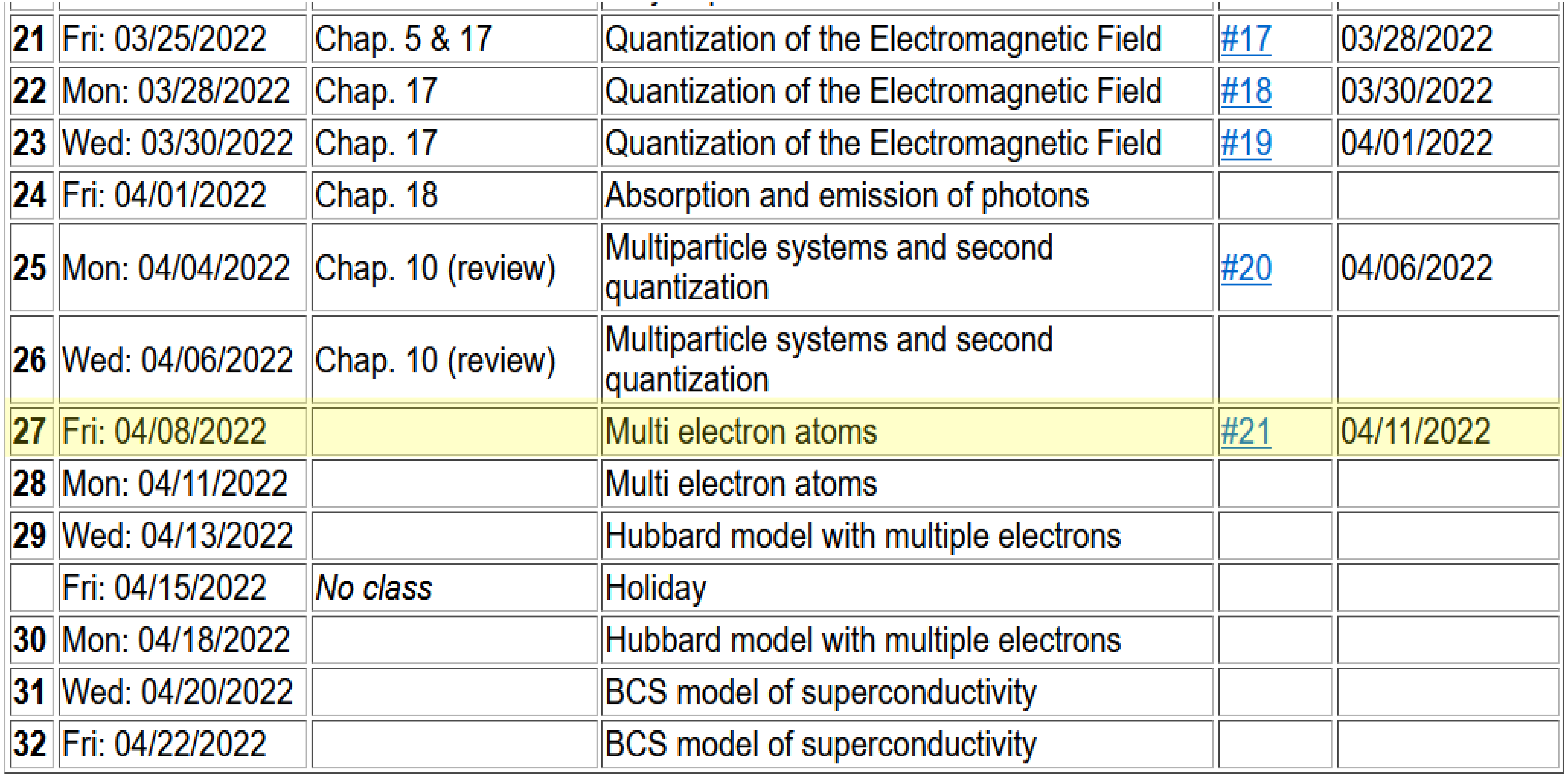
PHY 742 Quantum Mechanics II
12-12:50 AM MWF Olin 103
Notes for Lecture 27

Quantum mechanics of multiple particle systems

Atom example systems -- using second quantization formalism and focusing on Fermi particles

1. He atom in its ground state
2. He atom in an excited state
3. Other atomic systems -- multiplet splittings



21	Fri: 03/25/2022	Chap. 5 & 17	Quantization of the Electromagnetic Field	#17	03/28/2022
22	Mon: 03/28/2022	Chap. 17	Quantization of the Electromagnetic Field	#18	03/30/2022
23	Wed: 03/30/2022	Chap. 17	Quantization of the Electromagnetic Field	#19	04/01/2022
24	Fri: 04/01/2022	Chap. 18	Absorption and emission of photons		
25	Mon: 04/04/2022	Chap. 10 (review)	Multiparticle systems and second quantization	#20	04/06/2022
26	Wed: 04/06/2022	Chap. 10 (review)	Multiparticle systems and second quantization		
27	Fri: 04/08/2022		Multi electron atoms	#21	04/11/2022
28	Mon: 04/11/2022		Multi electron atoms		
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 #21

April 8, 2022

Review Notes for Lecture 27.

1. Evaluate the ground state energy of a He atom using the single particle basis of the He$^+$ ion, evaluating the expressions obtained in class. (Hint: some of these evaluations were discussed in Lecture 1.)

Review -- Multiparticle systems using “second” quantization formalism

Start with a basis of functions that can span the space of our multiparticle system. Typically, the basis functions are formed from single particle states.

Eigenstates of a single particle Hamiltonian $h(\mathbf{r})$:

$$h(\mathbf{r})\varphi_a(\mathbf{r}) = \varepsilon_a \varphi_a(\mathbf{r})$$

$$h(\mathbf{r})\varphi_b(\mathbf{r}) = \varepsilon_b \varphi_b(\mathbf{r})$$

$$\vdots$$

$$h(\mathbf{r})\varphi_z(\mathbf{r}) = \varepsilon_z \varphi_z(\mathbf{r})$$

The states $\left|\varphi_a(\mathbf{r})\right\rangle$ represent a "first" quantization.
The occupations of these states in the multiparticle wave function use the notiont of "second" quantization.

We now assume that the single particle eigenstates $\left\{\varphi_a(\mathbf{r})\right\}$ span the function space available to each particle.

Representing the single particle system within the basis:

$$h(\mathbf{r}_1) = \sum_a \left|\varphi_a(\mathbf{r}_1)\right\rangle \varepsilon_a \left\langle\varphi_a(\mathbf{r}_1)\right|$$

Second quantization for Fermi particles described in this basis

$$N_a = f_a^\dagger f_a$$

Fermi particle anticommutation relations:

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

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

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

Second quantized creation and annhilation Fermi operators

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

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

$$f^\dagger{}_a \left|n_a\right\rangle = \sqrt{1-n_a} \left|1-n_a\right\rangle$$

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

Non-trivial operations:

$$f_a \left|0_a\right\rangle = 0 \qquad f_a \left|1_a\right\rangle = \left|0_a\right\rangle$$

$$f_a^\dagger \left|0_a\right\rangle = \left|1_a\right\rangle \qquad f_a^\dagger \left|1_a\right\rangle = 0$$

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

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

Some details --

Second quantized creation and annhilation Fermi operators

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

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

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

$$= \left(f_a - f_a f_a^\dagger f_a \right) \left| n_a \right\rangle = f_a \left(1 - n_a \right) \left| n_a \right\rangle$$

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

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

$$\left| K \right|^2 = \left\langle n_a \right| f_a^\dagger f_a \left| n_a \right\rangle = n_a \qquad \Rightarrow f_a \left| n_a \right\rangle = \sqrt{n_a} \left| 1 - n_a \right\rangle$$

Similarly, $\Rightarrow f_a^\dagger \left| n_a \right\rangle = \sqrt{1 - n_a} \left| 1 - n_a \right\rangle$

From “first” quantization --

$$h(\mathbf{r}_1) = \sum_a \left|\varphi_a(\mathbf{r}_1)\right\rangle \varepsilon_a \left\langle \varphi_a(\mathbf{r}_1)\right|$$

To “second” quantization --

$$\left|\varphi_a(\mathbf{r})\right\rangle \Leftrightarrow f_a^\dagger \left|0\right\rangle$$

$$h = \sum_a f_a^\dagger f_a \, \varepsilon_a$$

More general treatment of multiparticle system (focusing on Fermions)

$$H(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=\sum_{i=1}^{N}h(\mathbf{r}_i)+V(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)$$

interparticle
interaction

Often: $V(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=\sum_{i=1\ (i>j)}^{N}\sum_{j=1}^{N}v(\mathbf{r}_i-\mathbf{r}_j)$

In this case, the second quantized forms can be written for Fermi particles

$$H(\mathbf{r}_1,\mathbf{r}_2\ldots.\mathbf{r}_N)\Rightarrow\sum_{a}\varepsilon_a f_a^\dagger f_a+\sum_{abcd}v_{abcd}f_a^\dagger f_b^\dagger f_d f_c$$

Here v_{abcd} denotes matrix elements such as

$$v_{abcd}=\int d^3r_1\int d^3r_2\ \varphi_a^*(\mathbf{r}_1)\varphi_b^*(\mathbf{r}_2)v(\mathbf{r}_1-\mathbf{r}_2)\varphi_c(\mathbf{r}_1)\varphi_d(\mathbf{r}_2)$$

Example of a multi-electron atom – He atom with 2 electrons and Z=2

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

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

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

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

Single particle basis:

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

For example:

$$h(\mathbf{r})\left|\varphi_{1s}\right\rangle = \left(-\frac{\hbar^2\nabla^2}{2m}-\frac{2e^2}{r}\right)\left|\varphi_{1s}\right\rangle = \varepsilon_{1s}\left|\varphi_{1s}\right\rangle$$

More complete considerations --

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

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

Second quantized version of the He atom Hamiltonian

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

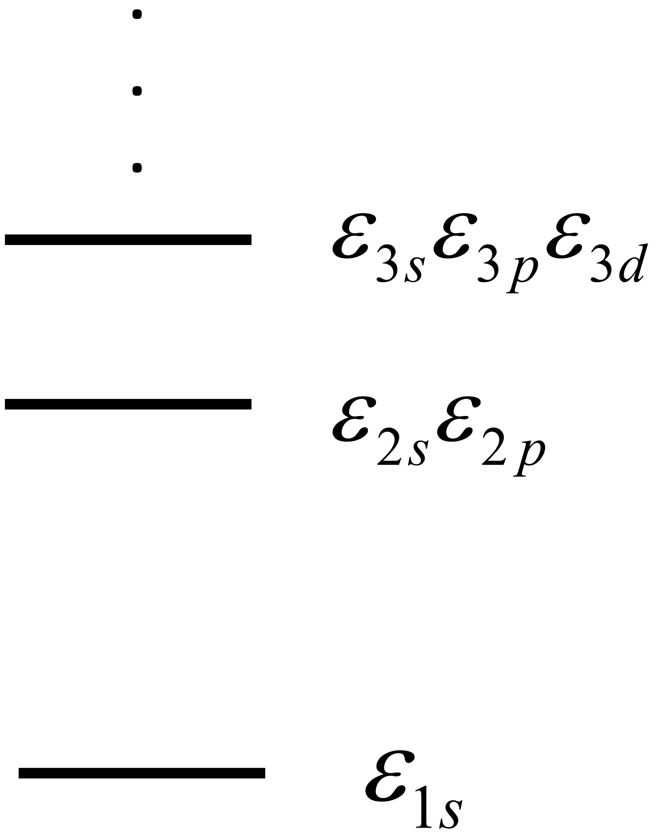
Here v_{ijkl} denotes matrix elements such as

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

The matrix element $i \equiv nlmm_s$

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

Spectrum of single particle states for He atom (schematic)

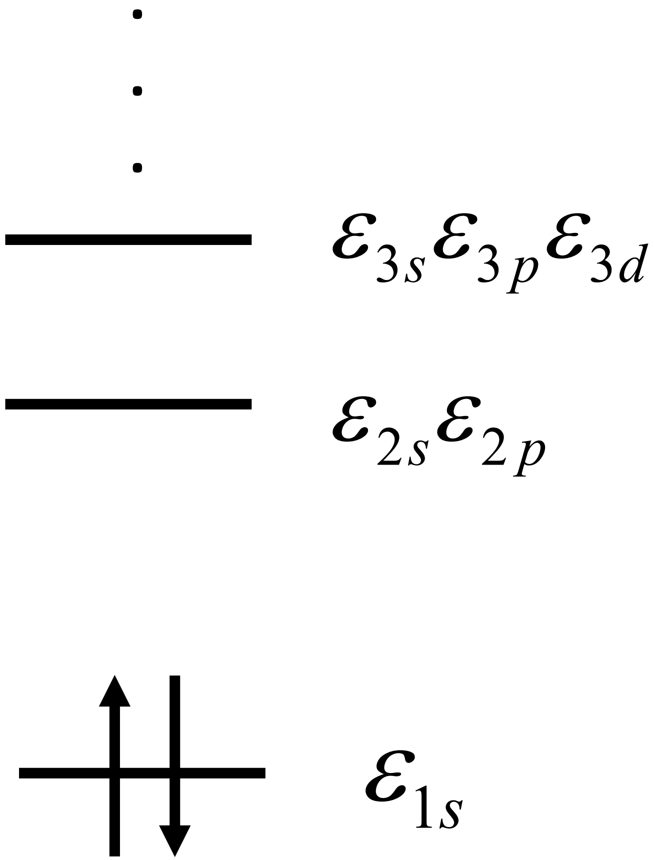


$\varepsilon_{3s}\varepsilon_{3p}\varepsilon_{3d}$

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

ε_{1s}

Ground state configuration for He atom



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

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 $i \neq j$

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

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

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

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

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

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

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

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

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 single particle terms according to

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

Now consider the interaction term

Here we assume that $i \neq j$ and $k \neq l$

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

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

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

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_j f_i f_i^\dagger f_j^\dagger |0\rangle = 1 \qquad \Rightarrow v_{ijij}$$

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

$$\Rightarrow \langle 0 | f_j f_i f_i^\dagger f_j^\dagger f_i f_j f_i^\dagger f_j^\dagger |0\rangle = -1 \qquad \Rightarrow -v_{ijji}$$

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

Evaluation of two particle term, continued

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

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

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

$$v_{ijji} = 0$$

Why?

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

$$\langle \psi | H | \psi \rangle = 2\varepsilon_{1s} + v_{1s1s1s1s}$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{2e^2}{r} \right) |\varphi_{1s}\rangle = \varepsilon_{1s} |\varphi_{1s}\rangle \qquad v_{1s1s1s1s} = \int d^3r d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi_{1s}(r)|^2 |\varphi_{1s}(r')|^2$$

Note: HW21 asks you to evaluate these expressions and compare the results with a variational approach discussed in Lecture #1.

Discussion – how accurate is our treatment of the ground state of the He atom?

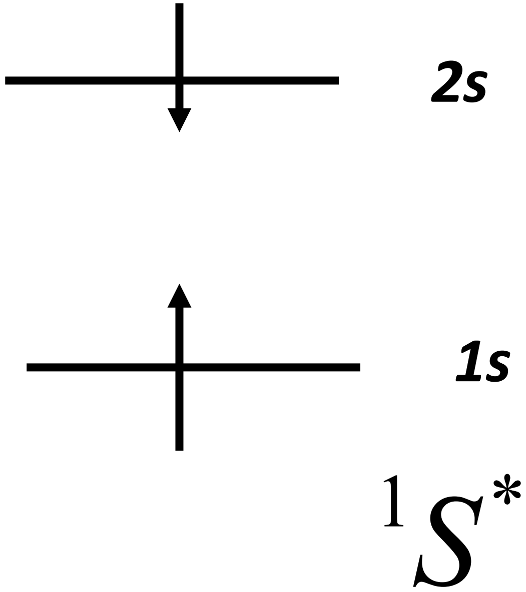
a. We get a numerical result – it must be correct.
b. The variational approach used in Lecture 1 was more accurate.

If (b) is the conclusion – what is the problem with the second quantization approach?

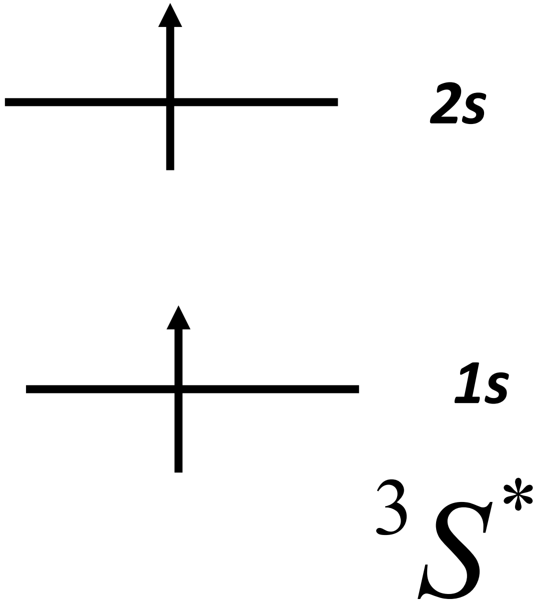
c. It should only be used for qualitative analysis
d. Second quantization approach is in principle exact, but we can improve our solution.

Continuing our example of He as an illustration of the second quantization formalism, but using simple expectation values --

He atom (Z=2) in terms of single particle states representing excited configurations



$^1S^*$

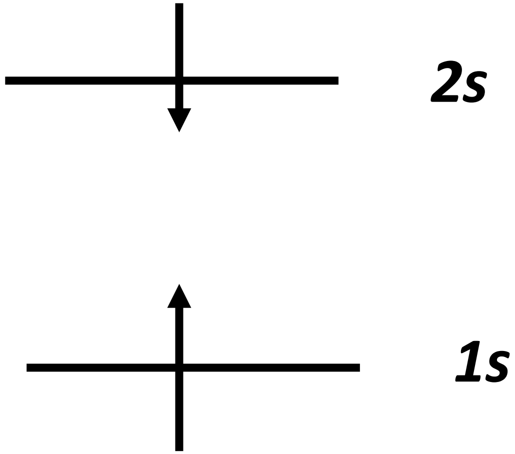


$^3S^*$

Digression of atomic term notation

$$^{(2S+1)}L$$

Here we assume no spin-orbit interaction and total electron spin S and total electron orbital angular momentum L are "good quantum numbers".

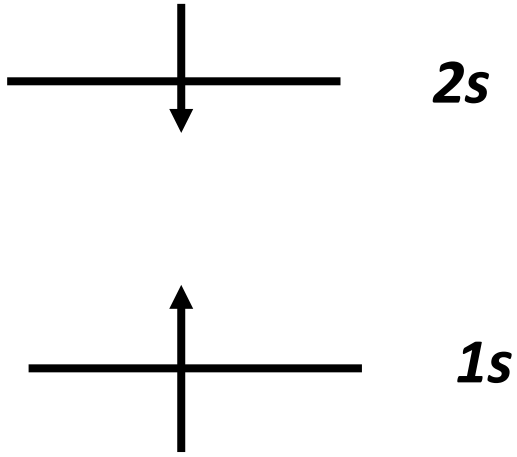


$$^{1}S^{*}$$

$$\left|\Psi(^{1}S^{*})\right\rangle = ??$$

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

$$f^{\dagger}_{2s\beta} f^{\dagger}_{1s\alpha}\left|0\right\rangle \quad \text{or} \quad f^{\dagger}_{2s\alpha} f^{\dagger}_{1s\beta}\left|0\right\rangle$$



$$^1S^*$$

What should we do?

a. **Use one or the other?**
b. **Use linear combination of both solutions?**

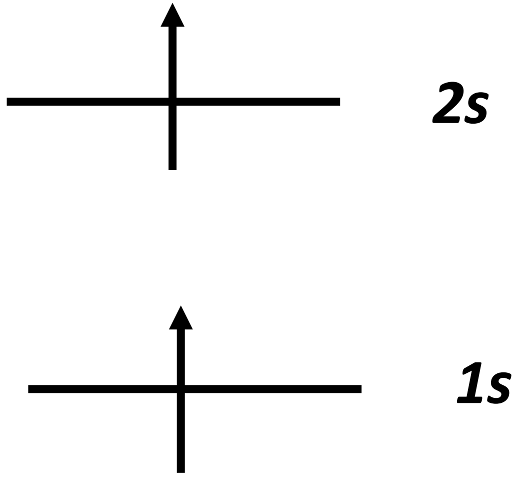
Actually, in this case, we can use our knowledge of addition of angular momentum to know that For *S=0*, the spatial part of the 2 particle wavefunction is symmetric in particle exchange.

$$\left|\Psi(^1S^*)\right\rangle = ??$$

$$f^\dagger_{2s\beta} f^\dagger_{1s\alpha}\left|0\right\rangle \quad \text{or} \quad f^\dagger_{2s\alpha} f^\dagger_{1s\beta}\left|0\right\rangle$$

$$\left\langle\Psi(^1S^*)\right|H\left|\Psi(^1S^*)\right\rangle =$$

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



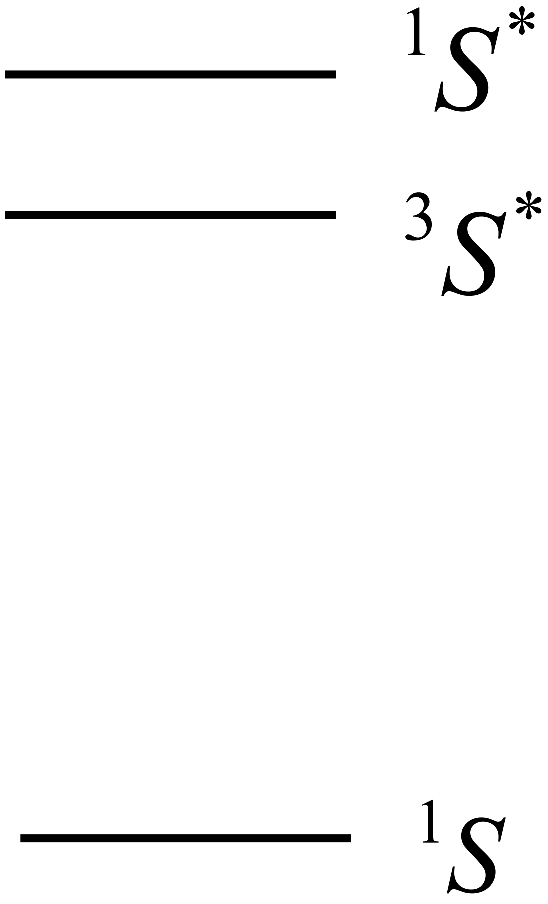
$$^3S^*$$

In this case, our knowledge of addition of angular momentum to know that For *S=1*, the spatial part of the 2 particle wavefunction is antisymmetric in particle exchange.

$$\left\langle \Psi(^3S^*) \middle| H \middle| \Psi(^3S^*) \right\rangle =$$

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

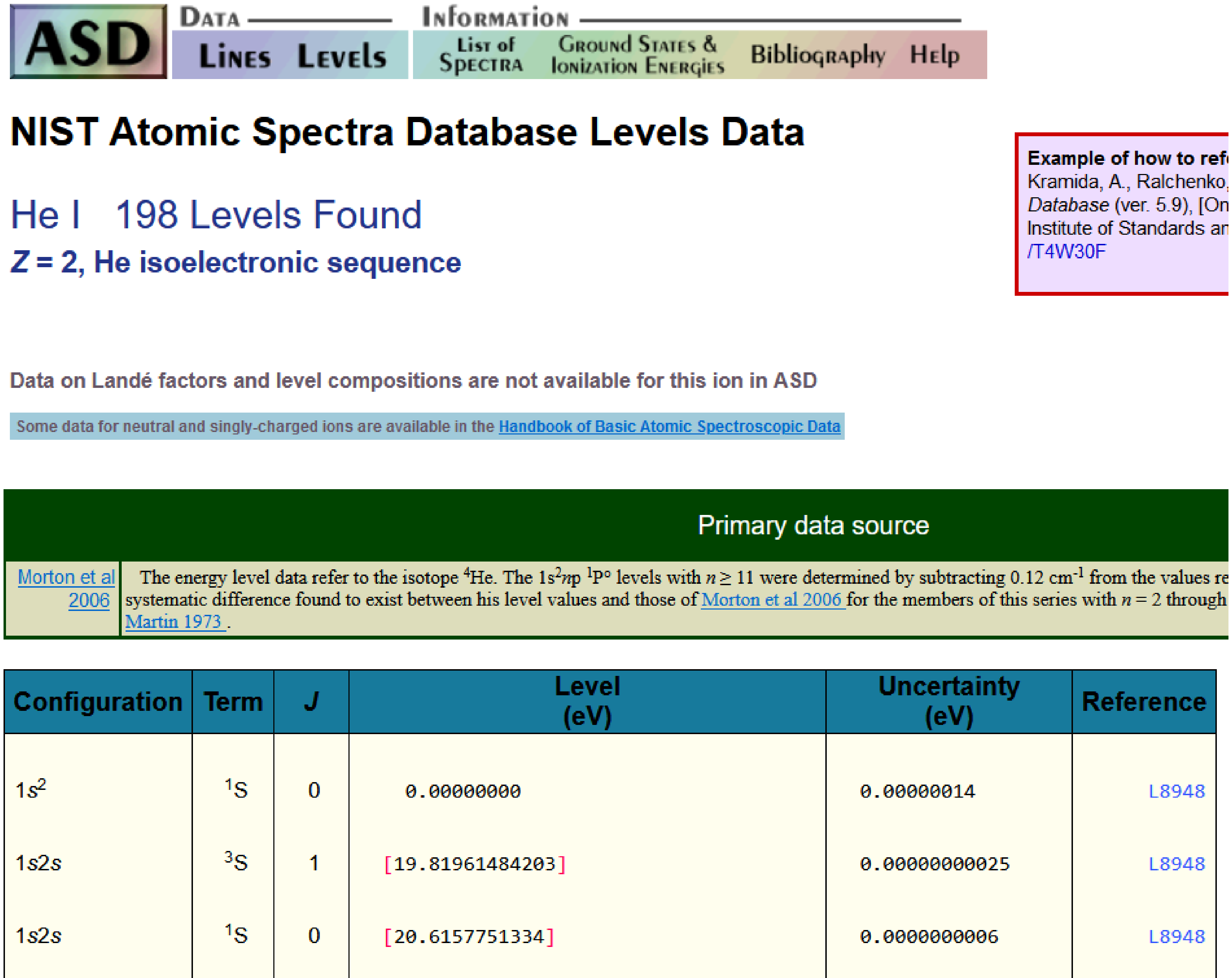
Summary of results for excited state He atom in this approximation



$$^{1}S^{*} \qquad \varepsilon_{1s}+\varepsilon_{2s}+v_{1s2s1s2s}+v_{1s2s2s1s}$$

$$^{3}S^{*} \qquad \varepsilon_{1s}+\varepsilon_{2s}+v_{1s2s1s2s}-v_{1s2s2s1s}$$

$$^{1}S \qquad 2\varepsilon_{1s}+v_{1s1s1s1s}$$



NIST Atomic Spectra Database Levels Data

Example of how to ref
Kramida, A., Ralchenko,
Database (ver. 5.9), [On
Institute of Standards an
/T4W30F

He I   198 Levels Found

Z = 2, 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
Morton et al 2006	The energy level data refer to the isotope ^{4}He. The $1s^2np$ $^1P^o$ levels with $n \geq 11$ were determined by subtracting 0.12 cm^{-1} from the values re systematic difference found to exist between his level values and those of Morton et al 2006 for the members of this series with $n = 2$ through Martin 1973 .

Configuration	Term	*J*	Level (eV)	Uncertainty (eV)	Reference
$1s^2$	^{1}S	0	0.00000000	0.00000014	L8948
$1s2s$	^{3}S	1	[19.81961484203]	0.00000000025	L8948
$1s2s$	^{1}S	0	[20.6157751334]	0.0000000006	L8948