

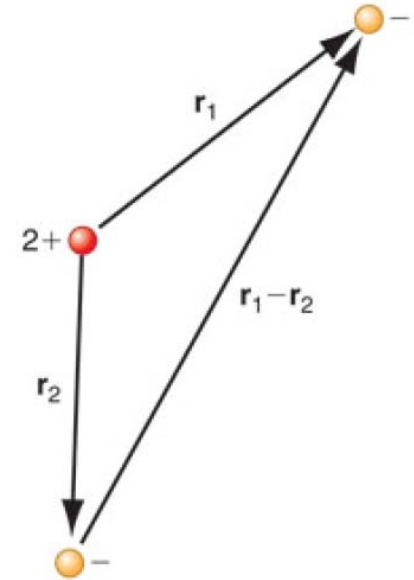
## Ground State of Helium Atom

$$H = H^{(0)} + H^{(1)}$$

$$H^{(0)} = H_1 + H_2, \quad H_i = -\frac{1}{2} \nabla_i^2 - \frac{2}{r_i}, \quad i = 1, 2$$

$H^{(0)}$  separates into two  $H^+$  atom-like Hamiltonians

Full  $H$  does not separate



$$\psi = \psi_{1s}(r_1)\psi_{1s}(r_2) \quad \text{trial function}$$

$$E^{(0)} = -\frac{4}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) = -4, \quad \begin{array}{l} 4x \text{ energy of } H \text{ atom} \\ 2x \text{ energy of } He^+ \end{array}$$

$$E^{(1)} = \left\langle \psi_{1s}(r_1)\psi_{1s}(r_2) \left| \frac{1}{r_{12}} \right| \psi_{1s}(r_1)\psi_{1s}(r_2) \right\rangle \quad \text{Coulomb interaction between two spherical charge distributions}$$

$$= \int |\psi_{1s}(r_1)|^2 \frac{1}{r_{12}} |\psi_{1s}(r_2)|^2 d\vec{r}_1 d\vec{r}_2$$

$$E^{(1)} = \frac{5}{8} Z = \frac{5}{4} \text{ (in } au\text{)}$$

$$E^{(0)} + E^{(1)} = \left(-4 + \frac{5}{4}\right) au = \frac{11}{4} au = -2.75 au$$

Best  $1s(r_1)1s(r_2) - 2.86 au$

Exact  $- 2.90 au$

Error  $\sim 1.1 eV$

Electron correlation energy

The reason we can't get to the exact energy with this type of trial function is that the true wavefunction does not separate.

## 1s2s state of He

$$\left\langle 1s(1)2s(2) \left| H_1 + H_2 + \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle = H_{11}$$
$$= E_{1s} + E_{2s} + J_{12}$$

↖ Coulomb integral between 1s+2s orbitals

Different from  
 $J_{11}$  above

but since we cannot tell which electron is which, we also have to consider  $2s(1)1s(2)$  and the new integral

$$\left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 2s(1)1s(2) \right\rangle = H_{12} = K_{12} \leftarrow \text{Exchange (no classical counterpart)}$$

The 2x2 determinant is

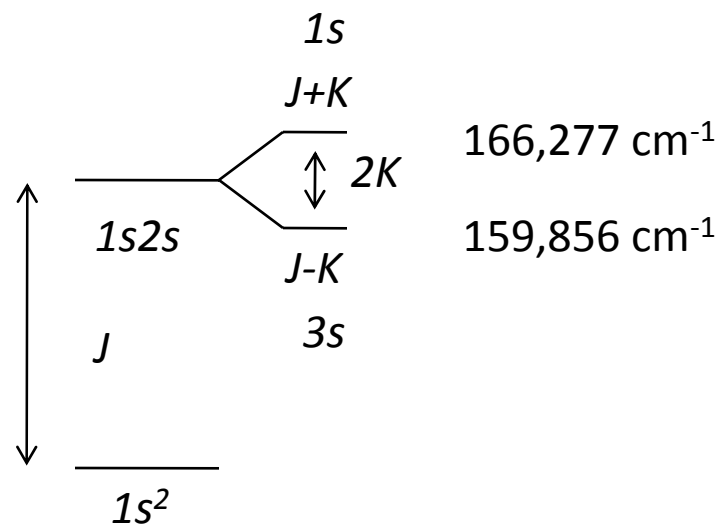
$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0, \quad H_{11} = H_{22}$$

$$E = \frac{E_{1s} + E_{2s}}{2} + J_{12} \pm K_{12}$$

$$\psi = 1s2s \pm 2s1s$$

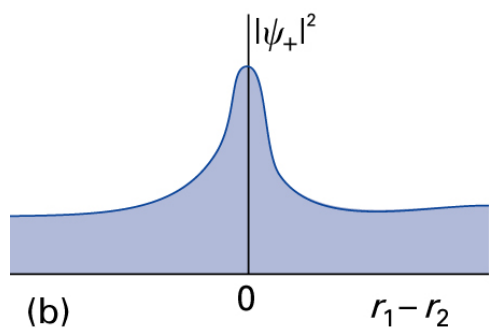
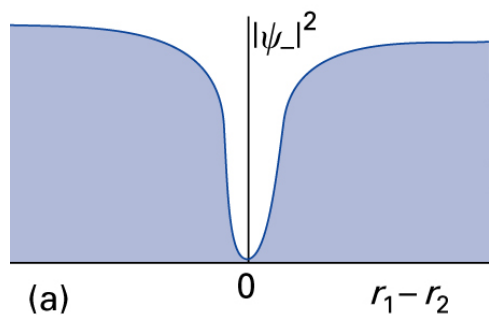
+ singlet

- triplet



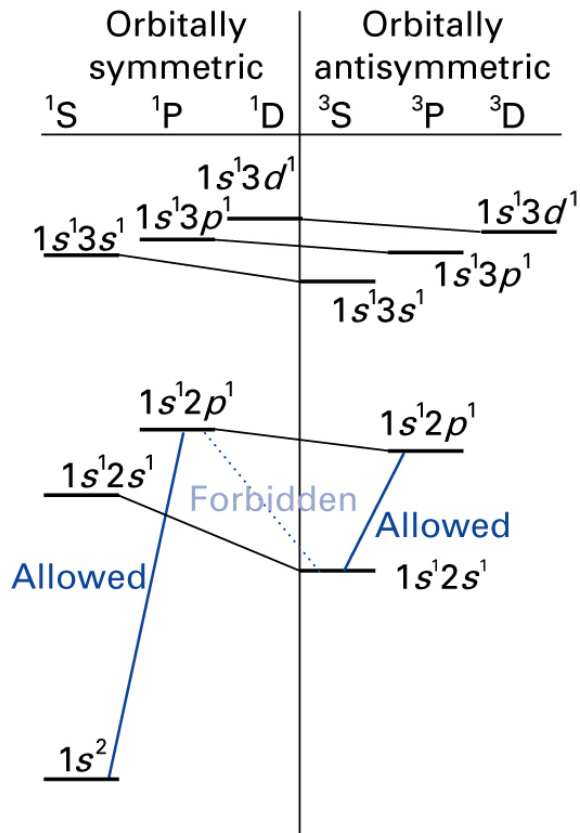
$$\Delta E = 6421 \text{ cm}^{-1} = 0.8 \text{ eV}$$

$$\Rightarrow K_{1s2s} \sim 0.4 \text{ eV}$$



$$\psi_- = \frac{1}{\sqrt{2}} [1s(r_1)2s(r_2) - 2s(r_1)1s(r_2)]$$

$$= 0 \text{ when } r_1 = r_2$$



Energy level diagram for He

singlet  $\longleftrightarrow$  triplet transitions are forbidden

- spin is conserved
- singlet states – symmetrical
- triplet states - antisymmetrical

$$\vec{\mu} = -e \int \underbrace{\psi_+^*(\vec{r}_1, \vec{r}_2)(\vec{r}_1 + \vec{r}_2)\psi_-(\vec{r}_1, r_2)}_{\text{changes sign of } r_1, r_2 \text{ swapped}} d\tau_1 d\tau_2$$

changes sign of  $r_1, r_2$  swapped  
not possible so  $\int = 0$

Transition forbidden

## Pauli Principle

for identical fermions total wave function must be antisymmetric wrt exchange of coordinates (space + spin)

$$(ab + ba)(\alpha\beta - \beta\alpha) \longleftarrow \text{singlet}$$

$$(ab - ba) \left\{ \begin{array}{l} \alpha\alpha \\ \alpha\beta + \beta\alpha \\ \beta\beta \end{array} \right\} \text{ triplet}$$

shorthand nomenclature  
assuming coordinate 1  
precedes coordinate 2

e.g.,  $a(\vec{r}_1)b(\vec{r}_2)$   
 $\alpha(\sigma_1)\beta(\sigma_2)$   
 .....  $\uparrow$  spin coordinate

### Pauli exclusion principle

no two electrons can occupy  
the same state

Consider  $1s(r_1)1s(r_2)\alpha(\sigma_1)\alpha(\sigma_2) \longleftarrow$

does not change sign under  
exchange of coordinates

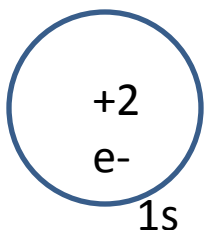
So spin quantum #s must differ

$$1s1s(\alpha\beta - \beta\alpha)$$

Correct form of the wavefunction

He 2s orbital below 2p – why?

He<sup>+</sup> core with either a 2s or 2p orbital



e<sup>-</sup> would see a charge of +1 if its distribution did not penetrate that of the 1s orbital

Since the 2s orbital penetrates the 1s distribution more than the 2p does, causing the 2s orbital to be lower in energy.

Inner electrons shield the outer electrons from the full nuclear charge

*Li* 1s<sup>2</sup>2s    *IP* ~ 5.4 eV    it would be much greater if the 2s electron experienced the full +3 nuclear charge

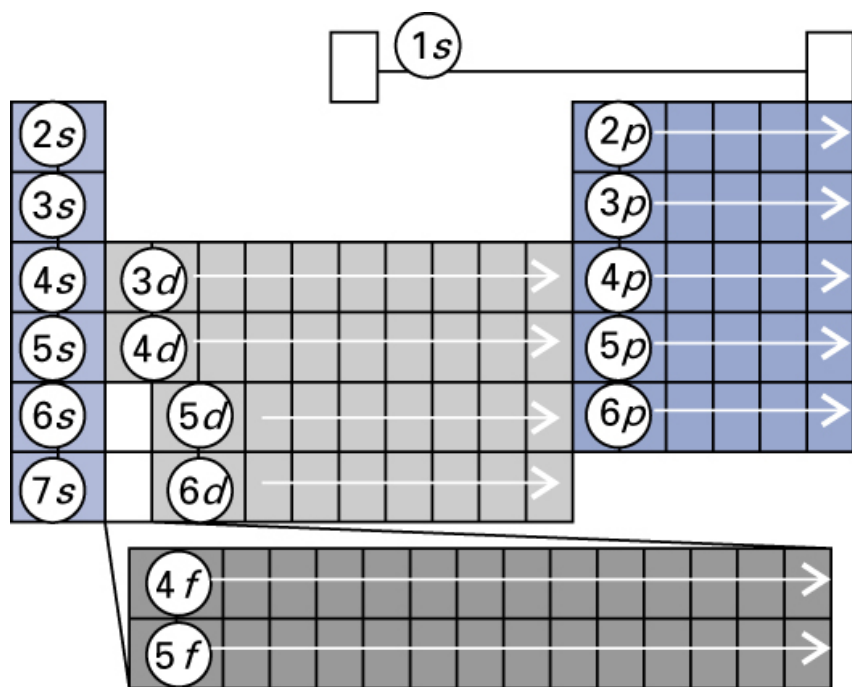
This is > *IP* of the 2s orbital of H due to charge penetration

$$\psi = e^{-Zr/a_0} \quad \text{vary } Z, \text{ get } Z_{\text{eff}} = 1.3$$

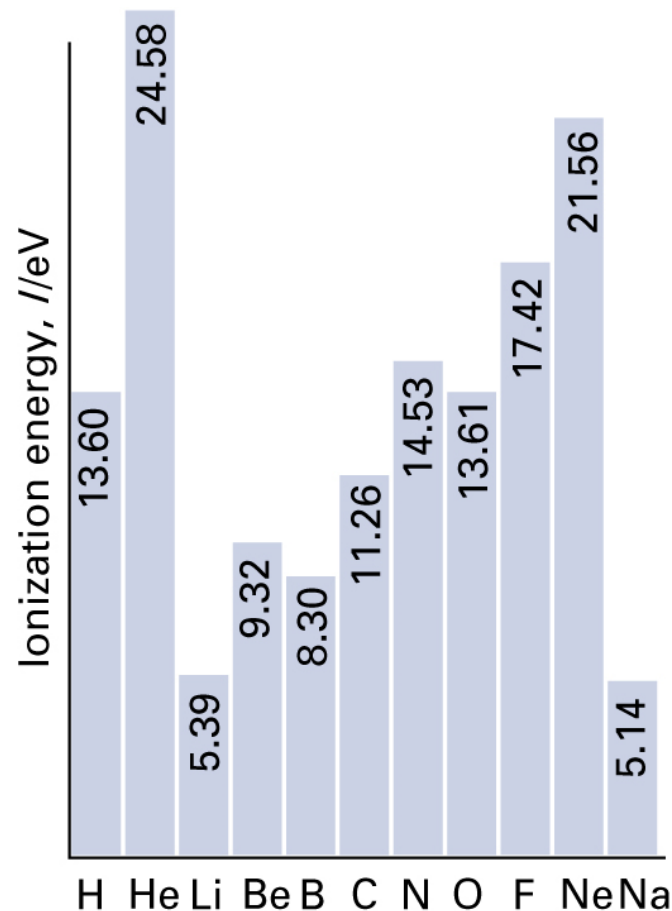
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The shielding effects are responsible for the  
 $s < p < d < f$  filling of shells

$4s$  drops below  $3d$ ,  $5s$  below  $4d$ , etc.,  
Responsible for Ca having  $4s^2$  rather than  $3d^2$ .



Sequence of filling of the atomic orbitals along the periodic table



Trend in IPs

## Slater-type orbitals

$$\psi_{nlm_\ell} = N r^{n_{\text{eff}} - 1} e^{-Z_{\text{eff}} \rho / n_{\text{eff}}} Y_{\ell m_\ell}(\theta, \phi)$$

In practice, use  $\psi = N e^{-\alpha r}$   $s$

$$N \begin{pmatrix} x \\ y \\ z \end{pmatrix} e^{-\alpha' r} \quad p, \text{ etc.}$$

For molecules, most quantum chemistry programs actually use functions of the form

$$\psi_s \sim \sum c_i e^{-\alpha_i r^2}$$

$$\psi_{p_x} \sim \sum c_i x e^{-\alpha_i r^2} \quad \text{etc.}$$

## Self-consistent field methods (Hartree-Fock)

Each electron moves in the average field of the other electrons

$$\Psi_{trial} = |\phi_1 \bar{\phi}_1 \cdots \phi_n \bar{\phi}_n|, \quad \text{"-"} \Rightarrow \beta, \quad \text{no "-" } \Rightarrow \alpha$$

for closed-shell systems

$$E = \frac{\langle \Psi_{trial} | H | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle}$$

Optimize parameters in orbitals to minimize energy subject to constraint the orbitals are orthonormal

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

Set of equations which define the orbitals and the orbital energies

But the operator  $V_i^{eff}$  depends on the orbitals we are trying to find!!

So this is not an eigenvalue problem in the usual sense

$$V^{eff} = \sum_r (2J_r - K_r)$$

$$J_r \phi_s(1) = \left[ \int \phi_r^*(2) \frac{1}{r_{12}} \phi_r(2) dr_2 \right] \phi_s(1)$$

$$K_r \phi_s(1) = \left[ \int \phi_r^*(2) \frac{1}{r_{12}} \phi_s(2) dr_2 \right] \phi_r(1)$$

note exchange

$$\varepsilon_s = \langle s | h_1 | s \rangle + \sum_r (2J_{sr} - K_{sr})$$

$h_1$  involves the kinetic energy and electron-nuclear interactions

$$E = 2 \sum_s \varepsilon_s - \sum_{r,s} (2J_{rs} - K_{rs})$$

Coulomb and exchange subtracted off to prevent double counting

Check on *He* atom

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

$$E = 2\varepsilon_{1s} - [2J_{1s,1s} - K_{1s,1s}] = 2\varepsilon_{1s} - J_{1s,1s} = 2E_{1s} + J_{1s,1s}$$

## How does one actually solve the Hartree-Fock equations?

Guess a set of orbitals

- build  $J_r, K_r$
- calculate  $E$
- solve for  $\phi_s, \varepsilon_s$



Iterate until convergence is achieved