

11	Mon., 11/10 Tues. 11/11 Wed., 11/12 Fri., 11/14	5.2 Atoms (Q9.2) 5.3 Solids (Unit T7.2) 8.1-.2 WKB Approximation & Tunneling	Daily 11.M Weekly 11 Daily 11.W Daily 11.F
12	Mon., 11/17 Tues. 11/18	6.1 Time-independent Perturbation, non-degenerate	Daily 12.M Weekly 12

Daily: Kyle Jacob   Spencer   Gigja   Anton   Jessica   Sean   Antwain   Jonathan   Casey   Jeremy   Mark   Connor   Brad

### Equipment

- Griffith's text
- Moore's Text
- Thornton & Rex Ch. 8 - Atoms

### Check dailies

### Announcements

- Test is graded and, here it is. On it, the corrected grade is because Connor pointed out that I'd ended up having 104 points total; I'd initially subtracted all the missed points from 100.
- Course grades are also there; underwhich I've noted what areas were holding you back – for most folks it's simply the daily lecture prep – logging on to Google Moderator. It's only 5% of your grade; but if you never do it, that's 5% of your grade!

"We should spend some time looking at the periodic table examples. Having a "real world" application has been pretty rare so I'd love to spend time on this." [Casey P](#)  
I would love to do this as well. I've been hoping to see how everything we've been doing connects to Chem for this entire course. [Anton](#)  
This would be excellent. [Bradley W](#)

"Can we talk about the notation that griffiths is trying to explain in 5.2.2 and maybe do an example using it?" [Jessica](#)  
I'd also like to go over this, particularly how it's used in Table 5.1. [Spencer](#)  
I would also like to go over (the last column in) Table 5.1. [Gigja](#)

"I am not sure the the value for  $E_0$  is determined in equation 5.31. I do not see how it relates to equation 5.29 when there is an 8 rather than a 4." [Kyle B](#)

I'd also like to go over this, particularly how it's used in Table 5.1.  
[Spencer](#)

## 5. Identical Particles

### 5.2 Atoms

Here we take a moment to, at least qualitatively, make the leap from the Hydrogen atom, which we'd treated pretty rigorously, to a general understanding of more complicated atoms. We're certainly ready for seeing the form of the Schrodinger Equation, if not really solving it.

You probably noticed how skimpy and qualitative this section is for the importance of what it's discussing; that's for two reasons – Griffiths imagines you've had a traditional 'modern physics' class in which all this was gone into in greater, if not completely rigorous, detail, and he knows that later chapters will deal with some of this with the rigor it deserves. So all he's after in this chapter is really looking at the implications of four things we *have* dealt with rigorously

- Electronic wavefunctions for Hydrogen
- How angular momentum freedoms mix (be they the  $l$  and  $s$  of an individual electron or the  $l$ 's and  $s$ 's of a pair of electrons)
- The need for over-all anti-symmetric (upon exchange) multi-electron states
- That anti-symmetric / symmetric *spatial* states on average have the electrons closer to / further from each other.

Across the hall, in Phys 231, we'd start this problem by spelling out all the forms of energy in the system, and then focusing on just those that will vary as the system evolves:

For the atom, there would be

$$E_{atom} = E_{rest.nucleus} + K_{nucleus} + \sum_j \left\{ E_{rest.e.j} + K_{e.j} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} + \sum_{k>j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{j,k}} \right\}$$

Now, to the extent that we're not going to be considering any interactions that will affect anybody's rest energy or even the nucleus's kinetic energy, what we'd focus on is just the energy that will change with the motions of the electrons. That's what we'll focus on, and translate into the tools of quantum mechanics:

$$\hat{H}_{e's} \approx \sum_j \left\{ \frac{\hat{p}_{e,j}^2}{2m_e} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} + \sum_{k>j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{j,k}} \right\}$$

(the  $k>j$  ensures we don't double count each interaction between each pair of electrons)

Or

$$\frac{\hbar}{i} \frac{\partial}{\partial t} \approx \sum_j \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} + \sum_{k>j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{j,k}} \right\}$$

What we're neglecting in this expression (and is picked up in the next chapter) is the magnetic interactions of all these circulating charges (spinning and orbiting electrons and spinning protons), but since magnetic effects are generally far smaller than accompanying electric effects (unless you've got an electrically neutral object), that will be only a small correction.

The solutions will depend upon the positions of all the electrons as well as their spins,

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z, t) \chi(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z)$$

### Combined Electron Wavefunction Symmetry

As we'd learned in the previous section, since electrons have  $\frac{1}{2}$ -integer spins, their combinations are described by anti-symmetric wavefunctions; that is, if you swapped any pair of electrons in your wavefunction expression, you'd get a new wavefunction that differed by an overall sign. That can be because the spatial wavefunction is anti-symmetric with a symmetric spin combination, or that can be because the spatial wavefunction is symmetric with an anti-symmetric spin combination.

**Q:** which of these two has the electrons being, on average, closer to each other?

**A:** the anti-symmetric spatial configuration (with symmetric spin – triplet). Since electrons are electrically repulsive to each other, this means it's a higher-energy, less-favorable configuration.

Strictly speaking, thanks to the electron-electron potential energy term, which depends on the relative separations of pairs of electrons, the wavefunctions that solve this equation are *not* separable.

### Electron-Electron Potential Effect

Qualitatively, what's the effect of the electron-electron Coulombic interaction term?

Imagine one among many electrons orbiting a nucleus.

**Q:** To the extent that its orbit is *inside* that of the other electrons, and their orbits are spherically symmetric, how would the other electrons affect our electron?

**A:** A Gaussian argument tells us that it wouldn't even notice they were there.

**Q:** To the extent that its orbit is *outside* that of the other electrons, and they're spherically symmetric, how would they affect our electron?

**A:** A Gaussian argument tells us that it would be just like having those other electrons in the nucleus, i.e., a weaker nuclear charge. So that will be the main Coulombic effect – to 'shield' outer electron orbitals from the nucleus.

Of course, we know that for the Hydrogen atom, which we could solve exactly, electrons don't live at fixed orbital radii, rather they have distributions, so no electron is *completely* inside or outside another's orbit, but this is the general effect we'd expect.

What about two electrons that are equidistant from the nucleus, in the same orbital? Jumping ahead of ourselves just a tad, Problem 5.11 invites you to demonstrate that for Helium the two electrons would average about  $5a/4$  apart, whereas they average  $a/2$  from the nucleus which has twice the charge – so you'd imagine the electron-electron effect to be significant but not dominant.

## 5.2.1 Helium

Okay, we'll start with the simplest approximation for the simplest 'multi-electron' atom: Helium. The Schrodinger equation for the electrons (neglecting magnetic interactions or motion of the nucleus) is

$$\frac{\hbar}{i} \frac{\partial}{\partial t} \approx \left( \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right) + \left( \frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right) + \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{1,2}}$$

Again, if it weren't for that pesky cross-term that relates the two electrons' positions to each other, the solution would simply be

$$\psi(\vec{r}_1, \vec{r}_2) \chi(\vec{s}_1, \vec{s}_2) = A(\psi_{n_a l_a m_a}(\vec{r}_1) \psi_{n_b l_b m_b}(\vec{r}_2) \pm \psi_{n_b l_b m_b}(\vec{r}_1) \psi_{n_a l_a m_a}(\vec{r}_2)) \chi_{\mp}(\vec{s}_1, \vec{s}_2)$$

Where what I mean by  $\chi_{\mp}(\vec{s}_1, \vec{s}_2)$  is that its either the anti-symmetric singlet state or the symmetric triplet state.

Now, Chapter 7's discussion of the Vibrational approach shows how to build upon this simple guess and refine it to approximately incorporate the electron-electron interaction. Not even venturing that far, Griffiths argues that a reasonable 0<sup>th</sup>-order approximate solution, one that gets us in the right ballpark and the right general behavior is the solution to

$$\frac{\hbar}{i} \frac{\partial}{\partial t} \approx \left( \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right) + \left( \frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right)$$

Which *is* separable.

In fact, the only difference between the terms in brackets and the Hydrogen potential that we'd worked with last chapter is the 2 that accompanies  $e^2$  (for the 2 protons in the nucleus.)

So we can immediately quote and adapt results from last chapter.

### Approximate Helium Ground State

For example, putting both electrons at the lowest energy state possible,  $n = 1$  (which dictates  $l = m = 0$  since  $|m| \leq l < n$ ),

We have

$$\psi_o(\vec{r}_1, \vec{r}_2) \chi(\vec{s}_1, \vec{s}_2) = A(\psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \pm \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2)) \chi_{\mp}(\vec{s}_1, \vec{s}_2)$$

**Q:** which sign must we choose in the expression for the combination of spatial wavefunctions?

**Q:** since they're Fermions / spin 1/2, what sign must be in the mix of spin states?

$\psi_o(\vec{r}_1, \vec{r}_2) \chi(\vec{s}_1, \vec{s}_2) = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) |1,0\rangle$  Note: the only way they can have the same  $n, l, m$  numbers is if they are in the anti-symmetric, singlet spin state.  $|1,0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow)$

For each,

$$\psi_{100}(\vec{r}_1) = \frac{1}{\sqrt{\pi a_{He}^3}} e^{-r/a_{He}}$$

**Q:** Looking back at equation 4.72 for the Bohr Radius,  $a$ , what must be the expression for the corresponding  $a_{He}$ ?

**A:** where  $a_{\text{He}} = \frac{4\pi\epsilon_0\hbar^2}{m2e^2} = \frac{1}{2}a$  where the 2 comes along with the  $e^2$  for the 2 protons.

So

$$\psi_{100}(\vec{r}_1) = \frac{2}{\sqrt{\pi a^3/2}} e^{-2r/a}$$

And

$$\psi_o(\vec{r}_1, \vec{r}_2)\chi(\vec{s}_1, \vec{s}_2) = \frac{8}{\pi a^3} e^{-2r_{(1+r_2)/a}} |1,0\rangle$$

Similarly,

Putting this expression for the wavefunction into our approximate equation,

$$\frac{\hbar}{i} \frac{\partial}{\partial t} \approx \left( \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right) + \left( \frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right)$$

Would return that the energies are

$$E_{\text{He}} \approx -\frac{2e^2}{8\pi\epsilon_0 a_{\text{He}}} - \frac{2e^2}{8\pi\epsilon_0 a_{\text{He}}} = -\frac{2e^2}{4\pi\epsilon_0 a_{\text{He}}} = -\frac{4e^2}{4\pi\epsilon_0 a} = -8 \cdot 13.6\text{eV} = -109\text{eV}$$

Or plugging in our expression for  $a$  and generalizing back out to other  $n$  values,

$$E_{\text{He}} \approx 4 \left( \frac{-13.6\text{eV}}{n_1^2} + \frac{-13.6\text{eV}}{n_2^2} \right)$$

Now, what effect would the electron-electron interaction have? They're repulsive, so it would reduce the bonding strength, that is, make the energy less negative. Problem 5.11 yields that, assuming the two electrons are in the ground state, their average separation is about  $5a/4$ . To ballpark the energy associated with that,

$$E_{e-e} \approx \frac{e^2}{4\pi\epsilon_0(5a/4)} = \frac{4}{5} \frac{e^2}{4\pi\epsilon_0 a} = \frac{8}{5} \frac{e^2}{8\pi\epsilon_0 a} = \frac{8}{5} (13.6\text{eV})$$

So, we'd correct the helium's ground-state energy to be about

$$E_{\text{He}} \approx -8 \cdot 13.6\text{eV} + \frac{8}{5} \cdot 13.6\text{eV} = -8 \cdot \frac{4}{5} \cdot 13.6\text{eV} = -87.04\text{eV}$$

Which is closer to the experimental value around  $-78.975\text{eV}$ .

### Approximate Helium Excited State

The next excited state we might consider has one electron in the ground state and the other in some other state.

$$\psi(\vec{r}_1, \vec{r}_2)\chi(\vec{s}_1, \vec{s}_2) = A(\psi_{100}(\vec{r}_1)\psi_{n_b l_b m_b}(\vec{r}_2) \pm \psi_{n_b l_b m_b}(\vec{r}_1)\psi_{100}(\vec{r}_2))\chi_{\mp}(\vec{s}_1, \vec{s}_2)$$

**Q:** What restrictions are there on the possible signs now?

**A:** Can choose either sign for spatial, as long as the opposite is chosen for spin.

**Q:** Once we do allow for electron-electron interactions, in light of the *exchange force* discussion in the previous section, which will end up being the higher energy (less strongly-bound) state, that with the *symmetric spatial & anti-symmetric spin* or that with the *anti-symmetric spatial & symmetric spin*?

**A:** The one with the anti-symmetric spatial and symmetric spin will have the average separation between the electrons being closer. Thus it will have the *higher, less-favorable* energy. That's the **Parahelium**.

Again, in chapter 7, Griffiths presents the Variational approach to wrapping in the electron-electron interaction, but we've managed to reason out some useful ball-park properties of Hydrogen without handling that too rigorously.

## 5.2.2 The Periodic Table

We extend this kind of reasoning to consider multi-electron atoms. Now, the first-order picture is to imagine building atoms of Hydrogen-like orbitals, each of which must respect

$$|m| \leq l < n \text{ which adds up to there being } 2n^2 \text{ 'slots' for electrons with a given } n.$$

Where the energy of an electron in a given level is approximately

$$E_{e_j} \approx -\frac{m}{2\hbar^2} \left( \frac{Z_{\text{eff},j} e^2}{4\pi\epsilon_0 n} \right)^2 = -\left( \frac{Z_{\text{eff},j}}{n} \right)^2 |E_0|$$

$$Z_{\text{eff},j} \approx Z - \left( \frac{\#_{\text{same\_radius}}}{\#_{\text{same\_radius}} + 1} + \#_{\text{inside}} \right)$$

where  $Z_{\text{eff},j}$  is roughly the number of electron states of lower  $n$  that are already occupied (since those have their electrons mostly within the orbit of the  $j^{\text{th}}$  electron.)

Note, number in a filled shell is  $2n^2$ , so the  $\#_{\text{inside}}$  will be around  $2(n-1)^2 + 2(n-2)^2 + \dots + 2$  so  $Z_{\text{eff}}$  hovers around 1, giving the energies around that of Hydrogen.

### Filling Orbitals

With these ideas, we can start populating the periodic table.

#### Problem 5.12 a

While we're doing so, notice that we cycle through similar outer shells: H, Li, Na, K, all have a single  $l = 0$  electron in the highest energy level / outermost orbital

Similarly, C, Si, Ge,.. all have 2 in an  $l = 1$  state furthest out. Keep in mind that  $Y_l^m$  orbital has its distinct shape; that, combined with the number of open/occupied electron states in a level dictate how each element interacts with other elements.

**What about spin alignment?**

We have the qualitative understanding that anti-symmetric combinations of electrons are lower-energy than symmetric ones, since they allow the electrons to be further apart.

**Hund’s first rule:** This leads to one of “Hund’s rules”: the state with the highest total spin (S) will have the lowest energy (i.e., the electrons will have aligned spin, and thus anti-symmetric spatial)

**Hund’s second rule:** Though we haven’t yet considered magnetic interactions, you might appreciate that orbiting charges interact magnetically, and, like two bar magnets, the lowest energy configuration has charge circulations (orbital angular momenta) aligned.

**Hund’s third rule:** less obviously says that its lowest energy for spins to be anti-aligned with orbits. We’ll see that in section 6.3.

**Problem 5.12 b**

It’s a matter of finding the possible combined  $l$ ’s and the possible combined  $s$ ’s and then the possible alignments. It gets interesting for Carbon:

With electrons in the following states: 2 in  $\psi_{100}$ , 2 in  $\psi_{200}$ , 2 in  $\psi_{2lm}$

$(1s)^2(2s)^2(2p)^2$

Total orbital angular momentum: the electrons in the  $s$  ( $l = 0$ ) orbitals don’t contribute, and each in the  $p$  ( $l = 1$ ) do. What alignments can there be? Obviously, they can be completely aligned  $l = 2$  or anti-aligned  $l = 0$ . Less obviously, they can be partly aligned to give a total orbital angular momentum of  $l = 1$ . (see Clebsch-Gordan  $1 \times 1$  table:  $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ )

Total spin angular momentum: the electrons filling a shell have opposite spins, so those don’t contribute to the total; it’s up to the 2 in the  $2p$  level. Obviously, they can be aligned,  $s = 1$ , or anti aligned,  $s = 0$ .

$l$	$s$			$2s+l$	
$\uparrow$	$\uparrow$	$l = 2, s = 1$	$j = 3$	$\rightarrow$	$^3D_3$
$\uparrow$	$\rightarrow$	$l = 2, s = 1$	$j = 2$		$^3D_2$
$\uparrow$	$\downarrow$	$l = 2, s = 1$	$j = 1$		$^3D_1$
$\uparrow$	0	$l = 2, s = 0$	$j = 2$		$^1D_2$
$\uparrow$	$\uparrow$	$l = 1, s = 1$	$j = 2$		$^3P_2$
$\uparrow$	$\downarrow$	$l = 1, s = 1$	$j = 0$		$^3P_0$
$\uparrow$	0	$l = 1, s = 0$	$j = 1$		$^1P_1$

$\uparrow$	$\rightarrow$	$l = 1, s = 1$	$j = 1$	${}^3P_1$
0	$\uparrow$	$l = 0, s = 1$	$j = 1$	${}^3S_1$
0	0	$l = 0, s = 0$	$j = 0$	${}^1S_0$

*What happens after krypton?*

While  $n$  slowly marches the *average* radii further and further out, it also increases the radial undulations. One with a higher number of undulations actually has a significant concentration *inside* the longer-wavelength, lower  $n$  wavefunction, and so is *less* shielded by that than otherwise and is *better* bound and has a *lower* energy.