Multielectron atoms

Now that we've beaten the hydrogen atom (+ any single-electron atom, for that matter) into the ground, let's think about what happens when you take higher Z atoms + add more electrons. You know that physical systems want to be in the lowest energy state, so presumably when you add more electrons, they should all pile up in the $n=1$ state - right?

Wrong! Helium works okay - its 2 electrons have $n=1$, but when you move up to Lithium its third electron has $n=2$, and all the higher Z atoms have electron states corresponding to $n \geq 2$.

[Aside: How do we know this? From spectroscopy. For excited atoms with $Z>2$, we don't get transitions to the $n=1$ state if the atoms aren't ionized, i.e., if they have all their electrons.

The reasons for this are quite general in Quantum mechanics, and are not specific to atoms. To understand this, we have to consider some features of quantum mechanics that are actually quite general and do not depend on the fact that we're interested in electrons in atoms.

Identical particles

So we have to consider how identical particles should be treated in quantum mechanics. Classically, this is not an issue — all particles have definite, well-defined trajectories, and in principle we can follow the motion of any individual particle and distinguish it from all other particles.

In quantum mechanics, the uncertainty principle doesn't allow this — keeping track of individual particles requires observing them, and if we have a system of identical particles the act of observation would disturb them enough that we might not be able to tell them apart — we might have overlapping wave functions.

(Aside: In the H atom, in the ground state for example, the e + p wave fns overlap, but we can distinguish them because of their mass, charge, etc.]

This indistinguishability of identical particles is fundamental and it must be reflected in our mathematical description of systems involving them, i.e.

> our calculation of any measurable quantity must be independent of the labeling of identical particles: we must get the same result if we interchange the labels of identical particles

because in our observations we cannot distinguish them.

This is a strong constraint on the possible forms of multiparticle wave functions (from which we calculate observables) and it has profound physical. consequences, Note, BTW, that it's not the wave function itself that has to be independent of the assignment of labels, but the observables you calculate from it.

Two identical particles

So let's look at a system of two identical particles, and for simplicity we'll ignore any interactions between them. You can think of two particles in a box as an example, but the result doesn't depend on the details.

So let the particles have mass m, and let their coordinates be labeled, respectively, by x_1, y_1, z_1, + x_2, y_2, z_2

Let ψ_T be the total wave function for the system. It's described by the Schrödinger eq'n

$$-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)\psi_T(\vec{x}_1,\vec{x}_2) + V_T(\vec{x}_1,\vec{x}_2)\,\psi_T = \underset{\substack{\uparrow \\ \text{total energy}}}{E_T}\,\psi_T$$

If there are no interactions btwn the particles we can write the potential as a sum

$$V_T = V(\vec{x}_1) + V(\vec{x}_2)$$

with the same potential for both because the particles are identical. Now we can do the usual separation, writing

$$\psi_T(\vec{x}_1, \vec{x}_2) = \psi(\vec{x}_1)\,\psi'(\vec{x}_2)$$

not necessarily the same fn, but see below

We need to be a little more specific. Any given eigenstate can be specified by 4 quantum numbers: 3 associated with space (e.g. n, l, m_l in the H atom) and 1 associated with spin (e.g. m_s). Instead of writing all of the quantum numbers, let's use α (or β) to stand in for the whole set. Also instead of writing $\psi(\vec{x}_1)$ let's write $\psi(1)$. So

$$\psi_\alpha(1)$$

means the eigenfunction described by the set of quantum numbers α as a function of the coordinates $\vec{x}_1$.

Now let's look at the consequences of the indistinguishability requirement. The Schr. eq'n allows as a sol'n something like

$$\psi_T = \psi_\alpha(1)\,\psi_\beta(2)$$

or any linear combination of such terms. We need to check an observable; the simplest one is the probability density $\psi_T^* \psi_T$. So we have

$$\psi_T^* \psi_T = \psi_\alpha^*(1)\,\psi_\alpha(1)\,\psi_\beta^*(2)\,\psi_\beta(2)$$

Now to check the indistinguishability condition. We must be able to interchange the labels for particles 1 + 2 without changing the probability density

$$\psi_T^* \psi_T \xrightarrow[1\leftrightarrow 2]{} \psi_\alpha^*(2)\,\psi_\alpha(2)\,\psi_\beta^*(1)\,\psi_\beta(1)$$

⇒ not the same as the original probability density.

Not surprising because $\psi_T \xrightarrow[1\leftrightarrow 2]{} \psi_\alpha(2)\,\psi_\beta(1)$. So this won't work for the total wave function. But what will work is a combination of the original ψ_T and the ψ_T you get on interchanging indices. There are two possibilities:

$$\psi_s = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\,\psi_\beta(2) + \psi_\beta(1)\,\psi_\alpha(2)\right]$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\,\psi_\beta(2) - \psi_\beta(1)\,\psi_\alpha(2)\right]$$

where the factors of $\frac{1}{\sqrt{2}}$ guarantee that ψ_s + ψ_A are normalized if ψ_α + ψ_β are normalized.

These work, their transformation properties on interchanging particle labels are

$$\psi_s \rightarrow \frac{1}{\sqrt{2}}\left[\psi_\alpha(2)\psi_\beta(1) + \psi_\beta(2)\psi_\alpha(1)\right] = +\psi_s \quad \text{symmetric}$$

$$\psi_A \rightarrow \frac{1}{\sqrt{2}}\left[\psi_\alpha(2)\,\psi_\beta(1) - \psi_\beta(2)\,\psi_\alpha(1)\right] = -\psi_A \quad \text{antisymmetric.}$$

and the probability densities transform as

$$\psi_s^*\psi_s \rightarrow (+1)^2\psi_s^*\psi_s = \psi_s^*\psi_s$$

$$\psi_A^*\psi_A \rightarrow (-1)^2\,\psi_A^*\psi_A = \psi_A^*\psi_A$$

You can convince yourself that these wave functions do the trick for other observables as well.

In general, to preserve observables, multiparticle wave functions must be symmetric or antisymmetric under interchange of any pair of particle labels.

Normalization:

The fact that the $\frac{1}{\sqrt{2}}$ gives the correct normalization is actually not trivial, but it follows from a general property of eigenfunctions: "orthogonality." We'll illustrate this with ψ_S; ψ_A works the same except for a couple of minus signs. We have

$$\int \psi_S^* \psi_S \, d^3x_1 \, d^3x_2 = \frac{1}{2} \int \Big[\underbrace{|\psi_\alpha(1)|^2 |\psi_\beta(2)|^2 + |\psi_\alpha(2)|^2 |\psi_\beta(1)|^2}_{①}$$

$$+ \underbrace{\psi_\alpha^*(1) \psi_\beta(1) \psi_\alpha(2) \psi_\beta^*(2) + \psi_\alpha(1) \psi_\beta^*(1) + \psi_\alpha^*(2) \psi_\beta(2)}_{②} \Big]$$

$$* \, d^3x_1 \, d^3x_2$$

Look at the terms in ①: They are

$$\underbrace{\int |\psi_\alpha(1)|^2 d^3x_1}_{=1} \; \underbrace{\int |\psi_\beta(2)|^2 d^3x_2}_{=1} + \underbrace{\quad 1 \leftrightarrow 2 \quad}_{=1}$$

assuming the ψ_α + ψ_β are normalized

In ② we have terms like

$$\int \psi_\alpha^*(1) \psi_\beta(1) d^3x_1 = 0 , \quad \alpha \neq \beta$$

It is a property of eigenfunctions that this integral is equal to zero if $\alpha \neq \beta$.

[Aside: If $\alpha = \beta$ we can use $\psi_T = \psi_\alpha(1)\,\psi_\beta(2) = \psi_\alpha(1)\,\psi_\alpha(2)$]

We can verify explicitly that

$$I = \int \psi_\alpha^*(x)\,\psi_\beta(x)\,dx = 0,$$

where the system is a particle in a box and α and β are the ground state and first excited state, respectively. We don't care about the overall normalization. The wave functions are

$$\psi_\alpha(x) = \psi_{gs}(x) \propto \cos\frac{\pi x}{a}$$

$$\psi_\beta(x) = \psi_{1^{st}\text{ exc. state}}(x) \propto \sin\frac{2\pi x}{a}$$

So $I \propto \displaystyle\int_{-a/2}^{a/2} \cos\frac{\pi x}{a}\,\sin\frac{2\pi x}{a}\,dx$

There are a number of ways to evaluate this. My favorite (besides looking it up...) is to use complex exponentials to find the appropriate trig identity:

$$\cos y \sin z = \left(\frac{e^{iy} + e^{-iy}}{2}\right)\left(\frac{e^{iz} - e^{-iz}}{2i}\right)$$

$$= \frac{1}{4i}\left[e^{i(y+z)} - e^{-i(y+z)} + e^{-i(y-z)} - e^{i(y-z)}\right]$$

$$= \frac{1}{2}\left[\sin(y+z) - \sin(y-z)\right]$$

So
$$I \propto \int_{-a/2}^{a/2} \sin\left(3\frac{\pi x}{a}\right) dx + \underset{\substack{\uparrow \\ \text{absorbing 2 minus signs}}}{\int_{-a/2}^{a/2}} \sin\left(\frac{\pi x}{a}\right) dx$$

$$= \frac{a}{3\pi}\left[-\cos\frac{3\pi x}{a}\Big|_{-a/2}^{a/2}\right] + \frac{a}{\pi}\left[-\cos\frac{\pi x}{a}\Big|_{-a/2}^{a/2}\right]$$

$$= \quad 0 \quad\quad + \quad 0$$

Actually a simpler way to see this is to notice that the original integral

$$I \sim \int_{-a/2}^{a/2} \cos\frac{\pi x}{a} \sin\frac{2\pi x}{a}\, dx$$

has an odd integrand and symmetric limits of integration.

Either way, we have

$$I = 0$$

end of example

So going back to the normalization of ψ_S, we have (assuming $\alpha \neq \beta$)

$$\int \psi_S^* \psi_S\, d^3x_1 d^3x_2 = \frac{1}{2}\left[1 + 1 + 0 + 0\right] = 1$$

Exclusion principle; spin + wave fn symmetry.

now we have two general possibilities symmetric & antisymmetric for multiparticle wave functions. How do we know when to apply which one, or what conditions/particles each corresponds to? It turns out, as we'll see below, that it depends on a particle's spin!

Meanwhile, let's go back to the puzzle we began this chapter with. Why don't the ground states of multielectron atoms have all the electrons piled up in the $n=1$ state? Pauli figured out the answer, which is called the Pauli Exclusion Principle. As applied to atoms, where he first figured it out, it says no two atomic electrons can be in the same quantum state. It turns out to be more general — in any system, you can't have more than one electron in a given quantum state.

Now what happens if we take ψ_A & make α & β the same? We get

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\,\psi_\alpha(2) - \psi_\alpha(2)\,\psi_\alpha(1)\right] = 0$$

$\Rightarrow$ antisymmetric wave functions don't allow more than one particle in the same state, i.e. they automatically satisfy the exclusion principle as written above.