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

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

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

atomic units $\quad \left.\begin{array}{l} \hbar = 1 \\ e = 1 \\ m_e = 1 \\ 4\pi\varepsilon_0 = 1 \end{array}\right\}$ energy: 1 a.u. = 27.211 eV
distance 1 au = 0.529 Å

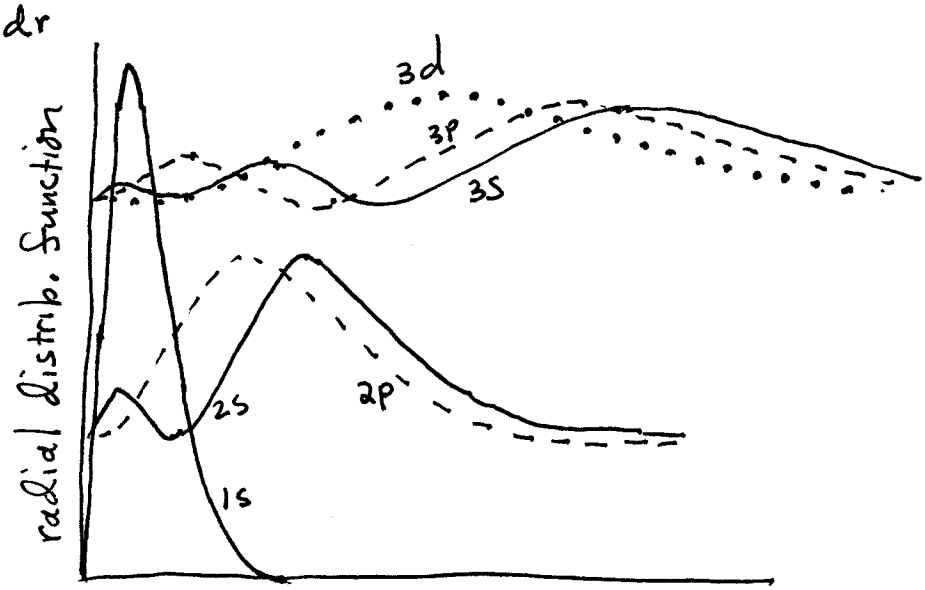
Note: we really should be using μ instead of m_e.

H, D, T have slightly different μ's, and thus can be distinguished spectroscopically.

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

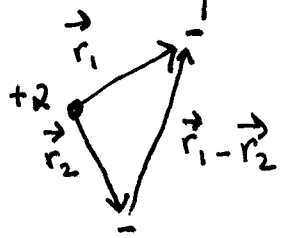
Radial distribution function → integrate over angular degrees of freedom

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



Chpt. 10 many e^- atoms

He atom: $\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right)\psi = E\psi$ | 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

$\psi = \phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)$ <u>orbital</u> approximation

Simplest approach: simply throw away the $\frac{1}{r_{12}}$ term
very poor approximation

Better approach: each e^- experiences a potential from the averaged charge distributions of the other e^-.

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

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

To proceed further, we must consider e^- spin

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

spin wavefunctions: α $m_s = 1/2$ $\uparrow$
β $m_s = -1/2$ $\downarrow$

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

$\hat{s}^2\beta = 3/4\,\beta$

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

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

<u>Indistinguishability</u> of electrons

wavefunction must be <u>antisymmetric</u> wrt exchange of two e^-

$$He: \quad \psi = \underset{\vec{r}_1}{\phi_{1s}(1)} \; \underset{\vec{r}_2}{\phi_{1s}(2)} \left[\underset{\sigma_1}{\alpha(1)} \underset{\sigma_2}{\beta(2)} - \beta(1)\alpha(2) \right]$$

$\left\{ \begin{array}{l} \text{Pauli} \\ \text{exclusion} \\ \text{principle} \end{array} \right\}$

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

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

when $\phi_{1s} \equiv 1s$

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

$m = n/2$, if n even
$= \frac{n+1}{2}$, if n odd

Slater determinant

Two electrons cannot have all quantum #'s the same.

excited states

2s	↓	↑	↓	↑
1s	↑	↑	↓	↓

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

<u>Variational method</u> approximate wavefunction Φ

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

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

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 parameter is α.

if $\alpha = 0 \longrightarrow E = 0.125 \frac{h^2}{8ma^2}$

$\alpha \neq 0 \quad \partial E / \partial \alpha = 0 \Rightarrow \alpha = -0.345 \longrightarrow E = 0.127 \frac{h^2}{8ma^2}$

$E_{exact} = 0.125 \frac{h^2}{8ma^2}$

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.

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

depends on orbitals that we are trying to solve for.

guess a set of orbitals

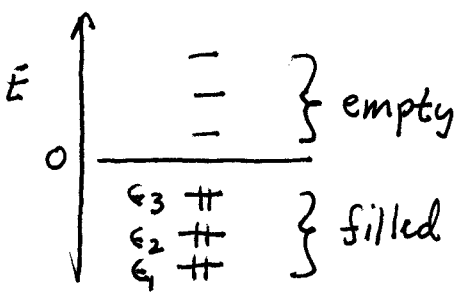
construct V_i^{eff}

solve for orbitals + energies

Iterate until energies and orbitals are converged

$$E_{total} = 2\sum_i \varepsilon_i - \underbrace{\sum_{j>i} (2J_{ij} - K_{ij})}_{\text{to remove double counting in } 2\sum_i \varepsilon_i}$$

J_{ij}: coulomb; K_{ij}: exchange



$IP_i = -\varepsilon_i$ for filled orbitals

$EA_j = -\varepsilon_j$ for empty orbitals

Koopmans theorem

$\underbrace{\varepsilon_{ns} < \varepsilon_{np} < \varepsilon_{nd}}_{\text{many electron atoms}}, \ldots$ $\qquad$ $\varepsilon_{ns} = \varepsilon_{np} = \varepsilon_{nd}, \ldots$ H atom

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

Energy

3 d	He $1s^2$	2
4 s	Ne $1s^2 2s^2 2p^6$	2+8 = 10
3 p	Ar $1s^2 2s^2 2p^6 3s^2 3p^6$	2+8+8 = 18
3 s		
2 p		
2 s		
1 s		

Sc [Ar] $4s^2 3d$
Ti [Ar] $4s^2 3d^2$
V [Ar] $4s^2 3d^3$
Cr [Ar] $4s 3d^5$

Mn [Ar] $s^2 3d^5$
Fe [Ar] $4s^2 3d^6$
Co [Ar] $4s^2 3d^7$
Ni [Ar] $4s^2 3d^8$

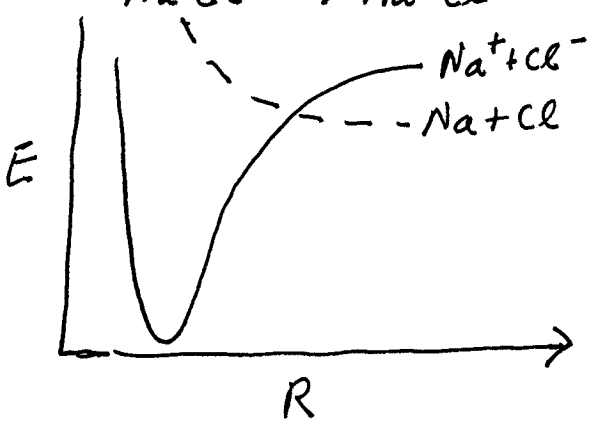
Cu [Ar] $4s 3d^{10}$
Zn [Ar] $4s^2 3d^{10}$

Cr $\underline{4s\ 3d^5}$ vs. $4s^2 3d^4$

$$\underbrace{\uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{d^5}$$

Cu $\underline{4s\ 3d^{10}}$ vs. $4s^2 3d^9$

$NaCl \rightarrow Na^+ Cl^-$ $\qquad \Delta E = IP_{Na} - EA_{Cl} = 5.1 - 3.6 = 1.5\,eV$



Electronegativity: $\chi = IP + EA$ ← definition due to Mulliken

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Many electron atoms:

$n,\ l,\ m_l,\ m_s$ not good quantum #'s

$L = \sum_i l_i$, $S = \sum s_i$ ← vector sums

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

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 $\vec{J} = \vec{L} + \vec{S}$ | $Z \gtrsim 40$

the good quantum #'s or J, M_J

<u>terms + states</u>

| ^{2S+1}L

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

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

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

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

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

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

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

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

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 $1s2s$

1	2	
α	β	$M_S = 0$
β	α	$M_S = 0$
α	α	$M_S = 1$
β	β	$M_S = -1$

There must be a $S=1$ state.

$S=1 \Rightarrow M_S = -1, 0, 1.$

There must also be a $S=0$ state $\Rightarrow M_S = 0$

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

$\left.\begin{matrix}\uparrow\downarrow \\ \downarrow\uparrow\end{matrix}\right\}$ S, T $\rightarrow$ $\psi_S = \frac{1}{2}(1s2s + 2s1s)(\alpha\beta - \beta\alpha)$

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

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

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

The T + S states are different energy $E_T < E_S$

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

multiplicity

Filled shells $\rightarrow$ ^1S

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

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

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

$\left.\begin{matrix}2p - 6 \text{ choices} \\ 3d - 10 \text{ choices}\end{matrix}\right\}$ 60 states

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

^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 princ.

p^2

m_{ℓ_1}	m_{ℓ_2}	M_L	m_{s_1}	m_{s_2}	M_S	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	
1	-1	0	-1/2	1/2	0	$^1D, {}^3P, {}^1S$
			1/2	-1/2	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

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

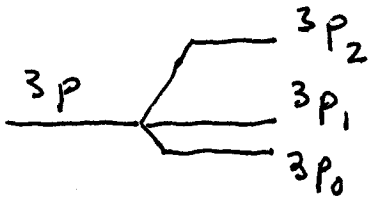
C: $1s^2 2p^2$ $\quad {}^3P < {}^1D < {}^1S$

S.O. coupling $\quad {}^3P \rightarrow {}^3P_2, {}^3P_1, {}^3P_0$

J

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

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

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

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

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

coulomb $\rightarrow J_{12}$

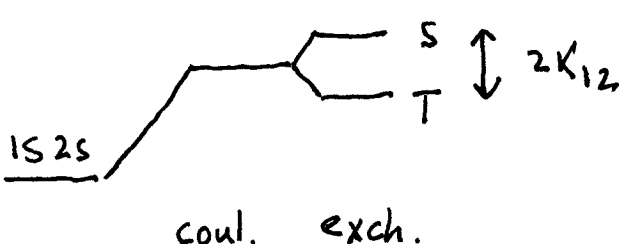
exchange $\rightarrow K_{12}$

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

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

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

$$= E_{1s} + E_{2s} + J_{12} - K_{12}$$, J, K are positive



K_{12} arises from the antisymmetrization of Ψ.