Quantum Mechanics and Atomic Physics

Lecture 21:

Pauli Exclusion Principle and Multi-electron atoms

http://www.physics.rutgers.edu/ugrad/361

Prof. Sean Oh

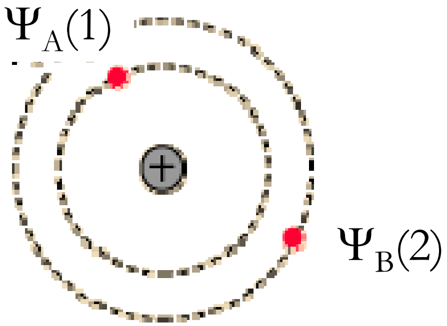
Last time

$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$: Fine structure constant

- Electron mass : mc^2 : ~0.5 MeV
- Bohr energies: of order $\alpha^2 mc^2$: ~10 eV
- Fine structure: of order $\alpha^4 mc^2$: ~10^{-4} eV
- Lamb shift: of order $\alpha^5 mc^2$: ~10^{-6} eV
- Hyperfine splitting: of order $(m/m_p)\alpha^4 mc^2$: ~10^{-6} eV

Multi-Electron Atoms

- Atoms with 2 or more electrons have a new feature:
  - **Electrons are indistinguishable!**
  - There is no way to tell them apart!
- Any measurable quantity (probability, expectation value, etc.) must not depend on which electron is labeled 1, 2, etc.



S.E. for Multi-electron atoms

- Let’s consider two electrons in Helium with coordinates:

$$(x_1, y_1, z_1) \qquad (x_2, y_2, z_2)$$

or

$$(\vec{r}_1) \qquad (\vec{r}_2)$$

- The total Hamiltonian operator for this system is

$$H_{op} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V_{TOT}$$

- So the Schrodinger equation is:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_{TOT} - \frac{\hbar^2}{2m_2}\nabla_2^2\psi_{TOT} + V_{TOT}\psi_{TOT} = E_{TOT}\psi_{TOT}$$

S.E. for Multi-electron atoms

- The total potential V_{tot} has 3 contributions:
  1. V between electron 1 and the nucleus
  2. V between electron 2 and the nucleus
  3. V between electron 1 and electron 2
- For now, let's consider only #1 and #2
- So,

$$V_{TOT} = V_1(x_1, y_1, z_1) + V_2(x_2, y_2, z_2)$$

or

$$V_{TOT} = V_1(\vec{r}_1) + V_2(\vec{r}_2)$$

- Note that the potential function is the same for both electrons

S.E. for Multi-electron atoms

$$-\frac{\hbar^2}{2m_1}\nabla^2\Psi_{TOT} - \frac{\hbar^2}{2m_2}\nabla_2^2\Psi_{TOT} + V_1\Psi_{TOT} + V_2\Psi_{TOT} = E_{TOT}\Psi_{TOT}$$

- We get the usual separation of variables

$$\Psi_{TOT} = \Psi_A(x_1,y_1,z_1)\Psi_B(x_2,y_2,z_2)$$

- Each Ψ will depend on quantum numbers

  n, ℓ, m_ℓ, m_s
- So, A and B stand for the particular sets of quantum numbers
- So, let's call $\Psi_A(1)$ eigenfunction for electron #1 and has the quantum numbers symbolized by A.

S.E. for Multi-electron atoms

- So, total eigenfunction solution is:

$$\psi_{TOT} = \psi_A(1)\,\psi_B(2)$$

- And with this separability assumption, the S.E. becomes:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_A\psi_B - \frac{\hbar^2}{2m_2}\nabla_2^2\psi_A\psi_B + V_1\psi_A\psi_B + V_2\psi_A\psi_B = E_{TOT}\psi_A\psi_B$$

$$\left\{-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_A + V_1\psi_A\right\}\psi_B + \left\{-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_B + V_2\psi_B\right\}\psi_A = E\psi_A\psi_B$$

- This equation suggests that we write the total energy E as:

$$E = E_A + E_B$$

S.E. for Multi-electron atoms

- So, we can separate this neatly into two independent expressions:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_A + V_1\psi_A = E_A\psi_A$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_B + V_2\psi_B = E_B\psi_B$$

- (This can be extended to any number of non-interacting particles!)

Exchange electrons

- So, we said that the total eigenfunction is:

$$\psi_{TOT} = \psi_A(1)\,\psi_B(2)$$

- If we exchange electrons 1 and 2 we get:

$$\psi_{TOT} = \psi_B(1)\,\psi_A(2)$$

- But the first equation gives:

$$\psi_{TOT}^{*}\,\psi_{TOT} = \psi_A^{*}(1)\,\psi_B^{*}(2)\,\psi_A(1)\,\psi_B(2)$$

- And the second (exchanged) equation gives:

$$\psi_{TOT}^{*}\,\psi_{TOT} = \psi_A^{*}(2)\,\psi_B^{*}(1)\,\psi_A(2)\,\psi_B(1)$$

- But these two probabilities are different!
    - This is not acceptable!
    - This means that the expressions for Ψ_{tot} above are not valid solutions!

Exchange electrons

- Since:

$$\psi^* \psi = |\psi|^2$$

- We need this to be satisfied:

$$|\psi(\text{after exchange})|^2 = |\psi(\text{before exchange})|^2$$

- So the total eigenfunction:

$$\psi_{(\text{after exchange})} = \pm \psi \, (\text{before exchange})$$

- + sign: Symmetric eigenfunction Ψ_{Symm}
- - sign: Anitsymmetric eigenfunction Ψ_{Anti}

Symmetric and Antisymmetric

$$\Psi_{Symm} = \frac{1}{\sqrt{2}}\left[\Psi_A(1)\Psi_B(2) + \Psi_B(1)\Psi_A(2)\right]$$

$$\Psi_{Anti} = \frac{1}{\sqrt{2}}\left[\Psi_A(1)\Psi_B(2) - \Psi_B(1)\Psi_A(2)\right]$$

- Ψ_{Symm} and Ψ_{Anti} are degenerate!
  - Same energy
  - They exhibit “exchange degeneracy”
- They have the right properties:

$$\Psi_{Symm}\,(\text{after exchange}) = +\Psi_{Symm}\,(\text{before exchange})$$

$$\Psi_{Anti}\,(\text{after exchange}) = -\Psi_{Anti}\,(\text{before exchange})$$

- Note $1/\sqrt{2}$ is for normalization, assuming that Ψ_{tot} is normalized:

$$\int \Psi_{Symm}^{*}\,\Psi_{Symm}\,dx = \frac{1}{2}\left[\int \Psi_{TOT}^{*}\Psi_{TOT} + \int \Psi_{TOT}^{*}\Psi_{TOT}\right] = 1$$

Pauli Exclusion Principle

- Principle was formulated by Wolfgang Pauli in 1925.
- "Weak form":
    - In an atom, no two electrons can be in the same quantum state, i.e. the same set of quantum numbers: n, ℓ, m_ℓ, m_s

Pauli Exclusion Principle

- Suppose electrons 1 and 2 are in the same quantum state A. Then:

$$\psi_{symm} = \frac{1}{\sqrt{2}}\left[\psi_A(1)\psi_A(2) + \psi_A(1)\psi_A(2)\right]$$

$$= \sqrt{2}\,\psi_A(1)\psi_A(2) \neq 0$$

  - So, Ψ_{Symm} permits 2 electrons in the same state.
  - So, Ψ_{Symm} violates the Pauli exclusion principle

$$\psi_{Anti} = \frac{1}{\sqrt{2}}\left[\psi_A(1)\psi_A(2) - \psi_A(1)\psi_A(2)\right] = 0$$

- Ψ_{Anti} obeys the Pauli exclusion principle.

Pauli Exclusion Principle

- "Strong" form of Pauli Exclusion Principle:
  - A multi-electron system must have an antisymmetric total eigenfunction.
  - "Strong" because it also incorporates indistinguishability.
  - All particles of half-integer spin (1/2, 3/2, …) have antisymmetric total eigenfunctions and are called "Fermions", obeying **Fermi-Dirac statistics**
    - Electrons, protons, neutrons
  - All particles of integer spin (0, 1, 2, …) have symmetric total eigenfunctions, and are called "Bosons", obeying **Bose-Einstein statistics.**
    - Photons, alpha, W and Z particles

Required for Bosons

$$\Psi_{tot} \propto \Psi_A(1)\Psi_B(2) \pm \Psi_A(2)\Psi_B(1)$$

Required for Fermions

Helium Example

- Normal Helium ($^{4}{}_{2}$He)
    - Even number of spin 1/2 constituents
    - 2 protons, 2 neutrons and 2 electrons
    - Is a Boson
- Helium-3 ($^{3}{}_{2}$He)
    - 2 protons, 1 neutrons, 2 electrons
    - Is a Fermion
- Generally, Even number sum of protons+neutrons+electrons → Boson

  Odd number sum → Fermion

Total Fermion Eigenfunction

- So, for Fermion, total eigenfunction must be antisymmetric
- Can write:

$$\Psi_{Anti} = \Psi(space)\,\Psi(spin)$$

- So, Ψ(space) and Ψ(spin) must have opposite symmetry in order for Ψ_{Anti} to be antisymmetric
- We had used A and B as abbreviations for particular sets of n, ℓ, m_ℓ, m_s
- Now let's use a and b as abbreviations for particular sets of n, ℓ, m_ℓ
  - i.e. just the space part

Space and Spin Eigenfunctions

$$\psi_{symm}(space) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]$$

$$\psi_{anti}(space) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)\right]$$

- The space wavefunctions are analogous to RΘΦ for Hydrogen

- For spins, there is no spatial wavefunction, so
  - Symbolically,

$$\chi(m_s \text{ for electron } 1,\ m_s \text{ for electron } 2)$$

Spin Eigenfunctions

- Example: $\chi(+\frac{1}{2},-\frac{1}{2})$
- But this does not have definite symmetry:

$$\chi(\text{after exchange}) \neq \pm\chi(\text{before exchange})$$

- So, the antisymmetric χ, corresponding to Ψ_{Symm}(space) (singlet state):

$$\chi_{\text{Anti}} = \frac{1}{\sqrt{2}}\left[\chi(+\tfrac{1}{2},-\tfrac{1}{2}) - \chi(-\tfrac{1}{2},+\tfrac{1}{2})\right]$$

- The symmetric χ, corresponding to Ψ_{Anti}(space); there are <u>three</u> ways to do it (triplet state):

$$\chi_{\text{Symm}} = \begin{cases} \chi(+1/2,+1/2) \\ \frac{1}{\sqrt{2}}\left[\chi(+\tfrac{1}{2},-\tfrac{1}{2}) + \chi(-\tfrac{1}{2},+\tfrac{1}{2})\right] \\ \chi(-1/2,-1/2) \end{cases}$$

Spin Angular Momentum

- In a two electron atom (Helium) the spin angular momentum of the two electrons couple to give the total spin:

$$\vec{S}' = \vec{S}_1 + \vec{S}_2$$

$$S' = |\vec{S}'| = \sqrt{s'(s'+1)}\,\hbar$$

$$S_z' = m_{s'}\hbar$$

$$m_{s'} = -s', -s'+1, \ldots +s'$$

- But what is s'?

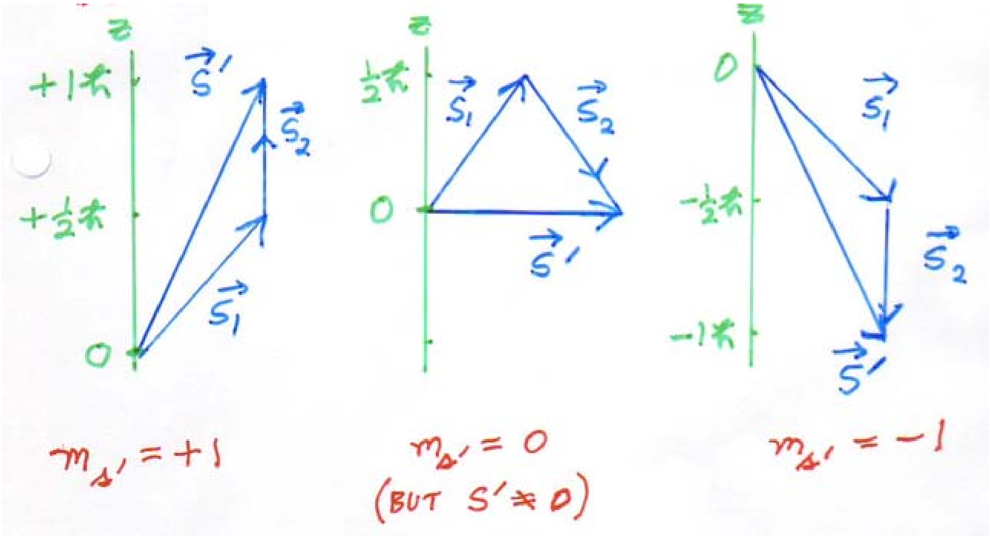
$$s_1 = s_2 = 1/2 \qquad s' = |s_1 - s_2|,\ |s_1 - s_2| + 1 \ldots (s_1 + s_2)$$

$$= 0 \text{ or } 1$$

Spin Angular Momentum

- If s'=0, $m_{s'} = 0$ only, and this is the singlet state, which is antisymmetric.
  - We have opposite spins, and **S'**=0

- If s'=1, $m_{s'}$ = -1, 0, +1, and this is why we get the triplet state which is symmetric.
  - We have parallel spins



Parallel Spins

- For parallel spins:
  - s’=1
  - triplet state in Helium (called Orthohelium)
  - χ symmetric
  - Ψ(space) antisymmetric.
- Suppose electrons get close, so a=b (same spatial quantum numbers):

$$\psi_{Anti}(space) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)\right] = 0$$

  - Low probability for electrons to have similar coordinates
  - Parallel-spin electron repel each other, over and above the Coulomb repulsion.
  - This “exchange” force mainly reflects the exclusion principle

Antiparallel Spins

- For antiparallel spins:
  - s'=0
  - Singlet state in Helium (called Parahelium)
  - χ antisymmetric
  - Ψ(space) symmetric
- Suppose electrons get close, so a=b (same spatial quantum numbers):

$$\Psi_{symm}(space) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_a(2) + \psi_a(1)\psi_a(2)\right] = \sqrt{2}\,\psi_a(1)\psi_b(2)$$

- This is large, so antiparallel-spin electrons <u>attract</u> each other via the "exchange" force.

Example

- Construct total (spatial+spin) ground state electron configuration of a Helium atom using the spatial hydrogenic wavefunction notation of

$\psi_{n\ell m}$

Example

- Construct total (spatial+spin) first excited state configuration of a Helium atom using the spatial hydrogenic wavefunction

ψ_{100} & ψ_{200}

- If you consider Coulomb repulsion between electrons, will the first excited state be in a singlet state (parahelium) or in a triplet state (orthohelium)?

Example

- If we put 5 electrons (fermions!) in an infinite square well, what is the ground state energy?
  - Recall the energies for an infinite square well are:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = n^2E_1, \text{ where } E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$

  - Since electrons are fermions, 2 electrons will populate n=1, 2 in n=2, and 1 in n=3.
  - So, the ground state energy of this system is:

$$E = 2\cdot(E_1) + 2\cdot(4E_1) + 1\cdot(9E_1) = 19E_1$$

- What if we put 5 bosons in the well?
  - All 5 bosons can go into n=1!
  - So ground state energy is $E=5E_1$

Example

- For two electrons in an infinite potential well, construct the total wavefunction of the ground state.

- For two electrons in an infinite potential well, construct total wavefunctions of the first excited state, with and without consideration of the electron-electron Coulomb potential

Summary/Announcements

- Next time:
    - Multi-electrons

- HW 12 will be posted on Nov. 30th (Wednesday).

- There will be a quiz next class (30th)