

Polyelectronic atoms

TEMA: POLYELECTRONIC ATOMS

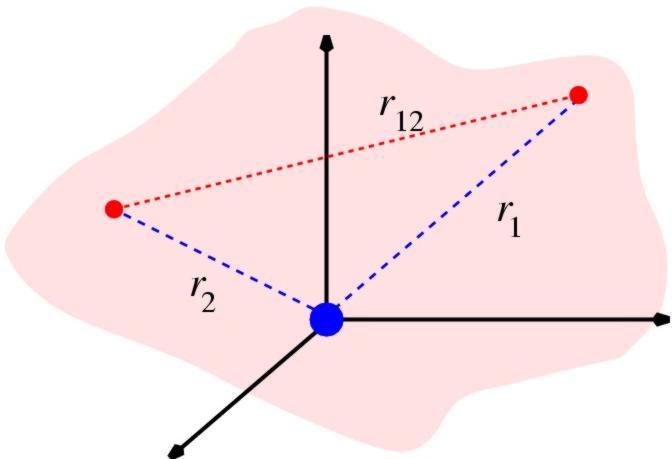
Introduction



I.	Spin-orbital functions	2
I.A.	Interelectronic repulsion	2
I.B.	Slater determinants	3
II.	Perturbation treatment	6
II.A.	Perturbation treatment	6
II.B.	Variational treatment	8
II.C.	Hartree-Fock approximation	9
III.	Electronic configurations	11
III.A.	Electronic configurations	11



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

POLYELECTRONIC
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I. Spin-orbital functions

3

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

spin $\left\{ \begin{array}{l} \alpha(1)\alpha(2) \rightarrow \text{Symmetric} \\ \beta(1)\beta(2) \rightarrow \text{Symmetric} \\ \alpha(1)\beta(2) \\ \beta(1)\alpha(2) \end{array} \right\}$ 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

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I. Spin-orbital functions



- Li $\Rightarrow \dot{\epsilon} 1s^3 ? \Rightarrow 1s(1)1s(2)1s(3) \Rightarrow$ 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.



I.B. Slater determinants

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I. Spin-orbital functions

5

■ Slater determinants

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

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

II.A. Perturbation treatment

II. Perturbation treatment

■ Lithium atom

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

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

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

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

- 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

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

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



II.B. Variational treatment

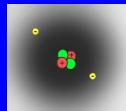
- Screening and effective nuclear charge $\Rightarrow Z^* = Z - \sigma$

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

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

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

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



II.C. Hartree-Fock approximation

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II. Perturbation treatment

6

- Factorable function

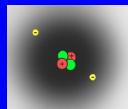
$$\phi = g_1(r_1, \theta_1, \phi_1)g_2(r_2, \theta_2, \phi_2) \cdots g_n(r_n, \theta_n, \phi_n)$$

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

- Hartree-Fock approximation

$$\left[-\frac{\hbar^2}{2\mu} \nabla_1^2 - k \frac{Ze^2}{r_1} + \langle g(2) | k \frac{e^2}{r_{12}} | g(2) \rangle \right] g(1) = \varepsilon_1 g(1)$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_2^2 - k \frac{Ze^2}{r_2} + \langle g(1) | k \frac{e^2}{r_{12}} | g(1) \rangle \right] g(2) = \varepsilon_2 g(2)$$



I.I.C. Hartree-Fock approximation

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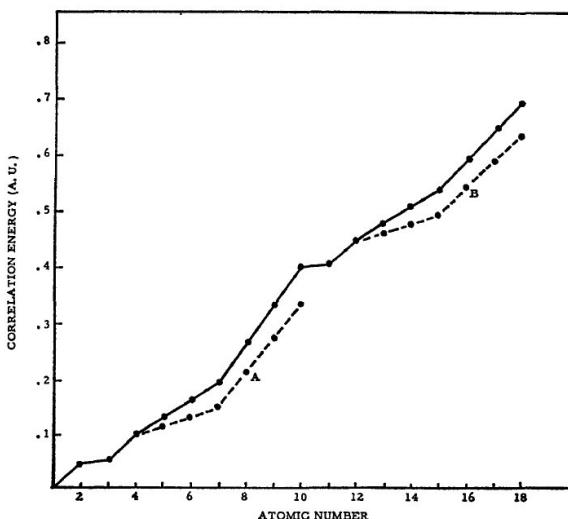
II. Perturbation treatment

10

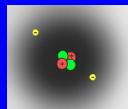
- Li \Rightarrow Error = 0.6 %
- Correlation energy $\Rightarrow E_{\text{corr}} = E_{\text{exac}} - E_{\text{HF}}$

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 $\uparrow Z$



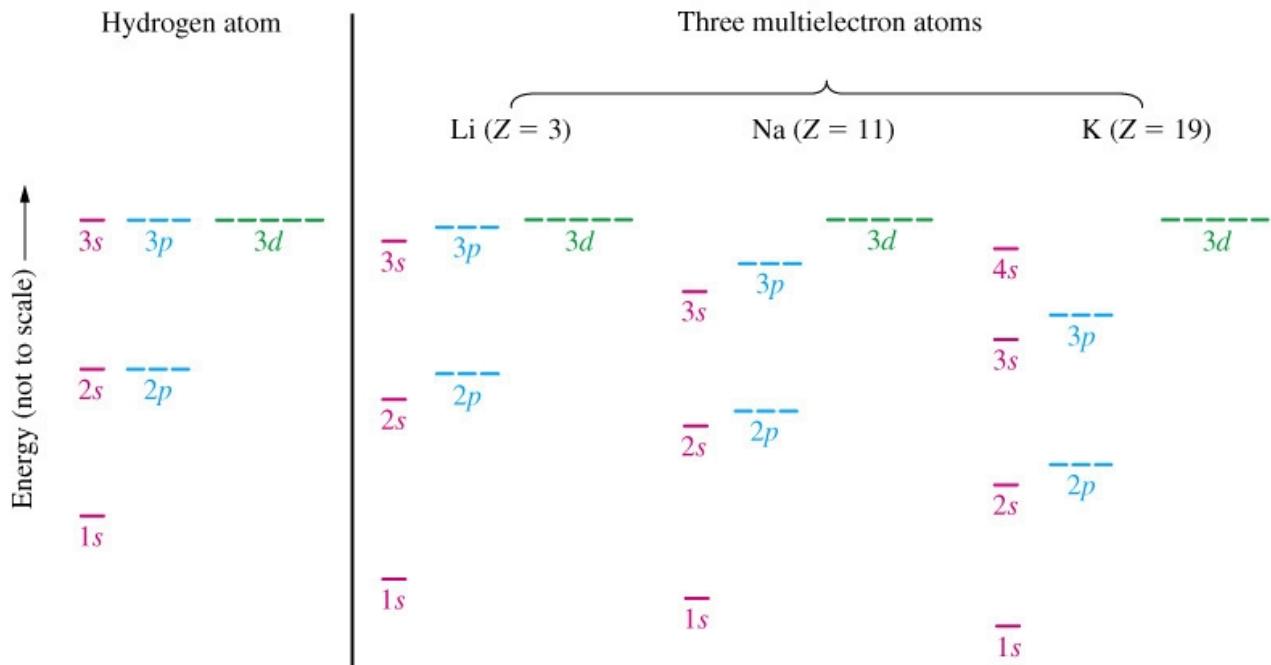
III.A. Electronic configurations

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III. Electronic configurations

11

■ Energy levels





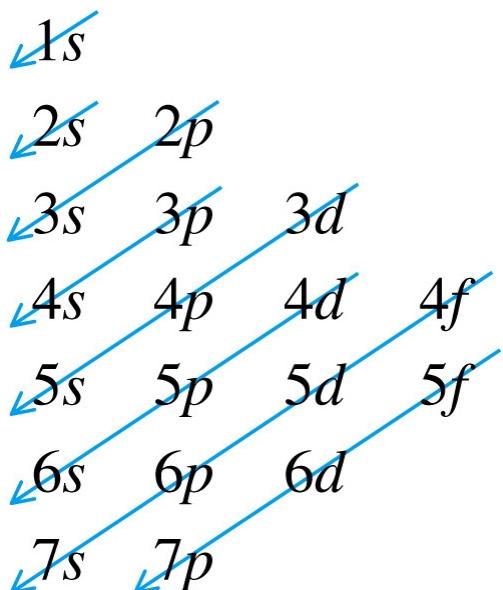
III.A. Electronic configurations

POLYELECTRONIC
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III. Electronic configura-
tions

12

■ Aufbau rule



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



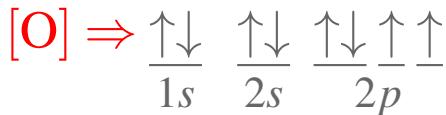
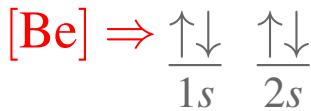
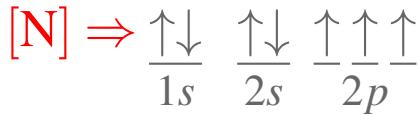
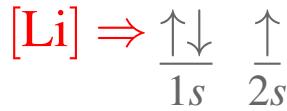
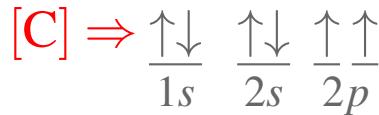
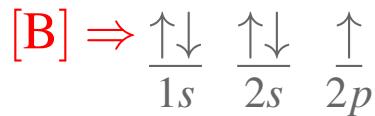
III.A. Electronic configurations

POLYELECTRONIC
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III. Electronic configurations

13

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





III.A. Electronic configurations

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III. Electronic configurations

14

Main-group elements																		
s block																		
1	(1s) H	2																
3	(2s) Li	4	(2s) Be															
11	(3s) Na	12	(3s) Mg															
19	(4s) K	20		21	22	23	24	25	26	27	28	29	30					
				Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn					
37	(5s) Rb	38	(5s) Sr		39	40	41	42	43	44	45	46	47	48				
				Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd					
55	(6s) Cs	56	(6s) Ba		57	72	73	74	75	76	77	78	79	80				
				La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg					
87	(7s) Fr	88	(7s) Ra		89	104	105	106	107	108	109	110	111	112				
				Ac†	Rf	Db	Sg	Bh	Hs	Mt								
Transition elements																		
d block																		
13	14	15	16	17	18													
5	6	7	(2p) N	O	F	He												
13	14	15	(3p) P	S	Cl	Ar												
31	32	33	(4p) As	Se	Br	Kr												
49	50	51	(5p) Sb	Te	I	Xe												
81	82	83	(6p) Po	At	Rn													
Inner-transition elements																		
f block																		
*	58	59	60	61	62	63	64	(4f) Gd	65	66	67	68	69	70	71			
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
†	90	91	92	93	94	95	96	(5f) Cm	97	98	99	100	101	102	103			
	Th	Pa	U	Np	Pu	Am	Bk	Cf	Es	Fm	Md	No	Lr					