

Duane's Science Enrichment Series

Where Those Strange Quantum Numbers Come From

Keywords: Chemistry, Physics, Quantum Mechanics

Target: College General Chemistry

If you've had a class in chemistry, you've learned about the quantum numbers in atoms. You know, they go like this: n can be any integer greater than 0. l can be any integer from 0 to $n-1$. m_l can be any integer from $-l$ to $+l$. m_s can be either $-1/2$ or $+1/2$. They're easy to remember, but what they never teach you in general chemistry is why those numbers are like that. How did mother nature set those rules, and why? Is she a bit cracked?

You got a clue in high school physics when you talked about vibrations. You saw something like this figure, and looking at it, it seems obvious why the standing waves in a string between two fixed points have to exist in multiples of $1/2$. Your book probably gave you an equation with an n in it to indicate which of those waves you're talking about. That's a quantum number, and it turns out it's the same quantum number as the n that refers to atomic orbitals.



As a matter of fact, nature is not cracked at all. It all boils down to something called eigensystems. You find out about these in linear algebra, or differential equations, or maybe both, and most people taking general chemistry haven't studied those subjects. They're usually brought up regarding matrix algebra, but functions can have eigensystems, too. An eigensystem looks like this:

$$\hat{O}f = \lambda f$$

Where f is some function and \hat{O} is an operator that when applied to f returns the same function times some constant. The trick is to find all the functions this works for. Let's look at something you've probably seen in Calculus 1:

$$\frac{d}{dx}e^{-2x} = -2e^{-2x}$$

Look! It's an eigensystem. The derivative operator acts on the exponential function to return the same function times a constant (-2). When this works out, the function is called an *eigenfunction* and the constant is its *eigenvalue*. Now let's try another function with the same operator.

$$\frac{d}{dx}\tan\frac{x}{2} = \frac{1}{2}\sec^2\frac{x}{2}$$

Well, that spits out a totally different function, so $\tan\frac{x}{2}$ is obviously not an eigenfunction of the derivative

operator. Only certain functions will work out just right, and they're in the minority. In quantum mechanics, the orbitals that exist are the only functions that solve the eigensystem for the atom or molecule.

In quantum mechanics, the typical eigensystem to solve is the Schrödinger equation:

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

The function $\psi(r, \theta, \phi)$ is the wavefunction that describes the shape of the orbitals. The operator \hat{H} is the Hamiltonian, which describes the complete energy environment of the electron, which includes information about its distance from the nucleus as well as all the spins involved. Since the Hamiltonian is in terms of energy, the constant E is the energy of its associated wavefunction.

It should be noted that it is very difficult to completely solve this equation. It has been done only for the hydrogen atom and H_2^+ , and analytically impossible for everything else. Hold onto your hats now. Here is the solution for hydrogen:

$$\psi_{nlm_l}(r, \theta, \phi) = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2Z}{na_0}\right)^{l+\frac{3}{2}} r^l e^{\frac{-Zr}{na_0}} L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) (-1)^{m_l} \sqrt{\frac{(2l+1)(l-m_l)!}{4\pi(l+m_l)!}} L_l^{m_l}(\cos\theta) e^{im_l\phi}$$

Aren't you glad that wasn't on the quiz? The $L_b^a(x)$'s are *associated Laguerre functions*, which you can look up. The different values of n , l , and m_l all define different wavefunctions that solve the eigensystem and each one has an energy eigenvalue associated with it. Look under the first radical. You'll see that if l ever gets bigger than $n-1$, you end up with the factorial of a negative number. Bad¹. Look under the second radical. You'll see that if m_l gets smaller than $-l$ or bigger than $+l$, then there is a negative number under the radical sign, and you can't take the square root of a negative number and get out something real.

Numbers that don't work in the equation are part of the explanation of where the quantum number rules come from, but there is more to it than that. It's simply that if you put together a function with the wrong values, then it no longer solves the eigensystem, so it can't be a real wavefunction. This is where the values get constrained to integers. Fractional values don't solve the eigensystem.

You might have noticed something missing. The equation above has n , l , and m_l but no m_s . Is the Schrödinger equation wrong? Well, sort of. It doesn't take into account Einstein's special theory of relativity, and we live in a universe that does. To take that into account, solve the Dirac equation. Yeah, right!

$$\left(\beta mc^2 + \sum_{k=1}^3 \alpha_k p_k c \right) \psi(\mathbf{x}, t) = i\hbar \frac{\partial \psi(\mathbf{x}, t)}{\partial t}$$

It might not look too hard until you realize that some of those symbols are 4-dimensional tensors. The solutions give wavefunctions that look like the Schrödinger wavefunctions, and energy levels that are very, very close to the Schrödinger ones. But it also pops out something else: m_s . And the only values that work for that are $+1/2$ and $-1/2$. To explain why they are the only ones that work is something you probably don't want to get into. Google "bispinor" if you're a masochist.

So you see, nature isn't actually crazy. It all comes out in the math. Think of an orbital as a vibrating string in three dimensions.

¹ Actually, you can do factorials of negative numbers using the gamma function, but negative integers and zero give you +/- infinity, which isn't good, either.