Multi-electron atoms

Today:
Using hydrogen as a model.
The Periodic Table

HWK 13 available online.

Please fill out the online participation survey. Worth 10 points on HWK 13.

Final Exam is Monday, Dec. 15 10:30A-1P HERE
Duane G1B20
n=1, 2, 3 ... = Principle Quantum Number

\[ E_n = -\frac{E_1}{n^2} \]  (for Hydrogen, same as Bohr)

l=s, p, d, f ... = Angular Momentum Quantum Number
=0, 1, 2, 3  (restricted to 0, 1, 2 ... n-1)

\[ |\vec{L}| = \sqrt{l(l + 1)} \hbar \]

m = ... -1, 0, 1.. = z-component of Angular Momentum
(restricted to -l to l)

\[ L_z = m\hbar \]

An electron in hydrogen is excited to Energy = -13.6/9 eV. How many different wave functions \( \psi_{nlm} \) in H have this energy? [graded indep. but use groups]
a. 1   b. 3   c. 6   d. 9   e. 10
An electron in hydrogen is excited to Energy = $-\frac{13.6}{9}$ eV. How many different wave functions in H have this energy?

- a. 1
- b. 3
- c. 6
- d. 9
- e. 10

**n** = Principle Quantum Number: \[ E_n = -\frac{E_1}{n^2} \quad \rightarrow \quad n=3 \]

\[ l = \text{(restricted to 0, 1, 2 ... n-1)} \quad \rightarrow \quad l=0,1,2 \]

\[ m = \text{(restricted to } -l \text{ to } l) \]

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m</th>
<th>3s states</th>
<th>3p states ((l=1))</th>
<th>3d states ((l=2))</th>
</tr>
</thead>
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<td>{3s states}</td>
<td>{3p states ((l=1))}</td>
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<td>{3d states ((l=2))}</td>
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</table>

Answer is d: 9 states all with the same energy

Isn’t this cool…

Chemists had already figured out rules for how many electrons could be in each shell. Didn’t know why. Solving Schrödinger equation explains WHY!
Energy Diagram for Hydrogen

In HYDROGEN, energy only depends on $n$, not $l$ and $m$.

(NOT true for multi-electron atoms!)
What is the magnitude of the angular momentum of the ground state of Hydrogen?

a. 0  

b. $\hbar$  

c. $\sqrt{2}\hbar$  

d. not enough information

Answer is a.

n=1 so  $l=0$ and $m=0$ ... Angular momentum is 0 ...
Schrodinger finds quantization of energy and angular momentum:

\[ n=1, 2, 3 \ldots \quad l=0, 1, 2, 3 \text{ (restricted to } 0, 1, 2 \ldots n-1) \]

\[ E_n = -\frac{E_1}{n^2} \quad |\vec{L}| = \sqrt{l(l+1)} \, \hbar \]

How does Schrodinger compare to what Bohr thought?

I. The energy of the ground state solution is **same**

II. The angular momentum of the ground state solution is **different**

III. The location of the electron is **different**

a. same, same, same
b. same, same, different
c. same, different, different
d. different, same, different
e. different, different, different

Bohr got energy right, but he said angular momentum \( L=nh \), and thought the electron was a point particle orbiting around nucleus.
Schroedinger solved S’s equation for hydrogen:
  wave functions, energies, angular momentum

In atom with **multiple electrons**, what do you expect to change in the way you set up the problem? and in the solutions?

Student Ideas:

A. Electron shielding
B. Need to know position of each electron
C. Pauli!
D. Time in V??
E. Boundary conditions? On each electron.
F. Multiple equations??
G. Spin?? Pauli too??
A brief review of chemistry

Electron configuration in atoms:
How do the electrons fit into the available orbitals?
What are energies of orbitals?

1s
2s
2p
3s
3p
3d

Total Energy

3d ___ ___ ___ ___ ___ ___
A brief review of chemistry

Electron configuration in atoms:
  How do the electrons fit into the available orbitals?
  What are energies of orbitals?

Filling orbitals ... lowest to highest energy, 2 e's per orbital

H
He
Li
Be
B
C
N
O

Total Energy

Oxygen = 1s\(^2\) 2s\(^2\) 2p\(^4\)

3d __ __ __ __ __ __

3p __ __ __

3s __ __

2p ee e e e

2s ee

1s ee

Shell not full – reactive
Shell full – stable
Will the 1s orbital be at the same energy level for each atom? Why or why not? What would change in Schrödinger's equation?

No. Change number of protons … Change potential energy in Schrödinger’s equation … 1s held tighter if more protons.

The energy of the orbitals depends on the atom.
A brief review of chemistry

Electron configuration in atoms:
How do the electrons fit into the available orbitals?
What are energies of orbitals?

1, 2, 3 … principle quantum number, tells you *some* about energy
s, p, d … tells you *some* about geometric configuration of orbital

Shell 1

Shell 2
Can Schrödinger make sense of the periodic table?

Schrödinger’s solution for multi-electron atoms

Need to account for all the interactions among the electrons
Must solve for all electrons at once! (use matrices)

\[ V \text{ (for } q_1) = k q_{\text{nucleus}} \frac{q_1}{r_{n-1}} + k q_2 \frac{q_1}{r_{2-1}} + k q_3 \frac{q_1}{r_{3-1}} + \ldots \]
Schrodinger’s solution for multi-electron atoms

What’s different for these cases?
Potential energy (V) changes!
(Now more protons AND other electrons)

\[
V \text{ (for } q_1) = k q_{\text{nucleus}} q_1/r_{n-1} + k q_2 q_1/r_{2-1} + k q_3 q_1/r_{3-1} + \ldots.
\]

Need to account for all the interactions among the electrons
Must solve for all electrons at once! (use matrices)

Gets very difficult to solve ... huge computer programs!

Solutions change:
- wave functions change
  higher \( Z \rightarrow \) more protons \( \rightarrow \) electrons in 1s more strongly bound \( \rightarrow \) radial distribution quite different
  general shape (p-orbital, s-orbital) similar but not same
- energy of wave functions affected by \( Z \) (# of protons)
  higher \( Z \rightarrow \) more protons \( \rightarrow \) electrons in 1s more strongly bound (more negative total energy)
For a given atom, Schrödinger predicts allowed wave functions and energies of these wave functions. SIMILAR STRUCTURE:

Why would behavior of Li be similar to Na?

a. because shape of outer most electron is similar.
b. because energy of outer most electron is similar.
c. both a and b
d. some other reason
In case of Na, what will energy of outermost electron be and why?

a. much more negative than for the outermost electron in Li
b. similar to the energy of the outermost electron in Li
c. much less negative than for the outermost electron in Li
In case of Na, what will energy of outermost electron be and WHY?

b. very similar to the energy of the outermost electron in Li AND somewhat (within a factor of 3) of the ground state of H

**Wave functions for sodium**

**What affects total energy of outermost electron?**

1. The effective charge (force) it feels towards center of atom.
2. It’s distance from the nucleus.

**What effective charge does 3s electron feel pulling it towards the nucleus?**

Close to 1 proton… 10 electrons closer in shield (cancel) a lot of the nuclear charge.

**What about distance?**

**In H**, 3s level is on average 9x further than 1s, so 9*Bohr radius.

**In Na**, 11 protons pull 1s, 2s, 2p closer to nucleus distance of 3s not as far out.

Electron in 3s is a bit further than 1s in H, but ~same as 2s in Li. Proximity of electrons in 1s, 2s, 2p is what makes 3s a bit bigger.

In case of Na, what will energy of outermost electron be and WHY?
Schrodinger predicts wave functions and energies of these wave functions.

Why would behavior of Li be similar to Na?

a. because shape of outer most electron is similar.
b. because energy of outer most electron is similar.
c. both a and b
d. some other reason
Why does ionization energy increase and size decrease as you add electrons in p orbitals?
As we go from Li to N, we end up with 3 electrons in the 2p subshell (one in each orbital).

Why is ionization energy larger and size smaller than in Li?

(Develop reasoning)

P orbitals each have direction… electrons in $p_x$ do not effectively shield electrons in $p_y$ from the nucleus.

So electrons in $p$ orbitals:
1. feel larger effective positive charge
2. are held closer to nucleus.
All atoms in this row have common filling of outermost shell (valence electrons), common shapes, similar energies ... so similar behavior.
Hydrogen (1p, 1e)

n=1

1s

l=0, m=0

Energy only depends on n

n=2

2s

3s

2p

3p

n=3

3s

2s

3p

3d

l=0, l=1, l=2

Energy depends on n and l

Boron (5p, 5e’s)

NOT TO SCALE!

Energy levels (shielding)

Splitting of s and p

m=-1, 0, 1
In multi-electron atoms, energy of electron level depends on \( n \) and \( l \) quantum numbers:

- \( l = 0 \):
  - \( m = -1, 0, 1 \)
  - Orbitals: 4p

- \( l = 1 \):
  - \( m = -2, -1, 0, 1, 2 \)
  - Orbitals: 3d

- \( l = 2 \):
  - \( m = -2, -1, 0, 1, 2 \)
  - Orbitals: 4d

What is electron configuration for atom with 20 electrons? Write it out (1s\(^2\) etc… !)

a. 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^4\)
b. 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 3d\(^2\)
c. 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^2\), 3d\(^6\)
d. 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^2\)
e. none of the above

Answer is d! Calcium: Fills lowest energy levels first

Which orbitals are occupied effects: chemical behavior (bonding, reactivity, etc.)
In multi-electron atoms, energy of electron level depends on \( n \) and \( l \) quantum numbers:

\[
\begin{align*}
 l &= 0 \\
 m &= -1, 0, 1 \\
 l &= 1 \\
 m &= -2, -1, 0, 1, 2 \\
 l &= 2 \\
 m &= -2, -1, 0, 1, 2
\end{align*}
\]

Calcium has 3 complete shells.

Incomplete shell: Chemical behavior & bonding determined by electrons in outer most shell (furthest from the nucleus).
Electronic structure of atom determines its form (metal, semi-metal, non-metal):
- related to electrons in outermost shell
- how these atoms bond to each other

Semiconductors
How does Schrodinger model of atom compare with other models? Why is it better?

• Bohr model:
  – Gives correct energies.
  – Postulates fixed energy levels.
  – Doesn’t explain WHY energy levels fixed.
  – Describes electron as point particle moving in circle.

• deBroglie model:
  – Also gives correct energies.
  – Explains fixed energy levels by postulating electron is standing wave, not orbiting particle.
  – Only looks at wave around a ring: basically 1D, not 3D
  – Gets angular momentum wrong.
  – Can’t generalize to multi-electron atoms.
How does Schrodinger model of atom compare with other models? Why is it better?

- Schrodinger model:
  - Gives correct energies.
  - Gives correct angular momentum.
  - Describes electron as 3D wave of probability.
  - Quantized energy levels result from boundary conditions.
  - Schrodinger equation can generalize to multi-electron atoms.
Why is each model useful?

• Bohr – useful for thinking about energy levels, predicting spectral lines.
• deBroglie – useful for giving simple model of how wave properties lead to quantization.
• Schrodinger – useful for describing how atoms interact, shells, chemistry, atoms with more than one electron.