10 - Atomic Structure

- Aim of Section:
  - Analyze structure of multi-electron atoms.

Introduction

- Energy eigenvalue problem for ground-state of neutral atom with Z electrons has form

$$\left[\sum_{i=1,Z}\left(-\frac{\hbar^2\,\nabla_i^{\,2}}{2\,m_e}-\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}+\frac{1}{2}\sum_{j=1,Z}^{j\neq i}\frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\right)\right]$$
$$\times\psi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_Z)=E\,\psi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_Z).$$

- This is partial differential equation in $3\,Z$ dimensions.
- For Z not too much greater than unity, it is possible to solve such an equation numerically.
- However, as Z increases, a direct numerical solution of the above equation becomes very rapidly infeasible.
- In following, will describe approximate approach based on variational principle that is feasible for any value of Z.

Variational Method - I

- Consider trial spatial wavefunction of form

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_Z) = \phi_1(\mathbf{x}_1)\,\phi_2(\mathbf{x}_2)\cdots\phi_Z(\mathbf{x}_Z).$$

- Suppose that

$$\int |\phi(\mathbf{x}_i)|^2\, d^3\mathbf{x}_i = 1,$$

for $i = 1, Z$.

Variational Method - II

- Expectation value of Hamiltonian can be written

$$\langle H\rangle = \sum_{i=1,Z}\int \phi_i^\ast(\mathbf{x}_i)\left(-\frac{\hbar^2\,\nabla_i^2}{2\,m_e}-\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}\right)\phi_i(\mathbf{x}_i)\,d^3\mathbf{x}_i$$
$$+\frac{1}{2}\sum_{i,j=1,Z}^{j\neq i}|\phi_i(\mathbf{x}_i)|^2\,\frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\,|\phi_j(\mathbf{x}_j)|^2\,d^3\mathbf{x}_i\,d^3\mathbf{x}_j. \quad (1)$$

Variational Method - III

- Wish to choose $\phi(\mathbf{x}_i)$ so as to minimize $\langle H \rangle$.
- Now, if $\phi(\mathbf{x}_i)$ were such as to minimize $\langle H \rangle$ then alteration of these functions by infinitesimal amount,

  $$\phi_i(\mathbf{x}_i) \to \phi_i(\mathbf{x}_i) + \lambda\, f_i(\mathbf{x}_i), \tag{2}$$

  should only change $\langle H \rangle$ by order λ^2.
- Alterations must be made such that

  $$\int |\phi_i(\mathbf{x}_i) + \lambda\, f_i(\mathbf{x}_i)|^2\, d^3\mathbf{x}_i = 1. \tag{3}$$

Variational Method - IV

- Expanding (3), term that multiplies λ is

$$g_i = \int [\phi_i^*(\mathbf{x}_i)\, f_i(\mathbf{x}_i) + \phi_i(\mathbf{x}_i)\, f_i^*(\mathbf{x}_i)]\, d^3\mathbf{x}_i. \tag{4}$$

- Obviously, to maintain proper normalization up to order λ, we require

$$g_i = 0, \tag{5}$$

  for $i = 1, Z$.

- Let us compute terms that that multiply λ when (2) is substituted into (1).

Variational Method - V

- Kinetic energy terms in (1) yield

$$\sum_{i=1,Z}\int\left\{\phi_i^*(\mathbf{x}_i)\left[-\frac{\hbar^2}{2\,m_e}\nabla_i^{\,2}f_i(\mathbf{x}_i)\right]+f_i^*(\mathbf{x}_i)\left[-\frac{\hbar^2}{2\,m_e}\nabla_i^{\,2}\phi_i(\mathbf{x}_i)\right]\right\}d^3\mathbf{x}_i.$$

- Integrating first term by parts twice, and using fact that $f_i(\mathbf{x}_i)$ must vanish at infinity if $\phi_i(\mathbf{x}_i)$ is to remain square integrable, we get

$$\sum_{i=1,Z}\int\left\{f_i(\mathbf{x}_i)\left[-\frac{\hbar^2}{2\,m_e}\nabla_i^{\,2}\phi_i^*(\mathbf{x}_i)\right]+f_i^*(\mathbf{x}_i)\left[-\frac{\hbar^2}{2\,m_e}\nabla_i^{\,2}\phi_i(\mathbf{x}_i)\right]\right\}d^3\mathbf{x}_i. \tag{6}$$

Variational Method - VI

- Electron-nucleus interaction terms in (1) yield

$$-\sum_{i=1,Z}\int\left[f_i^*(\mathbf{x}_i)\,\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}\,\phi_i(\mathbf{x}_i)+\phi_i^*(\mathbf{x}_i)\,\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}\,f_i(\mathbf{x}_i)\right]d^3\mathbf{x}_i. \tag{7}$$

Variational Method - VII

- Electron-electron interaction terms in (1) yield

$$\frac{1}{2}\sum_{i,j=1,Z}^{j\neq i}\iint\frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\left\{[f_i^{\,*}(\mathbf{x}_i)\,\phi_i(\mathbf{x}_i)+f_i(\mathbf{x}_i)\,\phi_i^*(\mathbf{x}_i)]\,|\phi_j(\mathbf{x}_j)|^2\right.$$

$$\left.+[f_j^{\,*}(\mathbf{x}_j)\,\phi_j(\mathbf{x}_j)+f_j(\mathbf{x}_j)\,\phi_j^*(\mathbf{x}_j)]\,|\phi_i(\mathbf{x}_i)|^2\right\}d^3\mathbf{x}_i\,d^3\mathbf{x}_j.$$

- However, if we swap dummy summation indices in second term then we get

$$\sum_{i,j=1,Z}^{j\neq i}\iint\frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\,[f_i^{\,*}(\mathbf{x}_i)\,\phi_i(\mathbf{x}_i)+f_i(\mathbf{x}_i)\,\phi_i^*(\mathbf{x}_i)]\,|\phi_j(\mathbf{x}_j)|^2$$

$$\times\,d^3\mathbf{x}_i\,d^3\mathbf{x}_j. \tag{8}$$

Variational Method - VIII

- Summing (6), (7), and (8), we get

$$G = \sum_{i=1,Z} \int \left[f_i(\mathbf{x}_i)\, F_i^\ast(\mathbf{x}_i) + f_i^\ast(\mathbf{x}_i)\, F_i(\mathbf{x}_i)\right] d^3\mathbf{x}_i, \tag{9}$$

  where

$$\begin{aligned} F_i(\mathbf{x}_i) &= -\frac{\hbar^2}{2\, m_e}\, \nabla_i^2 \phi_i(\mathbf{x}_i) - \frac{Z\, e^2}{4\pi\, \epsilon_0\, |\mathbf{x}_i|}\, \phi_i(\mathbf{x}_i) \\ &\quad + \sum_{j=1,Z}^{j\neq i} \left(\int \frac{e^2\, |\phi_j(\mathbf{x}_j)|^2}{4\pi\, \epsilon_0\, |\mathbf{x}_i - \mathbf{x}_j|}\, d^3\mathbf{x}_j\right) \phi_i(\mathbf{x}_i). \end{aligned} \tag{10}$$

Variational Method - IX

- We cannot just set G to zero, because the $f_i(\mathbf{x}_i)$ are constrained by (5).
- We can account for constraints using method of Lagrange multipliers. In other words, we set

$$G - \sum_{i=1,Z} \epsilon_i \, g_i = 0,$$

where the ϵ_i are Lagrange multipliers.

Variational Method - X

- Making use of (4), (9), and (10), we get

$$\sum_{i=1,Z}\int\left[f_i(\mathbf{x}_i)\,H_i^\ast(\mathbf{x}_i)+f_i^\ast(\mathbf{x}_i)\,H_i(\mathbf{x}_i)\right]d^3\mathbf{x}_i=0, \tag{11}$$

  where

$$\begin{aligned}H_i(\mathbf{x}_i)= &-\frac{\hbar^2}{2\,m_e}\,\nabla_i^2\phi_i(\mathbf{x}_i)-\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}\,\phi_i(\mathbf{x}_i)\\ &+\sum_{j=1,Z}^{j\neq i}\left(\int\frac{e^2\,|\phi_j(\mathbf{x}_j)|^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}d^3\mathbf{x}_j\right)\phi_i(\mathbf{x}_i)-\epsilon_i\,\phi_i(\mathbf{x}_i).\end{aligned}$$

Variational Method - XI

- We wish to minimize $\langle H \rangle$ with respect to arbitrary variations of the $\phi_i(\mathbf{x}_i)$. In other words, for arbitrary $f_i(\mathbf{x}_i)$ and $f_i^*(\mathbf{x}_i)$.
- Note that $f_i(\mathbf{x}_i)$ and $f_i^*(\mathbf{x}_i)$ are independent functions, because $f_i(\mathbf{x}_i)$ has independent real and imaginary parts.
- We can achieve this goal by setting coefficients multiplying $f_i(\mathbf{x}_i)$ and $f_i^*(\mathbf{x}_i)$ in (11) to zero. This implies that

$$H_i(\mathbf{x}_i) = 0,$$

for $i = 1, Z$.

Variational Method - XII

- Deduce that single-electron wavefunctions that minimize $\langle H\rangle$ satisfy

$$\left[-\frac{\hbar^2}{2\,m_e}\,\nabla_i^2-\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}+\sum_{j=1,Z}^{j\neq i}\int\frac{e^2\,|\phi_j(\mathbf{x}_j)|^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\,d^3\mathbf{x}_j\right]\phi_i(\mathbf{x}_i)=\epsilon_i\,\phi_i(\mathbf{x}_i). \tag{12}$$

- Previous equation has straightforward interpretation. It is energy eigenvalue equation for electron i, located at $\mathbf{x}_i$, that moves in effective potential

$$V_i(\mathbf{x}_i)=-\frac{Z\,e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i|}+\sum_{j=1,Z}^{j\neq i}\int\frac{e^2\,|\phi_j(\mathbf{x}_j)|^2}{4\pi\,\epsilon_0\,|\mathbf{x}_i-\mathbf{x}_j|}\,d^3\mathbf{x}_j. \tag{13}$$

- Total electronic energy of atom is

$$E=\sum_{i=1,Z}\epsilon_i. \tag{14}$$

Variational Method - XIII

- According to (13), each electron generates effective charge density $\rho_i(\mathbf{x}_i) = -e\,|\phi_i(\mathbf{x}_i)|^2$.
- Of course, electron is not affected by its own charge density (i.e., it cannot exert a force on itself).
- We can further simplify problem if we replace $V_i(\mathbf{r}_i)$ by its angular average,

$$V_i(|\mathbf{x}_i|) = \oint V_i(\mathbf{x}_i)\,\frac{d\Omega_i}{4\pi}. \tag{15}$$

- In this case, each electron moves in central effective potential.
- Hence, orbital angular momentum of each electron is separately conserved.

Variational Method - XIV

- Follows that we can write

$$\phi_i(\mathbf{x}_i) = \mathcal{R}_{n_i,l_i}(r_i)\, Y_{l_i}^{m_i}(\theta_i, \phi_i), \tag{16}$$

  where

$$\int_0^\infty r_i^2\, \mathcal{R}_{n_i,l_i}^2(r_i)\, dr_i = 1.$$

- As usual, total orbital angular momentum squared of ith electron is $l_i\,(l_i+1)\,\hbar^2$, whereas projection of angular momentum along z-axis is $m_i\,\hbar$.
- Full (i.e., including spin) single-electron state is

$$|n_i, l_i, m_i, \sigma_i\rangle = \mathcal{R}_{n_i,l_i}(r_i)\, Y_{l_i}^{m_i}(\theta_i, \phi_i)\, \chi_{\sigma_i},$$

  where $\chi_{\sigma_i=\pm 1/2} = \chi_\pm$.
- Thus, each electron is characterized by four quantum numbers, n_i, l_i, m_i, and σ_i.

Variational Method - XV

- Let $\rho_i = r_i/a_0$, $\hat{\mathcal{R}}_{n_i,l_i} = a_0^{3/2}\,\mathcal{R}_{n_i,l_i}$, and $\hat{\epsilon}^{\,(n_i,l_i)} = \epsilon_i/|E_0|$.
- (12), (15), and (16) yield

$$\frac{d^2\hat{\mathcal{R}}_{n_i,l_i}}{d\rho_i^2} + \frac{2}{\rho_i}\,\frac{d\hat{\mathcal{R}}_{n_i,l_i}}{d\rho_i} + \left[-\frac{l_i\,(l_i+1)}{\rho_i^2} + \frac{2\,Z}{\rho_i} - \hat{U}_i(\rho_i) + \hat{\epsilon}^{\,(n_i,l_i)}\right]\hat{\mathcal{R}}_{n_i,l_i} = 0. \tag{17}$$

- Here,

$$\hat{U}_i(r_i) = 2\sum_{j=1,Z}^{j\neq i}\left[\frac{1}{\rho_i}\int_0^{\rho_i}\rho_j^2\,[\hat{\mathcal{R}}_{n_j,l_j}(\rho_j)]^2\,d\rho_j + \int_{\rho_j}^{\infty}\rho_j\,[\hat{\mathcal{R}}_{n_j,l_j}(\rho_j)]^2\,d\rho_j\right].$$

Variational Method - XVI

- Moreover, use has been made of

$$\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|}=\sum_{l=0,\infty}\sum_{m=-l,l}\frac{4\pi}{2l+1}\,\frac{r_<^{\,l}}{r_>^{\,l+1}}\,Y_{l_i}^{m_i\,*}(\theta_i,\phi_i)\,Y_{l_j}^{m_j}(\theta_j,\phi_j),$$

  where $r_<$ is lesser of r_i and r_j, and $r_>$ is greater, as well as orthonormal properties of spherical harmonics.
- Rather than trying to solve (17) directly, let us expand $\hat{\mathcal{R}}_{n_i,l_i}(\rho_i)$ in terms of known orthogonal radial wavefunctions that have the correct behavior at small and large ρ_i.
- In fact, let

$$\hat{\mathcal{R}}_{n_i,l_i}(\rho_i)=\sum_{k=1,\infty}\alpha_k^{(n_i,l_i)}\,\hat{R}_{l_i+k,l_i}(\rho_i),$$

  where $\hat{R}_{n,l}(\rho)=a_0^{3/2}\,R_{n,l}(a_0\,\rho)$, and $R_{n,l}(r)$ is a properly normalized hydrogen radial wavefunction.

Variational Method - XVII

- Proper normalization of single-electron wavefunction requires

$$\sum_{k=1,\infty} \left|\alpha_k^{(n_i,l_i)}\right|^2 = 1. \tag{18}$$

- Making use of properties of hydrogen radial wavefunctions, (17) reduces to

$$M_{k,k'}^{(l_i)}\,\alpha_{k'}^{(n_i,l_i)} = \hat{\epsilon}^{(n_i,l_i)}\,\alpha_k^{(n_i,l_i)}, \tag{19}$$

where

$$\begin{aligned} M_{k,k'}^{(l_i)} &= -\frac{\delta_{k,k'}}{(l_i+k)^2} - 2\,(Z-1)\,N_{k,k'}^{(l_i)} \\ &\quad + \sum_{j=1,Z}^{j\neq i}\ \sum_{k'',k'''=1,\infty} \alpha_{k''}^{(n_j,l_j)}\,L_{k,k',k'',k'''}^{(l_i,l_j)}\,\alpha_{k''''}^{(n_j,l_j)}. \end{aligned} \tag{20}$$

Variational Method - XVIII

- Here,

$$N_{k,k'}^{(l_i)} = \int_0^\infty \rho\, \hat{R}_{l_i+k,l_i}(\rho)\, \hat{R}_{l_i+k',l_i}(\rho)\, d\rho, \tag{21}$$

$$L_{k,k',k'',k''}^{(l_i,l_j)} = \int_0^\infty \rho\, \hat{R}_{l_i+k,l_i}(\rho)\, \hat{R}_{l_i+k',l_i}(\rho)\, \hat{U}_{k'',k'''}^{(l_j)}(\rho)\, d\rho, \tag{22}$$

$$\begin{aligned} \hat{U}_{k,k'}^{(l_i)}(\rho) = 2 \int_0^\rho \rho'^{\,2}\, \hat{R}_{l_i+k,_i}(\rho')\, \hat{R}_{l_i+k',_i}(\rho')\, d\rho' \\ + 2\,\rho \int_\rho^\infty \rho'\, \hat{R}_{l_i+k,_i}(\rho')\, \hat{R}_{l_i+k',_i}(\rho')\, d\rho'. \end{aligned} \tag{23}$$

- Note that $n_i = 1$ corresponds to the lowest eigenvalue of (19), whereas $n_i = 2$ corresponds to the next lowest, and so on.

Variational Method - XIX

- (18)–(23) constitute a non-linear matrix eigenvalue problem that can be solved by iteration to obtain electron energy levels, $\epsilon^{(n_i,l_i)} = \hat{\epsilon}^{(n_i,l_i)}\,|E_0|$.
- Ground-state energy of atom is then calculated by placing Z electrons in lowest available energy levels. This approach to finding ground-state energy due to D.R. Hartree.
- Might think that minimum energy state obtained by putting all electrons in $n = 1$, $l = 0$ state.
- However, we have not taken into account fact that overall multi-electron wavefunction must be anti-symmetric with respect to interchange of any two electrons.
- We could try to redo analysis with properly anti-symmetric multi-electron wavefunctions. This is known as Hartree-Fock approach, and is very difficult to implement.

Variational Method - XX

- Alternatively, we can adopt ansatz that symmetry requirements forbid electrons from having same set of four quantum numbers, n, l, m, and σ. This ansatz known as Pauli exclusion principle.
- Effective potential, (15), no longer has $1/r$ form. Thus, states with same n quantum number, but different l quantum numbers are no longer degenerate (because degeneracy of these levels in hydrogen atom is special property of $1/r$ potential).

Variational Method - XX

- Lowest energy states occur in following order:

Shell	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	5d	6p	7s	5f
$n+l$	1	2	3	3	4	4	5	5	5	6	6	6	7	7	7	7	8

- Recall that s, p, d, f correspond to $l = 0, 1, 2, 3$, respectively.
- Relative energy of states predicted by Madelung's rules:
  1. Energy increases with increasing $n + l$.
  2. For states with same value of $n + l$, energy increases with increasing n.

Periodic Table - I

- Can use insights gained by previous analysis to explain structure of periodic table of elements.
- Let us build up our atoms by successively adding electrons, and placing them in lowest available energy state. This is known as aufbau principle.
- Since Pauli exclusion principle forbids two electrons from having same set of quantum numbers, maximum number of electrons that can be placed in s, p, d, and f orbital is 2 (i.e., spin-up and spin-down), 6, 10, and 14, respectively.
- Madelung's rules specify order in which orbitals filled.

Periodic Table - II

- We start by filling $1s$ orbital. We get:

Z	Element	Configuration	Term
1	H	$(1s)$	$^2S_{1/2}$
2	He	$(1s)^2$	$^1S_0$

- Here, $(1s)$ means one electron in $1s$ orbital, and $(1s)^2$ means two electrons in $1s$ orbital.

Periodic Table - III

- Next we fill $2s$ orbital. We get:

Z	Element	Configuration	Term
3	Li	$(\mathrm{He})(2s)$	$^2S_{1/2}$
4	Be	$(\mathrm{He})(2s)^2$	$^1S_0$

- Here, (He) means electronic structure of helium: that is, $(1s)^2$.

Periodic Table - IV

- Next we fill $2p$ orbital. We get:

Z	Element	Configuration	Term
5	B	$(\mathrm{He})(2s)^2(2p)$	$^2\mathrm{P}_{1/2}$
6	C	$(\mathrm{He})(2s)^2(2p)^2$	$^3\mathrm{P}_0$
7	N	$(\mathrm{He})(2s)^2(2p)^3$	$^4\mathrm{S}_{3/2}$
8	O	$(\mathrm{He})(2s)^2(2p)^4$	$^3\mathrm{P}_2$
9	F	$(\mathrm{He})(2s)^2(2p)^5$	$^2\mathrm{P}_{3/2}$
10	Ne	$(\mathrm{He})(2s)^2(2p)^6$	$^1\mathrm{S}_0$

Periodic Table - V

- Next we fill $3s$ orbital. We get:

Z	Element	Configuration	Term
11	Na	(Ne)($3s$)	$^2S_{1/2}$
12	Mg	(Ne)$(3s)^2$	$^1S_0$

Periodic Table - VI

- Next we fill $3p$ orbital. We get:

Z	Element	Configuration	Term
13	Al	$(\mathrm{Ne})(3s)^2(3p)$	$^2\mathrm{P}_{1/2}$
14	Si	$(\mathrm{Ne})(3s)^2(3p)^2$	$^3\mathrm{P}_0$
15	P	$(\mathrm{Ne})(3s)^2(3p)^3$	$^4\mathrm{S}_{3/2}$
16	S	$(\mathrm{Ne})(3s)^2(3p)^4$	$^3\mathrm{P}_2$
17	Cl	$(\mathrm{Ne})(3s)^2(3p)^5$	$^2\mathrm{P}_{3/2}$
18	Ar	$(\mathrm{Ne})(3s)^2(3p)^6$	$^1\mathrm{S}_0$

Periodic Table - VII

- Next we fill 4*s* orbital. We get:

Z	Element	Configuration	Term
19	K	$(\mathrm{Ar})(4s)$	$^2\mathrm{S}_{1/2}$
20	Ca	$(\mathrm{Ar})(4s)^2$	$^1\mathrm{S}_0$

Periodic Table - VIII

- Next we fill $3d$ orbital. We get:

Z	Element	Configuration	Term
21	Sc	$(\mathrm{Ar})(4s)^2(3d)$	$^2\mathrm{D}_{3/2}$
22	Ti	$(\mathrm{Ar})(4s)^2(3d)^2$	$^3\mathrm{F}_2$
23	V	$(\mathrm{Ar})(4s)^2(3d)^3$	$^4\mathrm{F}_{3/2}$
24	Cr	$(\mathrm{Ar})(4s)(3d)^5$	$^7\mathrm{S}_3$
25	Mn	$(\mathrm{Ar})(4s)^2(3d)^5$	$^6\mathrm{S}_{3/2}$
26	Fe	$(\mathrm{Ar})(4s)^2(3d)^6$	$^5\mathrm{D}_4$
27	Co	$(\mathrm{Ar})(4s)^2(3d)^7$	$^4\mathrm{F}_{9/2}$
28	Ni	$(\mathrm{Ar})(4s)^2(3d)^8$	$^3\mathrm{F}_4$
29	Cu	$(\mathrm{Ar})(4s)(3d)^{10}$	$^2\mathrm{S}_{1/2}$
30	Zn	$(\mathrm{Ar})(4s)^2(3d)^{10}$	$^1\mathrm{S}_0$

- These elements known as transition elements. Note irregular structure of Cr and Cu.

Periodic Table - IX

- Next we fill $4p$ orbital. We get:

Z	Element	Configuration	Term
31	Ga	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)$	$^2\mathrm{P}_{1/2}$
32	Ge	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^2$	$^3\mathrm{P}_0$
33	As	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^3$	$^4\mathrm{S}_{3/2}$
34	Se	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^4$	$^3\mathrm{P}_2$
35	Br	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^5$	$^2\mathrm{P}_{3/2}$
36	Kr	$(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^6$	$^1\mathrm{S}_0$

Periodic Table - X

- Next we fill $5s$ orbital. We get:

Z	Element	Configuration	Term
37	Rb	$(\mathrm{Kr})(5s)$	$^2\mathrm{S}_{1/2}$
38	Sr	$(\mathrm{Kr})(5s)^2$	$^1\mathrm{S}_0$

Periodic Table - XI

- Next we fill *4d* orbital. We get:

Z	Element	Configuration	Term
39	Y	$(\mathrm{Kr})(5s)^2(4d)$	$^2\mathrm{D}_{3/2}$
40	Zr	$(\mathrm{Kr})(5s)^2(4d)^2$	$^3\mathrm{F}_2$
41	Nb	$(\mathrm{Kr})(5s)(4d)^4$	$^6\mathrm{D}_{1/2}$
42	Mo	$(\mathrm{Kr})(5s)(4d)^5$	$^7\mathrm{S}_3$
43	Tc	$(\mathrm{Kr})(5s)^2(4d)^5$	$^6\mathrm{S}_{5/2}$
44	Ru	$(\mathrm{Kr})(5s)(4d)^7$	$^5\mathrm{F}_5$
45	Rh	$(\mathrm{Kr})(5s)(4d)^8$	$^4\mathrm{F}_{9/2}$
46	Pd	$(\mathrm{Kr})(4d)^{10}$	$^1\mathrm{S}_0$
47	Ag	$(\mathrm{Kr})(5s)(4d)^{10}$	$^2\mathrm{S}_{1/2}$
48	Cd	$(\mathrm{Kr})(5s)^2(4d)^{10}$	$^1\mathrm{S}_0$

- Note irregular structures of many elements.

Periodic Table - XII

- Next we fill $5p$ orbital. We get:

Z	Element	Configuration	Term
49	In	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)$	$^2\mathrm{P}_{1/2}$
50	Sn	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)^2$	$^3\mathrm{P}_0$
51	Sb	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)^3$	$^4\mathrm{S}_{3/2}$
52	Te	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)^4$	$^3\mathrm{P}_2$
53	I	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)^5$	$^2\mathrm{P}_{3/2}$
54	Xe	$(\mathrm{Kr})(5s)^2(4d)^{10}(5p)^6$	$^1\mathrm{S}_0$

Periodic Table - XIII

- Next we fill $6s$ orbital. We get:

Z	Element	Configuration	Term
55	Cs	(Xe)$(6s)$	$^2S_{1/2}$
56	Ba	(Xe)$(6s)^2$	$^1S_0$

Periodic Table - XIV

- Next we fill $4f$ orbital. We get:

Z	Element	Configuration	Term
57	La	$(\mathrm{Xe})(6s)^2(5d)$	${}^2\mathrm{D}_{3/2}$
58	Ce	$(\mathrm{Xe})(6s)^2(4f)(5d)$	${}^3\mathrm{H}_5$
59	Pr	$(\mathrm{Xe})(6s)^2(4f)^3$	${}^4\mathrm{I}_{9/2}$
60	Nd	$(\mathrm{Xe})(6s)^2(4f)^4$	${}^5\mathrm{I}_4$
61	Pm	$(\mathrm{Xe})(6s)^2(4f)^5$	${}^6\mathrm{H}_{5/2}$
62	Sm	$(\mathrm{Xe})(6s)^2(4f)^6$	${}^7\mathrm{F}_0$
63	Eu	$(\mathrm{Xe})(6s)^2(4f)^7$	${}^8\mathrm{S}_{7/2}$
64	Gd	$(\mathrm{Xe})(6s)^2(4f)^7(5d)$	${}^9\mathrm{D}_2$
65	Tb	$(\mathrm{Xe})(6s)^2(4f)^9$	${}^6\mathrm{H}_{15/2}$
66	Dy	$(\mathrm{Xe})(6s)^2(4f)^{10}$	${}^5\mathrm{I}_8$
67	Ho	$(\mathrm{Xe})(6s)^2(4f)^{11}$	${}^4\mathrm{I}_{15/2}$
68	Er	$(\mathrm{Xe})(6s)^2(4f)^{12}$	${}^3\mathrm{H}_6$
69	Tm	$(\mathrm{Xe})(6s)^2(4f)^{13}$	${}^2\mathrm{F}_{7/2}$
70	Yb	$(\mathrm{Xe})(6s)^2(4f)^{14}$	${}^1\mathrm{S}_0$

- These elements known as Lanthanides or rare earths.

Periodic Table - XV

- Next we fill $5d$ orbital. We get:

Z	Element	Configuration	Term
71	Lu	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)$	$^3\mathrm{D}_{3/2}$
72	Hf	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^2$	$^3\mathrm{F}_2$
73	Ta	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^3$	$^4\mathrm{F}_{3/2}$
74	W	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^4$	$^5\mathrm{D}_0$
75	Re	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^5$	$^6\mathrm{S}_{5/2}$
76	Os	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^6$	$^5\mathrm{D}_4$
77	Ir	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^7$	$^4\mathrm{F}_{9/2}$
78	Pt	$(\mathrm{Xe})(6s)(4f)^{14}(6d)^9$	$^3\mathrm{D}_3$
79	Au	$(\mathrm{Xe})(6s)(4f)^{14}(5d)^{10}$	$^2\mathrm{S}_{1/2}$
80	Hg	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}$	$^1\mathrm{S}_0$

Periodic Table - XVI

- Next we fill $6p$ orbital. We get:

Z	Element	Configuration	Term
81	Tl	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)$	$^2\mathrm{P}_{1/2}$
82	Pb	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)^2$	$^3\mathrm{P}_0$
83	Bi	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)^3$	$^4\mathrm{S}_{3/2}$
84	Po	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)^4$	$^3\mathrm{P}_2$
85	At	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)^5$	$^2\mathrm{P}_{3/2}$
86	Rn	$(\mathrm{Xe})(6s)^2(4f)^{14}(5d)^{10}(6p)^6$	$^1\mathrm{S}_0$

Periodic Table - XVII

- Next we fill $7s$ orbital. We get:

Z	Element	Configuration	Term
87	Fr	$(\mathrm{Rn})(7s)$	?
88	Ra	$(\mathrm{Rn})(7s)^2$	$^1\mathrm{S}_0$

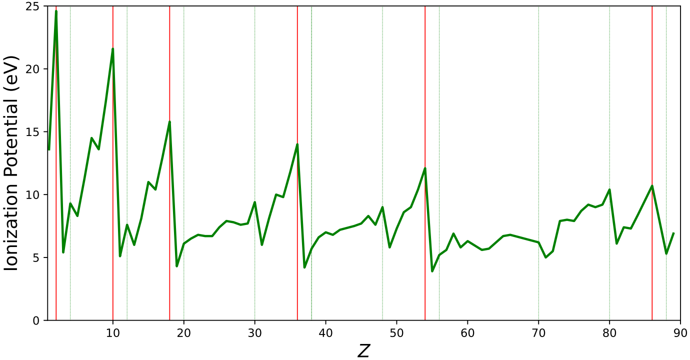
Periodic Table - XVII

- Next we fill $5f$ orbital. We get:

Z	Element	Configuration	Term
89	Ac	$(\mathrm{Rn})(7s)^2(6d)$	$^2\mathrm{D}_{3/2}$
90	Th	$(\mathrm{Rn})(7s)^2(6d)^2$	$^3\mathrm{F}_2$
91	Pa	$(\mathrm{Rn})(7s)^2(5f)^2(6d)$	$^4\mathrm{K}_{11/2}$
92	U	$(\mathrm{Rn})(7s)^2(5f)^3(6d)$	$^5\mathrm{L}_6$
93	Np	$(\mathrm{Rn})(7s)^2(5f)^4(6d)$	$^6\mathrm{L}_{11/2}$
94	Pu	$(\mathrm{Rn})(7s)^2(5f)^6$	$^7\mathrm{F}_0$

- At this point, we have run out of elements with stable atomic nucleii.

Periodic Table - XVII



- Figure shows ionization potentials of elements (i.e., energy needed to take one electron from them). Vertical red lines indicate filled shells that result in noble gases. Green lines indicate other filled shells.

Periodic Table - XVIII

- Noble gases (Helium, Neon, Argon, Krypton, Xenon, and Radon), which are characterized by full shells, have highest ionization potentials. This explains chemical inertness of such elements (they do not want to donate any of their electrons to form chemical bonds).
- Halogens (Fluorine, Chlorine, Bromine, Iodine, Astatine) are one electron short of a noble shell. This explains their eagerness to form chemical bonds in which they gain a single electron.
- Alkali metals (Lithium, Sodium, Potassium, Rubidium, Cesium, and Francium) have noble shells plus a single electron. This explains their eagerness to form chemical bonds in which they lose a single electron: e.g., sodium chloride, which consists of Na^+ and Cl^- ions with compete shells.

Periodic Table - XIX

- Continuing in this manner, we can explain most of chemical properties of elements on basis of how many electrons they have in their outer shells.
- In particular, we can predict valance of elements: i.e., how many electron they want to donate or lose when forming chemical bonds.

Spectroscopic Description of Ground-States - I

- Let $\mathbf{L}$ be total orbital angular momentum of electrons in given atom, and let L be associated quantum number. (Let M be quantum number associated with L_z.)
- Let $\mathbf{S}$ be total spin angular momentum of electrons in given atom, and let S be associated quantum number. (Let M_s be quantum number associated with S_z.)
- Finally, let $\mathbf{J} = \mathbf{L} + \mathbf{S}$ be total angular momentum of electrons in given atom, and let J be associated quantum number.
- Easily appreciated that filled orbital has zero net angular momentum of any kind. In other words, it is characterized by $L = S = J = 0$.
- Thus, it is only electrons in unfilled orbitals that affect angular momentum state of atomic ground-state.
- Angular momentum state conventionally represented as ${}^{2S+1}\mathrm{X}_{\mathrm{J}}$, where $\mathrm{X} = \mathrm{S}$, P, D, F, G, H, and I as $L = 0$, 1, 2, 3, 4, 5, and 6.

Spectroscopic Description of Ground-States - II

- Angular momentum state of atomic ground-state matters because of selection rules for electric dipole transitions.
- Selection rules state that if atom makes transition from excited state to ground-state then

$$\Delta S = 0,$$

$$\Delta L = \pm 1,$$

$$\Delta J = 0, \pm 1.$$

- Note that a $J = 0$ to a $J = 0$ transition is not allowed.
- Selection rules severely constrain which excited states can decay to ground-state.

Spectroscopic Description of Ground-States - III

- For light elements ($Z < 40$), spectroscopic state of ground-state can be predicted by Hund's rules:
  1. State with largest S value has lowest energy.
  2. For given S value, state with maximum L value has lowest energy.
  3. For a given S and L value, if incomplete shell not more than half-filled then lowest energy state has $J = |L - S|$, otherwise $J = L + S$.
- When applying Hund's rules, care must be taken not to violate Pauli exclusion principle.
- Hund's rules fail for heavier atoms because electron motion becomes relativistic, which changes manner in which electrons interact.

Spectroscopic Description of Ground-States - IV

- As example, consider Carbon.
- Carbon's unfilled subshell contains two $2p$ electrons.
- In accordance with Rule 1, we want both electrons to have same spin (spin-up, say), in order to maximize S. In fact, spins add to give $S = 1$.
- Want to maximize L, in accordance with Rule 2. However, cannot put two spin-up electrons in $m = +1$ state, because this violates Pauli exclusion principle. Best we can do is to put one electron in $m = +1$ state, and one in $m = 0$ state. So, $M_{\rm max} = 1$, which means that $L = 1$.
- Shell is less than half full, so Rule 3 tells us that $J = L - S = 0$.
- Hence, spectroscopic state of Carbon ground-state is ${}^3\mathrm{P}_0$.
- According to selection rules, only excited states that can decay to ground-state are ${}^3\mathrm{D}_1$ and ${}^3\mathrm{S}_1$.

Spectroscopic Description of Ground-States - V

- As a second example, consider Oxygen.
- Oxygen's unfilled subshell contains four $2p$ electrons.
- In accordance with Rule 1, we want all electrons to have same spin, in order to maximize S. However, there are only three m states, and Pauli exclusion principle forbids us from putting two electrons with same spin in one of these states. Hence, we have to put first three electrons in $m = -1$, 0, and $+1$ states. Fourth electron must have opposite spin. Maximum possible value of M_s is 1. Hence, $S = 1$.
- Want to maximize L, in accordance with Rule 2. So, to get maximum value of M we put fourth electron in $m = +1$ state. So, $M_{\rm max} = 1$, which means that $L = 1$.
- Shell is more than half full, so Rule 3 tells us that $J = L + S = 2$.
- Hence, spectroscopic state of Oxygen ground-state is ${}^3{\rm P}_2$.
- According to selection rules, only excited states that can decay to ground-state are ${}^3{\rm D}_{3,2,1}$ and ${}^3{\rm S}_1$.