PHY 742 Quantum Mechanics II
12-12:50 AM MWF Olin 103

Notes for Lecture 26

Quantum mechanics of multiple particle systems

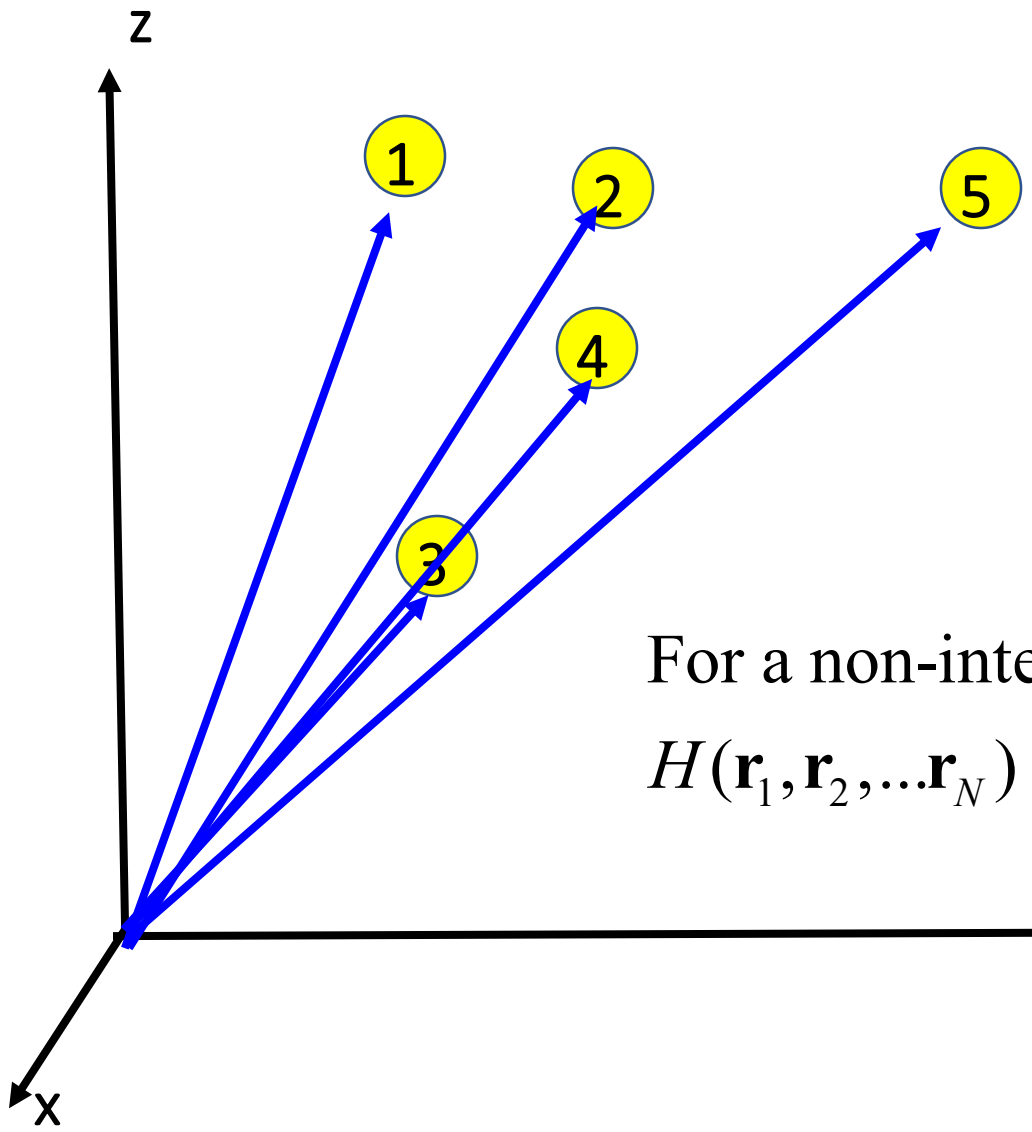
Continue reviewing Professor Carlson's textbook: Chapter 10. Multiple particles (Sec. A&B)

1. Non-interacting particles
   a. Second quantized formalism for Bose particles
   b. Second quantized formalism for Fermi particles
2. Interaction terms

Tenative plan --

21	Fri: 03/25/2022	Chap. 5 & 17	Quantization of the Electromagnetic Field	#17	03/28/2022
22	Mon: 03/28/2022	Chap. 17	Quantization of the Electromagnetic Field	#18	03/30/2022
23	Wed: 03/30/2022	Chap. 17	Quantization of the Electromagnetic Field	#19	04/01/2022
24	Fri: 04/01/2022	Chap. 18	Absorption and emission of photons		
25	Mon: 04/04/2022	Chap. 10 (review)	Multiparticle systems and second quantization	#20	04/06/2022
26	Wed: 04/06/2022	Chap. 10 (review)	Multiparticle systems and second quantization		
27	Fri: 04/08/2022		Multi electron atoms		
28	Mon: 04/11/2022		Multi electron atoms		
29	Wed: 04/13/2022		Hubbard model with multiple electrons		
	Fri: 04/15/2022	*No class*	Holiday		
30	Mon: 04/18/2022		Hubbard model with multiple electrons		
31	Wed: 04/20/2022		BCS model of superconductivity		
32	Fri: 04/22/2022		BCS model of superconductivity		

Quantum mechanical treatment of multiparticle systems



For a non-interacting system:

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

Quantum mechanical treatment of multiparticle systems

For a non-interacting system:

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

Here we are using *h*(r) to denote single particle contributions.

Energy eigenstates:

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

Simplification for separable Hamiltonian

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

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

$$E = \varepsilon_a + \varepsilon_b + \ldots.\varepsilon_z$$

Does not take into account particle symmetry.

Refinement of the results for treatment of distinguishable or indistinguishable particles

$\mathcal{P}$=permutation operator

$$\mathcal{P}(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)) \equiv \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)$$

For distinguishable particles:

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

Two types of indistinguishable particles:

Fermi particles: $\psi_F(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i\ldots\mathbf{r}_j\ldots\mathbf{r}_N) = -\psi_F(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_j\ldots\mathbf{r}_i\ldots\mathbf{r}_N)$

$$\Rightarrow \psi_F(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i\ldots\mathbf{r}_j\ldots\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}(-1)^{\mathcal{P}}\mathcal{P}\left(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\varphi_c(\mathbf{r}_3)\ldots\varphi_z(\mathbf{r}_N)\right)$$

Bose particles: $\psi_B(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i\ldots\mathbf{r}_j\ldots\mathbf{r}_N) = +\psi_B(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_j\ldots\mathbf{r}_i\ldots\mathbf{r}_N)$

$$\Rightarrow \psi_B(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i\ldots\mathbf{r}_j\ldots\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}\mathcal{P}\left(\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\varphi_c(\mathbf{r}_3)\ldots\varphi_z(\mathbf{r}_N)\right)$$

Energy eigenstates: $H(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N) = E\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)$

$$E = \varepsilon_a + \varepsilon_b + \ldots.\varepsilon_z$$

Treating multiparticle systems using "second" quantization formalism

Consider a non-interacting system:

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

For a system of non-interacting identical particles,

the single particle Hamiltonians $h(\mathbf{r}_1)$ are also identical.

Eigenstates of the single particle Hamiltonian:

$$h(\mathbf{r})\varphi_a(\mathbf{r}) = \varepsilon_a \varphi_a(\mathbf{r})$$

$$h(\mathbf{r})\varphi_b(\mathbf{r}) = \varepsilon_b \varphi_b(\mathbf{r})$$

$$\vdots$$

$$h(\mathbf{r})\varphi_z(\mathbf{r}) = \varepsilon_z \varphi_z(\mathbf{r})$$

We now assume that the single particle eigenstates $\{\varphi_a(\mathbf{r})\}$

span the function space available to each particle.

Treating multiparticle systems using "second" quantization formalism -- continued

$$h(\mathbf{r}_1) = \sum_\alpha \left|\varphi_\alpha(\mathbf{r}_1)\right\rangle \varepsilon_\alpha \left\langle\varphi_\alpha(\mathbf{r}_1)\right|$$

$$\left\langle\varphi_\alpha(\mathbf{r}_1)\middle|\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)\right\rangle = n_\alpha$$

=number of times basis function $\varphi_\alpha(\mathbf{r}_1)$ appears in the product representation

Second quantization representation:

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

$$H(\mathbf{r}_1,\mathbf{r}_2\ldots.\mathbf{r}_N) \Rightarrow \sum_\alpha \varepsilon_\alpha N_\alpha$$

Here the notation N_α indicates an operator

where the number operator acts as follows:

$$N_\alpha \left|n_a n_b n_c \ldots. n_z\right\rangle = n_\alpha \left|n_a n_b n_c .. n_\alpha .. n_z\right\rangle$$

In general, the number operator can be expressed in terms of a product of two operators. For the case of Bose particles, these operators are very similar to the raising and lowering operators of the harmonic oscillator.

$$N_\alpha = b_\alpha^\dagger b_\alpha$$

Bose particle commutation relations:

$$[b_\alpha, b_\beta] \equiv b_\alpha b_\beta - b_\beta b_\alpha = 0$$

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

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

Second quantization for Bose particles, continued

$$b_\alpha^\dagger b_\alpha \left| n_\alpha \right\rangle = n_\alpha \left| n_\alpha \right\rangle$$

$$b_\alpha \left| n_\alpha \right\rangle = \sqrt{n_\alpha} \left| n_\alpha - 1 \right\rangle$$

$$b_\alpha^\dagger \left| n_\alpha \right\rangle = \sqrt{n_\alpha + 1} \left| n_\alpha + 1 \right\rangle$$

For example: $b_\alpha^\dagger \left| 0_\alpha \right\rangle = \left| 1_\alpha \right\rangle$

$$b_\alpha^\dagger \left| 1_\alpha \right\rangle = \sqrt{2} \left| 2_\alpha \right\rangle$$

$$\left(b_\alpha^\dagger \right)^n \left| 0_\alpha \right\rangle = \sqrt{n!} \left| n_\alpha \right\rangle$$

$$\Rightarrow n_\alpha = 0, 1, 2, \ldots\ldots \infty$$

To represent 3 states: $\left| n_1 n_2 n_3 \right\rangle = \dfrac{\left(b_3^\dagger \right)^{n_3}}{\sqrt{n_3!}} \dfrac{\left(b_2^\dagger \right)^{n_2}}{\sqrt{n_2!}} \dfrac{\left(b_1^\dagger \right)^{n_1}}{\sqrt{n_1!}} \left| 0 \right\rangle$

Second quantization for Fermi particles

$$N_\alpha = f_\alpha^\dagger f_\alpha$$

Fermi particle anticommutation relations:

$$\left\{ f_\alpha , f_\beta \right\} \equiv f_\alpha f_\beta + f_\beta f_\alpha = 0$$

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

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

Second quantized creation and annhilation Fermi operators

$$f_\alpha^\dagger f_\alpha \left| n_\alpha \right\rangle = n_\alpha \left| n_\alpha \right\rangle$$

$$f_\alpha \left| n_\alpha \right\rangle = \sqrt{n_\alpha} \left| 1 - n_\alpha \right\rangle$$

$$f^\dagger{}_\alpha \left| n_\alpha \right\rangle = \sqrt{1 - n_\alpha} \left| 1 - n_\alpha \right\rangle$$

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

Non-trivial operations:

$$f_\alpha \left| 0_\alpha \right\rangle = 0 \qquad f_\alpha \left| 1_\alpha \right\rangle = \left| 0_\alpha \right\rangle$$

$$f_\alpha^\dagger \left| 0_\alpha \right\rangle = \left| 1_\alpha \right\rangle \quad f_\alpha^\dagger \left| 1_\alpha \right\rangle = 0$$

$$\Rightarrow n_\alpha = 0 \text{ or } 1$$

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

Some details --

Second quantized creation and annhilation Fermi operators

Starting with the result: $f_a^\dagger f_a \left| n_a \right\rangle = n_a \left| n_a \right\rangle$

We want to show: $f_a \left| n_a \right\rangle = \sqrt{n_a} \left| 1 - n_a \right\rangle$

Consider: $f_a^\dagger f_a \left(f_a \left| n_a \right\rangle \right) = f_a^\dagger f_a f_a \left| n_a \right\rangle = \left(1 - f_a f_a^\dagger \right) f_a \left| n_a \right\rangle$

$$= \left(f_a - f_a f_a^\dagger f_a \right) \left| n_a \right\rangle = f_a \left(1 - n_a \right) \left| n_a \right\rangle$$

This implies that $f_a \left| n_a \right\rangle = K \left| 1 - n_a \right\rangle$

Assuming normalized eigenstates $\left\langle 1 - n_a \right| \left. 1 - n_a \right\rangle = 1$

$$\left| K \right|^2 = \left\langle n_a \right| f_a^\dagger f_a \left| n_a \right\rangle = n_a$$

Second quantized creation and annhilation Fermi operators

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

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

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

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

Note that the symmetry of the wavefunction is built into the formalism for Bose particles

$$b_a^\dagger b_b^\dagger \left|0\right\rangle = b_b^\dagger b_a^\dagger \left|0\right\rangle$$

Note that the antisymmetry of the wavefunction is built into the formalism for Fermi particles

$$f_a^\dagger f_b^\dagger \left|0\right\rangle = -f_b^\dagger f_a^\dagger \left|0\right\rangle$$

In this case, the second quantized forms for the non-interacting system can be written:

$$H(\mathbf{r}_1, \mathbf{r}_2 .... \mathbf{r}_N) \Rightarrow \sum_\alpha \varepsilon_\alpha b_\alpha^\dagger b_\alpha \quad \text{for Bose particles}$$

$$H(\mathbf{r}_1, \mathbf{r}_2 .... \mathbf{r}_N) \Rightarrow \sum_\alpha \varepsilon_\alpha f_\alpha^\dagger f_\alpha \quad \text{for Fermi particles}$$

More general treatment of multiparticle system

$$H(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=\sum_{i=1}^{N}h(\mathbf{r}_i)+V(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)$$

interparticle interaction

$$\text{Often: } V(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=\sum_{i=1}^{N}\sum_{(i>j)\ j=1}^{N}v(\mathbf{r}_i-\mathbf{r}_j)$$

In this case, the second quantized forms can be written

$$H(\mathbf{r}_1,\mathbf{r}_2\ldots.\mathbf{r}_N)\Rightarrow\sum_{\alpha}\varepsilon_\alpha b_\alpha^\dagger b_\alpha+\sum_{\alpha\beta\gamma\delta}v_{\alpha\beta\gamma\delta}b_\alpha^\dagger b_\beta^\dagger b_\delta b_\gamma \quad \text{for Bose particles}$$

$$H(\mathbf{r}_1,\mathbf{r}_2\ldots.\mathbf{r}_N)\Rightarrow\sum_{\alpha}\varepsilon_\alpha f_\alpha^\dagger f_\alpha+\sum_{\alpha\beta\gamma\delta}v_{\alpha\beta\gamma\delta}f_\alpha^\dagger f_\beta^\dagger f_\delta f_\gamma \quad \text{for Fermi particles}$$

Here $v_{\alpha\beta\gamma\delta}$ denotes matrix elements such as

$$v_{\alpha\beta\gamma\delta}=\int d^3r_1\int d^3r_2\ \varphi_\alpha^{\ *}(\mathbf{r}_1)\varphi_\beta^{\ *}(\mathbf{r}_2)v(\mathbf{r}_1-\mathbf{r}_2)\varphi_\gamma(\mathbf{r}_1)\varphi_\delta(\mathbf{r}_2)$$

Pros and Cons for using second quantization –

Pros –

1. **Beautiful, compact, ….**
2. **Worthy of physicists …**

Cons –

1. **Does not really introduce new physics**
2. **Slater determinants and symmetrization/antisymmetrization operators are good enough**

Example of a multi-electron atom – He atom with 2 electrons and Z=2

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

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

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

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?

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

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

Second quantized version of the He atom Hamiltonian

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

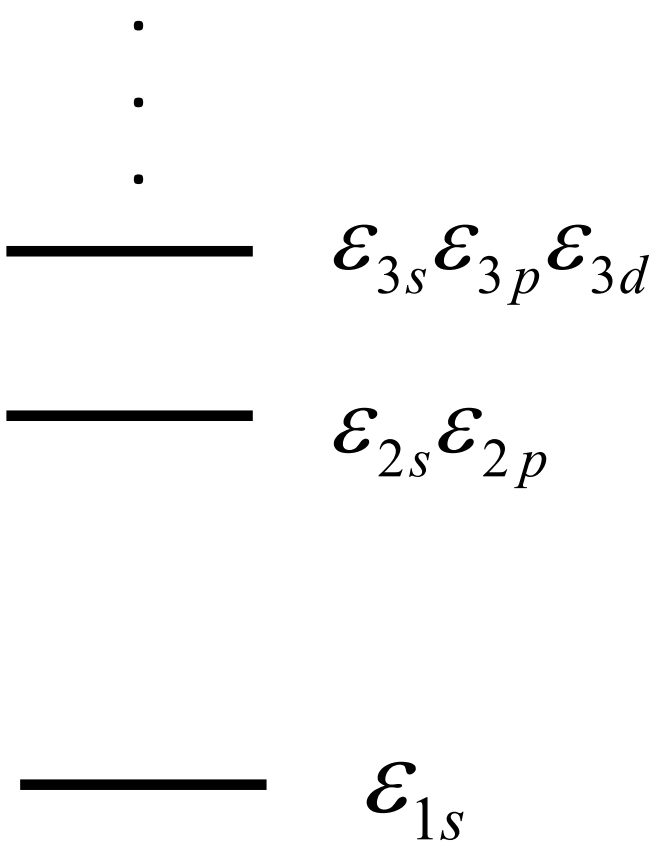
Here v_{ijkl} denotes matrix elements such as

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

The matrix element $i \equiv nlmm_s$

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

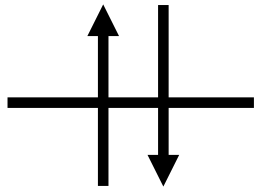
Spectrum of single particle states for He atom (schematic)



Ground state configuration for He atom

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

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



ε_{1s}

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

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

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

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

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

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

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

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

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

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

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

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 $l = j$: $f_j f_i f_i^\dagger f_j^\dagger f_j f_i f_i^\dagger f_j^\dagger = f_i f_i^\dagger f_j f_j^\dagger f_i f_i^\dagger f_j f_j^\dagger$

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_j f_i f_i^\dagger f_j^\dagger | 0 \rangle = 1 \qquad \Rightarrow v_{ijij}$$

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

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_i f_j f_i^\dagger f_j^\dagger | 0 \rangle = -1 \qquad \Rightarrow -v_{ijji}$$

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 $\psi = f^\dagger_{1s\alpha} f^\dagger_{1s\beta} |0\rangle$

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

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

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

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

$$v_{ijji} = 0$$

Why?

Next time, we will analyze this result and consider extension of the analysis to excited electronic states of He.