PHY 742 Quantum Mechanics II

1-1:50 AM MWF via video link:

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

Plan for Lecture 28

Quantum mechanics of a multi electron atom

Continue reading Professor Carlson's textbook: Chapter X. Multiple particles (Sec. F)   Also review Chapter VIII. Spin and Adding Angular Momentum (Sec. C)

1. **Digression on atomic term analysis**
2. **Excited states of the He atom**

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

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	Chap. 10	Multielectron atoms		
	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		

No new homework assignment.   Time for completing any "outstanding" homework and planning for projects.

In principle, we can calculate the electronic structure for any atom in the periodic table. Last time we considered the ground state of the He atom.

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

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

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

$$= \qquad h(\mathbf{r}_1) \qquad + \qquad h(\mathbf{r}_2) \quad + v(\mathbf{r}_1,\mathbf{r}_2)$$

Single particle basis:

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

Setting up the basis for the problem.   In fact the analysis is equivalent to a first order perturbation theory for the interaction term v.

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 within the second quantization formalism.

Ground state configuration for He atom

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

$$\varepsilon_{2s}\varepsilon_{2p} \qquad \psi = f_{1s\alpha}^{\dagger} f_{1s\beta}^{\dagger} \left|0\right\rangle$$

$$\varepsilon_{1s}$$

Consider first the lowest energy state of this system.

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?

While the ground state of the He atom is a very simple case, it illustrates the general properties of many electron atoms in a spherical environments. Because of the spherical symmetry, total angular moment of the system is conserved. If we assume that spin-orbit interactions are negligible, then total spin angular momentum and total orbital angular momentum are each separately conserved. Please review Chapter 8 of your textbook to know how to "add" angular momentum using Clebsch-Gordan coefficients.

$$|jm\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 j_2; m_1 m_2\rangle \langle j_1 j_2; m_1 m_2 | jm\rangle \tag{8.12a}$$

$$|j_1 j_2; m_1 m_2\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^{j} |jm\rangle \langle jm | j_1 j_2; m_1 m_2\rangle \tag{8.12b}$$

Here $|jm\rangle$ describes the total angular moment quantum numbers, while $|j_1 j_2; m_1 m_2\rangle$ describes the product of two angular momenta $|j_1 j_2; m_1 m_2\rangle \equiv |j_1 m_1\rangle |j_2 m_2\rangle$. "$j$" can represent orbital or spin angular moment.

Note, for practical calculations of Clebsch-Gordan coefficients, a good source is NIST's DLMF -- https://dlmf.nist.gov/34.1

An often used alternative to the $3j$ symbol is the Clebsch–Gordan coefficient

34.1.1 $\quad \left(j_1 \, m_1 \, j_2 \, m_2 \mid j_1 \, j_2 \, j_3 \, m_3\right) = (-1)^{j_1 - j_2 + m_3} (2j_3 + 1)^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix};$

Professor Carlson also has a working maple script on his website.

For the spherical atom without spin-orbit coupling, the total spin angular momentum S and the total orbital angular momentum L are both conserved. The atomic term notation is ^{2S+1}L

Examples: $\quad ^1S, \, ^3S, \, ^1P, \, ^1D, \, ^4G....$

Example from NIST

NIST Atomic Spectra Database Levels Data

He I   198 Levels Found
Z = 2, He isoelectronic sequence

Configuration	Term	J	Level (eV)
$1s^2$	^{1}S	0	0.00000000
$1s2s$	^{3}S	1	[19.81961468]
$1s2s$	^{1}S	0	[20.61577496]
$1s2p$	^{3}P°	2	[20.96408703]
		1	[20.96409651]
		0	[20.96421899]
$1s2p$	^{1}P°	1	[21.21802284]

The atomic spectra of all of the elements have been well studied over the years and NIST has collected the data in the form of a table of atomic energy levels such as shown here for He.   The ground state of each atom is chosen as the zero of energy.   In this case, the lowest energy excitations are at higher energy by at approximately 20 eV or more.

Example from NIST

NIST Atomic Spectra Database
Levels Data

C I   435 Levels Found

Z = 6, C isoelectronic sequence

Configuration	Term	J	Level (eV)
$2s^2 2p^2$	^3P	0	0.0000000000
		1	0.0020354130
		2	0.0053825826
$2s^2 2p^2$	^1D	2	1.2637284
$2s^2 2p^2$	^1S	0	2.6840136

The atomic levels of C are very interesting. For the ground state configuration of 1s^2 2s^2 2p^2, we see that there are different arrangements leading to 3 different atomic terms. The lowest term has the designation ^3P while the highest term has the designation ^1S, having an energy 2.84 eV higher.

Back to the discussion of He

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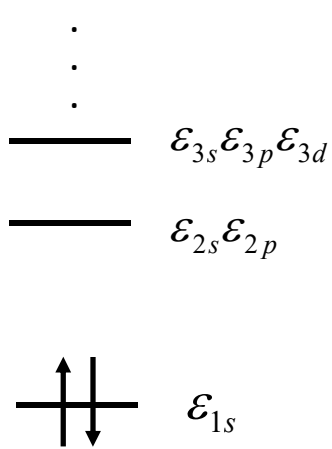
$$\psi = f^{\dagger}_{1s\alpha} f^{\dagger}_{1s\beta} \left|0\right\rangle$$

$\vdots$

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

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

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

$$S = 0 \qquad L = 0$$

$\uparrow\!\!\downarrow$ ε_{1s}

Atomic term: ^1S

This slide summarizes the analysis of the ground state wavefunction.

Digression --   How do we know that the total spin of this state is S=0?

$$\frac{1}{\sqrt{2}}\left(\alpha_1\beta_2 - \alpha_2\beta_1\right)$$

Clearly M_S=0 --   but do we really know that S=0?

What do you think?

Back to the discussion of He

A possible excited state:

$$\psi = f^{\dagger}_{1s\alpha} f^{\dagger}_{2s\alpha} \left| 0 \right\rangle$$

$$\psi =$$

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

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

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

$$S = 1 \qquad L = 0$$

ε_{1s}

Atomic term: $\quad {}^3S$

Now consider a possible excited state.   Notice that the spin degeneracy is specified as 3, while only one spin configuration is mentioned.   What can explain this?

Energy estimate of the ^3S excited state of He

$$\psi = f^\dagger_{1s\alpha} f^\dagger_{2s\alpha} \left| 0 \right\rangle$$

$$H = \sum_i \varepsilon_i f^\dagger_i f_i + \sum_{ijkl} v_{ijkl} f^\dagger_i f^\dagger_j f_l f_k$$

Evaluation of $\left\langle \psi \left| H \right| \psi \right\rangle$ for $\psi = f^\dagger_k f^\dagger_l \left| 0 \right\rangle \;\; (k \neq l)$

$$\left\langle \psi \left| H \right| \psi \right\rangle = \varepsilon_k + \varepsilon_l + v_{klkl} - v_{kllk}$$

$$= \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$$

This follows the analysis we discussed in Lecture 27.

Excited state energies -- continued

$$\langle \psi | H | \psi \rangle = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$$

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

$$v_{1s2s1s2s} = \int d^3r_1 d^3r_2 |\varphi_{1s}(\mathbf{r}_1)|^2 |\varphi_{2s}(\mathbf{r}_2)|^2 v(\mathbf{r}_1 - \mathbf{r}_2)$$

$$v_{1s2s2s1s} = \int d^3r_1 d^3r_2 \left(\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_1) \right)\left(\varphi_{1s}(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2) \right) v(\mathbf{r}_1 - \mathbf{r}_2)$$

Writing the spatial parts of the matrix elements in a way that we can evaluate them.

Specific basis states for He atom $\;Z=2\;$ in terms of $a_0\;$ (Bohr radius)

$$\varphi_{1s}(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}$$

$$\varphi_{2s}(\mathbf{r}) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^3\left(2-\frac{Zr}{a_0}\right)e^{-Zr/(2a_0)}$$

In this spherically symmetric case, the integrals can be evaluated:

$$v_{1s2s1s2s} = (4\pi)^2\int_0^\infty r_1^2 dr_1\int_0^\infty r_2^2 dr_2\left(\varphi_{1s}(r_1)\right)^2\left(\varphi_{2s}(r_2)\right)^2\frac{1}{r_>} = \frac{e^2}{a_0}\frac{17}{81}$$

$$v_{1s2s2s1s} = (4\pi)^2\int_0^\infty r_1^2 dr_1\int_0^\infty r_2^2 dr_2\left(\varphi_{1s}(r_1)\varphi_{2s}(r_1)\right)\left(\varphi_{1s}(r_2)\varphi_{2s}(r_2)\right)^2\frac{1}{r_>} = \frac{e^2}{a_0}\frac{16}{729}$$

Explicit formulas for He evaluated using Maple.

Maple script for evaluating integrals --

> $assume(Z > 0);\ assume(a > 0);$

> $f1s := r \rightarrow \dfrac{1}{\text{sqrt}(\text{Pi})} \cdot \left(\dfrac{Z}{a}\right)^{\frac{3}{2}} \exp\left(-\dfrac{Z \cdot r}{a}\right);$

$$f1s := r \mapsto \dfrac{\left(\dfrac{Z}{a}\right)^{3/2} e^{-\frac{Zr}{a}}}{\sqrt{\pi}}$$

> $f2s := r \rightarrow \dfrac{1}{\text{sqrt}(32 \cdot \text{Pi})} \cdot \left(\dfrac{Z}{a}\right)^{\frac{3}{2}} \cdot \left(2 - \dfrac{Z \cdot r}{a}\right) \exp\left(-\dfrac{Z \cdot r}{2 \cdot a}\right);$

$$f2s := r \mapsto \dfrac{\left(\dfrac{Z}{a}\right)^{3/2} \left(2 - \dfrac{Zr}{a}\right) e^{-\frac{Zr}{2a}}}{\sqrt{32\,\pi}}$$

> $v1 := (4 \cdot \text{Pi})^2 \cdot \left(int\!\left(x \cdot (f1s(x))^2 \cdot int(y^2 \cdot (f2s(y))^2,\, y=0..x),\, x=0..\text{infinity}\right) + int\!\left(x^2 \cdot (f1s(x))^2 \cdot int(y \cdot (f2s(y))^2,\, y=x..\text{infinity}),\, x=0..\text{infinity}\right)\right);$

$$v1 := \dfrac{17\, Z\!\sim}{81\, a\!\sim}$$

> $v2 := (4 \cdot \text{Pi})^2 \cdot \left(int\!\left(x \cdot (f1s(x) \cdot f2s(x)) \cdot int(y^2 \cdot (f1s(y) \cdot f2s(y)),\, y=0..x),\, x=0..\text{infinity}\right) + int\!\left(x^2 \cdot (f1s(x) \cdot f2s(x)) \cdot int(y \cdot (f1s(y) \cdot f2s(y)),\, y=x..\text{infinity}),\, x=0..\text{infinity}\right)\right);$

$$v2 := \dfrac{16\, Z\!\sim}{729\, a\!\sim}$$

Maple script for this case.

Summary of results for excited state:

$$\psi = f^{\dagger}_{1s\alpha} f^{\dagger}_{2s\alpha} \left| 0 \right\rangle$$

$$S = 1 \qquad L = 0$$

Atomic term: $\quad {}^{3}S$
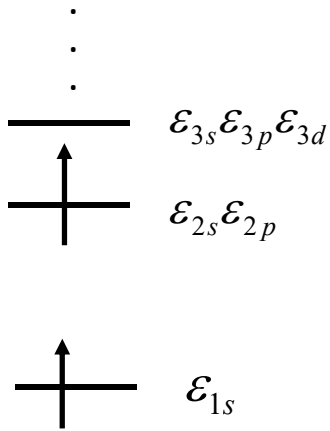
$$\langle \psi | H | \psi \rangle = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$$

$$= \frac{e^2}{2a_0}\left(-4 - \frac{4}{4} + \frac{68}{81} - \frac{64}{729} \right)$$

$$= \frac{e^2}{2a_0}(-4.25)$$

.
.
.

$\overline{}$ $\varepsilon_{3s}\varepsilon_{3p}\varepsilon_{3d}$
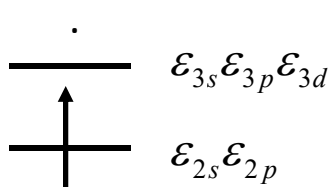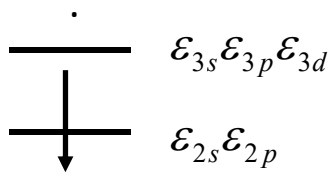
$\varepsilon_{2s}\varepsilon_{2p}$

ε_{1s}

Summary of the results just analyzed.

Consider another excited state of He
 While these two states are orthogonal to each other, they are mixed by the
 Hamiltonian, so we must consider them together

$$\psi_A := f^\dagger_{1s\alpha} f^\dagger_{2s\beta} |0\rangle \qquad \psi_B = f^\dagger_{1s\beta} f^\dagger_{2s\alpha} |0\rangle$$

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

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

ε_{1s}

Now consider a different excited state configuration, this time with total spin projection
M_S=0.   In this case, there are two configurations that we need to consider together.

Consider another excited state of He -- continued

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

$$\psi_A = f_{1s\alpha}^\dagger f_{2s\beta}^\dagger |0\rangle \qquad \psi_B = f_{1s\beta}^\dagger f_{2s\alpha}^\dagger |0\rangle$$

$$\langle \psi_A | H | \psi_A \rangle = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} = \langle \psi_B | H | \psi_B \rangle$$

$$\langle \psi_A | H | \psi_B \rangle = -v_{1s2s2s1s} = \langle \psi_B | H | \psi_A \rangle$$

Evaluating the Hamiltonian in the A and B basis.

Consider another excited state of He – continued

   Since the two states are mixed by the Hamiltonian, we need to consider their linear combination:

$$\psi = C_A \psi_A + C_B \psi_B \quad \text{for} \quad \psi_A = f_{1s\alpha}^\dagger f_{2s\beta}^\dagger \left|0\right\rangle \text{ and } \psi_B = f_{1s\beta}^\dagger f_{2s\alpha}^\dagger \left|0\right\rangle$$

$$ A B$$

$$H = \begin{array}{c} A \\ B \end{array} \begin{pmatrix} \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} & -v_{1s2s2s1s} \\ -v_{1s2s2s1s} & \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} \end{pmatrix}$$

Two solutions:

$$\psi = \frac{1}{\sqrt{2}}\left(\psi_A \pm \psi_B\right) \varepsilon_\pm = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} \mp v_{1s2s2s1s}$$

Summary of results.

Consider another excited state of He – continued

One solution:

$$\psi_{+} = \frac{1}{\sqrt{2}}\left(\psi_{A} + \psi_{B}\right) \qquad \varepsilon_{+} = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$$

$\Rightarrow$ This solution is another example of the spin triplet ($S=1$) solution that we analyzed previously

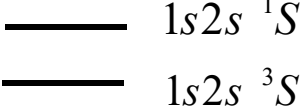**Another solution:**

$$\psi_{-} = \frac{1}{\sqrt{2}}\left(\psi_{A} - \psi_{B}\right) \qquad \varepsilon_{-} = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} + v_{1s2s2s1s}$$

$\Rightarrow$ This solution is a spin singlet ($S=0$) solution with higher energy

How do we really understand how to separate out the singlet and triplet state for this case?

Summary of analysis of ground state and lowest excited states of He atom

Single particle states	Two particle states (first order perturbation)	Energies	
		Calc. (eV)	NIST (eV)

$$\mathcal{E}_{2s}$$

$$1s2s\ {}^{1}S \quad 19.4 \quad 20.6$$

$$1s2s\ {}^{3}S \quad 17.0 \quad 19.8$$

$$\mathcal{E}_{1s}$$

$$1s^{2}\ {}^{1}S \quad 0.00 \quad 0.00$$

Summary of the numerical results.   Do you call this success?   How could the calculation be improved?