

Again as in the H-atom, first-order perturbation theory gives:

$$E_J = E^{(o)} + \int \psi_{nJM_JLS}^{(o)*} \zeta(L, S) \hat{L} \cdot \hat{S} \psi_{nJM_JLS}^{(o)} d\tau$$

$$= E^{(o)} + \frac{\zeta(L, S)}{2} [J(J+1) - L(L+1) - S(S+1)]$$

The energy intervals are:

$$E_{J+1} - E_J = \frac{\zeta [(J+1)(J+2) - J(J+1)]}{2} = \xi(J+1)$$

This is the **Landé interval rule**: the spin-orbit splitting between sequential J levels in a term is proportional to the larger of the J values.

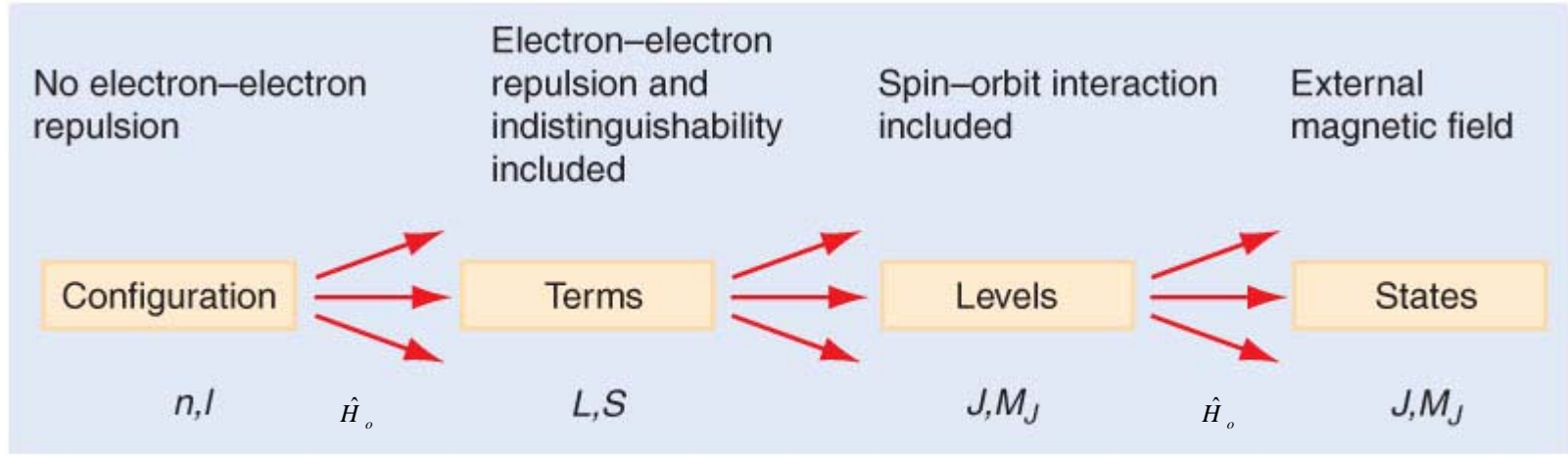
Whether the level with the largest value of J lies highest or lowest energy is determined by the sign of ζ .

If $\zeta > 0$, the term is said to be regular (as for C), and If $\zeta < 0$, the term is inverted (as for O)

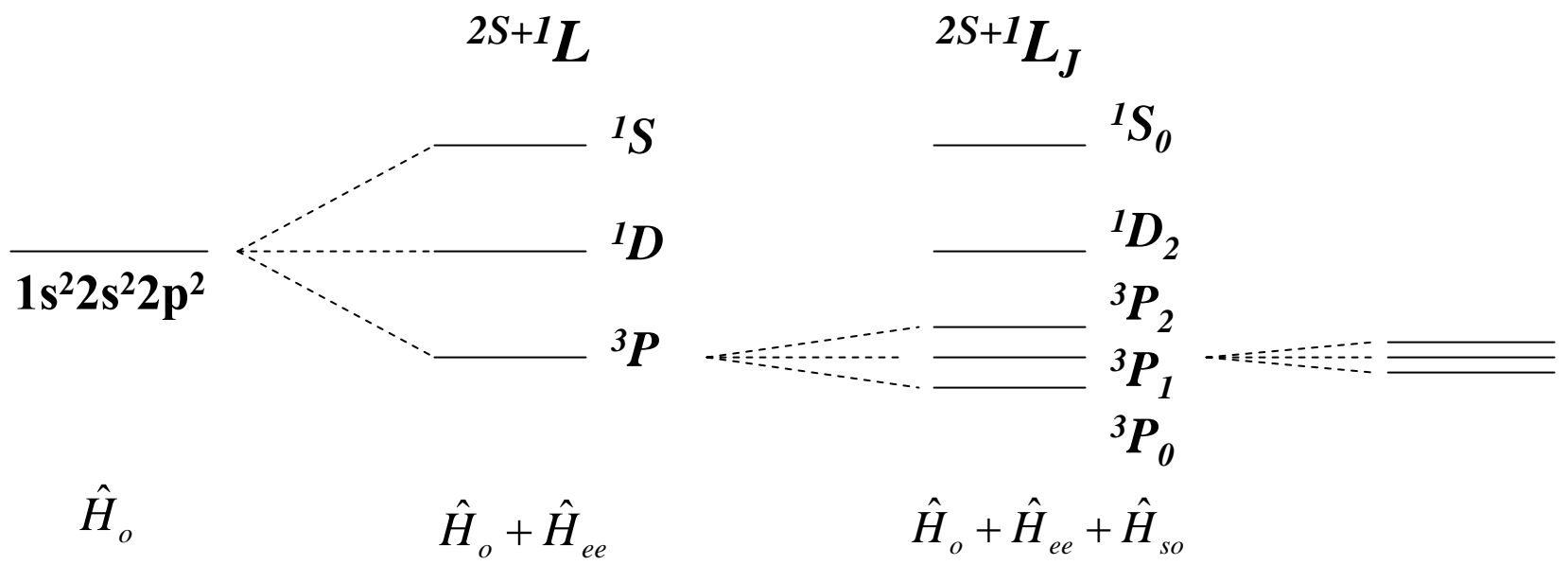
Hund's third rule:

If the ground term arises from a configuration for which valence electrons make up a less than half-filled subshells (e.g., C), then the lowest energy term will be regular, whereas If the configuration is more than half-filled subshells (e.g., O), then the lowest energy term will be inverted.

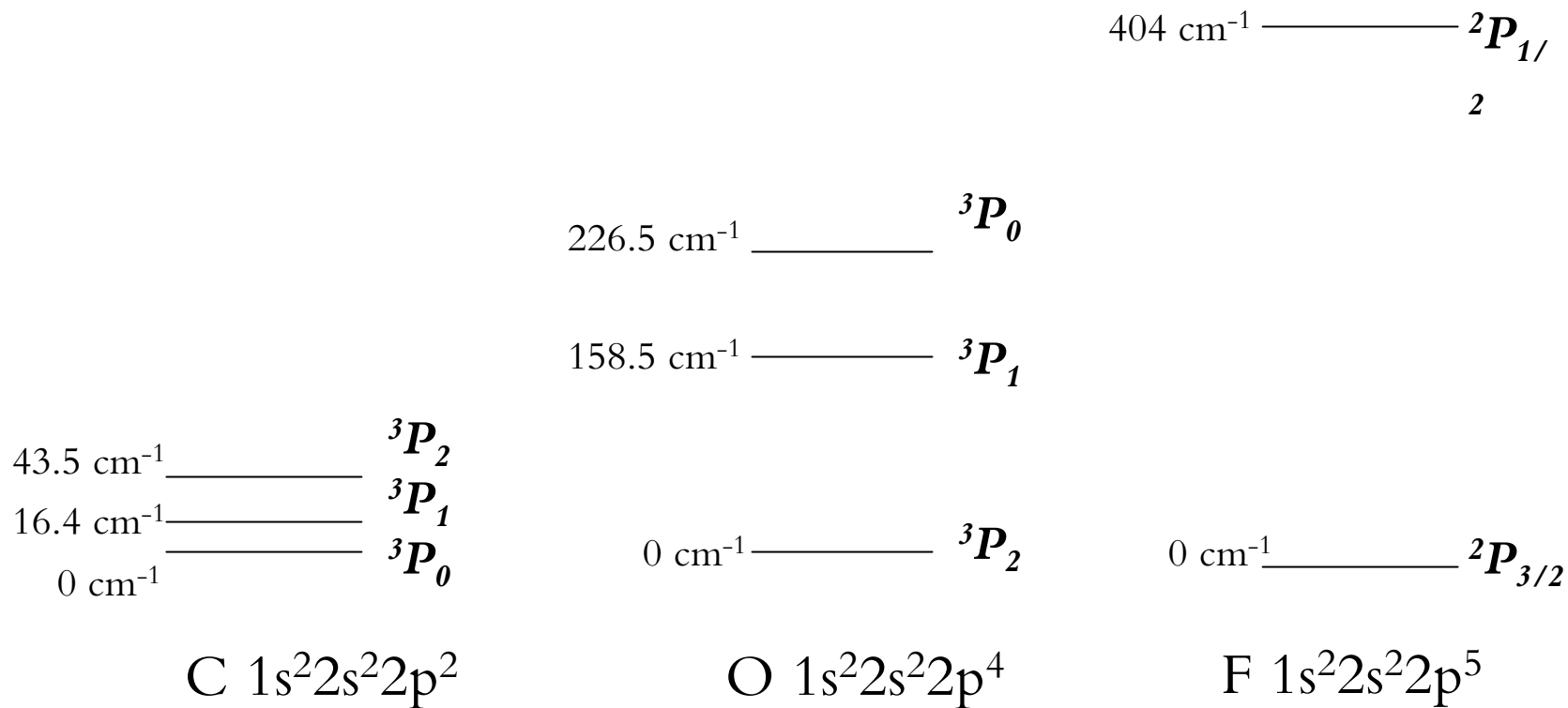
The Process of Successive Approximation



e.g., the ground state of C



Examples of Hund's Third Rule



The multiplet splitting for the lowest energy term of the C, O and F atoms

5. ELECTRONIC STRUCTURE OF THE ELEMENTS

Table 5.1. Reviewed 2005 by C.G. Wohl (LBNL). The electronic configurations and the ionization energies are from the NIS “Ground Levels and Ionization Energies for the Neutral Atoms,” W.C. Martin, A. Musgrove, S. Kotochigova, and J.E. Sanson <http://physics.nist.gov> (select “Physical Reference Data”). The electron configuration for, say, iron indicates an argon electr argon) plus six 3*d* electrons and two 4*s* electrons. The ionization energy is the least energy necessary to remove to infinity one ele atom of the element.

Element			Electron configuration (3 <i>d</i> ⁵ = five 3 <i>d</i> electrons, etc.)	Ground state ^{2<i>S</i>+1} <i>L</i> _{<i>J</i>}	Ionization energy (eV)
1	H	Hydrogen	1 <i>s</i>	² <i>S</i> _{1/2}	13.5984
2	He	Helium	1 <i>s</i> ²	¹ <i>S</i> ₀	24.5874
3	Li	Lithium	(He)2 <i>s</i>	² <i>S</i> _{1/2}	5.3917
4	Be	Beryllium	(He)2 <i>s</i> ²	¹ <i>S</i> ₀	9.3227
5	B	Boron	(He)2 <i>s</i> ² 2 <i>p</i>	² <i>P</i> _{1/2}	8.2980
6	C	Carbon	(He)2 <i>s</i> ² 2 <i>p</i> ²	³ <i>P</i> ₀	11.2603
7	N	Nitrogen	(He)2 <i>s</i> ² 2 <i>p</i> ³	⁴ <i>S</i> _{3/2}	14.5341
8	O	Oxygen	(He)2 <i>s</i> ² 2 <i>p</i> ⁴	³ <i>P</i> ₂	13.6181
9	F	Fluorine	(He)2 <i>s</i> ² 2 <i>p</i> ⁵	² <i>P</i> _{3/2}	17.4228
10	Ne	Neon	(He)2 <i>s</i> ² 2 <i>p</i> ⁶	¹ <i>S</i> ₀	21.5645
11	Na	Sodium	(Ne)3 <i>s</i>	² <i>S</i> _{1/2}	5.1391
12	Mg	Magnesium	(Ne)3 <i>s</i> ²	¹ <i>S</i> ₀	7.6462
13	Al	Aluminum	(Ne)3 <i>s</i> ² 3 <i>p</i>	² <i>P</i> _{1/2}	5.9858
14	Si	Silicon	(Ne)3 <i>s</i> ² 3 <i>p</i> ²	³ <i>P</i> ₀	8.1517
15	P	Phosphorus	(Ne)3 <i>s</i> ² 3 <i>p</i> ³	⁴ <i>S</i> _{3/2}	10.4867
16	S	Sulfur	(Ne)3 <i>s</i> ² 3 <i>p</i> ⁴	³ <i>P</i> ₂	10.3600
17	Cl	Chlorine	(Ne)3 <i>s</i> ² 3 <i>p</i> ⁵	² <i>P</i> _{3/2}	12.9676
18	Ar	Argon	(Ne)3 <i>s</i> ² 3 <i>p</i> ⁶	¹ <i>S</i> ₀	15.7596
19	K	Potassium	(Ar) 4 <i>s</i>	² <i>S</i> _{1/2}	4.3407
20	Ca	Calcium	(Ar) 4 <i>s</i> ²	¹ <i>S</i> ₀	6.1132
21	Sc	Scandium	(Ar) 3 <i>d</i> 4 <i>s</i> ²	² <i>D</i> _{3/2}	6.5615
22	Ti	Titanium	(Ar) 3 <i>d</i> ² 4 <i>s</i> ²	³ <i>F</i> ₂	6.8281
23	V	Vanadium	(Ar) 3 <i>d</i> ³ 4 <i>s</i> ²	⁴ <i>F</i> _{3/2}	6.7462
24	Cr	Chromium	(Ar) 3 <i>d</i> ⁵ 4 <i>s</i>	⁷ <i>S</i> ₃	6.7665
25	Mn	Manganese	(Ar) 3 <i>d</i> ⁵ 4 <i>s</i> ²	⁶ <i>S</i> _{5/2}	7.4340
26	Fe	Iron	(Ar) 3 <i>d</i> ⁶ 4 <i>s</i> ²	⁵ <i>D</i> ₄	7.9024
27	Co	Cobalt	(Ar) 3 <i>d</i> ⁷ 4 <i>s</i> ²	⁴ <i>F</i> _{9/2}	7.8810
28	Ni	Nickel	(Ar) 3 <i>d</i> ⁸ 4 <i>s</i> ²	³ <i>F</i> ₄	7.6398
29	Cu	Copper	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i>	² <i>S</i> _{1/2}	7.7264
30	Zn	Zinc	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ²	¹ <i>S</i> ₀	9.3942
31	Ga	Gallium	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i>	² <i>P</i> _{1/2}	5.9903
32	Ge	Germanium	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i> ²	³ <i>P</i> ₀	7.8994
33	As	Arsenic	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i> ³	⁴ <i>S</i> _{3/2}	9.7886
34	Se	Selenium	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i> ⁴	³ <i>P</i> ₂	9.7524
35	Br	Bromine	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i> ⁵	² <i>P</i> _{3/2}	11.8138
36	Kr	Krypton	(Ar) 3 <i>d</i> ¹⁰ 4 <i>s</i> ² 4 <i>p</i> ⁶	¹ <i>S</i> ₀	13.9996
37	Rb	Rubidium	(Kr) 5 <i>s</i>	² <i>S</i> _{1/2}	4.1771
38	Sr	Strontium	(Kr) 5 <i>s</i> ²	¹ <i>S</i> ₀	5.6949
39	Y	Yttrium	(Kr) 4 <i>d</i> 5 <i>s</i> ²	² <i>D</i> _{3/2}	6.2173
40	Zr	Zirconium	(Kr) 4 <i>d</i> ² 5 <i>s</i> ²	³ <i>F</i> ₂	6.6339
41	Nb	Niobium	(Kr) 4 <i>d</i> ⁴ 5 <i>s</i>	⁶ <i>D</i> _{1/2}	6.7589
42	Mo	Molybdenum	(Kr) 4 <i>d</i> ⁵ 5 <i>s</i>	⁷ <i>S</i> ₃	7.0924
43	Tc	Technetium	(Kr) 4 <i>d</i> ⁵ 5 <i>s</i> ²	⁶ <i>S</i> _{5/2}	7.28
44	Ru	Ruthenium	(Kr) 4 <i>d</i> ⁷ 5 <i>s</i>	⁵ <i>F</i> ₅	7.3605
45	Rh	Rhodium	(Kr) 4 <i>d</i> ⁸ 5 <i>s</i>	⁴ <i>F</i> _{9/2}	7.4589
46	Pd	Palladium	(Kr) 4 <i>d</i> ¹⁰	¹ <i>S</i> ₀	8.3369
47	Ag	Silver	(Kr) 4 <i>d</i> ¹⁰ 5 <i>s</i>	² <i>S</i> _{1/2}	7.5762
48	Cd	Cadmium	(Kr) 4 <i>d</i> ¹⁰ 5 <i>s</i> ²	¹ <i>S</i> ₀	8.9938

49	In	Indium	(Kr)4d ¹⁰ 5s ² 5p			² P _{1/2}	5.7864
50	Sn	Tin	(Kr)4d ¹⁰ 5s ² 5p ²			³ F ₀	7.3439
51	Sb	Antimony	(Kr)4d ¹⁰ 5s ² 5p ³			⁴ S _{3/2}	8.6084
52	Te	Tellurium	(Kr)4d ¹⁰ 5s ² 5p ⁴			³ F ₂	9.0096
53	I	Iodine	(Kr)4d ¹⁰ 5s ² 5p ⁵			² F _{3/2}	10.4513
54	Xe	Xenon	(Kr)4d ¹⁰ 5s ² 5p ⁶			¹ S ₀	12.1298
55	Cs	Cesium	(Xe) 6s			² S _{1/2}	3.8939
56	Ba	Barium	(Xe) 6s ²			¹ S ₀	5.2117
57	La	Lanthanum	(Xe) 5d 6s ²			² D _{3/2}	5.5769
58	Ce	Cerium	(Xe)4f 5d 6s ²			¹ G ₄	5.5387
59	Pr	Praseodymium	(Xe)4f ³ 6s ²		L	⁴ I _{9/2}	5.473
60	Nd	Neodymium	(Xe)4f ⁴ 6s ²		a	⁵ I ₄	5.5250
61	Pm	Promethium	(Xe)4f ⁵ 6s ²		n	⁶ H _{5/2}	5.582
62	Sm	Samarium	(Xe)4f ⁶ 6s ²		t	⁷ F ₀	5.6437
63	Eu	Europium	(Xe)4f ⁷ 6s ²		h	⁸ S _{7/2}	5.6704
64	Gd	Gadolinium	(Xe)4f ⁷ 5d 6s ²		a	⁹ D ₂	6.1498
65	Tb	Terbium	(Xe)4f ⁹ 6s ²		n	⁶ H _{15/2}	5.8638
66	Dy	Dysprosium	(Xe)4f ¹⁰ 6s ²		i	⁵ I ₈	5.9389
67	Ho	Holmium	(Xe)4f ¹¹ 6s ²		d	⁴ I _{15/2}	6.0215
68	Er	Erbium	(Xe)4f ¹² 6s ²		e	³ H ₆	6.1077
69	Tm	Thulium	(Xe)4f ¹³ 6s ²		s	² F _{7/2}	6.1843
70	Yb	Ytterbium	(Xe)4f ¹⁴ 6s ²			¹ S ₀	6.2542
71	Lu	Lutetium	(Xe)4f ¹⁴ 5d 6s ²			² D _{3/2}	5.4259
72	Hf	Hafnium	(Xe)4f ¹⁴ 5d ² 6s ²		T	³ F ₂	6.8251
73	Ta	Tantalum	(Xe)4f ¹⁴ 5d ³ 6s ²		r	⁴ F _{3/2}	7.5496
74	W	Tungsten	(Xe)4f ¹⁴ 5d ⁴ 6s ²		a	⁵ D ₀	7.8640
75	Re	Rhenium	(Xe)4f ¹⁴ 5d ⁵ 6s ²		n	⁶ S _{5/2}	7.8335
76	Os	Osmium	(Xe)4f ¹⁴ 5d ⁶ 6s ²		s	⁵ D ₄	8.4382
77	Ir	Iridium	(Xe)4f ¹⁴ 5d ⁷ 6s ²		i	⁴ F _{9/2}	8.9670
78	Pt	Platinum	(Xe)4f ¹⁴ 5d ⁹ 6s		t	³ D ₃	8.9588
79	Au	Gold	(Xe)4f ¹⁴ 5d ¹⁰ 6s		i	² S _{1/2}	9.2255
80	Hg	Mercury	(Xe)4f ¹⁴ 5d ¹⁰ 6s ²		o	¹ S ₀	10.4375
81	Tl	Thallium	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p		n	² P _{1/2}	6.1082
82	Pb	Lead	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ²			³ F ₀	7.4167
83	Bi	Bismuth	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ³			⁴ S _{3/2}	7.2855
84	Po	Polonium	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴			³ F ₂	8.414
85	At	Astatine	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵			² F _{3/2}	
86	Rn	Radon	(Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶			¹ S ₀	10.7485
87	Fr	Francium	(Rn) 7s			² S _{1/2}	4.0727
88	Ra	Radium	(Rn) 7s ²			¹ S ₀	5.2784
89	Ac	Actinium	(Rn) 6d 7s ²			² D _{3/2}	5.17
90	Th	Thorium	(Rn) 6d ² 7s ²			³ F ₂	6.3067
91	Pa	Protactinium	(Rn)5f ² 6d 7s ²		A	⁴ K _{11/2} *	5.89
92	U	Uranium	(Rn)5f ³ 6d 7s ²		c	⁵ L ₆ *	6.1941
93	Np	Neptunium	(Rn)5f ⁴ 6d 7s ²		t	⁶ L _{11/2} *	6.2657
94	Pu	Plutonium	(Rn)5f ⁶ 7s ²		i	⁷ F ₀	6.0260
95	Am	Americium	(Rn)5f ⁷ 7s ²		n	⁸ S _{7/2}	5.9738
96	Cm	Curium	(Rn)5f ⁷ 6d 7s ²		i	⁹ D ₂	5.9914
97	Bk	Berkelium	(Rn)5f ⁹ 7s ²		d	⁶ H _{15/2}	6.1979
98	Cf	Californium	(Rn)5f ¹⁰ 7s ²		e	⁵ I ₈	6.2817
99	Es	Einsteinium	(Rn)5f ¹¹ 7s ²		s	⁴ I _{15/2}	6.42
100	Fm	Fermium	(Rn)5f ¹² 7s ²			³ H ₆	6.50
101	Md	Mendelevium	(Rn)5f ¹³ 7s ²			² F _{7/2}	6.58
102	No	Nobelium	(Rn)5f ¹⁴ 7s ²			¹ S ₀	6.65
103	Lr	Lawrencium	(Rn)5f ¹⁴ 7s ² 7p?			² P _{1/2} ?	4.9?
104	Rf	Rutherfordium	(Rn)5f ¹⁴ 6d ² 7s ² ?			³ F ₂ ?	6.0?

* The usual *LS* coupling scheme does not apply for these three elements. See the introductory note to the NIST table from which this table is taken.

8. Many electron atoms

Need a suitable wave function to describe such N-electron atomic systems, $N \geq 2$.

Consider perturbation approach. Split Hamiltonian in the following way:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \sum_{i=1}^N \vec{\nabla}_i^2 - Ze^2 \sum_{i=1}^N \frac{1}{r_i}$$

$$\hat{V} = e^2 \sum_{i>j=1}^N \frac{1}{r_{ij}}$$

\mathbf{H}_0 represents the unperturbed problem of N electrons which do not interact with each other (only with the nucleus) and \mathbf{V} is the perturbation which accounts for the electron-electron interaction via Coulomb's Law

It is convenient to write:

$$\hat{H}_0 = \sum_{i=1}^N \hat{H}_i$$

$$\hat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 - Z \frac{e^2}{r_i}$$

This means the unperturbed Hamiltonian can be written as a sum of H-like Hamiltonian operators for each individual electron, i , in the atom. We know the solutions:

$$\hat{H}_i \phi_{\rho_i}(i) = E_{n_i} \phi_{\rho_i}(i)$$

$$\rho_i = \left(n_i, l_i, m_{l_i}, s_i = \frac{1}{2}, m_s \right)$$

$$\phi_{\rho_i}(i) = R_{n_i, l_i}(r_i) Y_{l_i}^{m_{l_i}}(\theta_i, \varphi_i) \times (\alpha_i \text{ or } \beta_i)$$

$$E_{n_i} = -\frac{Z^2 e^2}{2n_i^2 a_0}$$

The spatial part of ϕ_{ρ_i} namely RY is called an atomic orbital. The complete function (with spin) is called a spin atomic orbital or spinor.

Since $\mathbf{H}^{(0)}$ is separable, the eigenfunctions have the form:

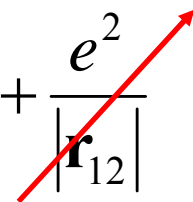
$$\prod_{i=1}^N \phi_{\rho_i}(i) = \phi_{\rho_1}(1) \phi_{\rho_2}(2) \cdots \phi_{\rho_N}(N) = \Phi_0 = \text{standard configuration for N-electron problem.}$$

The corresponding eigenvalues of \mathbf{H}_0 are given by:

$$E^{(0)} = \sum_{i=1}^N E_{n_i} = -\frac{Z^2 e^2}{2a_o} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} + \cdots + \frac{1}{n_N^2} \right)$$

Consider the case of the Helium atom. It is very similar to the hydrogen atom except that we have a $Z=+2e$ nuclear charge.

The Hamiltonian where the electron-electron repulsion term is neglected is:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{|\mathbf{r}_1|} - \frac{Ze^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_{12}|}$$


$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{|\mathbf{r}_1|}}_{e^- \text{ one}} \underbrace{-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{|\mathbf{r}_2|}}_{e^- \text{ two}}$$

If we assume the particles are non-interaction then the resulting Schrodinger Equation is separable and we can write the Hamiltonian and wave function as:

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(1,2) = \Psi(1)\Psi(2)$$

This a **product wave function** again is only exact if the electrons are non-interacting

With this approximation the energy of the system is given by:

$$E = E_{n_1}^1 + E_{n_2}^2 = -\frac{Z^2 e^2}{n_1^2 2a_o} + -\frac{Z^2 e^2}{n_2^2 2a_o} \quad n_1 = 1, 2, 3... \text{ \& } n_2 = 1, 2, 3...$$

How good is this approximation? We can compare the ground state energy of the independent electron helium atom and compare it to that determined experimentally.

$$E_o(\text{H with } Z=2) = -54.4 \text{ eV}$$

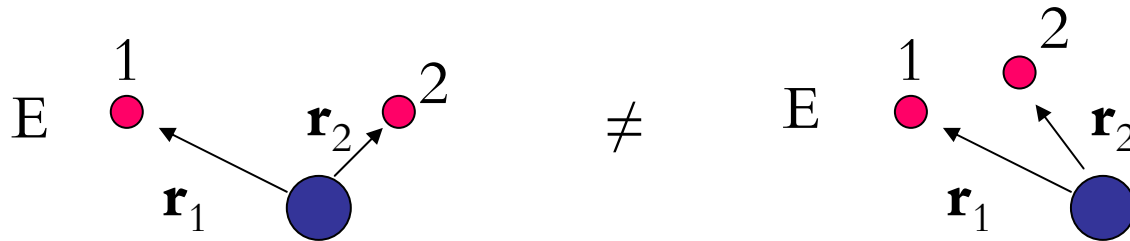
$$E_o(\text{He}) = -54.4 - 54.4 = -108.8 \text{ eV}$$

The true value is -79.0 eV. Thus the independent electron approximation is surprisingly good; i.e., it is in the right order of magnitude.

$\Psi(1,2)$ versus $\Psi(1)\Psi(2)$ - What's the Difference?

Consider a two electron system. The true many electron wave function should indicate that:

The probability of finding the electron at \mathbf{r}_1 , should depend on where the other electron is.



Does the product wave function account for this?

NO

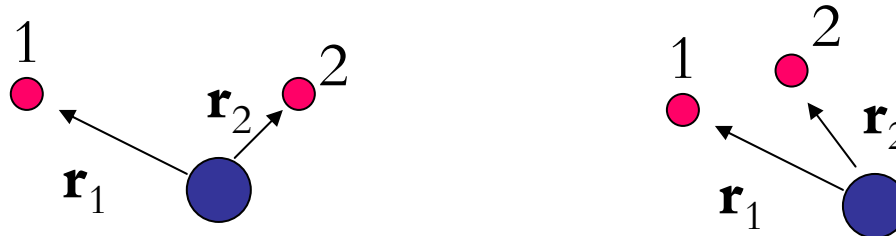
Lets examine this a bit more closely.

$$P(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2)^* \Psi(\mathbf{r}_1, \mathbf{r}_2) = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2$$

Expressing the many-electron wave function as a product wave function we have:

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) &= \Psi_1(\mathbf{r}_1)^* \Psi_2(\mathbf{r}_2)^* \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2) \\ &= |\Psi_1(\mathbf{r}_1)|^2 |\Psi_2(\mathbf{r}_2)|^2 = P_1(\mathbf{r}_1) P_2(\mathbf{r}_2) \end{aligned}$$

These are independent functions



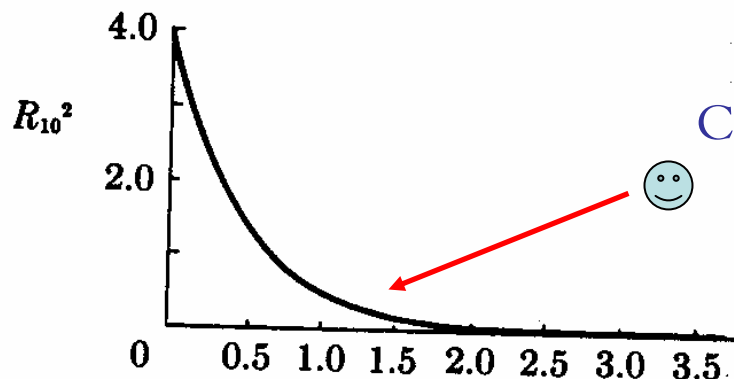
The probabilities are independent, so can these type of approximate wave functions account for any electron-electron repulsion? No but...

Although the product wave function is only EXACT for non-interacting particles, the approximation does allow us to approximately include the effect of the electron-electron interaction (by perturbation theory).

The product wave function approximation of the many electron wave function can be a very good approximation. It is the most widely used approximation used in research involving calculations in chemistry.

Average Shielding Approximation

In this approximation, we assume the effect of the other electron is to shield the nuclear charge from the other electron.



Consider our electron out here

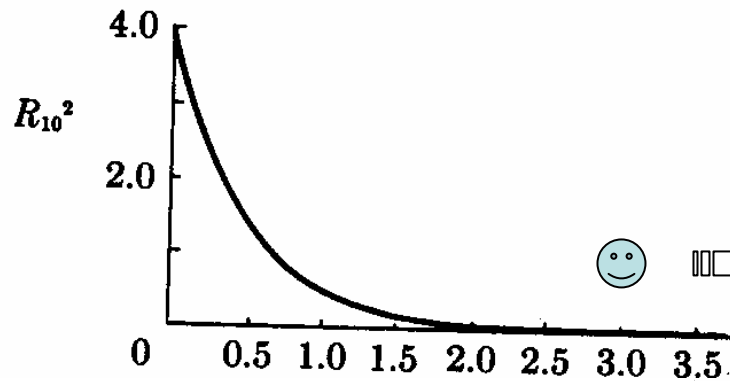
The charge distribution of the other electron 'shields' the nuclear charge from the other electron.

Within the independent electron approximation, we can therefore do better than just using Z by defining an effective nuclear charge, Z_{eff}

$$E = -\frac{Z_{\text{eff}}^2}{n_1^2} \frac{e^2}{2a_0} - \frac{Z_{\text{eff}}^2}{n_2^2} \frac{e^2}{2a_0}$$

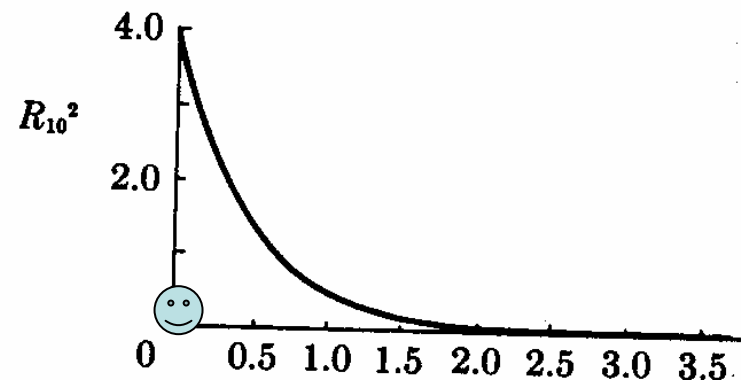
What is the value of Z_{eff} ?

Consider both electrons in their ground 1s state.



Out here, the other electron screens out 1e worth of the nuclear charge, so if $r_2 = \infty$ then $Z_{\text{eff}} = +1e$

In contrast at the nucleus, the other electron does not screen the nuclear charge at all, so at $r_2 = 0$ then $Z_{\text{eff}} = +2e$.



Thus, $1 < Z_{\text{eff}} < 2$

In fact, it should be a function of r such that $Z_{\text{eff}} = Z_{\text{eff}}(r)$

There are many ways of estimating the effective nuclear charge Z_{eff} from calculation and experimental data.

$$E_{\text{He}} = -\frac{Z_{\text{eff}}^2 e^2}{n_1^2 2a_o} - \frac{Z_{\text{eff}}^2 e^2}{n_2^2 2a_o}$$

For example, given that experimental the first ionization potential of He is 24.6 eV, find an estimate for Z_{eff}

$$\text{Use: } \frac{e^2}{a_o} = 1 \text{ Hartree} = 27.211 \text{ eV}$$

$$\therefore 24.6 = \frac{Z_{\text{eff}}^2 e^2}{2a_o} = \frac{Z_{\text{eff}}^2 \cdot 27.211}{2}$$

$$\Rightarrow Z_{\text{eff}} = 1.34$$

A better estimate involving a calculation of $\langle H \rangle$ yields $Z_{\text{eff}}^2 = 1.6875$

Will see that shielding determines many trends associated with the Periodic Table