“ The Pauli Exclusion Principle”

(This “short’ draft received a B).

Although students in many levels of chemistry and physics use the Pauli exclusion principle at an elementary level, many of them do not actually understand the concept which dictates this law. As many people know it, the Pauli exclusion principle simply states that each orbital, which holds two electrons, cannot contain two electrons of the same spin projection ($m_s = \pm 1/2$). In other words, if an orbital has one “spin-up” electron, the level can only be filled up with a “spin-down” electron. This rule is used blindly by many students when examining the makeup of atoms on the periodic table. Let’s examine the theory behind this very important principle.

In order to understand the Pauli exclusion principle fully, some basic knowledge of quantum mechanics is required. Quantum mechanics is the study of small-scale phenomena that cannot be described in classical terms.[1] Whereas classical mechanics is governed by Newton’s three laws, quantum mechanics is governed by the Schrödinger equation. In quantum mechanics, every system is assigned a wave function, $\Psi(x,t)$ which follows this equation, defined as

$$H\,\Psi(x,t) = i\hbar \frac{\delta \Psi(x,t)}{\delta t}, \qquad (1)$$

where “H”, is the Hamiltonian, “$\Psi(x,t)$” is the wave function, “i” is an imaginary number, “$\hbar$” is a constant, and $\frac{\delta \Psi(x,t)}{\delta t}$ is the first derivative of the wave function with respect to time. The wave function is a function of both position and time. When properly normalized, the wave function can be used to find the probability of finding a particle in a position “x” at a given time “t”. This means that a system’s wave function changes with time, and so too does the probability of finding a particle in any given position, “x”. So, one must choose a value for “t”, and can still get information only about the probability of finding a particle at a certain position.

There is yet another distinct difference between classical and quantum mechanics. In classical mechanics, it is possible to distinguish between identical objects. For instance if there are two identical balls, they can be labeled in such a way that they can be distinguished from each other. This characteristic of macroscopic objects allows one to know the position of any given object in a system of identical objects at any given time. In quantum mechanics, however, we are dealing with identical particles that cannot be labeled. One can know the probable position of two particles at an initial point in time, and know the probable position of those two particles later in time, but cannot determine which particle went where. This property of very small particles is called indistinguishability.

It was this notion of indistinguishable particles that sparked the idea of the Pauli exclusion principle. Because two identical particles are indistinguishable, when one deals with a system of two such particles, the wave function must be constructed such that it is non-committal; meaning it is valid regardless of which particle is in which state.[3] Assuming we assign one of the electrons with the wave function, Ψ_a, and the other electron with the wave function, Ψ_b, there are two ways to construct a wave-function for a system of two identical particles:

$$\Psi(r_1, r_2) = A\,[\Psi_a(r_1)\,\Psi_b(r_2) \pm \Psi_b(r_2)\,\Psi_a(r_1)]\,, \tag{2}$$

where “A” is a normalization constant, and “r1” and “r2” are the positions of particle 1 and 2 respectively. The world is constructed such that bosons, particles with integer spins, possess a symmetric wave function, while fermions, particles with half-integer spins, possess an anti-symmetric wave function. So, if we are dealing with two non-interacting fermions, the wave function for the two-particle system is given by

$$\Psi(r_1, r_2) = A\,[\Psi_a(r_1)\,\Psi_b(r_2) - \Psi_b(r_2)\,\Psi_a(r_1)]. \tag{3}$$

Now that we have determined the wave function for a two-fermion system, we can see the logic behind the Pauli exclusion principle. Let us assume that both fermions are in the same quantum state. This means that both fermions will be characterized by the same wave function, Ψ_a. So, substituting Ψ_a for both wave functions in equation 3 yields

$$\Psi(r_1, r_2) = A\,[\Psi_a(r_1)\,\Psi_a(r_2) - \Psi_a(r_2)\,\Psi_a(r_1)] = 0, \tag{4}$$

an impossible situation, for the wave function for this two-particle system would then disappear. The common formulation of the Pauli exclusion principle stems from this result. It states that no two fermions can occupy the same quantum state. So here, we see that the Pauli Exclusion Principle not only applies to electrons, but to all identical fermions.[3]

The Pauli exclusion principle has had great impact on many different aspects of science, including molecular spectral intensities[4], the collapse of stars to form white dwarfs, the further collapse of stars into degenerate objects such as neutron stars, and the concept of the Fermi level in the band theory of solids.[5] But, by far, the Pauli Exclusion Principle has been most useful in helping to explain the structure of the periodic table. In this context, the Pauli exclusion principle says that two electrons cannot share the same quantum state. In other words, although two electrons can be in the same sub-shell, they must have the opposite spin in order to do so. Without this fundamental principle, all electrons in an atom could simply fill up the lowest sub-shell, and the arrangement of the Periodic Table as we know it, would be inherently different.

References

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[5] http://hyperphysics.phy-astr.gsu.edu/hbase/pauli.html#c2