

## **PHY 742 Quantum Mechanics II**

**1-1:50 AM MWF via video link:**

**<https://wakeforest-university.zoom.us/my/natalie.holzwarth>**

### **Extra notes for Lecture 25**

#### **Quantum mechanics of multiple particle systems**

**Read Professor Carlson's textbook: Chapter X. Multiple particles**

#### **1. Non-interacting particles**

**a. Distinguishable, Fermi, Bose**

**b. Second quantized formalisms**

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In this lecture, we will begin our consideration of multiple particle systems which is discussed in Chapter 10 of your textbook. First we consider the ideal situation that the multiple particles do not interact with each other.

## 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

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Here is the course outline that we have been following.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	<a href="#">#17</a>	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	<a href="#">#18</a>	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	<a href="#">#19</a>	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	<a href="#">#20</a>	04/03/2020
26	Fri: 04/03/2020				
27	Mon: 04/06/2020				
28	Wed: 04/08/2020				
	Fri: 04/10/2020	No class	<i>Good Friday</i>		
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 #20 asks you to do a problem from the end of Chapter 10 of Professor Carlson's textbook.

## Your questions:

### From Trevor

Slide 8 asks what would happen if  $\psi_{\text{A}}$  and  $\psi_{\text{B}}$  have exactly the same shape. Looking at the equation on that slide, the total wavefunction would be zero. Is this a demonstration of the Pauli exclusion principle, since in essence it's saying that two fermi particles can't be in the same state?

### From Surya

1. We can express wave function for n-fermions easily using Slater determinant. Can we write wave function for 3-Bosons just like we do for two bosons with two states in slide 13?
2. Is it possible to explain non-interacting Bose/Fermi particle using DFT?

**Some answers –**

**Question:** Slide 8 asks what would happen if  $\phi_a$  and  $\phi_b$  have exactly the same shape. Looking at the equation on that slide, the total wavefunction would be zero. Is this a demonstration of the Pauli exclusion principle, since in essence it's saying that two fermi particles can't be in the same state?

Example for two Fermi particles:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1))$$

In this case, if  $\phi_a(\mathbf{r}) \equiv \phi_b(\mathbf{r})$ , then  $\psi(\mathbf{r}_1, \mathbf{r}_2) = 0$ . This result is consistent with the Pauli exclusion principle that two identical Fermi particles cannot simultaneously occupy the same state.

**Question:** We can express wave function for n-fermions easily using Slater determinant. Can we write wave function for 3-Bosons just like we do for two bosons with two states in slide 13?

Example for two Bose particles:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1))$$

For three Bose particles:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) \end{vmatrix}_+$$

← **Determinant but without minus signs.**

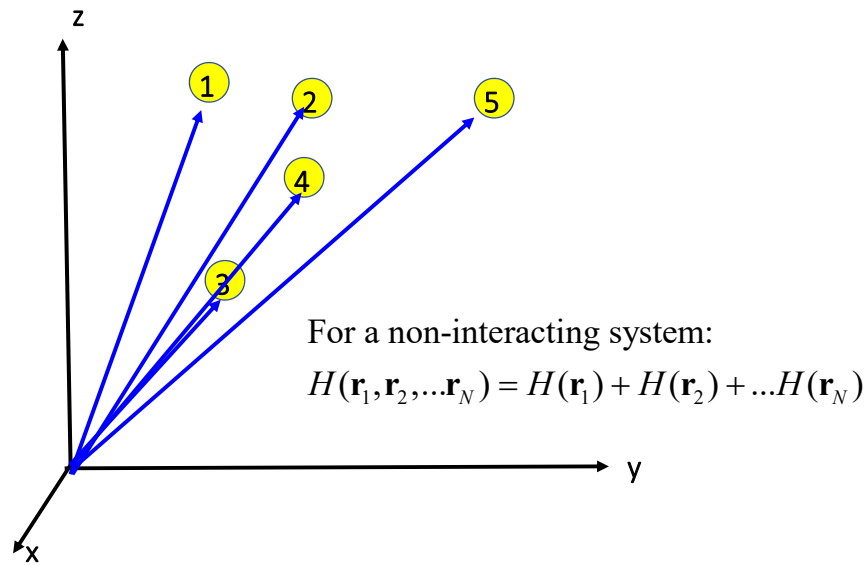
**Question:** Is it possible to explain non-interacting Bose/Fermi particle using DFT?

**Comment:** DFT (density functional theory) is called a “mean field” theory which refers to the fact that the “mean values” of interactions are used self-consistently in the evaluations. This leads to an effective single particle formulation of the system. If the system is non-interacting, then the system can be treated exactly as independent particles. However in nature, there are very few cases of non-interacting particles.

**Slides from original lecture --**



## Quantum mechanical treatment of multiparticle systems



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This diagram illustrates a general system to be considered where  $N$  particles are described by  $N$  different coordinates. For the moment, we will be considering systems which do not vary in time. This can be generalized later.

## Quantum mechanical treatment of multiparticle systems

For a non-interacting system:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = H(\mathbf{r}_1) + H(\mathbf{r}_2) + \dots H(\mathbf{r}_N)$$

Energy eigenstates:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Simplification for separable Hamiltonian

$$\text{For: } H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1)$$

$$H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2)$$

Solution to the many particle problem

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\dots\varphi_z(\mathbf{r}_N)$$

$$E = \varepsilon_a + \varepsilon_b + \dots\varepsilon_z$$

← Turns out to not be generally correct.

In order to describe our system we need to account for the coordinates of our N particles in the probability amplitude  $\psi$ . Since the particles do not interact with each other, we can analyze the individual particle states by solving each single particle Schrodinger equation in terms of their probability amplitudes  $\varphi$ . The many particle probability amplitude is then simply the product of the single particle functions and the eigenstate energy is the sum of the single particle energies.

## Quantum mechanical treatment of multiparticle systems – non-interacting particles

The treatment given on previous slides, assumes that the particles are **distinguishable**.

A more sophisticated treatment is needed for **indistinguishable** particles.

Two types of indistinguishable particles:

Fermi particles:  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$

Bose particles:  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = +\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$

However the product of single particle states is missing some of the known properties of indistinguishable multiparticle systems. In particular, it is known that there are two types of particles, named Fermi particles and Bose particles which behave differently. The difference between the two is represented in terms of how their probability amplitudes are affected by the exchange of two particles in the function.

Consider two particles in a one-dimension labeled with coordinates  $x_1$  and  $x_2$ . Identify each of them as Fermi, Bose, or neither in terms of the functional forms.

1.  $\psi(x_1, x_2) = e^{-\alpha|x_1-x_2|}$

2.  $\psi(x_1, x_2) = (x_1 - x_2)e^{-\alpha|x_1-x_2|}$

3.  $\psi(x_1, x_2) = x_1e^{-\alpha|x_1-x_2|}$

**Quantum mechanical treatment of multiparticle systems –  
non-interacting Fermi particles**

Fermi particles:  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$

Example for two particles:

$$H(\mathbf{r}_1, \mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\text{For: } H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1)$$

$$H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2)$$

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1))$$

$$E = \varepsilon_a + \varepsilon_b$$

Returning to the non-interacting particles. By construction, this form of psi satisfies the Fermi particle exchange equation. What do you think happens of the two functions phi<sub>a</sub> and phi<sub>b</sub> have exactly the same shape?

**Quantum mechanical treatment of multiparticle systems –  
non-interacting Fermi particles**

Fermi particles:  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$

Example for  $N$  particles using Slater determinant:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix}$$

$$E = \varepsilon_a + \varepsilon_b + \dots + \varepsilon_z$$

The antisymmetrization of single particle states can be conveniently be written in terms of a so-called Slater determinant.

**Quantum mechanical treatment of multiparticle systems –  
non-interacting Bose particles**

Bose particles:  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$

Example for two particles:

$$H(\mathbf{r}_1, \mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\text{For: } H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1)$$

$$H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2)$$

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1))$$

$$E = \varepsilon_a + \varepsilon_b$$

Returning to the non-interacting particles. By construction, this form of psi satisfies the Bose particle exchange equation. What do you think happens if the two functions  $\varphi_a$  and  $\varphi_b$  have exactly the same shape?

**Quantum mechanical treatment of multiparticle systems –  
non-interacting particles; multiplicity of eigenstates**

**Consider a system with two independent particle states  
and two particles:**

$$\begin{array}{ll} \text{————} & \varepsilon_b & H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1) \\ \text{————} & \varepsilon_a & H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2) \end{array}$$

Possible states for distinguishable particles:

$$\begin{array}{ll} \psi_I(\mathbf{r}_1, \mathbf{r}_2) = \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) & E_I = \varepsilon_a + \varepsilon_b \\ \psi_{II}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1) & E_{II} = \varepsilon_a + \varepsilon_b \\ \psi_{III}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_a(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) & E_{III} = 2\varepsilon_a \\ \psi_{IV}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_b(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) & E_{IV} = 2\varepsilon_b \end{array}$$

Here we can find 4 different 2-particle states for the distinguishable particle case.



**Quantum mechanical treatment of multiparticle systems –  
non-interacting particles; multiplicity of eigenstates**

**Consider a system with two independent particle states  
and two particles:**

$$\begin{array}{ll} \text{————} & \varepsilon_b & H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1) \\ \text{————} & \varepsilon_a & H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2) \end{array}$$

Possible states for Fermi particles:

$$\psi_I(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)) \quad E_I = \varepsilon_a + \varepsilon_b$$

Is there really only one possibility here?

**Quantum mechanical treatment of multiparticle systems –  
non-interacting particles; multiplicity of eigenstates**

**Consider a system with two independent particle states  
and two particles:**

$$\begin{array}{ll} \text{————} & \varepsilon_b & H(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) = \varepsilon_a\varphi_a(\mathbf{r}_1) \\ \text{————} & \varepsilon_a & H(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) = \varepsilon_b\varphi_b(\mathbf{r}_2) \end{array}$$

Possible states for Bose particles:

$$\psi_I(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)) \quad E_I = \varepsilon_a + \varepsilon_b$$

$$\psi_{II}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_a(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) \quad E_{II} = 2\varepsilon_a$$

$$\psi_{III}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_b(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) \quad E_{III} = 2\varepsilon_b$$

How could it be that there are more possibilities here?

### Treating multiparticle systems using “second” quantization formalism

Consider a non-interacting system:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = H(\mathbf{r}_1) + H(\mathbf{r}_2) + \dots H(\mathbf{r}_N)$$

For a system of non-interacting identical particles, the single particle Hamiltonians  $H(\mathbf{r}_i)$  are also identical. Suppose we have a complete basis set that describes each single-particle state;

$$\Phi(\mathbf{r}, t) = \sum_{\alpha} C_{\alpha} \varphi_{\alpha}(\mathbf{r}) e^{-i\varepsilon_{\alpha} t / \hbar}$$

These basis functions can be used to represent the many particle wavefunctions.

It turns out that the creation and annihilation operators can be used to help us with a convenient formalism to take the particle symmetry into account. We need to start with a complete set of single particle basis functions.

### Operators for Bose system

$$\text{Creation operator: } b_{\alpha}^{\dagger} |0\rangle = |1_{\alpha}\rangle \quad b_{\alpha}^{\dagger} |n_{\alpha}\rangle = \sqrt{n_{\alpha} + 1} |n_{\alpha} + 1\rangle$$

$$\text{Destruction operator: } b_{\alpha} |1_{\alpha}\rangle = |0_{\alpha}\rangle \quad b_{\alpha} |n_{\alpha}\rangle = \sqrt{n_{\alpha}} |n_{\alpha} - 1\rangle$$

### Commutator notation

$$b_{\alpha}^{\dagger} b_{\beta}^{\dagger} = b_{\beta}^{\dagger} b_{\alpha}^{\dagger}$$

$$[b_{\alpha}^{\dagger}, b_{\beta}^{\dagger}] = 0$$

$$b_{\alpha} b_{\beta} = b_{\beta} b_{\alpha}$$

$$[b_{\alpha}, b_{\beta}] = 0$$

$$[b_{\alpha}, b_{\beta}^{\dagger}] = \delta_{\alpha\beta}$$

From our experience with creation and annihilation operators we can deduce the following relationships .

### Example for Fermi particles

Slater determinant for  $N$  particles:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix}$$

Second quantization representation:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle \Rightarrow |n_a n_b n_c \dots n_z\rangle$$

**For Fermi particles, the occupation eigenvalues can be  $n_a=0$  or  $1$**

Now, consider the case for Fermi particles. Why are the occupation eigenvalues restricted as stated for Fermi particles?

### Operators for Fermi system

Creation operator:  $f_{\alpha}^{\dagger} |0\rangle = |1_{\alpha}\rangle$

Destruction operator:  $f_{\alpha} |1_{\alpha}\rangle = |0_{\alpha}\rangle$

#### Anti commutator notation

$$f_{\alpha}^{\dagger} f_{\beta}^{\dagger} = -f_{\beta}^{\dagger} f_{\alpha}^{\dagger}$$

$$\{f_{\alpha}^{\dagger}, f_{\beta}^{\dagger}\} = 0$$

$$f_{\alpha} f_{\beta} = -f_{\beta} f_{\alpha}$$

$$\{f_{\alpha}, f_{\beta}\} = 0$$

$$\{f_{\alpha}, f_{\beta}^{\dagger}\} = \delta_{\alpha\beta}$$

We will show next time, that we construct creation and annihilation operators for Fermi particles as well. These ideas will be elaborated next time.