

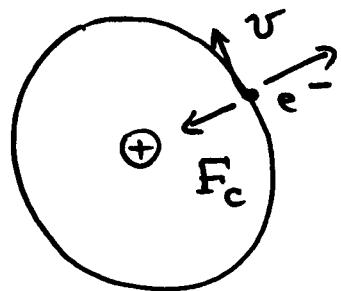
Atomic orbitals

Ch. 4 @ HB

Bohr model

The Rutherford planetary model assumes that electrons are moving around a charged nucleus in circular orbitals

H:



Equilibrium condition:

$$\sum_i \vec{F}_i = 0$$

$$-\frac{e^2}{4\pi\epsilon_0 r^2} + \frac{mv^2}{r} = 0$$

$$E = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r}$$

Bohr assumption: angular momentum is quantized

$$mv r = \hbar n$$

$$m^2 v^2 = \frac{m e^2}{4\pi\epsilon_0 r} = \frac{\hbar^2 n^2}{r^2}$$

$$E_0 = \frac{e^2}{4\pi\epsilon_0 a_0} = 27.211 \text{ eV} =$$

$$= 627.51 \text{ kcal/mol}$$

$$= 1 \text{ Hartree}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

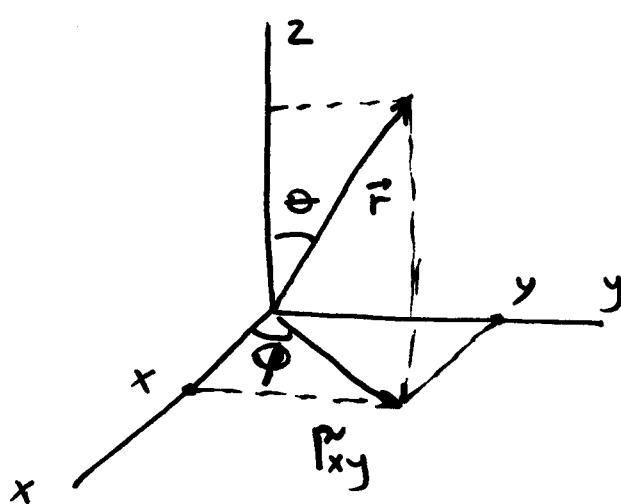
$$= 0.529 \text{ \AA}$$

Hydrogen atom:

$$E_n = -\frac{E_0}{2n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

Angular momentum. Definition.

Polar coordinates (p. 111 @ HB)



$$z = r \cos \theta$$

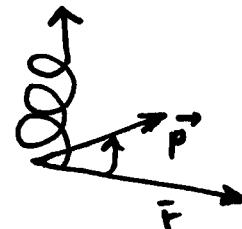
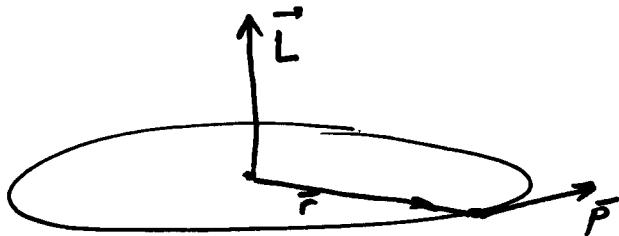
$$r_{xy} = r \sin \theta$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

In classical mechanics:

$$\vec{L} = \vec{r} \times \vec{p}$$



$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

In quantum mechanics:

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Example: $\hat{L}_x y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) y = i\hbar z$

Homework: Calculate

$$\hat{L}_y \hat{L}_x (z^2 y)$$

Commutation relations

$$\begin{aligned}\hat{L}_x \hat{L}_y f &= -\hbar^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial z} \right) = \\ &= -\hbar^2 \left[y \frac{\partial^2 f}{\partial x \partial z} + yz \frac{\partial^2 f}{\partial x \partial z} - z^2 \frac{\partial^2 f}{\partial y \partial x} - xy \frac{\partial^2 f}{\partial z^2} + zx \frac{\partial^2 f}{\partial y \partial z} \right]\end{aligned}$$

$$\begin{aligned}\hat{L}_y \hat{L}_x f &= -\hbar^2 \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \left[y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right] \\ &= -\hbar^2 \left[zy \frac{\partial^2 f}{\partial x \partial z} - z^2 \frac{\partial^2 f}{\partial x \partial y} - xy \frac{\partial^2 f}{\partial z^2} + x \frac{\partial^2 f}{\partial y \partial z} - xz \frac{\partial^2 f}{\partial z \partial y} \right]\end{aligned}$$

$$(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) f = -\hbar^2 \left[y \frac{\partial^2 f}{\partial x \partial z} - x \frac{\partial^2 f}{\partial y \partial z} \right] = i\hbar \hat{L}_z f$$

$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$

\hat{L}_x and \hat{L}_y do not commute:
x and y projections of the
angular momentum cannot
be observed simultaneously!

By cyclic permutation of x, y, and z one gets
other commutation rules:

$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$

Commutator with \hat{L}^2

$$\begin{aligned}
 [\hat{L}^2, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\
 &= \hat{L}_y [\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x] \hat{L}_y + \hat{L}_z [\hat{L}_z, \hat{L}_x] + \\
 &\quad + [\hat{L}_z, \hat{L}_x] \hat{L}_z = -\hat{L}_y i\hbar \hat{L}_z - i\hbar \hat{L}_z \hat{L}_y + \\
 &\quad + \hat{L}_z i\hbar \hat{L}_y + i\hbar \hat{L}_y \hat{L}_z = 0
 \end{aligned}$$

Homework: Check that $[\hat{L}_i^2, \hat{L}_j] = [\hat{L}_i^2, \hat{L}_k] = 0$!

\hat{L}^2 and one component can be observed simultaneously.
Traditionally one considers \hat{L}_z and \hat{L}^2 .

$\hat{L}_{x,y,z}$ in polar coordinates:

$$\hat{L}_x = i\hbar \left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right)$$

$$\hat{L}_y = -i\hbar \left(\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

Eigenfunctions of \hat{L}_z and \hat{L}^2

$$\hat{L}_z Y(\theta, \varphi) = b Y(\theta, \varphi)$$

$$Y(\theta, \varphi) = S(\theta) \Phi(\varphi)$$

$$\hat{L}^2 Y(\theta, \varphi) = c Y(\theta, \varphi)$$

$$-i\hbar \frac{d\Phi(\varphi)}{d\varphi} = b\Phi(\varphi)$$

$$\Phi(\varphi) = A e^{i\theta\varphi/\hbar}, \quad \Phi(\varphi + 2\pi) = \Phi(\varphi) \rightarrow b = m\hbar$$

$$Y(\theta, \varphi) = A S(\theta) e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$\begin{aligned} \hat{L}^2 Y(\theta, \varphi) &= -A\hbar^2 e^{im\varphi} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} S(\theta) - \frac{m^2}{\sin^2\theta} S(\theta) \right] = \\ &= c A e^{im\varphi} S(\theta) \end{aligned}$$

$$\frac{d^2S}{d\theta^2} + \cot\theta \frac{dS}{d\theta} - \frac{m^2}{\sin^2\theta} S = -\frac{c}{\hbar^2} S$$

The solution of the above equation is

$$S_{e,m} = \left[\frac{(2e+1)}{2} \frac{(e-lm)!}{(e+lm)!} \right]^{\frac{1}{2}} \underline{\underline{P_e^{lm}(\cos\theta)}}$$

associated Legendre
Polynomials

$$Y_{em}(\theta, \varphi) = \frac{1}{\sqrt{2\pi}} S_{em}(\theta) e^{im\varphi}$$

← spherical function

Angular momentum summary

The angular momentum is characterized by two quantum numbers, l and m

$$\hat{L}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi)$$

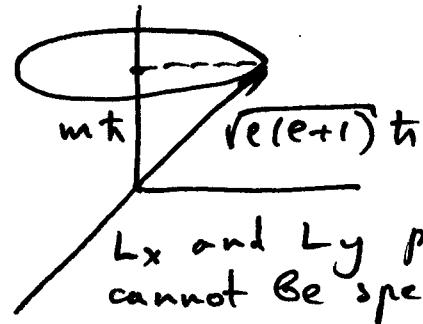
$$\hat{L}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi)$$

magnetic quantum number

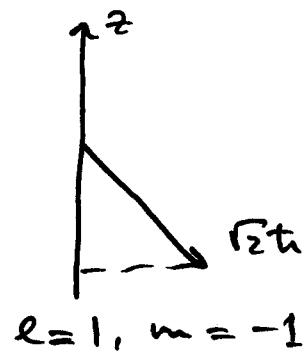
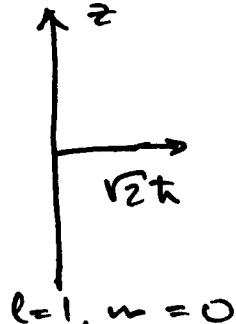
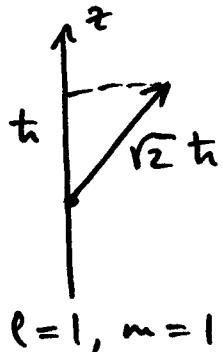
azimuthal quantum number
 $l = 0, 1, 2, \dots$

$$m = -l, -l+1, \dots, 0, 1, \dots, l$$

$2l+1$



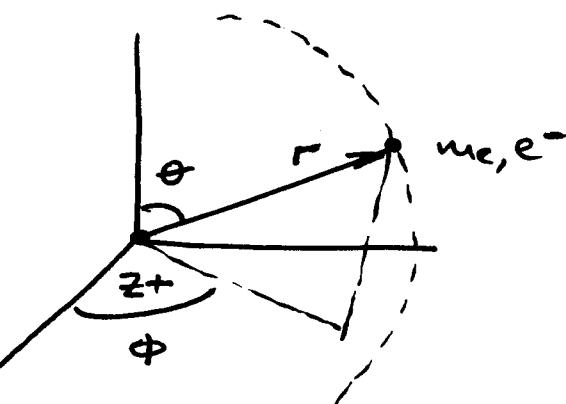
$l=1$:



Homework: Draw a similar picture for $l=2$

Homework: Show that the spherical functions are eigenfunctions of $\hat{L}_x^2 + \hat{L}_y^2$. Find the eigenvalues.

Hydrogen atom



$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{ze^2}{4\pi\epsilon_0 r}$$

Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In the spherical coordinates:

$$\nabla^2 = \nabla_r^2 - \frac{1}{r^2 h^2} \vec{L}^2$$

defines the radial extent
of the wave-function

defines the angular distribution
of the electronic density

Solution of the Schrödinger equation:

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

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{e(e+1)\hbar^2}{2mr^2} - \frac{ze^2}{4\pi\epsilon_0 r} \right] R_{nl} = E_n R_{nl}$$

$n = 1, 2, 3, 4, \dots$ ← principle quantum number

$l = 0, 1, 2, \dots, n-1$ ← azimuthal quantum number

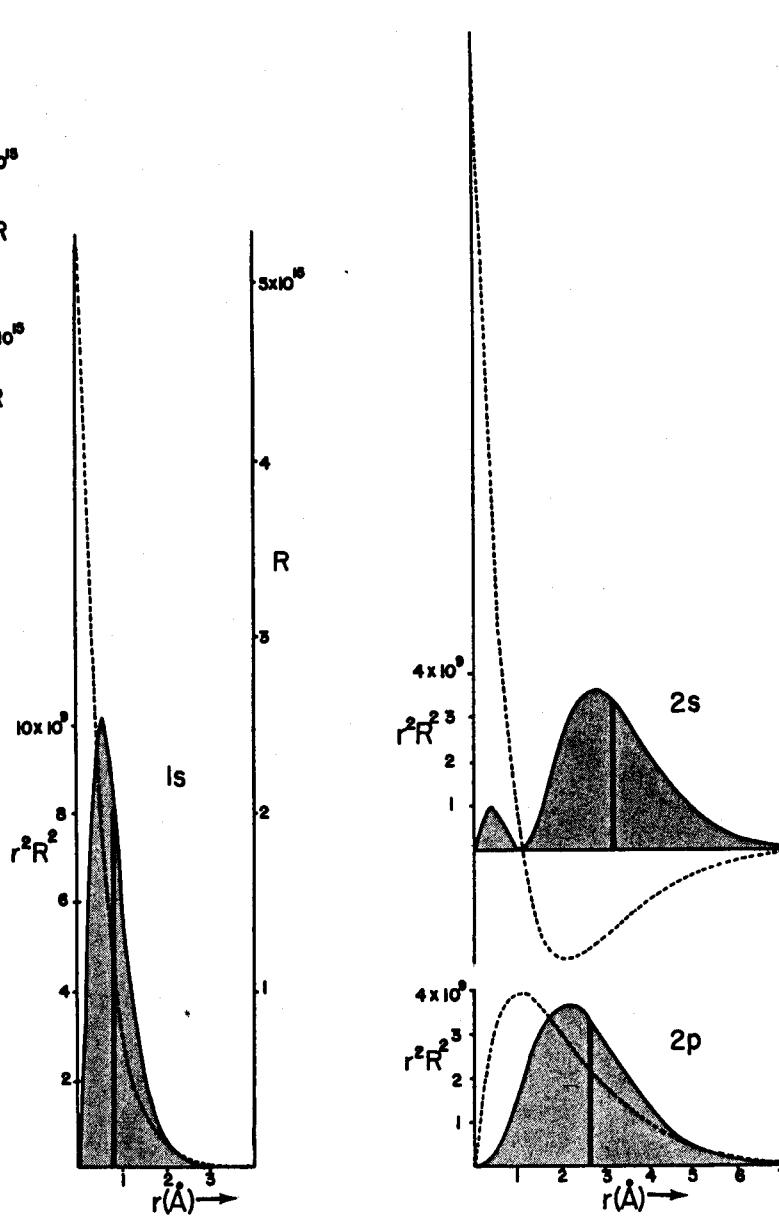
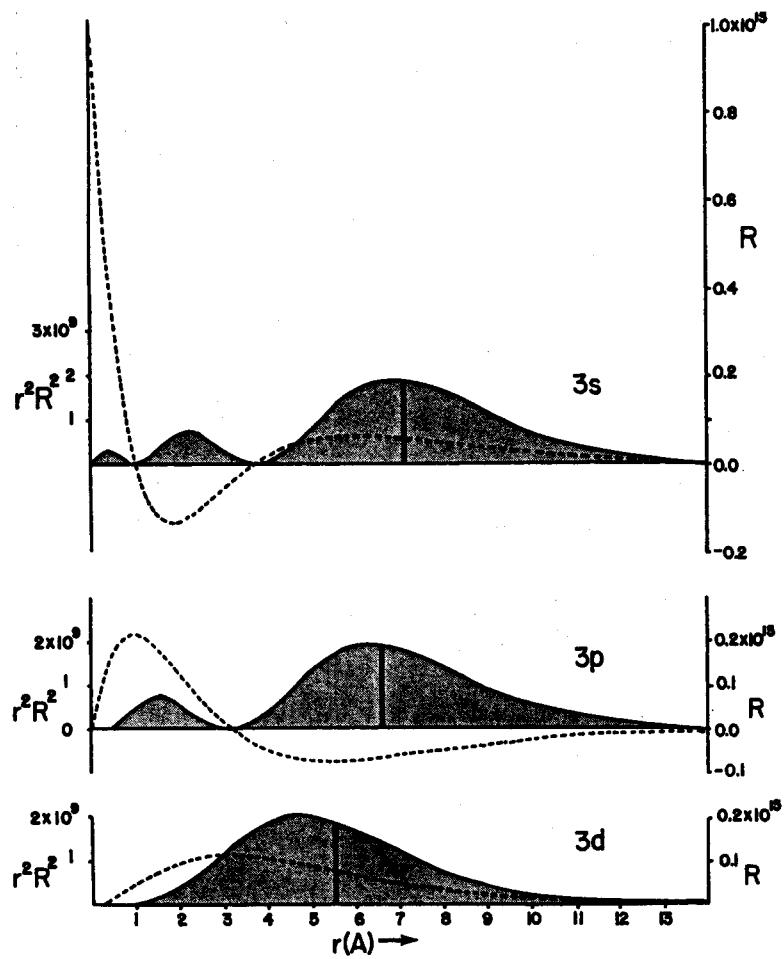
$m_l = -l, \dots, 0, \dots, l$ ← magnetic quantum number

$$E_n = -\frac{ze^2}{2a_0 n^2} = -\frac{z^2 \text{ Hartree}}{2n^2}$$

$$\max(L^2) = \hbar^2 n(n-1) \quad \left. \right\} \quad \begin{aligned} \max(L_x) &= (n-1)\hbar \\ L^2 &= n^2 \hbar^2 \end{aligned} \quad \begin{aligned} \text{instead of Bohr's} \\ L^2 = n^2 \hbar^2 \end{aligned}$$

charge of the nucleons

Radial wave functions



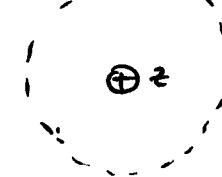
Angular wave functions

$$n=1, \ell=0, m=0$$

$$\Psi(1s) = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$R_{10} = 2 \left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$$



$$n=2, \ell=1, 0, m=-1, 0, 1$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

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

$$Y_{11} = -\sqrt{\frac{3}{4\pi}} \frac{\sin\theta}{\sqrt{2}} e^{i\phi}$$

$$R_{21} = \frac{1}{2\sqrt{6}} \left(\frac{z}{a_0}\right)^{5/2} r e^{-zr/2a_0}$$

$$Y_{1-1} = -\sqrt{\frac{3}{4\pi}} \frac{\sin\theta}{\sqrt{2}} e^{-i\phi}$$

$$\Psi_{2s} = R_{20} Y_{00},$$

$$\Psi_{2p_z} = R_{21} Y_{11}$$

$$\Psi_{2p_0} = R_{21} Y_{10}$$

$$\Psi_{2p_{-1}} = R_{21} Y_{1-1}$$

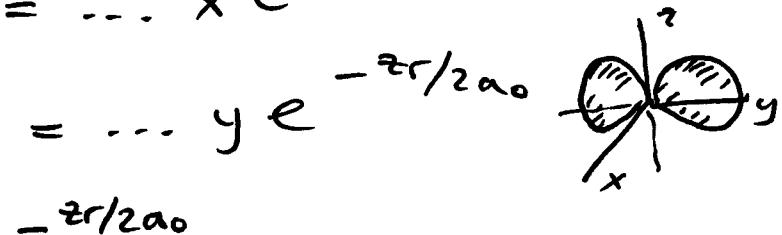
eigenfunctions
of \hat{L}^2 and \hat{L}_z

Forming real wave-functions:

$$\Psi_{2p_x} = \frac{1}{\sqrt{2}} (\Psi_{2p_{-1}} + \Psi_{2p_1}) = \dots x e^{-zr/2a_0}$$

$$\Psi_{2p_y} = \frac{1}{\sqrt{2}i} (\Psi_{2p_1} - \Psi_{2p_{-1}}) = \dots y e^{-zr/2a_0}$$

$$\Psi_{2p_z} = \Psi_{2p_0} = \dots z e^{-zr/2a_0}$$



$$\underline{n=3}, \quad l=0, 1, 2, \quad -l \leq m \leq l$$

$$R_{32} = \frac{4}{81\sqrt{30}} \left(\frac{z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{2r}{3a_0}}$$

$$Y_{20} = \sqrt{\frac{5}{4\pi}} \frac{1}{2} (3\cos^2\theta - 1)$$

$$Y_{21} = -\sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{2}} \sin\theta \cos\theta e^{i\phi}, \quad Y_{2-1} = Y_{21}^*$$

$$Y_{22} = \sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{8}} \sin^2\theta e^{2i\phi}, \quad Y_{2-2} = Y_{22}^*$$

Five orbitals: $R_{32} Y_{20}$, $R_{32} Y_{21}$, $R_{32} Y_{2-1}$,
 $R_{32} Y_{22}$, $R_{32} Y_{2-2}$

Real wave-functions:

$$\begin{aligned} \Psi_{3d_{x^2-y^2}} &= \frac{1}{\sqrt{2}} R_{32} (Y_{22} + Y_{-2}) = \dots \sin^2\theta \cos 2\phi \\ &= \dots \sin^2\theta (\cos^2\phi - \sin^2\phi) = \dots (x^2 - y^2) \end{aligned}$$

Homework: Build the wave-function $\Psi_{3d_{xz}}$ and plot its contour in the xz -plane at $r=a_0, z=1$

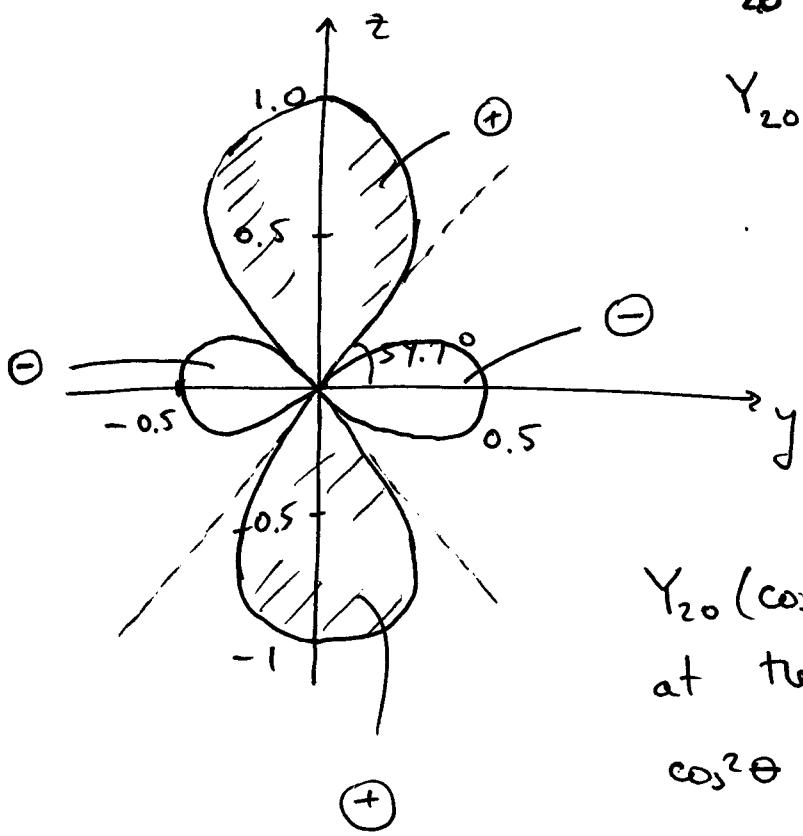
$3d_{z^2}$

$$\Psi_{3d_{z^2}} = R_{32} Y_{20} (\cos \theta)$$

$$Y_{20} (\cos \theta) = \frac{1}{2} (3\cos^2 \theta - 1)$$

$$Y_{20} (\theta = 0^\circ) = 1$$

$$Y_{20} (\theta = 90^\circ) = -\frac{1}{2}$$



$$Y_{20} (\cos \theta) = 0$$

at the "magic" angle:

$$\cos^2 \theta = \frac{1}{3}$$

$$\theta = 54.7^\circ$$

Atomic States

Total orbital momentum:

$$\vec{L} = \sum_{i=1}^n \vec{L}_i \quad M_L = \sum_{i=1}^n (m_e)_i$$

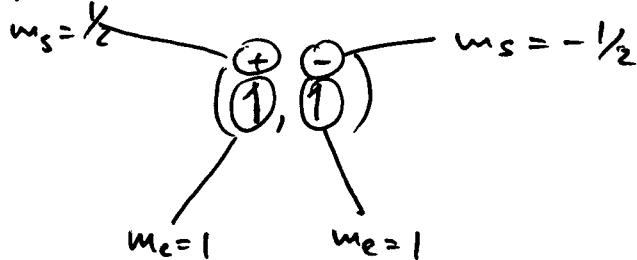
Total spin:

$$\vec{S} = \sum_{i=1}^n \vec{S}_i \quad S = \sum_{i=1}^n (m_s)_i$$

$$M_L = L, L-1, L-2, \dots, -L$$

$$M_S = S, S-1, S-2, \dots, -S$$

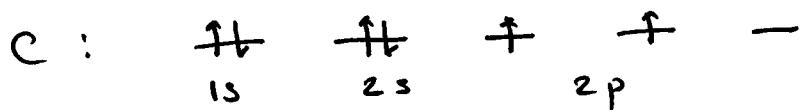
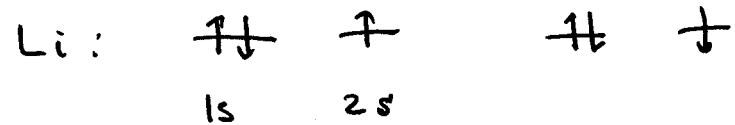
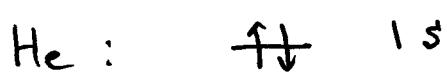
Analysis of microstates of p^2 configuration of C:



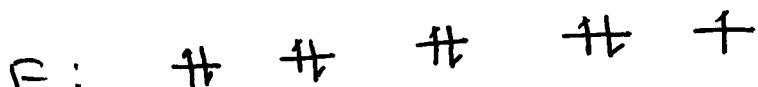
	M_S	1	0	1
M_L				
2			(↑, ↓)	
1		(↑, 0) (0, ↑)	(↑, 0)	
0		(↑, ↓) (↓, ↑)	(↓, ↓)	
-1		(-↑, 0) (-0, ↑)	(-↑ 0)	
-2			(-↑, -↓)	

	M_S	1	0	-1
M_L				
2				1
1		1	2	1
0		1	3	1
-1		1	2	1
-2				1

Electronic configurations



Hund's first rule: The configuration with the greatest number of unpaired spins has the lowest energy.



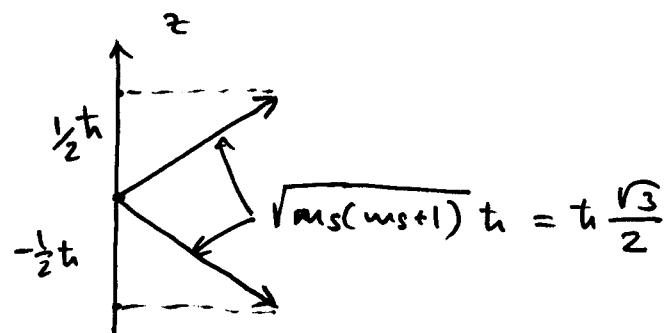
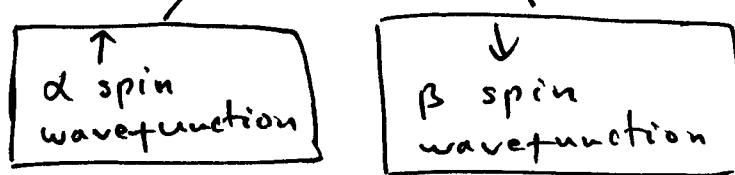
Atomic Configurations

- * The energy of a many-electron orbital depends on both n and ℓ (2 ℓ +1) degenerate

- * The order of orbital energies is :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d \dots$$

- * Electrons have an intrinsic angular momentum called spin. Spin quantum number is $\frac{+1}{2}$ or $\frac{-1}{2}$



- * Pauli exclusion principle: no two electrons in an atom can have the same set of quantum numbers

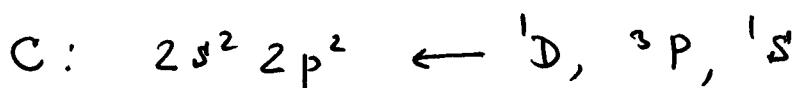
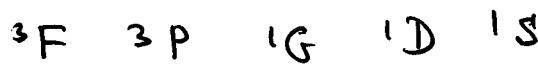
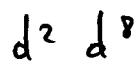
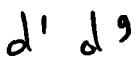
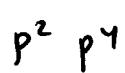
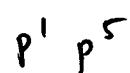
Russell-Saunders (LS) coupling

In the RS scheme the orbital and spin angular momentum separately determine the energy of the state. The atomic state is given by the symbol

$$^{2S+1}L$$

L	0	1	2	3	4	5
Letter	S	P	D	F	G	H

States which arise from common configurations:



Hund's second rule: for states of the same spin multiplicity the state with greater orbital angular momentum will usually be lower in energy.

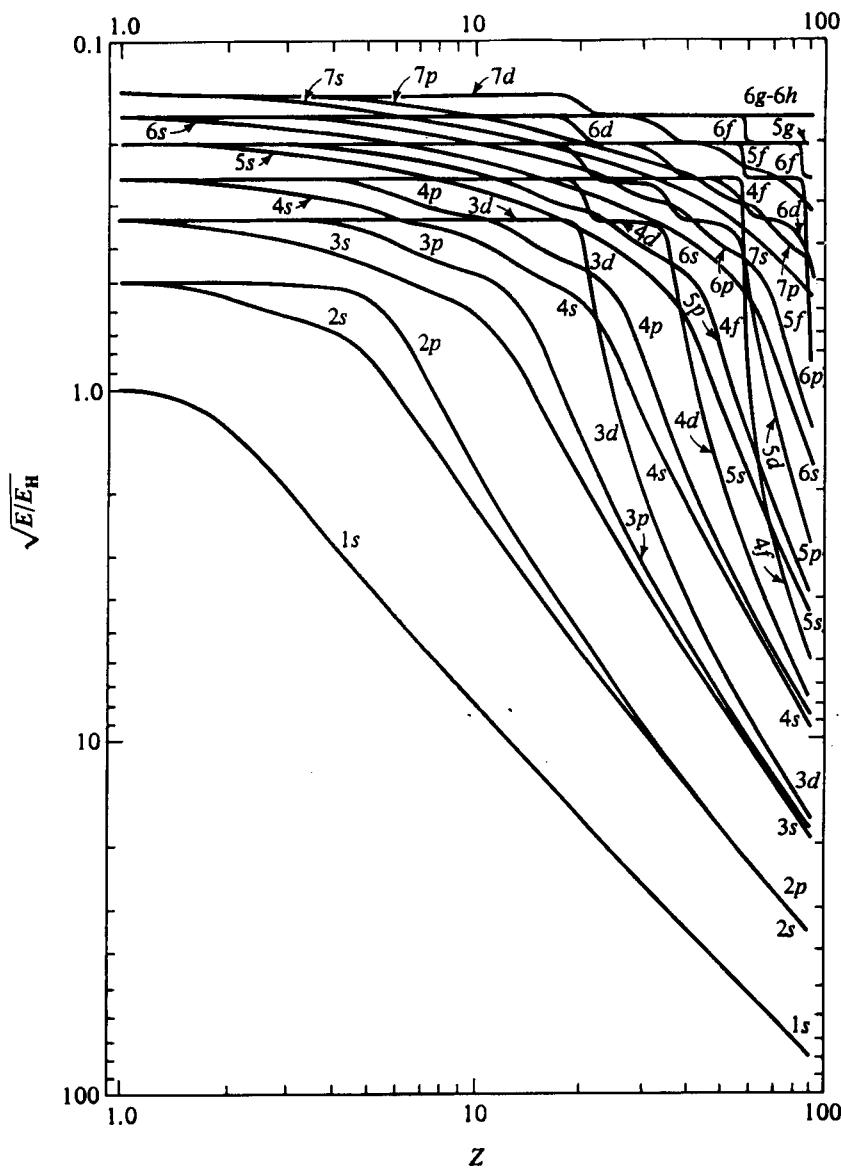


FIGURE 11.2 Atomic-orbital energies as a function of atomic number for neutral atoms, as calculated by Latter. [Figure redrawn by M. Kasha from R. Latter, *Phys. Rev.* **99**, 510 (1955). Used by permission.] Note the logarithmic scales. E_H is the ground-state hydrogen-atom energy, 13.6 eV.

He atom: $1s^2$

Hamiltonian: $H = K_1 + K_2 + \boxed{H_{\text{int}}} + V_1 + V_2$

↑ ↑
kinetic energy

$$H_{\text{int}} = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Total angular momentum operator:

$$\hat{L} = \hat{L}_1 + \hat{L}_2$$

$$H = H_0 + H_{\text{int}} \quad \leftarrow \begin{matrix} \text{non-radial} \\ \text{interaction energy} \end{matrix}$$

radial Hamiltonian

$$\hat{L}_z \frac{1}{r_{12}} = \frac{1}{r_{12}} L_z + \frac{1}{i} \left(\frac{\partial r_{12}^{-1}}{\partial \varphi_1} + \frac{\partial r_{12}^{-1}}{\partial \varphi_2} \right) \quad [L_{z1}, H_0] = 0$$

$$[L_{z2}, H_0] = 0$$

$$[L_1^2, H_0] = [L_2^2, H_0] = 0$$

r_{12} depends on $|\varphi_1 - \varphi_2|$, therefore

$$\frac{\partial r_{12}^{-1}}{\partial \varphi_1} = - \frac{\partial r_{12}^{-1}}{\partial \varphi_2}$$

$$[\hat{L}_z, H] = 0$$

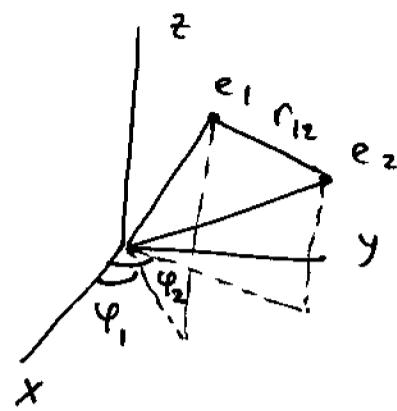
$$[\hat{L}_z, \frac{1}{r_{12}}] = 0$$

L^2 and L_z are constants of motion for many-electron atoms

$$\text{However, } [L_{z1}, \frac{1}{r_{12}}] \neq 0$$

Definite values of ℓ and m_ℓ for individual electrons do not have physical meaning

Coulomb attraction



Total angular momentum

Total angular momentum is the vector sum of the total orbital and spin angular momenta:

$$\vec{J} = \vec{L} + \vec{S}$$

\vec{J} always commute with the Hamiltonian \rightarrow

\vec{J} can be observed in a given electronic state

\vec{L} and \vec{S} commute with \hat{H} only when the spin-orbit coupling is neglected

$$\hat{H} = \hat{H}_0 + A_{LS} \vec{L} \cdot \vec{S}$$

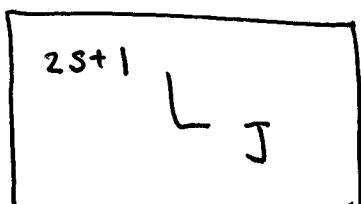
! Homework: Show that $[\vec{L}, H] \neq 0$

The RS coupling scheme is the result of neglect of spin-orbit coupling.

J states

Hund's third rule: In atoms with a less-than-half-filled subshell (e.g. p^2), the level of lowest J will be lowest in energy (${}^3P_0 < {}^3P_1 < {}^3P_2$). In atoms with a greater-than-half-filled subshell (p^4) the level of highest J will be lowest in energy.

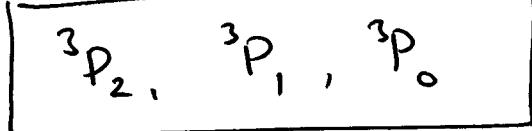
Full atomic configuration:



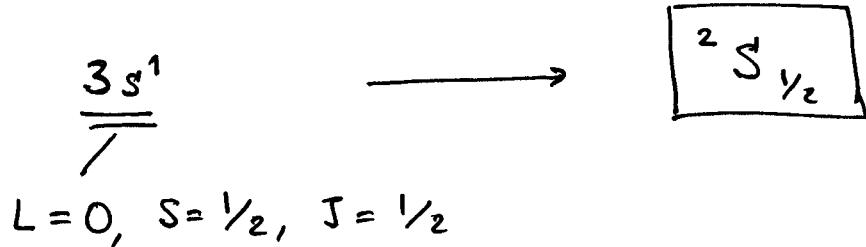
$$J = L+S, L+S-1, L+S-2, \dots, |L-S|$$

$S=1$
↓
 3P
↑
 $L=1$

$$J = 1+1, 1+1-1, 1+1-2$$



4-7

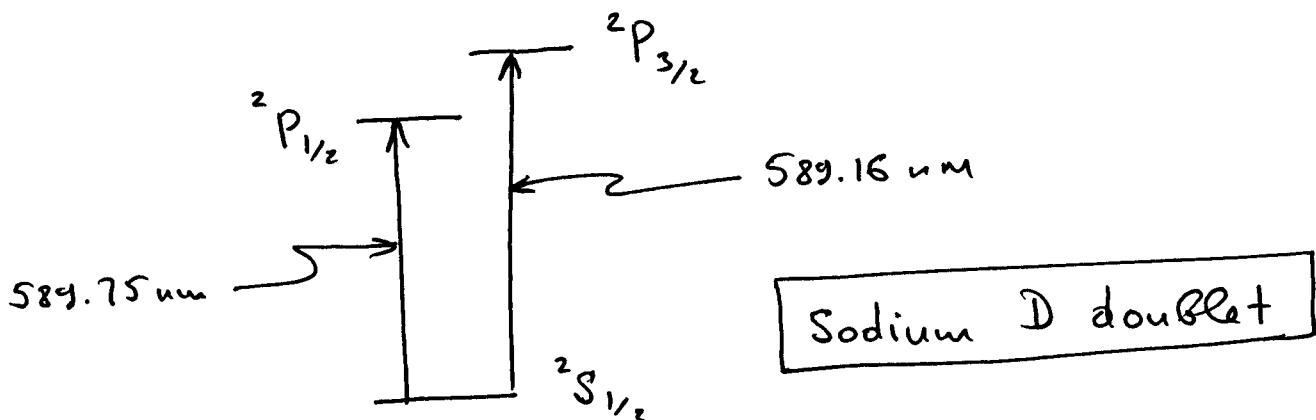
Ground state of Na $\rightarrow 3s^1$ First excited state of Na $\rightarrow 3p^1$ 

$$\begin{array}{c} \overline{\overline{3p^1}} \\ \nearrow \\ L=1, S=\frac{1}{2}, J=\frac{3}{2}, \frac{1}{2} \end{array}$$

M_L	M_S	$\frac{1}{2}$	$-\frac{1}{2}$
1	1	1	
0	1	1	
-1	1	1	

$\rightarrow ^2P : {}^2P_{3/2}, {}^2P_{1/2}$

Third Hund's rule: $E({}^2P_{1/2}) < E({}^2P_{3/2})$



Homework: Find the energy separation (in cm^{-1}) between two lines of the D doublet.

!

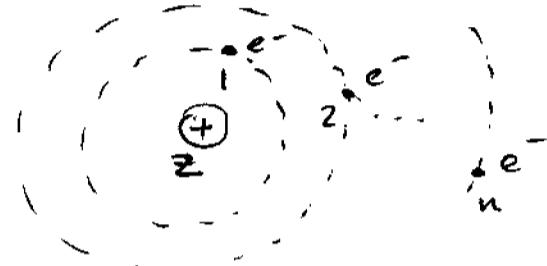
QM Basis of Hund's rules

Atomic Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{rep}} + \hat{H}_{\text{so}}$$

Hydrogenic Hamiltonian:

$$\hat{H}_0 = \sum_{i=1}^n \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{ze^2}{4\pi\epsilon_0 r_i} \right]$$



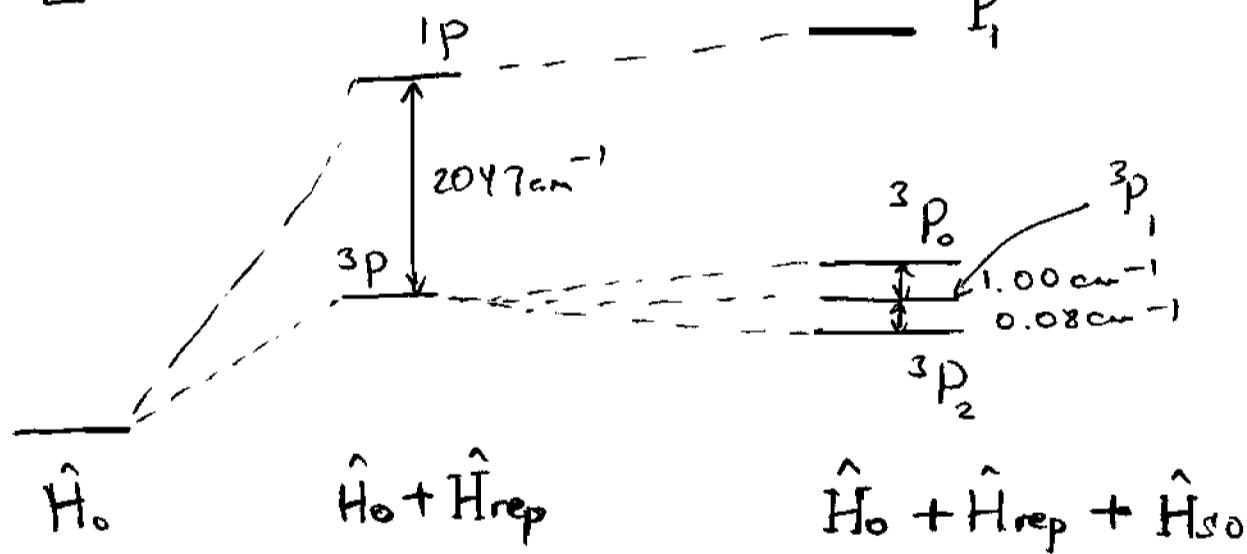
Interelectronic repulsion:

$$H_{\text{rep}} = \sum_{i < j} \sum_{i=1}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$



Spin-orbit interaction:

$$H_{\text{so}} = \sum A_i \vec{L}_i \cdot \vec{S}_i$$

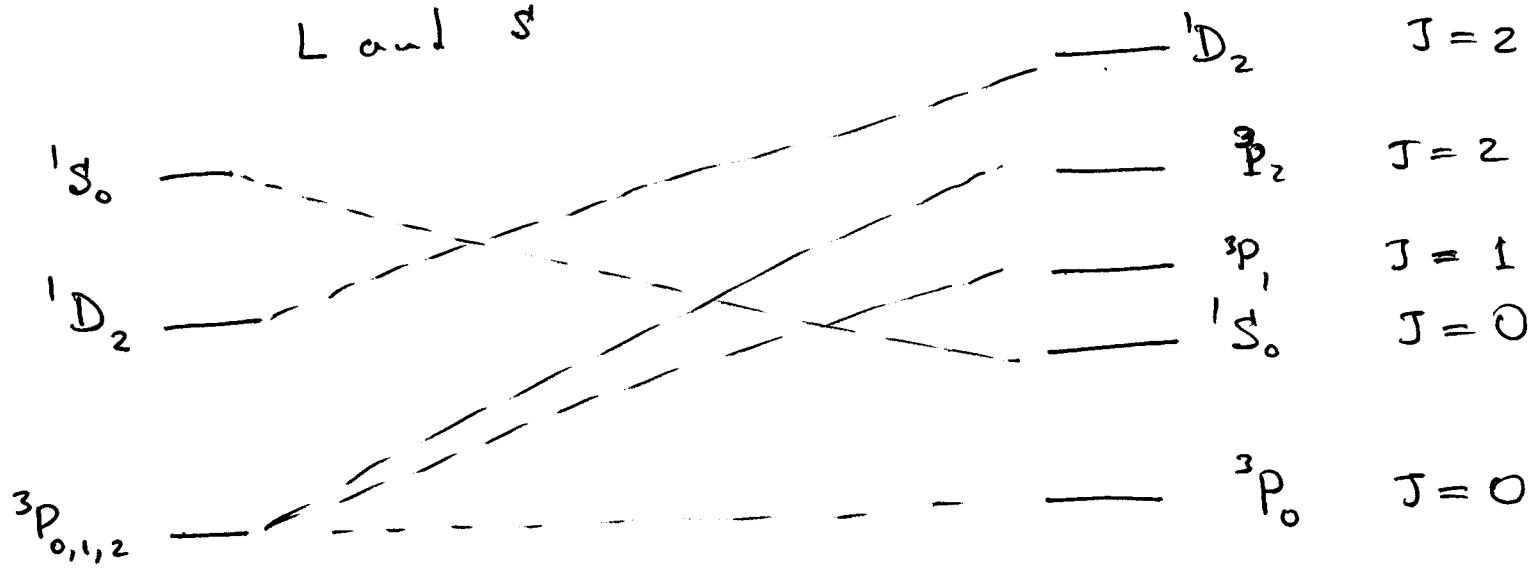


1s1p configuration of He

jj - coupling

In the LS coupling scheme the energy levels are placed based on individual magnitudes of L and S. Three Hund's rules are used:

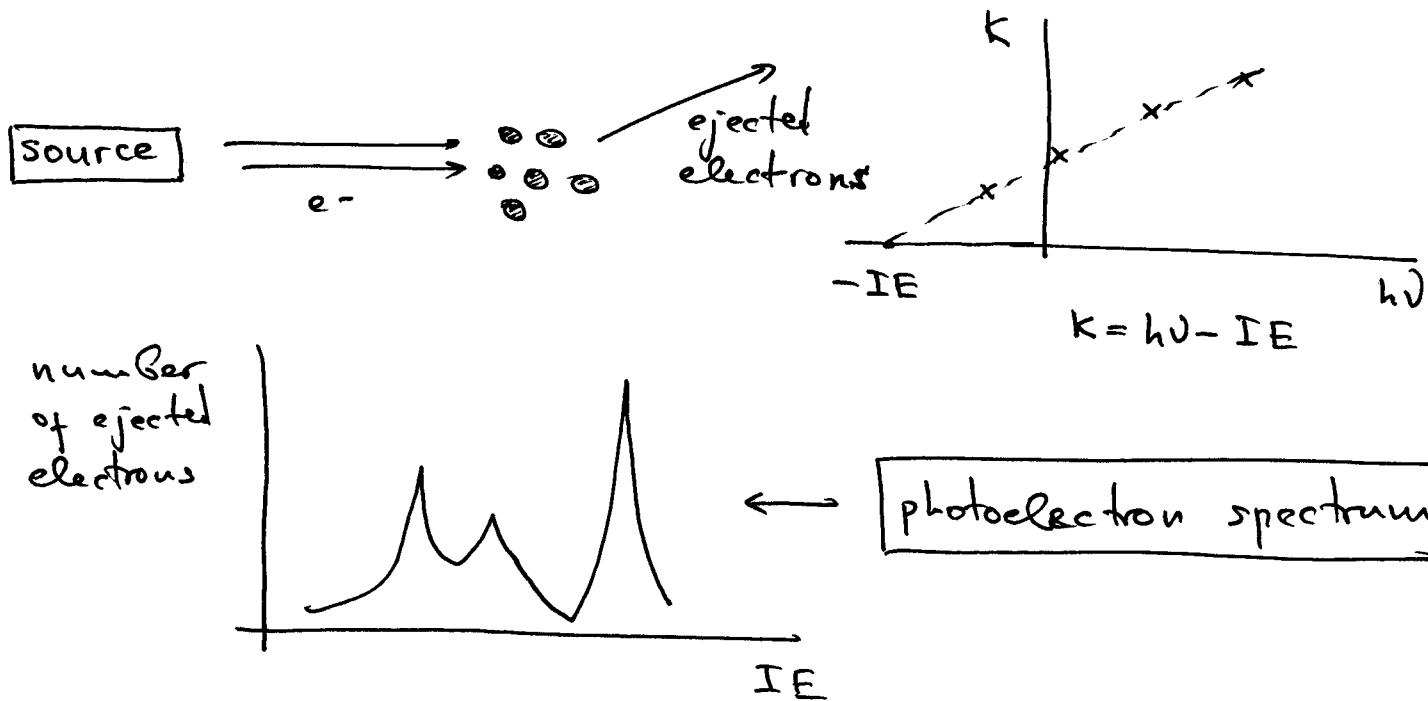
- ① First, highest spin multiplicity is chosen
- ② Second, for states with the same spin, states with greater L are placed at lower energy.
- ③ J - splitting is introduced at the same L and S



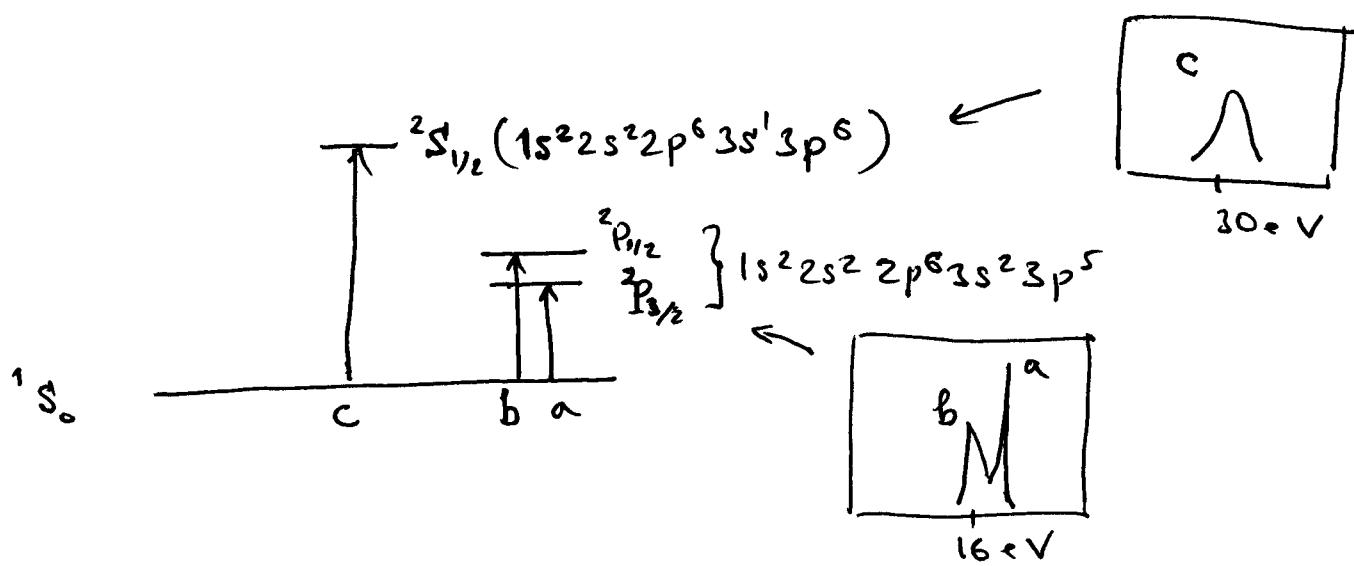
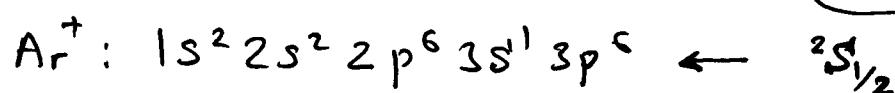
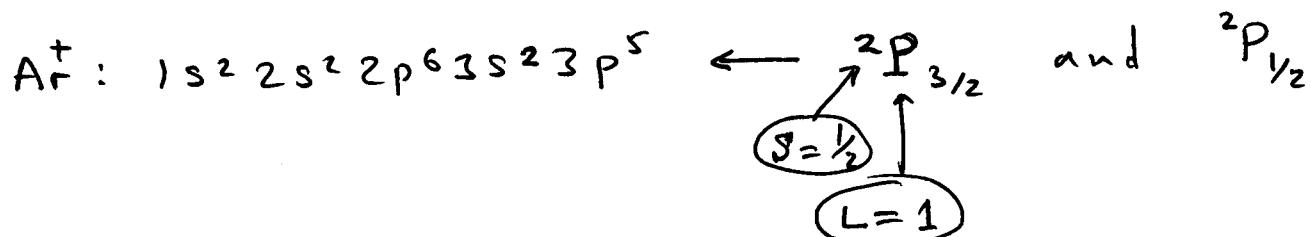
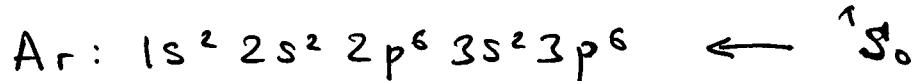
Russell-Saunders
LS coupling

jj - coupling

Photoelectron spectroscopy



PE spectrum of argon:



Matrix formulation of QM

The observable value for an operator G :

$$\langle G \rangle = \langle \psi | G | \psi \rangle$$

$$= \sum_i |i\rangle \langle i| \quad \sum_j |j\rangle \langle j|$$

$$= \sum_{ij} \langle \psi | i \rangle \langle i | G | j \rangle \langle j | \psi \rangle =$$

$$|\psi\rangle = \sum_i c_i |i\rangle = \sum_i \langle i | \psi \rangle |i\rangle$$

$$= \sum_i c_i \langle i | G | j \rangle c_j$$

$$G = H$$

$$\boxed{\langle H \rangle = \sum c_i c_j H_{ij}}$$

matrix elements of
the Hamiltonian

Quantum chemistry looks for solutions of this equation in terms of optimizing c_i coefficients!

Dirac notation

Shorthand notation:

$$\psi_i(x) \equiv |i\rangle$$

$$\psi_i^*(x) \equiv \langle i|$$

$$a(x) \equiv |a\rangle$$

$$a^*(x) \equiv \langle a|$$

Ket

Bra

The scalar product is defined as a Bra - Ket

$$\int dx a^*(x) b(x) \equiv \langle a | b \rangle$$

Bra - Ket

$$\int dx \varphi^*(x) \varphi(x) = \langle \varphi | \varphi \rangle = 1$$

For eigenfunctions belonging to different eigenvalues

$$\int \varphi_i^*(x) \varphi_j(x) dx = \langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

δ_{ij} is the Kronecker symbol:

$$\delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases}$$

Linear expansion and operators

Any wave function $\Psi(x)$ can be expanded in a complete set of eigenfunctions of some operator G : $G\varphi_i = g_i \varphi_i$.

$$\Psi(x) = \sum c_i \varphi_i(x) \rightarrow c_i = \int \varphi_i^*(x) \Psi(x) dx$$

In bra-ket notation

$$|\Psi\rangle = \sum_i \langle i | \Psi \rangle |i\rangle = \sum_i |i\rangle \langle i | \Psi \rangle$$

$$\boxed{\sum_i |i\rangle \langle i| = 1}$$

For states depending on x :

$$\sum_i |\Psi_i(x)\rangle \langle \Psi_i(x')| = \delta(x-x')$$

Dirac delta-function

$$\delta(x) = \lim_{\varepsilon \rightarrow 0} \delta_\varepsilon(x)$$

$$\delta_\varepsilon(x) = \begin{cases} \frac{1}{2\varepsilon}, & -\varepsilon \leq x \leq \varepsilon \\ 0, & \text{otherwise} \end{cases}$$

