

Roadmap to the structure of N -electron atoms

Hydrogenic systems:

Quantum defect Foot 4.2



2-electron systems:

Perturbation treatment - very crude Foot 3.1

Antisymmetric wavefunctions - very important Foot 3.2.1

N -electron systems:

Central field approximation Foot 4.3

Configurations Foot 4.1

The periodic table of elements

LS -coupling: Foot 5

Detailed energy structure within a configuration

Electrostatic interaction in 2-electron systems.

Neglect finestructure just to simplify notations

$$\left(-\frac{\hbar^2}{2m}\hat{\nabla}_1^2 - \frac{Ze^2}{4\pi\epsilon_0\hat{r}_1} - \frac{\hbar^2}{2m}\hat{\nabla}_2^2 - \frac{Ze^2}{4\pi\epsilon_0\hat{r}_2} + \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}}\right)\Psi(1,2) = E \cdot \Psi(1,2)$$

$$(\hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}})\Psi(1,2) = E \cdot \Psi(1,2)$$

$$\hat{r}_{12} = |\hat{r}_1 - \hat{r}_2|$$

First approximation: neglect the whole repulsion!!

$$\hat{H}_0 = \hat{H}_1 + \hat{H}_2$$

$$\hat{H}_i\phi_i(i) = E_i\phi_i(i), i = 1, 2.$$

$$E_i = -R\frac{Z^2}{n_i^2}$$

$$\phi_i(i) = R_{n_i\ell_i}(r_i) \cdot Y_{\ell_i, m_{\ell_i}}(\theta_i, \varphi_i) \cdot \chi_{m_{s_i}}(sz_i)$$

$$\Psi_0(1,2) = \phi_1(1) \cdot \phi_2(2) \quad (i) = (r_i, \theta_i, \varphi_i, sz_i)$$

$$E_0 = E_1 + E_2$$

First order perturbation calculation:

$$E = E_0 + \left\langle \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}} \right\rangle_{\Psi_0}$$

Table 2.2 Radial hydrogenic wavefunctions $R_{n,l}$ in terms of the variable $\rho = Zr/(na_0)$, which gives a scaling that varies with n . The Bohr radius a_0 is defined in eqn 1.40.

$$R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0}\right)^{3/2} 2(1 - \rho) e^{-\rho}$$

$$R_{2,1} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{2}{\sqrt{3}} \rho e^{-\rho}$$

$$R_{3,0} = \left(\frac{Z}{3a_0}\right)^{3/2} 2 \left(1 - 2\rho + \frac{2}{3}\rho^2\right) e^{-\rho}$$

$$R_{3,1} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \rho \left(1 - \frac{1}{2}\rho\right) e^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \rho^2 e^{-\rho}$$

Normalisation: $\int_0^\infty R_{n,l}^2 r^2 dr = 1$

Antisymmetric wavefunctions

A particle with half integer spin (fermion) must be described by an antisymmetric wavefunction

$$\Psi(\bar{q}_1, \bar{q}_2) = \frac{1}{\sqrt{2}} [\phi_1(1) \cdot \phi_2(2) - \phi_1(2) \cdot \phi_2(1)]$$

coordinates

$$\bar{q} = (r, \theta, \varphi, sz)$$

quantum numbers

$$\phi_i = R_{n_i \ell_i}(r_j) \cdot Y_{\ell_i, m_{\ell_i}}(\theta_j, \varphi_j) \cdot \chi_{m_{s_i}}(sz_j)$$

$$i = 1, 2. \quad j = 1, 2.$$

- $1/\sqrt{2}$ due to normalisation
- $\Psi(\bar{q}_2, \bar{q}_1) = -\Psi(\bar{q}_1, \bar{q}_2)$
- "+" sign will give the symmetric function
- 2 electrons cannot have ALL 4 quantum numbers equal $\Rightarrow$ Pauli principle

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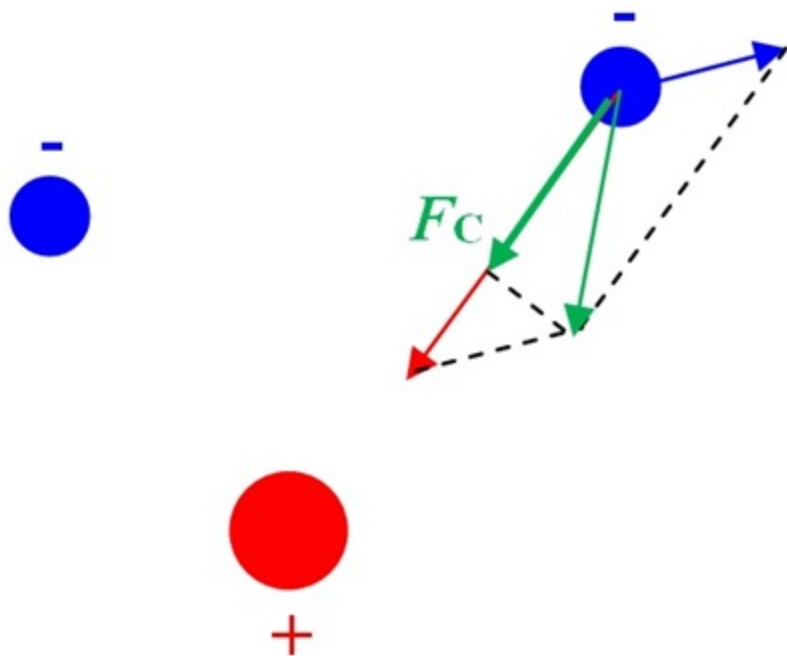
LS -coupling: Foot 5

Detailed energy structure within a configuration

The central field approximation

N -electron atoms

- Each electron moves independently of the others in the electrostatic field from the nucleus and the other $N - 1$ electrons.
- This field is assumed to be spherically symmetric.



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Independent

Unknown but spherically symmetric

$$\hat{H}\Psi = E\Psi$$
$$\hat{H} = \sum_{i=1}^N \hat{H}_i = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \hat{\nabla}_i^2 + \hat{V}_i(r_i) \right)$$
$$\Psi = \prod_{i=1}^N \phi_i \quad E = \sum_{i=1}^N \varepsilon_i \quad \hat{H}_i \phi_i = \varepsilon_i \phi_i$$
$$\phi_i = R_{n_i \ell_i}(r_i) \cdot Y_{\ell_i, m_{\ell_i}}(\theta_i, \varphi_i) \cdot \chi_{m_{s_i}}(s_{z_i})$$

Determined numerically

The diagram illustrates the central field approximation by showing the total Hamiltonian and wavefunction as sums and products of single-electron terms. Annotations highlight the independent nature of these terms and the spherically symmetric but unknown potential, which is then determined numerically.

(Physically acceptable wavefunctions Ψ must then be anti-symmetrized.)

One-electron atoms in spherical coordinates

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 \cdot r} \\ &= -\frac{\hbar^2}{2\mu} \cdot \left[\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \right] - \frac{Ze^2}{4\pi\epsilon_0 \cdot r} \\ &= -\frac{\hbar^2}{2\mu} \cdot \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\textcolor{red}{L}^2}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi\epsilon_0 \cdot r} \end{aligned}$$

Generally, any spherical
potential, $U(\vec{r})=U(r)$

$$\Psi(r, \theta, \varphi, s_z) = R_{n,\ell}(r) \cdot Y_{\ell, m_\ell}(\theta, \varphi) \cdot \chi_{s, m_s}(s_z)$$

Self consistent field technique.

$$\hat{H} = \sum_{i=1}^N \hat{H}_i = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \hat{\nabla}_i^2 + \hat{V}_i(r_i) \right)$$

$$E = \sum_{i=1}^N \varepsilon_i \quad \hat{H}_i \phi_i = \varepsilon_i \phi_i$$

$$\phi_i = R_{n_i l_i}(r_i) \cdot Y_{l_i, m_{l_i}}(\theta_i, \varphi_i)$$

1. Guess $R_i(r_i)$ $i = 1, 2, \dots, N$
2. Calculate the potential, V_i , experienced by electron i due to the attraction of the nucleus and the repulsion from the charge distributions, $e \cdot |\phi_j|^2$ $j \neq i$, of the other $N-1$ electrons. (see Ex 25, H2)
3. Solve $\hat{H}_i \phi_i = \varepsilon_i \phi_i$ numerically $\Rightarrow R_i$ and ε_i
4. Repeat 3 for all N electrons $\Rightarrow$ improved $R(r)$.
5. Iterate from 2 until energies and wavefunctions reach a desired consistency.

Ionization energies (cm⁻¹) in He-like systems in different approximations.

$$E_{\text{ion}}^{\text{He}} = \left| E_{\text{He}}(1s^2) - E_{\text{He}^+}(1s) \right| = \left| E_{\text{He}}(1s^2) - R \frac{Z^2}{1^2} \right|$$

Approx	He I	ΔE / %	C V	ΔE / %
E_0	438920	-	3950352	-
E_1	164605	17	3127370	1.1
E_{CFA}	189116	4.6	3163975	0.05
E_{exp}	198310.66637(20) ^a		3162408(20) ^b	

E_0 : No repulsion at all! $E(1s^2) = -2 \cdot R \cdot \frac{Z^2}{1^2}$

E_1 : First order perturbation. $E(1s^2) = -2 \cdot R \cdot \frac{Z^2}{1^2} + \frac{5}{4} R \cdot Z$

E_{CFA} Central field approximation

^a) D. Z. Kandula *et al.*, Phys. Rev. Lett. **105**, 063001 (2010)

^b) L. Engström *et al.*, J. Phys. B: At. Mol. Opt. Phys. **25**, 2459 (1992)

Note that since binding energies scale with Z^2 and the electron repulsion only as Z , the CFA gets better as Z increases along an isoelectronic sequence

The CFA leads naturally to the concept of a configuration, i.e. a list of the n and ℓ quantum numbers for all electrons:

$$(n_1 \ell_1)^{w_1} (n_2 \ell_2)^{w_2} \cdot \dots \cdot (n_m \ell_m)^{w_m}$$

where w is the number of equivalent electrons (having the same n and ℓ) in the orbital.

Compare with
$$\Psi = \prod_{i=1}^N \phi_i$$

The configuration has a single energy value

$$E = \sum_{i=1}^N \varepsilon_i$$

being sum of the energies of all

electrons involved.

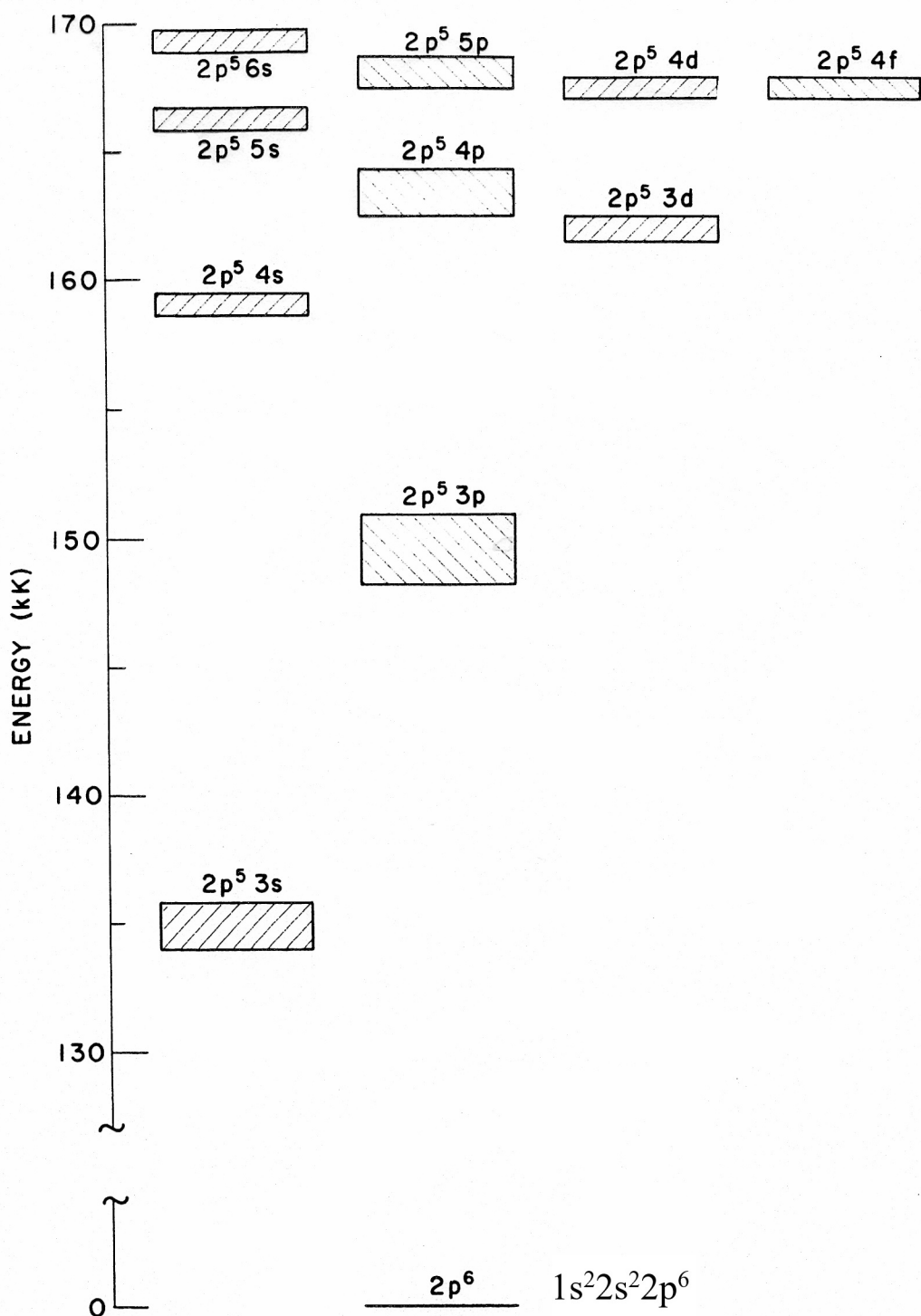


Fig. 4-1. Block diagram of the lowest configurations of Ne I. The levels of each configuration lie within the limited energy range shown by the corresponding shaded block. (There is one level in $2p^6$, and there are four levels in each p^5s configuration, ten levels in each p^5p , and twelve levels in each p^5d or p^5f configuration.)

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period																			
1	1 H 1.008																	2 He 4.0026	
2	3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948	
4	19 K 39.098	20 Ca 40.078		21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62		39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]
*Lanthanoids			*	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05		
**Actinoids			**	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		

What is the ground configuration of the elements, and why do we write it in this way??

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The physical background to the periodic table of the elements.

1. Number of quantum states N :

a) Given n and ℓ . Orbital / subshell

$N = 2 \cdot (2\ell + 1)$ due to m_s and m_ℓ .

b) Given n . Shell

$$N = 2n^2$$

$$N = \sum_{\ell=0}^{n-1} 2(2\ell+1) = \sum_{\ell=0}^{n-1} 4\ell + \sum_{\ell=0}^{n-1} 2 = 4 \frac{n(n-1)}{2} + 2n = 2n^2$$

2. Highest binding energy for low n and ℓ due to the quantum defect

3. Pauli principle, i.e. antisymmetric wave-functions, demanding that no 2 electrons have all 4 quantum numbers identical

Periodic System (first four rows)

H 1s																	He 1s ²	Filled K-shell
Li 2s	Be 2s ²											B 2p	C 2p ²	N 2p ³	O 2p ⁴	F 2p ⁵	Ne 2p ⁶	Filled L-shell
Na 3s	Mg 3s ²											Al 3p	Si 3p ²	P 3p ³	S 3p ⁴	Cl 3p ⁵	Ar 3p ⁶	8 outer electrons 3s ² 3p ⁶
K 4s	Ca 4s ²	Sc 3d	Ti 3d ²	V 3d ³	Cr 3d ⁴	Mn 3d ⁵	Fe 3d ⁶	Co 3d ⁷	Ni 3d ⁸	Cu 3d ⁹	Zn 3d ¹⁰	Ga 4p	Ge 4p ²	As 4p ³	Se 4p ⁴	Br 4p ⁵	Xe 4p ⁶	8 outer electrons 4s ² 4p ⁶

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Alkali metals

Alkaline earths

Halogens

Noble gases

Ionization energy, eV

