

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

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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.

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	<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		

Need more feedback from you – including lecture questions, outstanding homework, and project topics.

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

Slides from original lecture --

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
Physical Measurement Laboratory www.nist.gov

Standard Reference Data www.nist.gov

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

Solids
 Liquids
 Gases
 Artificially Prepared

*Based upon ¹²C. () 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 900 (July 2019)

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2 ¹S₀

He

Helium
4.0026
¹s²
24.5874

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)

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

Single particle basis:

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

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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

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

The matrix element $i \equiv nlm m_s$

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

Defining single particle and two particle interaction terms within the second quantization formalism.

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.

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?

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 momentum 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.

$$|jm\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1j_2; m_1m_2\rangle \langle j_1j_2; m_1m_2 | jm\rangle \quad (8.12a)$$

$$|j_1j_2; m_1m_2\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^j |jm\rangle \langle jm | j_1j_2; m_1m_2\rangle \quad (8.12b)$$

Here $|jm\rangle$ describes the total angular momentum quantum numbers, while $|j_1j_2; m_1m_2\rangle$ describes the product of two angular momenta $|j_1j_2; m_1m_2\rangle \equiv |j_1m_1\rangle |j_2m_2\rangle$. "j" can represent orbital or spin angular momentum.

This material is covered in Chapter 8 of your textbook.

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

$$2S+1 \mathbf{L} \quad \text{Examples: } {}^1S, {}^3S, {}^1P, {}^1D, {}^4G \dots$$

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	1S	0	0.00000000
1s2s	3S	1	[19.81961468]
1s2s	1S	0	[20.61577496]
1s2p	3P°	2	[20.96408703]
		1	[20.96409651]
		0	[20.96421899]
1s2p	1P°	1	[21.21802284]

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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

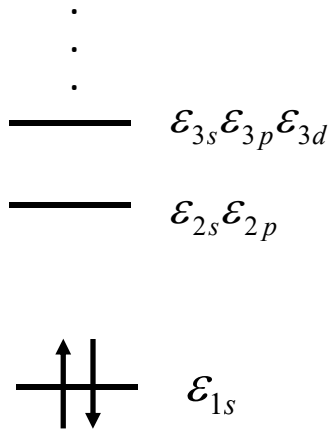
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The atomic levels of C are very interesting. For the ground state configuration of $1s^2 2s^2 2p^2$, we see that there are different arrangements leading to 3 different atomic terms. The lowest term has the designation 3P while the highest term has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

Back to the discussion of He



Ground state:

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

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

$$S = 0 \quad L = 0$$

Atomic term: 1S

Energy estimate: $\langle \psi | H | \psi \rangle = 2\epsilon_{1s} + v_{1s1s1s1s}$

This slide summarizes the analysis of the ground state wavefunction.

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

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

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

- 1. We don't know**
- 2. We know because ??**

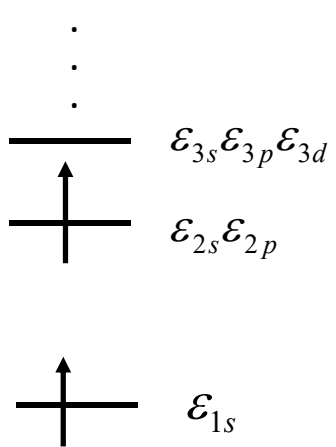
What do you think?

Back to the discussion of He

A possible excited state:

$$\psi = f_{1s\alpha}^\dagger f_{2s\alpha}^\dagger |0\rangle$$

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



$$S = 1 \quad L = 0$$

Atomic term: 3S

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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

$$\psi = f_{1s\alpha}^\dagger f_{2s\alpha}^\dagger |0\rangle$$

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

Evaluation of $\langle \psi | H | \psi \rangle$ for $\psi = f_k^\dagger f_l^\dagger |0\rangle$ ($k \neq l$)

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \epsilon_k + \epsilon_l + v_{klkl} - v_{kllk} \\ &= \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s} \end{aligned}$$

This follows the analysis we discussed in Lecture 27.

Excited state energies -- continued

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

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

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

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

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:

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

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

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Explicit formulas for He evaluated using Maple.

Maple script for evaluating integrals --

```

> assume(Z > 0); assume(a > 0);
> f1s := r -> 1/sqrt(Pi) * (Z/a)^(3/2) * exp(-Z*r/a);

```

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

```

> f2s := r -> 1/sqrt(32*Pi) * (Z/a)^(3/2) * (2 - Z*r/a) * exp(-Z*r/a);

```

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

```

> v1 := (4*Pi)^2 * (int(x*(f1s(x))^2 * int(y^2*(f2s(y))^2, y = 0..x), x = 0..infinity) + int(x^2*(f1s(x))^2 * int(y*(f2s(y))^2, y = x..infinity), x = 0..infinity));

```

$$v1 := \frac{17 Z^2}{81 a^2}$$

```

> v2 := (4*Pi)^2 * (int(x*(f1s(x)*f2s(x)) * int(y^2*(f1s(y)*f2s(y)), y = 0..x), x = 0..infinity) + int(x^2*(f1s(x)*f2s(x)) * int(y*(f1s(y)*f2s(y)), y = x..infinity), x = 0..infinity));

```

$$v2 := \frac{16 Z^2}{729 a^2}$$

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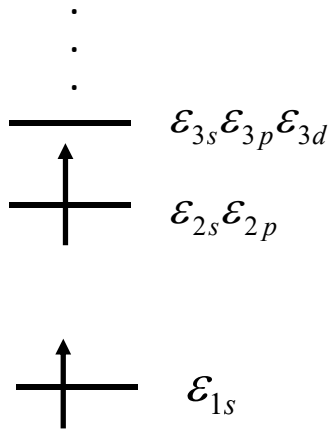
Maple script for this case.

Summary of results for excited state:

$$\psi = f_{1s\alpha}^\dagger f_{2s\alpha}^\dagger |0\rangle$$

$$S = 1 \quad L = 0$$

Atomic term: 3S



$$\begin{aligned} \langle \psi | H | \psi \rangle &= \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s} \\ &= \frac{e^2}{2a_0} \left(-4 - \frac{4}{4} + \frac{68}{81} - \frac{64}{729} \right) \\ &= \frac{e^2}{2a_0} (-4.25) \end{aligned}$$

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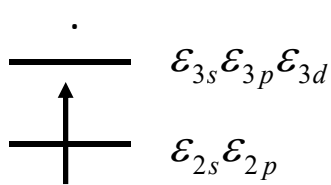
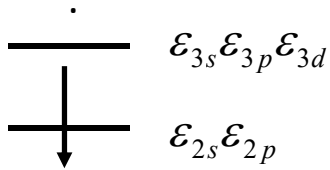
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Summary of the results just analyzed.

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

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



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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

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

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

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

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

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:

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

A
 B

$$H = \begin{matrix} A & \left(\begin{array}{cc} \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} & -v_{1s2s2s1s} \\ -v_{1s2s2s1s} & \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} \end{array} \right) \\ B & \end{matrix}$$

Two solutions:

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

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Summary of results.

Consider another excited state of He – continued

One solution:

$$\psi_+ = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \quad \epsilon_+ = \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$$

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


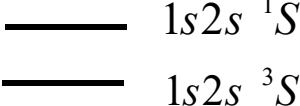


Another solution:

$$\psi_- = \frac{1}{\sqrt{2}}(\psi_A - \psi_B) \quad \epsilon_- = \epsilon_{1s} + \epsilon_{2s} + v_{1s2s1s2s} + v_{1s2s2s1s}$$

⇒ 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}		19.4	20.6
 \mathcal{E}_{1s}		0.00	0.00

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

What do you think about these results

1. Very discouraging
2. Very encouraging
3. Needs more work

Other formulations

- Form basis functions that are eigenfunctions of total spin
- Eigenfunctions of total spin may be symmetric or antisymmetric wrt particle exchange.

$$\Psi = \Psi_{\text{Space}} \Psi_{\text{Spin}}$$

or

Sym	Anti
Anti	Sym