

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.

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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.

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:

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

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

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

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

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

PERIODIC TABLE
Atomic Properties of the Elements

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

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS
Based on 1993 CODATA recommended values, with the exception of the speed of light in vacuum, which is exact.

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	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
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86	1159.0186	1161.0186	1163.0186	1165.0186	1167.0186	1169.0186	1171.0186	1173.0186	1175.0186	1177.0186	1179.0186	1181.0186	1183.0186	1185.0186	1187.0186	1189.0186	1191.0186	1193.0186	1195.0186	1197.0186	1199.0186	1201.0186	1203.0186	1205.0186	1207.0186	1209.0186	1211.0186	1213.0186	1215.0186	1217.0186	1219.0186	1221.0186	1223.0186	1225.0186	1227.0186	1229.0186	1231.0186	1233.0186	1235.0186	1237.0186	1239.0186	1241.0186	1243.0186	1245.0186	1247.0186	1249.0186	1251.0186	1253.0186	1255.0186	1257.0186	1259.0186	1261.0186	1263.0186	1265.0186	1267.0186	1269.0186	1271.0186	1273.0186	1275.0186	1277.0186	1279.0186	1281.0186	1283.0186	1285.0186	1287.0186	1289.0186	1291.0186	1293.0186	1295.0186	1297.0186	1299.0186	1301.0186	1303.0186	1305.0186	1307.0186	1309.0186	1311.0186	1313.0186	1315.0186	1317.0186	1319.0186	1321.0186	1323.0186	1325.0186	1327.0186	1329.0186	1331.0186	1333.0186	1335.0186	1337.0186	1339.0186	1341.0186	1343.0186	1345.0186	1347.0186	1349.0186	1351.0186	1353.0186	1355.0186	1357.0186	1359.0186	1361.0186	1363.0186	1365.0186	1367.0186	1369.0186	1371.0186	1373.0186	1375.0186	1377.0186	1379.0186	1381.0186	1383.0186	1385.0186	1387.0186	1389.0186	1391.0186	1393.0186	1395.0186	1397.0186	1399.0186	1401.0186	1403.0186	1405.0186	1407.0186	1409.0186	1411.0186	1413.0186	1415.0186	1417.0186	1419.0186	1421.0186	1423.0186	1425.0186	1427.0186	1429.0186	1431.0186	1433.0186	1435.0186	1437.0186	1439.0186	1441.0186	1443.0186	1445.0186	1447.0186	1449.0186	1451.0186	1453.0186	1455.0186	1457.0186	1459.0186	1461.0186	1463.0186	1465.0186	1467.0186	1469.0186	1471.0186	1473.0186	1475.0186	1477.0186	1479.0186	1481.0186	1483.0186	1485.0186	1487.0186	1489.0186	1491.0186	1493.0186	1495.0186	1497.0186	1499.0186	1501.0186	1503.0186	1505.0186	1507.0186	1509.0186	1511.0186	1513.0186	1515.0186	1517.0186	1519.0186	1521.0186	1523.0186	1525.0186	1527.0186	1529.0186	1531.0186	1533.0186	1535.0186	1537.0186	1539.0186	1541.0186	1543.0186	1545.0186	1547.0186	1549.0186	1551.0186	1553.0186	1555.0186	1557.0186	1559.0186	1561.0186	1563.0186	1565.0186	1567.0186	1569.0186	1571.0186	1573.0186	1575.0186	1577.0186	1579.0186	1581.0186	1583.0186	1585.0186	1587.0186	1589.0186	1591.0186	1593.0186	1595.0186	1597.0186	1599.0186	1601.0186	1603.0186	1605.0186	1607.0186	1609.0186	1611.0186	1613.0186	1615.0186	1617.0186	1619.0186	1621.0186	1623.0186	1625.0186	1627.0186	1629.0186</

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 $n\{0123..\}$

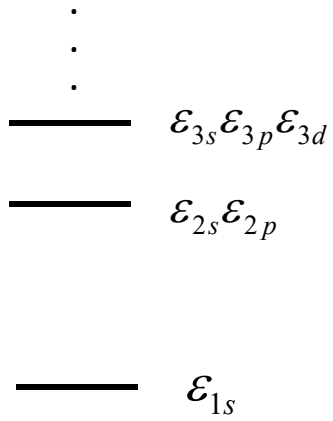
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Defining single particle and two particle interaction terms. Do you notice something odd on this slide?

Spectrum of single particle states for He atom (schematic)



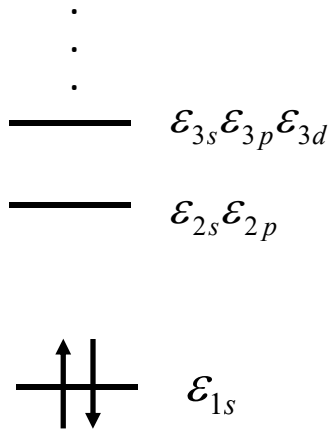
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Non-interacting particle energy diagram

Ground state configuration for He atom



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

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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

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

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

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?