\[ \langle n \ell m_\ell | n \ell m_\ell \rangle \]
\[ \sum_i |i \rangle \langle i | = 1 \]
\[ \beta = \langle 1 | \hat{H} | 2 \rangle \]
H atom atomic orbitals form an orthonormal set

Now use “bra-ket” notation for the same thing ....

\[
\langle \ell', m_{\ell}' \mid \ell, m_{\ell} \rangle \equiv \int_{\text{all}} Y_{\ell', m_{\ell}'}^* (\theta, \phi) Y_{\ell, m_{\ell}} (\theta, \phi) d\Omega
\]

\[= \delta_{\ell \ell'} \delta_{m_{\ell} m_{\ell}'} \]

Ket: \[\mid \ell, m_{\ell} \rangle \doteq Y_{\ell, m_{\ell}} (\theta, \phi) \]

Bra = complex conjugate of ket: \[\langle \ell, m_{\ell} \mid \equiv Y_{\ell, m_{\ell}}^* (\theta, \phi) \]

\[\langle \mid \rangle \] = integrate over all space

\[\dot{\equiv} \text{ “dot equals” means “is represented by”} \]}
OPERATORS
are mathematical instructions that represent physical quantities like energy or momentum. They perform various operations on wave functions or kets, like differentiation, multiplication etc. The result of such an operation may be:
• The same function or ket, multiplied by a constant. In this case we say the function is an EIGENFUNCTION of that operator and the constant is the EIGENVALUE associated with that eigenfunction.

\[
\hat{H} \varphi(r, \theta, \phi) = E \varphi(r, \theta, \phi) \quad \hat{H} \left| \varphi_{n, l, m_l, m_s} \right> = E_{n, l, m_l, m_s} \left| \varphi_{n, l, m_l, m_s} \right>
\]

\[
-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sin(kx) = \frac{\hbar^2 k^2}{2m} \sin(kx)
\]
OPERATORS
are mathematical instructions that represent physical quantities like energy or momentum. They perform various operations on wave functions or kets, like differentiation, multiplication etc. The result of such an operation may be:

• A different function or ket (or sum of kets) multiplied by a constant. In this case we say the function is NOT an eigenfunction of that operator.

\[ \hat{p} \varphi(r) \neq p \varphi(r) \]

\[ \frac{\hbar}{i} \frac{d}{dx} \sin(kx) = \frac{\hbar k}{i} \cos(kx) \]
OPERATORS

can also be represented as matrices. In this case, the operator is just a table of projections!

\[
H = \begin{pmatrix}
\langle 1 | H | 1 \rangle & \langle 1 | H | 2 \rangle & \langle 1 | H | 3 \rangle \\
\langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle & \langle 2 | H | 3 \rangle \\
\langle 3 | H | 1 \rangle & \langle 3 | H | 2 \rangle & \langle 3 | H | 3 \rangle 
\end{pmatrix}
\]

Now IF …..

\[\hat{H} | 1 \rangle = E_1 | 1 \rangle\]
\[\hat{H} | 2 \rangle = E_2 | 2 \rangle\]
\[\hat{H} | 3 \rangle = E_1 | 3 \rangle\]
OPERATORS

can also be represented as matrices. A square matrix acts on a column vector or ket. The result of such an operation may be:

• The *same* column vector or ket, multiplied by a constant. In this case we say the function is an EIGENVECTOR of that operator and the constant is the EIGENVALUE associated with that eigenvector.

\[
\begin{pmatrix}
E_1 & 0 & 0 \\
0 & E_2 & 0 \\
0 & 0 & E_3 \\
\end{pmatrix}
\begin{pmatrix}
1 \\
0 \\
0 \\
\end{pmatrix} = E_1 \begin{pmatrix}
1 \\
0 \\
0 \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
E_1 & 0 & 0 \\
0 & E_2 & 0 \\
0 & 0 & E_3 \\
\end{pmatrix}
\begin{pmatrix}
0 \\
1 \\
0 \\
\end{pmatrix} = E_2 \begin{pmatrix}
0 \\
1 \\
0 \\
\end{pmatrix}
\]
If an **OPERATOR** acts on a ket, to produce a new ket, we can project the new ket onto some bra. Choose the kets

\[
\begin{align*}
|p_x\rangle &= \frac{1}{\sqrt{2}} \left[ |Y_{1,-1}\rangle - |Y_{1,1}\rangle \right] \\
|p_y\rangle &= \frac{i}{\sqrt{2}} \left[ |Y_{1,-1}\rangle + |Y_{1,1}\rangle \right] \\
|p_z\rangle &= |Y_{1,0}\rangle
\end{align*}
\]

These are (degenerate) eigenfunctions of the "angular-momentum-squared" operator. The states have definite angular momentum.

Now project these new kets onto the three bras. You get 9 numbers .... Organize them in a matrix
Represent the $L^2$ OPERATOR in the basis of $|p_x>, |p_y>, |p_z>$,

$$\langle p_x | \hat{L}^2 | p_z \rangle = \langle p_x | 2\hbar^2 | p_z \rangle = \langle p_x | p_z \rangle = 0$$

$$\langle p_y | \hat{L}^2 | p_z \rangle = 0$$

$$\langle p_z | \hat{L}^2 | p_z \rangle = 2\hbar^2$$

$$\hat{L}^2 = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}$$

Sutton 2.13

$$\hat{L}^2 = \begin{pmatrix}
L^2_{11} & L^2_{12} & L^2_{13} \\
L^2_{21} & L^2_{22} & L^2_{23} \\
L^2_{31} & L^2_{32} & L^2_{33}
\end{pmatrix}$$
Represent the $L_z$ OPERATOR in the basis of $|p_x>$, $|p_y>$, $|p_z>$,

$$\langle p_x | \hat{L}_z | p_z \rangle = \langle p_x | 0 \hbar | p_z \rangle = 0$$

$$\hat{L}_z | p_x \rangle = \frac{\hbar}{\sqrt{2}} \left[ -|Y_{1,-1}\rangle - |Y_{1,1}\rangle \right] = i\hbar | p_y \rangle$$

$$\hat{L}_z | p_y \rangle = \frac{i\hbar}{\sqrt{2}} \left[ -|Y_{1,-1}\rangle + |Y_{1,1}\rangle \right] = -i\hbar | p_x \rangle$$

$$\hat{L}_z = \hbar \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
Multi-electron Atoms

Much more complicated: e-p; e-e interactions change Schrödinger equation. We don't need to worry too much about all of this.

\[ \hat{H} \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2) \]

6 coordinates, not 3 (plus spin)

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \]
Multi-electron Atoms

- Much more complicated: e-p; e-e interactions change Schrödinger equation
- Radial wave functions change, but angular character is very similar to H atom wave functions
- Still makes sense to talk about s, p, d, f orbitals
- Energy levels no longer degenerate w.r.t. n
- Leads to consistent picture of elements - periodic table - with ns, np, etc orbitals filled with 2 electrons each (spin) in accordance with Pauli exclusion principle and Hund’s rules.

Sutton Table 1.2 for electronic configuration.
Multi-electron atoms - some $n$-degeneracy is lifted

(a) Hydrogen
Multi-electron Atoms

http://www.vcs.ethz.ch/chemglobe/ptoe/
## Multi-electron Atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>Name of element</th>
<th>Atomic number</th>
<th>1s</th>
<th>2s</th>
<th>2p_x</th>
<th>2p_y</th>
<th>2p_z</th>
<th>3s</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Hydrogen</td>
<td>1</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>Helium</td>
<td>2</td>
<td>↑↓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>Lithium</td>
<td>3</td>
<td>↑↓</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>Beryllium</td>
<td>4</td>
<td>↑↓</td>
<td>↑↓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
<td>5</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
<td>6</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
<td>7</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
<td>8</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Fluorine</td>
<td>9</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>Neon</td>
<td>10</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
<td>11</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑</td>
</tr>
</tbody>
</table>

http://wps.prenhall.com