Multi-Particle States

Lecture 31

Physics 342
Quantum Mechanics I

Friday, April 16th, 2010

Just as quantum mechanics in one dimensions is meant to motivate and inform (and, in some specific cases, to model), quantum mechanics applied to a single particle in an external field is a fundamentally incomplete, albeit useful, picture. After all, an electron is not alone in the universe with a Coulomb field. Something is generating the Coulomb field, and we are honor bound to treat the entirety of the system, not just the electron in isolation. Indeed, we can establish the relative correctness of an electron in isolation only by considering its relation to other electrons and particles.

This is the task we now undertake: A description of wavefunctions of systems. Particles in isolation is itself a classical concept – fundamentally, quantum particles and more generally, quantum fields are all part of the "master wave-function of the universe". Think of the program of multi-particle classical mechanics: We have a position vector $\mathbf{r}(t) \in \mathbb{R}^{3N}$ for N particles, and the goal is to find the motion of each particle from Newton's second law (or some Euler-Lagrange equivalent). In the quantum mechanical analogue of this problem, the wave function is still the goal, but we don't get a vector $\boldsymbol{\psi} \in \mathbb{R}^{3N}$ wave function, instead we want a one-dimensional wave function that depends on $3N$ *coordinates* (plus time, of course).

31.1   Multi-Particle Wave Functions

It is easy to think about what we mean by multiple particles interacting in quantum mechanics. Take two particles with some interaction potential $V(\mathbf{r}_1, \mathbf{r}_2)$ for particle coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. Then the classical Hamiltonian

$$H = \frac{p_1^2}{2\,m_1} + \frac{p_2^2}{2\,m_2} + V(\mathbf{r}_1, \mathbf{r}_2) \tag{31.1}$$

becomes the quantum mechanical operator

$$H = -\frac{\hbar^2}{2\,m_1}\,\nabla_1^2 - \frac{\hbar^2}{2\,m_2}\,\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2) \qquad (31.2)$$

where ∇_1 is the gradient operator w.r.t. the first particle's coordinates, ∇_2 refers to the second particle's. Our wave function is now $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$, a function of the six coordinates and time. The statistical interpretation carries over:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2\, d\tau_1\, d\tau_2 \qquad (31.3)$$

is the probability of finding particle 1 in the volume $d\tau_1$ about $\mathbf{r}_1$ and particle 2 in the volume $d\tau_2$ about $\mathbf{r}_2$. The normalization is over all possible locations of the first and second particles

$$\int |\Psi|^2\, d\tau_1\, d\tau_2 = 1. \qquad (31.4)$$

Finally, provided the potential is time-independent, we can separate Schrödinger's equation as usual, letting $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = e^{-i\frac{E\,t}{\hbar}}\,\psi(\mathbf{r}_1, \mathbf{r}_2)$ with ψ solving the time-independent eigenvalue equation:

$$\left(-\frac{\hbar^2}{2\,m_1}\,\nabla_1^2 - \frac{\hbar^2}{2\,m_2}\,\nabla_2^2 + V\right)\psi = E\,\psi. \qquad (31.5)$$

31.2 Distinguishable and Indistinguishable Particles

Consider a separable potential, i.e. one which acts only on one particle or the other, $V(\mathbf{r}_1, \mathbf{r}_2) = V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2)$, then Schrödinger's equation itself separates, and we can consider a wavefunction that is a multiplicative separation $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\,\psi_2(\mathbf{r}_2)$. The two particles are each in some individual state of the sort we have been considering (in our one-particle discussions), and they only combine in the sense that a full system's Hamiltonian must include all particles in the system.

The above separation assumes it is possible to distinguish between the particles somehow: They have different masses, or interact differently with a potential. For indistinguishable particles (like any two electrons, same mass, same interaction), we can have either particle in either state (just a relabelling $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, ultimately integrated over anyway). So which should be put

in which state? There are two obvious choices, adjusted by normalization:

$$\psi_\pm(\mathbf{r}_1, \mathbf{r}_2) = A\left(\psi_1(\mathbf{r}_1)\,\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_2)\,\psi_2(\mathbf{r}_1)\right). \tag{31.6}$$

The two choices are fundamentally different, particles that combine according to the positive sign are called *bosons* and particles that combine according to the bottom one are called *fermions*. There is an easy (but deep) way to characterize fermions and bosons by their spins – all particles with integer spin are bosons, all particles with half-integer spin are fermions. So nature tells us which sign to choose based on which type of particle we are considering. Fermions, using the minus sign above, cannot occupy the same state, since then $\psi_1 = \psi_2$ and $\psi_- = 0$, a statement of the Pauli exclusion principle. No such restriction holds for bosons.

If we define the exchange operator P that acts on the composite wavefunction via: $P\,\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$, then if a Hamiltonian involves indistinguishable particles $(m_1 = m_2)$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$, we have $H(1 \leftrightarrow 2) = H$. In this case, the Hamiltonian commutes with P:

$$[P, H]\,f(\mathbf{r}_1, \mathbf{r}_2) = H(1 \leftrightarrow 2)\,f(\mathbf{r}_2, \mathbf{r}_1) - H\,f(\mathbf{r}_2, \mathbf{r}_1) = 0. \tag{31.7}$$

Then there are mutual eigenstates of P and H. The eigenstates of P have eigenvalue ± 1 – to see this, suppose we have an eigenstate $\psi(\mathbf{r}_1, \mathbf{r}_2)$ – that is, $P\,\psi(\mathbf{r}_1, \mathbf{r}_2) = \alpha\,\psi(\mathbf{r}_1, \mathbf{r}_2)$, then applying P again (to any function, eigenfunction or not) gives back $\psi(\mathbf{r}_1, \mathbf{r}_2)$ (exchange twice), so

$$P\left(P\psi(\mathbf{r}_1, \mathbf{r}_2)\right) = \alpha^2\,\psi(\mathbf{r}_1, \mathbf{r}_2) \longrightarrow \alpha = \pm 1. \tag{31.8}$$

We see that the symmetry/antisymmetry of a wavefunction is allowed since ψ is a simultaneous eigenstate of P and H, so it is possible to find eigenstates of H that have

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1). \tag{31.9}$$

In fact, this is strengthened by the natural observation that eigenstates of H for identical particles *must be* in either a symmetric or antisymmetric state – not just *can be*. So our "choice" of bosons or fermions is forced, and exhaustive.

31.3   Identical, Non-Interacting Electrons

We have not included spin as a part of the wavefunction yet, but it is easy to do. Consider two non-interacting electrons, so that the Hamiltonian is

$$\left(-\frac{\hbar^2}{2\,m}\,\nabla_1^2 - \frac{\hbar^2}{2\,m}\,\nabla_2^2 + V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2) \right)\,\psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\psi(\mathbf{r}_1,\mathbf{r}_2), \qquad (31.10)$$

for the spatial wavefunction. But this H commutes with the total spin operator S^2, so that we must be able to find eigenstates of each. The eigenstates of S^2 for two electrons are just the singlet and triplet configurations that we saw last time. The exchange operator P is not just a matter of interchanging the spatial positions, we must also interchange the spins, and it is the *combination* of the two that must be antisymmetric or symmetric. To be explicit, we can write $P = P_{\mathbf{r}}\,P_m$, the spatial and spin exchanges together form the full exchange.

The wavefunction can be thought of as $\psi(\mathbf{r}_1,\mathbf{r}_2) = \phi(\mathbf{r}_1,\mathbf{r}_2)\,\chi$ where χ is the spin portion[1], and $\phi(\mathbf{r}_1,\mathbf{r}_2)$ is the spatial portion satisfying the above time-independent Schrödinger equation. Now suppose we choose the singlet configuration for the spins, i.e.

$$\chi = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\,\frac{1}{2}\right\rangle \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle - \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle \left|\frac{1}{2}\,\frac{1}{2}\right\rangle \right) \qquad (31.11)$$

then $P_m\chi = -\chi$, since χ is antisymmetric in the interchange of the two electrons. Since electrons are fermions, the entire wavefunction must be antisymmetric, which tells us that $P_{\mathbf{r}}\phi = +\phi$, i.e. we take the symmetric combination for the spatial wavefunction (denoted by $+$ to indicate that it is the zero-total-spin singlet form – symmetric):

$$\phi_+(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_1(\mathbf{r}_1)\,\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\,\phi_2(\mathbf{r}_1) \right) \qquad (31.12)$$

where $\phi_1(\mathbf{r}_1)$ is the solution to the 1 portion of the above Hamiltonian (a one-particle state) and $\phi_2(\mathbf{r}_2)$ is the solution to the 2 portion.

The triplet, $s = 1$ eigenstates of S^2 are all symmetric in interchange of the two electrons, hence the spatial wavefunction must be *antisymmetric* to make the entire wavefunction antisymmetric: $P_{\mathbf{r}}\phi = -\phi$, and here we take

$$\phi_-(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_1(\mathbf{r}_1)\,\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\,\phi_2(\mathbf{r}_1) \right). \qquad (31.13)$$

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[1]Notice that the χ spin part of the wavefunction does *not* itself separate multiplicatively.

Now, the point – if we ask what is the probability that one particle is in the vicinity $d\tau_1$ of $\mathbf{r}_1$ and that the second particle is in the vicinity $d\tau_2$ of $\mathbf{r}_2$, the answer, according to our statistical interpretation, is (this is a spatial question, spins don't matter)

$$
\begin{aligned}
|\phi|^2 \, d\tau_1 \, d\tau_2 = \frac{1}{2} & \left[|\phi_1(\mathbf{r}_1)|^2 \, |\phi_2(\mathbf{r}_2)|^2 + |\phi_1(\mathbf{r}_2)|^2 \, |\phi_2(\mathbf{r}_1)|^2 \right. \\
& \left. \pm (\phi_1^*(\mathbf{r}_1) \, \phi_1(\mathbf{r}_2) \, \phi_2^*(\mathbf{r}_2) \, \phi_2(\mathbf{r}_1) + \phi_1(\mathbf{r}_1) \, \phi_1^*(\mathbf{r}_2) \, \phi_2(\mathbf{r}_2) \, \phi_2^*(\mathbf{r}_1)) \right] d\tau_1 \, d\tau_2 \\
= \frac{1}{2} & \left[|\phi_1(\mathbf{r}_1)|^2 \, |\phi_2(\mathbf{r}_2)|^2 + |\phi_1(\mathbf{r}_2)|^2 \, |\phi_2(\mathbf{r}_1)|^2 \right. \\
& \left. \pm 2 \, \mathrm{Re}(\phi_1^*(\mathbf{r}_1) \, \phi_1(\mathbf{r}_2) \, \phi_2^*(\mathbf{r}_2) \, \phi_2(\mathbf{r}_1)) \right] d\tau_1 \, d\tau_2.
\end{aligned}
$$

(31.14)

It is only the final term that distinguishes between the singlet and triplet states. In the triplet (minus sign) case, the probability of finding the electrons at the same location ($\mathbf{r}_1 = \mathbf{r}_2$) is zero, and the electrons "avoid" each other. For the singlet, it is more likely to find the electrons occupying the same spatial location. In addition, we can see why a free electron on one side of the room can be taken as spatially distinct from an electron on the other – if we think of $\mathbf{r}_1$ and $\mathbf{r}_2$ as widely separated, with $\phi_1(\mathbf{r})$ large near $\mathbf{r}_1$ and $\phi_2(\mathbf{r})$ large around $\mathbf{r}_2$, then the dominant term above is just $|\phi_1(\mathbf{r}_1)|^2 \, |\phi_2(\mathbf{r}_2)|^2$. But this is the probability density for two independent particles – meaning that we can treat them separately.

31.4 Exchange "Force"

The above calculation (31.14) has a term that depends on the symmetrization or antisymmetrization of the state, and it is called the "exchange density". In general, there will be an observable difference associated with the symmetry requirements. If we ignore spin, and consider just the spatial wavefunction $\psi_\pm$ with ψ_+ for bosons, ψ_- for fermions, we can characterize a sort of symmetry pressure by considering the expectation value of the distance between the two particles (squared so we don't get cancellation) – we'll work in one dimension here for simplicity:

$$
\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 \, x_2 \rangle.
$$

(31.15)

31.4.1 Distinguishable Particles

If $\psi = \psi_1(\mathbf{r}_1) \, \psi_2(\mathbf{r}_2)$, so that we are talking about two different particles, then we just need the usual expectation values:

$$\langle x_1^2 \rangle = \int \psi_1(x_1)^* \, x_1^2 \, \psi_1(x_1) \, dx_1 \int \psi_2^*(x_2) \, \psi_2(x_2) \, dx_2 = \langle x^2 \rangle_1$$
$$\langle x_2^2 \rangle = \langle x^2 \rangle_2$$
$$\langle x_1 \, x_2 \rangle = \langle x \rangle_1 \, \langle x \rangle_2$$

(31.16)

where the top line shows how the calculation goes, and we write $\langle x^2 \rangle_1$ (and similarly for $\langle x^2 \rangle_2$) to indicate that we just have the x^2 expectation value w.r.t. the state $\psi_1(x)$. Our distinguishable particles are then, on average,

$$\langle (x_1 - x_2)^2 \rangle_{di} = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2 \, \langle x \rangle_1 \, \langle x \rangle_2. \qquad (31.17)$$

31.4.2 Indistinguishable Particles

Here, we have

$$\psi_\pm = \frac{1}{\sqrt{2}} \left(\psi_1(x_1) \, \psi_2(x_2) \pm \psi_1(x_2) \, \psi_2(x_1) \right). \qquad (31.18)$$

The relevant expectation values are

$$\langle x_1^2 \rangle = \frac{1}{2} \left[\langle x^2 \rangle_1 + \langle x^2 \rangle_2 \pm \int \psi_1^*(x_1) \, x_1^2 \, \psi_2(x_1) \, dx_1 \int \psi_2^*(x_2) \, \psi_1(x_2) \, dx_2 \right.$$
$$\left. \pm \int \psi_2^*(x_1) \, x_1^2 \, \psi_1(x_2) \, dx_1 \int \psi_1^*(x_2) \, \psi_2(x_2) \, dx_2 \right],$$

(31.19)

and provided $\psi_1(x) \neq \psi_2(x)$ (in the fermion case, at least, they cannot) – then orthonormality gives $\int \psi_1^*(x) \, \psi_2(x) \, dx = 0$, and the above reduces to $\langle x_1^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_1 + \langle x^2 \rangle_2)$. The expectation value $\langle x_2^2 \rangle = \langle x_1^2 \rangle$ since there is no distinguishing between the particles.

The difference comes in the cross-term, of course:

$$
\begin{aligned}
\langle x_1\, x_2 \rangle = \frac{1}{2} \Bigg[&\int \psi_1^*(x_1)\, x_1\, \psi_1(x_1)\, dx_1 \int \psi_2^*(x_2)\, x_2\, \psi_2(x_2)\, dx_2 \\
&+ \int \psi_1^*(x_2)\, x_2\, \psi_1(x_2)\, dx_2 \int \psi_2^*(x_1)\, x_1\, \psi_2(x_1)\, dx_1 \\
&\pm \int \psi_1^*(x_1)\, x_1\, \psi_2(x_1)\, dx_1 \int \psi_2^*(x_2)\, x_2\, \psi_1(x_2)\, dx_2 \\
&\pm \int \psi_2^*(x_1)\, x_1\, \psi_1(x_1)\, dx_1 \int \psi_1^*(x_2)\, x_2\, \psi_2(x_2)\, dx_2 \Bigg] \\
= &\, \langle x \rangle_1\, \langle x \rangle_2 \pm \langle x \rangle_{12}^2
\end{aligned}
\tag{31.20}
$$

where the last term is just the obvious $\int \psi_1^*(x)\, x\, \psi_2(x)\, dx$. Written in terms of the distinguishable case, we have

$$
\langle (x_1 - x_2)^2 \rangle_{ind\pm} = \langle x \rangle_1^2 + \langle x \rangle_2^2 - 2\left(\langle x \rangle_1\, \langle x \rangle_2 \pm \langle x \rangle_{12}^2 \right) = \langle (x_1 - x_2)^2 \rangle_{di} \mp 2\, \langle x \rangle_{12}^2,
\tag{31.21}
$$

so for the bosonic $+$ case, the particles are slightly closer together than distinguishable particles, and for fermions, they are slightly further apart. Again, we see that the cross term goes away if the wave functions do not significantly overlap, another indication that localization (i.e. a classical interpretation) works at some level.

The "force" is fictitious in a classical sense, but we can think of a bosonic attractive force pulling two electrons closer together, and a fermionic repulsive force tending to push two particles apart, this is the so-called "exchange" force.

31.5   Atoms and the Periodic Table

The discussion of non-interacting electrons in the presence of some central potential is the crudest possible model for multi-electron atoms. Electrons, of course, interact via electrostatics (at the very least), so throwing out the interaction potential cannot be quite right. Yet, the basic physics of spin and statistics does inform atomic structure, up to a point.

Homework

Reading: Griffiths, pp. 201–210.

Problem 31.1

Griffiths 5.1. Two particle view of Hydrogen.

Problem 31.2

Griffiths 5.6. Measurable differences from the particle-interchange eigenstates.