

H atom

$$E = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3, \dots$$

$$a_0 = \frac{\epsilon_0 h^2}{\pi m_e e^2} = 0.529 \text{ \AA}$$

$$E = -\frac{1}{2} \frac{m_e e^4}{(4\pi\epsilon_0)^2 n^2 \hbar^2} \quad \frac{-1}{2n^2} \quad \text{in a. u.}$$

atomic units

$$\hbar = 1$$

$$e = 1$$

$$m_e = 1$$

$$4\pi\epsilon_0 = 1$$

energy: 1 a.u. = 27.211 eV

distance 1 a.u. = 0.529 \text{ \AA}

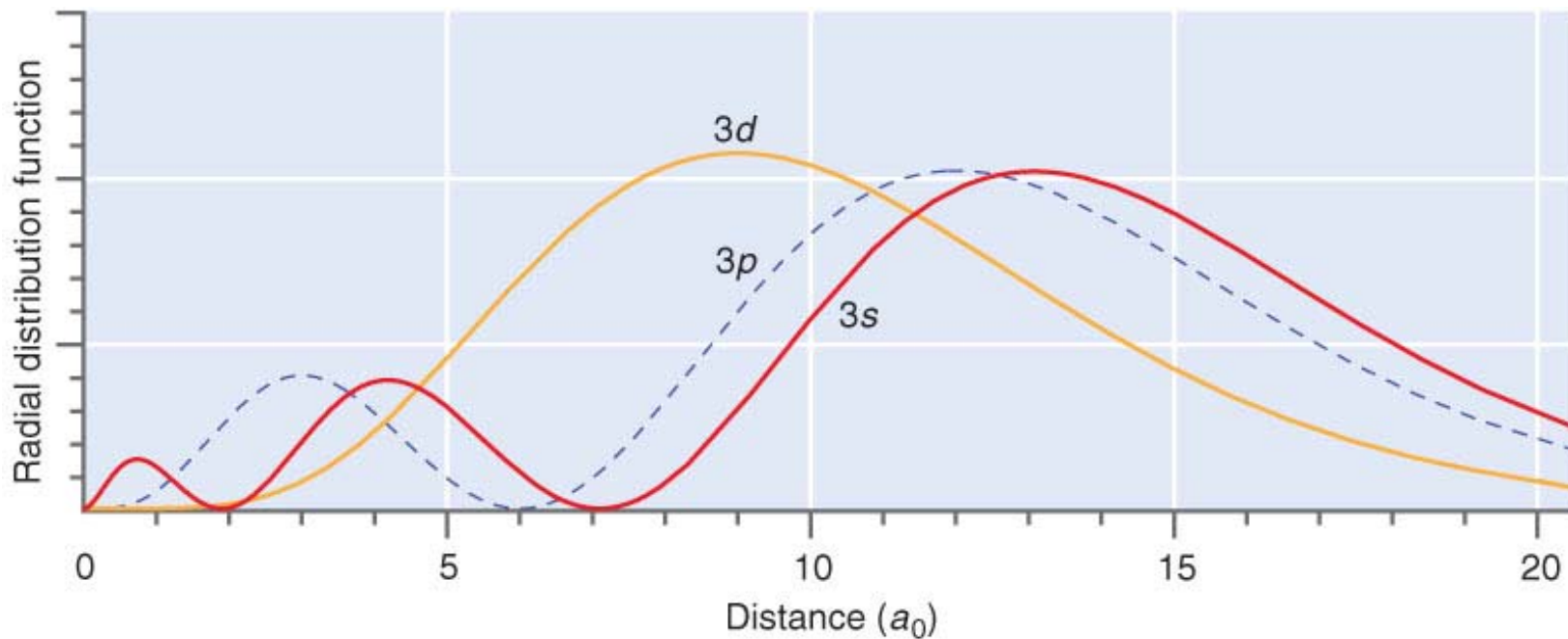
Note: We really should be using  $\mu$  instead of  $m_e$ .

H, D, T have slightly different  $\mu$  and thus can be distinguished spectroscopically

Treatment of H atom applies to  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ...  $\text{U}^{91+}$

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

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



## Chapter 10 Many e<sup>-</sup> atoms

$$\text{He atom: } \left( -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right) \psi = E\psi \quad \text{in a.u.}$$

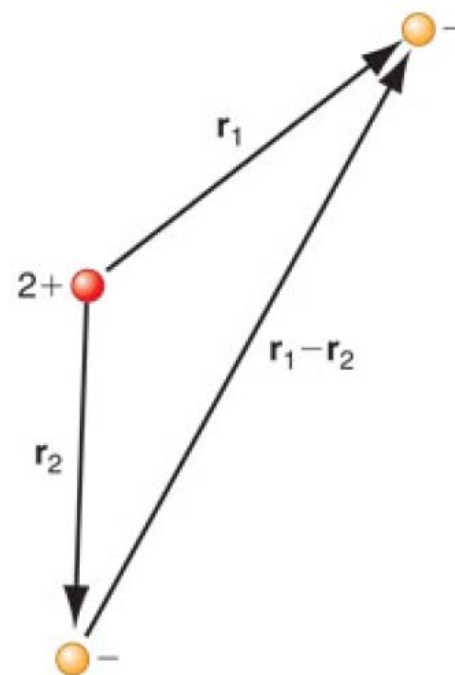
cannot separate due to  $\frac{1}{r_{12}}$  term

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

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

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

Better approach: each e<sup>-</sup> experiences a potential from the average charge distribution of the other e<sup>-</sup>



$$V_1^{eff}(\vec{r}_1) = -\frac{2}{r_1} + \int \phi_2(\vec{r}_2) \frac{1}{r_{12}} \phi_2(\vec{r}_2) d\vec{r}_2 \quad \left| \text{Hartree model} \right.$$

N electrons  $\rightarrow$  N one-electron hamiltonians  $\rightarrow$   $\{\phi_i, \varepsilon_i\}$

To proceed further, we must consider  $e^-$  spin

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

spin wavefunctions:

$\alpha$	$m_s = \frac{1}{2}$	$\uparrow$
$\beta$	$m_s = -\frac{1}{2}$	$\downarrow$

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

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

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

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


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### Indistinguishability of electrons

wavefunction must be **antisymmetric** wrt exchange of two e<sup>-</sup>

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

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

Pauli  
exclusion  
principle

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

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

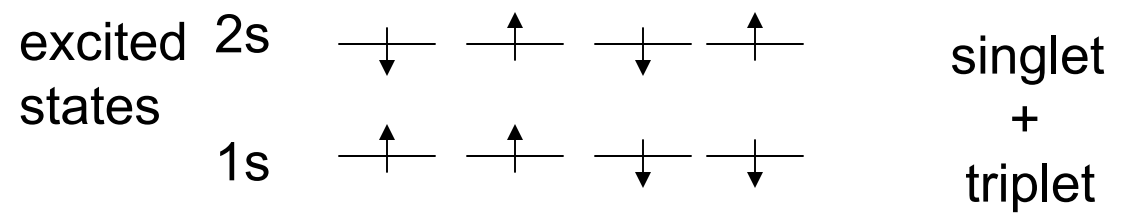
$$\text{In general } \psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \dots & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \dots & \phi_m(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \dots &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

$$m = n/2, \text{ if } n \text{ even}$$

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

### Slater determinant

Two electrons cannot have all quantum #s the same.



$$\left\{ \begin{array}{l} \psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha & 2s\beta \\ 1s\alpha & 2s\beta \end{vmatrix} \\ \psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha & 2s\alpha \\ 1s\alpha & 2s\alpha \end{vmatrix} \\ \psi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta & 2s\beta \\ 1s\beta & 2s\beta \end{vmatrix} \\ \psi_4 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta & 2s\alpha \\ 1s\beta & 2s\alpha \end{vmatrix} \end{array} \right.$$

**Variational method:** approximate wavefunction  $\Phi$

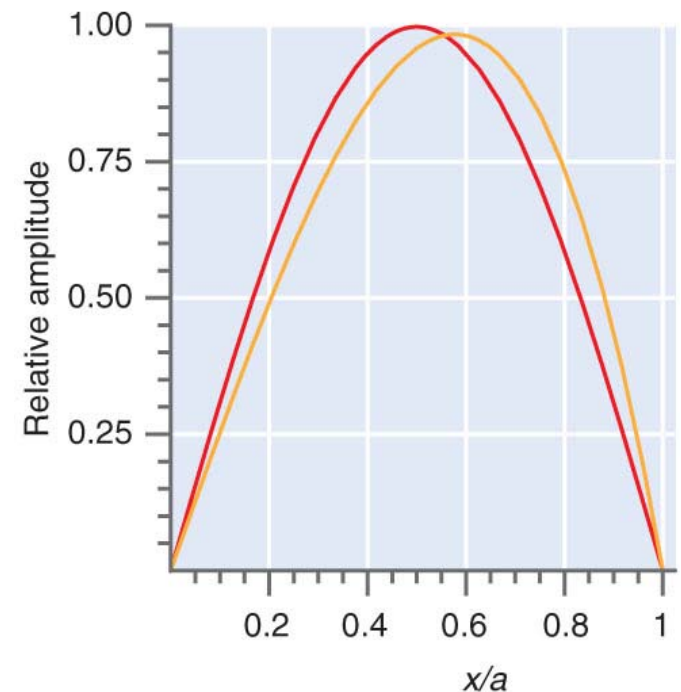
$$H\Phi \neq E\Phi$$

$$E = \frac{\int \Phi^* H \Phi d\tau}{\int \Phi^* \Phi d\tau} \quad \leftarrow \quad \text{If } \Phi \text{ has a parameter, } b, \text{ solve } \partial E / \partial b = 0$$

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

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

The variational parameter is  $\alpha$



Plot of the exact and approximate wavefunctions

$$\text{if } \alpha = 0 \rightarrow E = 0.203 \frac{h^2}{ma^2}$$

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

$$E_{\text{exact}} = 0.125 \frac{h^2}{ma^2}$$

The energy can never fall below the exact energy

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Hartree-Fock Self-Consistent Field method

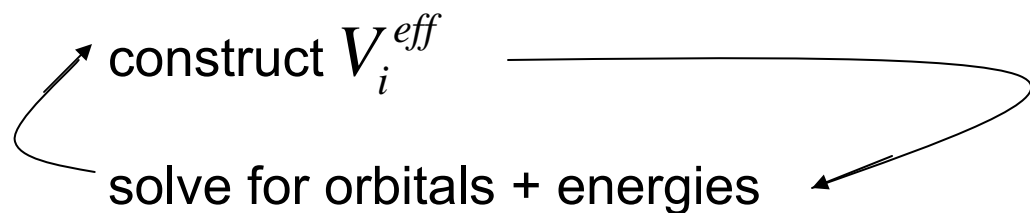
$\Phi$  is taken to be a Slater determinant  
parameters in orbitals are varied

$$\left[ -\frac{1}{2} \nabla_i^2 + V_i^{\text{eff}}(r_i) \right] \phi_i(r_i) = \varepsilon_i(r_i)$$

↑ depends on orbitals that we are trying to solve for



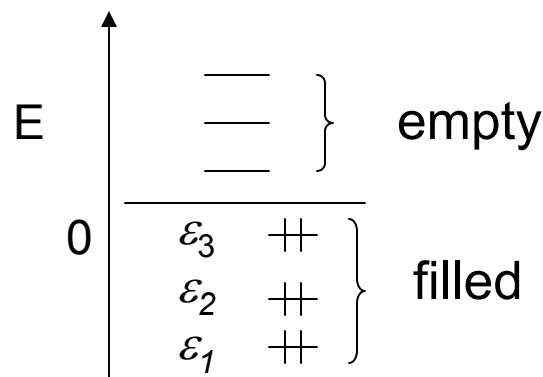
Guess a set of orbitals



Iterate until energies and orbitals are converged.

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

$\uparrow$  Coulomb                       $\uparrow$  exchange



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

$$\left. \begin{aligned} IP_i &= -\varepsilon_i && \text{for filled orbitals} \\ EA_j &= -\varepsilon_j && \text{for empty orbitals} \end{aligned} \right\} \text{Koopmans theorem}$$

many electron atoms

$$\epsilon_{ns} < \epsilon_{np} < \epsilon_{nd}, \dots$$

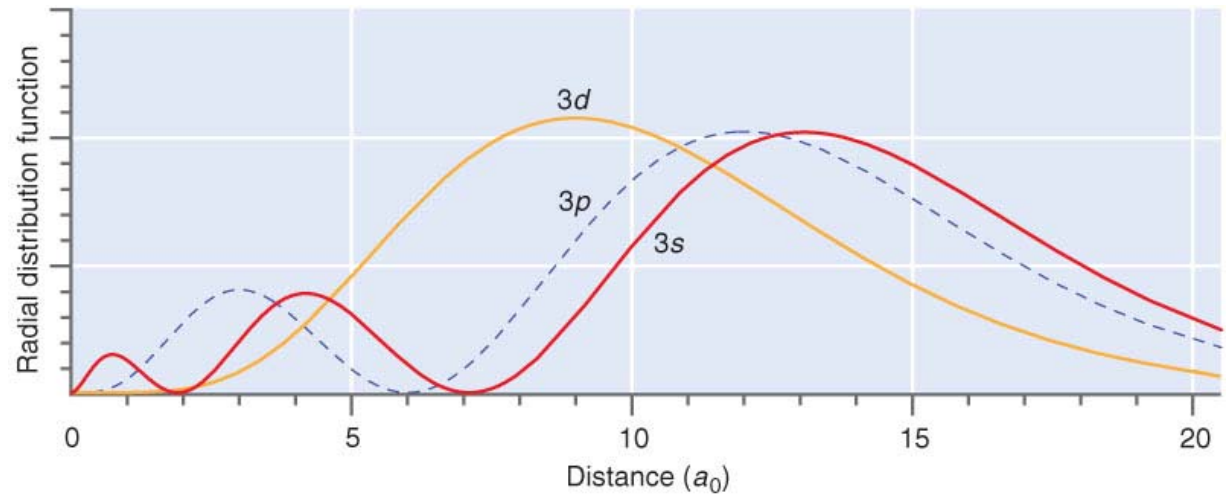
deshielding



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

H atom

$$\epsilon_{ns} = \epsilon_{np} = \epsilon_{nd}, \dots$$



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*He*  $1s^2$  2

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

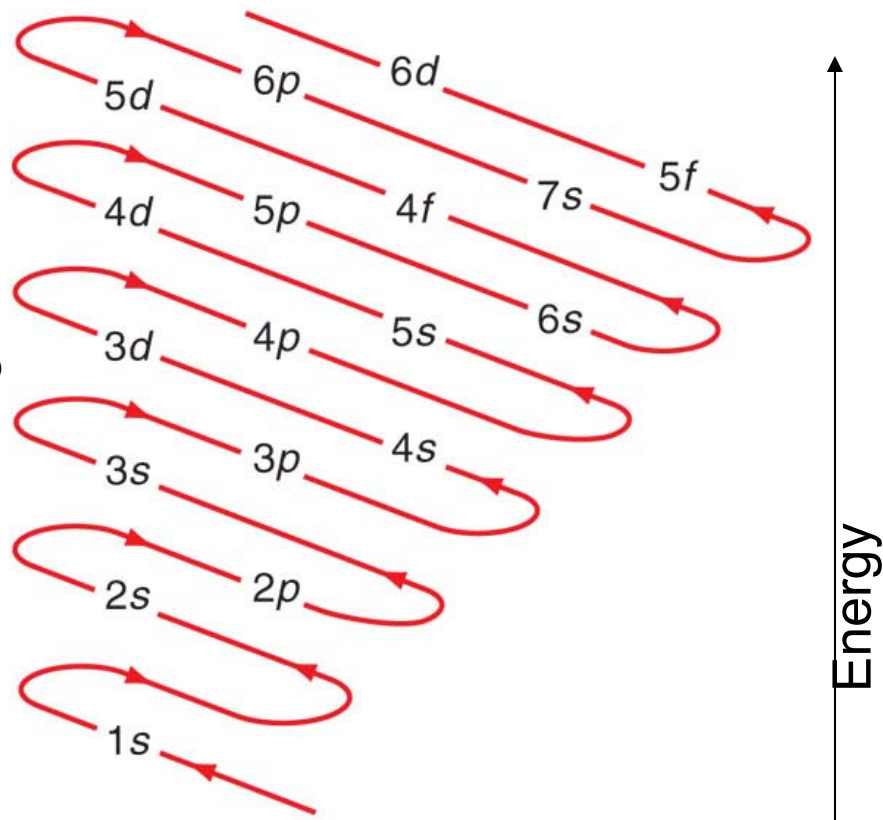
*Ar*  $1s^2 2s^2 2p^6 3s^2 3p^6$  2+8+8=18

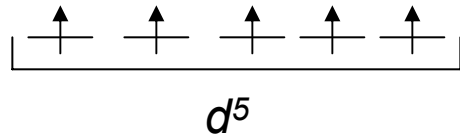
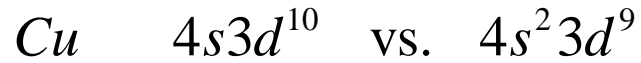
*Sc*[Ar] $4s^2 3d$     *Mn*[Ar] $s^2 3d^5$     *Cu*[Ar] $s 3d^{10}$

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

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

*Cr*[Ar] $4s 3d^5$     *Ni*[Ar] $4s^2 3d^8$





Especially stable

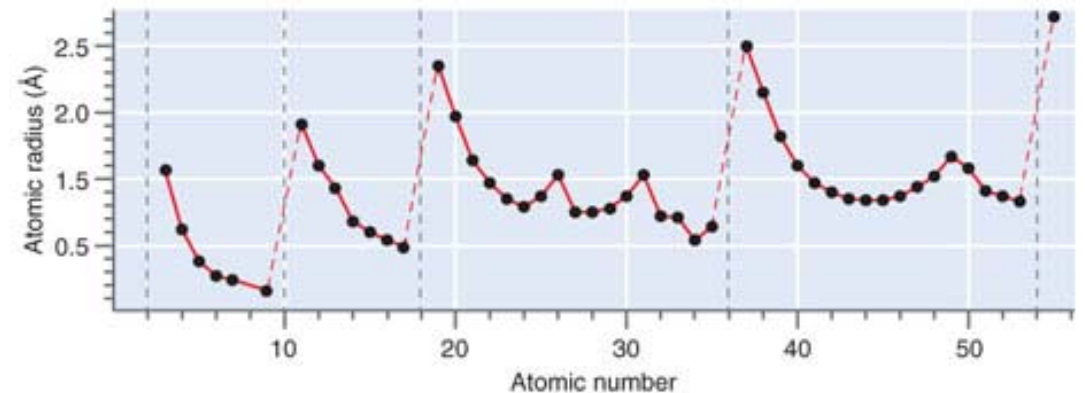
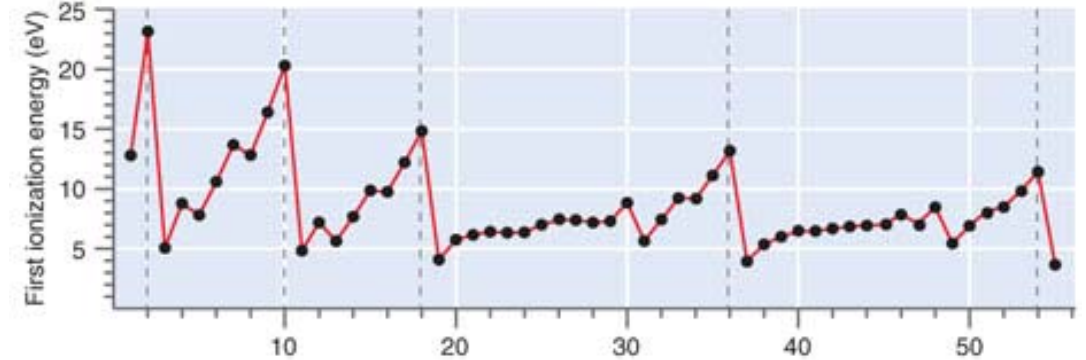
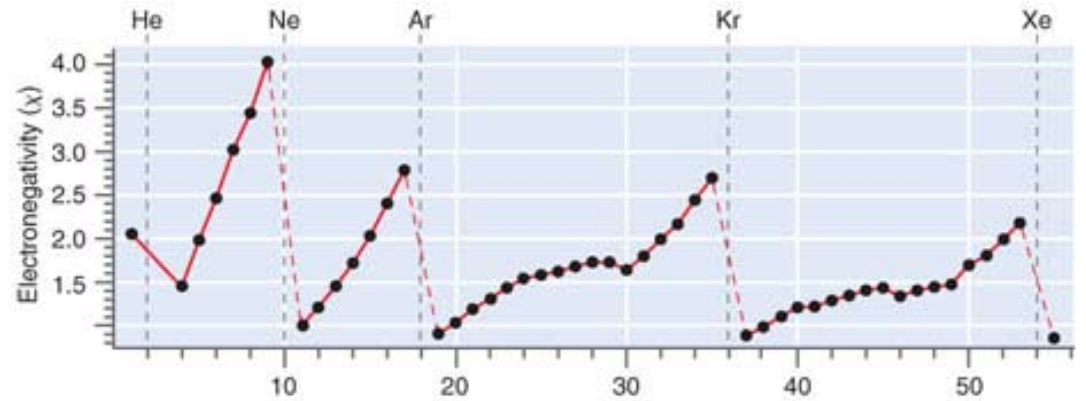
Electronegativity:  $X = IP + EA$

definition due to Mulliken

Does Na transfer an  $e^-$  to Cl?

$$\Delta E = IP_{Na} - EA_{Cl} =$$

$$5.1 - 3.6 = 1.5 eV \quad \rightarrow$$



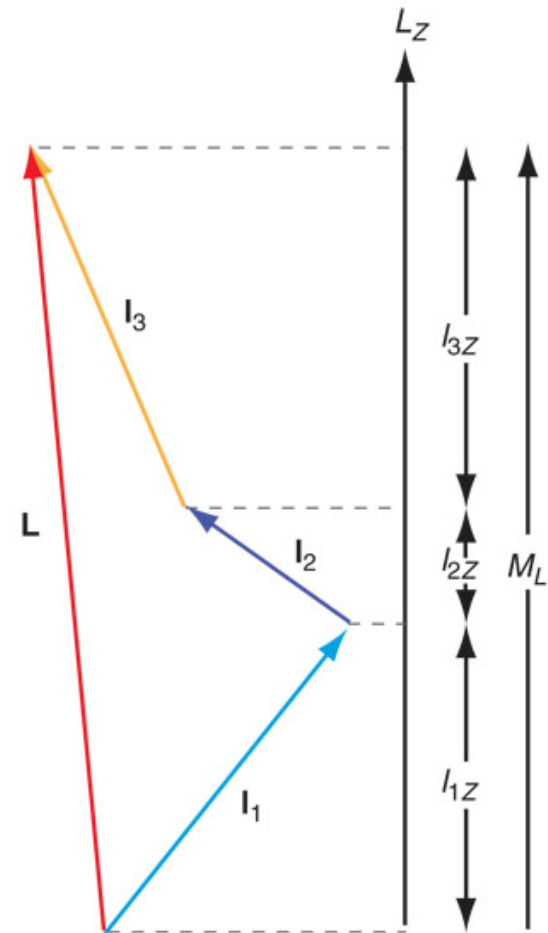
## Many electron atoms:

$n, \ell, m_\ell, m_s$  not good quantum #s

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

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

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



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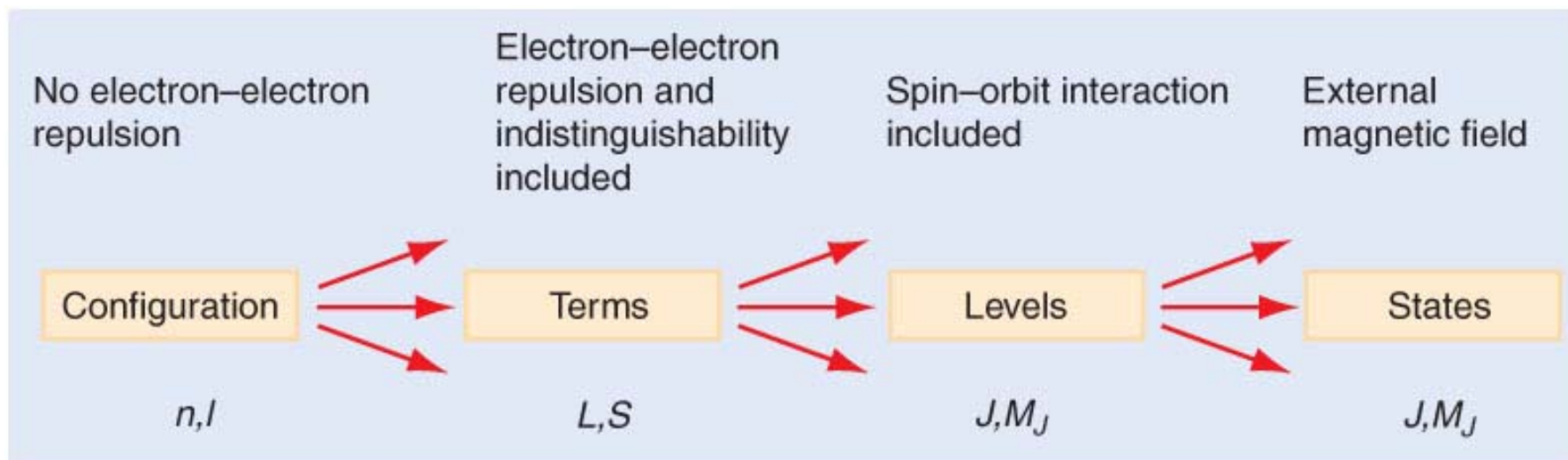
Actually, for heavy elements, one needs to add a **spin-orbit coupling** term to  $\hat{H}$ .

$\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$  no longer commute with  $\hat{H}$

with spin-orbit coupling, need to use  $\vec{J} = \vec{L} + \vec{S}$

$z \gtrsim 40$

the good quantum #s are  $J, M_J$



## Terms + States

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

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

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

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

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

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

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

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

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

Term symbol  $2S+1L$

multiplicity

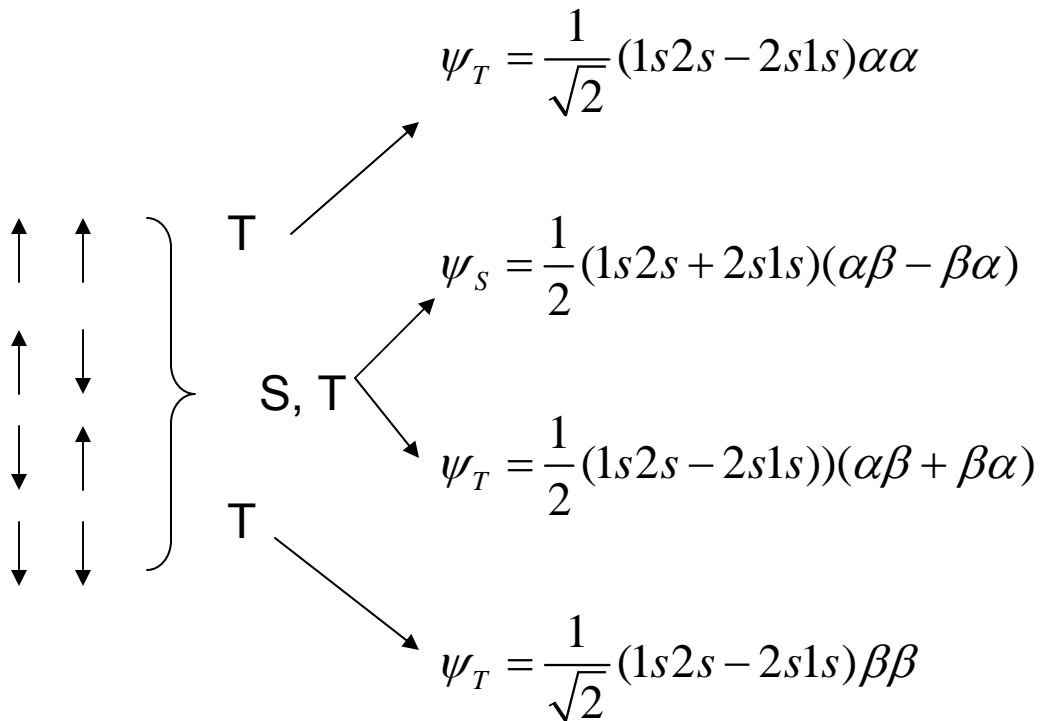
# A closer look at spin

		1	2	
He 1s2s	{	$\alpha$	$\beta$	$M_s = 0$
		$\beta$	$\alpha$	$M_s = 0$
		$\alpha$	$\alpha$	$M_s = 1$
		$\beta$	$\beta$	$M_s = 1$

There must be a  $S = 1$  state.

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

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





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

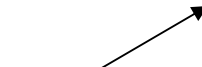
filled shells  $\rightarrow ^1S$        $C: 1s^2 2p 3d \quad L = 3, 2, 1, \quad S = 1, 0$

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

$21 + 7 + 15 + 5 + 9 + 3 = 60$  states

2p: 6 choices  
3d: 10 choices

60 states



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

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

$$C: 1s^2 2p^2 \rightarrow {}^3P, {}^1S, {}^1D$$

(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	${}^1D$
			-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	${}^3P$
			-1/2	-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	${}^1D$

$m_i$															
+1						↓	↓	↑		↑	↓	↓	↑	↑	↑↓
0		↓	↑	↓	↑				↑↓		↓	↑	↓	↑	
-1	↑↓	↑	↓	↓	↑	↓	↑	↓		↑					
$M_S$	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
$s^1$	2	S
$p^1, p^5$	2	P
$p^2, p^4$	1	S, $^1D$ , $^3P$
$p^3$	2	P, $^2D$ , $^4S$
$d^1, d^9$	2	D
$d^2, d^8$	1	S, $^1D$ , $^1G$ , $^3P$ , $^3F$
$d^3, d^7$	4	F, $^4P$ , $^2H$ , $^2G$ , $^2F$ , $^2D$ (2), $^2P$
$d^4, d^6$	5	D, $^3H$ , $^3G$ , $^3F$ (2), $^3D$ , $^3P$ (2), $^1I$ , $^1G$ (2), $^1F$ , $^1D$ (2), $^1S$ (2)
$d^5$	6	S, $^4G$ , $^4F$ , $^4D$ , $^4P$ , $^2I$ , $^2H$ , $^2G$ (2), $^2F$ (2), $^2D$ (3), $^2P$ , $^2S$

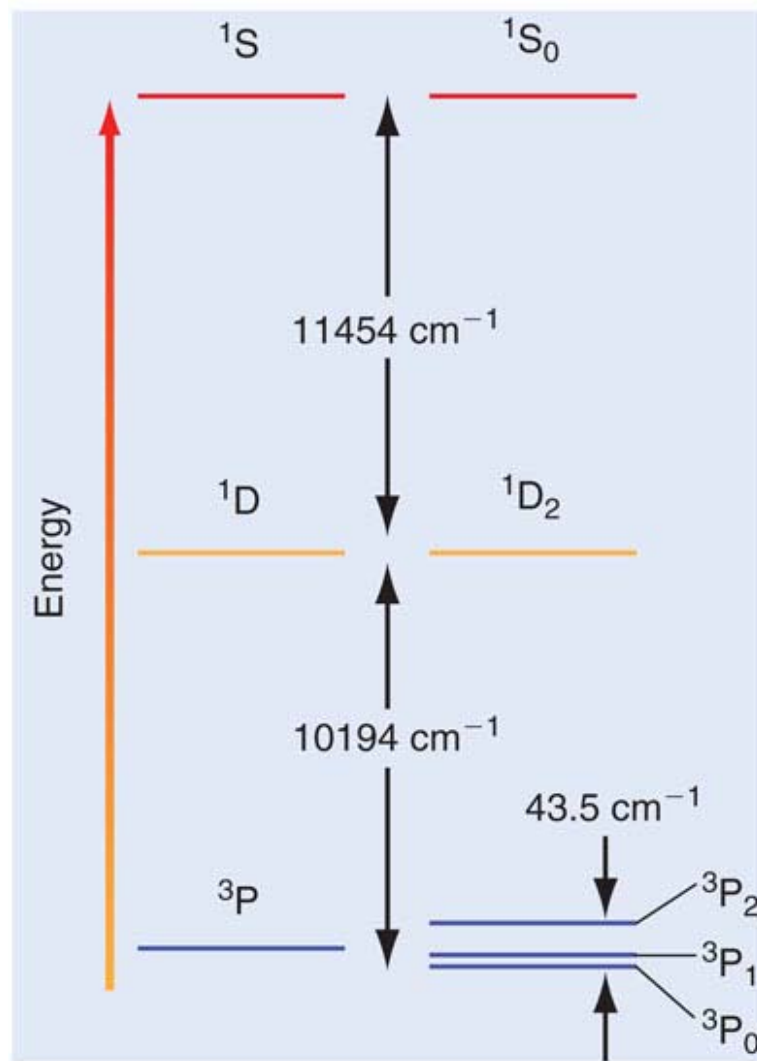
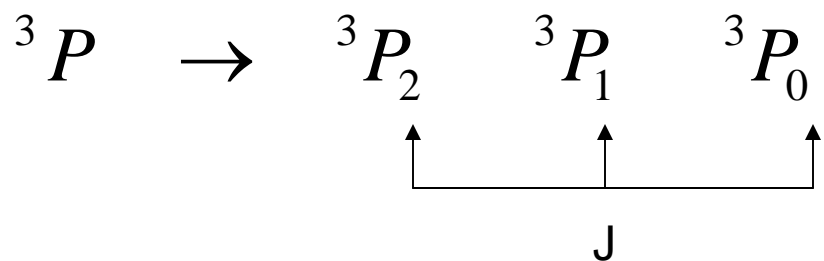
Note  $p, p^5$ ;  $p^2, p^4$ ;  $d^2, d^8$ ;  $d^3, d^7$  etc. give the same states for each pair.

### Hund's Rules:

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

$$C: 1s^2 2p^2 \quad {}^3P < {}^1D < {}^1S$$

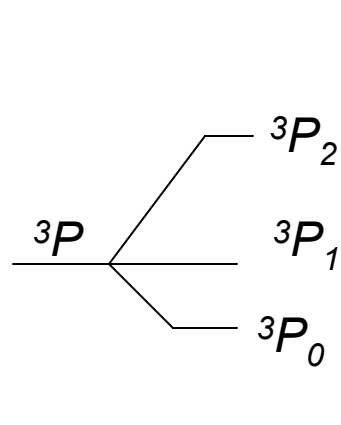
S. O. Coupling



Energy level diagram for C atom

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

generally can ignore for light atoms



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



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

## Return to the 1s2s singlet/triplet problem

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

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

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

coulomb  exchange 

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

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

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

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

$J, K$  are positive

$K_{12}$  arises from the antisymmetrization of  $\psi$ .

