

Classroom



In this section of Resonance, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. "Classroom" is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

Exchange and Sign-change: The Pauli Exclusion Principle

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A mystery in the early part of the century was why the atom is stable. According to classical electrodynamics, an electron orbiting around the nucleus should rapidly radiate out its energy and fall into the nucleus. So though Rutherford's experiments had established that the atom consists of a small positively charged nucleus and a cloud of electrons presumably orbiting it, this picture seemed inconsistent with theory.

In 1913 Bohr gave his model of the hydrogen atom, in which the allowed orbits of the electrons are quantized because (he assumed) their orbital angular momentum is quantized in units of Planck's constant. This meant that the electrons can exist only in specific discrete energy levels, and an electron in the lowest level cannot lose any further energy. He also said that an electron moves between levels by emitting or absorbing a quantum of radiation corresponding to the energy difference of the levels. This theory accounted very well for the hydrogen atom spectrum. A shell model of the atom arose in the next few years, where electrons were assigned to distinct orbitals classified by quantum numbers. This accounted well for the observed spectroscopic features of the atoms: the grouping of spectral lines, allowed transitions, and so on, but it could not predict energies except in the



hydrogen atom. To account for splittings in magnetic fields (the 'Zeeman effect'), Uhlenbeck and Goudsmit postulated in 1925 that electrons carry a 'spin', or intrinsic magnetic moment, apart from their orbital moment.

Around that time, too, Pauli suggested his 'exclusion principle': two electrons in an atom cannot have all their quantum numbers the same, and if they occupy the same orbital, they must have different spin. This was needed to explain why all electrons in an atom could not sit in the lowest orbital, to minimize the energy.

This gave a fairly complete picture of the atom for those days, and students even today are initially given this picture. However, this is not a consistent theory, but a collection of ad hoc assumptions, each of which was made to accommodate an awkward experimental fact. At the time when Pauli suggested his exclusion principle, the quantum theory was a mess. Moreover, it could make no quantitative prediction, except for the hydrogen atom.

The situation changed rapidly in the next two years, with the birth of 'quantum mechanics'. The ad hoc assumptions above were explained using a new, vastly successful theory which, based on a few fundamental ideas, accounted for everything in atomic structure and various other phenomena besides.

In quantum mechanics, the Pauli principle can be stated in a much deeper way, and Pauli's statement is one consequence of that. So let us review how to describe an atom in quantum mechanics. An atom – or, indeed, any interacting system of particles – is described by a 'wave function'. This is a function of all the coordinates and 'internal variables' such as spin, of all the particles. So for a collection of electrons, where the n th electron has position \mathbf{r}_n and spin $\sigma_n = \pm 1/2$, the wave function is a function of all these variables

$$\psi = \psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_n, \sigma_n, \dots)$$

The wave function is, in general, complex-valued. The meaning of this wave function is this: The system is not in a state where all particles have definite positions. At best, we can say a particle has a particular probability of being in a particular region of space. The absolute square of the wave function for a particular set of coordinates $\{\mathbf{r}_n, \sigma_n\}$ is a measure of the probability that, if we made a measurement, the electrons were actually at these positions and had these spins. The wave function evolves according to Schrödinger's equation. Just as the positions of the particles are not certain, the energy of the system is typically not certain either, but there are special states of the system which are states of definite energy, and these states do not change with time: it is most convenient to describe the system in terms of these states.

This is easiest to follow for a single particle. Let us make the approximation that the nucleus is so heavy that it doesn't move much, so we treat it just as a potential field rather than as another particle. Then let us think of a one electron atom (the hydrogen atom). The wave function is a function of three coordinates of this electron, and its spin. Solving Schrödinger's equation gives us a set of allowed 'stationary states' for this electron. In practice, only the ground state is truly stationary: the excited states will quickly decay into lower states with the emission of radiation.

Suppose we had two electrons, but the two electrons did not interact with each other: they only interacted with the nucleus. Then applying Schrödinger's equation naively we may think that we can just put both electrons into the ground state. And if we had three electrons, we could put all three into the ground state, and so on: since they aren't interacting, it doesn't matter.

Pauli's principle says we cannot do that. The electrons must be in different states, so at most two electrons can be in the ground state, one of which must have spin up and the other spin down. But the reason for Pauli's principle is rather deep: it is the fact that all electrons are identical and indistinguishable.



Classically, one can always imagine two identical particles but can distinguish them by simply watching one of them wherever it goes. In quantum mechanics, the very idea is meaningless: particles don't have any trajectories. Therefore, if all electrons are identical, we must build that into the structure of quantum mechanics, and not allow the possibility of distinguishing them. In particular, if we have a wave function, that wave function must remain basically the same (ie change by a phase factor at most) if we exchange two particles. Since exchanging them again will give us back our original wave function, the phase factor must be $\phi = \pm 1$ (so that $\phi^2 = 1$). So we have two possibilities:

$$\begin{aligned}\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) &= + \psi(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1) \text{ or} \\ \psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) &= - \psi(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1)\end{aligned}$$

It was proved by Pauli in 1940, when relativity theory and quantum mechanics were combined, that all particles with half integer spin must satisfy the latter condition, and all particles with integer spins the former. The half integer spin particles are called 'fermions' and the integer spin particles 'bosons'. Electrons are fermions (spin half), so exchanging two electrons must reverse the sign of the wave function (we say the wave function is 'antisymmetric' under exchange of particles). This automatically means that we cannot put two electrons in the same state: for if we exchange them, it remains the same state, but it also changes sign, so it must be zero. So the exclusion principle can be stated as follows: The wave function of a set of identical fermions must be antisymmetric under pairwise exchange of their coordinates.

Thus, if we had two electrons in independent non-interacting states $\psi_1(\mathbf{r}, \sigma)$ and $\psi_2(\mathbf{r}, \sigma)$, then we cannot simply write the combined wave function as

$$\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \psi_1(\mathbf{r}_1, \sigma_1) \psi_2(\mathbf{r}_2, \sigma_2)$$

because this is not antisymmetric. We can, however, write

$$\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \psi_1(\mathbf{r}_1, \sigma_1) \psi_2(\mathbf{r}_2, \sigma_2) - \psi_2(\mathbf{r}_1, \sigma_1) \psi_1(\mathbf{r}_2, \sigma_2)$$

(you can check that this changes sign if you exchange the particles). With three or more particles, we can write a wave function in the form of a determinant (the above is really a 2×2 determinant). The most general wave function would be a sum of such determinants.

Now comes the question of how to treat a real atom, where electrons are all interacting with one another as well as with the nucleus. In principle, one should write down a Schrödinger equation for this full many-body wave function and solve it, but this is impossible even for the helium atom. So we make various approximations. The simplest, and very effective, approximation is to assume that electrons continue to be in independent 'orbitals' like the hydrogen atom states, but the orbitals are now modified by the presence of the other electrons. So we can try and find a modified set of orbitals, with corresponding energies, and populate them with electrons. Note that this is an *approximation*: the picture of single electron energy levels is not strictly correct.

Early on, Hartree suggested the following scheme. Assume some initial, independent wave function for each electron (say, the unperturbed hydrogen atom wave function.) Then account for the effect of all the other electrons on the first electron, by replacing them with an average charge density (the sum of the absolute squares of each single-electron wave function), and solving for the first electron in the potential created by this average charge distribution. We will now get a different wave function for the first electron. Then do the same for the second electron, and the third, and so on. (Actually, we can assume the first two electrons have the same wave function since their spins are different.) We keep doing this until our revised wave functions don't change any more: when we recalculate our first electron wave function, we get back nearly the same one we started with. Then calculate the total energy of the system. This is called the 'self consistent field' method and gives rather good results.



One problem with this method is that the Pauli principle is put in by hand: the electrons are initially assigned to different orbitals, but the wave function, being a simple product of single electron wave functions, doesn't satisfy the antisymmetry condition. Fock modified the method to start off with a properly antisymmetric wave function (a determinant of the single electron wave functions). The resulting energy calculation has two pieces, the old 'Hartree' term and a new 'Fock' or 'exchange' term. This 'Hartree-Fock' method is one of the most commonly used in physics: not just for atomic structure, but for molecules and solids too.

Thus the Hartree-Fock method is a justification for the picture people had of the atom in 1925: electrons exist in shells around the nucleus, each shell has a distinct energy level, and the number of electrons in a shell is limited by the Pauli exclusion principle. In the framework of quantum mechanics, and making a few reasonable approximations, we can recreate this picture and understand why the old model worked so well.



Pauli's rudeness to his collaborators was taken for granted as part of his personality; none of them was put out on being called an incompetent idiot in public if Pauli had found an error in his work. Even Niels Bohr, usually treated with a modicum of politeness, was not safe from Pauli's sarcasm, as in this letter to Bohr's wife: "... you wrote two weeks ago that Niels would answer my letter on Thursday; but you didn't say which Thursday. However, a reply written on any other day of the week would be equally welcome ..."

Otto Frisch