PHY 742 Quantum Mechanics II
1-1:50 AM MWF via video link:
https://wakeforest-university.zoom.us/my/natalie.holzwarth

Plan for Lecture 17

Quantum mechanics of a multi electron atom

Continue reading Professor Carlson's textbook: Chapter X. Multiple particles (Sec. F)

1. He atom
   a. Accounting for spin.
   b. Ground state.
   c. Excited states.

In this lecture, we will consider what we learned about Fermi particles and apply it to Fermi particles in multielectron atoms, starting with He.

Topics for Quantum Mechanics II

Single particle analysis

- **Single particle interacting with electromagnetic fields – EC Chap. 9**
- **Scattering of a particle from a spherical potential – EC Chap. 14**
- **More time independent perturbation methods – EC Chap. 12, 13**
- **Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6**
- **Time dependent perturbation methods – EC Chap. 15**
- **Relativistic effects and the Dirac Equation – EC Chap. 16**
- **Path integral formalism (Feynman) – EC Chap. 11.C**

Multiple particle analysis

- **Quantization of the electromagnetic fields – EC Chap. 17**
- **Photons and atoms – EC Chap. 18**
- **Multi particle systems; Bose and Fermi particles – EC Chap. 10**
- **Multi electron atoms and materials**
  - **Hartree-Fock approximation**
  - **Density functional approximation**

Here is the course outline that we have been following.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020				
	Fri: 04/10/2020	No class	*Good Friday*		
29	Mon: 04/13/2020				
30	Wed: 04/15/2020				
31	Fri: 04/17/2020				
32	Mon: 04/20/2020				
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

Homework #22 involves rederiving the results shown on the lecture slides and evaluating the expectation value of the energy of a He atom.

In the past lectures, we have considered how to represent the quantum mechanics of identical particles. For treating a many electron atom, the focus is on representing the Fermi properties of the electrons. For example, in a basis with state labels *a,b,c*…. the second quantization operators work as follows.

Second quantization for Fermi particles

$$N_a = f_a^\dagger f_a$$

Fermi particle anticommutation relations:

$$\left\{ f_a, f_b \right\} \equiv f_a f_b + f_b f_a = 0$$

$$\left\{ f_a^\dagger, f_b^\dagger \right\} = 0$$

$$\left\{ f_a, f_b^\dagger \right\} = \delta_{ab}$$

Review of Fermi creation and annihilation operators.

Second quantized creation and annhilation Fermi operators

$$f_a^\dagger f_a \left|n_a\right\rangle = n_a \left|n_a\right\rangle$$

$$f_a \left|n_a\right\rangle = \sqrt{n_a}\left|1-n_a\right\rangle$$

$$f^\dagger{}_a \left|n_a\right\rangle = \sqrt{1-n_a}\left|1-n_a\right\rangle$$

These results follow from the anti commutator relations of the operators.

Non-trivial operations:

$$f_a \left|0_a\right\rangle = 0 \qquad f_a \left|1_a\right\rangle = \left|0_a\right\rangle$$

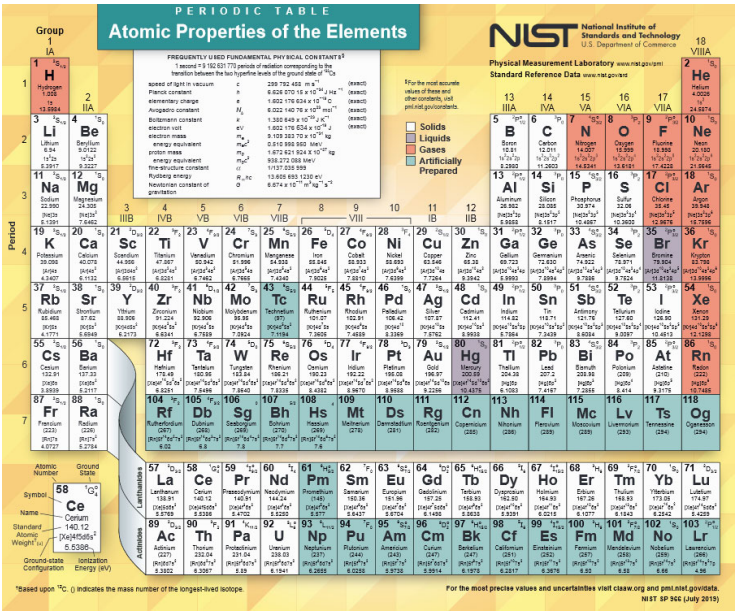
$$f_a^\dagger \left|0_a\right\rangle = \left|1_a\right\rangle \quad f_a^\dagger \left|1_a\right\rangle = 0$$

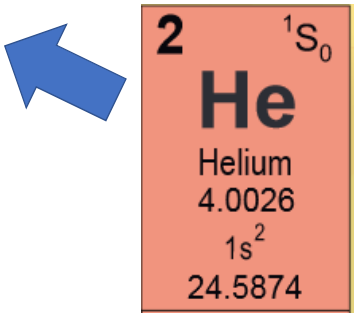
$$\Rightarrow n_a = 0 \text{ or } 1$$

To represent 3 states: $\left|n_a n_b n_c\right\rangle = \left(f_c^\dagger\right)^{n_c}\left(f_b^\dagger\right)^{n_b}\left(f_a^\dagger\right)^{n_a}\left|0\right\rangle$

These results follow from the anti-commutation relations

https://www.nist.gov/system/files/documents/2019/12/10/nist_periodictable_july2019_crop.pdf





You probably know this notation. If not, please pose questions.

The Hamiltonian for an He atom (Z=2): (cgs Gaussian units)

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

$$= \underbrace{-\frac{\hbar^2\nabla_1^2}{2m} - \frac{2e^2}{r_1}}_{h(\mathbf{r}_1)} + \underbrace{-\frac{\hbar^2\nabla_2^2}{2m} - \frac{2e^2}{r_2}}_{h(\mathbf{r}_2)} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$= h(\mathbf{r}_1) + h(\mathbf{r}_2) + v_{\text{int}}(\mathbf{r}_1,\mathbf{r}_2)$$

Single particle basis:

$$h(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) \equiv h(\mathbf{r}_1)\varphi_{nlm}(\mathbf{r}_1) = \varepsilon_n\varphi_{nlm}(\mathbf{r}_1)$$

What is missing from this analysis?

What is missing?

Electron spin.

1. **Electron spin does not appear in this Hamiltonian and therefore cannot effect the analysis?**
2. **Electron spin does not appear in this Hamiltonian but can have a profound effect on the analysis?**

Single particle basis with spin:

$$h(\mathbf{r}_1)\varphi_{am_s}(\mathbf{r}_1) \equiv h(\mathbf{r}_1)\varphi_{nlmm_s}(\mathbf{r}_1) = \varepsilon_{nlm}\varphi_{nlmm_s}(\mathbf{r}_1)$$

Other convenient notations

$$m_s = \tfrac{1}{2} \quad \Rightarrow \alpha \text{ or } \uparrow \qquad m_s = -\tfrac{1}{2} \quad \Rightarrow \beta \text{ or } \downarrow$$

Various alternative notations.

Second quantized version of the He atom Hamiltonian

$$H(\mathbf{r}_1,\mathbf{r}_2) \Rightarrow \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here v_{ijkl} denotes matrix elements such as

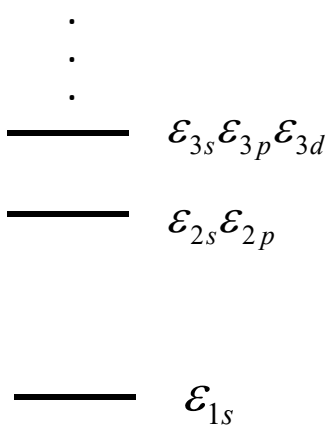
$$v_{ijkl} = \left\langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \middle| v(\mathbf{r}_1-\mathbf{r}_2) \middle| \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \right\rangle$$

The matrix element $i \equiv nlmm_s$

In general, we will use $nl \Rightarrow n\{spdf..\}$ for $n\{0123..\}$

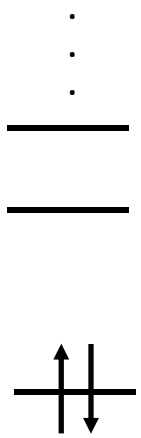
Defining single particle and two particle interaction terms. Do you notice something odd on this slide?

Spectrum of single particle states for He atom (schematic)



Non-interacting particle energy diagram

Ground state configuration for He atom



$\varepsilon_{3s}\varepsilon_{3p}\varepsilon_{3d}$

$\varepsilon_{2s}\varepsilon_{2p}$

ε_{1s}

$$\psi = f^{\dagger}_{1s\alpha} f^{\dagger}_{1s\beta} \left|0\right\rangle$$

Consider first the lowest energy state of this system.

Expectation value of Hamiltonian for ground state of He atom

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_k f_l$$

Need to evaluate $\langle \psi | H | \psi \rangle$ for $\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$

First consider the single particle terms; here we assume $i \neq j$

$\langle \psi | f_i^\dagger f_i | \psi \rangle$ for $\psi = f_i^\dagger f_j^\dagger |0\rangle$

$\langle \psi | f_i^\dagger f_i | \psi \rangle = \langle 0 | f_j f_i f_i^\dagger f_i f_i^\dagger f_j^\dagger | 0 \rangle$

$f_j f_i f_i^\dagger f_i f_i^\dagger f_j^\dagger = -f_i f_j f_i^\dagger f_i f_i^\dagger f_j^\dagger = f_i f_i^\dagger f_j f_i f_i^\dagger f_j^\dagger$

$= -f_i f_i^\dagger f_i f_j f_i^\dagger f_j^\dagger = f_i f_i^\dagger f_i f_i^\dagger f_j f_j^\dagger$

$f_j f_i f_i^\dagger f_i f_i^\dagger f_j^\dagger |0\rangle = f_i f_i^\dagger f_i f_i^\dagger f_j f_j^\dagger |0\rangle = |0\rangle$

$$\{f_a, f_b\} = 0$$

$$\{f_a^\dagger, f_b^\dagger\} = 0$$

$$\{f_a, f_b^\dagger\} = \delta_{ab}$$

Evaluating the expectation value in terms of the creation and annihilation operators.

Expectation value of Hamiltonian for ground state of He atom

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Need to evaluate $\langle \psi | H | \psi \rangle$ for $\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$

The results on the previous slide evaluate the single particle terms according to

$$\left\langle \psi \left| \sum_i \varepsilon_i f_i^\dagger f_i \right| \psi \right\rangle = \varepsilon_{1s\alpha} + \varepsilon_{1s\beta} = 2\varepsilon_{1s}$$

Here we make use of the fact that the energy does not depend on spin.

Now consider the interaction term

Here we assume that $i \neq j$ and $k \neq l$

$$\langle \psi | f_i^\dagger f_j^\dagger f_l f_k | \psi \rangle \quad \text{for } \psi = f_i^\dagger f_j^\dagger |0\rangle$$

$$\langle \psi | f_i^\dagger f_j^\dagger f_l f_k | \psi \rangle = \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_l f_k f_i^\dagger f_j^\dagger | 0 \rangle$$

For $k = i$ and $l = j$: $f_j f_i f_i^\dagger f_j^\dagger f_j f_i f_i^\dagger f_j^\dagger = f_i f_i^\dagger f_j f_j^\dagger f_i f_i^\dagger f_j f_j^\dagger$

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_j f_i f_i^\dagger f_j^\dagger | 0 \rangle = 1$$

For $k = j$ and $l = i$: $f_j f_i f_i^\dagger f_j^\dagger f_i f_j f_i^\dagger f_j^\dagger = -f_i f_i^\dagger f_j f_j^\dagger f_i f_i^\dagger f_j f_j^\dagger$

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_i f_j f_i^\dagger f_j^\dagger | 0 \rangle = -1$$

Evaluating the two particle interaction terms, specializing to the choices of k and l that give nontrivial results.

Expectation value of Hamiltonian for ground state of He atom

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Need to evaluate $\langle \psi | H | \psi \rangle$ for $\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$

The results on the previous slide evaluate the two particle terms according to

$$\left\langle \psi \left| \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k \right| \psi \right\rangle = v_{ijij} - v_{ijji}$$

Here $i \equiv 1s\alpha \qquad j \equiv 1s\beta$

Evaluation of two particle term, continued

$$v_{ijkl} \equiv \left\langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \middle| v(\mathbf{r}_1 - \mathbf{r}_2) \middle| \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \right\rangle$$

$$\text{Here} \quad i \equiv 1s\alpha \qquad j \equiv 1s\beta$$

$$v_{ijij} = \int d^3r_1 d^3r_2 \left|\varphi_{1s\alpha}(\mathbf{r}_1)\right|^2 \left|\varphi_{1s\beta}(\mathbf{r}_2)\right|^2 v(\mathbf{r}_1 - \mathbf{r}_2)$$

$$v_{ijji} = 0$$

Why is v_{ijji}=0?

Summary of results

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Need to evaluate $\langle \psi | H | \psi \rangle$ for $\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$

$$\langle \psi | H | \psi \rangle = 2\varepsilon_{1s} + v_{ijij}$$

Note that in coordinate and spin representation,

$$\psi = \frac{1}{\sqrt{2}} \varphi_{1s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)\left(\alpha_1\beta_2 - \alpha_2\beta_1\right)$$

What is the total electron spin of this He atom?