

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 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.

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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

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

Your questions –

From Surya:

1. Can you explain why the Hamiltonian of is expressed in second quantized form? The hamiltonian is totally unique when expressing in terms of creations and annihilation operators. But I don't understand how we can come up with those expressions.
2. I am still not getting how we can get $f|n\rangle = (n)^{1/2}|1-n\rangle$ using anticommutation relation. Would you mind giving a hint?

From Trevor:

1. On slide 16, taking a guess for why $v_{ijji} = 0$: is it because ϕ_{1sa} and ϕ_{1sb} are linearly independent eigenstates due to their different spins? so when you integrate over $(\phi_{1sa}(r1))^*(\phi_{1sb}(r1))$ it comes out as zero, I would think.

Question: Can you explain why the Hamiltonian of is expressed in second quantized form? The Hamiltonian is totally unique when expressing in terms of creations and annihilation operators. But I don't understand how we can come up with those expressions.

Comments: It is totally reasonable to question the use of second quantization for treating many particle problems. It is in fact just a mathematical device, to help the analysis. In fact, the Hamiltonian is not completely "unique" since it relies on the use of a particular basis set. As a point in its favor, it has been very productively used to solve some very complicated many body problems (with the help of diagram formalisms and computer analysis, etc.) I personally find that it most productive to go back and forth between second and first quantization formalisms.

Question: On slide 16, taking a guess for why $v_{ijji} = 0$: is it because ϕ_{1sa} and ϕ_{1sb} are linearly independent eigenstates due to their different spins? so when you integrate over $(\phi_{1sa}(r_1))^*(\phi_{1sb}(r_1))$ it comes out as zero, I would think.

Comment: Your analysis is correct.

$$v_{ijkl} \equiv \langle \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2) \rangle$$

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

$$v_{ijji} = \langle \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \rangle$$

$$v_{ijji} = 0 \quad \text{because } \langle \alpha | \beta \rangle = 0$$

Question: I am still not getting how we can get $f|n\rangle = \sqrt{n} |1-n\rangle$ using anticommutation relations. Would you mind giving a hint?

Second quantized creation and annihilation Fermi operators

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

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

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

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

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

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

Slides from original lecture --

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, \dots the second quantization operators work as follows.

Second quantization for Fermi particles

$$N_a = f_a^\dagger f_a$$

Fermi particle anticommutation relations:

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

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

$$\{f_a, f_b^\dagger\} = \delta_{ab} \qquad f_a f_a^\dagger + f_a^\dagger f_a = 1$$

Review of Fermi creation and annihilation operators.

Second quantized creation and annihilation Fermi operators

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

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

$$f_a^\dagger |n_a\rangle = \sqrt{1-n_a} |1+n_a\rangle$$

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

Non-trivial operations:

$$f_a |0_a\rangle = 0 \quad f_a |1_a\rangle = |0_a\rangle$$

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

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

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

These results follow from the anti-commutation relations

PERIODIC TABLE
Atomic Properties of the Elements

NIST National Institute of Standards and Technology
U.S. Department of Commerce

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS^a
(Based on 1983 CODATA recommended values, with the exception of the two hyperfine splits of the ground state of ¹³³Cs)

Physical Measurement Laboratory www.nist.gov
Standard Reference Data

For the most accurate values of these and other constants, visit www.nist.gov/constants.

Solids
 Liquids
 Gases
 Artificially Prepared

1 1s ¹ H Hydrogen 1.00794 1.00811	2 1s ² He Helium 4.0026 4.002603253(15)	3 2s ¹ Li Lithium 6.941 6.94087	4 2s ² Be Beryllium 9.012 9.012182	5 2s ² 2p ¹ B Boron 10.811 10.8107	6 2s ² 2p ² C Carbon 12.011 12.0107	7 2s ² 2p ² N Nitrogen 14.007 14.00643	8 2s ² 2p ² O Oxygen 15.999 15.99903	9 2s ² 2p ² F Fluorine 18.998 18.998403223	10 2s ² 2p ² Ne Neon 20.180 20.1797	11 3s ¹ Na Sodium 22.990 22.98976928	12 3s ² Mg Magnesium 24.305 24.30409	13 3s ² 3p ¹ Al Aluminum 26.982 26.9815385	14 3s ² 3p ² Si Silicon 28.086 28.0855836	15 3s ² 3p ² P Phosphorus 30.974 30.973761998	16 3s ² 3p ² S Sulfur 32.065 32.064	17 3s ² 3p ² Cl Chlorine 35.453 35.4527	18 3s ² 3p ² Ar Argon 39.948 39.9481634	19 3d ¹ 4s ¹ K Potassium 39.098 39.0983	20 3d ¹ 4s ¹ Ca Calcium 40.078 40.0783	21 3d ² 4s ¹ Sc Scandium 44.956 44.9559376	22 3d ² 4s ¹ Ti Titanium 47.883 47.8828	23 3d ² 4s ¹ V Vanadium 50.942 50.9415	24 3d ³ 4s ¹ Cr Chromium 51.996 51.9961	25 3d ³ 4s ¹ Mn Manganese 54.938 54.938044	26 3d ⁵ 4s ¹ Fe Iron 55.845 55.8452	27 3d ⁶ 4s ¹ Co Cobalt 58.933 58.933194	28 3d ⁷ 4s ¹ Ni Nickel 58.933 58.933194	29 3d ⁸ 4s ¹ Cu Copper 63.546 63.546	30 3d ¹⁰ 4s ¹ Zn Zinc 65.38 65.38	31 3d ¹⁰ 4s ¹ Ga Gallium 69.723 69.7231	32 3d ¹⁰ 4s ¹ Ge Germanium 72.631 72.63081	33 3d ¹⁰ 4s ¹ As Arsenic 74.922 74.9216	34 3d ¹⁰ 4s ¹ Se Selenium 78.972 78.9718	35 3d ¹⁰ 4s ¹ Br Bromine 79.904 79.904	36 3d ¹⁰ 4s ¹ Kr Krypton 83.796 83.796	37 4d ¹ 5s ¹ Rb Rubidium 85.468 85.4678	38 4d ¹ 5s ¹ Sr Strontium 87.62 87.62	39 4d ² 5s ¹ Y Yttrium 88.906 88.90584	40 4d ² 5s ¹ Zr Zirconium 91.224 91.2242	41 4d ² 5s ¹ Nb Niobium 92.906 92.90638	42 4d ⁴ 5s ¹ Mo Molybdenum 95.94 95.94	43 4d ⁵ 5s ¹ Tc Technetium 98.906 98.906251	44 4d ⁵ 5s ¹ Ru Ruthenium 101.07 101.072	45 4d ⁶ 5s ¹ Rh Rhodium 102.91 102.91	46 4d ⁷ 5s ¹ Pd Palladium 106.36 106.36	47 4d ⁸ 5s ¹ Ag Silver 107.87 107.8682	48 4d ¹⁰ 5s ¹ Cd Cadmium 112.41 112.411	49 4d ¹⁰ 5s ¹ In Indium 114.82 114.818	50 4d ¹⁰ 5s ¹ Sn Tin 118.71 118.710	51 4d ¹⁰ 5s ¹ Sb Antimony 121.76 121.757	52 4d ¹⁰ 5s ¹ Te Tellurium 127.60 127.603	53 4d ¹⁰ 5s ¹ I Iodine 126.91 126.90545	54 4d ¹⁰ 5s ¹ Xe Xenon 131.29 131.294	55 4d ¹⁰ 5s ¹ Cs Cesium 132.91 132.905451963	56 4d ¹⁰ 5s ¹ Ba Barium 137.33 137.327	57 4f ¹ 5d ¹ La Lanthanum 138.91 138.90547	58 4f ¹ 5d ¹ Ce Cerium 140.12 140.124	59 4f ¹ 5d ¹ Pr Praseodymium 140.91 140.90766	60 4f ¹ 5d ¹ Nd Neodymium 144.24 144.242	61 4f ¹ 5d ¹ Pm Promethium 144.91 144.91288	62 4f ¹ 5d ¹ Sm Samarium 150.36 150.36	63 4f ¹ 5d ¹ Eu Europium 151.96 151.964	64 4f ¹ 5d ¹ Gd Gadolinium 157.25 157.254	65 4f ¹ 5d ¹ Tb Terbium 158.93 158.92535	66 4f ¹ 5d ¹ Dy Dysprosium 162.50 162.50014	67 4f ¹ 5d ¹ Ho Holmium 164.93 164.93032	68 4f ¹ 5d ¹ Er Erbium 167.26 167.259	69 4f ¹ 5d ¹ Tm Thulium 168.93 168.934	70 4f ¹ 5d ¹ Yb Ytterbium 173.05 173.054	71 4f ¹ 5d ¹ Lu Lutetium 174.97 174.96706	72 4f ¹⁴ 5d ¹ Hf Hafnium 178.49 178.49	73 4f ¹⁴ 5d ¹ Ta Tantalum 180.95 180.94788	74 4f ¹⁴ 5d ¹ W Tungsten 183.84 183.84	75 4f ¹⁴ 5d ¹ Re Rhenium 186.21 186.207	76 4f ¹⁴ 5d ¹ Os Osmium 190.23 190.23	77 4f ¹⁴ 5d ¹ Ir Iridium 192.22 192.222	78 4f ¹⁴ 5d ¹ Pt Platinum 195.08 195.083	79 4f ¹⁴ 5d ¹ Au Gold 196.97 196.966569	80 4f ¹⁴ 5d ¹ Hg Mercury 200.59 200.59	81 4f ¹⁴ 5d ¹ Tl Thallium 204.38 204.38	82 4f ¹⁴ 5d ¹ Pb Lead 207.2 207.2	83 4f ¹⁴ 5d ¹ Bi Bismuth 208.98 208.9804	84 4f ¹⁴ 5d ¹ Po Polonium 209 209	85 4f ¹⁴ 5d ¹ At Astatine 210 210	86 4f ¹⁴ 5d ¹ Rn Radon 222 222	87 5d ¹ 6s ¹ Fr Francium 223 223	88 5d ¹ 6s ¹ Ra Radium 226 226	89 4f ¹⁴ 5d ¹ 6s ¹ Ac Actinium 227 227	90 4f ¹⁴ 5d ¹ 6s ¹ Th Thorium 232.04 232.0377	91 4f ¹⁴ 5d ¹ 6s ¹ Pa Protactinium 231.04 231.036888	92 4f ¹⁴ 5d ¹ 6s ¹ U Uranium 238.03 238.02891	93 4f ¹⁴ 5d ¹ 6s ¹ Np Neptunium 237.05 237.0481734	94 4f ¹⁴ 5d ¹ 6s ¹ Pu Plutonium 244.06 244.0643083	95 4f ¹⁴ 5d ¹ 6s ¹ Am Americium 243.06 243.061381	96 4f ¹⁴ 5d ¹ 6s ¹ Cm Curium 247.07 247.070351	97 4f ¹⁴ 5d ¹ 6s ¹ Bk Berkelium 247.07 247.070351	98 4f ¹⁴ 5d ¹ 6s ¹ Cf Californium 251.08 251.083208	99 4f ¹⁴ 5d ¹ 6s ¹ Es Einsteinium 252.08 252.083208	100 4f ¹⁴ 5d ¹ 6s ¹ Fm Fermium 257.10 257.10	101 4f ¹⁴ 5d ¹ 6s ¹ Md Mendelevium 258.10 258.10	102 4f ¹⁴ 5d ¹ 6s ¹ No Nobelium 259.10 259.10	103 4f ¹⁴ 5d ¹ 6s ¹ Lr Lawrencium 260.10 260.10	104 5d ¹ 6s ¹ Rf Rutherfordium 261.10 261.10	105 5d ¹ 6s ¹ Db Dubnium 262.10 262.10	106 5d ¹ 6s ¹ Sg Seaborgium 263.10 263.10	107 5d ¹ 6s ¹ Bh Bohrium 264.10 264.10	108 5d ¹ 6s ¹ Hs Hassium 265.10 265.10	109 5d ¹ 6s ¹ Mt Meitnerium 266.10 266.10	110 5d ¹ 6s ¹ Ds Darmstadtium 267.10 267.10	111 5d ¹ 6s ¹ Rg Roentgenium 268.10 268.10	112 5d ¹ 6s ¹ Cn Copernicium 269.10 269.10	113 5d ¹ 6s ¹ Nh Nihonium 270.10 270.10	114 5d ¹ 6s ¹ Fl Flerovium 271.10 271.10	115 5d ¹ 6s ¹ Mc Moscovium 272.10 272.10	116 5d ¹ 6s ¹ Lv Livermorium 273.10 273.10	117 5d ¹ 6s ¹ Ts Tennessine 274.10 274.10	118 5d ¹ 6s ¹ Og Oganesson 275.10 275.10
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^aBased upon ¹³³Cs. () indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit www.nist.gov and www.nist.gov/constants.
NIST SP 960 (July 2019)

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2 1s⁰

He

Helium

4.0026

1s²

24.5874

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

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

$$\begin{aligned}
 H(\mathbf{r}_1, \mathbf{r}_2) &= -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &= -\frac{\hbar^2\nabla_1^2}{2m} - \frac{2e^2}{r_1} - \frac{\hbar^2\nabla_2^2}{2m} - \frac{2e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &= \underbrace{-\frac{\hbar^2\nabla_1^2}{2m} - \frac{2e^2}{r_1}}_{h(\mathbf{r}_1)} + \underbrace{-\frac{\hbar^2\nabla_2^2}{2m} - \frac{2e^2}{r_2}}_{h(\mathbf{r}_2)} + v_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2)
 \end{aligned}$$

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

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

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

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

The matrix element $i \equiv nlm m_s$

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

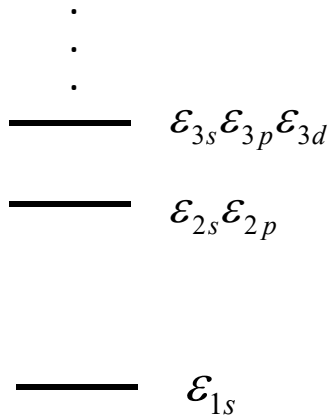
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Defining single particle and two particle interaction terms. Do you notice something odd on this slide?

Spectrum of single particle states for He atom (schematic)



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Non-interacting particle energy diagram

Ground state configuration for He atom

⋮
⋮
⋮
— $\mathcal{E}_{3s}\mathcal{E}_{3p}\mathcal{E}_{3d}$

— $\mathcal{E}_{2s}\mathcal{E}_{2p}$

↑ ↓
— \mathcal{E}_{1s}

$$\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$$

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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 $i \neq j$

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

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

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

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

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

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

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

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

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

Expectation value of Hamiltonian for ground state of He atom

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

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

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

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 $k \neq l$

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

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

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

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

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

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

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

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

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

Evaluation of two particle term, continued

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

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

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

$$v_{ijji} = 0$$

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,

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

What is the total electron spin of this He atom?

What is the total spin of the ground state of the He atom?

1. $S=0$?
2. $S=1$?
3. None of the above?

What do you know/want to know about atomic term analysis?

1. I'm good.
2. I would like to know more.
3. Please don't subject me to this nightmare!