First discuss the handout:

- Look at trends in the shape of $R_{nl}(r)$
- Look at graphs of probability density

\[|\psi(r, \theta, \phi)|^2 \, dV,\] where $dV$ is a small volume, tells us the probability of finding an electron in the volume $dV$ centered at $r, \theta, \phi$.

$|\psi(r, \theta, \phi)|^2$ by itself is called "probability density".

- Calculate probability that $e^-$ is in a shell of radius $r$, thickness $dr$

\[
\text{Prob} = \int_0^\pi \int_0^{2\pi} |\psi(r, \theta, \phi)|^2 \, r^2 \sin \theta \, d\theta \, d\phi \, dr
\]

\[= 4\pi r^2 |R_{nl}(r)|^2 \, dr
\]

(using the fact \( \int_0^\pi \int_0^{2\pi} |Y_{lm}(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi = 4\pi \))

- Comment on multi-electron atoms (see next page)
MULTIELECTRON ATOMS

Plot \( V(r) \) for the last electron entering a multielectron atom, compare to \( \frac{e^2}{4\pi \varepsilon_0 r} \).

- For large \( r \), the last electron feels a net charge \( +1e \) from the screened nucleus.
- For small \( r \), the last electron feels a net charge of \( +Ze \) from the unscreened nucleus.

Comparing wavefunctions with equal \( n \) but different \( l \), the probability density near \( r=0 \) determines how much the wavefunction is shifted down in energy.

The effect is non-linear with \( r \); ... prob density at smaller \( r \) is disproportionately more important. \( s \)-orbitals get the biggest downward shift.
Summary

* The properties of atomic orbitals play a central role in the properties of solids.

* There are different ways of visualizing orbitals
  - \( Y(r, \theta, \phi) \) plotted on \( r \) axis + globe
  - \( |Y(r, \theta, \phi)|^2 \) plotted on \( x-z \) plane
  - \( \frac{2\pi}{\bar{\Psi}} \) plot
    ...
    many more

Visualization of orbitals will be important in the class project.
ORTHOGONAL FUNCTIONS & BRA-KET NOTATION

What does it mean for functions to be orthogonal?

Recall the vector algebra definition:

Example 1

\( \vec{a} \) & \( \vec{b} \) are not orthogonal

\[
\vec{a} = \begin{bmatrix} 2 \\ 1 \end{bmatrix}, \quad \vec{b} = \begin{bmatrix} 1 \\ 2 \end{bmatrix}
\]

\[
\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y = 2 + 2 = 4
\]

This operation is called "dot product"

The vectors \( \vec{a} \) & \( \vec{b} \) are orthogonal if and only if \( \vec{a} \cdot \vec{b} = 0 \)

Example 2

\( \vec{a} \) & \( \vec{b} \) are orthogonal

\[
\vec{a} \cdot \vec{b} = \begin{bmatrix} 2 \\ 1 \end{bmatrix} \cdot \begin{bmatrix} -1 \\ 2 \end{bmatrix} = -2 + 2 = 0
\]
Consider much longer vectors which list the values of functions (the functions would be evaluated at discrete points)

\[
\mathbf{u} = \begin{bmatrix}
0 \\
0.1 \\
0.2 \\
0.25 \\
0.3 \\
0.25 \\
\vdots
\end{bmatrix}
\quad \text{and} \quad
\mathbf{v} = \begin{bmatrix}
0 \\
0.2 \\
0.3 \\
0.2 \\
0 \\
-0.2 \\
\vdots
\end{bmatrix}
\]

\[
\mathbf{u} \cdot \mathbf{v} = \sum_i u_i v_i
\]

where \( i \) refers to the \( i \)th component of the vector.

If the functions are evaluated at enough closely spaced points, the sum can be written as an integral

\[
\int u(x)v(x)\,dx
\]

(The index \( i \) has been replaced by the argument of the function.)

Two real-valued functions are orthogonal over the range \( x' \to x'' \) if

\[
\int_{x=x'}^{x''} u(x)v(x)\,dx = 0
\]
Two complex-valued functions are orthogonal over the range \( x' \rightarrow x'' \) if

\[
\int_{x'=x'}^{x''} u^*(x) v(x) \, dx = 0
\]

* means "complex conjugate"

A function is normalized over the range \( x' \rightarrow x'' \) if

\[
\int_{x'=x'}^{x''} u^*(x) u(x) \, dx = 1
\]

All QM wavefunctions describing single particles are normalized.

For example

\[
\int_{\text{all space}} \Psi_{n,l,m}^*(r,\theta,\phi) \Psi_{n',l',m'}(r,\theta,\phi) \, dV = 1
\]

Not only are the H atom wavefunctions normalized, they are orthogonal to one another. They form an "orthonormal set".
It is a remarkable property of diff. eqns such as the S. Eqn that the solutions are guaranteed to form an orthonormal set.

Example of orthogonal fns

\[ \sin \theta \quad \text{---} \quad \sin 2\theta \]

\[ \int_{0}^{2\pi} \sin \theta \sin 2\theta \, d\theta = 0 \quad \text{(The sin)} \]

In QM, we often need to evaluate the "dot product" of two quantum wavefunctions. It is cumbersome to always write

\[ \int_{\text{all space}} y_{n_1, l_1, m_1} \ast y_{n_2, l_2, m_2} \, dV \]

\[ \langle n_1 l_1 m_1 | n_2 l_2 m_2 \rangle \text{ is not a function, it is a single number.} \]
\[ \int_{\text{all space}} 4_n^* 4_{n', l', m'} \, dV = \langle n', l', m' | n, l, m \rangle \]

Notes:

\[ \langle n', l', m' | \] is called a "bra" with \[ 4_n^* \]
\[ | n, l, m \rangle \] is called a "ket" and can be interchanged with \[ 4_n \]

Whenever a bra comes from left and meets a ket coming from the right, they invoke the dot product operation

\[ \langle n', l', m' | \begin{array}{c} n, l, m \end{array} \]

Proof!

Zero or one

The outcome of the dot product operation is a single number.

i.e. \[ \langle n' l' m' | n l m \rangle \] is not a function, it is a single number.
Since the ket $|n, l, m\rangle$ is interchangeable with $\psi_{nlm}(r, \theta, \phi)$, we can rewrite the S. Eqn using bra-ket notation

$$\frac{\hat{A}^2}{2m} + V(\hat{r}) \psi(\hat{r}) = E \psi(\hat{r})$$

$\hat{H}$ is called the Hamiltonian operator.

Once again, bra-ket notation is more concise (less ink) than other choices.

**LINEAR COMBINATIONS OF ATOMIC ORBITALS (LCAOs)**

Now that we've streamlined the notation, it's easy to introduce LCAOs.

Consider any LCAO wave function $\frac{1}{\sqrt{2}}(|2,1,1\rangle + |2,1,-1\rangle)$

*This is a linear combination of degenerate orbitals

We know that $\hat{H} |2,1,1\rangle = E_z |2,1,1\rangle$

and $\hat{H} |2,1,-1\rangle = E_z |2,1,-1\rangle$

Therefore $\hat{H} \left[ \frac{1}{\sqrt{2}} \left( |2,1,1\rangle + |2,1,-1\rangle \right) \right] = E_z \left[ \frac{1}{\sqrt{2}} \left( |2,1,1\rangle + |2,1,-1\rangle \right) \right]$
Key point: There are 3 orbitals with \( n=2 \) & \( l=1 \). They all have energy \( E_2 \). Any linear combination of these orbitals will also satisfy the Schrödinger Eqn with energy \( E_2 \).

Adding together orthogonal atomic orbitals, like \( 1,2,1 \), and \( 1,2,1 \) can create new and physically relevant electron distributions.

\[
\psi_{2,1,1} = \frac{1}{\sqrt{24}} \frac{\alpha^{3/2}}{\alpha} e^{-1/2a} \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}
\]

\[
\psi_{2,1,-1} = -\frac{1}{\sqrt{24}} \frac{\alpha^{3/2}}{\alpha} e^{-1/2a} \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}
\]

\[
\psi_{2,1,1} + \psi_{2,1,-1} = \frac{1}{\sqrt{24}} \frac{\alpha^{3/2}}{\alpha} e^{-1/2a} \sqrt{\frac{3}{8\pi}} \sin \theta \left(e^{i\phi} - e^{-i\phi}\right)
\]

\[
= 2 \sin \phi
\]

Now a \( p_z \) orbital.

Maximal when \( \phi = \frac{\pi}{2} \) and \( \phi = \frac{3\pi}{2} \).