Multielectron atoms, Pauli Exclusion Principle, and the Periodic Table

• Final is on Mon. Dec. 16 from 7:30pm-10:00pm in this room.
• Homework Set #12 due next Wed.
• Rest of the semester:
  – Today we will cover multielectron atoms, the Pauli Exclusion Principle and figure out the Periodic table.

Wolfgang Pauli
1900 – 1958
Did you know that minus 40 degrees is the same regardless of the scale used?

Yep, 40 below is 40 below in both Celsius and Fahrenheit.

But …., mercury freezes at minus 38 degrees Celsius. So if it gets really cold, your old-fashioned mercury thermometer will stop at minus 38 degrees.
Record lows don't cause colds—viruses do. Rhinovirus just happens to be more prevalent in the U.S. during the winter, largely due to migration patterns from other countries. In fact, the biggest contributor to cold-weather colds is found in the warm indoors where people (and their germs) are confined together.
Try this Experiment

When there's a huge temperature gradient between water and the outside air, when a pot of boiling water measuring 212 degrees Fahrenheit (100 C) is splashed into air measuring minus 30 F (-34 C) a surprising effect occurs. **The boiling water will instantly turn to snow, and blow away.**

Extremely cold air is very dense, with molecules spaced so closely there isn't much room left for carrying water vapor. Boiling water, on the other hand, emits vapor very readily. When the water is thrown into the air it breaks into droplets, which have even more surface area for vapor to rise off of. This presents a problem. There's more vapor being emitted than the air can hold, so the vapor "precipitates out" by clinging to microscopic particles in the air, such as sodium or calcium, and forming crystals. This is just what goes into the formation of snowflakes.
What’s the Mpemba Effect?

The Mpemba effect, named after Erasto Mpemba, is the assertion that warmer water can freeze faster than colder water.

After an invited lecture, Tanzanian student Erasto Mpemba asked the question "If you take two similar containers with equal volumes of water, one at 35 °C (95 °F) and the other at 100 °C (212 °F), and put them into a freezer, the one that started at 100 °C (212 °F) freezes first. Why?" only to be ridiculed by his classmates and his teacher.

After initial consternation, Dr. Osborne experimented on the issue back at his workplace and confirmed Mpemba's finding. They published the results together in 1969.
Mpemba Effect cont.

**Evaporation**: The evaporation of the warmer water reduces the mass of the water to be frozen.

**Frost**: The lower temperature water tends to freeze from the top, reducing further heat loss by radiation and air convection, while the warmer water tends to freeze from the bottom and sides because of water convection.

**Convection**: Reduction of water density below 39 °F tends to suppress convection currents that cool lower part of the liquid mass; the lower density of hot water would reduce this effect, perhaps sustaining more rapid initial cooling. Higher convection in the warmer water may also spread ice crystals around faster.

In 2012, the Royal Society of Chemistry offered 1000 Pounds for the best paper offering an explanation to the Mpemba effect and more than 22,000 people entered. Still being debated.

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Energy Shifts

• Have solved Schrodinger eq. (non-relativistic) using kinetic energy $= \frac{1}{2} mv^2$ and potential energy $= -kZe^2/r$.

Talked about spin-orbital correction on Wednesday, and found $\Delta E \propto \mathbf{S} \cdot \mathbf{L} \approx 10^{-4} \text{ eV}$ + shift was up or down depending on spin of the atomic electron (depends on $\ell + m$)

Another effect of comparable size is the relativistic correction for kinetic energy – with spin orbit coupling called “fine structure”

$E = T + V = \frac{p^2}{2m} + V$

$T_{\text{Rel}} = \sqrt{c^2 p^2 + m^2 c^4} - mc^2$

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Relativistic Correction

\[ T_{\text{Rel}} = \sqrt{c^2p^2 + m^2c^4} - mc^2 \]

\[ E_{\text{Rel}} = T_{\text{Rel}} + V \]

\[ E_{\text{Rel}} = mc^2 \left[ \left( 1 + \frac{p^2}{m^2c^2} \right)^{\frac{1}{2}} - 1 \right] + V \]

\[ E_{\text{Rel}} \approx mc^2 \left[ 1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} - 1 \right] + V \]

\[ E_{\text{Rel}} \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + V \]

\[ \Delta E_{\text{Rel}} = -\frac{p^4}{8m^3c^2} \]
Relativistic Correction

\[ \Delta E_{\text{Rel}} = - \frac{p^4}{8m^3c^2} = - \frac{T^2}{2mc^2} \]

\[ \Delta E_{\text{Rel}} = - \frac{T^2}{2mc^2} = - \frac{(E - V)^2}{2mc^2} = - \frac{E^2 + V^2 - 2EV}{2mc^2} \]

Now, \( E = E_n \) and \( V = -KZe^2/r \) and can expectation value

\[
< \Delta E_{\text{Rel}} >= - \frac{1}{2mc^2} \iiint \psi_{nljm}^* (E^2 + V^2 - 2EV)_{op} \psi_{nljm} r^2 \sin \theta dr d\theta d\phi
\]

\[
< \Delta E_{\text{Rel}} >= - \frac{E_n^2}{2mc^2} - \frac{k^2Z^2e^4}{2mc^2} \iiint \psi_{nljm}^* \frac{1}{r^2} \psi_{nljm} r^2 \sin \theta dr d\theta d\phi
\]

\[ - \frac{E_n kZe^2}{2mc^2} \iiint \psi_{nljm}^* \frac{1}{r} \psi_{nljm} r^2 \sin \theta dr d\theta d\phi \]

Evaluation yields

\[ \Delta E_{\text{Rel}} = - \frac{k^2Z^2 |E_n| \alpha^2}{n} \left( \frac{2}{2\ell + 1} - \frac{3}{n} \right) \]
Fine Structure Plots

3D_{5/2}  3D_{3/2}
3P_{3/2}  3D_{3/2}
3S_{1/2}  3P_{1/2}

3D_{5/2}  3D_{3/2}
3P_{3/2}  3D_{3/2}
3S_{1/2}  3P_{1/2}

2P_{3/2}  2S_{1/2}  2P_{1/2}

2P_{3/2}  2S_{1/2}  2P_{1/2}

1S_{1/2}  1S_{1/2}

unperturbed  + fine structure
Atomic wavefunctions and quantum numbers

Each atomic electron can be identified by four quantum numbers:

- \( n = 0, 1, 2, \ldots \) = principal quantum number
- \( \ell \) gives total orbital angular momentum: \( L = \sqrt{\ell(\ell + 1)}\hbar \)
- \( m \) gives z-component of orbital angular momentum: \( L_z = m\hbar \)
- \( m_s = \pm \frac{1}{2} \) gives the z-component of spin: \( S_z = m_s\hbar \)

The atom itself has angular momentum which is the vector sum of orbital and intrinsic angular momenta of the electrons. \( \vec{J} = \vec{L} + \vec{S} \)

Thus, the Stern-Gerlach experiment actually measures the z-component of the total angular momentum: \( J_z = L_z + S_z \)

Useful information for homework problem 3
Approximations for multielectron atoms

When there are multiple electrons we have to consider the effect of the electrons on each other. This is difficult to do precisely.

So we need to make approximations.

The outer electrons are screened by the inner electrons so the effective charge they feel is less than $Ze$ which we can write as $Z_{\text{eff}}e$. If one electron is well outside of the other $Z-1$ electrons it feels a charge of just $1e$ (i.e. $Z_{\text{eff}}=1$).

The innermost electrons feel nearly the full charge of $Ze$ so $Z_{\text{eff}} \approx Z$.

We can use our findings for hydrogen-like ions by replacing $Z$ with $Z_{\text{eff}}$ so the energy is

$$E_n = -Z_{\text{eff}}^2 E_R / n^2$$

and the most probable radius is

$$r_{mp} \approx n^2 a_B / Z_{\text{eff}}$$
Lithium has $Z=3$. Two electrons are in a 1s state and one electron is in a 2p state. About how many times farther out is the 2p electron compared to the 1s electrons?

A. 3
B. 4
C. 6
D. 8
E. 12

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$$r_{mp} \approx n^2 a_B / Z_{\text{eff}}$$
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A. 3
B. 4
C. 6
D. 8
E. 12

The 1s state is always closest to the nucleus and thus will feel nearly the full force of all $Z$ protons so $Z_{\text{eff}} \approx Z$. This gives a radius of $r_{1s} \approx a_B / 3$.

The 2p electron will be screened by the two 1s electrons and will only feel a net charge of 1e. So $Z_{\text{eff}} = 1$. So $r_{2s} \approx 4a_B$.

Taking the ratio we find $r_{2p}/r_{1s} = 12$.

For hydrogen and hydrogen-like ions this ratio is only $n^2 = 4$. 

$E_n = -Z_{\text{eff}}^2 E_R / n^2 \quad r_{mp} \approx n^2 a_B / Z_{\text{eff}}$
Multielectron atom energy levels

For a given principal quantum number $n$, the $\ell$ states have different radial distributions.

Since $Z_{\text{eff}}$ depends on how far out the electron is, different $\ell$ states have different energies for the same value of $n$.

The main criterion is how close the electrons get to the nucleus.

The closer the electrons get to the nucleus, the higher $Z_{\text{eff}}$ is and the lower (more negative) the energy.

$$E_n = -Z_{\text{eff}}^2 E_R / n^2$$

Higher $\ell$ electrons don’t get close to the nucleus so $Z_{\text{eff}}$ is smaller.

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Clicker question 2

Lithium has $Z=3$. Two electrons are in a 1s state and one electron is excited into the 3d state. How does the energy of this excited electron compare to the energy of the electron in a hydrogen atom which is also in the 3d state?

A. The lithium electron energy is significantly higher (less negative)  
B. The lithium electron energy is significantly lower (more negative)  
C. The lithium electron energy is about the same  
D. Impossible to tell

\[ E_n = -Z_{\text{eff}}^2 E_R / n^2 \quad r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}} \]
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\[ E_n = -Z_{\text{eff}}^2 E_R / n^2 \]
\[ r_{mp} \approx n^2 a_B / Z_{\text{eff}} \]

The outermost electron in lithium will be screened by the two 1s electrons and will only feel a net charge of 1e. So \(Z_{\text{eff}} = 1\). This is the same as for the hydrogen atom!

So in both cases, \(E_3 = -E_R / 9\)

Experimentally it is -1.513 eV for lithium and -1.512 eV for hydrogen

Related to homework problem 5

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Energy levels for multielectron atoms

For a given \( n \), as \( \ell \) increases, the energy increases (becomes less negative).

So energy depends on both \( n \) and \( \ell \) for multielectron atoms.

There are now more energy levels so the degeneracy of each level is less.

Note that the 4s state is actually below the 3d state.
Building up electron configurations

We know the hydrogen ground state is 1s.

Makes sense: electrons want to be in the lowest potential energy state.

Helium has two electrons. What are their energy states?

Both helium electrons are in the 1s state (lowest potential energy).

Lithium has three electrons. What are their energy states?

Two electrons are in the 1s state but one electron is in the 2s state!

Why aren’t all 3 electrons in the 1s state?!
Q. In 1925, Wolfgang Pauli came up with the Pauli Exclusion Principle which states ...

A. The position and momentum of a particle cannot both be precisely known.

B. No two electrons in a quantum system can occupy the same quantum state.

C. Two components of an atom’s angular momentum cannot both be precisely known.

D. Multiple bosons in a quantum system can have the same quantum numbers.

E. None of the above

As far as understanding atoms, this means that no two electrons in an atom can have the same quantum numbers.
Filling orbitals

For multielectron atoms, energy levels are specified by \( n \) and \( \ell \). A specification of \( n\ell m \) is termed the orbital.

Electrons fill the lowest energy orbitals but have to obey the Pauli Exclusion Principle so there are at most two electrons per orbital.

Hydrogen (H): \( n=1, \ell=0, m=0, m_s=\pm\frac{1}{2} \)

Total angular momentum = \( \pm\frac{1}{2} \)

Helium (He): \[
\begin{align*}
n=1, \ell=0, m=0, m_s=+\frac{1}{2} \\
n=1, \ell=0, m=0, m_s=-\frac{1}{2}
\end{align*}
\]

Total angular momentum = 0

Lithium (Li): \[
\begin{align*}
n=1, \ell=0, m=0, m_s=+\frac{1}{2} \\
n=1, \ell=0, m=0, m_s=-\frac{1}{2} \\
n=2, \ell=0, m=0, m_s=\pm\frac{1}{2}
\end{align*}
\]

Total angular momentum = \( \pm\frac{1}{2} \)
Filling orbitals

We can continue filling orbitals.

The electron configuration is given by writing the $n\ell$ value and a superscript with the number of electrons for the energy level.

Oxygen: $1s^22s^22p^4$

B C N O

Li: $1s^22s^1$  Be: $1s^22s^2$

H: $1s^1$  He: $1s^2$

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Q. What is the electron configuration for an atom with 20 electrons?

A. \(1s^22s^22p^63s^23p^4\)

B. \(1s^22s^22p^63s^23p^63d^2\)

C. \(1s^22s^22p^63s^23p^44s^23d^6\)

D. \(1s^22s^22p^63s^23p^64s^2\)

E. none of the above
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A. $1s^22s^22p^63s^23p^4$
B. $1s^22s^22p^63s^23p^63d^2$
C. $1s^22s^22p^63s^23p^64s^23d^6$
D. $1s^22s^22p^63s^23p^64s^2$
E. none of the above

To minimize energy, two electrons fill the 4s orbital before the 3d orbital.
Periodic table of the elements

Periodic table created by Dmitri Mendeleev in 1869. He grouped elements which behaved similarly. Big success was predicting new elements which were later found.
Chemical behavior is generally determined by the outer (loosely bound) electrons.

Elements in the same column have similar outer electrons and similar energies so they behave similarly.

So quantum mechanics can explain the periodic table!