Polyelectronic atoms

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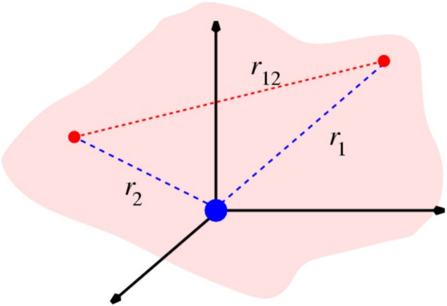
PHYSICAL CHEMISTRY I

Index

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 ⇒ hydrogenic Hamiltonians
- Interelectronic repulsion ⇒ coupled motions
- Schrödinger's equation ⇒ no analytic solution

Slater determinants

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

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

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

Slater determinants

- Li $\Rightarrow 1s^3? \Rightarrow 1s(1)1s(2)1s(3) \Rightarrow$ 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.

Slater determinants

- Slater determinants

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

$$\psi_{\mathrm{Li},1s^22s} = \frac{1}{\sqrt{6}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$= \left|1s\overline{1s}2s\right|$$

Perturbation treatment

- Lithium atom

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

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

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

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

Perturbation treatment

- Independent electron approximation

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

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

- First order correction

$$E^{(1)}=2\iint|1s(1)2s(2)|^2\frac{e^2}{r_{12}}dv_1\,dv_2+\iint|1s(1)1s(2)|^2\frac{e^2}{r_{12}}dv_1\,dv_2$$

$$-\iint 1s(1)^*2s(2)^*1s(2)2s(1)\frac{e^2}{r_{12}}dv_1\,dv_2$$

$$=\underbrace{2J_{1s2s}+J_{1s1s}}_{\text{Coulomb int.}}-\underbrace{K_{1s2s}}_{\text{exchange int.}}=83.5\text{ eV}$$

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

Variational treatment

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

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

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

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

$b_1 = 2.686$, $b_2 = 1.776$ y $W = -201.2$ eV ⇒ Error 1.1 %

Hartree-Fock approximation

- Factorable function

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

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

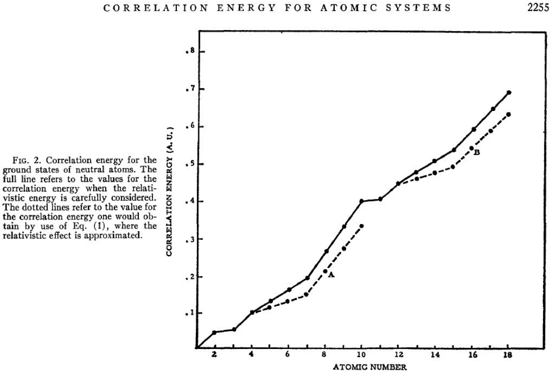
- Hartree-Fock approximation

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

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

Hartree-Fock approximation

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



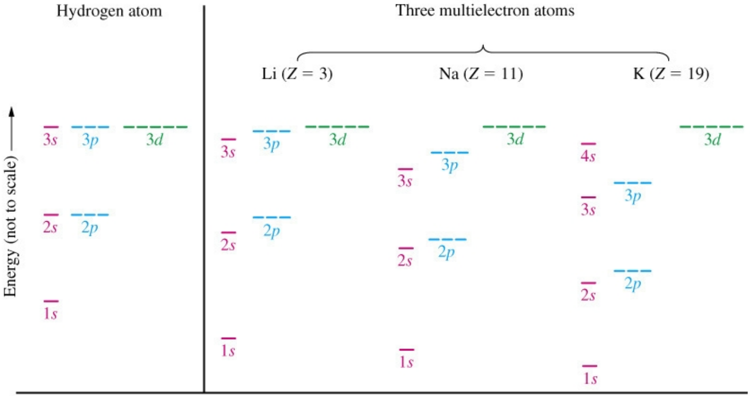
CORRELATION ENERGY FOR ATOMIC SYSTEMS 2255

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 $\uparrow Z$

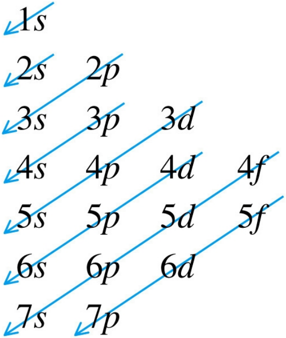
Energy levels

- Energy levels



Aufbau rule

- Aufbau rule



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

Hund's rule

- Hund's rule ⇒ The sum of the spins must be maximun

$$[\mathrm{H}] \Rightarrow \underset{1s}{\underline{\uparrow}}$$

$$[\mathrm{He}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}$$

$$[\mathrm{Li}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow}}$$

$$[\mathrm{Be}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow\downarrow}}$$

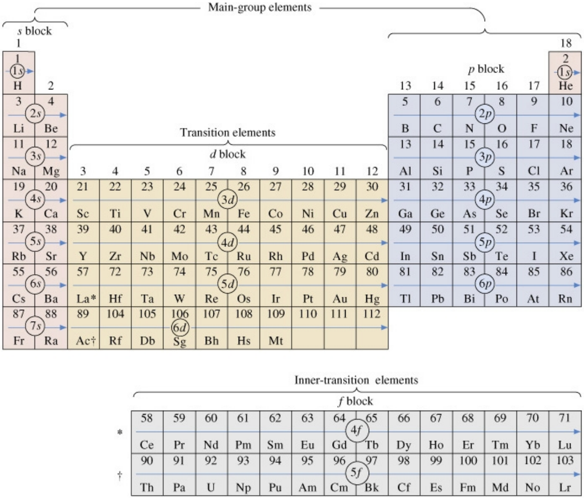
$$[\mathrm{B}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p}{\underline{\uparrow}}$$

$$[\mathrm{C}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p}{\underline{\uparrow}\,\underline{\uparrow}}$$

$$[\mathrm{N}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p}{\underline{\uparrow}\,\underline{\uparrow}\,\underline{\uparrow}}$$

$$[\mathrm{O}] \Rightarrow \underset{1s}{\underline{\uparrow\downarrow}}\quad \underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p}{\underline{\uparrow\downarrow}\,\underline{\uparrow}\,\underline{\uparrow}}$$

Periodic table of the elements



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112						

*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr