Atoms

Daniel Wysocki and Nicholas Jira

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Introduction

Neutral Atom

- atomic number Z
- nucleus has charge Ze
- surrounded by Z electrons
  - mass m
  - charge $-e$

Hamiltonian

$$H = H_{\text{nucleus}} + H_{\text{electrons}}$$

- H_{nucleus} is the total kinetic and potential energy resulting from the nucleus' electric field on the electrons
- $H_{\text{electrons}}$ is the potential energy resulting from the electrons' mutual repulsion

Hamiltonian

$$H_{\text{nucleus}} = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\varepsilon_0}\right)\frac{Ze^2}{r_j} \right\}$$

$$H_{\text{electrons}} = \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{\|\mathbf{r}_j - \mathbf{r}_k\|}$$

Hamiltonian

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\varepsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{\|\mathbf{r}_j - \mathbf{r}_k\|}$$

$$H\psi = E\psi$$

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$$

Acceptable Solutions to Schrödinger Equation

- electrons are identical fermions, so not all solutions are acceptable
  - no two electrons can occupy the same state

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_Z)$$

- $\psi \cdot \chi$ must be anti-symmetric with respect to interchange of two electrons

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Solutions to Schrödinger Equation

- only atom with a known analytic solution is $Z = 1$ (hydrogen)
- approximations must be made for heavier elements

Helium

Hamiltonian

$$H = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|}$$

- two hydrogenic Hamiltonians with charge $2e$
- electron repulsion term makes things difficult

Ignoring Repulsion

- if we ignore the difficult term, we find

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n\ell m}(\mathbf{r}_1)\psi_{n'\ell' m'}(\mathbf{r}_2)$$

$$E = 4(E_n + E_{n'})$$

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{8}{\pi a^3} \exp(-2(r_1 + r_2)/a)$$

$$E_0 = 8(-13.6\,\text{eV}) = -109\,\text{eV}$$

Helium Ground State

- neglecting electron repulsion we found $E_0 = -109\,\text{eV}$
- experimentation reveals $E_0 = -78.975\,\text{eV}$
  - evidently electron repulsion is responsible for an additional $30\,\text{eV}$ of energy

Helium Excited States

- consist of one electron in hydrogenic ground state, and the other in an excited state

$$\psi_{n\ell m}\psi_{100}$$

- if both electrons are in excited states
  - one immediately drops to the ground state
  - releases enough energy to knock the other out of the atom
  - produces helium ion (He^+)

Helium Excited States

- both symmetric and anti-symmetric spin configurations exist
- anti-symmetric spin configurations (singlet)
  - parahelium
- symmetric spin configuration (triplet)
  - orthohelium
- electrons closer together in symmetric configuration
  - parahelium states have higher energy than orthohelium counterparts

The Periodic Table

Orbitals

- n^2 unique hydrogenic position wave functions with energy E_n
  - $2n^2$ wave functions when spin ($\uparrow\downarrow$) is considered
- if rows of periodic table corresponded to # shells, they would have lengths 2, 8, 18, 32, 50, ...
  - instead they have lengths 2, 8, 8, 18, 18, ...

Orbitals

- Hydrogen: (1, 0, 0) has ↑

Orbitals

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- Helium: (1, 0, 0) has $\uparrow\downarrow$

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- Helium: $(1, 0, 0)$ has $\uparrow\downarrow$
- Lithium: $(1, 0, 0)$ full, $(2, \ell, 0)$ has $\uparrow$

Lithium Orbitals

$$(2, \ell, 0)$$

- for $n = 2$, ℓ can be 0 or 1
- in absence of electron-electron interactions, both have same energy
- in presence of of $e - e$ interactions, higher angular momentum (ℓ) tends to send particle outwards
  - lower ℓ is thus favored

$$(2, 0, 0)$$

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- Helium: (1, 0, 0) has $\uparrow\downarrow$
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- Helium: (1, 0, 0) has $\uparrow\downarrow$
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- Neon: (1, 0, 0) full, . . . (2, 1, 1) full, (2, 1, 0) full, (2, 1, -1) full

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- Boron: (1, 0, 0) full, (2, 0, 0) full, (2, 1, 0) has ↑
- ⋮
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- Sodium: (3, 0, 0) has ↑

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- Boron: (1, 0, 0) full, (2, 0, 0) full, (2, 1, 0) has ↑
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- Neon: (1, 0, 0) full, . . . (2, 1, 1) full, (2, 1, 0) full, (2, 1, -1) full
- Sodium: (3, 0, 0) has ↑
- Magnesium: (3, 0, 0) has ↑↓

Orbitals

- for the next six (aluminum through argon), $\ell = 1$
  - two for each value of m (-1, 0, $+1$)
- the next 10 *would* fill (3, 2, m), but electron-electron interactions change that
  - Potassium and Calcium fill (4, 0, 0)
  - Scandium through Zinc fill (3, 2, m)
- another jump occurs after Krypton, which fills (4, 1, m)
  - Rubidium starts to fill (5, 0, 0)

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  - "fundamental"
- the rest come alphabetically after f, skipping over j
  - h, i, k, l, ...

Nomenclature

- consider the ground state of Carbon

$$(1s)^2(2s)^2(2p)^2$$

- there are two electrons in $(1, 0, 0)$
- there are two electrons in $(2, 0, 0)$
- there are two electrons in some combination of

$$(2, 1, 1), (2, 1, 0), (2, 1, -1)$$

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- remaining two electrons in $(2p)$ state could be in singlet or triplet state
  - total spin quantum number S could be 1 or 0
- grand total $J = L + S$ could be 3, 2, 1, or 0

Hund's Rules

- methods for figuring out the totals
- result written as

$$^{2S+1}L_J$$

- ground state of Carbon is $^3P_0$

Hund's Rules

1. Consistent with the Pauli principle, the state with the highest total spin (S) will have the lowest energy.
2. For a given spin, the state with the highest total orbital angular momentum (L), consistent with overall anti-symmetrization, will have the lowest energy.
3. If a subshell (n, ℓ) is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy.

Thank You