10	Fri., 11/7	**5.1** Identical Particles: 2-Particle Systems (Q8.6, 11.5)	**Daily 10.F**
11	Mon., 11/10	**5.2** Atoms (Q9.2)	**Daily 11.M**
	Tues. 11/11		**Weekly 11**
	Wed., 11/12	**5.3** Solids (Unit T7.2)	**Daily 11.W**
	Fri., 11/14	**8.1-.2** WKB Approximation & Tunneling	**Daily 11.F**

Equipment
- Griffith's text
- Moore's Text
- Spatial physics talk for particle – physics slides

Check dailies

"Im confused what griffiths means when he wavefunctions can overlap. Also can we go over the symmetrization requirement?" Jessica

"How do we determine whether a state is symmetric or antisymmetric? For example, the singlet and triplet states Griffiths mentions at the end of the chapter." Spencer

Identical Particles

5.1   Two-Particle Systems

Classically

If you had a system of two interacting particles, perhaps it's the Earth and the Sun or two masses on either end of a spring, then the system's energy would be expressible as

$$E_{1,2} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V_{1,2}$$

Quantum Mechanically

Then we should be able to generate a Schrodinger equation for the whole *system* by replacing the Energy and momentum with the appropriate operators

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V_{1,2}$$

1

$$\frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m_1}\nabla_1^2 + \frac{-\hbar^2}{2m_2}\nabla_2^2 + V_{1,2}$$

Where the two derivatives are intended to return the momenta for the two members of the system. Evidently, so one derivative pulls out just one particle's momentum and the other pulls out the other particle's momentum, we need to describe the two particle's in terms of two different position vectors. So the wave function is of the form $\Psi_{1,2} = \Psi(\vec{r}_1, \vec{r}_2, t)$.

Then the probability of finding the two parts of the system *anywhere*, that is, if you look for particle 1 at *all* possible r_1's and particle 2 at *all* possible r_2's, should be 1:

$$1 = \int\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 dVol_1 dVol_2$$

Mind you, it's not that these are *different* volumes, it's that we're individually looking for particle 1 and particle 2 over all space.

What can you do with such a *system* wavefunction? For example,

$$\langle p_1 \rangle = \int\int \Psi^*(\vec{r}_1, \vec{r}_2, t)\hat{p}_1 \Psi(\vec{r}_1, \vec{r}_2, t)dVol_1 dVol_2$$

Separable? While the kinetic energy terms are distinct, if the two particles are interacting, the potential energy will likely depend upon $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$ in a non-separable way. Which means that the solution isn't separable either.

Correct Hydrogen
You might rightly think 'but shouldn't we have treated the Hydrogen atom's electron and proton like this?' Yes indeed. The Coulomb potential isn't really the 'electron's', it's a property of the electron-proton system, and in principle the proton is free to respond to that interaction. In practice, the proton's being so much more massive than the electron means it's a pretty good approximation that it remains stationary, but to be more accurate,

$$\hat{H}_H = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \frac{e^2}{4\pi\varepsilon_o r}$$

As problem 5.1 suggests, if you change variables from $\vec{r}_e$ and $\vec{r}_p$ to $\vec{r} = \vec{r}_e - \vec{r}_p$ and

$\vec{R} = \dfrac{m_e\vec{r}_e + m_p\vec{r}_p}{m_e + m_p}$ (the center of mass), the Hamiltonian can be rephrased as

$$\hat{H}_H = \frac{\hat{p}_R^2}{2(m_e + m_p)} + \frac{\hat{p}_r^2}{2\frac{m_p m_e}{m_p + m_e}} - \frac{e^2}{4\pi\varepsilon_o r}$$

Which is exactly how you'll treat the Earth orbiting the sun in Classical Mechanics. This equation *does* have separate dependence on R and r, so the wavefunction can be written as separable factors,

$$\Psi_H = \Psi(\vec{R}, t)\Psi(\vec{r}, t).$$

The one wavefunction describes the center of mas of the Hydrogen, in other words, how the Hydrogen atom might move around the room, and the other describes how the separation between the proton and electron can change.

We could go so far as to separate out the energies:

$$\hat{H}_R = \frac{\hat{p}_R^2}{2(m_e + m_p)}$$ Hydrogen as a whole is a free particle

$$\hat{H}_r = \frac{\hat{p}_r^2}{2\frac{m_p m_e}{m_p + m_e}} - \frac{e^2}{4\pi\varepsilon_o r}$$ which looks just like the approximate relation when we imagined

the proton was locked at the origin. So all the results will be the same, including the spectrum for transitions between energy levels, excel we have $\frac{m_p m_e}{m_p + m_e}$ instead of m_e. Which means the energies are off by a factor of about 0.999 – not too bad.

5.1.1 Bosons and Fermions

Though it may not be terribly realistic, the simplest case to consider is two *non*-interacting particles. If we make them indistinguishable, we see something really interesting and fundamental.

Distinguishable

First off, let's imagine we have two *distinguishable* particles, like the electron and the proton in the Hydrogen atom, but we'll just call them particles 1 and 2. Let's say Particle 1 is in state *a* and particle *2* is in state *b*.

$$\psi_{1,2}_D = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

Indistinguishable / Identical

Now, if the two particles *aren't* distinguishable, say they're both electrons, and one is in the $n = 1$ state and the other is in the $n = 2$ state, but they're otherwise identical (including being in the same spin state- otherwise you could use that to tell them apart) then we can't tell which electron is in which state. So then the wavefunction for the whole system must be some linear combination that would, upon swapping the two particles (1 and 2) between the two states (a and b) give the same *physical* results.

$$\psi_{1,2} = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))$$

Clearly, if we choose the + sign,

$$\psi_{1,2}_+ = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))$$

$$\psi_{2,1}_+ = A(\psi_a(\vec{r}_2)\psi_b(\vec{r}_1) + \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)) = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)) = \psi_{1,2}_+$$

But you may object that 'the negative sign would mean that the wavefunction after swapping the two particles states would give the *opposite* wavefunction:

$$\psi_{1,2}_- = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1))$$

$$\psi_{2,1}_- = A(\psi_a(\vec{r}_2)\psi_b(\vec{r}_1) - \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)) = -(\psi_a(\vec{r}_2)\psi_b(\vec{r}_1) - \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)) = -\psi_{1,2}_-$$

And those two *are distinguishable!* Yes and no. The *wavefunctions* are different; however, they do not lead to *physically* distinguishable *results*! That's because probabilities and thus measurments depend on the probability density, $|\psi|^2$, so a difference of sign in the wavefunction isn't physically meaningful.

How do we choose the sign?

Feynman's Exchange by Rotation. Griffiths notes that the answer comes from relativistic quantum mechanics. Feynman wasn't satisfied with that and argued that it the exchange must correspond to a physical process that you can imagine doing. The process he proposed that gives the same results as relativistic quantum mechanics is if the 'exchange' operator corresponded with the physical process of rotating your perspective, I'll call it $\hat{R}$ for rotate. The idea is something like this: if you identify r_1 as the vector pointing to your right and r_2 as the vector pointing to your left, then you just spin yourself (your reference frame) around 180° and r_1 is now to your left while r_2 is now to your right. Of course, rotating your reference frame $\Delta\phi_{coordintes} = -\pi$ is equivalent to rotating your system $\Delta\phi_{system} = \pi$. The effect of that is

$$\hat{R}\psi_a(\vec{r}_1) = \psi_a(\vec{r}_2)e^{im\pi} \text{ and } \hat{R}\psi_b(\vec{r}_2) = \psi_b(\vec{r}_1)e^{im\pi}$$

So, the product $\hat{R}(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)) = \psi_b(\vec{r}_1)e^{im\pi}\psi_a(\vec{r}_2)e^{im\pi} = e^{im2\pi}\psi_b(\vec{r}_1)\psi_a(\vec{r}_2) = \pm\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)$ where you get $+$ if m is an integer and $-$ if m is a half-integer.

There we have it. Now, this rotation is equivalent to exchanging particles (just swapping the 1's and 2's) *if*

$$\psi_{1,2_B} = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)) \text{ for integer spin particles, } \textbf{Bosons}$$

$$\psi_{1,2_F} = A(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)) \text{ for half-integer spin particles, } \textbf{Fermions}$$

Particles in the same state

Now, what if the two particles happen to be in the *same* state? Like both are in the *n = 1* state.

Bose-Einstein Condensate
For *Bosons,* there's no problem,
$$\psi_{1,2_B} = A(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)) = 2A\psi_a(\vec{r}_2)\psi_a(\vec{r}_1)$$
So it's completely allowed for two Bosons to have the same state. In statistical mechanics, you'll see that this freedom leads, in the most extreme case, to a Bose-Einstein Condensate, in which an awful lot of the bosons in a population 'condense' down into the system's ground state at low temperatures.

Pauli Exclusion Principle
However, for *Fermions,* things don't look so good,
$$\psi_{1,2_F} = A(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)) = 0$$
The composite wavefunction is 0, so the probability of finding these two in the same state anywhere is 0. It can't happen. This is known as the Pauli Exclusion Principle. In statistical

mechanics, this will mean that even at 0 temperature, higher-energy states will be occupied if the lower energy ones are 'full.'

> 1. *Conceptual*: List several properties of bosons vs. fermions.

Considering Spin

Now, I really relied upon there being spin to appeal to this rotation as being analogous to exchange. Griffiths comments that the overall composite state of the system, $\psi_{a,b}(\vec{r}_1,\vec{r}_2)|l_{a,b},m_{a,b}\rangle$ will be symmetric for Bosons and anti-symmetric for Fermions. Since the Triplet spin state is itself symmetric, that means the spatial part must be anti-symmetric, but since the singlet spin state is anti-symmetric, that means that the spatial part must be symmetric.

This is consistent with the exchange operator being

$$\hat{R}\psi_{a,b}(\vec{r}_1,\vec{r}_2)|l_{a,b},m_{a,b}\rangle = e^{il_{a,b}\pi}\psi_{a,b}(\vec{r}_1,\vec{r}_2)|l_{a,b},m_{a,b}\rangle$$

(I have to figure out why it should be *l* when its *m* that appears to be right. But need *l* for mixed triplet state)

Or spelling out the options:

$$\chi = \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = \uparrow\uparrow \quad \text{or} \quad \chi = \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = \downarrow\downarrow, \text{ so the total state of the system is}$$

$$\psi_{1,2_F}\chi_{triplet} = A\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\right)\begin{bmatrix}\uparrow_1\uparrow_2\\ \frac{1}{\sqrt{2}}\left(\uparrow_1\downarrow_2+\downarrow_1\uparrow_2\right)\\ \downarrow_1\downarrow_2\end{bmatrix}$$

Or

$$\psi_{1,2_F}\chi_{sin glet} = A\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)+\psi_b(\vec{r}_2)\psi_a(\vec{r}_1)\right)\tfrac{1}{\sqrt{2}}\left(\downarrow_1\uparrow_2-\uparrow_1\downarrow_2\right)$$

> 2. *Starting Weekly HW*: Griffiths problem 5.4

5.1.2 Exchange Forces

The "exchange force" isn't really a force at all, but the effect of the wavefunction's being symmetric or anti-symmetric. It's most easily seen in considering the average separation of two particles in the three different cases: distinguishable particles, identical particles in a symmetric spatial state, and identical particles in an anti-symmetric spatial state.

Case 1: Distinguishable Particles

$$\psi_{1,2} = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$
$$\underset{D}{}$$

$$\left\langle\left\langle (\vec{r}_1 - \vec{r}_2)^2\right\rangle_a\right\rangle_b = \left\langle\left\langle r_1^2\right\rangle_a\right\rangle_b + \left\langle\left\langle r_2^2\right\rangle_a\right\rangle_b - 2\left\langle\left\langle x_1 x_2 + y_1 y_2 + z_1 z_2\right\rangle_a\right\rangle_b$$

Where, what I mean by this double-bracket notation is we've got both wavefunctions a and b in there.

$$\left\langle\left\langle r_1^2\right\rangle_a\right\rangle_b = \int \psi_{1,2}^* \, r_1^2 \psi_{1,2} dVol_1 dVol_2 = \int \psi_a(\vec{r}_1)^* \psi_b(\vec{r}_2)^* r_1^2 \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) dVol_1 dVol_2$$

$$= \int \psi_a(\vec{r}_1)^* r_1^2 \psi_a(\vec{r}_1) dVol_1 \int \psi_b(\vec{r}_2)^* \psi_b(\vec{r}_2) dVol_2 = \left\langle r^2\right\rangle_a \left\langle \psi_b | \psi_b\right\rangle = \left\langle r^2\right\rangle_a$$

Similarly, $\left\langle r_2^2\right\rangle_{a,b} = \left\langle r^2\right\rangle_b$ and $\left\langle x_1 x_2 + y_1 y_2 + z_1 z_2\right\rangle_{a,b} = \left\langle x\right\rangle_a\left\langle x\right\rangle_b + \left\langle y\right\rangle_a\left\langle y\right\rangle_b + \left\langle z\right\rangle_a\left\langle z\right\rangle_b$

So,

$$\underset{D}{\left\langle (\vec{r}_1 - \vec{r}_2)^2\right\rangle_{a,b}} = \left\langle r^2\right\rangle_a + \left\langle r^2\right\rangle_b - 2\left(\left\langle x\right\rangle_a\left\langle x\right\rangle_b + \left\langle y\right\rangle_a\left\langle y\right\rangle_b + \left\langle z\right\rangle_a\left\langle z\right\rangle_b\right)$$

Ok, having seen what this looks like in 3-D, there's no real conceptual gain to working here rather than for 1-D, so, like Griffiths, let's focus on a 1-D problem. Then

$$\underset{D}{\left\langle (x_1 - x_2)^2\right\rangle_{a,b}} = \left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b - 2\left\langle x\right\rangle_a\left\langle x\right\rangle_b$$

Case 2: Identical Particles

$$\underset{\pm}{\psi_{1,2}} = \tfrac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$$

So,

$$\underset{\pm}{\left\langle (x_1 - x_2)^2\right\rangle_{a,b}} = \left\langle x_1^2\right\rangle_{a,b} + \left\langle x_2^2\right\rangle_{a,b} - 2\left\langle x_1 x_2\right\rangle_{a,b}$$

Where this time,

$$\left\langle x_1^2\right\rangle_{a,b} = \left\langle \tfrac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)\middle| x_1^2 \tfrac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)\right\rangle$$

$$= \tfrac{1}{2}\left(\left\langle \left(\psi_{a,1}\psi_{b,2} \pm \psi_{a,2}\psi_{b,1}\right)\middle| x_1^2\left(\psi_{a,1}\psi_{b,2} \pm \psi_{a,2}\psi_{b,1}\right)\right\rangle\right)$$

$$= \tfrac{1}{2}\left(\left\langle \psi_{a,1}\psi_{b,2}\middle| x_1^2\psi_{a,1}\psi_{b,2}\right\rangle + \left\langle \psi_{a,2}\psi_{b,1}\middle| x_1^2\psi_{a,2}\psi_{b,1}\right\rangle \pm \left\langle \psi_{a,1}\psi_{b,2}\middle| x_1^2\psi_{a,2}\psi_{b,1}\right\rangle \pm \left\langle \psi_{a,2}\psi_{b,1}\middle| x_1^2\psi_{a,1}\psi_{b,2}\right\rangle\right)$$

$$= \tfrac{1}{2}\left(\left\langle \psi_{a,1}\middle| x_1^2\psi_{a,1}\right\rangle\left\langle \psi_{b,2}\middle| \psi_{b,2}\right\rangle + \left\langle \psi_{b,1}\middle| x_1^2\psi_{b,1}\right\rangle\left\langle \psi_{a,2}\middle| \psi_{a,2}\right\rangle \pm \left\langle \psi_{a,1}\middle| x_1^2\psi_{b,1}\right\rangle\left\langle \psi_{b,2}\middle| \psi_{a,2}\right\rangle \pm \left\langle \psi_{b,1}\middle| x_1^2\psi_{a,1}\right\rangle\left\langle \psi_{a,2}\middle| \psi_{b,2}\right\rangle\right)$$

$$= \tfrac{1}{2}\left(\left\langle \psi_a\middle| x^2\psi_a\right\rangle + \left\langle \psi_b\middle| x^2\psi_b\right\rangle \pm 0 \pm 0\right)$$

$$= \tfrac{1}{2}\left(\left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b\right)$$

where terms vanished because we'll assume ortho-normality.

Similarly,

$$\left\langle x_2^2\right\rangle_{a,b} = \tfrac{1}{2}\left(\left\langle x^2\right\rangle_a + \left\langle x^2\right\rangle_b\right)$$

As for the cross term,

$$\langle x_1 x_2 \rangle_{a,b} = \left\langle \tfrac{1}{\sqrt{2}}\left(\psi_{a,1}\psi_{b,2} \pm \psi_{a,2}\psi_{b,1} \right) \middle| x_1 x_2 \, \tfrac{1}{\sqrt{2}}\left(\psi_{a,1}\psi_{b,2} \pm \psi_{a,2}\psi_{b,1} \right) \right\rangle$$

$$= \tfrac{1}{2}\left(\langle \psi_{a,1}\psi_{b,2} | x_1 x_2 \psi_{a,1}\psi_{b,2} \rangle + \langle \psi_{a,2}\psi_{b,1} | x_1 x_2 \psi_{a,2}\psi_{b,1} \rangle \pm \langle \psi_{a,1}\psi_{b,2} | x_1 x_2 \psi_{a,2}\psi_{b,1} \rangle \pm \langle \psi_{a,2}\psi_{b,1} | x_1 x_2 \psi_{a,1}\psi_{b,2} \rangle \right)$$

$$= \tfrac{1}{2}\left(\langle \psi_a | x\psi_a \rangle\langle \psi_b | x\psi_b \rangle + \langle \psi_a | x\psi_a \rangle\langle \psi_b | x\psi_b \rangle \pm \langle \psi_a | x\psi_b \rangle\langle \psi_b | x\psi_a \rangle \pm \langle \psi_b | x\psi_a \rangle\langle \psi_a | x\psi_b \rangle \right)$$

$$= \left(\langle x \rangle_a \langle x \rangle_b \pm \langle x \rangle_{ba}\langle x \rangle_{ab} \right) = \langle x \rangle_a \langle x \rangle_b \pm \left| \langle x \rangle_{ba} \right|^2$$

<center>where the last two terms involve mixed inner products</center>

So,

$$\left\langle (x_1 - x_2)^2 \right\rangle_{a,b}^{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\left(\langle x \rangle_a \langle x \rangle_b \pm \left| \langle x \rangle_{ba} \right|^2 \right)$$

Comparing with the distinguishable case,

$$\left\langle (x_1 - x_2)^2 \right\rangle_{a,b}^{\pm} = \left\langle (x_1 - x_2)^2 \right\rangle_{a,b}^{D} \mp 2\left| \langle x \rangle_{ba} \right|^2$$

The moral is that if the two indistinguishable particles are in anti-symmetric spatial state, they are *further* apart than if they were distinguishable, but if they are in the symmetric spatial state, then they are *closer* than if they were distinguishable.

Covalent bonds.

Recall that spin-1/2 particles can be in the symmetric spatial state if they are in the anti-symmetric, i.e., singlet, anti-aligned, spin state. So, in that case, two electrons shared by two atoms would tend *toward* each other, bridging the gap between the two atoms.

You may recall that Moore argued this would be the lower-energy configuration since being symmetric means that the shared wavefunction *doesn't* have to go to 0 in the middle, so the wavelength can by broader / the concavity can be less / the kinetic energy can be less.

1. *Conceptual*: Explain, using Quantum Mechanics, the source of the covalent bond.

2. *Starting Weekly HW*: Griffiths problem 5.6