

14.2: The Orbitals

The specific functions $\psi(\vec{r})$ (or $\psi(x, y, z)$, or $\psi(r, \theta, \phi)$) that work with the Schrödinger equation are the eigenfunctions of the Hamiltonian operator. Because we don't know necessarily when we start what those functions are, even though we've now specified the operator, we have to go through a process in order to figure out what the possible functions $\psi(\vec{r})$ are.¹ Therefore, we call those functions the “solutions” of the Schrödinger equation. The exact functional form of these solutions aren't particularly illuminating. However, they do have some general features, the existence of which underlie all of atomic structure. In the previous chapter, we talked about some solutions that could be described by energy levels. For instance, the solutions to the one-dimensional simple harmonic oscillator have evenly spaced energy levels indexed by an integer n . In three dimensions, it will take three different “quantum numbers” to index the solutions. The numbers we choose to represent the states are the ones that have a most direct physical interpretation.

We call the solutions “orbitals” rather than just energy levels. In Hydrogen, there are usually multiple orbitals that share the same energy. In other atoms, fewer orbitals will share the same energy. These orbitals represent states available to the electron. Each state has an energy, a total angular momentum, and a z component of orbital angular momentum associated with it.² Those three values are the observables for which the orbitals are eigenstates. It's not surprising that the orbitals are energy eigenstates, because we produced them by finding states represented by wave functions that solve the Schrödinger equation, which is the energy eigenfunction equation. It is less obvious why they would be angular momentum eigenstates. It turns out that it's possible to break the kinetic energy operator into two parts, a “radial” part and a part that is the orbital angular momentum operator. That means that the Schrödinger equation includes the orbital angular momentum eigenvalue equation inside it.

These orbitals are not, however, eigenstates for position or for momentum. In particular, not being position eigenstates, electrons in atomic orbitals do not have definite position. Rather, there is a probability density for them to be at different positions, just as an electron in the $|+z\rangle$ spin state is not in a definite state of x spin and has probabilities to be found with positive and negative x spin. While the name “orbital” suggests that the electron is circling the nucleus in a manner analogous to how the Earth circles the Sun, this is not what is happening at all. The electron doesn't follow any particular path through space around the nucleus. Instead, the orbital is a probability cloud representing the effective amplitude for the electron to be found in any one tiny region of space around the nucleus. One consequence of this is that the negative charge associated with the electron is spread throughout this cloud. Whereas the Earth's mass is always at the position the Earth is in its orbit at any given moment, there is no single position for an electron in an atom, so there's no single place where the electron's charge is. The charge of the electron is more diffuse. Additionally, the center of the cloud is right at the nucleus. For the ground state, where the probability distribution is spherically symmetric, to something “far” from the atom (i.e. far enough away that the probability for the electron being found that far away or farther is negligible) the atom acts as if it were entirely neutral, with the effective charge of the electron being at exactly the same place as the effective charge of the proton.

Of the three quantum numbers that represent the electron orbitals, the quantum number n , the principle quantum number, is sometimes called the shell number. The average distance of the electron from the nucleus is determined primarily by n . In a single-electron atom, to first order the energy of the atom is determined entirely by n . (There are second order effects, such as the magnetic interaction between the spin and orbit of the electron, that are beyond the scope of this class.) The ground state has $n = 1$, and higher shells have larger values of n .

The second quantum number, l , indexes the total orbital angular momentum of an electron in that state. It too must be a non-negative integer; that is, it can be 0 or a positive integer. The angular momentum represented by l does not include the spin angular momentum of the electron. Electrons remain electrons, and as such their total spin angular momentum is $\frac{\sqrt{3}}{2}\hbar$, and the possible projection along any axis is quantized to $+\hbar/2$ and $-\hbar/2$. The total angular momentum in the electron cloud of an atom depends on the orbital and spin angular momenta of all the electrons. Combining those angular momenta is fairly complicated, and involves taking into account the fact that electrons are indistinguishable particles. It turns out that for a given state, the angular momentum quantum number l must be less than the principle quantum number n . Thus, for the ground state, $n = 1$, we know that $l = 0$. The next shell out, $n = 2$, there are two possible values of l : $l = 0$ and $l = 1$. The orbital angular momentum associated with a given value of l is $\hbar\sqrt{l(l+1)}$. Notice that this means that the ground state orbital has zero orbital angular momentum! This highlights the degree to which these orbitals are not analogous to planets circling stars, for a planet circling a star assuredly does have orbital angular momentum.

The third quantum number, m , indexes the z projection of the angular momentum. Just as electron spin angular momentum is quantized, so is electron orbit angular momentum. However, there's a difference. Instead of having half-integral values, orbital

angular momentum has integral values. As a spin-1/2 particle, we could say that the quantum number for the total spin of every electron is $s = 1/2$. The z projection, which we've called S_z , is then either $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. We could say that there are quantum numbers, perhaps m_s , associated with electron spin that give the electron two possible spin states, one with $m_s = 1/2$, the other with $m_s = -1/2$.

In electron orbits, the total angular momentum l is an integer. m can be either positive or negative (representing angular momentum that's in the positive or negative z directions). Unlike electron spin, m can also be zero. However, m cannot get any larger than l . Thus, for a given value of l , there are $2l + 1$ possible projections: $m = -l, m = -l + 1, \dots, m = 0, \dots, m = l - 1, m = l$.³ The z component of orbital angular momentum associated with an orbital with quantum number m is just $m\hbar$. Notice that, just as with electron spin, it's impossible to have a z component of angular momentum that is equal to the total angular momentum of the state. Just like electron spin, the x , y , and z components of angular momentum are all represented by non-commuting operators. That is, an orbital can only be in a definite state for one of them. Thus, while a classical particle would have multiple different states (effectively) for a given l and m (as there would be different x and y projections of angular momentum available), a quantum particle's orbit is completely specified by just the total angular momentum quantum number l , and the z projection quantum number m .

The solution to the Schrödinger equation provides a dazzling wealth of orbitals available to the electron in the Hydrogen atom. Strictly speaking, we've solved for the orbitals as energy eigenstates. This means that if an electron is in one of those states, in the absence of observations or interactions it will stay in that state. (If it's in an indeterminate energy state, if you somehow manage to measure the energy of the atom you will collapse the atom's wave vector and it will drop into an eigenstate.) However, observationally, atoms that are in excited states do not stay there forever. After a while, they will spontaneously decay, with the electron dropping down to a lower state, and eventually with the electron reaching the ground state (which is stable. This would imply that the atom must somehow be interacting with something, if it is able to change from one eigenstate to another. Indeed, it does; it is interacting with the electromagnetic field. Even if there isn't any light (i.e. any "excitations of the electromagnetic field") around us, the field is always there. What's more, there are always virtual photons, as a result of the energy/time version of Heisenberg's Uncertainty Principle (Section 11.4.1). The interaction of the atom with the electromagnetic field yields a probability in any given time interval that the atom may emit a photon and drop to a lower energy state. The energy of that photon corresponds exactly to the difference in energy between the upper and lower states of the transition.

¹That process is much more advanced than what could be covered here and involves differential equations.

²Remember that if a system is in a definite state for the z component of angular momentum, it can not have a definite value for x and y angular momentum. This is true for orbital angular momentum as well as for the intrinsic spin of particles. Whereas in a classical system, x , y , and z components of angular momentum would give you three "degrees of freedom", three things that could be varied, the orthogonality of those observables in quantum mechanics means that you only have two: total angular momentum, and one component.

³So for $l = 1$, there are three possible values of m : -1, 0, and 1. For $l = 2$, there are five possible values of m : -2, -1, 0, 1, and 2. And so forth.

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