Week 6 & 7: H Atom & Periodic Table Announcements

Hydrogen Atom (Solution 3)

- Use the V from Coulombic potential energy of one proton and one electron (H atom) in S.

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0 \qquad V(r) = \frac{-Zq^2}{4\pi\varepsilon_0 r}$$

- Get a separable wave function in spherical coordinates

$$\psi(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$

Quantum Numbers

- Since the wave function ψ must be well behaved, continuous, etc., there are only certain values of the quantum numbers: n,l, $m_{l,}$ and m_s which can be used
- Principal quantum number:
- Orbital angular momentum number:
- Magnetic quantum number:
- Spin

Radial Wave Function

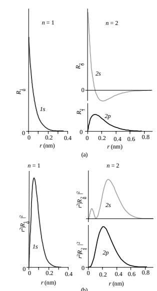

Fig. 3.21: (a) Radial wavefunctions of the electron in a hydrogenic atom for various *n* and ℓ values. (b) *r*2*Rn*,ℓ2 28

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Spherical Harmonic Wave Function

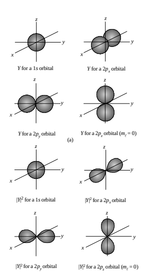

Fig. 3.22: (a) The polar plots of $Y_{n,\ell}(\theta,\phi)$ for 1*s* and 2*p* states. (b) The angular dependence of the probability distribution which is proportional to $|Y_{n,\ell}(\theta,\phi)|^2$. 29

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Orbitals

- These are **not orbits but an orbitals!**
- For **s-states**, Ψ function does not depend on r
  - R(r) is spherical symmetric and we think of s states as spherical orbitals, where the electron density is constant everywhere
  - Probability highest in a shell near
  - For example for H atom: $r=a_o=0.0529$ nm
    - This is the **1st Bohr radius** of the H atom
    - a_o is the radius of the ground state
- **P-states** have directionality: these come about in Y (angular) component

Energy Levels

- The energy of the level is determined by n

$$E_n = -\frac{mq^4 Z^2}{8\varepsilon_0^2 h^2 n^2}$$

- Now for H, where Z=1, the lowest energy state is 1s, and the energy of that state is called <u>ionization energy</u>: $E_I = \frac{mq^4}{8\varepsilon_0^2 h^2} = 13.6eV$

- For other atoms and other energy levels:

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

Energy Levels of H Atom

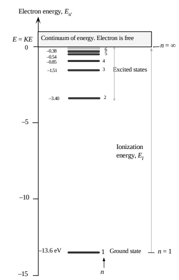

Fig. 3.23: The energy of the electron in the hydrogen atom (Z = 1). 30

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Electron in a Box

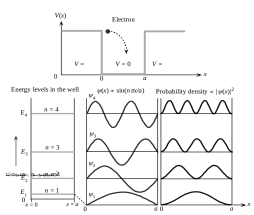

Fig. 3.15: Electron in a one-dimensional infinite PE well. The energy of the electron is quantized. Possible wavefunctions and the probability distributions for the electron are shown. 23

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Compare Energy States of H with Electron in a Box

- Unlike the electron in a box, the energy states get closer together as n increases, instead of further apart.
- Higher states have smaller (negative) energy values…Why the difference??

Absorption & Emission Spectra

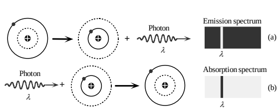

Fig. 3.24: The physical origin of (a) emission and (b) absorption spectra.

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Excitation & Emission

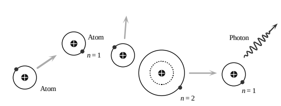

Fig. 3.25: An Atom can become excited by a collision with another atom. When it returns to its ground energy state, it emits a photon.

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Orbital Angular Momentum: l

- l and m_l: Quantize the magnitude of the orbital angular momentum (just like energy is quantized)
- Orbital angular momentum exists due to the fact that the electron is attracted to the nucleus with a certain force

$$L = \hbar[l(l+1)]^{1/2}$$

- l gives the shape of the orbitals

Orbital Angular Momentum

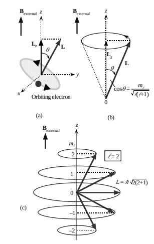

Fig. 3.26:(a) The electron has an orbital angular momentum which has a quantized component, L_z, along an external magnetic field, $\mathbf{B}_{external}$. (b) The orbital angular momentum vector **L** rotates about the *z*-axis. Its component L_z is quantized and therefore the orientation of **L**, the angle θ, is also quantized. **L** traces out a cone. (c) According to quantum mechanics, only certain orientations (θ) for **L** are allowed as determined by ℓ and m_ℓ.

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Magnetic Quantum Number: m_l

- In the presence of an external magnetic field: the orbital angular momentum becomes quantized according to m_l

$$L_z = m_l \hbar$$

Absorption/ Emission

- When an atom absorbs energy, an electron can be excited up a level
- When an electron drops down a level, energy can be emitted
- Electrons & photons must obey conservation of momentum
- If a photon is given off or absorbed, the momentum of the electron must change

Selection Rules: rules that govern allowable electron transitions

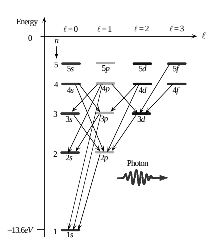

Fig. 3.27: An illustration of the allowed photon emission processes. Photon emission involves ? ℓ = ±1.

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- n must change
- $\Delta l = \pm 1$
- $\Delta m_l = 0, \pm 1$

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Spin: m_s

- Each state has two electrons
- Each electron has a "spin" ±1/2
  - "spin" is not really accurate
  - a better way to picture that our electrons have two states is to keep in mind that moving charge has a magnetic field associated with it and picture the 2 spin options as equivalent to N & S of a magnet

Spin

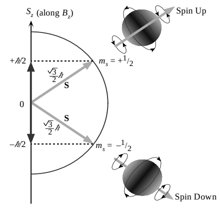

Fig. 3.28: Spin angular momentum exhibits space quantization. Its magnitude along *z* is quantized so that the angle of ***S*** to the *z*-axis is also quantized.

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Calculations with Quantum Numbers

$$L = \hbar[l(l+1)]^{1/2}$$

$$L_z = m_l \hbar$$

$$S = \hbar[s(s+1)]^{1/2}$$

$$s = \frac{1}{2}$$

$$S_z = m_s \hbar$$

Multi-electron Atoms

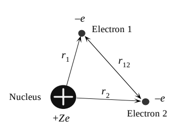

Fig. 3.32: A helium-like atom. The nucleus has a charge of +*Ze*, where for He *Z* = 2. If one electron is removed, we have the He+ ion which is equivalent to the hydrogenic atom with *Z* = 2.

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Multi-electron Atoms

- In atoms with more than one electron, there is an "effective nuclear charge": SCREENING
  - Outer electrons are far from the ion core
  - Inner electron charges can screen the positive nuclear charge
- He atoms has 2 electrons
  - V(r) now depends also on inter-electron distance
  - Where r_{12} is the distance between the 2 electrons
  - First is Coulombic attraction, the second is repulsion
- This causes the SWE to have a different set of wave functions as solutions
  - Since the "l" quantum numbers determine the orientation of the electron orbitals, the energy now depends not just on n but also on l
  - $E_{n,l}$ increases with both n and l

Energy Levels in Multi-electron Atoms

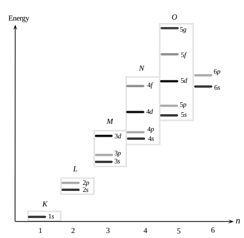

Fig. 3.33: Energy of various one-electron states. The energy depends on both n and ℓ

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Aufbang Chart

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d 6f

Use Chart for Filling Orbitals

- **Example** Fe (26)

- PEP does not tell us how electrons distribute themselves among the energy levels when there is degeneracy.
- Suppose we have 6 electrons
  - 2 x 1s states. 2 x 2s states.
  - How do the other 2 occupy the 2p states, since there is room for 6 electrons?
  - They could pair their spins and occupy only one m_l state
  - or align their spins and occupy different m_l states.

Hund's Rule:

- Observations show: electrons in same n,l subshell prefer to have spins parallel
- This is because by aligning spins, they occupy different orbitals
- If they were crammed into the same orbital with different spin states, there would be a large Coulombic repulsion because they occupy the same region of space.
- Try C(6), N(7), O(8), F(9), Ne(10)

Filling Orbitals

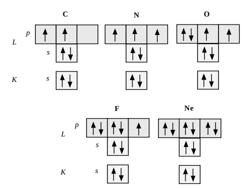

Fig. 3.36: Electronic configurations for C, N, O, F and Ne atoms. Notice that Hund's rule forces electrons to align their spins in C, N and O. The Ne atom has all the *K* and *L* orbitals full.

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