CHAPTER 9
Atomic Structure and Spectra

I. The Hydrogenic Atoms (one electron species). H, He$^{+1}$, Li$^{2+}$, ...

A. Clues from Line Spectra.

Reminder: fundamental equations of spectroscopy:

\[ \varepsilon_{\text{photon}} = h \nu \]

relation of energy of photon to its \( \nu \)

\[ \nu = \frac{c}{\lambda} \]

relation of frequency to \( \lambda \)

\[ \tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \]

definition of "wavenumber" \( \tilde{\nu} \) (units usually cm$^{-1}$)

When system (atom, oscillator, rotor, etc.) interacts with light and jumps from one state to another:

\[ \varepsilon_{\text{photon}} = \Delta E \]

spacing between energy levels

\[ \Delta E \]

emission

\[ \varepsilon_{\text{photon}} = \Delta E \]

absorption

= \( E_{\text{upper}} - E_{\text{lower}} \)

The pattern of emission lines from atomic hydrogen were fit by Rydberg equation:

\[ \tilde{\nu} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) ; \quad R_H = 109,677 \text{ cm}^{-1} \]

Balmer Series \[ n_1=2 \quad n_2=3,4,5,\ldots \]
Lyman \[ n_1=1 \quad n_2=2,3,4,\ldots \]
Paschen \[ n_1=3 \quad n_2=4,5,6,7 \]
Now know that $n_1$, $n_2$ are quantum levels

$n_1 =$ lower level
$n_2 =$ upper level

Level spacings $\Delta E = E_{n_2} - E_{n_1} = \varepsilon_{\text{photon}} = h\nu = \frac{hc}{\lambda} = h\tilde{\nu}$

$\Delta E = hc\tilde{\nu}$

$\Delta E = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

That Rydberg Eqn has two terms, and knowing that emissions are a result of transitions between two quantum energy levels, implies that energy levels of Hydrogen are given by an expression of the form:

$$E_n \propto \frac{\text{constant}}{n^2}$$

where the denominator contains the quantum number $n$

B. The Quantum Mechanical Structure of Hydrogenic Atoms.

1. Treat just like rigid rotor, but now radial dimension can vary. Place origin at center of mass. Since nuclear mass $m_N >> m_e$ (electron), center of mass is virtually at nucleus.
Reduced mass \( \mu = \frac{m_N m_e}{m_N + m_e} \approx m_e \)

2 particle problem reduced to effective 1 particle problem:
An e\(^-\) with effective mass \( \mu \approx m_e \) traveling around origin.

2. **Schroedinger Equation**

\[
\hat{H}\psi = \frac{-\hbar^2}{2\mu} \nabla^2 \psi + V(r)\psi = E\psi
\]

Kinetic energy operator \( \frac{-\hbar^2}{2\mu} \nabla^2 \) just like rigid rotor Hamiltonian except radial portion \( \neq 0 \) anymore.

Also potential energy operator \( V \) is no longer zero, but depends on radial coordinate (\( r=\)distance between nucleus and electron)

\[
V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}
\]

Coulomb's Law between point charges \( +Ze \) and \(-e\) at a separation distance of \( r \).

\( \varepsilon_0 \) = vacuum permittivity = \( 8.85 \times 10^{-12} \) J^{-1} C^{2} m^{-1}

3. **Solution (wave functions of H atom).**

Is obtained by technique of separation of variables which is made possible by the **centrosymmetric** potential.

\[
\psi_{n,\ell,m_\ell} = R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)
\]

3 quantum #'s
radial spherical harmonics, part of wave fct

n = principal q.n. = 1,2,3,4...\( \infty \)
\( \ell \) = angular mom. q.n. = 0,1,2... \( (n-1) \)
\( m_\ell \) = magnetic q.n. = \( -\ell,...0,...+\ell \)

4. **The angular wave equation for Y looks like something we have seen before containing the legendrian operator:**

\[
\hat{\Lambda}Y_{\ell,m_\ell}(\theta,\phi) = -\ell(\ell + 1)Y_{\ell,m_\ell}(\theta,\phi)
\]
5. The radial wave equation to solve looks like this:

\[ \frac{-\hbar^2}{2\mu} \frac{d^2}{dr^2} rR(r) + V_{\text{eff}} rR(r) = ErR(r) \]

where:

\[ V_{\text{eff}} = \frac{-Ze^2}{4\pi\varepsilon_o r} + \frac{\ell(\ell + 1)\hbar^2}{2\mu r^2} \]

Note that only the radial portion contains the energy eigenvalue \( E \), meaning the energy is fully determined by the radial part alone.

The first term in the effective potential \( V_{\text{eff}} \) is simply Coulomb’s law potential energy term.

The second term is the centrifugal effect which keeps the electron from getting too close to the nucleus. This in turn depends on the amount of angular momentum of the electron about the nucleus and so depends on the \( \ell \) quantum number.

6. Energies (depend only on principal quantum number \( n \) in hydrogenic atoms)

\[ E_n = \frac{-Ze^2\mu e^4}{32\pi^2\varepsilon_o^2\hbar^2} \left( \frac{1}{n^2} \right) \quad \text{where } n = 1, 2, 3... \]

\( e^4/32\pi^2\varepsilon_o^2\hbar^2 \) is the part that never varies, totally constants

also \( \mu \approx m_e \) so it hardly varies as one goes from H to He\(^+\) to Li\(^{2+}\)...etc.
$E_n = -Z^2 \times \mu \times (\text{constants}) \over n^2$

For hydrogen $Z=1$

$$E_n = \frac{-13.598 \text{eV}}{n^2} = \frac{-2.170 \times 10^{-18} \text{J}}{n^2}$$

For others, He$^+$, Li$^{+2}$

$$E_n \sim -Z^2 \times 13.6 \text{ eV} \over n^2$$

where $Z =$ atomic # of nucleus

Using this energy formula can you derive the Rydberg equation and find the Rydberg Constant?


The wavefunctions $\psi_{n, \ell, m_\ell}$ are called "atomic orbitals."

Each orbital is defined by 3 quantum #'s.

<table>
<thead>
<tr>
<th>Orbital name</th>
<th>$n$</th>
<th>$\ell$</th>
<th>$m_\ell$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2s</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2p (3 of them)</td>
<td>2</td>
<td>1</td>
<td>-1, 0, +1</td>
</tr>
<tr>
<td>3s</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3p</td>
<td>3</td>
<td>1</td>
<td>-1, 0, +1</td>
</tr>
<tr>
<td>3d (5 of them)</td>
<td>3</td>
<td>2</td>
<td>-2, -1, 0, 1, 2</td>
</tr>
</tbody>
</table>
s $\rightarrow$ $\ell = 0$ e.g. 4f (then n = 4 and $\ell = 3$)
p $\rightarrow$ $\ell = 1$
d $\rightarrow$ $\ell = 2$
f $\rightarrow$ $\ell = 3$

8. Degeneracy.

Lots of degeneracy, since $E \propto \frac{1}{n^2}$

E does not depend on $\ell, m_\ell$ for H $(n, \ell, m_\ell)$

\begin{align*}
\text{Energy} & \\
(3,0,0) & (3,1,-1) (3,1,0) (3,1,1) & (3,2,-2) (3,2,-1) (3,2,0) (3,2,1) (3,2,2) \\
(2,0,0) & (2,1,-1) (2,1,0) (2,1,1) & \\
\text{3p} & \text{3d} & \\
\text{2p} & & \\
(1,0,0) & & \\
\end{align*}

9. Shells and subshells

\begin{align*}
\text{Subshells} & \\
\text{s} & \text{p} & \text{d} & M \text{ shell, } n = 3 \\
& & & \text{L shell, } n = 2 \\
& & & \text{K shell, } n = 1 \\
\text{Shells} & \text{Orbitals} & & \\
\end{align*}
10. Ionization Energy

\[ \Delta E = E_\infty - E_{n=1} \]

\[ 0 - (-\hbar c R_H) = \hbar c R_H = 13.6 \text{ eV} \]

Now let’s see what $\psi$ looks like.

11. The Radial Wave function. $R_{n,r}(r)$

Atkins replaces $r$ variable with dimensionless $\rho$ variable where:

\[ \rho = \frac{2Z}{n} \left( \frac{\mu}{m_e} \right) \frac{r}{a_0} \]

this ratio is 0.99946 for H and even closer to 1.0000 for heavier nuclei
\[ \rho \equiv \frac{2Zr}{na_o} \quad \rho \propto r \]

where \( a_o = \text{Bohr radius} = 52.947 \text{ pm} = \frac{\hbar^2 4\pi \varepsilon_0}{\mu e^2} \)

\[ R_{n,\ell} = N_n \rho^\ell L_{n,\ell}(\rho)e^{-\rho/2} \] where \( L_{n,\ell} \) are “associated Laguerre polynomials”

\[ R(r) = (\text{norm const}) \times (\text{polynomial in } r) \times (\text{decaying exponential in } r) \]

Written as function of radial coordinate \( r \):

\[ R_{n,\ell} = R_{10}(r) = R_{1s} = \left( \frac{Z}{a_o} \right)^{3/2} 2e^{-Zr/a_o} \]

\[ R_{20}(r) = R_{2s} = \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_o} \right)^{3/2} \left( 2 - \frac{Zr}{a_o} \right) e^{-Zr/a_o} \]

<table>
<thead>
<tr>
<th>Orbital</th>
<th>( n )</th>
<th>( l )</th>
<th>( R_{n,\ell} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>0</td>
<td>[ 2 \left( \frac{Z}{a} \right)^{3/2} e^{-\rho/2} ]</td>
</tr>
<tr>
<td>2s</td>
<td>2</td>
<td>0</td>
<td>[ \frac{1}{8^{1/2}} \left( \frac{Z}{a} \right)^{3/2} (2 - \rho)e^{-\rho/2} ]</td>
</tr>
<tr>
<td>2p</td>
<td>2</td>
<td>1</td>
<td>[ \frac{1}{24^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \rho e^{-\rho/2} ]</td>
</tr>
<tr>
<td>3s</td>
<td>3</td>
<td>0</td>
<td>[ \frac{1}{243^{1/2}} \left( \frac{Z}{a} \right)^{3/2} (6 - 6\rho + \rho^2)e^{-\rho/2} ]</td>
</tr>
<tr>
<td>3p</td>
<td>3</td>
<td>1</td>
<td>[ \frac{1}{486^{1/2}} \left( \frac{Z}{a} \right)^{3/2} (4 - \rho)\rho e^{-\rho/2} ]</td>
</tr>
<tr>
<td>3d</td>
<td>3</td>
<td>2</td>
<td>[ \frac{1}{2430^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \rho^2 e^{-\rho/2} ]</td>
</tr>
</tbody>
</table>

\( \rho = \frac{(2Z/na)r}{\text{with } a = 4\pi \varepsilon_0 \hbar^2 / \mu e^2}. \) For an infinitely heavy nucleus (or one that may be assumed to be so), \( \mu = m_e \) and \( a = a_o \), the Bohr radius. The full wavefunction is obtained by multiplying \( R \) by the appropriate \( Y \) given in Table 9.3.
So, \# of radial nodes = n - ℓ - 1

12. Visualizing the s orbitals.

s orbitals have spherical symmetry and have radial nodes when n>1.

Convenient to describe \( \psi^2 \) in terms of “90\% boundary surfaces.”

i.e. sphere that enclose 90\% of probab. distribution

Also define mean radius of orbital as \( <r> \) (see Eq(10.19))

\[
<r> = \int r^2 \psi^2 d\tau = \int r^2 R^2 dr \int d\phi \int d\theta \sin \theta Y^2
\]

Also can talk about radial distribution function

\[
P(r)dr = 4\pi r^2 \psi^2 dr
\]

which gives probability of finding electron in a shell of thickness dr at a distance r from nucleus.
Here is radial distribution function for 1s:
13. Electron dot density diagrams:
14. Visualizing the p orbitals ($\ell=1$).

With $\ell > 0$ we start introducing angular momentum.

p orbitals and beyond have non-spherical symmetry

- Zero amplitude at $r=0$ (centrifugal effect)
- A nodal plane

The three p-orbitals are distinguished by quantum number $m_\ell = -1, 0, +1$

e.g.,

$$\psi_{(n=2,\ell=1,m_\ell=0)} = R_{2,1}(r)Y_{1,0}(\theta, \phi)$$

$$= \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a_o} \right)^{5/2} \exp^{-Zr/2a_o} \cos \theta$$

Standard practice is to construct real p-orbital $\psi$’s from linear comb of p orbitals, since they have complex $e^{\pm im}$ in them.

That’s what is usually plotted, as in the following boundary surface diagram:

Here is $3p_x$ orbital
Nodes summary:

angular = $\ell$
radial = $n - \ell - 1$
total = $n - 1$

Orbital angular momentum

$L = \sqrt{\ell(\ell + 1)\hbar}$

15. d orbitals ($\ell = 2$)

Have 2 nodal planes

Again linear comb of 3d $\psi$’s are used to construct a set of 5 real 3d orbitals for visualizing.

Here’s 3d$_{z^2}$

To conserve angular momentum,

\[ \Delta l \] must be equal to ±1
\[ \Delta m_l \] must be equal to 0, ±1

when H atom absorbs or emits light. All other transitions are forbidden.

\[ \Delta n \] can be anything.
Table 11.3. Real Hydrogen-like Energy Eigenfunctions

\[
\psi_{10} = \psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} e^{-Zr/a}
\]

\[
\psi_{20} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right) e^{-Zr/2a}
\]

\[
\psi_{21x} = \psi_{2px} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right) e^{-Zr/2a} \sin(\theta) \cos(\phi)
\]

\[
\psi_{21y} = \psi_{2py} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right) e^{-Zr/2a} \sin(\theta) \sin(\phi)
\]

\[
\psi_{300} = \psi_{3s} = \frac{1}{18\sqrt{3\pi}} \left( \frac{Z}{a} \right)^{3/2} \left[ 6 - \frac{8Zr}{a} + \left( \frac{2Zr}{3a} \right)^2 \right] e^{-Zr/3a}
\]

\[
\psi_{310} = \psi_{3pz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{6Zr}{a} - \frac{Z^2r^2}{a^2} \right) e^{-Zr/3a} \cos(\theta)
\]

\[
\psi_{31x} = \psi_{3px} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{6Zr}{a} - \frac{Z^2r^2}{a^2} \right) e^{-Zr/3a} \sin(\theta) \cos(\phi)
\]

\[
\psi_{31y} = \psi_{3py} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{6Zr}{a} - \frac{Z^2r^2}{a^2} \right) e^{-Zr/3a} \sin(\theta) \sin(\phi)
\]

\[
\psi_{320} = \psi_{3dz^2} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right)^2 e^{-Zr/3a} [3 \cos^2(\theta) - 1]
\]

\[
\psi_{3dxz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right)^2 e^{-Zr/3a} \sin(\theta) \cos(\theta) \cos(\phi)
\]

\[
\psi_{3dyz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right)^2 e^{-Zr/3a} \sin(\theta) \cos(\theta) \sin(\phi)
\]

\[
\psi_{dz^2-y^2} = \frac{1}{81\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right)^2 e^{-Zr/3a} \sin^2(\theta) \cos(2\phi)
\]

\[
\psi_{3dxy} = \frac{1}{81\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{3/2} \left( \frac{Zr}{a} \right)^2 e^{-Zr/3a} \sin^2(\theta) \sin(2\phi)
\]
II. Many-Electron Atoms (more than 1 e\textsuperscript{−}).

- extremely complicated due to e\textsuperscript{−} -- e\textsuperscript{−} repulsion
- no exact solutions in terms of known math functions
- accurate solutions available by numerical computations
- solution \( \psi(r_1, r_2, \ldots r_n) = \) function of every e\textsuperscript{−} coordinate

A. The Orbital Approx.

Says the wavefunction for a many-electron atom \( \psi(r_1, r_2, \ldots r_n) \) can be written as a product of one-electron wave functions:

\[
\psi(r_1, r_2, \ldots r_n) = \psi_1(r_1) \times \psi_2(r_2) \ldots \quad (\text{each e}^{-} \ \text{occupying own orbital})
\]

Further think of individual orbitals as \textit{hydrogenic orbitals}, but with modified nuclear charges.

This is starting point for mathematical treatment.

Now, use hydrogenic orbitals as the \textbf{basis set} for describing each one-electron orbital of the multi-electron atoms.

Orbital or wave function for electron \( i \) is written as a weighted linear combination of hydrogenic atomic orbitals.

\[
\psi_i = c_{1s}\phi_{1s} + c_{2s}\phi_{2s} + c_{2p_x}\phi_{2p_x} + \ldots \quad \text{where:}
\]

- \( c_{1s} \) is weighting coefficient
- \( \phi_{1s} \) is H-like atom 1s but with \( Z > 1 \)
- \( c_{2s} \) is weighting coeff.
- \( \phi_{2s} \) is H-like atom 2s

\[
\psi_i = c_{1s}\phi_{1s} + c_{2s}\phi_{2s} + c_{2p_x}\phi_{2p_x} + \ldots
\]

\( \text{e.g.} \) Helium’s 2 electrons go into orbitals that are quite similar to H 1s orbitals but with \( 2 > Z > 1 \).

Electron config of He = 1s\textsuperscript{2} (both in “1s-like” orbitals)

Each electron is interacting with a Z=+2e nucleus so He is smaller than H even though having 2 electrons.

As we go to more than 2 electrons, we find that:

- 1s\textsuperscript{3} is excluded, i.e. is forbidden.

\[
\text{Li} = 1s^22s^1
\]

- 2 e\textsuperscript{−} in 1s-like orbitals
- 3\textsuperscript{rd} e\textsuperscript{−} in a 2s-like orbital
The n=1 shell is said to be a **closed shell** once it has two electrons. We could also write the above then as:

\[ \text{Li} = [\text{He}]2s^1 \]

Pauli Exclusion Principle = no more than 2e\(^-\) per orbital, and their spins must be paired. (↑↓)

### B. Spin.

Electron has 1 more degree of freedom beyond 3 spatial degrees. Intrinsic ang. Mom.

Total spin q# \( S = 1/2 \) for electron, proton and neutron.

This is an intrinsic quantity which cannot change.

Total spin angular mom = \( \sqrt{s(s+1)} \hbar \)

Magnitude of spin about a particular axis (such as magnetic field direction in NMR) is controlled by quantum number \( m_s \), which can have possible values determined by \( s \):

\[ m_s = -s, \ldots +s \]

So for electron: \( m_s = -1/2 \) or \(+1/2\) \( \downarrow \) or \( \uparrow \)

No 2 e\(^-\) can have the same 4 quantum numbers.

\[ n, \ell, m_\ell, m_s \]

i.e. be in the same quantum state.

e.g. \( 1s (\uparrow) \ 1, 0, 0, +1/2 \) \( \quad \) Both are in same orbital 1s but in 2 unique quantum states.

\[ 1s (\downarrow) \ 1, 0, 0, -1/2 \]

See Atkins textbook p. 342 for a more full description of Pauli Principle, and the requirement of having an antisymmetric wave function.
C. Penetration and Shielding.

As we try to hang on to thinking about electrons of many-electron atoms occupying H-like orbitals, we are forced to introduce concept of shielding.

1. Shielding effect of $e^-$ in same s orbital is present but slight.

Each $e^-$ is in a 1s-like orbital, but $e^-$ does not experience full +2e charge of nucleus because of the repulsive interaction with the other electron.

Effective atomic # or **effective nuclear charge** experienced by the electrons in He

$$Z_{\text{eff}} = Z = 1.69$$ for He 1s electrons

$$Z_{\text{eff}} < Z = 2$$

$$Z_{\text{eff}} = Z - \sigma$$

(where $\sigma$ is “shielding constant”)

This means each $e^-$ in He occupies 1s orbital with $Z=1.69$ rather than $Z=2$ or $Z=1$.

(So we can substitute this $Z_{\text{eff}}$ for $Z$ in the radial wave function for 1s.)

2. Shielding of $e^-$ from the nuclear charge by $e^-$ in lower filled shells is great.
3. s orbitals **penetrate** more to the nucleus than p orbitals because $R(r) \neq 0$ at nucleus for s orbitals.

Therefore, when $e^- e^-$ repulsion is considered in many-e$^-$ atoms, 2s is below 2p in energy, rather than degenerate as in Hydrogen.

$$3s < 3p < 3d$$ also.

[Image of radial distribution function, $P$ vs $Zr/a_0$]

<table>
<thead>
<tr>
<th>Na</th>
<th>$Z = 11$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 e$^-$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$3s \uparrow \downarrow Z_{\text{eff}} = 2.5$</td>
<td></td>
</tr>
<tr>
<td>$2p \uparrow \uparrow \uparrow \downarrow \downarrow$</td>
<td></td>
</tr>
<tr>
<td>$Z_{\text{eff}} = 6.85$ fill 1st, lower in energy</td>
<td></td>
</tr>
<tr>
<td>$1s \uparrow \downarrow$</td>
<td></td>
</tr>
<tr>
<td>$Z_{\text{eff}} = 10.6$</td>
<td></td>
</tr>
</tbody>
</table>

Na $= 1s^2 2s^2 2p^6 3s^1$

filled filled valence e$^-$

<table>
<thead>
<tr>
<th>K shell</th>
<th>L shell</th>
</tr>
</thead>
</table>

$E = \frac{-Z_{\text{eff}}^2 13.6 \text{eV}}{n^2} = \frac{-2.5^2 (13.6)}{3^2}$
D. Aufbau Principle (building up principle).

1. Order of occupation of hydrogen-like orbitals in the ground state config of many e⁻ atoms.

1s  2s  2p  3s  3p  4s  3d  4p  5s  4d  5p  6s

sneaks in under the 3d

K

19 e⁻  1s²2s²2p⁶3s²3p⁶4s¹

instead of 3d¹

4s [———] ——— 3d[———] ——— ——— ———

3p │ │ │ │ │

2p │ │ │ │ │

2s │ │ │ │ │

1s │ │ │ │ │

4s and 3d are very close in energy

2. Feed e⁻ into orbitals in proper succession, max of 2 e⁻ per orbital.

3. Hund’s Rule = an atom in its ground state adopts a config with the greatest # of unpaired e⁻ (maximum multiplicity)

Why? Due to spin correlation. (Parallel spins repel each other less, causing the atom to shrink slightly, improving the electron-nuclear attraction.)

e⁻ occupy different orbitals in a subshell by energy preference.

N  7 e⁻

2s [———] ——— ——— 2p “subshell”

keep unpaired

1s [———] ———
Many-electron atoms \[\text{here } S = \frac{Z_{\text{eff}}}{n}\]

### Table 4.9 Best values of $\xi$ for the ground state of neutral atoms*

<table>
<thead>
<tr>
<th>$Z$</th>
<th>1$s$</th>
<th>2$s$</th>
<th>2$p$</th>
<th>3$s$</th>
<th>3$p$</th>
<th>4$s$</th>
<th>3$d$</th>
<th>4$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2</td>
<td>1.6875</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>2.6906</td>
<td>0.6396</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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*E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963); computed for ground state configuration, except for Cr([Ar]4$d^5$3$d^4$) and Co([Ar]4$d^9$5$d^0$).*
E. Periodicity of Ionization Energies.

1. Minimum energy to remove e\(^-\) from a many e\(^-\) atom is its first ionization energy \(I_1\).

\[
\text{Na(g)} \rightarrow \text{Na}^+ + \text{e}^- \quad \text{energy needed} = I_1
\]

\(I_2\) = 2\(^{nd}\) ioniz energy, etc.

IONIZATION ENERGY \(\sim\) difficulty of removing e\(^-\)

General trend \(I_1\) ↑ across row, \(I_1\) ↓ down column.

2. Li, Na, K (alkali metals) have low \(I_1\).

Have single s electron outside a filled shell, so \(Z_{\text{eff}}\) is low.

3. Compare Li and Be. \(I_1\) (Be) > \(I_1\) (Li)

Plus add another 2s electron which inadequately shields the other 2s electron.

**Table 9B.2 First and second ionization energies**

<table>
<thead>
<tr>
<th>Element</th>
<th>(I_1/\text{(kJ mol}^{-1}))</th>
<th>(I_2/\text{(kJ mol}^{-1}))</th>
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<tr>
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<td>1312</td>
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<tr>
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<tr>
<td>Mg</td>
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<td>1451</td>
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<tr>
<td>Na</td>
<td>496</td>
<td>4562</td>
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</table>

* More values are given in the Data section.
\[ Z_{eff} \ (2s) \uparrow \]

So \( I_1 \uparrow \) as \( Li \rightarrow Be \)

4. Now compare Be to B. \( I_1 \) goes down. Why?

\[
\begin{align*}
\text{Be} & \quad \text{N} \\
\text{Be} & \quad \text{O} \\
\text{B} & \quad \text{C} \\
\text{Li} & 
\end{align*}
\]

Added e\(^-\) goes into 2p (which has poor penetration toward nucleus). Nuclear charge goes up +1e, but 2p electron is well-shielded by compact 1s, 2s.

5. \( B \rightarrow C \rightarrow N \) \( I_1 \uparrow \) because nuclear charge is increasing, but e\(^-\) are filling spatially separated 2p orbitals which poorly shield one another.

\[
\begin{align*}
\text{B} & \quad \text{1e}^- \text{ in } 2p \\
\text{Be} & \quad \text{N} \\
\text{Be} & \quad \text{O} \\
\text{B} & \quad \text{C} \\
\text{Li} & 
\end{align*}
\]

6. \( N \rightarrow O \) \( I_1 \) takes a dip \( \downarrow \) slightly.

Now beginning to pair up e\(^-\) in 2p orbitals. e\(^-\) -- e\(^-\) repulsion increase in that paired orbitals, and e\(^-\) is easier to remove.
F. Electron Affinity, \( E_{ea} \)

1. \( E_{ea} = \) Energy released when an electron attaches to a gaseous atom.

\[
\text{Cl}(g) + e^- \rightarrow \text{Cl}^- + E_{ea}
\]

| \( \text{Cl} \) | 349 |
| \( \text{F} \) | 322 |
| \( \text{H} \) | 73  |
| \( \text{O} \) | 141 | \( \text{O}^- \) | -844 |

G. Numerical Computations of Many Electron Atomic Orbitals.

→ Hartree-Fock Self-Consistent Field Theory (SCF).

1. \( e^- -- e^- \) repulsion is the computational problem.

\[
H\psi = E\psi
\]

\[
\sum_{\text{all electrons}} \left\{-\frac{\hbar^2}{2m} \nabla_i^2 \psi - \frac{Ze^2}{4\pi\varepsilon_o r_i} \psi \right\} + \frac{e^2}{4\pi\varepsilon_o} \sum_{\text{pairs}} \frac{1}{r_{ij}} \psi = E\psi
\]

where:

\[
\sum_{\text{all electrons}} \quad \text{is the sum over all electrons}
\]

\[
-\frac{\hbar^2}{2m} \nabla_i^2 \psi \quad \text{is the KE term for each electron } i
\]

(easy part, separable)

\[
\frac{Ze^2}{4\pi\varepsilon_o r_i} \psi \quad \text{electron-nuclear interaction. Easy and separable.}
\]

\[
\frac{e^2}{4\pi\varepsilon_o} \sum_{\text{pairs}} \frac{1}{r_{ij}} \psi \quad \text{difficult part because inseparable.}
\]

Involves distances \( 1/r_{ij} \) between all electrons \( i \) & \( j \).

\( e^- -- e^- \) repulsion

Call this \( V_{ee} \)
2. **SCF:**
   a. Simplify $V_{ee}$ term by allowing each $e^-$ to interact with the $e^-$ cloud formed by all other $e^-$ (i.e. $\psi^2$) rather than interact with instantaneous position of the other electrons.

   b. Start with an initial guess of the solution by putting each $e^-$ in a **hydrogenic** orbital using Aufbau rules. This provides $1^{st}$ guess of $e^-$ cloud of each electron.

   c. Apply the approx S.E. to get improved set of orbitals.

   d. Repeat procedure until improved $\psi$'s are no longer changing between cycles of iteration.

   You have iterated to self-consistency!

3. The electron-electron interaction really contains two effects:

   - Coulombic repulsion
   - Spin-spin correlation

SCF solution for Na

Radial distribution fct.
H. The full wave function of many-electron atoms.

1. Full wave function must include spin state designation.

   e.g., Helium, a 2 e- system

   \[ \Psi(1,2) = \psi(1,2)(\uparrow \uparrow) \]

   spatial spin part part

   spin wave functions are combinations of \( \alpha(i) \) or \( \beta(i) \) which are one electron spin functions.

   \[ \Psi(1,2) = \psi(1)\psi(2)(\uparrow \uparrow) \]

   orbital 4 tentative possibilities approx for 2 spins

   \[ \begin{align*}
   \alpha(1)\alpha(2) & \quad \beta(1)\beta(2) & \quad \alpha(1)\beta(2) & \quad \alpha(2)\beta(1)
   \end{align*} \]

   In last two combinations \([\alpha(1)\beta(2) \text{ or } \alpha(2)\beta(1)]\), due to the indistinguishability condition of two electrons, you have to express these as linear combinations and there are two ways to do that:

   \[ \begin{align*}
   \sigma_+(1,2) &= \frac{1}{2^{\frac{1}{2}}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\
   \sigma_-(1,2) &= \frac{1}{2^{\frac{1}{2}}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) 
   \end{align*} \]

2. So four possible spin arrangements of 2 electrons:

   \[ \begin{align*}
   \alpha(1)\alpha(2) & \quad \beta(1)\beta(2) & \quad \sigma(1,2) & \quad \sigma(1,2)
   \end{align*} \]

   Now comes Pauli principle: when the labels (e.g. 1 and 2) of any two identical fermions are exchanged, the total wavefunction \( \Psi \) must change sign. (antisymmetric wavefunction requirement)

   \[ \Psi(1,2) = -\Psi(2,1) \]

   If just look at spatial wavefunctions alone & if both e- in same orbital:

   \[ \psi(1)\psi(2) = +\psi(2)\psi(1) \quad \text{(not antisymmetric)} \]

   Therefore the \( \text{spin} \) portion of total \( \Psi \) must be the antisymmetric part.
Of the four possible arrangements only $\sigma(1,2)$ is antisymmetric so:

$$\Psi(1,2) = \psi(1)\psi(2)\sigma_-(1,2)$$

$$= \frac{1}{2^{1/2}} \begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix}$$

Slater determinant

Therefore:

if 2 e- in same spatial atomic orbital, only one spin state available $\sigma(1,2)$ which is sins paired " $\uparrow\downarrow$ "

But when 2 e- are in different orbitals, all 4 of the spin combinations are possible.

$\alpha(1)\alpha(2) \quad \beta(1)\beta(2) \quad \sigma(1,2) \quad \sigma(1,2)$

The first three are parallel (triplet), the last is paired (singlet)

all three combos possess spin angular momentum (lower in energy)

no spin angular momentum

$L = 1$

$M_L = -1, 0, +1$

$L = 0$
III. Spectra of Complex Atoms.

A. General.

More complicated than hydrogenic spectra.

\[ h\nu = \frac{hc}{\lambda} = \Delta E \] differences between atomic energy levels

The problem is \( \Delta E \neq \) difference between orbital energies

E.g. He \( \rightarrow \) He* (electronically excited Helium)

B. Selection Rules for allowed transitions in many-electron atoms

1. No change of overall spin.

   Implies singlet \( \rightarrow \) singlet is allowed

   But singlet \( \rightarrow \) triplet is not allowed
2. Here are the allowed transitions in Helium (no singlet to triplet)

3. Sodium’s bright doublet emission:
4. Term symbols as labels of electronic states:

   e.g, what is meant by symbolism $^2P_{3/2}$

   S, P, D gives the total orbital angular momentum $L=0, 1, 2, \text{ etc}$

   Upper left superscript gives the spin multiplicity $1=\text{singlet,}$
   $2=\text{doublet, 3=triplet}$

   Lower right subscript gives the total angular momentum $J$

   Optional: See text if you desire a deeper understanding.