Lecture #15: Identical particles, multielectron atoms
E/R: Chapter 9

John Bowers
Bowers@ece.ucsb.edu
Lecture Today, Thursday, Friday (1 pm)
Identical Particles

• In classical physics, particles can be followed, and hence labels can be attached to each.

• In quantum physics, measurable results obtained from calculations should not depend on the assignment of labels to identical particles.
Example: Two identical particles in a box-no interaction between particles

\[ x_1 \quad \text{The position of particle 1} \]
\[ x_2 \quad \text{The position of particle 2} \]
\[ V(x_1, x_2) = 0 \text{ for } 0 < x_1, x_2 < L; \infty \text{ otherwise} \]
\[ \left[-\frac{\hbar^2}{2m} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + V(x_1, x_2) \right] \psi(x_1, x_2) = E \psi(x_1, x_2) \]
Example: Two identical particles in a box-no interaction between particles

\[ V(x_1, x_2) = 0 \text{ for } 0 < x_1, x_2 < L; \infty \text{ otherwise} \]

\[ \left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + V(x_1, x_2) \right] \psi(x_1, x_2) = E \psi(x_1, x_2) \]

This is separable since \( V \) depends on only one particle at a time.

\[ \psi(x_1, x_2) = \psi_{n_1}(x_1) \psi_{n_2}(x_2) \]

This can be substituted into SE, and the solution is

\[ \psi_{n_1}(x_1) = A_1 \sin \frac{n_1 \pi x_1}{L} \]

\[ \psi(x_1, x_2) = A_3 \sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L} \]

But, this is not symmetric under exchange of 1\( \rightarrow \)2
Example: Two identical particles in a box-no interaction between particles

\[ \psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) \]

This wavefunction is symmetric under exchange 1→2

\[ \psi_S(x_1, x_2) = \frac{1}{\sqrt{2}}(\psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_2}(x_1)\psi_{n_1}(x_2)) \]

This wavefunction changes sign under exchange, so \( \psi^*\psi \) is the same under exchange.

\[ \psi_A(x_1, x_2) = \frac{1}{\sqrt{2}}(\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2)) \]
Pauli Exclusion Principle

• In a multielectron atom, there can never be more than one electron in the same quantum state.

• Note that this is satisfied automatically by the antisymmetric state:

\[
\psi_{s_n l_1 l_2}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n l_1}(x_1)\psi_{n l_1}(x_2) + \psi_{n l_1}(x_1)\psi_{n l_1}(x_2)) = \sqrt{2}\psi_{n l_1}(x_1)\psi_{n l_1}(x_2)
\]

\[
\psi_{A_n l_1 l_2}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{n l_1}(x_1)\psi_{n l_1}(x_2) - \psi_{n l_1}(x_1)\psi_{n l_1}(x_2)) = 0
\]

• A system containing several electrons must be described by an antisymmetric total eigenfunction.
• Fermions: particles with half integral spin \((1/2, 3/2, \ldots)\) such as electrons and protons. Fermions obey the Pauli exclusion principle and have antisymmetric wavefunctions.

• Bosons: particles with integral spin \((0, 1, \ldots)\) such as photons. They need not obey the Pauli Exclusion Principle and have symmetric wavefunctions.
Multi-Electron Wave-functions
Independent Particle Approximation

For a system with two electrons:
Total Wave-function = (Spatial Component) X (Spin Component)
Independent electrons:
Spatial Component = \( \Psi_A(1) \times \Psi_B(2) \)

• Separation of Variables can be applied to the two-particle Hamiltonian if electrons are independent

• Also a consequence of the fact that the joint distribution of two independent random variables is a product of their individual distributions
Multi-Electron Wave-functions
Independent Particle Approximation

For a system with two electrons:
Total Wave-function = (Spatial Component) X (Spin Component)
Independent electrons:
Spatial Component = \( \Psi_\text{A}(1) \times \Psi_\text{B}(2) \)

• Labels (1) and (2) represent the two electrons

• A and B represent the energy levels they occupy respectively

• This state does not go into \( \pm \) itself on interchange of 1 and 2

• Problem: However, electrons are indistinguishable!

• \( |\Psi|^2 \) is physically measurable, must not depend on electron labeling
Multi-Electron Wave-functions
Independent Particle Approximation

Fix: Linear Combinations of Degenerate Solutions
Spatial Component = \((1/2)^{1/2} \left[ \Psi_A(1) \Psi_B(2) \pm \Psi_B(1) \Psi_A(2) \right] \)

- Labels (1) and (2) represent the two electrons
- A and B represent the energy levels they occupy respectively
- This state goes into \( \pm \) itself on interchange of 1 and 2
- Both physically acceptable, one (+) symmetric and the other (-) anti-symmetric under exchange
Multi-Electron Wave-functions
Independent Particle Approximation

For a system with two electrons:
Total Wave-function = (Spatial Component) X (Spin Component)

Spin Component
Terminology: $|\frac{1}{2}, -\frac{1}{2} >$

• Meaning: The first electron is spin-up, the second is spin-down

• Again there is lack of symmetry on exchange of particles 1 and 2
Spin Component, Contd.
Problem: Lack of Exchange Symmetry

Fix:

• Spin-symmetric states – Triplet:
  \[ |\frac{1}{2}, \frac{1}{2} > \]
  \[ |\frac{-1}{2}, \frac{-1}{2} > \]
  \[ (1/2)^{1/2} [ |\frac{1}{2}, \frac{-1}{2} > + |\frac{-1}{2}, \frac{1}{2} > ] \]

• Spin-anti-symmetric state: \((1/2)^{1/2} [ |\frac{1}{2}, \frac{-1}{2} > - |\frac{-1}{2}, \frac{1}{2} > ] \)
Hartree Theory

• Multielectron atomic theory
• First consider a nuclear attractive coulombic force: $+Ze$
• Include the coulombic repulsion due to the average position of other electrons: $-(Z-1)e$
• Assume each electron moves independently of each other.

• Schrödinger’s equation becomes separable into $Z$ separate equations for the motion of each electron:
  $$\frac{-\hbar^2}{2m} \nabla^2 \psi + V(r)\psi = E\psi$$
What is $V(r)$?

• First guess:
  
  – For $r \to 0$,
    
    $$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$
  
  – For $r \to \text{infinity}$
    
    $$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

• Then, solve SE and calculate $V(r)$
Hartree Solution

- Assume $V(r)$ (previous slide)
- Calculate the solutions
  \[ \psi_\alpha(r, \theta, \phi), \psi_\beta(r, \theta, \phi), \psi_\gamma(r, \theta, \phi), \ldots \]
  with energies
  \[ E_\alpha, E_\beta, E_\gamma, \ldots \]
- Put one electron in each state. Solution is the product of one electron states.
  \[ \psi = \psi_\alpha(r_1, \theta_1, \phi_1), \psi_\beta(r_2, \theta_2, \phi_2), \psi_\gamma(r_3, \theta_3, \phi_3), \ldots \]
- Note: $\alpha, \beta, \gamma$ includes space and spin
  \[ \alpha : \langle n = 1; l = 0; m_l = 0, \uparrow \rangle \]
  \[ \beta : \langle n = 1; l = 0; m_l = 0, \downarrow \rangle \]
Hartree Solution (cont)

- Use $\psi^*\psi$ to calculate $V(r)$
- Iterate:
  - Solve SE using new $V(r)$
  - Put one electron in each state to assemble $\psi$
  - Calculate $V(r)$
Hartree Fock Theory

• Hartree theory ignores the requirement of antisymmetric wave functions.
• Fock included this.
• For a N electron atom, N! terms are added in the expression for ψ (It is an N dimensional Slater determinant).
• The effect is only significant for the valence electrons.
Θ–φ Dependence

• The Θ–φ dependence is the same as for the hydrogen atom since we didn’t assume anything for the form of V(r).
Solution to SE in Spherical Coordinates

\[-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi\]

If \( V(r, \theta, \phi) = V(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \)

Then try separation of variables

\( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \)

Substitute and divide by \( R \Theta \Phi \)

\[-\frac{\hbar^2}{2mR} \left( \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) + \frac{1}{\Theta r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi r^2 \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} + V(r) = E \]
Separate $\phi$ dependence

Rearrange:

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d^2 \phi} = -\frac{2mr^2 \sin^2 \theta}{\hbar^2} (E - V(r)) - \frac{\sin^2 \theta}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta})$$

$LHS$ is a function of $\phi$ only.

No assumption on the form of $V(r)$!
Solution of $\Phi$

No assumption on the form of $V(r)!$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d^2 \phi} = -m_l^2$$

$$\Phi = Ae^{im_l \phi}$$

*Single valued means*

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

*Which means $m$ is an integer.*
Separation of $r$ and $\theta$

\[-m_i^2 = -\frac{2mr^2 \sin^2 \theta}{\hbar^2} (E - V(r)) - \frac{\sin^2 \theta}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) \]

Re-arrange:

\[-\frac{2mr^2}{\hbar^2} (E - V(r)) + \frac{1}{R} \left( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) \right) = \frac{m_i^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) \equiv l(l + 1) \]

_LHS is a function of $r$ only and RHS is a function of $\theta$ only._

**No assumption on the form of $V(r)$!**
Solution of $\Theta$

\[
\frac{m_l^2 \Theta}{\sin^2 \theta} - \frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d \Theta}{d \theta} \right) = l(l + 1)\Theta
\]

The solution is in Appendix N.
Use a power series expansion in $\cos \theta$.
The series terminates for

\[
l = |m_l|, |m_l + 1|, ...
\]

\[
\Theta = \sin^{m_l} \theta \ F_{lm_l} (\cos \theta)
\]

No assumption on the form of $V(r)$!
Results of Hartree Theory

• Eigenfunctions labeled by $n, l, m, m_l, m_s$
• $(E$ will not be given by $E_0 / n^2$)
• Important for solid state physics.
• Numerical calculation programs exist for Hartree and Hartree-Foch
Labeling of energy levels (shells)

- \( N=1,l=0 \) 1s 2 states (up, down) H, He
Labeling of energy levels (shells)

- N=1, l=0 1s 2 states (up, down) H, He
- N=2, l=0 2s 2 states (up, down) Li, Mg
Labeling of energy levels (shells)

• \( N=1, l=0 \)  
  \( 1s \)  
  2 states (up, down)  
  H, He

• \( N=2, l=0 \)  
  \( 2s \)  
  2 states (up, down)  
  Li, Mg

• \( N=2, l=1 \)  
  \( 2p \)  
  6 states (\( 2x|m_l|=-1,0,1 \))  
  B, C, N, O, F, Ne
Labeling of energy levels (shells)

- N=1, l=0
  - 1s
  - 2 states (up, down) H, He

- N=2, l=0
  - 2s
  - 2 states (up, down) Li, Mg

- N=2, l=1
  - 2p
  - 6 states (2x(m_l=-1,0,1))

- N=3, l=0
  - 3s
  - 2 states (2x(m_l=0))
Labeling of energy levels (shells)

- **N=1, l=0**  
  1s  2 states (up, down)  
  H, He

- **N=2, l=0**  
  2s  2 states (up, down)  
  Li, Mg

- **N=2, l=1**  
  2p  6 states (2x(m_l=-1,0,1))

- **N=3, l=0**  
  3s  2 states (2x(m_l=0))

- **N=3, l=1**  
  3p  6 states (2x(m_l=-1,0,1))
Order and Labeling of energy levels (shells)

- **N=1, l=0**  
  1s  2 states (up, down)  H, He

- **N=2, l=0**  
  2s  2 states (up, down)  Li, Mg

- **N=2, l=1**  
  2p  6 states (2x(m_l=-1,0,1))

- **N=3, l=0**  
  3s  2 states (2x(m_l=0))

- **N=3, l=1**  
  3p  6 states (2x(m_l=-1,0,1))

- **N=4, l=0**  
  4s  2 states (2x(m_l=0))

- **N=3, l=2**  
  3d  10 states (2x(m_l=-2,-1,0,1,2))

- **N=4, l=1**  
  4p  6 states (2x(m_l=-1,0,1))
Order and Labeling of energy levels (shells)

- $N=1, l=0$  
  1s  2 states

- $N=2, l=0$  
  2s  2 states

- $N=2, l=1$  
  2p  6 states

- $N=3, l=0$  
  3s  2 states

- $N=3, l=1$  
  3p  6 states

- $N=4, l=0$  
  4s  2 states

- $N=3, l=2$  
  3d  10 states

- $N=4, l=1$  
  4p  6 states

- $N=5, l=0$  
  5s  2 states

- $N=5, l=1$  
  5p  6 states

- $N=6, l=0$  
  6s  2 states

- $N=4, l=3$  
  4f  14 states
Chemistry

- Inner electrons affected by nucleus, not other atoms.
- Outer electrons see a potential of $+e$ or $+2e$ and are affected by adjacent atoms.
- The outer electrons are called valence electrons and are involved in bonding to other atoms.
- Atoms with the same valence structure behave similarly chemically.
Periodic Table (Mendeleev in 1869)

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- **Lanthanides**
  - 4f
    - Ce
    - Pr
    - Nd
    - Pm
    - Sm
    - Eu
    - Gd
    - Tb
    - Dy
    - Ho
    - Er
    - Tm
    - Yb
    - Lu
  - 5f
    - Th
    - Pa
    - U
    - Np
    - Pu
    - Am
    - Cm
    - Bk
    - Cf
    - Es
    - Fm
    - Md
    - No
    - Lw

- **Actinides**
Band Theory of Solids

- Isolated atom (B)

![Energy Levels Diagram]

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Band Theory of Solids

- Isolated $\rightarrow$ 2 atoms

![Energy Level Diagram]

- 1s
- 2s
- 2p
Band Theory of Solids

- Isolated $\rightarrow$ solid

- Splitting higher for outer electrons; more overlap.

- Splitting increases as the separation decreases.
Energy Bands

- Bands that originate from closed shells (e.g. 1s, 2s for boron) have filled bands.
- Shells that are partially filled result in bands that are partially filled.
- Filled bands give insulators.
- Partially filled bands give metals.
- Filled bands with empty bands close by (0.1 to 3 eV) are called semiconductors.
- Materials with odd number of electrons/atom are always metals.
Quantum Statistics

• How are electrons distributed versus energy?
• Classical answer: Maxwell Boltzman distribution

\[ P(E) = Ae^{-E/kT} \]

• However, this has most electrons at low energies, which violates the Pauli exclusion principle.
Quantum Statistics

• How are electrons distributed versus energy?
• Classical answer: Maxwell Boltzman distribution

\[ P(E) = Ae^{-E/kT} \]

• Quantum mechanical answer: Fermi Dirac distribution

\[ P(E) = \frac{A'}{1 + e^{(E-E_0)/kT}} \]

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Conduction

• A filled band has no net current flow. For every electron going in one direction, there is an electron going in the opposite direction.

• In general (for electron conduction only),

\[ n = \int_{-\infty}^{\infty} dE \ N(E) f(E) \]

\[ j = env \]