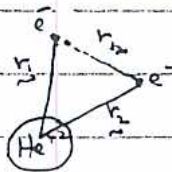


Chem. 1410  
Oct. 29, 2007

Two-electron atom



$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

atomic # [Z=2 for He]  
↓

$$\psi = \psi(r_1, r_2)$$

Attempt to approximate  $\psi$  by (temporarily) neglecting  $\frac{1}{r_{12}}$ ; Then  $\psi(r_1, r_2) \approx \psi(r_1) \psi(r_2)$

$\underbrace{n_1, l_1, m_1}_{\text{standard hydrogenic orbitals}}, \underbrace{n_2, l_2, m_2}$  } any set of H-like orbitals  $\rightarrow$  approx. soln. to S.E.

But, this approximation is not (generally) adequate; doesn't include

Pauli Excl. Principle:

(including spin)  
wavefn. for any many-electron system changes sign under exchange of any 2 electrons!

See

variational  
Principle  
supplement  
[to follow!]

For example, consider approximation for He g.s.:  $\psi(r_1, r_2) \approx \psi_{1s}(r_1) \psi_{1s}(r_2) \rightarrow \psi_{1s}(r_2) \psi_{1s}(r_1)$   
 unchanged [no good]

To patch up, graft on spin  $\psi_{1s}(r) \rightarrow \psi_{1s}(r) \begin{cases} \alpha(r) \\ \beta(r) \\ \text{down} \end{cases}$  [Spin "u.f." S.O.]  $\int d\tau \begin{cases} \beta(r)\beta(r) = 1 \\ \alpha(r)\alpha(r) = 1 \\ \alpha(r)\beta(r) = 0 \end{cases}$

Clearly,  $\psi(r_1, r_2) = \psi_{1s}(r_1) \psi_{1s}(r_2) \left\{ \alpha(r_1)\beta(r_2) - \alpha(r_2)\beta(r_1) \right\} \frac{1}{\sqrt{2}}$  is properly antisymmetric  
 ↑ just for normalization

For 2-electron system  $\psi = (\psi\text{-orbital})(\psi\text{-spin}) \Rightarrow$  relatively minor perturbation due to inclusion of spin, Pauli Ex. Princ.

For <sup>n-more</sup> 3-electron system, can't factorize  $\psi$  into "space x spin"; effects of spin/Pauli Ex. Princ. are profound.

ground state configuration of Many electron atoms:

H 1s  
 He 1s<sup>2</sup>  
 Li 1s<sup>2</sup> 2s ← Pauli Excl. principle ⇒ max. of 2 electrons/spatial orbital  
 [spins must be paired]

Qualitative consequences of Excl. Princib: Aufbau Principle: Imagine modified hydrogenic orbitals exist.

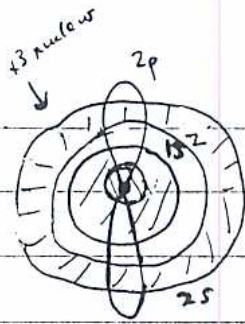
Energy ordering is

orbital degeneracy: 1 1 3 1 3 1 5 3 1 5  
 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d

significant break-down of hydrogenic orbital ordering

Issue: Why breakdown of orbital degeneracy? Ans: shielding and penetration ⇒ relative electrostatic (de)stabilization (4)

Eg: Li:



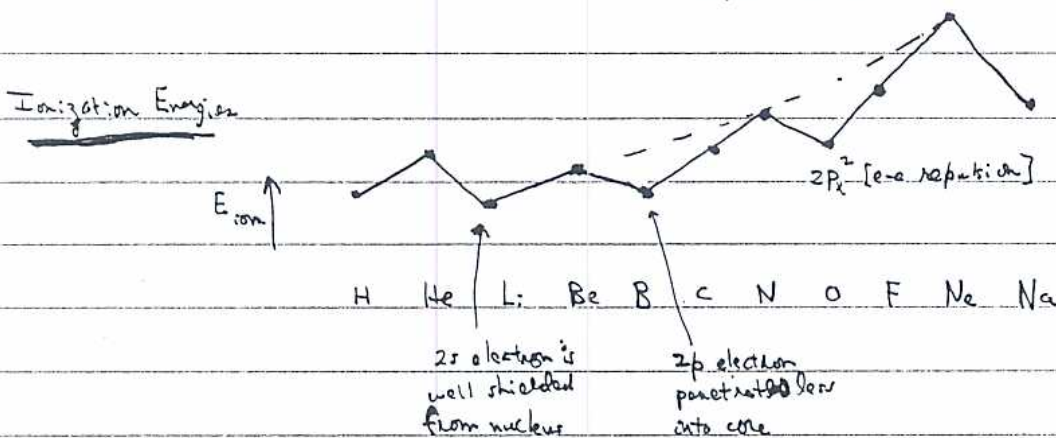
① fill up e's in pairs x orbital degeneracy

② e's fill different degenerate orbitals before pairing

③ Hund's rule: atom adopts config. w/ greatest # unpaired electrons (due to spin correlation)

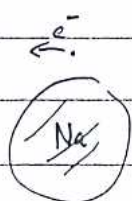
Eg: carbon g.s. =  $1s^2 2s^2 2p_x^1(\alpha) 2p_y^1(\alpha)$

↑  
triplet ← term to be explained below



SCF (Hartree-Fock) approx. for many electron atoms [retains 1-electron orbital concept; refines shape of hydrogenic orbitals + associated energies]

Consider g.s. of Na:  $1s^2 2s^2 2p^6 3s^1$   
core e's →





To extent that core electrons are frozen, 3s electron sees a fancy  $H^+$  nucleus [charge distributed over larger spatial region]

∴ a 1-electron problem!

what to use for frozen core electron charge distribution: why not  $\rho_c(r) = -ze|\psi_{3s}(r)|^2 - ze|\psi_{2s}(r)|^2 - ze|\psi_{2p_x}(r)|^2 - ze|\psi_{2p_y}(r)|^2 - ze|\psi_{2p_z}(r)|^2 = \rho_c(r)$

Then effective SE for 3s electron orbital is:

$$[1] \quad \frac{-\hbar^2}{2m_e} \nabla^2 \psi_{3s} - \frac{ze^2}{4\pi\epsilon_0 r} \psi_{3s} + \underbrace{V_{ee}(r)}_{\substack{\text{potnl. for} \\ \text{interaction} \\ \text{of 3s electron w/} \\ \text{"fixed" electron core}}} \psi_{3s} = E \psi_{3s} \Rightarrow \text{"modified 3s-type orbital"}$$

But!: How do we know appropriate  $\psi_{1s}, \psi_{2s}, \psi_{2p} \dots$

SCF procedure: ① Guess  $\psi_{1s}, \psi_{2s}, \psi_{2p}$  [e.g. Hydrogenic orbitals]

② Compute  $\psi_{3s}$  using Eq. [1]

use updated version!

③ using  $\psi_{1s}, \psi_{2s}, \psi_{3s} \Rightarrow$  use anal of eq [1]  $\psi_{2p}$   
input

④ using  $\psi_{1s}, \psi_{2p}, \psi_{3s} \Rightarrow \psi_{2s}$

⑤ Cycle thru till self-consistency achieved

## Slater determinants + the Pauli Exclusion Principle

Any acceptable N-electron w.f. can be written as (linear combo) of Slater determinants [ ← Build in proper anti-symmetry of w.f. under exchange ]

E.g. for  $N=3$

$$\psi(r_1, r_2, r_3) = \begin{vmatrix} \varphi_a(r_1) \alpha(1) & \varphi_a(r_2) \alpha(2) & \varphi_a(r_3) \alpha(3) \\ \varphi_b(r_1) \beta(1) & \varphi_b(r_2) \beta(2) & \varphi_b(r_3) \beta(3) \\ \varphi_c(r_1) \beta(1) & \varphi_c(r_2) \beta(2) & \varphi_c(r_3) \beta(3) \end{vmatrix} \Leftrightarrow \begin{array}{l} 1 \text{ electron in } \varphi_a, \alpha \\ 1 \text{ electron in } \varphi_b, \beta \\ 1 \text{ electron in } \varphi_c, \beta \end{array}$$

↑ suppress vector signs

↑ ignore normalization

Determinant fact:  $\det |M| = 0$  if any two rows or columns are same

Thus, can't have two electrons w. same spatial orbital index and same spin  $\Rightarrow$  alternate statement of Pauli Excl. Princ. for many electron atoms

(a, b, c)

"No 2 electrons can have the same <sup>set of</sup> g.n.'s [including spin]"

Practice w. Slater det's:  $1s^2$  (g.s.) config. of Helium

$$\psi(r_1, r_2) = \begin{vmatrix} \varphi_{1s}(r_1) \alpha(1) & \varphi_{1s}(r_2) \alpha(2) \\ \varphi_{1s}(r_1) \beta(1) & \varphi_{1s}(r_2) \beta(2) \end{vmatrix} = \varphi_{1s}(r_1) \varphi_{1s}(r_2) \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \}$$

↑  $r_1$

Singlet + triplet states: Consider  $1s^2 2s^1$  excited state configuration of He

(spin)

Construct

spin-orbitals which are acceptable approximate solutions of the Schröd Eq:

(7)

Four possibilities:  $\Psi_S = [\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$  [Neglect spin-normalization]

Singlet  $\rightarrow$

Triplet  $\rightarrow$

$$\Psi_T = [\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)] \left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{array} \right\}$$

If turn out: (i)  $\left\{ \begin{array}{l} \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \end{array} \right\}$  are eigenstates of  $\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)^2$  w/ eigenvalue  $\hbar^2 1(1+1)$   
 [ "triplet" ] ↑  
i.e.  $S=1$

while  $\hat{S}^2 [\alpha(1)\beta(2) - \alpha(2)\beta(1)] = 0$  [i.e.,  $S=0$ ] [ "singlet" ]

$\Rightarrow$  He  $1s^1 2s^1$

(ii) Triplet states lie lower in E by  $\sim 6400 \text{ cm}^{-1} \sim 0.8 \text{ eV}$

(that singlet state)

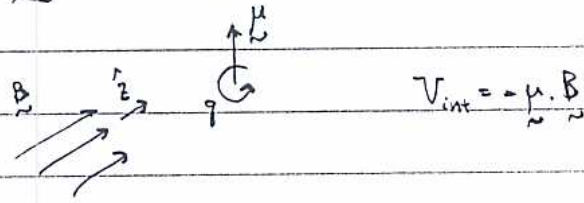
rather large, although

$\ll \Delta E_{1s}^{2s}$  in He<sup>+</sup>;  $\Delta E \sim 20 \text{ eV}$

[ Reason:  $\Psi = 0$  when  $r_1 = r_2$ , so electrons stay out of each other's way ]



# External Magnetic Fields [Zeeman effect]



Classically,  $\vec{\mu} = \gamma \vec{L}$  w.  $\gamma = \frac{q}{2m}$ ; Quantize this:  $\hat{\mu} = \gamma \hat{L}$

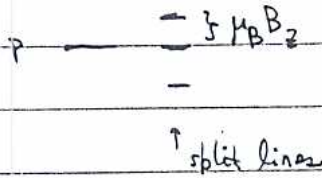
Thus, quantum mechanically:  $\hat{V}_{int} = -\gamma B_z \hat{L}_z$ ; allowed values of  $l_z = \frac{m \hbar}{l}$  [ $m \rightarrow M$  in

multi-electron atoms]

And,

$$E_{int} = - \left[ \frac{-e \hbar}{2m_e} \right] B_z \left( \frac{m \hbar}{l} \right) \equiv \mu_B \frac{m}{l} B_z ; \mu_B = \frac{\hbar e}{2m_e} = \text{"Bohr magneton"}$$

"Normal" Zeeman effect:



Pattern usually complicated by spin magnetic moment [→ "anomalous" Zeeman effect]

$$E_{int} = 2.0023 \mu_B \frac{m}{s} B_z \quad [m_s \rightarrow M_s \text{ in multielectron systems}] \Rightarrow \text{more complicated spectral line pattern}$$

↑ Spin contribution to

↑ [Landé' g factor]