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

Plan for Lecture 28

Quantum mechanics of a multi electron atom

Using second quantization formalism together with material from Professor Carlson's textbook: Chapter 10. Multiple particles (Sec. F) and also Chapter 8. Spin and Adding Angular Momentum (Sec. C)

- 1. Review of what we have learned so far
- 2. General discussion of atomic term analysis
- **3. Examples and comparison with NIST atomic database**

25	Mon: 04/04/2022		Multiparticle systems and second quantization	<u>#20</u>	04/06/2022
26	Wed: 04/06/2022		Multiparticle systems and second quantization		
27	Fri: 04/08/2022		Multi electron atoms	<u>#21</u>	04/11/2022
28	Mon: 04/11/2022		Multi electron atoms	<u>#22</u>	04/18/2022
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		

PHY 742 -- Assignment #22

April 11, 2022

The material for this homework follows Lecture 28

 In class, we evaluated the ground state of a He atom and its lowest two excited states using the single particle basis of eigenstates of the He⁺ H-like ion with Z=2. Evaluate the same analysis for Li⁺ using the single particle basis of eigenstates of the Li⁺⁺ H-like ion with Z=3. Compare your results with the NIST database. Focusing on multielectron systems --

$$H(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = \sum_{i=1}^{N} h(\mathbf{r}_{i}) + V(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N})$$

where: $V(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = \sum_{i=1}^{N} \sum_{(i>j)}^{N} \sum_{j=1}^{N} v(\mathbf{r}_{i} - \mathbf{r}_{j})$
Single particle basis: $h(\mathbf{r})\varphi_{k}(\mathbf{r}) = \varepsilon_{k}\varphi_{k}(\mathbf{r})$
In this basis and using second quantization formalism --
 $\left|\varphi_{k}(\mathbf{r})\right\rangle \Rightarrow f_{k}^{\dagger}f_{k}\left|0\right\rangle$

Second quantized Hamiltonian: $H = \sum_{i} \varepsilon_{i} f_{i}^{\dagger} f_{i} + \sum_{ijkl} v_{ijkl} f_{i}^{\dagger} f_{j}^{\dagger} f_{l} f_{k}$ where $v_{ijkl} \equiv \left\langle \varphi_{i}(\mathbf{r}_{1})\varphi_{j}(\mathbf{r}_{2}) \middle| v(\mathbf{r}_{1} - \mathbf{r}_{2}) \middle| \varphi_{k}(\mathbf{r}_{1})\varphi_{l}(\mathbf{r}_{2}) \right\rangle$

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

PERIODIC TABLE Atomic Properties of the Elements National Institute of Group Standards and Technology 18 J.S. Department of Commerce VIIIA IA FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANT 8 1 °S., Physical Measurement Laboratory www.nist.gov/pml 1 second = 9 192 631 770 periods of rediation corresponding to the н He transition between the two hyperfine levels of the ground state of ³³²Cs Standard Reference Data www.nist.gov/srd ⁵For the most accurate speed of light in vacuum 299 792 458 m s⁻¹ (exact) Hydroger 1.008 Helium 4.0026 6.626 070 15 x 10⁻³⁴ J Hz values of these and Planck constant (exact) 13 14 15 16 17 1.602 176 634 x 10⁻¹⁸ C other constants, visit elementary charge (exact) IIA IIIA IVA VA VIA VIIA pml.nist.gov/constants 13.5984 6.022 140 76 x 10²⁹ mol 24.5874 Avogadro constant (exact) 2S.0 ²P₁⁰ $^{2}P_{0}^{2}$ 3 1S 1.380 649 x 10⁻²⁹ J K⁻¹ (exact) Ър. "S.". 10 Boltzmann constant 5 18 (exact) Solids 1.602 176 634 x 10⁻¹⁸ J electron volt в F Li Be С Ν 0 Ne electron mass 9.109 383 70 x 10⁻³¹ kg Liquids Lithium Beryllium energy equivalent Boror Carbon Nitrogen 14.007 Oxygen 15.999 Fluorine Neor 0.510 998 950 MeV Gases 6.94 9.0122 10.81 12.011 18.998 20.180 1.672 621 924 X 10⁻²⁷ kg proton mass mp 15 25 15²25² 1s²2s²2p 18²28²2p² 18²28²2p 18 28 21 938.272 088 MeV Artificially energy equivalent 5.3917 8.2980 11.2603 14.5341 13.6181 17.4228 21.5645 9.3227 fine-structure constant 1/137.035 999 Prepared 11 ^{*}s, 12 's 13 °P: 14 ³P. 15 ⁴S^o₃₂₂ 16 17 °P: 18 Rydberg energy 13.605 693 1230 eV ³P R_hc Mg Newtonian constant of а 6.674 x 10⁻¹¹ m³kg⁻¹ s⁻¹ P s CI Na AI Si Ar gravitation Sodium Magnesiun Aluminum Silicon Phosphorus Sulfur Chlorine Argon 39.948 22,990 24.305 6 9 26.982 28.085 30.974 32.06 35.45 5 7 8 10 11 12 - 4 INel3s INe13s² [Ne]3s²3p [Ne]38²3p² [Ne]3s²3p² [Ne]3s²3p⁴ [Ne]35²3p² [Ne]3s²3p⁴ IIIB VB IB IVB VIB VIIB VIII IIB 5.1391 7.6462 5.9858 8.1517 10.4867 10.3600 12.9676 15.7596 Period 19 21 ²D₁₀ 22 F. 23 F. 24 25 's_{s2} 26 ⁵D₄ 27 ⁶F₈₂ 28 ³E. 29 2S. 30 31 °P: 33 ⁴S^o₃₂ 35 °P_{3/2} °S, 7S., ³P 36 20 °S, 32 34 κ Sc Ti v Cr Mn Fe Co Ni Cu Zn Ga Ge Ca As Se Br Kr Scendium Chromium Cobelt Nicke Copper Gellium Bromine 79.904 Celcium Titenium Venedium Manganese Zino Germanium Arsenic Selenium Potessium Iron Kryptor 55.845 63.546 65.38 69.723 72.630 74.922 78.971 83.798 40.078 47.867 50.942 54.938 58.933 58.693 39.098 44.956 51.996 [Ar]3d⁵4s⁵ [Ar]3d⁴45⁵ [Ar]3d^T4s² [Ar]3d⁹45⁵ [Ar]3d¹⁶4s² 4 [Ar]3d¹⁰4s⁵4p⁵ [Ar]3d¹⁰4s⁵4p [Ar]3d4s² [Ar]3d³4s² [Ar]3d²4s² [Ar]3d 4a [Ar]3d¹⁰4s [Ar]3d¹⁰4s⁵4p [Ar]3d¹⁰4s¹4p¹ [Ar]3d¹⁰4s³4p³ ¹ [Ar]3d¹⁰4s⁵4p³ IArl4: [Ar]43* 4.3407 6.1132 6.5615 6.8281 6.7462 6.7665 7.4340 7.9025 7.8810 7.6399 7.7264 9.3942 5.9993 7.8994 9.7886 9.7524 11.8138 13.9996 51 4s° 37 39 °D, 43 's., °S., 38 1s 40 °F, 41 °o, 42 's, 44 ⁱF. 45 °F,, 46 's. 47 ²s. 48 49 ²P₁₀ 50 52 ³P 53 ²P₃₂ 54 ³P Rb Zr Ru Rh Pd Sr Y Nb Mo TC Ag Cd In Sn Sb Те Xe Rubidium Strontium Yttrium Zirconium Niobiun lolvbdenum Technetiun Ruthenium Rhodium Palladium Silver Cedmium Indium Tin Antimony Tellurium Xenon 24.5874 85.468 87.62 88.906 91.224 92.906 95.95 101.07 102.91 106.42 107.87 112.41 114.82 118.71 121.76 127.60 126.90 131.29 [Kr]4d⁹5s [Kr]4d¹⁰5s²5p³ [Kr]4d¹⁰5s²5p⁴ [Kr]4d¹⁰5s²5p⁵ [Kr]4d¹⁰5s²5p [Kr]53¹ [Kr]4d²5a² [Kr]4d⁴55 [Kr]4d⁵55 [Kr]4d⁵53⁵ [Kr]4d¹⁰ (Kr)4d¹⁰5s 7.5762 [Kr]4d¹⁰5s⁵ [Kr]4d¹⁰5s²5p [Kr]4d¹⁰5s³5p 1Kr15s IKri4d5s [Kr]4d⁷5s 6.2173 7.1194 7.3439 4.1771 5.6949 6.6341 6.7589 7.0924 7.3605 7.4589 8.3369 8.9938 5.7864 8.6084 9.0097 10.4513 12.1298 55 °s., 56 72 °F. 73 'ғ" 74 °D. 75 's_{sa} 76 ۴D, 17 4Fag 78 °D, 79 °s., ¹S., 81 ²P. 82 ³P, 83 1st 84 ³P. 85 °P. 86 Re Pt Hg Cs Ва Ηf w Os Pb Bi Po At Rn Та Ir Au TI Cesium 132.91 Gold 196.97 Berium 137.33 Hafnium Tentalum 180.95 Tungsten 183.84 Rhenium Osmium Iridium Platinum Mercury 200.59 Thellium Lead 207.2 Bismuth Polonium Astatine Radon (222) 204.38 208.98 178.49 190.23 (209) (210)186.21 192.22 195.08 [Xe]6s [Xe]0s² [Xe]4f¹⁴5d²ds² [Xe]4f¹⁴5d²ds² [Xe]4f¹⁶5d⁴6s³ (Xe)41¹⁴5d⁵6s² [Xe]4f¹⁴Sd⁹ds³ (Xe)41¹⁴5d⁷6s (Xe]41¹⁴5d⁸6s (Xe]41¹⁴5d¹⁰6s [Xe]41⁷⁴5d¹⁰6s [Hg]őp [Hg]0p³ Holdo [Hg]0p⁴ [Ho]0p [Hg]6p^{*} 7.5496 7.4167 7.2855 8.414 9.3175 10.7485 3.8939 5.2117 6.8251 7.8640 7.8335 8.4382 8.9670 8.9588 9.2256 10.4375 6.1083 87 's,, 105 F₃₁₂ sa 108 88 's 104 °F. 106 107 109 110 111 112 113 114 115 116 117 118 Sg Hs FL Fr Ra Rf Db Bh Mt Ds Rg Cn Mc Og Nh Lv Ts Radium Seaborgium (269) Bohrium Frencium Rutherfordium Dubnium Hessium Meitnerium Dermstedtiur Flerovium Roentgeni (282) Copernicium Nihonium Moscowium. Livermorium Tennessine Ogene (223)(226)(267) (268) (270) (269) (278) (281) (285) (286) (289) (289) (293) (294) (294) [Rn]7s [Rn]7s² [Rn[5f¹⁴00²75²] [Rn[5f¹⁴00³75²] [Rn]5f¹⁴00⁴75² (Rn)5f¹⁴0d⁶7s² (Rn)5f¹⁴0d⁶7s³ 4.0727 5.2784 6.02 6.8 7.8 7.7 7.6 Atomic Ground 57 ¹D₃₂ 58 ¹G^o₄ 59 ⁴I^o₈₀ 60 ⁵I₄ 61 ⁶H^o₅₂ 62 ⁷F₀ 63 ⁶S^o₇₂ 64 ⁶D^o₂ 65 ⁶H^o₅₂ 66 ⁵I₄ 67 ⁶I^o₁₅₀ 68 ³H, 69 ³F⁹₇₂ 70 ¹S₀ 71 ²D₂₂ State Number Eu Dy Pr Nd Pm Sm Tb Ho Yb La Ce Gd Er Tm Lu 58 ¹G^o₄ Lanthanum Cerium eseodymiu Neodymium romethium Semarium Europium Gedolinium Terbium Dysprosium Holmium Erbium Thulium Ytterbium Lutetium Symbol 138.91 140.12 140.91 144.24 (145) 150.36 151.96 157.25 158.93 162.50 164.93 167.26 168.93 173.05 174.97 Се Diel5dds [Xe]4f5d0s³ [Xe]4f²0s² [Xe]41⁴03² (Xe)41⁶03³ 5.577 [Xe]41⁶03² [Xe]4f⁷6s² [Xe]47⁷5083⁵ 6.1498 [Xe]4f²0s² (Xe)41⁴⁰05⁵ 5.9391 [Xe]4f¹¹0s² D(e)4f¹²0s² [Xe]4f¹²0s² [Xe]4f¹⁴0s 6.2542 [Xe]41³⁴5685 Name 5.5769 5.5386 5.4702 5.5250 5.6437 5.6704 5.8638 6.0215 6.1077 6.1843 5.4259 Cerium 89 91 'K_{ma} 92 *D° 97 *H° 99 'I.;; °D30 90 °F. 93 °L... 94 95 °s_{?a} 96 98 100 ^ан. 101 ^аға, 102 's, 103 °P Standard 140.12 Bk Pu Th Pa U Np Cf Es Fm No Atomic [Xe]4f5d6s Ac Am Cm Md Lr Weight^T 5.5386-Actinium Thorium Protectinium Urenium Curium (247) Berkelium (247) Californium Einsteinium Fermium (257) Nobelium Neptunium (237) Plutoniun Americium Mendeleviur Lewrenciun 238.03 (227)232.04 231.04 (244) (243) (251) (258) (259) (266) (252) Ground-state Ionizatio [Rn]6d³7s³ (Rn)Sf²6d7s² [Rn]5f³6d7s³ (Rn)5f⁴6d7s³ [Rn]5f⁹7s³ [Rn]5f⁷75² [Rn]51⁷6d7s³ [Rn]Sf²7s² [Rn]Sf¹⁰7s³ [Rn]5f¹⁰7s³ IRn16d7s [Rn]5f¹¹7s² [Rn]5f¹²7s² IRn151¹⁴75 [[Rn]5f⁵⁴7s³7] Configuration Energy (eV) 5.9738 5.3802 6.3067 5.89 6.1941 6.2655 6.0258 5 9914 6.1978 6.2817 6.3676 6.50 6.58 6.66 4.96 *Based upon ¹²C. () Indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit claaw.org and pmi.nist.gov/data. NIST SP 966 (July 2019) ¹S₀

Helium

4.0026

 $1s^2$

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

$$H(\mathbf{r}_{1},\mathbf{r}_{2}) = -\frac{\hbar^{2}}{2m} (\nabla_{1}^{2} + \nabla_{2}^{2}) - 2e^{2} \left(\frac{1}{r_{1}} + \frac{1}{r_{2}}\right) + \frac{e^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|}$$

$$= -\frac{\hbar^{2} \nabla_{1}^{2}}{2m} - \frac{2e^{2}}{r_{1}} - \frac{\hbar^{2} \nabla_{2}^{2}}{2m} - \frac{2e^{2}}{r_{2}} + \frac{e^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|}$$

$$= -\frac{\hbar(\mathbf{r}_{1}) + h(\mathbf{r}_{2}) + v(\mathbf{r}_{1},\mathbf{r}_{2})$$

Single particle basis:

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

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PHY 742 -- Spring 2022 -- Lecture 28

Second quantized version of the He atom Hamiltonian

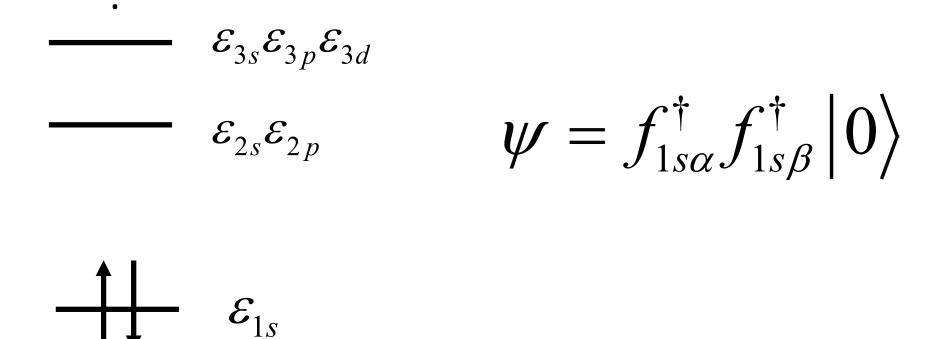
$$H(\mathbf{r}_1,\mathbf{r}_2) \Longrightarrow \sum_i \varepsilon_i f_i^{\dagger} f_i + \sum_{ijkl} v_{ijkl} f_i^{\dagger} f_j^{\dagger} f_l f_k$$

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 $n\{0123..\}$

Ground state configuration for He atom



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$$H = \sum_{i} \varepsilon_{i} f_{i}^{\dagger} f_{i} + \sum_{ijkl} v_{ijkl} f_{i}^{\dagger} f_{j}^{\dagger} f_{l} f_{k}$$
Need to evaluate $/v_{ijkl} H |v_{ijkl}\rangle$ for $v_{ijkl} - f_{ij}^{\dagger}$

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,

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

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.

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

Here $|jm\rangle$ describes the total angular moment 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.

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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 3 *j* symbol is the Clebsch–Gordan coefficient

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

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+1L

Examples:
$${}^{1}S, {}^{3}$$

 ${}^{3}S, {}^{1}P, {}^{1}D, {}^{4}G....$

Example from NIST

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NIST Atomic Spectra Database Levels Data

He I 198 Levels Found *z* = 2, He isoelectronic sequence

Configuration	Term	J	Level (eV)
1 <i>s</i> ²	¹ S	0	0.0000000
1 <i>s</i> 2 <i>s</i>	³ S	1	[19.81961468]
1 <i>s</i> 2 <i>s</i>	¹ S	0	[20.61577496]
1 <i>s</i> 2p	³ Ро	2 1 0	[20.96408703] [20.96409651] [20.96421899]
1 <i>s</i> 2p	¹₽°	1	[21.21802284]

Example from NIST

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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	ЗР	0 1 2	0.00000000 0.0020354130 0.0053825826
2s ² 2p ²	¹ D	2	1.2637284
2s ² 2p ²	1S	0	2.6840136

Back to the discussion of He

Ground state: $\psi = f_{1s\alpha}^{\dagger} f_{1s\beta}^{\dagger} \left| 0 \right\rangle$ • $\psi = \frac{1}{\sqrt{2}} \varphi_{1s}(\mathbf{r}_1) \varphi_{1s}(\mathbf{r}_2) \left(\alpha_1 \beta_2 - \alpha_2 \beta_1 \right)$ • $\mathcal{E}_{3s}\mathcal{E}_{3p}\mathcal{E}_{3d}$ L = 0S = 0 $\mathcal{E}_{2s}\mathcal{E}_{2v}$ ^{1}S Atomic term: \mathcal{E}_{1s} Energy estimate: $\langle \psi | H | \psi \rangle = 2\varepsilon_{1s} + v_{1s1s1s1s}$

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 ??

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Back to the discussion of He

A possible excited state:

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

$$\psi =$$

$$\psi =$$

$$\varphi =$$

$$\varphi_{1s} (\mathbf{r}_{1}) \varphi_{2s} (\mathbf{r}_{2}) - \varphi_{1s} (\mathbf{r}_{2}) \varphi_{2s} (\mathbf{r}_{1})) \alpha_{1} \alpha_{2}$$

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

$$\varphi =$$

$$E_{1s} \qquad \text{Atomic term:} \quad {}^{3}S$$

Energy estimate of the ³S excited state of He

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

$$H = \sum_{i} \varepsilon_{i} f_{i}^{\dagger} f_{i} + \sum_{ijkl} v_{ijkl} f_{i}^{\dagger} f_{j}^{\dagger} f_{l} f_{k}$$

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

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

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

Excited state energies -- continued

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

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

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

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

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

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

$$v_{1s2s1s2s} = (4\pi)^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 (\varphi_{1s}(r_1))^2 (\varphi_{2s}(r_2))^2 \frac{1}{r_2} = \frac{Ze^2}{a_0} \frac{17}{81}$$
$$v_{1s2s2s1s} = (4\pi)^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 (\varphi_{1s}(r_1)\varphi_{2s}(r_1)) (\varphi_{1s}(r_2)\varphi_{2s}(r_2)) \frac{1}{r_2} = \frac{Ze^2}{a_0} \frac{16}{729}$$

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Maple script for evaluating integrals --

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

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

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

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

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

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

$$vI := (4 \cdot \operatorname{Pi})^{2} \cdot \left(int(x \cdot (fIs(x))^{2} \cdot int(y^{2} \cdot (f2s(y))^{2}, y = 0 \cdot x), x = 0 \cdot \operatorname{infinity}) + int(x^{2} \cdot (fIs(x))^{2} \cdot int(y \cdot (f2s(y))^{2}, y = x \cdot \operatorname{infinity}), x = 0 \cdot \operatorname{infinity});$$

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

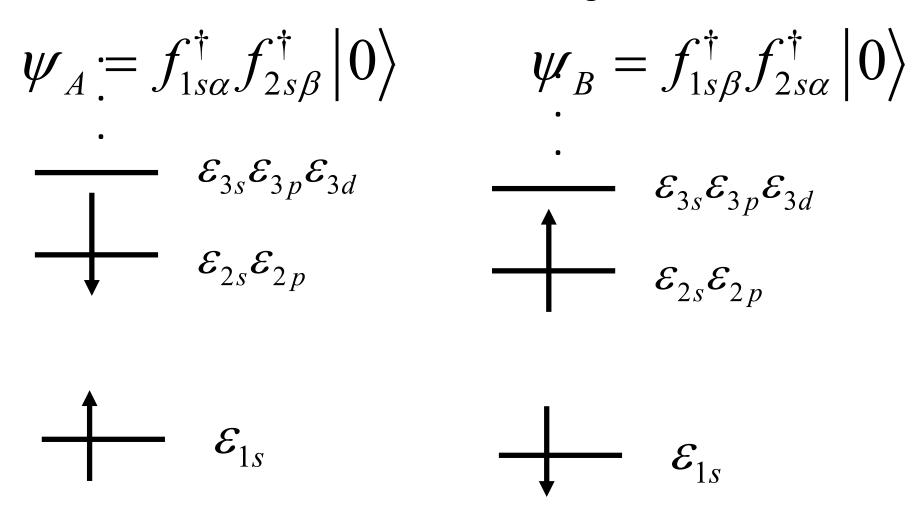
$$v2 := (4 \cdot \operatorname{Pi})^{2} \cdot \left(int(x \cdot (fIs(x) \cdot f2s(x)) \cdot int(y^{2} \cdot (fIs(y) \cdot f2s(y)), y = 0 \cdot x), x = 0 \cdot \operatorname{infinity}) + int(x^{2} \cdot (fIs(x) \cdot f2s(x)) \cdot int(y \cdot (fIs(y) \cdot f2s(y)), y = x \cdot \operatorname{infinity}), x = 0 \cdot \operatorname{infinity});$$

$$v2 := \frac{17 Z^{2}}{16 Z^{2}}$$

Summary of results for excited state: $\psi = f_{1s\alpha}^{\dagger} f_{2s\alpha}^{\dagger} \left| 0 \right\rangle$ S = 1 L = 0• ^{3}S Atomic term: • $\mathcal{E}_{3s}\mathcal{E}_{3p}\mathcal{E}_{3d}$ $\langle \psi | H | \psi \rangle = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} - v_{1s2s2s1s}$ $\mathcal{E}_{2s}\mathcal{E}_{2p}$ $=\frac{e^2}{2a_0}\left(-4-\frac{4}{4}+\frac{68}{81}-\frac{64}{729}\right)$ $=\frac{e^2}{2a}(-4.25)$ \mathcal{E}_{1s}

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



Consider another excited state of He -- continued

$$H = \sum_{i} \varepsilon_{i} f_{i}^{\dagger} f_{i} + \sum_{ijkl} v_{ijkl} f_{i}^{\dagger} f_{j}^{\dagger} f_{l} f_{k}$$

$$\psi_{A} = f_{1s\alpha}^{\dagger} f_{2s\beta}^{\dagger} \left| 0 \right\rangle \qquad \psi_{B} = f_{1s\beta}^{\dagger} f_{2s\alpha}^{\dagger} \left| 0 \right\rangle$$

$$\left\langle \psi_{A} \left| H \right| \psi_{A} \right\rangle = \varepsilon_{1s} + \varepsilon_{2s} + v_{1s2s1s2s} = \left\langle \psi_{B} \left| H \right| \psi_{B} \right\rangle$$
$$\left\langle \psi_{A} \left| H \right| \psi_{B} \right\rangle = -v_{1s2s2s1s} = \left\langle \psi_{B} \left| H \right| \psi_{A} \right\rangle$$

Consider another excited state of He – continued

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

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

$$A \qquad B$$

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

Two solutions:

Ē

$$\psi = \frac{1}{\sqrt{2}} \left(\psi_A \pm \psi_B \right)$$

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

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Consider another excited state of He – continued

One solution:

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

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

Another solution:

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

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

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

Single particle states

F

Two particle statesEnergies(first order perturbation)Calc. (eV)NIST (eV)

0.00

 \mathcal{E}_{1s}

 $1s^{2}$ S^{1}

0.00

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.

$$\psi = \psi_{\text{Space}} \psi_{\text{Spin}}$$

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

ASD Lines Levels	FORMATION	BibliogRaphy Help
NIST Atomic Spectra Da	tabase Levels F	orm
	Best view	red with the latest versions of Web browsers and JavaScript enabled
This form provides access to NIST crit	ically evaluated data on at	omic energy levels.
Spectrum: Li II e.g., Fe I	or Mg Li-like or Z=59 I	I or 198Hg I
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Energy ordered O		
Level Z Principal configuration		
information: ✓ Principal term ✓ Level ✓ Uncertainty		
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✓ Landé-g		
Leading percentages		
Bibliographic references:		

Li II 109 Levels Found *z* = 3, He isoelectronic sequence

Data on Landé factors and level compositions are not available for this ion in ASD

Some data for neutral and singly-charged ions are available in the Handbook of Basic Atomic Spectroscopic Data

Primary data source	
Unpublished level list prepared for line classifications published in Kelly 1987	These data are not critically evaluat

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Reference
1 <i>s</i> ²	¹ S	0	0.00000	0.000012	L3462
1s2s	³ S	1	59.020815	0.000012	
1 <i>s</i> 2s	¹ S	0	60.92269	0.00012	
1s2p	3 Þ 0	1 2 0	61.280575 61.280856 61.281244	0.000012 0.000012 0.000012	
1s2p	¹₽°	1	62.216336	0.000012	

What do you expect to be the atomic term for the lowest energy of Li I?

Examples of atoms in their ground state with complicated multiplet term splittings

C I 435 Levels Found

Z = 6, C isoelectronic sequence

Ti I 559 Levels Found

Z = 22, Ti isoelectronic sequence

Some data for neutral and singly-charged ions are available in the Handbook of

 Primary data source
 Query NIST Bibliographic

 Saloman 2012
 Image: Constraint of the second second

Configuration	Term	J	Level (eV)
3d ² 4s ²	a ³ F	2	0.0000000
		3	0.02109378
		4	0.04796626
3d ³ (⁴ F)4s	a ⁵F	1	0.8129437
		2	0.8181426
		3	0.82585949
		4	0.83599520
		5	0.8484192
3d ² 4s ²	a ¹ D	2	0.8995494
3d ² 4s ²	a ³ P	0	1.0460073
		1	1.05292613
		2	1.06655474

Some data for neutral and singly-charged ions are available in the Handbook of Basic Aton

Primary data source	Query NIST Bibliographic Databas
Haris & Kramida 2017	Literature on C I Energy

Configuration	Term	J	Level (eV)	
$2s^22p^2$	3р	0	0.000000000	
20 20		1	0.0020354130	
		2	0.0053825826	
2s ² 2p ²	¹ D	2	1.2637284	
2s ² 2p ²	1S	0	2.6840136	
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