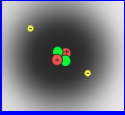


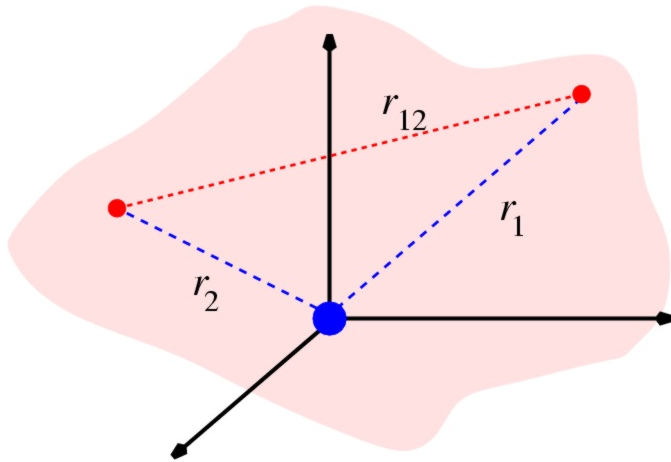
Polyelectronic atoms



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I.A. Interelectronic repulsion



■ Helium atom

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + k \frac{e^2}{r_{12}}$$

$$\hat{h}_1 = -\frac{\hbar^2}{2\mu} \nabla_1^2 - k \frac{Ze^2}{r_1}$$

$$\hat{h}_2 = -\frac{\hbar^2}{2\mu} \nabla_2^2 - k \frac{Ze^2}{r_2}$$

- h_1 y $h_2 \Rightarrow$ hydrogenic Hamiltonians
- Interelectronic repulsion \Rightarrow coupled motions
- Schrödinger's equation \Rightarrow no analytic solution



I.B. Slater determinants

- He $\Rightarrow 1s^2 \Rightarrow 1s(1)1s(2) \Rightarrow$ Symmetric with respect to $P_{1,2}$

$$\text{spin} \left\{ \begin{array}{l} \alpha(1)\alpha(2) \rightarrow \text{Symmetric} \\ \beta(1)\beta(2) \rightarrow \text{Symmetric} \\ \alpha(1)\beta(2) \\ \beta(1)\alpha(2) \end{array} \right\} \text{ No symmetry} \rightarrow \left\{ \begin{array}{l} \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \rightarrow \text{Symmetric} \\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \rightarrow \text{Antisymmetric} \end{array} \right.$$

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



I.B. Slater determinants

- $\text{Li} \Rightarrow \zeta 1s^3? \Rightarrow 1s(1)1s(2)1s(3) \Rightarrow \text{Symmetric.}$

There is no combination of $\alpha(1)$, $\alpha(2)$, $\alpha(3)$, $\beta(1)$, $\beta(2)$ y $\beta(3)$ antisymmetric with respect to $P_{1,2}$, $P_{1,3}$ y $P_{2,3}$ simultaneously.

- Pauli exclusion principle. Two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously.

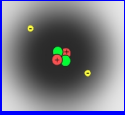


I.B. Slater determinants

- Slater determinants

$$\Psi_{\text{He},1s^2} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = 1s(1)1s(2) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

$$\begin{aligned} \Psi_{\text{Li},1s^2 2s} &= \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \\ &= |1s\bar{1}s2s| \end{aligned}$$



II.A. Perturbation treatment



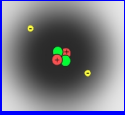
■ Lithium atom

$$\hat{H}(0) = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\hbar^2}{2m_e} \nabla_3^2 - k \frac{Ze^2}{r_1} - k \frac{Ze^2}{r_2} - k \frac{Ze^2}{r_3}$$

$$\hat{H}' = k \frac{e^2}{r_{12}} + k \frac{e^2}{r_{23}} + k \frac{e^2}{r_{13}}$$

$$\begin{aligned} \psi^{(0)} = & 6^{-1/2} [1s(1)1s(2)2s(3)\alpha(1)\beta(2)\alpha(3) - 1s(1)2s(2)1s(3)\alpha(1)\alpha(2)\beta(3) \\ & - 1s(1)1s(2)2s(3)\beta(1)\alpha(2)\alpha(3) + 1s(1)2s(2)1s(3)\beta(1)\alpha(2)\alpha(3) \\ & + 2s(1)1s(2)1s(3)\alpha(1)\alpha(2)\beta(3) - 2s(1)1s(2)1s(3)\alpha(1)\beta(2)\alpha(3)] \end{aligned}$$

$$E^{(0)} = E_{1s}^{(0)} + E_{1s}^{(0)} + E_{2s}^{(0)}$$



II.A. Perturbation treatment

- Independent electron approximation

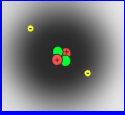
$$E^{(0)} = -\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2}\right) \left(\frac{Z^2 e^2}{2a_0}\right) = -\frac{81}{4} (13.606 \text{ eV}) = -275.5 \text{ eV}$$

$$E_{\text{exac}} = -203.5 \text{ eV} \Rightarrow \text{Error } -35.4 \%$$

- First order correction

$$\begin{aligned} E^{(1)} &= 2 \iint |1s(1)2s(2)|^2 \frac{e^2}{r_{12}} dv_1 dv_2 + \iint |1s(1)1s(2)|^2 \frac{e^2}{r_{12}} dv_1 dv_2 \\ &\quad - \iint 1s(1)^* 2s(2)^* 1s(2) 2s(1) \frac{e^2}{r_{12}} dv_1 dv_2 \\ &= \underbrace{2J_{1s2s} + J_{1s1s}}_{\text{Coulomb int.}} - \underbrace{K_{1s2s}}_{\text{exchange int.}} = 83.5 \text{ eV} \end{aligned}$$

$$E^{(0)} + E^{(1)} = -192.0 \text{ eV} \Rightarrow \text{Error } 5.7 \%$$



II.B. Variational treatment

- Screening and effective nuclear charge $\Rightarrow Z^* = Z - \sigma$

$$\phi = \frac{1}{\sqrt{6}} \begin{vmatrix} f(1)\alpha(1) & f(1)\beta(1) & g(1)\alpha(1) \\ f(2)\alpha(2) & f(2)\beta(2) & g(2)\alpha(2) \\ f(3)\alpha(3) & f(3)\beta(3) & g(3)\alpha(3) \end{vmatrix}$$

$$f = \frac{1}{\pi^{1/2}} \left(\frac{b_1}{a_0} \right)^{3/2} e^{-b_1 r/a_0}$$

$$g = \frac{1}{4(2\pi)^{1/2}} \left(\frac{b_2}{a_0} \right)^{3/2} \left(2 - \frac{b_2 r}{a_0} \right) e^{-b_2 r/2a_0}$$

$$b_1 = 2.686, b_2 = 1.776 \text{ y } W = -201.2 \text{ eV} \Rightarrow \text{Error } 1.1 \%$$



II.C. Hartree-Fock approximation



- Factorable function

$$\phi = g_1(r_1, \theta_1, \phi_1)g_2(r_2, \theta_2, \phi_2) \cdots g_n(r_n, \theta_n, \phi_n)$$

$$g_i = h_i(r_i)Y_{m_i}^{l_i}(\theta_i, \phi_i)$$

- Hartree-Fock approximation

$$\left[-\frac{\hbar^2}{2\mu} \nabla_1^2 - k \frac{Ze^2}{r_1} + \langle g(2) | k \frac{e^2}{r_{12}} | g(2) \rangle \right] g(1) = \epsilon_1 g(1)$$
$$\left[-\frac{\hbar^2}{2\mu} \nabla_2^2 - k \frac{Ze^2}{r_2} + \langle g(1) | k \frac{e^2}{r_{12}} | g(1) \rangle \right] g(2) = \epsilon_2 g(2)$$

II.C. Hartree-Fock approximation

- Li \Rightarrow Error = 0.6%
- Correlation energy $\Rightarrow E_{\text{corr}} = E_{\text{exac}} - E_{\text{HF}}$

CORRELATION ENERGY FOR ATOMIC SYSTEMS

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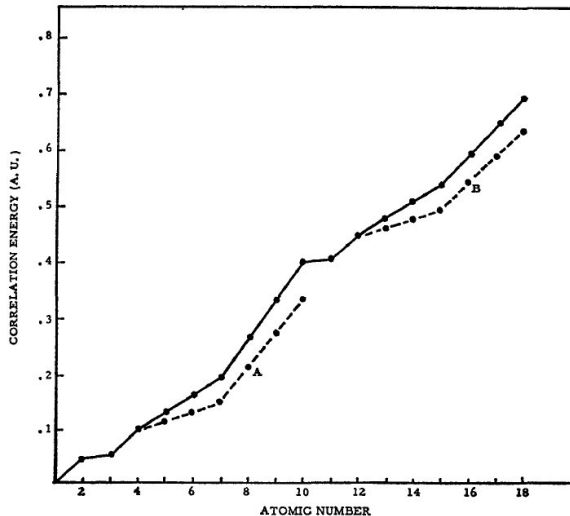
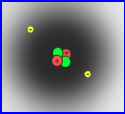


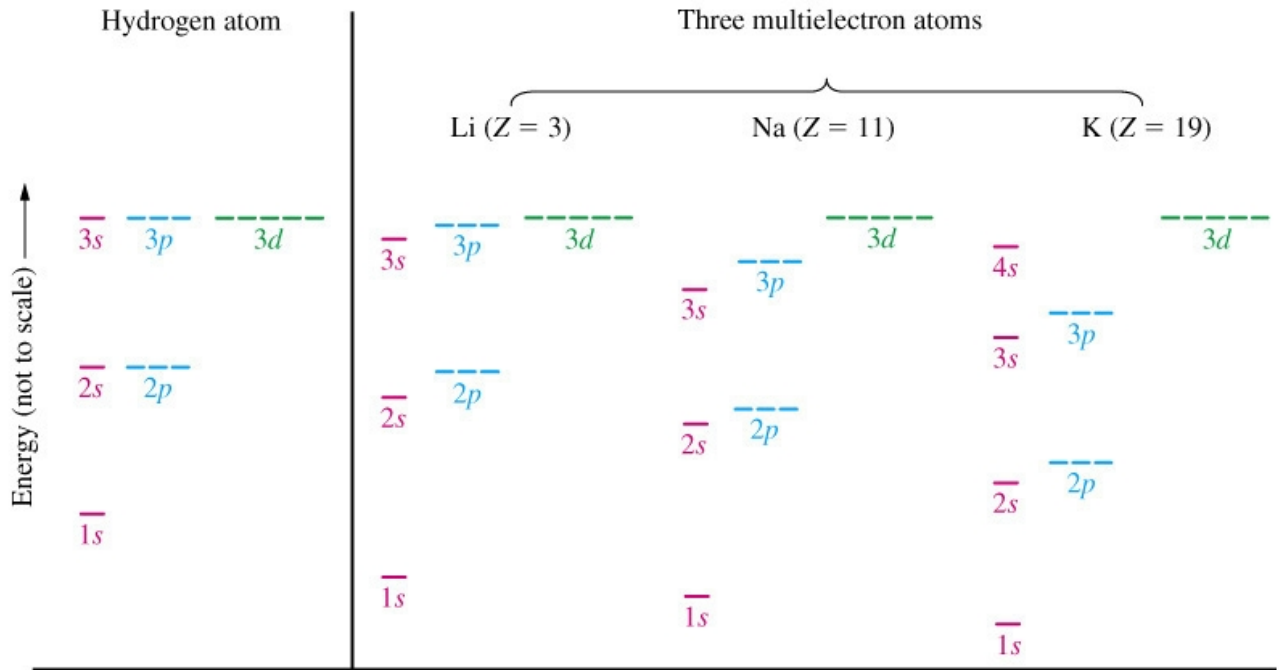
FIG. 2. Correlation energy for the ground states of neutral atoms. The full line refers to the values for the correlation energy when the relativistic energy is carefully considered. The dotted lines refer to the value for the correlation energy one would obtain by use of Eq. (1), where the relativistic effect is approximated.

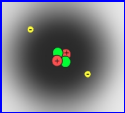
- 1 a.u. = 27 eV
- E. Clementi. J. Chem. Phys. 38, 2248 (1963).
- \downarrow Error if $\uparrow Z$



III.A. Electronic configurations

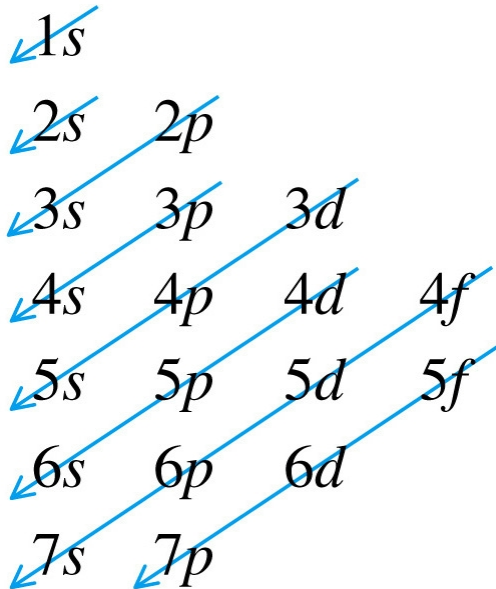
■ Energy levels



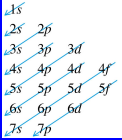


III.A. Electronic configurations

■ Aufbau rule



- Energy $\propto n + l$
- For a given $n + l$ lower energy for lower n



III.A. Electronic configurations

- Hund's rule \Rightarrow The sum of the spins must be maximum

