H atom

$$E = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3, \ldots$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 0.529\text{Å}$$

$$E = -\frac{1}{2}\frac{m_e e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2} \qquad\qquad \frac{-1}{2n^2} \qquad \text{in a.u.}$$

atomic units
$$\hbar = 1$$
$$e = 1$$
$$m_e = 1$$
$$4\pi\varepsilon_0 = 1$$

energy: 1 a.u. = 27.211 eV
distance 1 a.u. = 0.529 Å

$$E = \frac{-Z^2}{2n^2}$$
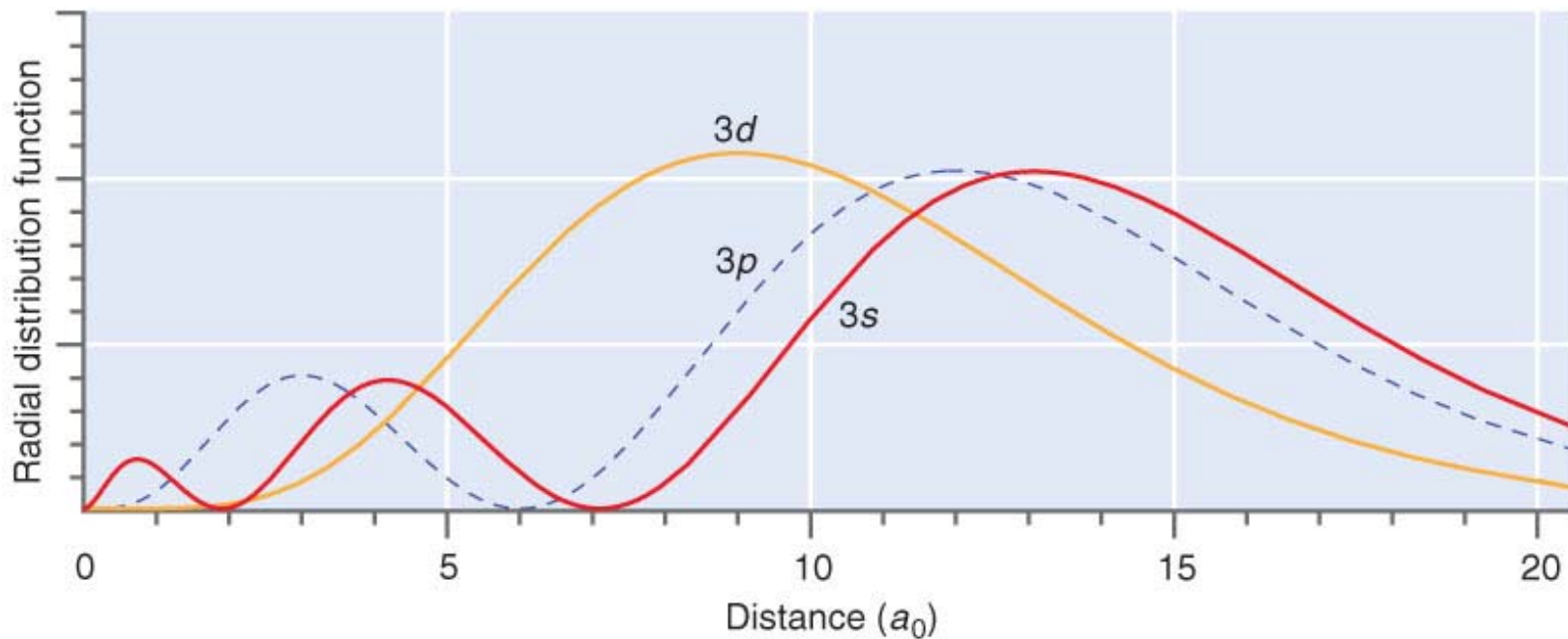
$$r = \frac{n^2 a_o}{Z}$$

General results for hydrogenic atoms (H^+, He^+, Li^{2+}, … U^{91+}), Z = nuclear charge

Note: We really should be using μ instead of m_e.

H, D, T have slightly different μ and thus can be distinguished spectroscopically

Radial distribution function $\rightarrow$ integrate over angular degrees of freedom

$$P(r)dr = r^2 \left[R(r) \right]^2 dr$$

Chapter 10   Many e⁻ atoms

He atom: $\left(-\dfrac{1}{2}\nabla_1^2 - \dfrac{1}{2}\nabla_2^2 - \dfrac{2}{r_1} - \dfrac{2}{r_2} + \dfrac{1}{r_{12}} \right)\psi = E\psi$ in a.u.
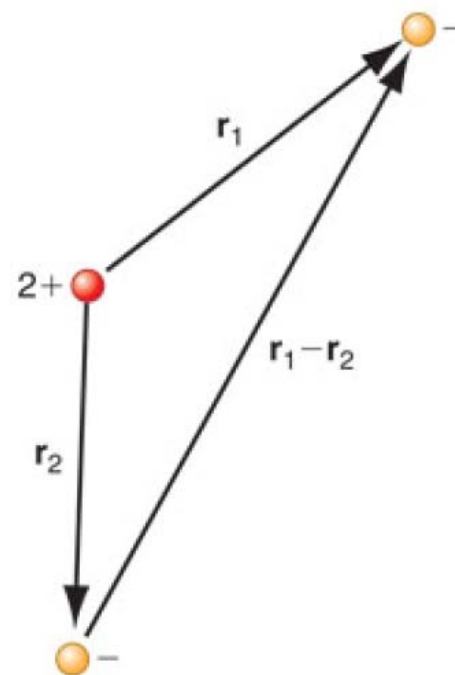
cannot separated due to $\dfrac{1}{r_{12}}$ term

However, it is still useful to use an approximate wavefunction that does separate

$\psi = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)$ orbital approximation

Simplest approach: neglect the $\dfrac{1}{r_{12}}$ term
                    poor approximation

Better approach: each e⁻ experiences a potential
                    from the average charge distribution of the other e⁻

$V_1^{eff}(\vec{r}_1) = -\dfrac{2}{r_1} + \int \phi_2(\vec{r}_2)\dfrac{1}{r_{12}}\phi_2(\vec{r}_2)\,d\vec{r}_2$ | Hartree model

N electrons → N one-electron hamiltonians → {ϕ_l, ε_i}

$h_i \varphi_i = \varepsilon_i \varphi_i$

Effective one
electron hamiltonian

To proceed further, we must consider e⁻ spin

spin of e⁻ = ½; two components $m_s = +1/2$, $m_s = -1/2$

spin eigenfunctions: $\alpha \quad m_s = \dfrac{1}{2} \quad \uparrow$

$\beta \quad m_s = -\dfrac{1}{2} \quad \downarrow$

$$\hat{s}^2 \alpha = \hbar^2 (s)(s+1)\alpha = \frac{3}{4}\alpha\hbar^2$$

$$\hat{s}^2 \beta \qquad\qquad = \frac{3}{4}\beta\hbar^2$$

$$\hat{s}_z \alpha = m_s \hbar \alpha = \frac{\hbar}{2}\alpha; \quad \hat{s}_z \beta = -\frac{\hbar}{2}\beta$$

$$\int \alpha^* \alpha \, d\sigma = \int \beta^* \beta \, d\sigma = 1; \quad \int \alpha^* \beta \, d\sigma = 0$$

Indistinguishability of electrons
wavefunction must be **antisymmetric** wrt exchange
of two e$^-$

He: $\psi = \phi_{1s}(1)\phi_{1s}(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$

$$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ \vec{r}_1 & \vec{r}_2 & \sigma_1 & \sigma_2 \end{array}$$

Pauli
exclusion
principle

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} 1s(1)1s(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$= \frac{1}{\sqrt{2}} 1s1s\left(\alpha\beta - \beta\alpha\right)$$

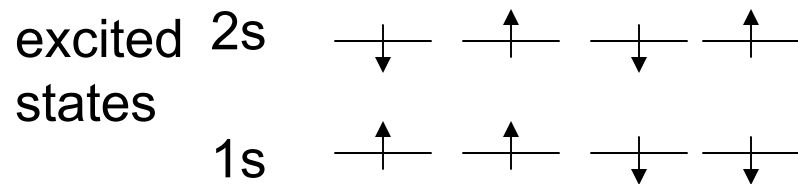Two electrons cannot have all quantum #s the same.

In general:
$$\psi(1,2,...n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1). & . & . & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2). & . & . & \phi_m(2)\beta(2) \\ ... & ... & & & ... \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n). & . & . & \phi_m(n)\beta(n) \end{vmatrix}$$

$m = n/2,$ if n even

$= \dfrac{n+1}{2},$ if n odd

Slater determinant

excited states

singlet
+
triplet

$$\psi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\alpha & 2s\beta \\ 1s\alpha & 2s\beta \end{vmatrix}$$

$$\psi_2 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\alpha & 2s\alpha \\ 1s\alpha & 2s\alpha \end{vmatrix}$$

$$\psi_3 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\beta & 2s\beta \\ 1s\beta & 2s\beta \end{vmatrix}$$

$$\psi_4 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\beta & 2s\alpha \\ 1s\beta & 2s\alpha \end{vmatrix}$$

2s

1s
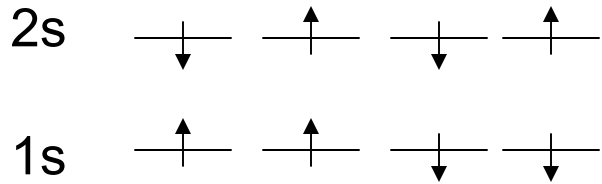
$\{1s(1)2s(2)+2s(1)1s(2)\}(\alpha\beta-\beta\alpha)$ Singlet, S = 0, M_s=0

$\{1s(1)2s(2)-(2s(1)1s(2)\}\alpha\alpha$

$\{1s(1)2s(2)-2s(1)1s(2)\}(\alpha\beta+\beta\alpha)$ Triplet, S = 1, M_s=1, 0, -1

$\{1s(1)2s(2)-2s(1)1s(2)\}\beta\beta$

Normally, the three components of the triplet give the same energy

Excited triple is energetically below excited singlet
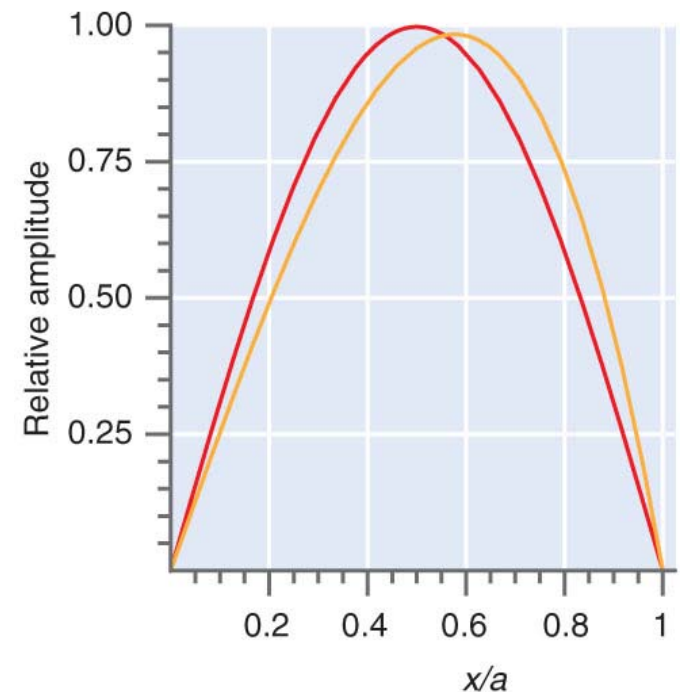
Variational method: approximate wavefunction Φ

$$H\Phi \neq E\Phi$$

$$E = \frac{\int \Phi^* H \Phi \, d\tau}{\int \Phi^* \Phi \, d\tau}$$

$\longleftarrow$ If Φ has a parameter, b, solve $\partial E / \partial b = 0$

example: $\Phi = \left(\dfrac{x}{a} - \dfrac{x^3}{a^3} \right) + \alpha \left(\dfrac{x^5}{a^5} - \dfrac{1}{2}\left(\dfrac{x^7}{a^7} + \dfrac{x^9}{a^9} \right) \right)$

for particle-in-box problem with $0 < x < a$

The variational parameter is α

Plot of the exact and approximate wavefunctions

if $\alpha = 0 \rightarrow \quad E = 0.203 \dfrac{h^2}{ma^2}$

$\alpha \neq 0 \quad \dfrac{2E}{2\alpha} = 0 \Rightarrow \alpha = -6.345 \rightarrow E = 0.127 \dfrac{h^2}{ma^2}$

$E_{exact} = 0.125 \dfrac{h^2}{ma^2}$
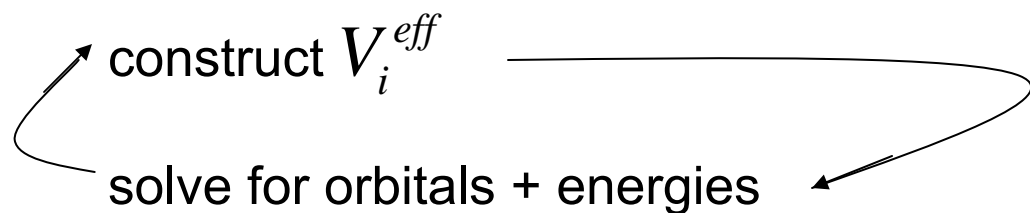
The energy can never fall below the exact energy

Hartree-Fock Self-Consistent Field method

Φ is taken to be a Slater determinant
    parameters in orbitals are varied

$$\left[-\frac{1}{2}\nabla_i^2 + V_i^{eff}(r_i) \right] \phi_i(r_i) = \varepsilon_i(r_i)$$
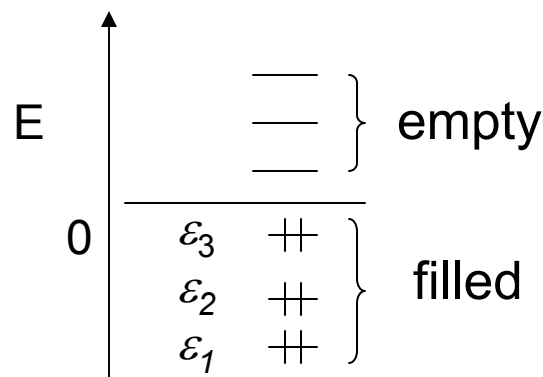
depends on orbitals that we are trying to solve for

Guess a set of orbitals

construct V_i^{eff}

solve for orbitals + energies

Iterate until energies and orbitals are converged.

$$E_{total} = 2\sum_i \varepsilon_i - \sum_{j>i}\left(2J_{ij} - K_{ij}\right)$$

exchange

Coulomb

to remove double counting in $2\sum_i \varepsilon_i$

E

$\left.\begin{array}{c} \underline{} \\ \underline{} \\ \underline{} \end{array}\right\}$ empty

0

ε_3 ⧺

ε_2 ⧺ $\Big\}$ filled

ε_1 ⧺

$IP_i = -\varepsilon_l$ for filled orbitals

$EA_j = -\varepsilon_j$ for empty orbitals

Koopmans theorem

many electron atoms

$$\varepsilon_{ns} < \varepsilon_{np} < \varepsilon_{nd}, \ldots$$

H atom

$$\varepsilon_{ns} = \varepsilon_{np} = \varepsilon_{nd}, \ldots$$

deshielding

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s has more weight near nucleus than does *p* which has more weight near nucleus than *d*.

$He \quad 1s^2$ 2

$Ne \quad 1s^2 2s^2 2p^6$ $2 + 8 = 10$

$Ar \quad 1s^2 2s^2 2p^6 3s^2 3p^6$ $2+8+8=18$

$Sc[Ar]4s^2 3d \quad Mn[Ar]4s^2 3d^5 \quad Cu[Ar]4s3d^{10}$

$Ti[Ar]4s^2 3d^2 \quad Fe[Ar]4s^2 3d^6 \quad Zn[Ar]s^2 3d^{10}$

$V[Ar]4s^2 3d^3 \quad Co[Ar]4s^2 3d^7$

$Cr[Ar]4s3d^5 \quad Ni[Ar]4s^2 3d^8$

Energy

5d   6p   6d

4d   5p   4f   7s   5f

3d   4p   5s   6s

3s   3p   4s

2s   2p

1s

$$Cr \quad 4s3d^5 \quad \text{vs.} \quad 4s^2 3d^4$$
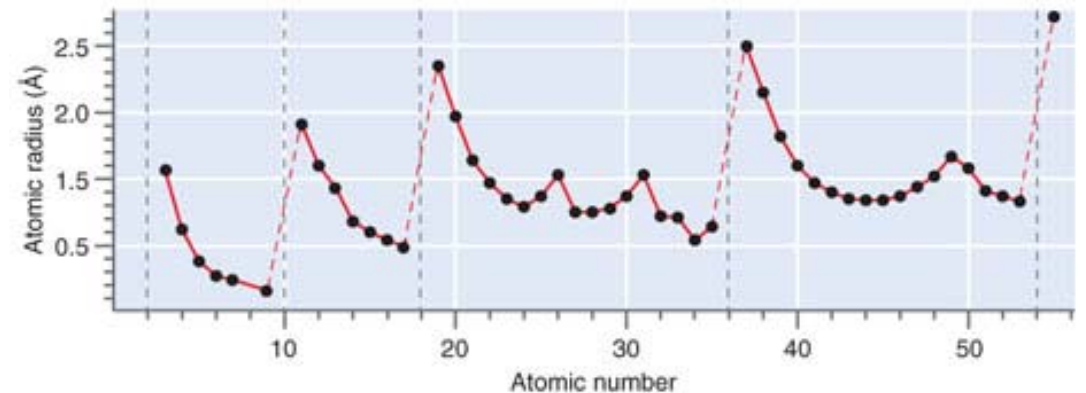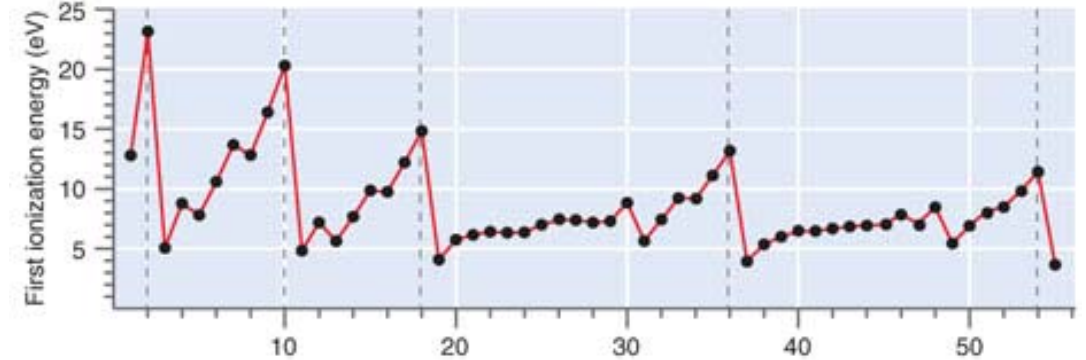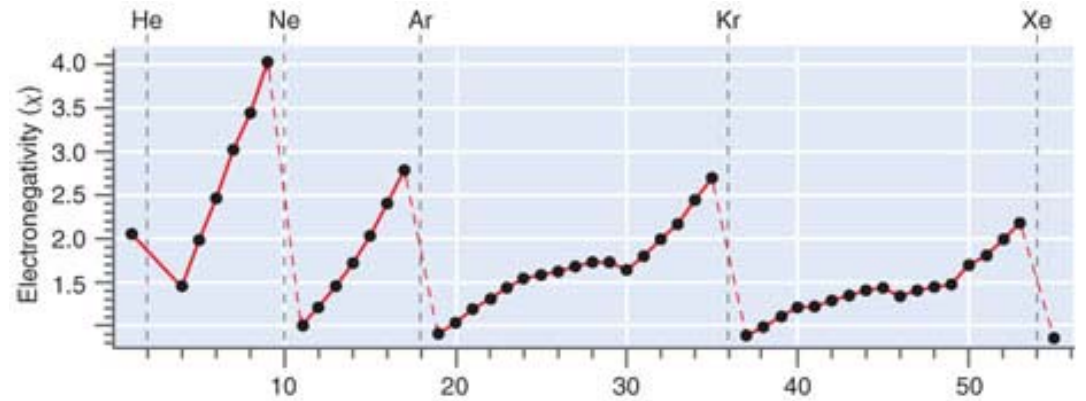$$Cu \quad 4s3d^{10} \quad \text{vs.} \quad 4s^2 3d^9$$

d^5
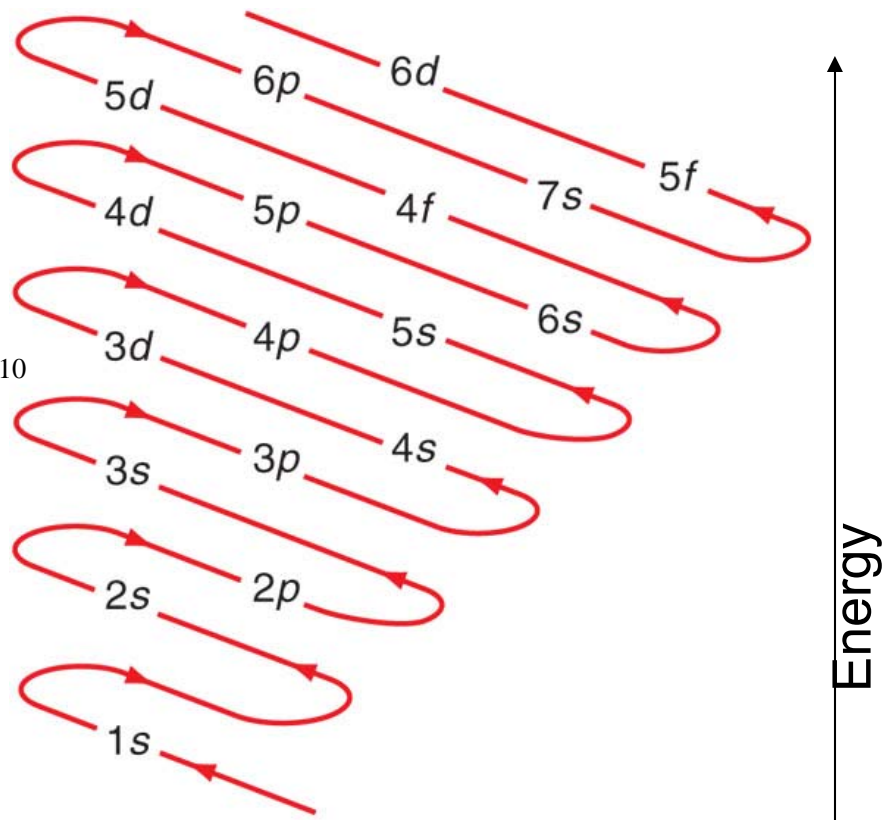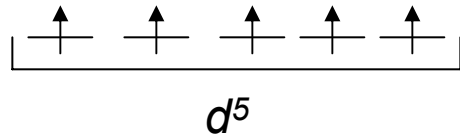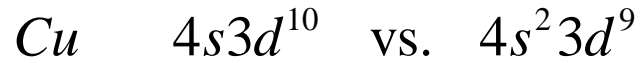
Especially stable

Electronegativity: $X = IP + EA$

definition due to Mulliken

Does Na transfer an e⁻ to Cl?

$$\Delta E = IP_{Na} - EA_{Cl} =$$
$$5.1 - 3.6 = 1.5 eV$$

Many electron atoms:

n, ℓ, m_ℓ, m_s not good quantum #s

$$L = \sum_i \ell_i, \quad S = \sum s_i$$

Lower case: individual orbitals

Upper case: many electron state

$$\hat{L}_z = \sum_i \hat{\ell}_{z,i}, \quad \hat{S}_z = \sum_i \hat{s}_{z,i}$$

L, S, M_L, M_S are the good quantum #s

Actually, for heavy elements, one needs to add a spin-orbit coupling term to $\hat{H}$.

$\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ no longer commute with $\hat{H}$
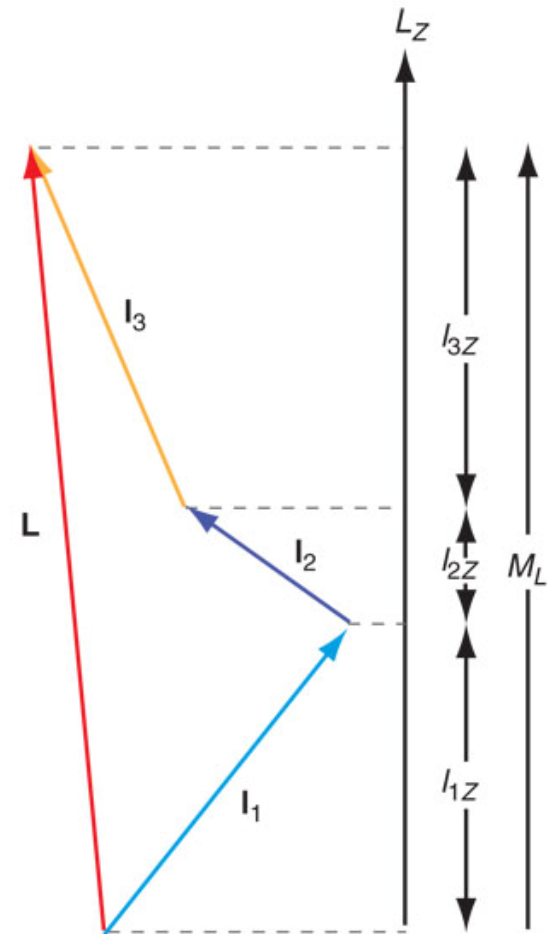
with spin-orbit coupling, need to use $\vec{J} = \vec{L} + \vec{S}$ $\quad$ $z \gtrsim 40$

the good quantum #s are J, M_J

No electron–electron repulsion	Electron–electron repulsion and indistinguishability included	Spin–orbit interaction included	External magnetic field
Configuration	Terms	Levels	States
n,l	L,S	J,M_J	J,M_J
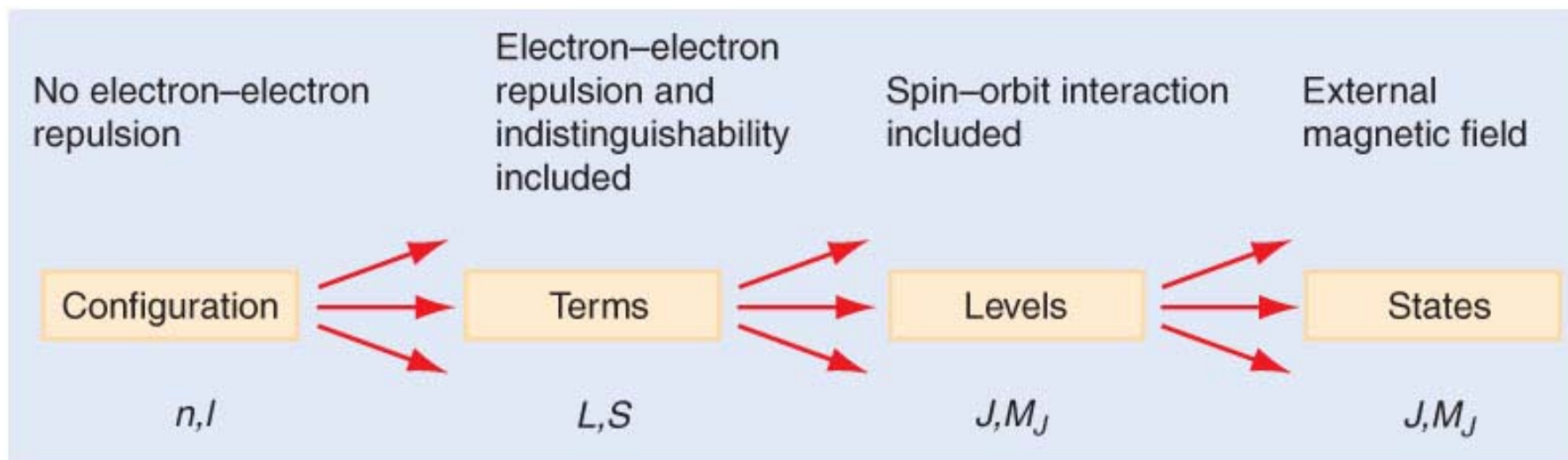
Terms + States

H	$1s$	$L = 0;\ S = \dfrac{1}{2} \rightarrow\ ^2S$	

Term symbol ^{2S+1}L

$\uparrow$

multiplicity

He $1s^2$ $L = 0;\ S = 0 \rightarrow\ ^1S$

B $1s^2 2s^2 2p$ $L = 1;\ S = \dfrac{1}{2} \rightarrow\ ^2P$

C $1s^2 2s^2 2p^2$ $L = 2,1,0;\ S = 1,0\ \rightarrow\ ^3P,\ ^1D,\ ^1S$

N $1s^2 2s^2 2p^3$ $L = 2,1,0;\ S = \dfrac{3}{2},\dfrac{1}{2}\ \rightarrow\ ^4S,\ ^2P,\ ^2D$

O $1s^2 2s^2 2p^4$ $L = 2,1,0;\ S = 1,0\ \rightarrow\ ^3P,\ ^1D,\ ^1S$

F $1s^2 2s^2 2p^5$ $L = 1;\ S = \dfrac{1}{2}\ \rightarrow\ ^2P$

Ne $1s^2 2s^2 2p^6$ $L = 0;\ S = 0\ \rightarrow\ ^1S$

Ti $[Ar]4s^2 3d^2$ $L = 4,3,2,1,0;\ S = 0,1\ \rightarrow\ ^1S,\ ^1D,\ ^1G,\ ^3P,\ ^3F$

A closer look at spin

He   1s2s

$$\begin{cases} \alpha \quad \beta \qquad M_s = 0 \\[1em] \beta \quad \alpha \qquad M_s = 0 \\[1em] \alpha \quad \alpha \qquad M_s = 1 \\[1em] \beta \quad \beta \qquad M_s = 1 \end{cases}$$

1   2

There must be a
$S = 1$ state.

$S = 1 \Rightarrow M_s = -1, 0, 1$

There must also be an
$S = 0$ state $\Rightarrow M_s = 0$

$$\psi_T = \frac{1}{\sqrt{2}}(1s2s - 2s1s)\alpha\alpha$$

$$\psi_S = \frac{1}{2}(1s2s + 2s1s)(\alpha\beta - \beta\alpha)$$

$$\psi_T = \frac{1}{2}(1s2s - 2s1s))(\alpha\beta + \beta\alpha)$$

$$\psi_T = \frac{1}{\sqrt{2}}(1s2s - 2s1s)\beta\beta$$

T

S, T

T
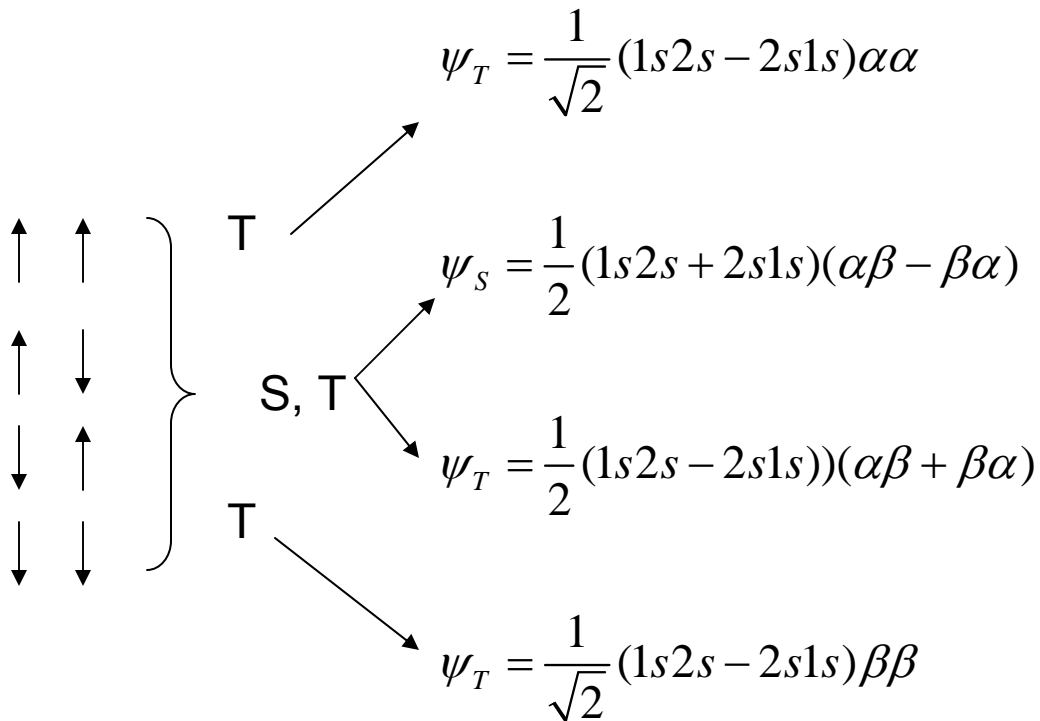
In the absence of a magnetic field, the three triplet components are degenerate.

The *T* and *S* states are different energy $E_T < E_s$

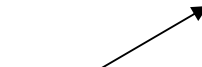term $^{2S+1}L \rightarrow (2S+1)(2L+1)$ degeneracy

filled shells $\rightarrow$ ^1S

$$C: \quad 1s^2 2p3d \quad L = 3,2,1, \quad S = 1,0$$

$$^3F, \, ^1F, \, ^3D, \, ^1D, \, ^3P, \, ^1P$$

$$21 + 7 + 15 + 5 + 9 + 3 = 60 \text{ states}$$

2p: 6 choices
3d: 10 choices $\Big\}$ 60 states

$C: \ 1s^2 2s^2 2p3p \qquad L = 2,1,0; \qquad S = 1,0$

$\qquad\qquad {}^3D, \ {}^1D, \ {}^3P, \ {}^1P, \ {}^3S, \ {}^1S$

$C: \ 1s^2 2p^2 \quad \rightarrow \quad {}^3P, \ {}^1S, \ {}^1D$ \qquad what happens to ${}^3D$, ${}^1P$, ${}^3S$?

violate the Pauli exclusion principle.

States and Terms for the np^2 Configuration

m_{l1}	m_{l2}	$M_L = m_{l1} + m_{l2}$	m_{s1}	m_{s2}	$M_S = m_{s1} + m_{s2}$	Term
−1	−1	−2	1/2	−1/2	0	${}^1D$
0	−1	−1	−1/2	−1/2	−1	${}^3P$
			−1/2	1/2	0	${}^1D, {}^3P$
			1/2	−1/2	0	
			1/2	1/2	1	${}^3P$
0	0	0	1/2	−1/2	0	${}^1D, {}^3P, {}^1S$
			−1/2	1/2	0	
			1/2	−1/2	0	
1	−1	0	−1/2	−1/2	−1	${}^3P$
			1/2	1/2	1	${}^3P$
1	0	1	−1/2	−1/2	−1	${}^3P$
			−1/2	1/2	0	${}^1D, {}^3P$
			1/2	−1/2	0	
			1/2	1/2	1	${}^3P$
1	1	2	1/2	−1/2	0	${}^1D$

| M_S | 0 | 0 | 0 | -1 | 1 | -1 | 0 | 0 | 0 | 1 | -1 | 0 | 0 | 1 | 0 |
| M_L | -2 | -1 | -1 | -1 | -1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 2 |

Possible Terms for Indicated Configurations

| Electron Configuration	Term Symbol
s^1	^2S
p^1, p^5	^2P
p^2, p^4	$^1S, \ ^1D, \ ^3P$
p^3	$^2P, \ ^2D, \ ^4S$
d^1, d^9	^2D
d^2, d^8	$^1S, \ ^1D, \ ^1G, \ ^3P, \ ^3F$
d^3, d^7	$^4F, \ ^4P, \ ^2H, \ ^2G, \ ^2F, \ ^2D \ (2), ^2P$
d^4, d^6	$^5D, \ ^3H, \ ^3G, \ ^3F \ (2), \ ^3D, \ ^3P \ (2), \ ^1I, \ ^1G \ (2), \ ^1F, \ ^1D \ (2),$ $^1S \ (2)$
d^5	$^6S, \ ^4G, \ ^4F, \ ^4D, \ ^4P, \ ^2I, \ ^2H, \ ^2G \ (2), \ ^2F \ (2), \ ^2D \ (3), \ ^2P, \ ^2S$

Note $p, p^5; \ p^2, p^4; \ d^2, d^8; \ d^3, d^7$ etc. give the same states for each pair.

<u>Hund's Rules</u>:
1. The lowest energy term is that with the highest spin

2. For terms that have the same spin, that with the greatest
    L value lies lowest in energy

$$C: \ 1s^2 2p^2 \qquad\qquad ^3P \ < \ ^1D \ < \ ^1S$$

S. O. Coupling
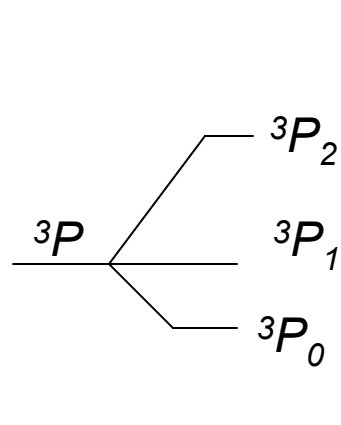
$$^3P \rightarrow \quad ^3P_2 \quad ^3P_1 \quad ^3P_0$$

J
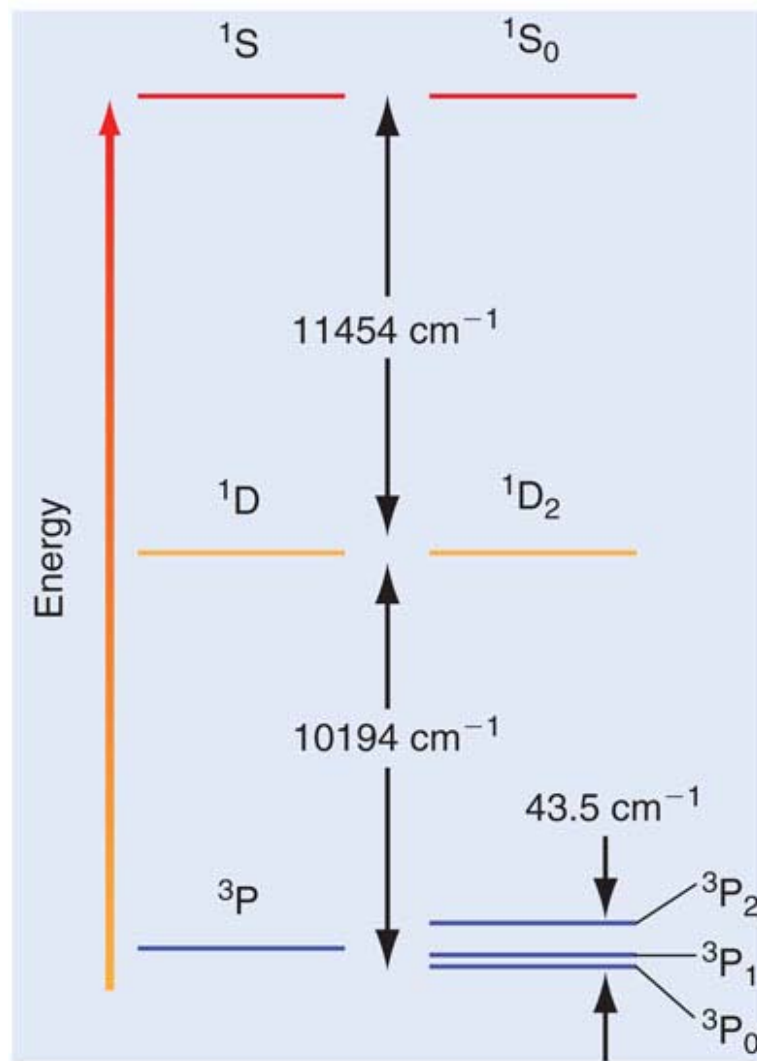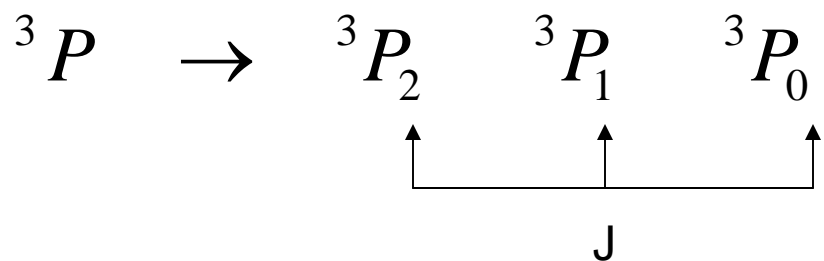
Energy level diagram for C atom

Spin-orbit coupling adds a term $\propto \vec{L} \cdot \vec{S}$ to $\vec{H}$

generally can ignore for light atoms

^3P $\Big\langle$ $^3P_2$
$^3P_1$
$^3P_0$

Hund's rule 3: If a subshell is $\geq$ half full, the level with the highest J is lowest in energy. If it is < half full, the level with the lowest J is lowest in energy

$^3P_1$ → splits into 3 levels upon application of magnetic field

Return to the 1s2s singlet/triplet problem

$$E_{singlet} = \frac{1}{2} \int (1s2s + 2s1s) \hat{H} (1s2s + 2s1s) d\tau_1 d\tau_2$$

$$= E_{1s} + E_{2s} + \frac{1}{2} \int (1s2s + 2s1s) \frac{1}{r_{12}} (1s2s + 2s1s) d\tau_1 d\tau_2$$

$$= E_{1s} + E_{2s} + J_{12} + K_{12}$$

$$J_{12} = \int 1s2s \frac{1}{r_{12}} 1s2s d\tau_1 d\tau_2$$

coulomb

exchange

$$K_{12} = \int 1s2s \frac{1}{r_{12}} 2s1s d\tau_1 d\tau_2$$

$$E_{triplet} = \frac{1}{2} \int (1s2s - 2s1s) \hat{H} (1s2s - 2s1s) d\tau_1 d\tau_2$$

$$= E_{1s} + E_{2s} + J_{12} - K_{12},$$

J, K are positive

K_{12} arises from the antisymmetrization of ψ.

1s2s   J   S $\uparrow$ 2K_{12}
               T $\downarrow$