Atomic Orbitals and Quantum Numbers

Bound electrons are delocalized in quantized energy levels that are three dimensional and called atomic orbitals.

Representations of atomic orbitals: s, p, and d orbitals (Fig. 7.15). Also, http://library.thinkquest.org/3659/structures/shapes.html

These pictures describe electron density, the region of space where the electron is likely to be found (Figs. 7.13 and 7.10).

They show the outer surface of the region that the electron occupies with 90% probability.

Orbitals are also called wave functions, a mathematical function that most correctly describes the region of space occupied by an electron.

Note that there are nodes, areas of zero electron density (0% probability of finding the electron).
We use quantum numbers to name the energy levels (the orbitals).

\( n \): principal quantum number, gives the energy, gives the size, shell, row.

\( n \) must be a positive integer \((n = 1, 2, 3, \ldots)\).

Larger \( n \) means the electron has more energy and occupies a larger region of space, i.e., the electron is in a larger orbital.

\( l \): azimuthal quantum number, gives the shape.

\( l \) is restricted by \( n \), can be zero or a positive integer less than \( n \) \((l = 0, 1, 2, \ldots, n-1)\).

\( l \) orbital / shape / location in the periodic table
0  \( s \) / sphere, 1 lobe, 0 nodes / left
1  \( p \) / 2 lobes, 1 node / right
2  \( d \) / 4 lobes, 2 nodes / middle
m<sub>l</sub>: “m sub l”, magnetic quantum number, specifies an orbital, gives orientation of the orbital, gives direction.

m<sub>l</sub> is restricted by l, can be any integer between -l and +l, including zero.  
m<sub>l</sub> = -l, ..., 0, ..., +l  (or, m<sub>l</sub> = 0, ±1, ±2, ..., ±l)

m<sub>s</sub>: “m sub s”, spin orientation quantum number, spin, gives orientation of the electron, “up” or “down”.

m<sub>s</sub> can be +1/2 or -1/2.

Electrons have a property called “spin” that can only have values of ±1/2. The electron is not literally spinning, but this is the name given for this property (Fig. 7.12).

With 3 quantum numbers (n, l, m<sub>l</sub>) we can label every atomic orbital (picture analogy p. 242).
With all 4 quantum numbers, we can give a unique label to every electron in every atom (picture analogy p. 242, Pauli exclusion principle).

Examples:
H: 1s orbital ($n=1, l=0, m_l=0$) and $m_s = +1/2$
He: 1s orbital and $m_s = +1/2$
1s orbital and $m_s = -1/2$

Orbital box diagrams

H:

He:

Electron configurations

Electron configuration notation ($1s^1$, $1s^2$, etc.)
H: $1s^1 = 1\, e^- \text{ in the } 1s \text{ orbital.}$

He: $1s^2 = 2\, e^- \text{ in the } 1s \text{ orbital.}$
The periodic table shows the order of orbital energy and stability. 1s is the lowest energy orbital. The periodic table also shows the s, p, d, and f blocks. Electron configurations of an atom can be built up (aufbau) by starting from the 1s orbital.

B:

C:

N:

O:

*Some orbitals have the same energy (called degenerate orbitals)

*Electrons repel each other
=> try not to pair up electrons, try for maximum spin (Hund)
Valence electrons are reactive; core electrons are not. (Chapters 8 and 9)

**Valence electrons**: outer electrons, electrons in orbitals with the highest $n$ or orbitals not completely filled.

**Core electrons**: inner electrons, electrons that have a lower $n$ than valence electrons.

C: $1s^22s^22p^2$

Na: $1s^22s^22p^63s^1$

Noble gas abbreviation = core electrons

C:

Na:
Electron clouds

Electrons surround the nucleus of an atom and form an electron cloud.

A collision between atoms is a collision between their electron clouds.

The clouds repel each other (the atoms bounce off each other) because electrons are negative. Example: hitting a table, gas particle collisions.

At the same time, the negative cloud of one atom is attracted to the positive nucleus of the other atom.

So atoms can come close to each other. Examples: condensation from gas to liquid, freezing from liquid into solid.
Sometimes atoms come close enough to react with each other if they have enough energy. Example: any chemical reaction.

The interaction between the electron clouds, like sharing clouds between atoms, is fundamental to chemical properties of atoms and compounds.

Chapters 7, 8, and 9 start examining electrons and the resulting chemical properties of atoms.
Practice: electronic configurations
For the element Ti (Z = 22),
Give the electronic configuration, with and without the noble gas abbreviation. (hint: 1s\(^2\)…)

Identify the valence and core electrons.

Draw the orbital box diagram.

Give the quantum numbers for the valence orbitals and electrons.
(hint: 
\( n = 1, 2, 3, \ldots \) 
\( l = 0, 1, 2, \ldots, n-1 \) 
\( m_l = -l, \ldots, 0, \ldots, +l \) 
\( m_s = +1/2 \text{ or } -1/2 \))
Unusual electron configurations

Transition metals: half-filled and fully-filled subshells have extra stability. $d^5s^1$ $d^{10}s^1$

Examples: Cr and Cu

Transition metal ions: $s$ and $d$ energy levels change order => all remaining $s$ and $d$ electrons move into the $d$ subshell.

Example: Ti$^{2+}$
Periodic Trends

1. Size (radius), Figs. 7.20, 7.21

a. Depends on $n$ and screening:

Larger $n$ means larger orbital size.
=> expect 2\textsuperscript{nd} row elements to be larger than 1\textsuperscript{st} row elements, etc.

Smaller $n$ orbitals (inner electrons) \textit{screen} higher $n$ orbitals (outer electrons) from the nucleus.

\textbf{Screening}: $e^-$ - $e^-$ repulsions between the inner electrons and the outer electrons partially cancel the pull of the nucleus on the higher $n$ electrons.
=> reduces the attraction force of the nucleus from its actual charge ($Z$) to an effective charge ($Z_{\text{eff}}$)
=> allows higher $n$ orbitals to expand away from the nucleus
=> expect 2\textsuperscript{nd} row elements to be larger than 1\textsuperscript{st} row elements, etc.
b. Depends on effective nuclear charge ($Z_{\text{eff}}$):

More protons ($Z$) means greater nuclear charge.
=> greater attractive force on electrons
=> electrons are pulled in closer
=> atoms get smaller
=> expect atoms to get smaller going to the right on the periodic table.

**Example:**
Which atom is larger, Li or K?
Which atom is larger, Na or P?

**General trends:**
Going down the periodic table

Going right across the periodic table

*These are general trends that hold mainly for s- and p-block elements.*
c. Depends on ionic charge:

Number of electrons vs. number of protons for cations (⁺) and anions (⁻).

Which is larger?

F or F⁻

Na or Na⁺

Rank in order from largest to smallest:

Na⁺

F⁻

Ne
2. Ionization Energy

**Ionization energy (IE):** the energy required to remove an electron from an atom or ion, \( \Delta E = IE \), generally depends on size (Fig. 7.22).

Measured for atoms in the gaseous state, \( \text{kJ/mol} \)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Reaction</th>
<th>Neutral Form</th>
<th>Ionized Form</th>
<th>IE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(g)</td>
<td>Li(g) → Li(^+)(g) + e(^-)</td>
<td>Li(^+)(g)</td>
<td>e(^-)</td>
<td>520</td>
</tr>
<tr>
<td>Na(g)</td>
<td>Na(g) → Na(^+)(g) + e(^-)</td>
<td>Na(^+)(g)</td>
<td>e(^-)</td>
<td>496</td>
</tr>
<tr>
<td>K(g)</td>
<td>K(g) → K(^+)(g) + e(^-)</td>
<td>K(^+)(g)</td>
<td>e(^-)</td>
<td>419</td>
</tr>
<tr>
<td>As(g)</td>
<td>As(g) → As(^+)(g) + e(^-)</td>
<td>As(^+)(g)</td>
<td>e(^-)</td>
<td>947</td>
</tr>
</tbody>
</table>

**General trends:**
Going down the periodic table

Going right across the periodic table
3. Electron Affinity

Electron affinity (EA): the energy required to add an electron to an atom or ion.

\[ \text{O(g)} + \text{e}^- \rightarrow \text{O}^-(g) \quad \text{EA} = -141 \text{ kJ/mol} \]
\[ \text{F(g)} + \text{e}^- \rightarrow \text{F}^-(g) \quad \text{EA} = -328 \text{ kJ/mol} \]

(negative energy means the process releases energy, other textbooks use a positive sign instead)

Not much of a general trend.
**Bonding**
Bonding orbital = atomic orbital overlap = shared electron density = chemical bond.

The most simple bonding orbital (bond) is to share the electrons between the nuclei.

**Examples:**

H\textsubscript{2}

HF

F\textsubscript{2}

Only use valence atomic orbitals to form bonding orbitals (only use valence electrons to form bonds).

**Covalent bond:** a bond formed by shared electrons, the bonding in molecular compounds. (as opposed to ionic bonds in ionic compounds, and metallic bonds in metals).