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 $\hbar = \dfrac{h}{2\pi}$.

- Uncertainty is, roughly, the experimental precision of the measurement.
- Position and momentum can't simultaneously both be known to arbitrary accuracy.

Why not?

- 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.
  - $$\left.\begin{array}{l}\text{Resolution } \Delta x \sim \lambda \\ \text{Kick } \Delta p_x \sim h/\lambda\end{array}\right\} \Delta x \Delta p_x \sim h > \frac{h}{4\pi}$$

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

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

or

$$\Delta v \geq \frac{\Delta p_x}{m_e} = 6 \times 10^{5}\,\mathrm{m/s}.$$

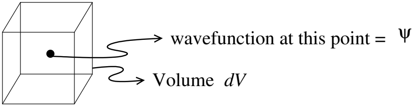
Important consequence:

- Bohr theory has orbits of fixed r, i.e. $\Delta r = 0$.
- The radial momentum component would then have to have infinite uncertainty.
  $(\Delta p_r = \dfrac{\hbar}{2\Delta r})$
- 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 ψ.
- Square of wavefunction = probability density

  $\psi^2\,dV$ = 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):

    $$E_n = -\frac{Z^2}{n^2} R_H$$

  ℓ: orbital angular momentum quantum number

  - Size of orbital angular momentum vector (L) depends on ℓ:

    $$L^2 = \ell(\ell + 1)\hbar^2$$

  m_ℓ: magnetic quantum number

  - z component of $\mathbf{L}$ depends on m_ℓ:

    $$L_z = m_\ell \hbar$$

Rules for hydrogenic quantum numbers

- n is a positive integer (1,2,3,...)
- ℓ can only take values between 0 and $n-1$

ℓ	0	1	2	3	4	5	...
code	s	p	d	f	g	h	...

- m_ℓ can only take values between $-\ell$ and ℓ

The orbitals are therefore the following:

n	ℓ	subshell	m_ℓ	number of orbitals
1	0	1s	0	1
2	0	2s	0	1
2	1	2p	-1, 0 or 1	3
3	0	3s	0	1
3	1	3p	-1, 0 or 1	3
3	2	3d	-2, -1, 0, 1 or 2	5
⋮				

Degeneracy

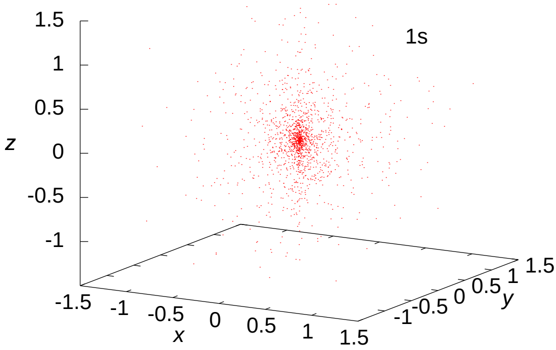
- All orbitals corresponding to the same value of n have the same energy.
  Different orbitals with the same energy are said to be degenerate.
- Example: The 2s, $2p_{-1}$, $2p_0$ and $2p_1$ orbitals all correspond to $n = 2$ and are degenerate in hydrogenic atoms.
- The degeneracy between orbitals can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

Real-valued orbitals

- The orbitals corresponding to the quantum numbers (n, ℓ, m_ℓ) 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_ℓ.
- We can replace the original set of orbitals with ones corresponding to the same values of n and ℓ (so same energy and angular momentum size), but that don't correspond to any particular value of m_ℓ, and that are real-valued.

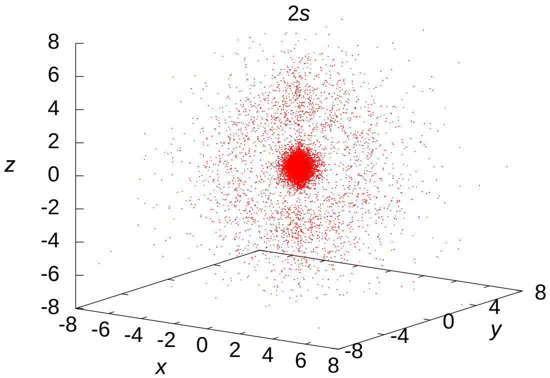
Electron density maps

$n = 1$



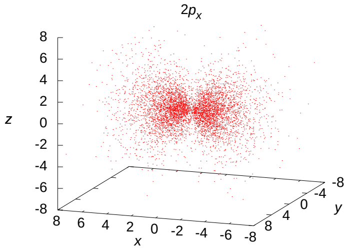
Electron density maps

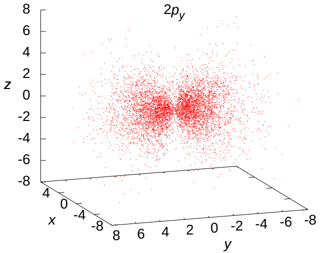
$n = 2$, $\ell = 0$

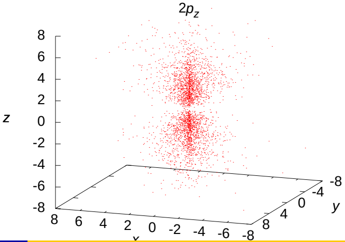


Electron density maps

$n = 2$, $\ell = 1$

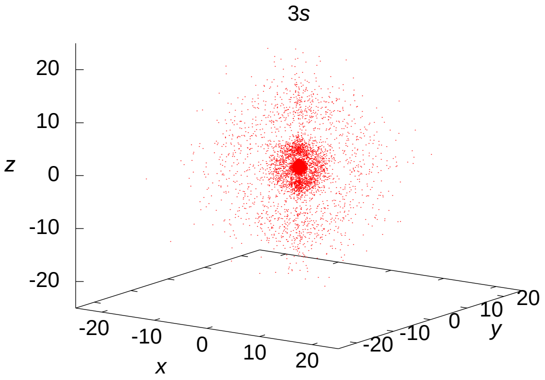






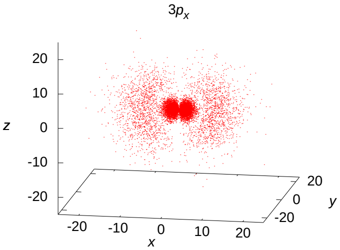
Electron density maps

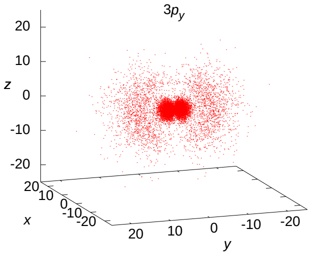
$n = 3$, $\ell = 0$

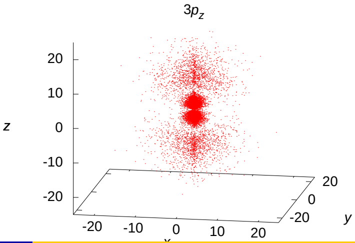


Electron density maps

$n = 3$, $\ell = 1$

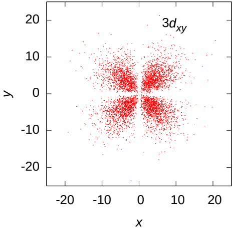


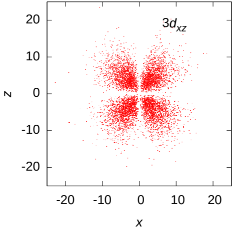


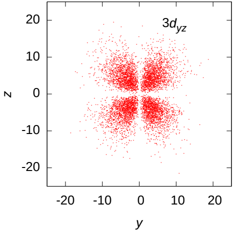


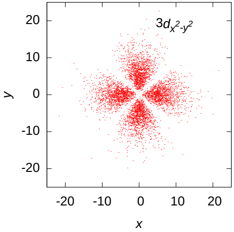
Electron density maps

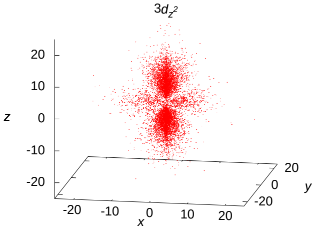
$n = 3$, $\ell = 2$









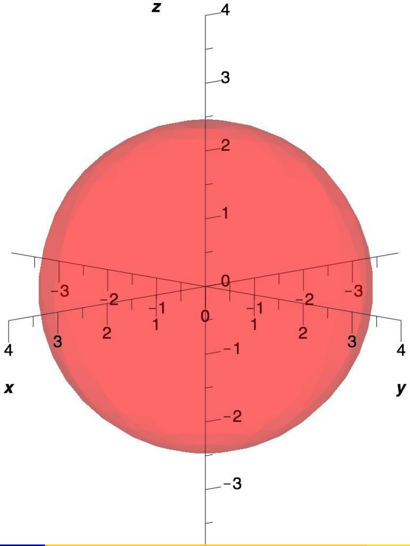


Wavefunctions have a phase

- The wavefunction has a phase, i.e. a sign.
- The sign changes at nodal surfaces.
- Diagrammatically, we represent the phase using color.

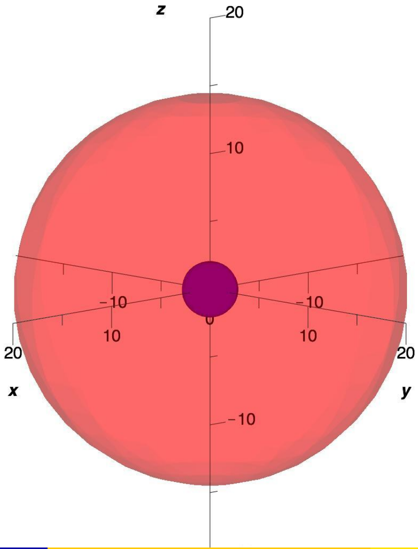
Hydrogenic orbital illustrations

1s orbital



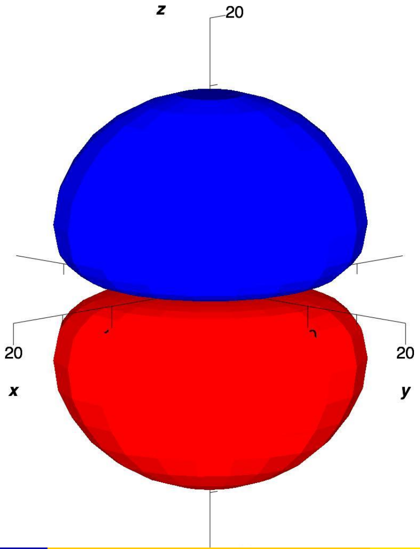
Hydrogenic orbital illustrations

2*s* orbital



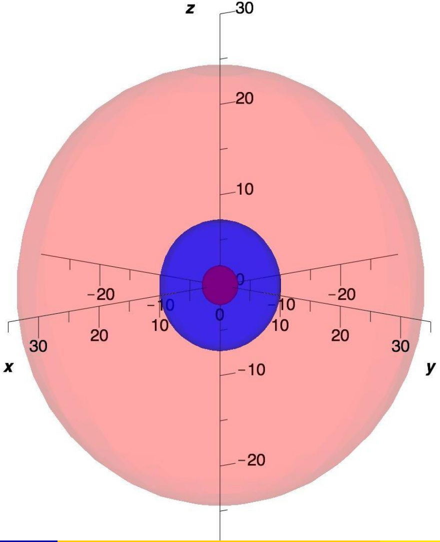
Hydrogenic orbital illustrations

$2p_z$ orbital



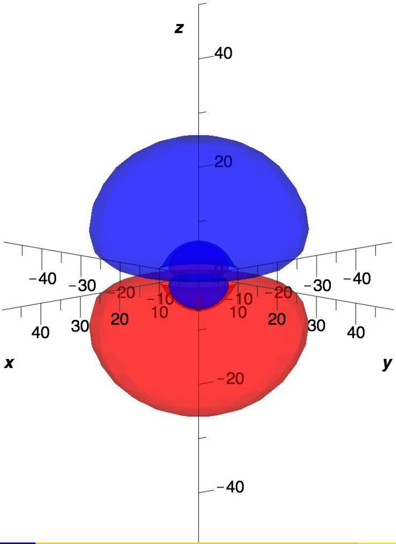
Hydrogenic orbital illustrations

3*s* orbital



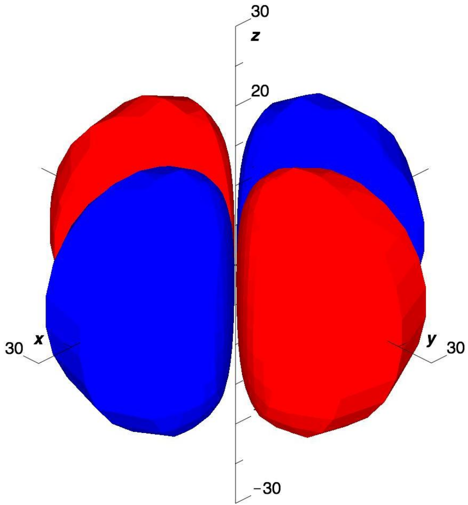
Hydrogenic orbital illustrations

$3p_z$ orbital



Hydrogenic orbital illustrations

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



Hydrogenic orbital illustrations

$3d_{z^2}$ orbital