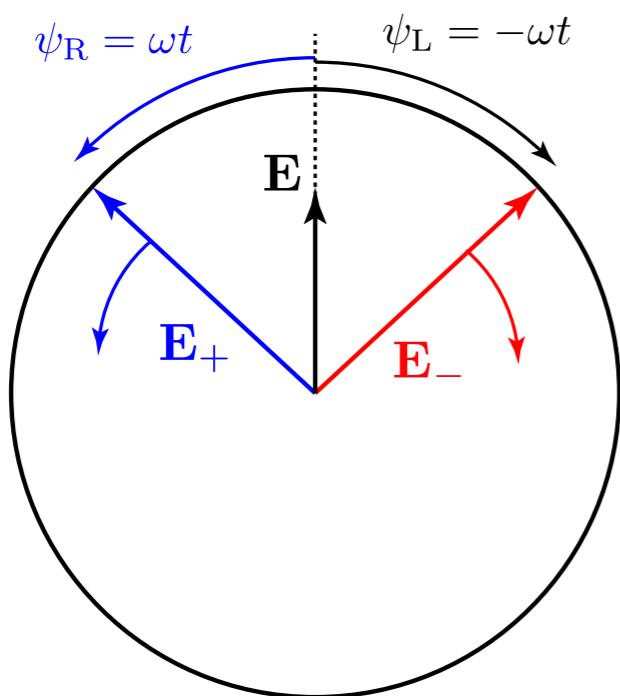
Let's define

$$\int_0^d k_{R,L} ds = \int_0^d k_0 ds \mp \frac{1}{2} \int_0^d \Delta k ds \equiv \phi \mp \varphi$$

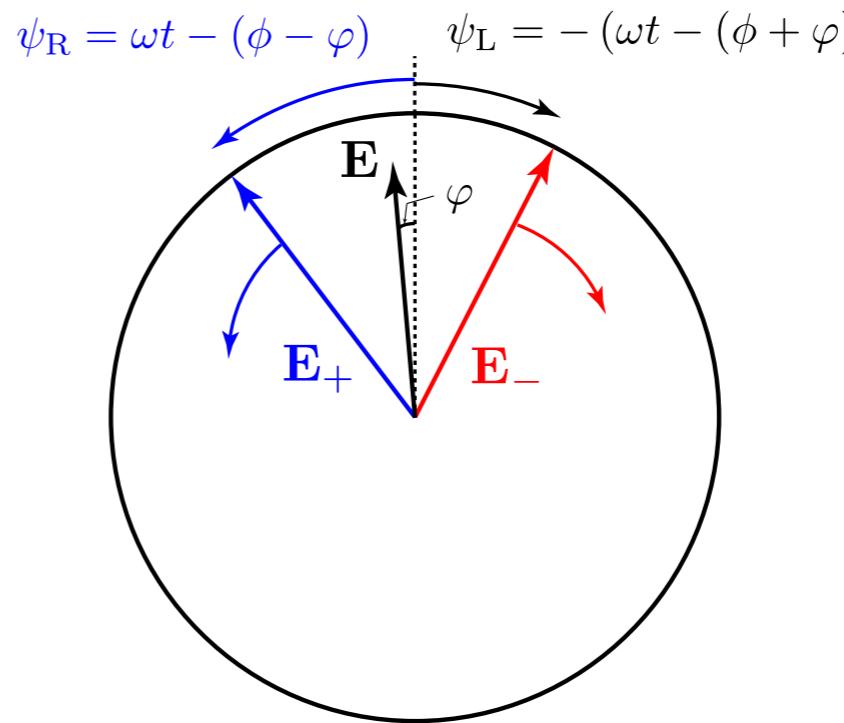
Then, after propagating a distance d through a magnetized plasma toward the observer, the electric field will be

$$\begin{aligned} \mathbf{E}(t) &= \frac{1}{2} \left[(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) e^{i(\phi-\varphi)} + (\hat{\mathbf{x}} - i\hat{\mathbf{y}}) e^{i(\phi+\varphi)} \right] E e^{-i\omega t} \\ &= (\hat{\mathbf{x}} \cos \varphi + \hat{\mathbf{y}} \sin \varphi) E e^{i(\phi-\omega t)} \end{aligned}$$

- The resulting electric field is also linearly polarized, but the polarization angle is rotated counterclockwise by angle φ (when viewed at a fixed position).



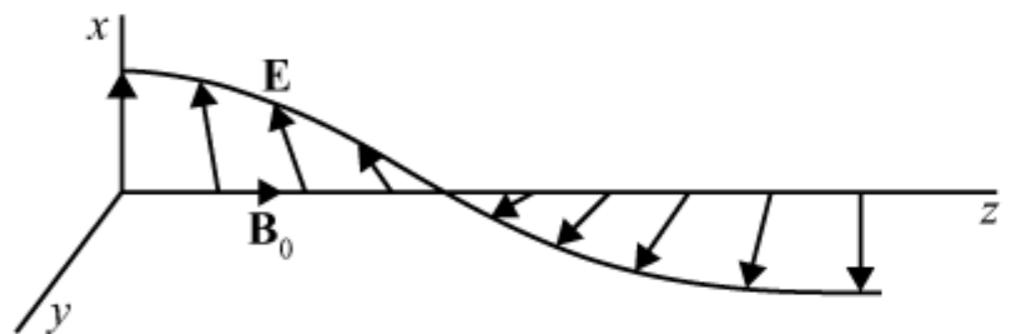
Before passing through the medium



After passing through the medium

- Radiation that starts linearly polarized in a certain direction is rotated by the Faraday effect through an angle φ after propagating a distance d through a magnetized plasma.

$$\varphi = \frac{1}{2} \int_0^d \Delta k ds = \frac{1}{2} \int_0^d \frac{\omega_p^2 \omega_B}{c \omega^2} ds = \frac{2\pi e^3}{m_e^2 c^2 \omega^2} \int_0^d n B_{\parallel} ds$$



- We cannot, of course, generally measure the absolute rotation angle, since we do not know the intrinsic polarization direction of the radiation when it started from the source.

However, since φ varies with frequency (as ω^{-2}), we can determine the value of integral $\int nB_{\parallel}ds$ by making measurements at several frequencies. This can give information about the interstellar magnetic field.

Rotation measure is defined by

$$\varphi = \frac{2\pi e^3}{m_e^2 c^2 \omega^2} \mathcal{RM} = \frac{e^3 \lambda^2}{2\pi m_e^2 c^4} \mathcal{RM}, \text{ where } \mathcal{RM} \equiv \int_0^d n_e B_{\parallel} ds$$

However, *the field changes direction often along the line of sight and this method gives only a lower limit to actual field magnitudes.*

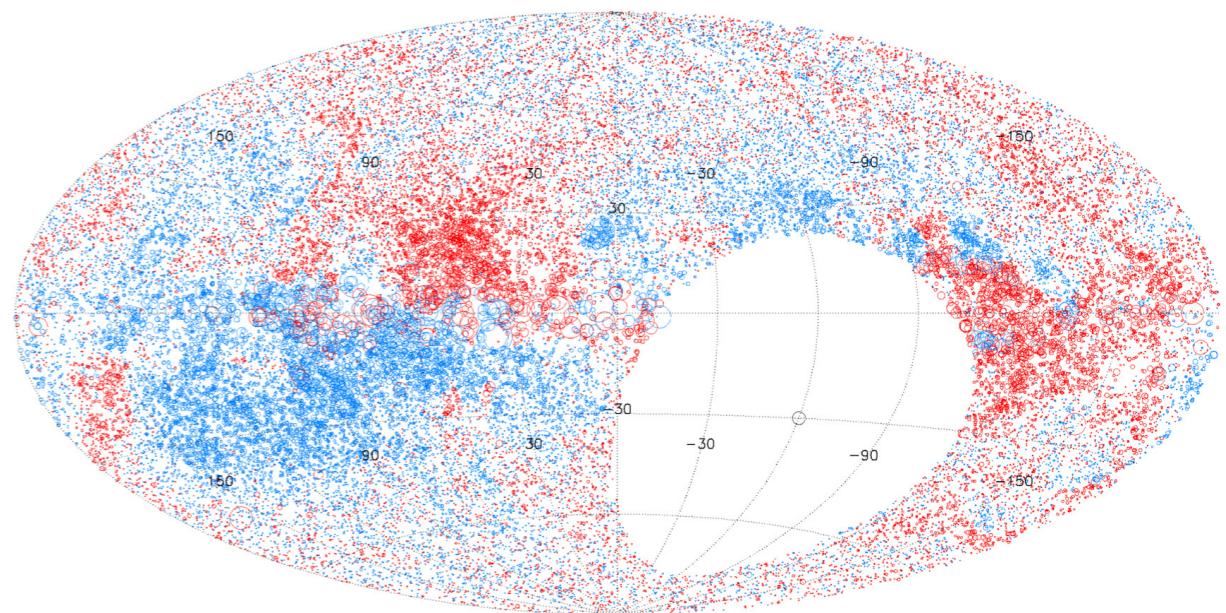
For measurements toward sources (pulsars) where the dispersion measure (DM) is also known, we can derive an estimate of the mean field strength along the line of sight.

$$\langle B_{\parallel} \rangle = \frac{\mathcal{RM}}{\mathcal{DM}} \quad \text{density-weighted magnetic field}$$

Radio astronomers have concluded that

$$\langle n_e \rangle \approx 0.03 \text{ cm}^{-3}$$

$$\langle B_{\parallel} \rangle \approx 3 \mu\text{G}$$



(Taylor, Stil, & Sunstrum 2009, ApJ, 702, 1230)

Red circles are positive RM and blue circles are negative.
The size of the circle scales linearly with magnitude of RM.

* [Plasma Effects in High-Energy Emission Processes] *

- Maxwell equations in dielectric medium:

$$\nabla \cdot (\epsilon \mathbf{E}) = 4\pi\rho$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial(\epsilon \mathbf{E})}{\partial t}$$

$$\mathbf{E} = -\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

These equations formally result from Maxwell's equation in vacuum by the substitutions.

$$\mathbf{E} \rightarrow \sqrt{\epsilon} \mathbf{E}$$

$$c \rightarrow c/\sqrt{\epsilon}$$

$$\mathbf{B} \rightarrow \mathbf{B}$$

$$e \rightarrow e/\sqrt{\epsilon}$$

$$\phi \rightarrow \sqrt{\epsilon}\phi$$

$$\mathbf{A} \rightarrow \mathbf{A}$$

These equations may be solved in the same manner as before for the retarded and Lienard-Wiechert potentials.

- Cherenkov Radiation

- Radiation from relativistic charges moving in a plasma with $n_r = \sqrt{\epsilon} > 1$.

In this case, the velocity of the charges can exceed the phase velocity:

$$v_p = \frac{c}{n_r} < v < c \rightarrow \beta n_r > 1$$

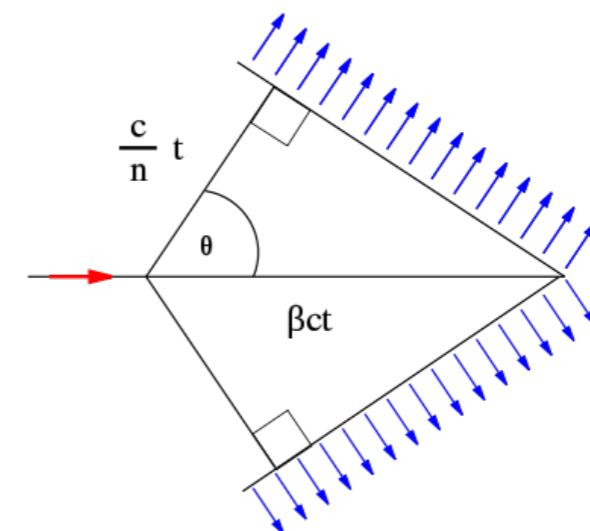
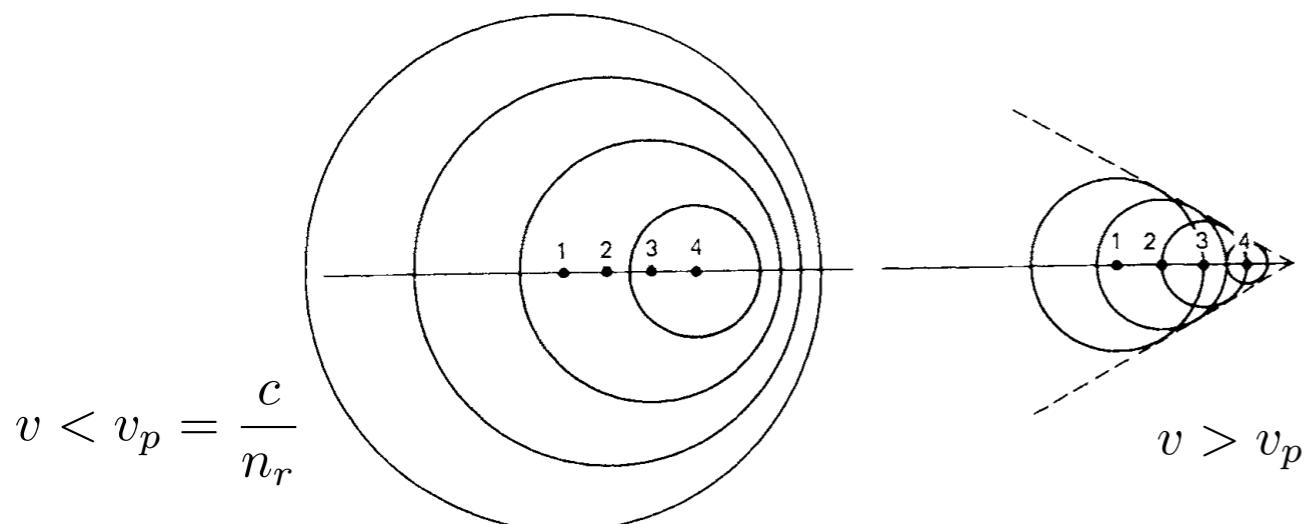
The beaming term of the Lienard-Wiechert potentials can vanish for an angle θ such that $\cos \theta = (n_r \beta)^{-1}$.

$$\kappa = 1 - (v/c) \cos \theta \rightarrow \kappa = 1 - \beta n_r \cos \theta$$

The potentials become infinite at certain places. In consequence, the uniformly moving particle can now radiate.

Cherenkov cone: Outside the cone, points feel no potentials yet. Inside the cone, each point is intersected by two spheres. The resulting radiation is called Cherenkov radiation.

A common analogy is the sonic boom of a supersonic aircraft or bullet.



- Razin-Tsytovich Effect

- When $n_r < 1$, Cherenkov radiation cannot occur.

The critical angle defining the beaming effect in a vacuum was shown to be $\theta_b \sim 1/\gamma = \sqrt{1 - \beta^2}$.

But in a plasma we have instead

$$\theta_b \sim \sqrt{1 - n_r^2 \beta^2}$$

If $n_r \ll 1$ and $\beta \sim 1$,

$$\theta_b \sim \sqrt{1 - n_r^2} = \sqrt{1 - \left(1 - \frac{\omega_p^2}{\omega(\omega \pm \omega_B)}\right)} \approx \frac{\omega_p}{\omega}$$

If $\omega < \gamma\omega_p$, $\theta_b > 1/\gamma$ and the beaming effect is suppressed.

Below the frequency $\gamma\omega_p$, the synchrotron spectrum will be cut off because of the suppression of beaming. This is called the Razin-Tsytovich effect.

As frequencies increase, θ_b decreases until it becomes of order of the vacuum value $1/\gamma$, and therefore the vacuum results apply.

Therefore, the plasma medium effect is unimportant when $\omega \gg \gamma\omega_p$.

Atomic Structure

References

- References for the atomic/molecular spectroscopy

Astronomical Spectroscopy [Jonathan Tennyson]

Physics and Chemistry of the Interstellar Medium [Sun Kwok]

Astrophysics of the Diffuse Universe [Michael A. Dopita & Ralph S. Sutherland]

⇒ many typos

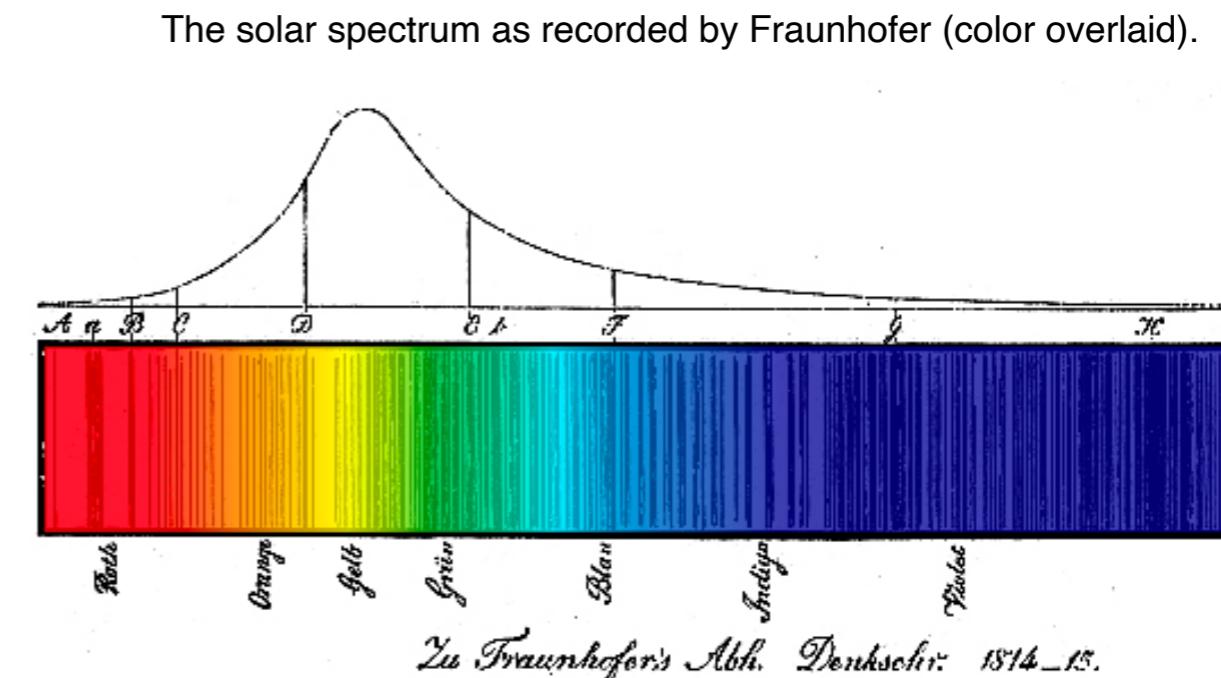
Atomic Spectroscopy and Radiative Processes [Egidio Landi Degl'Innocenti]

Atomic Astrophysics and Spectroscopy [Pradhan, A. K., & Nahar, S. N.]

History: Fraunhofer Lines

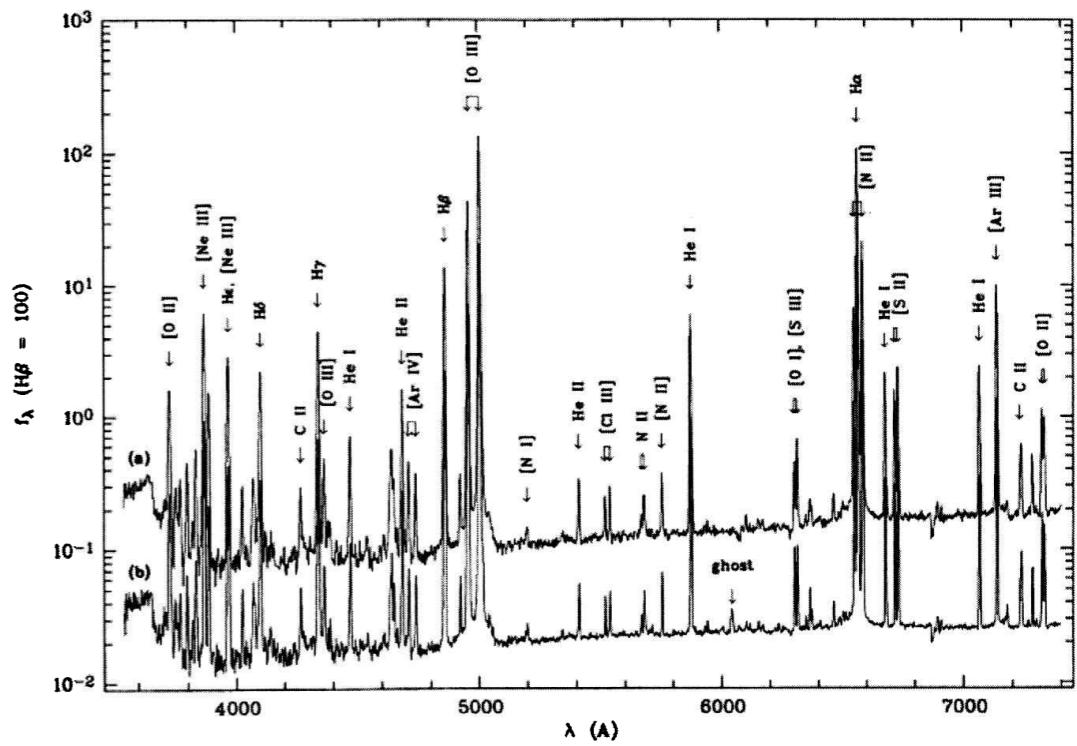
- In 1814, Joseph von Fraunhofer (1789-1826) used one of the high-quality prisms he had manufactured to diffract a beam of sunlight onto a whitewashed wall.
 - Besides the characteristic colors of the rainbow, he saw **many dark lines**.
 - He catalogued the exact wavelength of each dark line and labelled the strongest of them with letters. These are still known today as Fraunhofer lines. Many of these labels, such as the sodium D lines (5896\AA , 5890\AA ; Na I D₁, D₂) are still used today.
 - He did not know what caused the dark lines he observed.
 - However, he performed a similar experiment using light from the nearby star Betelgeuse and found that the pattern of dark lines changed significantly. He concluded correctly that **most of those features were somehow related to the composition of the object**.
- The first real step in understanding Fraunhofer's observations came in the middle of the 19th century with the experiments of Gustav Kirchhoff (1824-1887) and Robert Bunsen (1811-1891). They studied the color of the light emitted when metals were burnt in flames. In certain cases, the wavelength of the emitted light gave an exact match with the Fraunhofer lines. **These experiments demonstrated that the Fraunhofer lines were a direct consequence of the atomic composition of the Sun.**

In fact, some of the lines were due to the Earth's atmosphere, the so-called telluric lines.



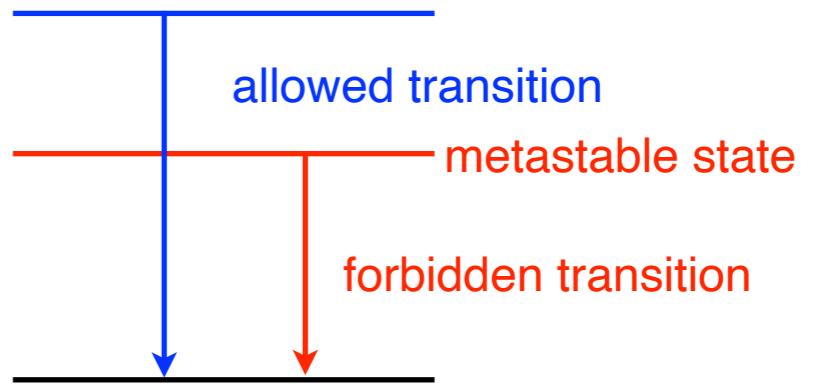
History: Nebulium?

- In 1918, extensive studies of the emission spectra of nebulae found a series of lines which had not been observed in the laboratory.
 - Particularly strong were features at 4959\AA and 5007\AA . For a long time, this pair could not be identified and these lines were attributed to a new element, '**nebulium**'.
 - In 1927, Ira Bowen (1898-1973) discovered that the lines were not really due to a new chemical element but instead **forbidden lines from doubly ionized oxygen** [O III].
 - He realized that in the diffuse conditions found in nebulae, atoms and ions could survive a long time without undergoing collisions. Indeed, ***under typical nebula conditions the mean time between collisions is in the range 10-10,000 secs.*** This means that ***there is sufficient time for excited, metastable states to decay via weak, forbidden line emissions.***
 - The forbidden lines could not be observed in the laboratory where it was not possible to produce collision-free conditions over this long timeframe.
 - **Other ‘nebulium’ lines turned out to be forbidden lines** originating from singly ionized oxygen [O II] and nitrogen [N III].



Optical spectra of NGC 6153, Liu et al. (2000, MNRAS)

[O III], [O II], [N II], etc:
We use a pair of square
brackets for a forbidden line.



Quantum Mechanics

- **The classical theory of radiation is unable to treat physical processes in which the interaction between matter and radiation takes place by means of single (or a few) photons.**

We have already dealt with some elementary aspects of this interaction when we discussed the Planck law and the Einstein coefficients.

However, to really solve problems we need to find explicit expressions for the A and B coefficients or equivalents.

This must involve detailed investigation of the structure of the matter that interacts with the radiation, its energy levels, and other physical properties.

- **Astrophysical spectral lines offer two important insights into the workings of our Universe.**

First, they are probes of the fundamental (QM) nature of matter because they originate from subatomic, atomic and molecular systems.

Second, they provide, via the Doppler effect, critical dynamical information on astrophysical systems ranging in scale from planetary system to superclusters of galaxies.

Schrödinger Equation

- A good starting point for a quantum mechanical understanding of spectral lines is the hydrogen atom, which is the simplest of all atoms, consisting of one proton and one electron.
- Since the H atom consists of only a proton and an electron, the Coulomb field experienced by the electron is spherically symmetric. The time-dependent Schrödinger equation for a system with **Hamiltonian H**:

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

Often we are interested in the stationary solutions found by separating the time and space parts of the wave function, which is possible *if H is independent of time*:

- The time-independent Schrödinger equation is obtained as follows:

$$\begin{aligned}\Psi(\mathbf{r}, t) &= \psi(\mathbf{r})e^{iEt/\hbar} \longrightarrow H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \\ H &= \frac{p^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\nabla^2 + V(r)\end{aligned}$$

momentum operator:

$$\mathbf{p} = \frac{\hbar}{i}\nabla$$

Here, in the spherical coordinates, the Laplace operator is given by

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \mathcal{R} + \frac{1}{r^2} \mathcal{L}^2\end{aligned}$$



Erwin Schrödinger

- Separation of variables: Since $V(r)$ depends only on r , we can try something like

$$\phi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Then, the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m} \mathcal{R}R(r) \right] Y(\theta, \phi) - \frac{\hbar^2}{2mr^2} [\mathcal{L}^2 Y(\theta, \phi)] R(r) + V(r)R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi)$$

→ $\frac{r^2 \mathcal{R}R(r)}{R(r)} + \frac{2mr^2}{\hbar^2} [E - V(r)] = -\frac{\mathcal{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} = \Lambda$ (a constant)

$$\mathcal{R}R(r) + \frac{2m}{\hbar^2} [E - V(r)] R(r) = \frac{\Lambda}{r^2} R(r)$$

$$\mathcal{L}^2 Y(\theta, \phi) = -\Lambda Y(\theta, \phi)$$

The left side depends only on r and the right side on θ and ϕ . Therefore, they should be a constant.

The solution of the second equation is known to be the spherical harmonics.

$$Y(\theta, \phi) = Y_{\ell m}(\theta, \phi) \text{ and } \Lambda = \ell(\ell + 1)$$

The solution for the radial component is given by the associated Laguerre polynomials.

$$R_{n\ell}(r) = -2 \left(\frac{1}{na_0} \right)^{3/2} \sqrt{\frac{(n - \ell - 1)!}{n [(n + \ell)!]^3}} \left(\frac{2r}{na_0} \right)^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1} \left(\frac{2r}{na_0} \right)$$

Summary of the Hydrogen atom

- momentum operator $\mathbf{p} = \frac{\hbar}{i}\nabla$
- Hamiltonian operator $H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$
- Expectation value of an operator

$$\langle F \rangle = \int \psi^* F \psi d^3x \quad \rightarrow \quad \langle F \rangle = \langle \psi | F | \psi \rangle$$

- Wavefunction for a hydrogen-like atom:

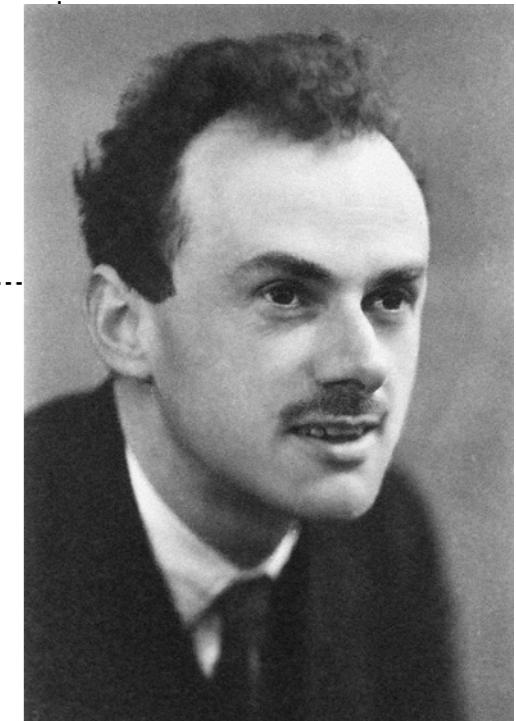
$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

bra-ket notation (Dirac notation)

ket vector : $|\psi\rangle$

bra vector : $\langle\phi| = |\psi\rangle^\dagger$

(\dagger : conjugate transpose)



radial function:

$$R_{nl}(r) = - \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

$\rho = \frac{2Z}{na_0}r$, $a_0 \equiv \frac{\hbar^2}{m_e c^2} = 0.529\text{\AA}$ (Bohr radius),
 L_{n+l}^{2l+1} = associated Laguerre polynomial

spherical harmonics

$$Y_{lm}(\theta, \phi) = (-1)^{(m+|m|)/2} \left[\frac{(l-|m|)!}{(l+|m|)!} \frac{2l+1}{4\pi} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\phi} \quad P_l^{|m|} = \text{associated Legendre function}$$

- **$n = 1, 2, 3, \dots$: principal quantum number**
- **$l = 0, 1, 2, \dots, n-1$: orbital angular momentum quantum number**
- **$m = -l, -l+1, \dots, 0, \dots, l-1, l$: magnetic quantum number**

Quantum Numbers / H-atom

- Each bound state of the hydrogen atom is characterized by a set of four quantum numbers (n, l, m, m_s)
 - $n = 1, 2, 3, \dots$: principal quantum number (shell)
 - $l = 0, 1, 2, \dots, n - 1$: **orbital angular momentum** quantum number (subshell)
 - ▶ By convention, the values of l are usually designated by small letters.
- | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|-----|
| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | ... |
| s | p | d | f | g | h | i | k | l | ... |
- $m = -l, -l + 1, \dots, 0, \dots, l - 1, l$: magnetic quantum number.
 - ▶ It determines the behavior of the energy levels in the presence of a magnetic field.
 - ▶ This is the projection of the electron orbital angular momentum along the z -axis of the system.
 - Spin
 - The electron possesses an intrinsic, **spin angular momentum** with the magnitude of $|s| = \frac{1}{2}$.
 - There are two states, $m_s = \pm \frac{1}{2}$, for the spin.
 - Degeneracy for a given n : $2 \times \sum_{l=0}^{n-1} (2l + 1) = 2n^2$

-
- Wavefunctions for a hydrogen-like atom

$$R_{1,0} = \left(\frac{Z}{a_0} \right)^{3/2} 2 e^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0} \right)^{3/2} 2 (1 - \rho) e^{-\rho}$$

$$R_{2,1} = \left(\frac{Z}{2a_0} \right)^{3/2} \frac{2}{\sqrt{3}} \rho e^{-\rho}$$

$$R_{3,0} = \left(\frac{Z}{3a_0} \right)^{3/2} 2 \left(1 - 2\rho + \frac{2}{3}\rho^2 \right) e^{-\rho}$$

$$R_{3,1} = \left(\frac{Z}{3a_0} \right)^{3/2} \frac{4\sqrt{2}}{3} \rho \left(1 - \frac{1}{2}\rho \right) e^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \rho^2 e^{-\rho}$$

Normalisation: $\int_0^\infty R_{n,l}^2 r^2 dr = 1$

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

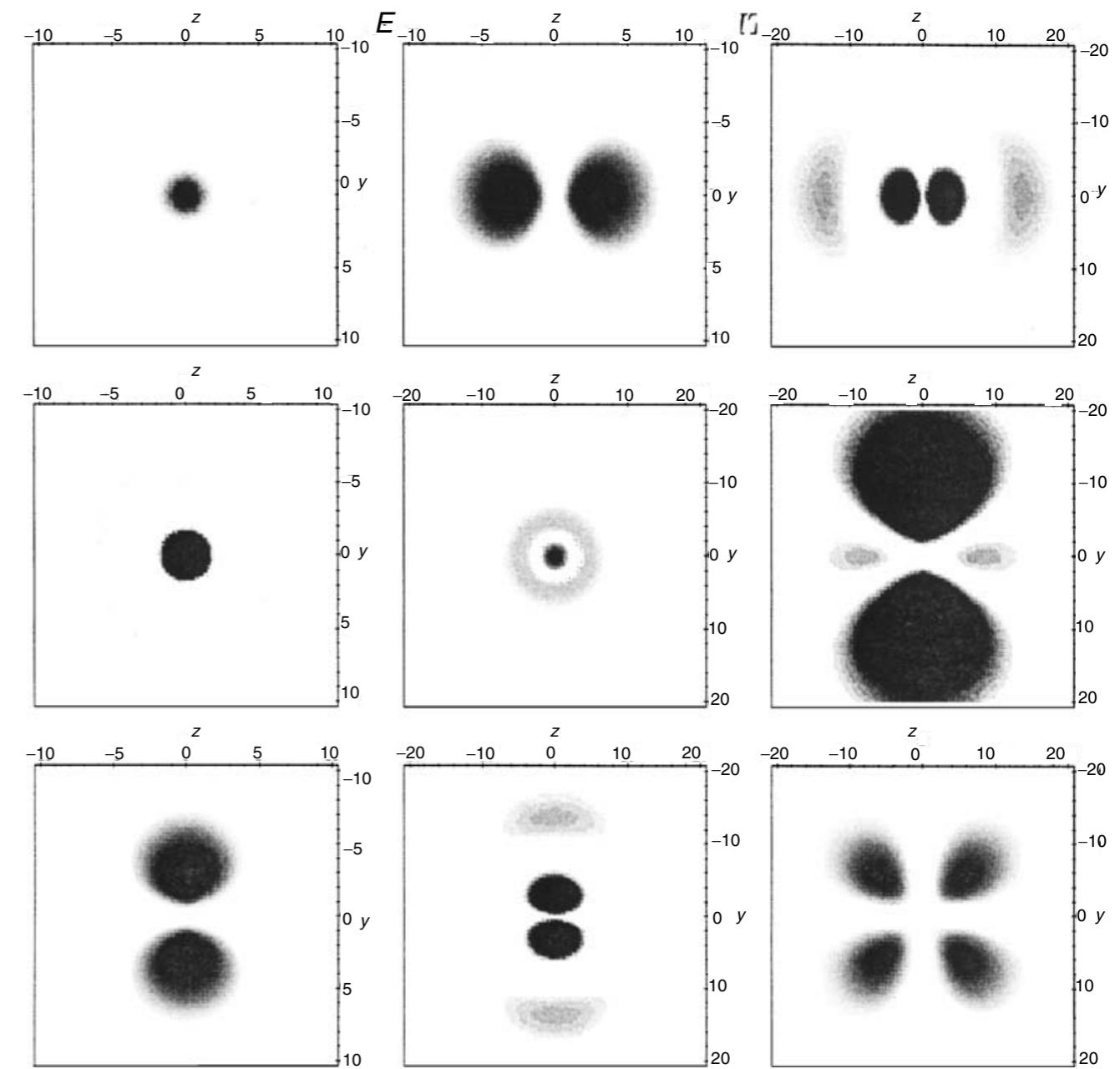
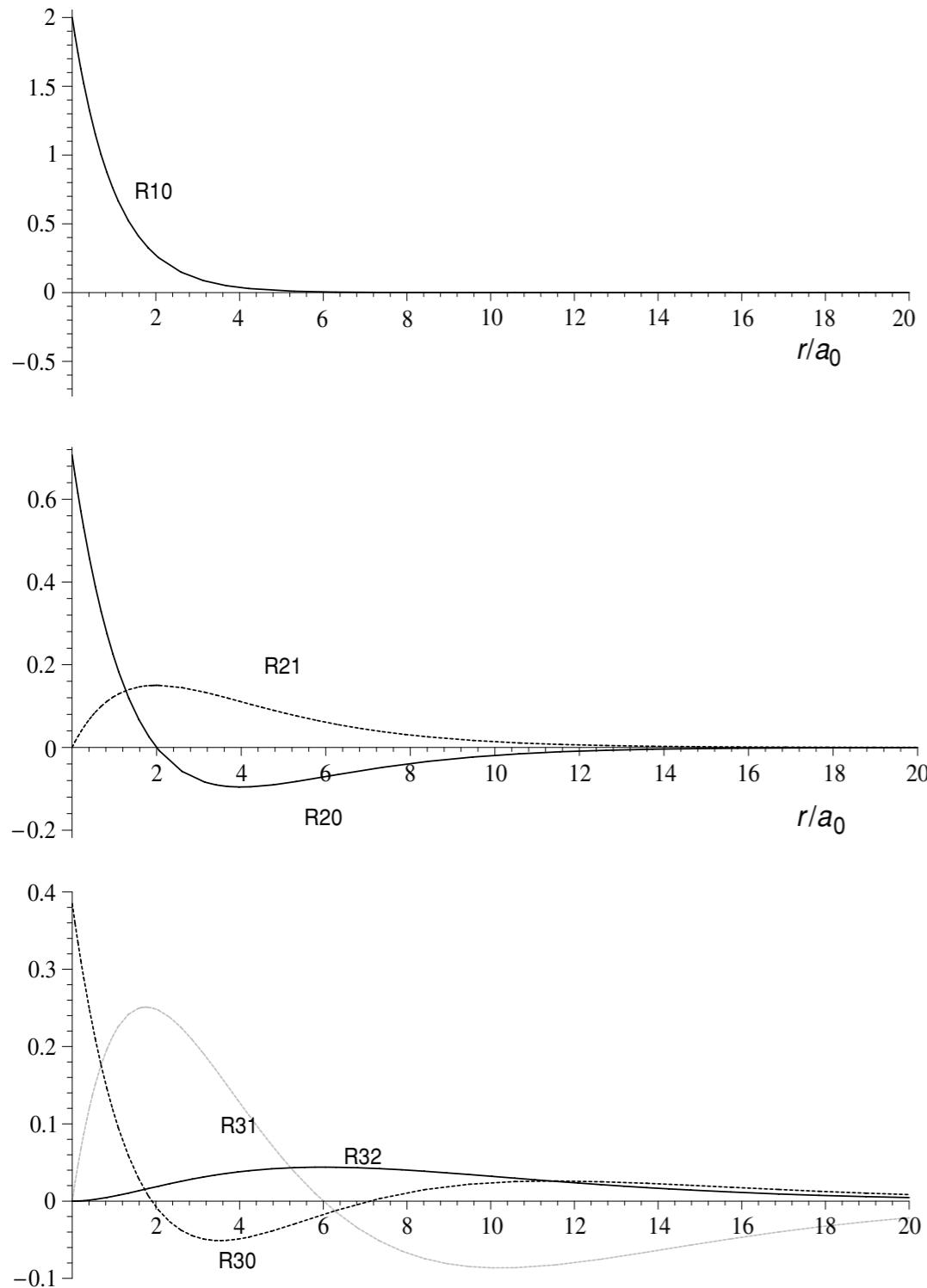
$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

Normalisation: $\int_0^{2\pi} \int_0^\pi |Y_{l,m}|^2 \sin \theta d\theta d\phi = 1$



Probability distributions (per unit volume). A slice through the $\phi = 0$ plane. The darker the shading the greater the probability density.

[Left] 1s, 2s, 2p0 from top to bottom
 [Center] 2p1, 3s, 3p0
 [Right] 3p1, 3d0, 3d1

[Angular Momentum]

- The orbital angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ has the following eigenvalue.

$$\mathbf{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, \quad L_z Y_{lm} = m\hbar Y_{lm}$$

Here, the ℓ can have values $\ell = 0, 1, \dots, n - 1$.

The magnitude of the angular momenta are

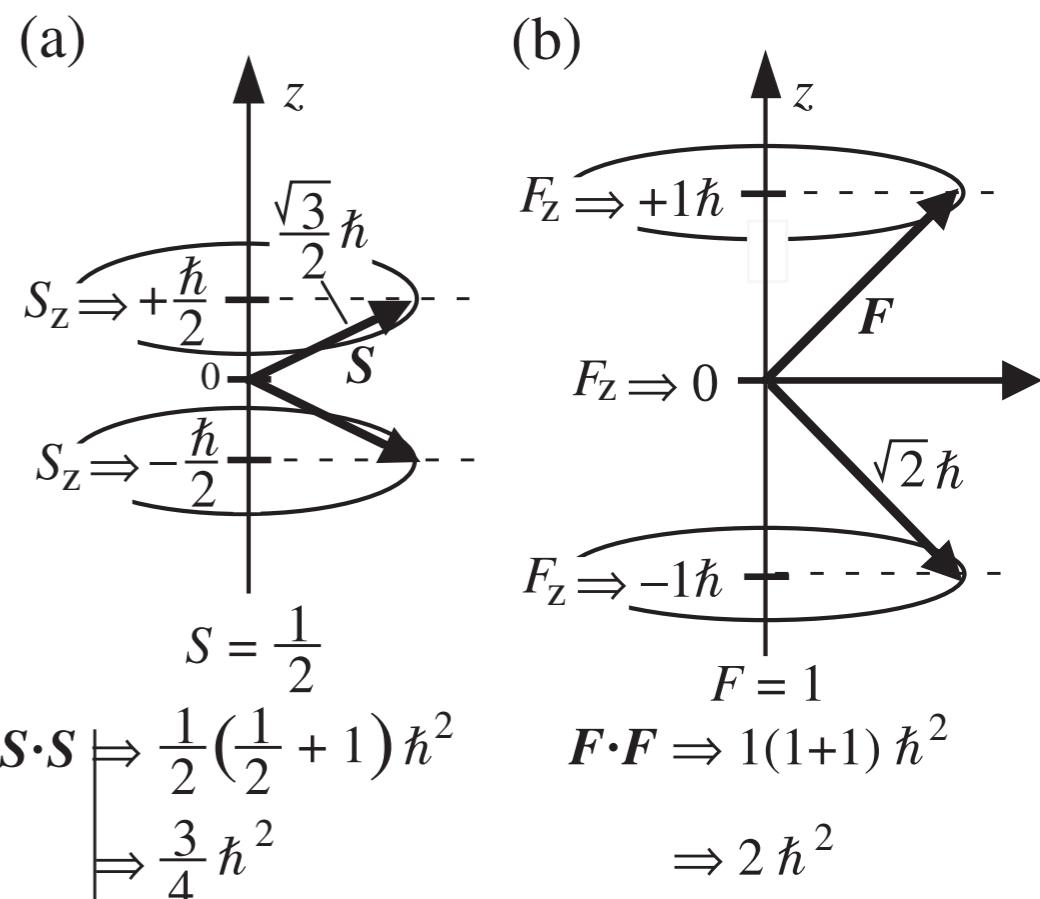
$$|\mathbf{L}| = \sqrt{\ell(\ell+1)}\hbar \quad \text{where } \ell = 0, 1, \dots, n-1$$

The z -component have the following values.

$$L_z = m\hbar \quad \text{where } m = -\ell, -\ell+1, \dots, \ell-1, \ell$$

- Electron has a spin of $s = \frac{1}{2}$ and it has two z -components:

$$s = \frac{1}{2}\hbar \rightarrow m_s = -\frac{1}{2}\hbar, \frac{1}{2}\hbar$$



- The spherical harmonics are eigenfunctions of the orbital angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.

$$\mathbf{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, \quad L_z Y_{lm} = m\hbar Y_{lm}$$

The sizes of the angular moment and z-component are

$$|\mathbf{L}| = \sqrt{l(l+1)}\hbar, \quad |L_z| = m\hbar$$

- Wavefunction (with $l=0$) at $r=0$

$$R_{10}(r) = \frac{2}{(a_0/Z)^{3/2}} e^{-r/(a_0/Z)}$$

$$R_{20}(r) = \frac{1}{(2a_0/Z)^{3/2}} \left(2 - \frac{r}{a_0/Z} \right) e^{-r/(2a_0/Z)}$$

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{1}{4\pi}}$$

$$|\psi_{n,l=0}(0)|^2 = \frac{1}{\pi} \left(\frac{Z}{na_0} \right)^3 \neq 0$$

This indicates that the electron can interact with the nucleus \Rightarrow hyperfine structure!

Probability of being located within a volume $d^3x = |\psi(r, \theta, \phi)|^2 d^3x = R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$

- Properties of the spherical harmonics:

$$\int_0^\pi \int_0^{2\pi} |Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1$$

$$\sum_{m=-l}^l |Y_{lm}(\theta, \phi)|^2 = \frac{2l+1}{4\pi}$$

No dependency on ϕ .

This property implies that **closed shells are spherically symmetric and have very little interaction with external electrons.**

- Orthonormality

$$\int d\Omega Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) = \delta_{\ell, \ell'} \delta_{m, m'}$$

$$\int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r) dr = \delta_{n, n'}$$

- Energy

$$E_n = -Z^2/2n^2$$

- Degeneracy for a given n .

$$2 \times \sum_{l=0}^{N-1} (2l + 1) = 2n^2$$

$n = 1, 2, 3, \dots$: principal quantum number

$l = 0, 1, 2, \dots, n-1$: orbital angular momentum quantum number

$m = -l, -l+1, \dots, 0, \dots, l-1, l$: magnetic quantum number

- Spin

The electron possesses an intrinsic angular momentum with the magnitude of $|s| = \frac{1}{2}$.

There are two states, $m_s = \pm \frac{1}{2}$, for the spin.

Wavefunctions:

$$\left| \frac{1}{2} \right\rangle \equiv \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \left| -\frac{1}{2} \right\rangle \equiv \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

To incorporate spin into the theory in a completely satisfactory way one should use the relativistic Dirac equation.

H-atom Spectra

- Spectral series of the H atom
 - The spectrum of H is divided into a number of series linking different upper levels n_2 with a single lower level n_1 value. ***Each series is denoted according to its n_1 value and is named after its discoverer.***
 - Within a given series, ***individual transitions are labelled by Greek letters.***

| $n_2 \longleftrightarrow n_1$ | | | |
|-------------------------------|-----------|--------|-----------------|
| n_1 | Name | Symbol | Spectral region |
| 1 | Lyman | Ly | ultraviolet |
| 2 | Balmer | H | visible |
| 3 | Paschen | P | infrared |
| 4 | Brackett | Br | infrared |
| 5 | Pfund | Pf | infrared |
| 6 | Humphreys | Hu | infrared |

$$\Delta n \equiv n_2 - n_1$$

$\Delta n = 1$ is α ,

$\Delta n = 2$ is β ,

$\Delta n = 3$ is γ ,

$\Delta n = 4$ is δ ,

$\Delta n = 5$ is ϵ .

Lyman series : Ly α , Ly β , Ly γ , ...

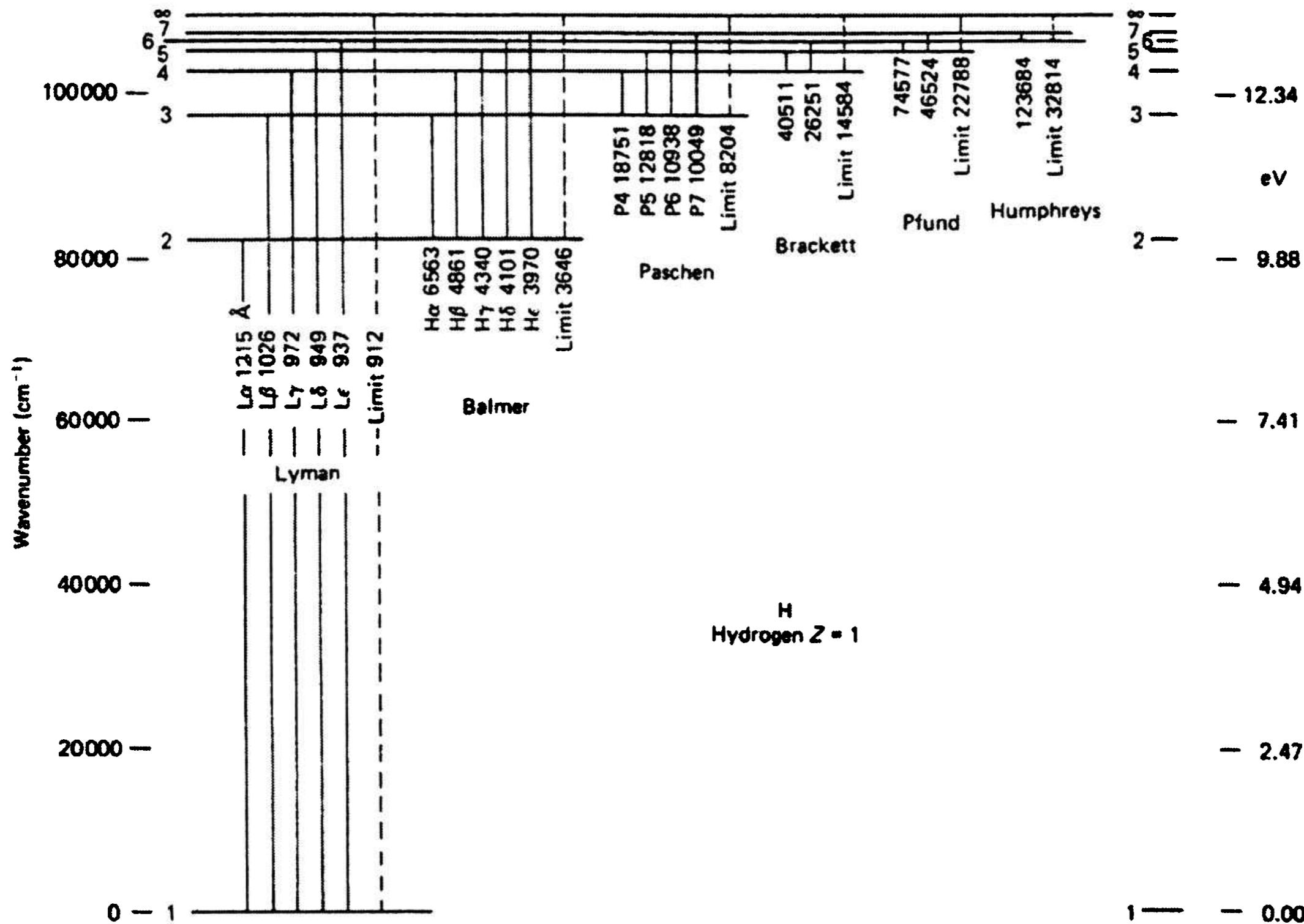
Balmer series : H α , H β , H γ , ...

Paschen series: P α , P β , P γ , ...

Brackett series : Br α , Br β , Br γ , ...

Transitions with high Δn are labelled by the n_2 . Thus, H15 is the Balmer series transition between $n_1 = 2$ and $n_2 = 15$.

Schematic energy levels of the hydrogen atom with various spectral series identified. The vertical numbers are wavelengths in Å.



Many electron systems

- The time-independent Schrödinger equation for an atom with N electrons and nuclear charge (atomic number) Z .

$$\left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r} \right) + \sum_{i=1}^{N-1} \sum_{j=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

where \mathbf{r}_i is the coordinate of the i th electron, with its origin at the nucleus.

The first term contains a kinetic energy operator for the motion of each electron and the Coulomb attraction between that electron and the nucleus.

The second term contains the electron-electron Coulomb repulsion term.

The Coulomb repulsion between pairs of electrons means the above equation is not analytically solvable, even for the simplest case, the helium atom for which $N = 2$.

Many-Electron Systems - [Central Field Approximation]

- Even in complex atoms with N electrons it is useful to consider single-electron states.

Hartree-Fock approximation (or self-consistent field approximation): We assume that each electron moves in the potential of the nucleus plus the averaged potential due to the other $N - 1$ electrons.

Central field approximation (or orbital approximation): In addition, when this averaged potential is assumed to be spherically symmetric, the force acting on each electron only depends on its distance from the nucleus at the center. It provides a useful classification of atomic states and also a starting point.

Let us assume that each electron moves in its own (angle-independent) central potential given by $V_i(r_i)$. This gives a simplified Schrödinger equation for the motion of each electron:

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_i(r_i) \right] \phi_i(\mathbf{r}_i) = E_i \phi_i(\mathbf{r}_i) \text{ where } V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j \neq i} \left\langle \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle$$

Note the average sign to make the potential angle-independent.

Orbitals: The solutions of the above equation are known as orbitals.

Using this approximation, the total energy and the total wave function of the system are given by the sum of single electron energies and the product of single electron wave functions, respectively.

$$E = \sum_i E_i$$

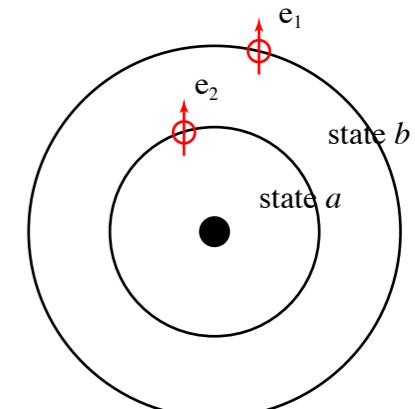
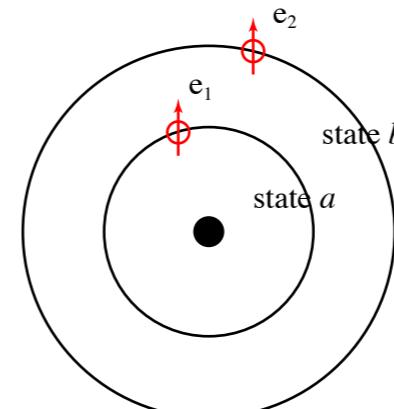
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

However, this wave function fails to satisfy a basic principle of quantum mechanics that one cannot distinguish between electron i and electron j .

[Indistinguishable Particles]

- Consider a system with **two identical particles**. We note that what is physically observable is not a wave function but a probability distribution. This distribution cannot be altered by interchanging the particles. This means that

$$|\Psi(a_1, b_2)|^2 = |\Psi(a_2, b_1)|^2$$



The equation has two possible solutions:

- symmetric solution

$$\Psi(a_1, b_2) = \Psi(a_2, b_1)$$

- antisymmetric solution

$$\Psi(a_1, b_2) = -\Psi(a_2, b_1)$$

Particles 1 and 2 are indistinguishable.

Pauli Exclusion Principle: *Wave functions are antisymmetric with respect to interchange of identical Fermions* (with a half-odd-integer spin). Within the central field approximation, a two-electron wave function which obeys the Pauli Principle can be written

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] = -\Psi(2, 1)$$

If the two spin-orbitals are the same ($\phi_a = \phi_b$), then the total wave function is zero, i.e., $\Psi(1,2) = 0$, and no physical (normalizable) state exists. The Pauli exclusion principle is summarized as "**No two electrons can occupy the same spin-orbital state.**"

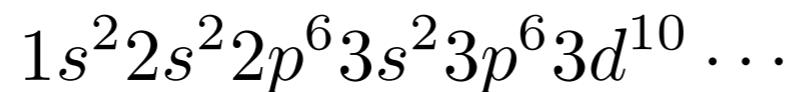
This exclusion provides the **degeneracy pressure** which holds up the gravitational collapse of white dwarfs and neutron stars.



Wolfgang Ernst Pauli

Complex Atoms : Electron Configuration

- The **configuration** is the distribution of electrons of an atom in atomic **orbitals**.
 - The configuration of an atomic system is defined by specifying the nl values of all the electron orbitals: nl^x means x electrons in the orbital defined by n and l .
 - Each orbital labelled nl actually consists of orbitals with $2l + 1$ different m values, each with two possible values of m_s . Thus the nl orbital can hold a maximum $2(2l + 1)$ electrons.



nl^x means x electrons in the orbital defined by n and l .

- **shells, subshells:**

- ***Principal quantum number = shell***: Shells correspond with the principal quantum numbers (1, 2, 3, ...). They are labeled alphabetically with letters used in the X-ray notation (K, L, M, ...).
- ***Orbital angular momentum quantum number = subshell***: Each shell is composed of one or more subshells. The first (K) shell has one subshell, called “1s”; The second (L) shell has two subshells, called “2s” and “2p”.

- **open shell configuration, closed shell configuration:**

the ground state configuration of carbon, which has six electrons: $1s^2 2s^2 2p^2$

the ground state configuration of neon atom, which has ten electrons: $1s^2 2s^2 2p^6$

A closed shell or sub-shell makes no contribution to the total orbital or spin angular momentum (L or S).

- Atomic ions which have the same number of electrons form what are called **isoelectronic series**.
- Electronically-excited states of atoms usually arise when one of the outermost electrons jumps to a higher orbital.

States with two electrons simultaneously excited are possible but are less important. For many systems, all of these states are unstable. They have sufficient energy to autoionize by spontaneously ejecting an electron.

[Electron Configuration]

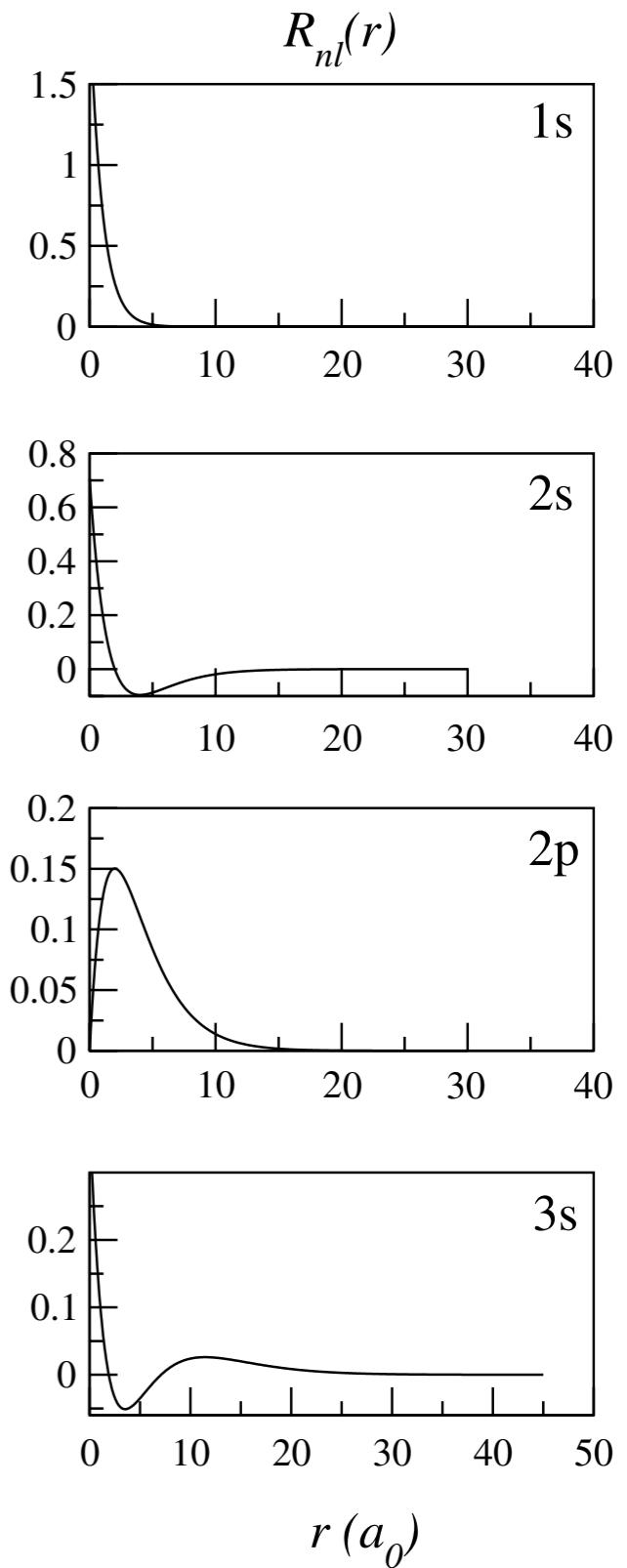
- **Energy ordering:**

For a hydrogen-like atom, the energy of the individual orbitals is determined by principal quantum number n .

$$E(1s) < E(2s) = E(2p) < E(3s) = E(3p) = E(3d) < E(4s) \dots$$

For complex atoms, the degeneracy on the orbital angular momentum quantum number l is lifted. This is because **electrons in low l orbits ‘penetrate’, i.e., get inside orbitals with lower n -values**. Penetration by the low l electrons means that they spend some of their time nearer the nucleus experiencing an enhanced Coulomb attraction. This lowers their energy relative to higher l orbitals which penetrate less or not at all.

$$E(1s) < E(2s) < E(2p) < E(3s) < E(3p) < E(4s) \lesssim E(3d) \dots$$



[Electron Configuration - Orbitals]

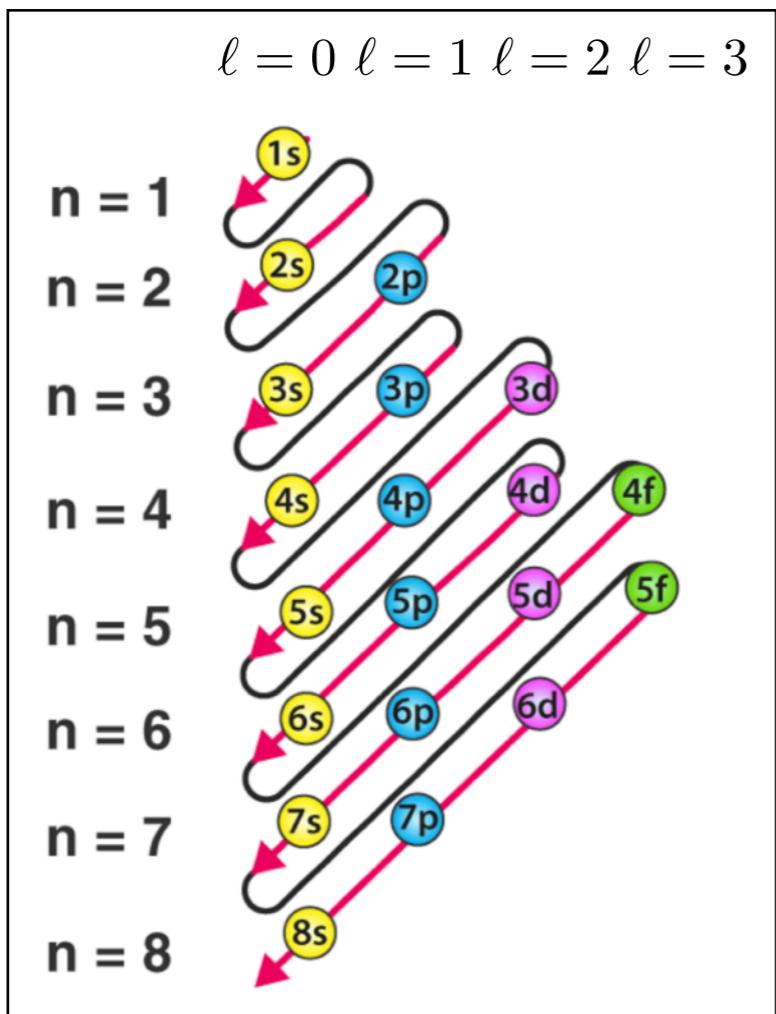
- $n = 1, 2, 3, \dots$: principal quantum number (주양자수)
- $l = 0, 1, 2, \dots, n-1$: orbital angular momentum (quantum number) for each electron (부양자수)

$n = 1, 2, 3, 4, 5 \dots$

$\ell = 0, 1, 2, 3, \dots, n-1 \rightarrow s, p, d, f, g, \dots$

- The electron configuration represents how the electrons are filled in shells and subshells.

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \dots$$



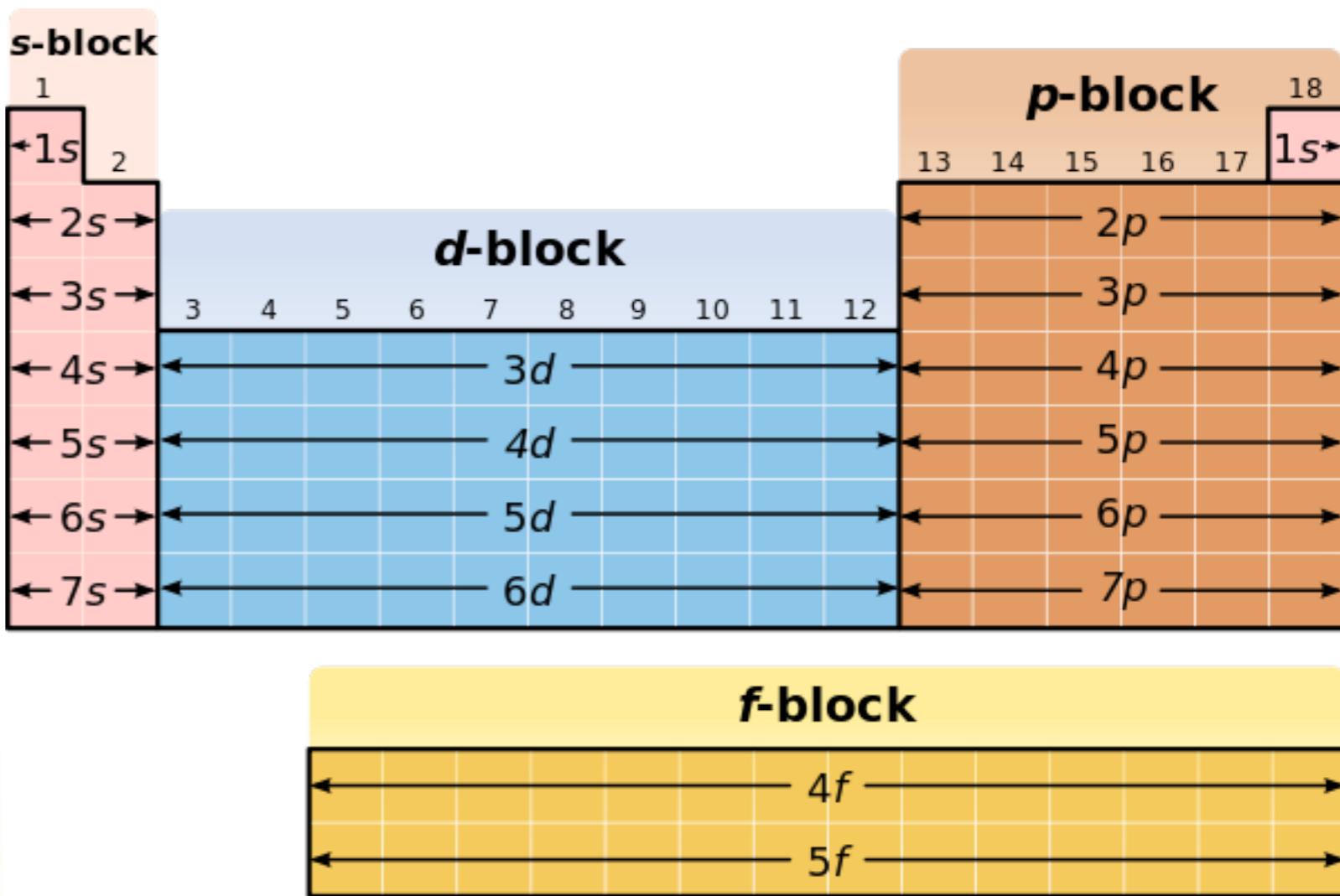
| Shell (Principle Quantum Number Value) | Subshell (Angular Momentum Quantum Number) | Notation | Maximum Number of electrons |
|--|--|----------|-----------------------------------|
| $n = 1$ | $l=0$ | 1s | 2 |
| $n = 2$ | $l=0$ | 2s | 2 |
| | $l=1$ | 2p | 6 |
| | $l=0$ | 3s | 2 |
| $n = 3$ | $l=1$ | 3p | 6 |
| | $l=2$ | 3d | 10 |
| | $l=0$ | 4s | 2 |
| | $l=1$ | 4p | 6 |
| $n = 4$ | $l=2$ | 4d | 10 |
| | $l=3$ | 4f | 14 |

표 9.2 원자의 전자 배열과 전리 에너지(Kramida et al. 2018)

| 원소/ 원자번호 | K | | L | | M | | N | | | 바닥상태 준위 | 전리 에너지(eV) | |
|-------------|-------|-------|-------|-----|----|----|----|----|---------------|------------|------------|--|
| | 1s | 2s 2p | 3s 3p | 3d | 4s | 4p | 4d | 4f | I → II | II → III | | |
| H 1 | 1 | | | | | | | | $^2S_{1/2}$ | 13.598 | | |
| He 2 | 2 | | | | | | | | 1S_0 | 24.587 | 54.418 | |
| Li 3 | 2 | 1 | | | | | | | $^2S_{1/2}$ | 5.392 | 75.640 | |
| Be 4 | 2 | 2 | | | | | | | 1S_0 | 9.323 | 18.211 | |
| B 5 | 2 | 2 | 1 | | | | | | $^2P_{1/2}^o$ | 8.298 | 25.155 | |
| C 6 | 2 | 2 | 2 | | | | | | 3P_0 | 11.260 | 24.385 | |
| N 7 | 2 | 2 | 3 | | | | | | $^4S_{3/2}^o$ | 14.534 | 29.601 | |
| O 8 | 2 | 2 | 4 | | | | | | 3P_2 | 13.618 | 35.121 | |
| F 9 | 2 | 2 | 5 | | | | | | $^2P_{3/2}^o$ | 17.423 | 34.971 | |
| Ne 10 | 2 | 2 | 6 | | | | | | 1S_0 | 21.565 | 40.963 | |
| Na 11 | | | 1 | | | | | | $^2S_{1/2}$ | 5.139 | 47.286 | |
| Mg 12 | | | 2 | | | | | | 1S_0 | 7.646 | 15.035 | |
| Al 13 | | | 2 1 | | | | | | $^2P_{1/2}^o$ | 5.986 | 18.829 | |
| Si 14 | Neon | | 2 2 | | | | | | 3P_0 | 8.152 | 16.346 | |
| P 15 | | 배열 | 2 3 | | | | | | $^4S_{3/2}^o$ | 10.487 | 19.769 | |
| S 16 | | | 2 4 | | | | | | 3P_2 | 10.360 | 23.338 | |
| Cl 17 | | | 2 5 | | | | | | $^2P_{3/2}^o$ | 12.968 | 23.814 | |
| Ar 18 | | | 2 6 | | | | | | 1S_0 | 15.760 | 27.630 | |
| K 19 | | | - | 1 | | | | | $^2S_{1/2}$ | 4.341 | 31.625 | |
| Ca 20 | | | - | 2 | | | | | 1S_0 | 6.113 | 11.872 | |
| Sc 21 | | | 1 | 2 | | | | | $^2D_{3/2}$ | 6.561 | 12.800 | |
| Ti 22 | | | 2 | 2 | | | | | 3F_2 | 6.828 | 13.576 | |
| V 23 | | | 3 | 2 | | | | | $^4F_{3/2}$ | 6.746 | 14.634 | |
| Cr 24 | | | 5 | 1 | | | | | 7S_3 | 6.767 | 16.486 | |
| Mn 25 | | | 5 | 2 | | | | | $^6S_{5/2}$ | 7.434 | 15.640 | |
| Fe 26 | | | 6 | 2 | | | | | 5D_4 | 7.902 | 16.199 | |
| Co 27 | Argon | | 7 | 2 | | | | | $^4F_{9/2}$ | 7.881 | 17.084 | |
| Ni 28 | | 배열 | 8 | 2 | | | | | 3F_4 | 7.640 | 18.169 | |
| Cu 29 | | | 10 | 1 | | | | | $^2S_{1/2}$ | 7.726 | 20.292 | |
| Zn 30 | | | 10 | 2 | | | | | 1S_0 | 9.394 | 17.964 | |
| Ga 31 | | | 10 | 2 1 | | | | | $^2P_{1/2}^o$ | 5.999 | 20.515 | |
| Ge 32 | | | 10 | 2 2 | | | | | 3P_0 | 7.899 | 15.935 | |
| As 33 | | | 10 | 2 3 | | | | | $^4S_{3/2}^o$ | 9.789 | 18.589 | |
| Se 34 | | | 10 | 2 4 | | | | | 3P_2 | 9.752 | 21.196 | |
| Br 35 | | | 10 | 2 5 | | | | | $^2P_{3/2}^o$ | 11.814 | 21.591 | |
| Kr 36 | | | 10 | 2 6 | | | | | 1S_0 | 14.000 | 24.360 | |

The subshell structure of elements up to argon ($Z = 18$) is filled up in a naturally straightforward manner, first according to n and then according to ℓ .

The 3p subshell is all occupied in argon (noble gas) with a closed sub shell $3p^6$. The next element potassium (K) ($Z = 19$), begins by filling in the 4s, instead of 3d.



[The Electrostatic Interaction, LS coupling, Terms]

- **The Electrostatic Interaction**

The specification of the electron configuration (the n, l values of all electrons) leaves a great deal of unspecified information, since we are not given the values of m_l and m_s . In the central field approximation all of these states are degenerate.

The exact Hamiltonian can be written as

$$\begin{aligned}
 H &= \sum_{i=1}^N \left(\frac{P_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i=1}^N \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + H_{\text{so}} \\
 &= \sum_{i=1}^N \left(\frac{P_i^2}{2m} + V_i(r_i) \right) + \sum_{i=1}^N \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{j \neq i} \left\langle \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle + H_{\text{so}} \\
 &= H_0 + H_{\text{es}} + H_{\text{so}}
 \end{aligned}$$

where $V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j \neq i} \left\langle \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle$

$H_0 \equiv$ central field approximation

$$H_{\text{es}} \equiv \sum_{i=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{j \neq i} \left\langle \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle$$

= electrostatic interaction

$H_{\text{so}} \equiv$ spin-orbit interaction

The term H_{es} represents the residual electrostatic interaction between electrons after the averaged central field has been subtracted.

The term H_{so} is the spin-orbit interaction, which causes the fine structure splitting.

- **LS coupling (Russell-Saunders coupling): Spectroscopic Terms**

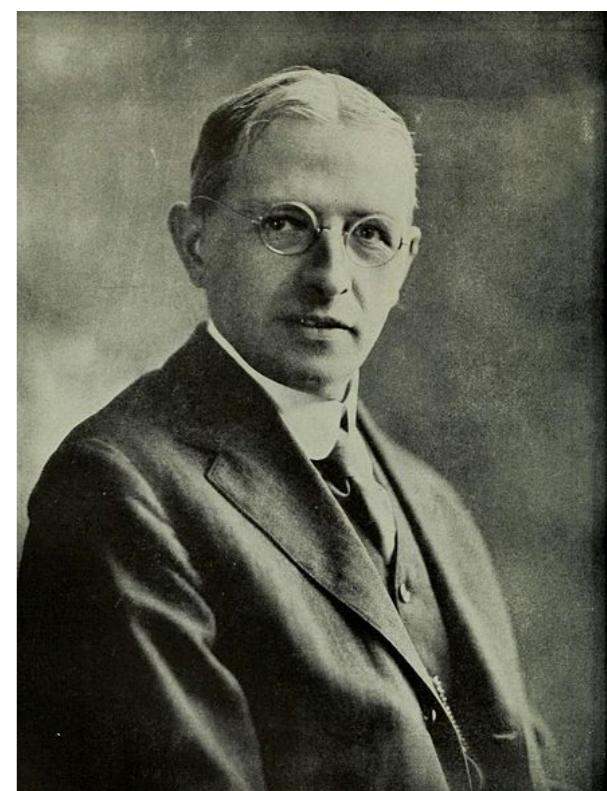
- The electrostatic interaction is the dominant splitting interaction of a configuration for many atoms (especially of low Z).
- The individual orbital angular momenta will not remain constant under this interaction, although their total $L = \sum_i l_i$ will be constant.

Also the sum of the spin angular momenta, $S = \sum_i s_i$, will be constant.

- The orbital and spin angular momenta of the electrons are added separately to give the total orbital angular momentum and the total electron spin angular momentum.
- According to perturbation theory, the configurations split into terms with particular values of L and S. These terms then split further by the action of the spin-orbit interaction.
- Physical origin of the electrostatic splitting: The electrons repel each other, and therefore their mutual electrostatic energy is positive. *The farther away the electrons get, the lower will be the contribution of the (positive) electrostatic energy to the total energy.*
 - ◆ A large spin implies that the individual spins are aligned in the same direction. Then, the electrons will be further apart on the average by the nature of the Pauli principle. Terms with larger spin tend to lie lower in energy because of lower, positive electrostatic energies.
 - ◆ There is a similar effect regarding the orbital angular moment. This effect is usually smaller than for the spin.
 - ◆ ⇒ The above two properties give rise to the so called Hund's rule.

Angular Momentum Coupling

- Atoms contain several sources of angular momentum.
 - electron orbital angular momentum L
 - electron spin angular momentum S
 - nuclear spin angular momentum I
 - The nuclear spin arises from the spins of nucleons. Protons and neutrons both have an intrinsic spin of a half.
- As in classical mechanics, only the total angular momentum is a conserved quantity.
 - It is therefore necessary to combine angular momenta together.
- Addition of two angular momenta:
 - The orbital and spin angular momenta are added vectorially as $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This gives the total electron angular momentum.
 - One then combines the total electron and nuclear spin angular momenta to give the final angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$.



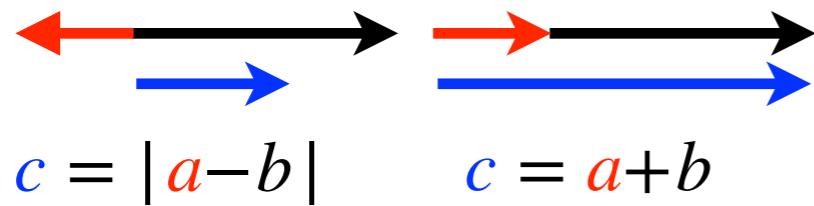
Henry Norris Russell

Hertzsprung-Russell diagram
Russell-Saunders coupling

Addition of two angular momenta

- In classical mechanics, adding vector a and vector b gives a vector c , whose length must lie in the range

$$|a - b| \leq c \leq a + b \quad \text{Here, } a, b, c \text{ are the lengths of their respective vectors.}$$



- In quantum mechanics, a similar rule applies except that the results are quantized. The allowed values of the quantized angular momentum, c , span the range from the sum to the difference of a and b in steps of one:

$$c = |a - b|, |a - b| + 1, \dots, a + b - 1, a + b$$

- For example, add the two angular momenta $L_1 = 2$ and $L_2 = 3$ together to give $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$. The result is

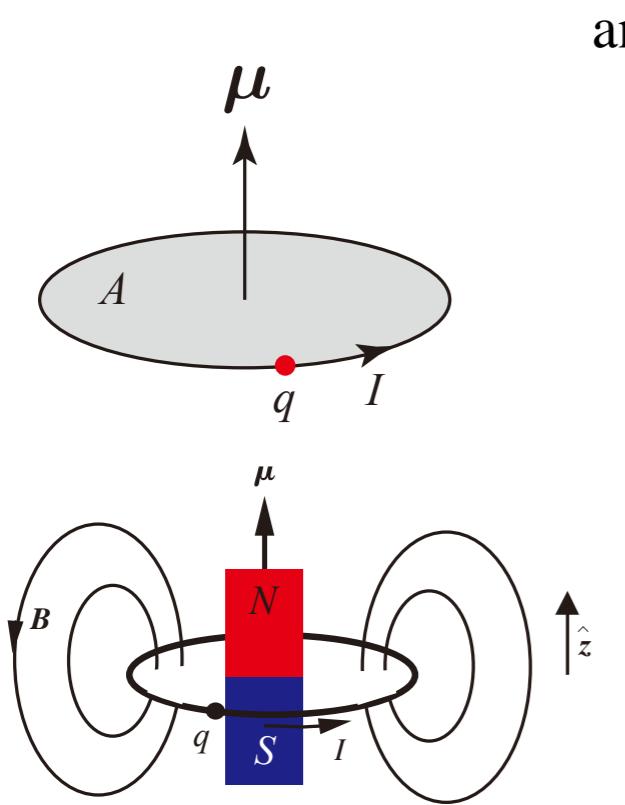
$$L = 1, 2, 3, 4, 5.$$

- Each angular momentum has z -components of. $m = -L, -L + 1, \dots, L, L + 1$.

[Magnetic moments]

- Relation between the magnetic moment and angular momentum

Consider a charge q with mass m that orbits in a circle at radius r about the z -axis with angular velocity ω .



angular momentum

$$\begin{aligned} \mathbf{J} &= \mathbf{r} \times \mathbf{p} \\ &= r \times (mv)\hat{\mathbf{z}} \\ &= mr^2\omega\hat{\mathbf{z}} \end{aligned}$$

magnetic momentum

$$\begin{aligned} \mu &= IA\hat{\mathbf{z}} \\ \text{current } I &= \frac{dq}{dt} = \frac{q}{P} = \frac{q\omega}{2\pi} \\ \text{area } A &= \pi r^2 \\ \mu &= \frac{1}{2}q\omega r^2\hat{\mathbf{z}} \end{aligned}$$

↑
period $P = \omega/2\pi$

Consequently, the classical relation between magnetic moment and angular momentum for an orbiting charge is

$$\mu = \frac{q}{2m}\mathbf{J}$$

Now consider a spinning sphere with uniform mass and charge distributions. It consists of many orbiting charge and mass elements, each obeying the above equation. Thus, the equation is also valid for the entire sphere.

In quantum mechanics, **the magnetic moment of the electron**, which is a point charge with zero radius, is given by

$$\boldsymbol{\mu}_e = -g_e \frac{e}{2m_e} \mathbf{S} \quad (\text{where } g_e = 2.0 \text{ in Dirac equation})$$

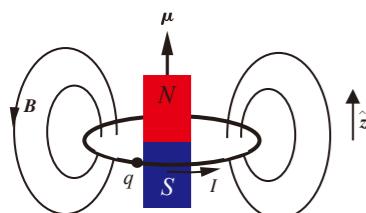
The magnetic moment of the electron is opposed to the direction of the spin \mathbf{S} , because of the negative charge.

Magnetic dipole in a magnetic field

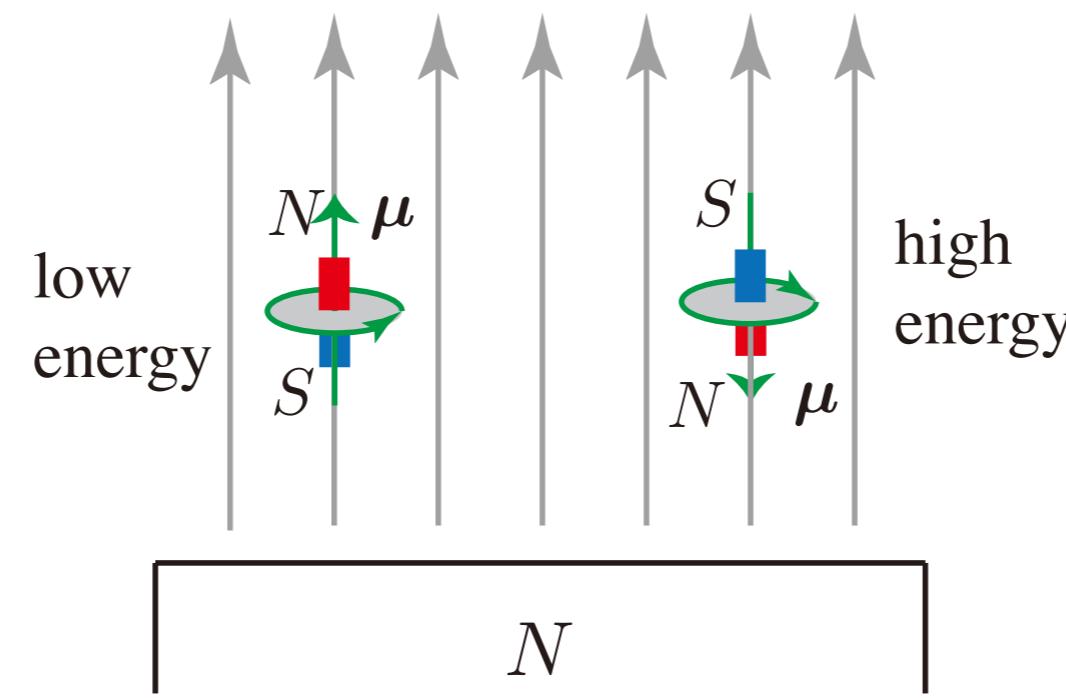
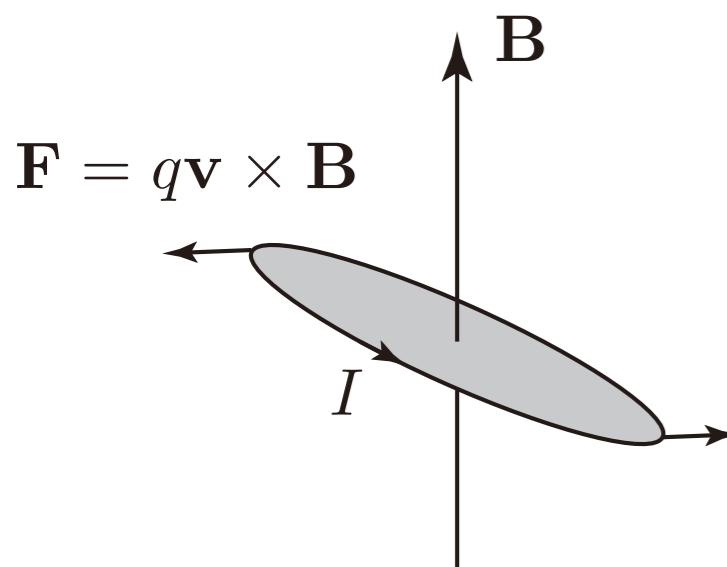
- A magnetic dipole will tend to align with an external magnetic field just as a compass needle aligns itself with the magnetic field of the earth.

One can visualize the external field acting on a magnet. This magnet experiences a torque tending to align it with the \mathbf{B} field.

Integration of this torque over the appropriate angles yields a potential energy that is a function of the angle θ between the magnetic field \mathbf{B} and magnetic moment μ vector. The lowest potential energy occurs when the two vectors are aligned. The potential energy E_{pot} turns out to be the negative dot product of the vectors μ and \mathbf{B} :



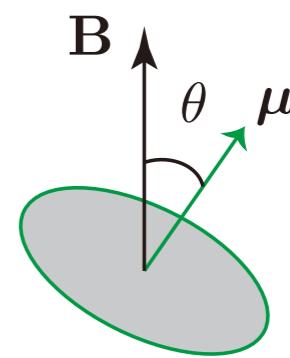
$$E_{\text{pot}} = -\mu \cdot \mathbf{B} = -\mu B \cos \theta$$



$$\text{torque } \tau = \mathbf{r} \times \mathbf{F}$$

$$E_{\text{pot}} < 0 \quad \text{if } \theta < \frac{\pi}{2}$$

$$E_{\text{pot}} > 0 \quad \text{if } \theta > \frac{\pi}{2}$$



$$E_{\text{pot}} = -\mu \cdot \mathbf{B}$$

[Spin-Orbit Coupling]

- The fact that the remaining spin-orbit splitting is much smaller makes the LS coupling scheme a very useful one.
- **Fine-structure splitting:** Relativistic effects couple electron orbital angular momentum and electron spin to give the so-called fine structure in the energy levels. Inclusion of relativistic effects splits the **terms** into **levels** according to their J value.
- When the electron will move around the nucleus with a non relativistic velocity \mathbf{v} , the electric field exerting on the electron will be $\mathbf{E} = Ze\frac{\mathbf{r}}{r^3}$. (Note that the nucleus has a positive charge Ze .)

In the electron rest frame, this electric field will be perceived as a magnetic field

$$\begin{aligned}\mathbf{B}' &= \mathbf{B}'_{\perp} = \gamma(\mathbf{B}_{\perp} - \boldsymbol{\beta} \times \mathbf{E}) = -\frac{\mathbf{v}}{c} \times \mathbf{E} \\ &= -\frac{Ze}{c} \frac{\mathbf{v} \times \mathbf{r}}{r^3} \\ &= \frac{Ze}{m_e c r^3} \mathbf{L} \quad (\mathbf{L} = \mathbf{r} \times \mathbf{p})\end{aligned}$$

Here, the magnetic field is perpendicular to the electron's orbital plane.

(where $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p} = m_e \mathbf{r} \times \mathbf{v}$ is the electron's orbital angular momentum)

- This magnetic field will interact with the electron's **magnetic moment**, which is

$$\boldsymbol{\mu} = -\frac{e}{m_e c} \mathbf{S} = 2\boldsymbol{\mu}_{\text{classical}}$$

definition of magnetic moment:

- Then, the interaction energy is

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{Ze^2}{m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

- For the sum of the interactions of all electrons will be

$$H_{\text{so}} = \xi (\mathbf{S} \cdot \mathbf{L})$$

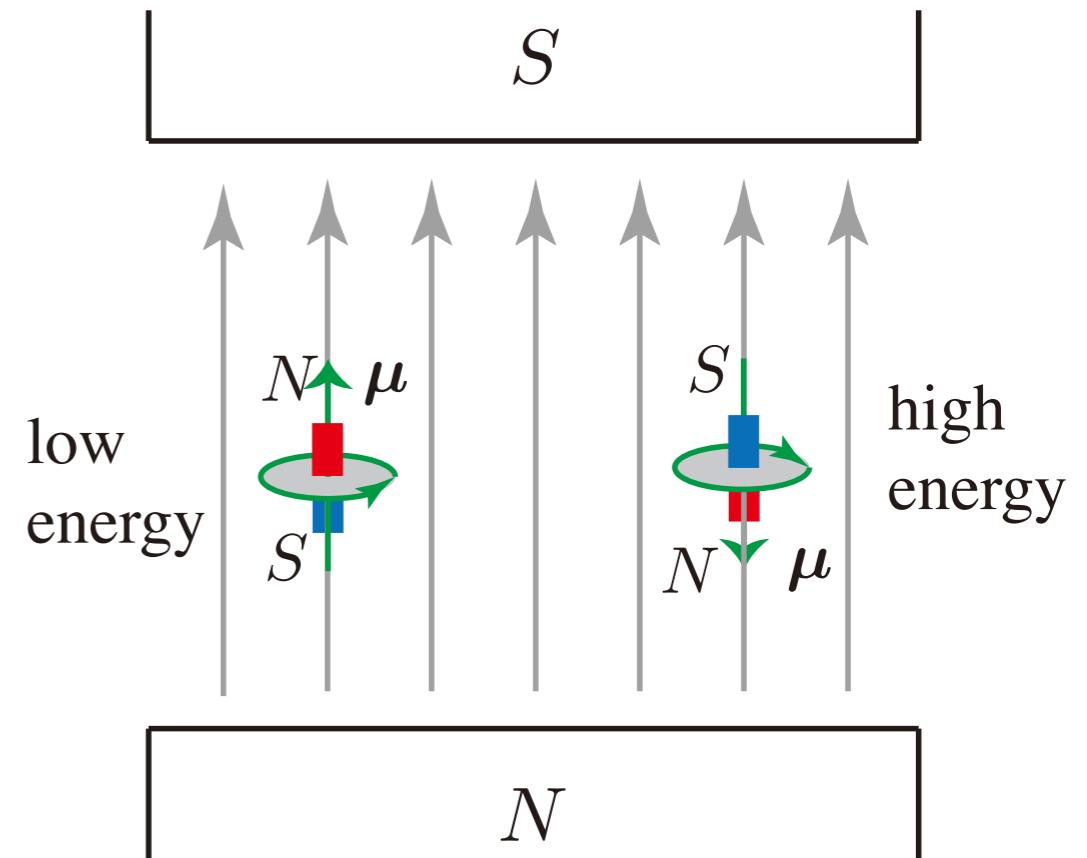
From the relation $\mathbf{J}^2 = |\mathbf{L} + \mathbf{S}|^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{S} \cdot \mathbf{L}$,

we obtain

$$H_{\text{so}} = \frac{1}{2}\xi (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

The eigen energy of the operator is given by

$$E_{\text{so}} = \frac{1}{2}C [J(J+1) - L(L+1) - S(S+1)]$$



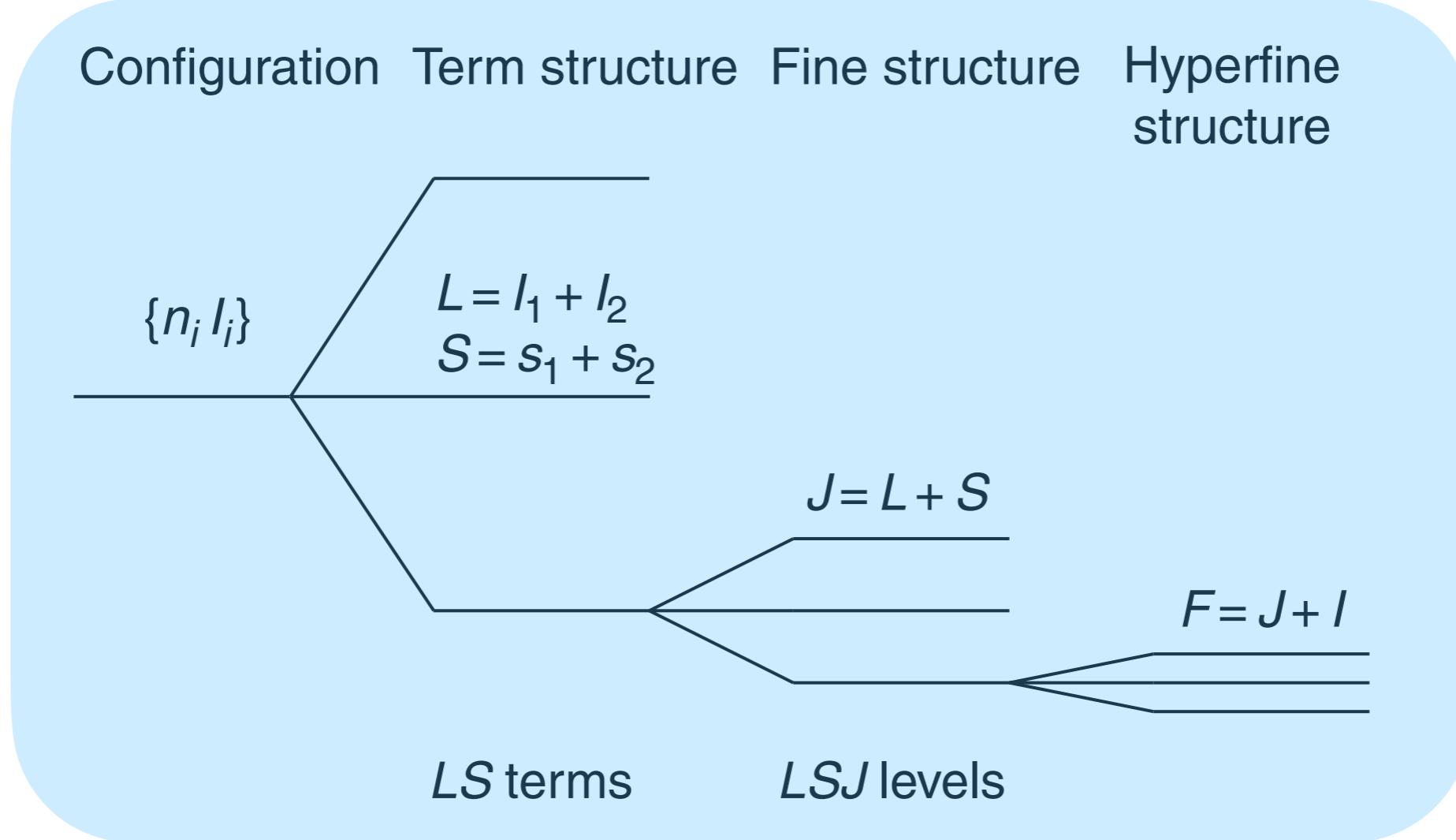
Note that

$$E_{\text{so}} = 0 \text{ for } L = 0 \text{ because } J = S$$

Therefore, there will be no fine structure for $L = 0$.

- Electronic configuration and energy level splitting

Configurations \Rightarrow Terms \Rightarrow Fine Structure (Spin-Orbit Interaction) \Rightarrow Hyperfine Structure (Interaction with Nuclear Spin)



- **Active electrons:** As a result of the Pauli Principle, closed shells and sub-shells have both $L = 0$ and $S = 0$. This means that it is only necessary to consider ‘active’ electrons, those in open or partially-filled shells.
- **Parity of the wave function**

The parity of the wave function is determined by how the wave function behaves upon inversion. The square of the wave function, i.e., the probability distribution of the electrons, must be unchanged by the inversion operation.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \pm \Psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N)$$

Even parity states are given by + sign and odd parity states are given by - sign.

The parity arising from a particular configuration can be determined simply by summing the orbital angular momentum quantum numbers for each of the electrons.

$$(-1)^{l_1+l_2+\dots+l_N}$$

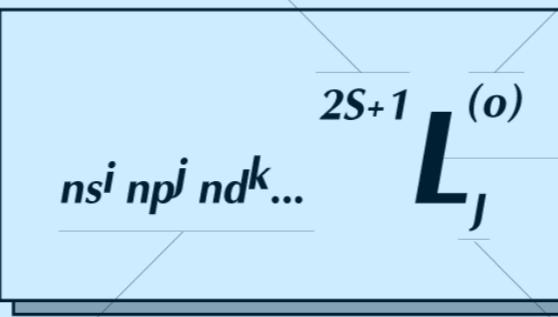
As closed shells and sub-shells have an even number of electrons, it is only necessary to explicitly consider the active electrons.

Spectroscopic Notation

- Spectroscopic Notation

Total Term Spin Multiplicity:
 S is vector sum of electron spins ($\pm 1/2$ each)
 Inner full shells sum to 0

Term Parity:
 o for odd, nothing for even



Total Term Orbital Angular Momentum:
 Vector sum of contributing electron orbitals.
 Inner full shells sum to 0.

The Number of levels in a term is the smaller of $(2S+1)$ or $(2L+1)$

Total Level Angular Momentum:
 Vector sum of L and S of a particular level in a term.

Electronic Configuration:
 the electrons and their orbitals
 (i.e. $1s^2 2s^2 3p^1$)

- A state with $S = 0$ is a ‘singlet’ as $2S+1 = 1$.
 - ▶ $J = L$ (singlet)
- A state with $S = 1/2$ is a ‘doublet’ as $2S+1 = 2$
 - ▶ $J = L - 1/2, L + 1/2$ (doublet if $L \geq 1$)
- One with $S = 1$ is a ‘triplet’ as $2S+1 = 3$
 - ▶ $J = L - 1, L, L + 1$ (triplet $L \geq 1$)

$$n = 1, 2, 3, 4, 5, \dots \rightarrow K, L, M, N, O, \dots$$

$$\ell = 0, 1, 2, 3, 4, \dots \rightarrow s, p, d, f, g, \dots$$

$$L = 0, 1, 2, 3, 4, \dots \rightarrow S, P, D, F, G, \dots$$

sharp, principal, diffuse, fundamental,...

Energy ordering for Terms and Levels

- Energy ordering: **Hund's rules**

Note that $H_{\text{so}} = \frac{1}{2}\xi(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$

- (1) **S-rule:** For a given configuration, the state with the maximum spin multiplicity is lowest in energy.

The electrons repel each other, and therefore their mutual electrostatic energy is positive. The farther away the electrons get, the lower will be the contribution of the electrostatic energy to the total energy.

- (2) **L-rule:** For a given configuration and spin multiplicity, the state with the maximum orbital angular momentum is the lowest in energy.

- (3) **J-rule:** The lowest energy is obtained for lowest value of J in the normal case and for highest J value in the inverted case.

The normal case is a shell which is less than half filled. The inverted case is a shell which is more than half full such as the ground state of atomic oxygen.



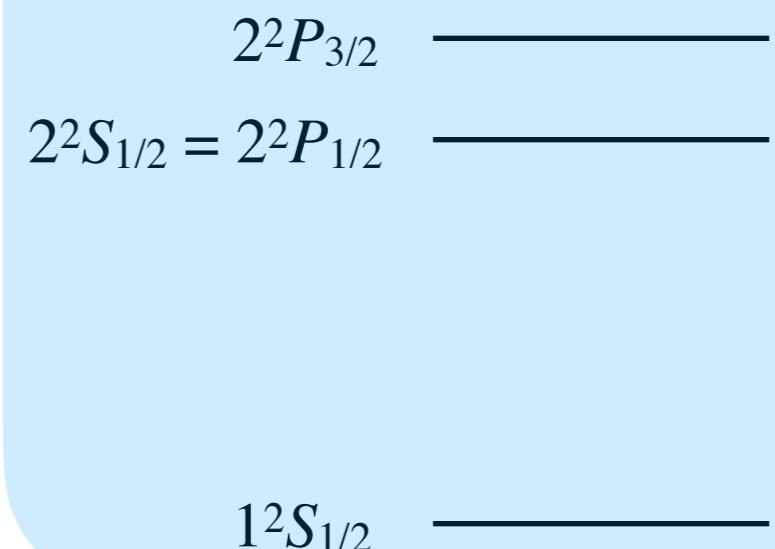
- The Hund's rules are only applicable within LS coupling. They are only rigorous for ground states. However, they are almost always useful for determining the energy ordering of excited states. The rules show increasing deviations with higher nuclear charge.

[Hydrogen Atom - Fine Structure]

- Fine structure of the hydrogen atom

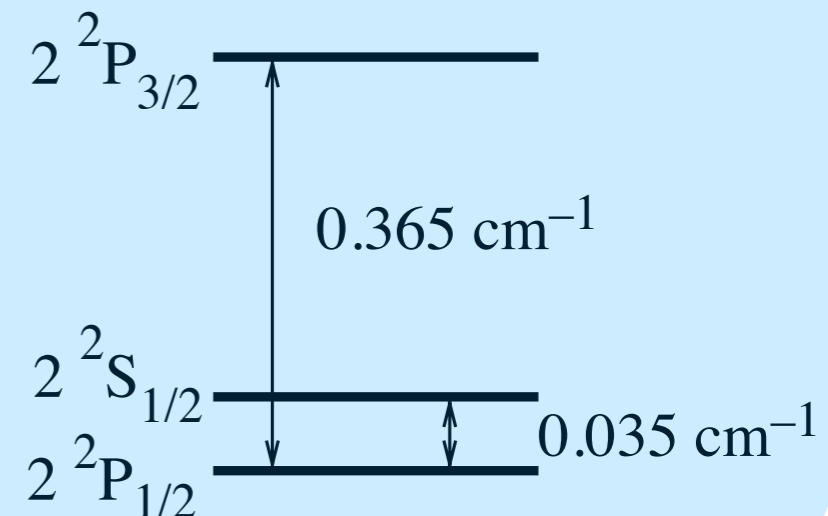
| configuration | L | S | J | term | level |
|---------------|---|-------|------------|---------|----------------------------|
| ns | 0 | $1/2$ | $1/2$ | 2S | $^2S_{1/2}$ |
| np | 1 | $1/2$ | $1/2, 3/2$ | $^2P^o$ | $^2P_{1/2}^o, ^2P_{3/2}^o$ |
| nd | 2 | $1/2$ | $3/2, 5/2$ | 2D | $^2D_{3/2}, ^2D_{5/2}$ |
| nf | 3 | $1/2$ | $5/2, 7/2$ | $^2F^o$ | $^2F_{5/2}^o, ^2D_{7/2}^o$ |

Relativistic QM (Dirac's eq)



- Splitting in the $n = 2$ levels of atomic hydrogen. The larger splitting is the fine structure and the smaller one the Lamb shift.
According to the Dirac equation, the $^2S_{1/2}$ and $^2P_{1/2}$ orbitals should have the same energies. However, the interaction between the electron and the vacuum (which is not accounted for by the Dirac equation) causes a tiny energy shift on $^2S_{1/2}$. (Quantum electrodynamics effect)

Quantum Electrodynamics



Hydrogen Atom : Hyperfine Structure

- Hyperfine Structure in the H atom

Coupling the nuclear spin I to the total electron angular momentum J gives the final angular momentum F . For hydrogen this means

$$F = J + I = J \pm \frac{1}{2}$$

