Chemistry 1000 Lecture 7: Hydrogenic orbitals

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Heisenberg uncertainty principle

Fundamental limitation to simultaneous measurements of position and momentum:

\[ \Delta x \Delta p_x \geq \frac{1}{2} \hbar \]

with \( \hbar = \frac{h}{2\pi} \).

- Uncertainty is, roughly, the experimental precision of the measurement.
- Position and momentum can’t simultaneously both be known to arbitrary accuracy.
Suppose that we want to locate an object in a microscope.

- Photons reflect (or refract) from the sample.
- Photons have momentum so they give the object a “kick” (i.e. change the momentum) during interaction with an object.

\[
\begin{align*}
\text{Resolution } \Delta x & \sim \lambda \\
\text{Kick } \Delta p_x & \sim \frac{h}{\lambda}
\end{align*}
\] 

\[\Delta x \Delta p_x \sim h > \frac{h}{4\pi}\]
Example: Suppose that we use X-rays to determine the position of an electron to within $10^{-10}$ m (diameter of a hydrogen atom). Since $\Delta x \Delta p_x \geq \frac{1}{2}\hbar$, we have

$$\Delta p_x \geq \frac{\hbar}{2 \Delta x} = 5 \times 10^{-25} \text{ kg m s}^{-1},$$

or

$$\Delta v \geq \frac{\Delta p_x}{m_e} = 6 \times 10^5 \text{ m/s}.$$
Important consequence:

- Bohr theory has orbits of fixed $r$, i.e. $\Delta r = 0$.
- The radial momentum component would then have to have infinite uncertainty.
  $$(\Delta p_r = \frac{\hbar}{2\Delta r})$$
- Infinite uncertainty in momentum not possible (sorry, Douglas Adams)
- $\therefore$ Bohr orbits not possible
Wavefunctions in modern quantum mechanics

- Quantum systems are described by a wavefunction $\psi$.
- Square of wavefunction $= \text{probability density}$
  \[ \psi^2 \, dV = \text{probability of finding the particle in a small volume } dV. \]

**Orbital:** one-electron wavefunction
Hydrogenic orbitals

- Depend on three quantum numbers
  - \( n \): principal quantum number
    - Total energy of atom depends on \( n \) (as in Bohr theory):
      \[
      E_n = -\frac{Z^2}{n^2} R_H
      \]
  - \( \ell \): orbital angular momentum quantum number
    - Size of orbital angular momentum vector (\( L \)) depends on \( \ell \):
      \[
      L^2 = \ell(\ell + 1)\hbar^2
      \]
    - \( m_\ell \): magnetic quantum number
      - \( z \) component of \( L \) depends on \( m_\ell \):
        \[
        L_z = m_\ell \hbar
        \]
Rules for hydrogenic quantum numbers

- $n$ is a positive integer (1, 2, 3, ...)
- $\ell$ can only take values between 0 and $n - 1$
  
  \[
  \begin{array}{c|ccccccc}
  \ell & 0 & 1 & 2 & 3 & 4 & 5 & \ldots \\
  \text{code} & s & p & d & f & g & h & \ldots \\
  \end{array}
  \]
- $m_{\ell}$ can only take values between $-\ell$ and $\ell$

The orbitals are therefore the following:

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>subshell</th>
<th>$m_{\ell}$</th>
<th>number of orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1s</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2s</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2p</td>
<td>−1, 0 or 1</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3s</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3p</td>
<td>−1, 0 or 1</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3d</td>
<td>−2, −1, 0, 1 or 2</td>
<td>5</td>
</tr>
</tbody>
</table>

...
Degeneracy

- All orbitals corresponding to the same value of $n$ have the same energy.
  Different orbitals with the same energy are said to be degenerate.
- Example: The $2s$, $2p_{-1}$, $2p_0$ and $2p_1$ orbitals all correspond to $n = 2$ and are degenerate in hydrogenic atoms.
- The degeneracy between orbitals can be lifted by external fields.
  Example: A magnetic field removes the degeneracy between orbitals with different values of $m_\ell$ (Zeeman effect).
The orbitals corresponding to the quantum numbers \((n, \ell, m_\ell)\) are complex-valued, i.e. they involve \(i = \sqrt{-1}\).

In many cases, there is no distinguished \(z\) axis, and therefore no particular meaning to the quantum number \(m_\ell\).

We can replace the original set of orbitals with ones corresponding to the same values of \(n\) and \(\ell\) (so same energy and angular momentum size), but that don’t correspond to any particular value of \(m_\ell\), and that are real-valued.
Electron density maps

\( n = 1 \)
Electron density maps

\( n = 2, \ell = 0 \)
Electron density maps

\( n = 2, \ell = 1 \)
Electron density maps

$n = 3, \ell = 0$
Electron density maps

$n = 3, \ell = 1$
Electron density maps

\( n = 3, \ell = 2 \)
Wavefunctions have a phase

- The wavefunction has a phase, i.e. a sign.

- The sign changes at nodal surfaces.

- Diagrammatically, we represent the phase using color.
Hydrogenic orbital illustrations

1s orbital
Hydrogenic orbital illustrations

2s orbital
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$2p_z$ orbital
Hydrogenic orbital illustrations

3s orbital
Hydrogenic orbital illustrations

$3p_z$ orbital
Hydrogenic orbital illustrations

$3d_{x^2-y^2}$ orbital
Hydrogenic orbital illustrations

$3d_{z^2}$ orbital