s orbital (l=0, m=0)

H 1s orbital:

\[ \psi_{n,l,m_l} = R_{n,l}(r) \cdot Y_{l,m_l}(\theta, \phi) \]

\[ \psi_{100} = (2e^{-r})(\frac{1}{2\sqrt{\pi}}) \]

Probability Density

This probability function gives the probability of finding the electron at any point in space.

\[ P(r) = \psi_{100}^2 = \frac{e^{-2r}}{\pi} \]

\[ \psi_{100}^2 = \frac{1}{\pi} \]
At what radius is it most probable to find the electron?

\[ P(r) = \psi_{100}^2 = \frac{e^{-2r}}{\pi} \]

**Is it at \( r=0 \)?**

Most probable radius: \( r + dr \)

Volume of the thin shell with thickness \( dr \)

\[ 4\pi r^2 dr \]

**Probability** = \( R^2(r)4\pi r^2 dr \)

\[ P/\text{dr} = R^2(r)4\pi r^2 \]

\( P/\text{dr} \), radial distribution function (RDF)

compares the probability of finding electron at different \( r \)

Also called radial probability function
H 1s orbital:

\[ RDF = 4\pi r^2 \left(2e^{-r}\right)^2 = 16\pi r^2 e^{-2r} \]

Most probable radius:

\[ \frac{\partial (RDF)}{\partial r} = 0 \]
Amplitude of the wavefunction: $R(r)$

Whenever the function changes sign, there is a **Radial Node:**

Radius at which the probability of finding the electron is zero.

No. of radial nodes = $n-l-1$

$$R_{2s} = \left(\frac{Z}{2a_0}\right)^{3/2} (2-\sigma)e^{-\sigma^2/2}$$

$$\sigma = \frac{Zr}{a_0}$$
No. of radial nodes = n - l - 1

volume: 
V = 4πr^3/3

incremental volume: 
dV = 4πr^2dr

weighted radial probability: 
R^2dV = 4πr^2R^2dr
Angular component: $Y$

No. of angular nodes = $l$

$l=0$  
$s$ orbital:  
$Y_{00} = \frac{1}{2\sqrt{\pi}}$

No angular dependence
Gerade (g): even with respect to inversion

Allowed  $m_i = 0$
Only one spatial orientation for a sphere
0 angular node

$l=1$  
$p$ orbital

$Y_{10} = \frac{\sqrt{3}}{2\sqrt{\pi}} \cos \theta$

Ungerade (u) : odd with respect to inversion

Allowed  $m_i = 0, \pm 1$
Three spatial orientations.
1 angular node

In cartesian coordinates
**l=2  d orbital**

\[ Y_{20} = \frac{\sqrt{30}}{2\sqrt{2}\pi} \cos \theta \sin \theta \cos \phi \]

Gerade (g)

Allowed \( m_l = 0, \pm 1, \pm 2 \)

Five spatial orientations.

2 angular nodes

\[
\frac{1}{4\sqrt{\pi}} \frac{15}{r^2} \frac{xz}{r^2}
\]

**Contour diagram**

\[
\frac{1}{2\sqrt{3\pi}} \frac{z}{r}
\]

3p<sub>z</sub>

- Orbital depiction is based on \( \psi^2 \)
- With the sign of \( \psi \) indicted (very important for bonding considerations)
- List all node planes
Orbital Radial Function \( R(r) \) Angular Function \( Y(x,y,z) \) Angular Function \( Y(\theta,\phi) \)

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Radial Function</th>
<th>Angular Function</th>
<th>Angular Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2p_z )</td>
<td>( \frac{1}{2\sqrt{6}} r e^{-r/2} )</td>
<td>( \frac{\sqrt{3}(x/r)}{2\sqrt{\pi}} )</td>
<td>( \frac{\sqrt{3}\cos\theta}{2\sqrt{\pi}} )</td>
</tr>
</tbody>
</table>

\[
\frac{1}{4} \sqrt{\frac{5}{\pi}} \frac{2z^2 - x^2 - y^2}{r^2}
\]
### Orbital Functions

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Radial Function $R(r)$</th>
<th>Angular Function $Y(x,y,z)$</th>
<th>Angular Function $Y(\theta,\phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3p_z$</td>
<td>$\frac{4}{81\sqrt{6}}(r^2 - 6r)e^{-r^3}$</td>
<td>$\frac{\sqrt{3}(x/r)}{2\sqrt{\pi}}$</td>
<td>$\frac{\sqrt{3} \cos \theta}{2\sqrt{\pi}}$</td>
</tr>
</tbody>
</table>

For hydrogen, $r$ with unit of $a_0$

For multiple electron systems, replace $r$ with $\sigma$,

$$\sigma = Zr / a_o$$

### Additional Orbital Functions

<table>
<thead>
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<th>Orbital</th>
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<th>Angular Function $Y(x,y,z)$</th>
<th>Angular Function $Y(\theta,\phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d_z^2$</td>
<td>$\frac{4}{81\sqrt{30}} r^2 e^{-r^3}$</td>
<td>$\frac{\sqrt{5}(3z^2 - r^2)}{4\sqrt{\pi}}$</td>
<td>$\frac{\sqrt{5}(3\cos^2 \theta - 1)}{4\sqrt{\pi}}$</td>
</tr>
</tbody>
</table>
All atomic orbitals (on same atom) are mutually orthogonal.

\[ \int \psi_1 \psi_2 dV = 0 \]

**Multielectron Atoms**

Orbital energies for hydrogen atom: 1s < 2s = 2p < 3s = 3p = 3d, etc....

Multielectron atom: three-body-problem; can’t solve exactly 1s < 2s < 2p < 3s < 3p etc....

1 electron approximation: borrow solutions to hydrogen atom; have to take into account shielding effects, electron-electron repulsion, spin correlation.

**Penetration and Shielding**

Radial distribution function

Distance from nucleus
1 electron system: Hydrogen

How about many-electron system?

1 electron with nuclear charge Z

Increasing electrostatic interaction
Orbital contract
Orbital energy drops

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

\[ E_n = -\frac{Z^2 \times 13.6\, eV}{n^2} \]

Example: For He\(^+\), Z=2, \( E_1 = -54.4 \, eV \)

For multi-electron atoms, Schrodinger equation can be set up, but cannot be solved exactly. *Use approximation.*

Build many-electron system:

1. **Pauli exclusion principle:**
   No two electrons in an atom can have the same set of four quantum numbers (\( n, l, m_l, m_s \))

\( m_s \): spin quantum number
Quantized, +1/2 or −1/2

Each atomic orbital can contain at most two electrons.
Aufbau principle: electron fill the atomic orbitals from the lowest energy up.

Dependence of orbital energies on $Z$

Useful guideline for placement of valence electrons:
$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 5s < 5p < 5d < 6s < 6p < 6d < 7s < 7p < 5f$
Example:

He: 1,0,0, ½ & 1,0,0, -1/2  \rightarrow  1s^2

Li: 1,0,0, ½; 1,0,0,-1/2; 2,0,0, ½  \rightarrow  1s^2 2s^1

Al: 13 electrons

\begin{align*}
1s^2 2s^2 2p^6 3s^2 3p^1 &= [Ne]3s^2 3p^1 \\
\end{align*}

Core electron  Valence electron

Recall in Hydrogen:

\[ E_n = -\frac{e^2}{2r_n} = -\frac{2\pi^2 m_e e^4}{n^2 \hbar^2} = -\frac{k}{n^2} \]

E(2s)=E(2p)

Why are they different in multi electron system?

Electron-electron repulsion

\[ + \quad \text{He} = \text{He} + \text{e} \]

First electron:

\[ E_n = -\frac{Z^2 \times 13.6eV}{n^2} \]

Second electron??
Ionization Energy (IE): energy required to remove an electron from the gaseous atom.

IE(He) = 24.6 eV

\[ E_1(He^+) = -54.4 eV \]

Each electron feels +2 nucleus and 1 electron.

In a many-electron atom, each electron is simultaneously:
- attracted to the protons in the nucleus
- repelled by other electrons (like-charge repulsion)

The net positive charge attracting the electron is called the effective nuclear charge

For He:

\[ Z_{\text{eff}} = 1.34 \]

\[ E = -\frac{Z_{\text{eff}}^2}{n^2} \times 13.6 eV \]

= -24.4 eV

IE(He) = 24.6 eV

Now, Li?
2s orbital penetrates the inner 1s electron shell better than 2p.

2s electron feel a greater effective nuclear charge $\Rightarrow$ lower $E$ for 2s

$$Z_{\text{eff}} (2s^1) > Z_{\text{eff}} (2p^1) \quad \Rightarrow \quad E(2s) < E(2p)$$

Ground State: $1s^2 2s^1$
For $Z > 1$:

$E(\text{ns}) < E(\text{np}) < E(\text{nd}) < E(\text{nf})$ for given $n$

$Z_{\text{eff}}$: \hspace{1cm} \rightarrow \text{low}$

Penetrating ability: \hspace{1cm} \rightarrow \text{poor}$

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

Shielding constant

---

**Slater's Rules:**

1) Write the electron configuration for the atom using the following design;

$$(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)$$

2) Any electrons to the right of the electron of interest contributes no shielding.

3) All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units.

4) **If the electron of interest is an $s$ or $p$ electron:** All electrons with one less value of the principal quantum number (n-1 shell) shield to an extent of 0.85 units of nuclear charge. All electrons with two less values of the principal quantum number (n-2 shell) shield to an extent of 1.00 units.

5) **If the electron of interest is an $d$ or $f$ electron:** All electrons to the left shield to an extent of 1.00 units of nuclear charge.

6) Sum the shielding amounts from steps 2 through 5 and subtract from the nuclear charge value to obtain the effective nuclear charge.
Example:

O:  \[ 1s^2 2s^2 2p^4 \]

\[ \sigma_{2p} = 2(0.85) + 5(0.35) = 4.55 \]

\[ Z_{\text{eff}} = Z - \sigma = 8 - 4.55 = 3.45 \]