

Atomic Structure

Initial questions: How can we identify atoms or molecules from their spectra? Put another way, given a set of lines, how can we be confident that we can figure out the composition?

In the next several lectures we're going to consider radiative processes related to transitions in atoms and molecules. In this lecture we'll take a basic look at the structure of atoms themselves. To do this right we need to use the equations of quantum mechanics, which would mean the Dirac equation or, for a good approximation, the Schrödinger equation with the Pauli exclusion principle. We will, in fact, use the Schrödinger equation. However, before going into those details it's helpful to see how one can get some insight with semiclassical approaches.

First, let's think of an atom purely classically. Imagine that we treat a hydrogen atom as an electron moving in circles around a proton. The electron is therefore accelerated, so it radiates. The total energy at a given instant is the (negative) potential energy plus the kinetic energy, and for a circular orbit the total energy is negative (it's half the potential energy, by the virial theorem). Therefore, loss of energy means that the electron moves closer to the proton, so the acceleration is greater and the energy loss is greater. Classically, this process would run away and within a tiny fraction of a second the atom would collapse.

As a semi-classical try to deal with this, Bohr suggested a quantization rule that the angular momentum of the electron had to be an integer multiple of \hbar . If we assume this but otherwise keep our classical "solar system" picture, then for the ground state we have $V = -e^2/r$, $K = \frac{1}{2}m_e v^2 = e^2/2r$ (from the virial theorem), and $L = m_e v r = \hbar$. The total energy is $-e^2/2r$, which for this angular momentum is $E = -m_e e^4 / 2\hbar^2 = -13.6$ eV. This happens to be exactly right, and if you put in $2\hbar$, $3\hbar$, and so on you get the right energy spacing ($E(n\hbar) \propto 1/n^2$).

But why should the angular momentum be quantized? Let's take a different approach: from the uncertainty principle we know that if an electron is confined to a small volume then it has a large momentum. In particular, let's say that $p = \hbar/\Delta x$, or if the electron is within a distance r of the proton then $p = \hbar/r$. Then, independent of quantization effects, we'd like to know the ground state of the atom, which is where the total energy is minimized. The total energy is $p^2/2m_e - e^2/r$, which is $\hbar^2/(2m_e r^2) - e^2/r$. This reaches a minimum at $r = \hbar^2/(m_e e^2)$, so that again we get the exact answer $E = -m_e e^4 / 2\hbar^2$.

This is too good to be true. In fact, we're just lucky to get the right factors in these cases, although getting the dependences right is *not* an accident. It is, however, helpful to have this general picture before moving on to the equations.

The fully quantum mechanical way to understand the structure of atoms, if they're nonrelativistic, is to use the Schrödinger equation. As you know, this takes the form

$$H\Psi = i\hbar\partial\Psi/\partial t \quad (1)$$

where H is the Hamiltonian operator and Ψ is the wavefunction. In classical physics the Hamiltonian is the total energy, i.e., the sum of the kinetic and potential energies. In quantum mechanics, it is the sum of the operators for the kinetic and potential energies. Conveniently, the kinetic energy depends only on momenta (or derivatives of position), whereas the potential energy depends only on positions. One can select a representation in which one wants to write the operators; in the coordinate representation $p = -i\hbar\nabla$, so if we use the nonrelativistic expression $E_K = p^2/2m$ then the Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V\right)\Psi = i\hbar\partial\Psi/\partial t. \quad (2)$$

If the solution is time-independent, then $\Psi = \psi(\mathbf{r})\exp(-iEt/\hbar)$, so we get the time-independent equation

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V\right)\psi = E\psi. \quad (3)$$

Before specializing to electric fields, let's think about how this would be generalized to relativistic energies. I want to say up front that I don't expect you to grasp all of this fully (I certainly don't understand all the implications!), and in no way do I intend to test you on it. I do, however, want to show you a little of the thinking that has gone into relativistic quantum mechanics, so that we can have a better perspective on the nonrelativistic approximations we'll be using.

Imagine that we have no potentials to worry about. Then $E^2 = p^2c^2 + m^2c^4$ for some general particle of mass m , so if we square the time-dependent version of the Schrödinger equation and rearrange we get

$$\left[\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) - \left(\frac{mc}{\hbar}\right)^2\right]\Psi = 0. \quad (4)$$

This is called the Klein-Gordon equation, because it was originally written down by Schrödinger. Looks fine, right? The difficulty, as discussed in Shu (beginning of chapter 25) is that for this equation (unlike the Schrödinger equation) one can't interpret Ψ as a wave function such that $|\Psi|^2$ is the probability density. That's why Schrödinger rejected this equation and it got named after other people. It does turn out that the Klein-Gordon equation can be used instead as a field equation for scalar (spin 0) particles.

The problem here is the introduction of a second time derivative. Dirac looked for a generalization of the Schrödinger equation that kept the linearity in time but had symmetry

between time and space (as required by special relativity). Thus, the Hamiltonian operator (without a potential) would be

$$H = \mathbf{a} \cdot \mathbf{P}c + bmc^2, \quad (5)$$

where \mathbf{a} and b are constants. This can be equated to $H = (P^2c^2 + m^2c^4)^{1/2}$; squaring and solving, we get the requirements

$$\begin{aligned} a_x a_x &= a_y a_y = a_z a_z = b b &= 1 \\ a_x a_y + a_y a_x &= a_y a_z + a_z a_y = a_z a_x + a_x a_z &= 0 \\ a_x b + b a_x &= a_y b + b a_y = a_z b + b a_z &= 0. \end{aligned} \quad (6)$$

We write it in this way instead of, say, writing $a_x b + b a_x = 2a_x b$ because in fact these equations can't be solved if you use ordinary numbers for a_x , a_y , a_z , and b . Instead, you have to use matrices. These 4x4 matrices are given in many places (e.g., Shu, page 268). As a result, the wave function needs to have four components (as Shu emphasizes, this does *not* make it a four-vector; it's just some internal space for the particles treated in this way). If we say $\Psi \rightarrow (\Psi_1, \Psi_2, \Psi_3, \Psi_4)$ and solve the matrix equation that way, then the probability density becomes $\rho = |\Psi_1|^2 + |\Psi_2|^2 + |\Psi_3|^2 + |\Psi_4|^2$. Dirac's equation turns out to represent electrons beautifully, taking into account their spin, being relativistic, and the whole shebang. We've diverted here because it's useful to see the full correct way of doing things every now and then, and Rybicki and Lightman don't cover this. Note, by the way, that the \mathbf{P} is not the canonical momentum (the one such that $\mathbf{p} = -i\hbar\nabla$), but the particle momentum; e.g., for an electromagnetic field $\mathbf{P} = \mathbf{p} - \frac{q}{c}\mathbf{A}$.

We will now return to using the Schrödinger equation. We can do this because for most atoms the energies are very non-relativistic, so all those attendant complications are just small perturbations.

Ask class: Suppose we have a hydrogen atom. What is the potential energy? It's $-e^2/r$, where r is the separation between the proton and electron. **Ask class:** what, then, is the Hamiltonian? It is

$$H = -(\hbar^2/2m)\nabla^2 - e^2/r. \quad (7)$$

The time-independent Schrödinger equation then becomes

$$[-(\hbar^2/2m)\nabla^2 - e^2/r] \psi = E\psi, \quad (8)$$

an eigenvalue/eigenvector equation. **Ask class:** now suppose we have a nucleus of charge Ze , and some number of electrons. Now what is the potential energy? It can be broken down into the potential energy of the electrons with the nucleus, and the potential energy of the electrons with themselves. If we sum over these and also sum over the kinetic energies of the electrons, the time-independent Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - E - Ze^2 \sum_j \frac{1}{r_j} + \sum_{i>j} \frac{e^2}{r_{ij}} \right) \psi = 0. \quad (9)$$

Let's start with a single-electron atom. As with other situations we've encountered (e.g., Maxwell's equations), the Schrödinger equation can in principle be solved directly by brute force, but in practice there are often shortcuts or things one can borrow from mathematical physics that simplify the analytical treatment. That's the case here as well. You could try to solve the equation by making an inspired guess (e.g., that the wavefunction should be the product of a polynomial in r with some exponential in r). That works. Or, you could use analogies with classical mechanics and electromagnetism to think about the full form of the wavefunction, which involves spherical harmonics.

Anyway, the single-electron approximation is more generally useful than you might think. The outermost electron of an atom can often be treated as if it is a single electron outside a point charge that is comprised of the nucleus plus the other electrons. The innermost electron of an atom can sometimes be treated as if it interacts just with the nucleus, with a constant contribution from the other electrons. These are special cases of two useful approximations: first, the self-consistent field approximation, in which each electron feels the nuclear potential plus the averaged potential of the other electrons; and second, the central field approximation, in which the averaged potential is assumed to be spherically symmetric. For rough estimates, these do well.

If one has a central potential (spherical symmetry), so that H depends only on r , then (as in other analogous situations) one can break down the wavefunction into

$$\psi(r, \theta, \phi) = r^{-1}R(r)Y_{lm}(\theta, \phi) , \quad (10)$$

where $R(r)$ is some function to be solved for and Y_{lm} are the spherical harmonics. Plugging this into the equation for hydrogen, for example, we find that the eigenvalues are indeed $E = -m_e e^4 / (2n^2 \hbar^2)$ for n a positive integer, as our simpler approach found as well. Thus, to this level, all states with a given n have the same energy; there is no dependence on the orbital quantum numbers l and m , let alone the spin quantum number m_s (which is needed because the electron spin can be $+1/2$ or $-1/2$). Still, to specify the particle state completely we need all four quantum numbers (n, l, m, m_s). Indeed, when higher-order effects are considered, or perturbations from external fields such as magnetic fields, the degeneracy in energy is broken.

What do you do if you have more than one electron? In that case the main new effects come from the *Pauli exclusion principle*: two identical fermions can't occupy the same quantum state. Applied to multielectron atoms, this means that the overall wavefunction must be perfectly antisymmetric. For example, let's represent the full wavefunction as a product of single-electron wavefunctions:

$$\Psi = u_a(1)u_b(2)u_c(3) \dots \quad (11)$$

where 1 means particle 1, 2 means particle 2, and so on, and a indicates some quantum state (n, l, m, m_s), b indicates another quantum state, and so on. If you take all possible

combinations of states, that forms a fine basis state but doesn't satisfy Pauli exclusion, so it's better to build that in from the start. A convenient way to do this is via the Slater determinant, which guarantees antisymmetry of the wave function if any two particles are interchanged.

That's all very well, you may say, but how do you actually *solve* the bloody equations?!? The problem is that, aside from the very simplest atoms (single-electron atoms) there are no longer any exact analytical solutions of the Schrödinger equation. Oops! Not only that, but even if you're prepared to spend arbitrary computer time on a problem, eigenvalue equations can't usually be solved by random functions. We need a systematic way to search for wave functions that are *almost* right, in the sense of giving us approximately the right eigenvalues.

Fortunately, such a method exists. It uses the variational condition that for any system the eigenfunctions are such that if one takes functions "nearby" the eigenfunctions, the expectation value of the Hamiltonian for those new functions will equal the energy of the eigenfunction, to first order. That is, $\delta\langle H \rangle = 0$ for eigenfunctions, but for no other functions. For example, this means that no function gives a lower expectation value than the ground state eigenfunction. To prove this, consider $\langle H \rangle = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$ for any function $|\psi\rangle$. We can expand $|\psi\rangle$ in the eigenfunctions $|\phi_n\rangle$ of H by

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle . \quad (12)$$

Since the eigenfunctions are orthonormal, this gives

$$\langle H \rangle = \sum_n |c_n|^2 E_n / \sum_n |c_n|^2 . \quad (13)$$

If $n = 0$ is the ground state, then $E_n \geq E_0$ so $\langle H \rangle \geq E_0$ for any state. Therefore, the ground state has the minimum possible energy, which means that any variation in the eigenfunction must give a change in energy that vanishes to first order (if it didn't, there would be a direction of change that lowered the energy). With slightly more effort, one can show that all eigenfunctions give zero first order variation in the energy. Variational principles apply all over the place in physics.

Variational principles are marvelous things. One picks a class of "trial" wave functions that satisfy the Pauli principle, then varies the parameters in that class to get an energy that is stationary to first order, using techniques from variational calculus (or numerically). When you do this for atoms, you get the Hartree-Fock equations. The net result is that one finds Schrödinger equations with two "potentials": the "direct" potential (electron-nucleus and one for the electron in question with the averaged charge density of the other electrons), and the "exchange" potential, which isn't really a potential per se but is instead the result of the Pauli exclusion principle. The exchange potential makes electrons avoid each other's

states. Application of this method gives decently accurate energies even for atoms with many electrons.

Let's do an explicit example to show how it works. Consider a hydrogen atom, with a Hamiltonian $H = -(\hbar^2/2m_e)\nabla^2 - e^2/r$. Let our trial wavefunction class be $\psi = C \exp(-r/r_0)$, where r_0 is our parameter and C is a normalizing constant. This is purely radial, so we can ignore the angular components and just use the radial part of the Laplacian:

$$\nabla^2 \rightarrow \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right). \quad (14)$$

Normalizing this means $\int_0^\infty \psi^* \psi 4\pi r^2 dr = 1$, where we have done the angular integrals under the assumption of spherical symmetry. The wavefunction is real, so $\psi^* = \psi = C \exp(-r/r_0)$. Performing the integral yields $C = (\pi r_0^3)^{-1/2}$.

The energy for a state is $E = \langle \psi | H | \psi \rangle$, or

$$E = -\frac{1}{\pi r_0^3} \int_0^\infty e^{-r/r_0} \left[\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} e^{-r/r_0} \right) + \frac{e^2}{r} e^{-r/r_0} \right] 4\pi r^2 dr. \quad (15)$$

Performing this integral yields

$$E(r_0) = \frac{\hbar^2}{2m_e r_0^2} - \frac{e^2}{r_0} \quad (16)$$

and minimizing this over r_0 gives $r_0 = \hbar^2/(m_e e^2)$ and $E = -m_e e^4/(2\hbar^2)$, which are both the actual minima. Thus in this case we got the exact right answer because we happened to choose the correct form for the wavefunction. Note, however, that in general we don't know the correct form (and indeed, in general, the correct form doesn't have a closed-form analytic expression). Then we have to choose plausible waveforms and minimize the energy. An exercise you can perform if you wish is to do the hydrogen atom problem but with trial wavefunctions of the form $\psi = C \exp(-r^2/r_0^2)$; how close do you get to the right energy in that case?

Recommended Rybicki and Lightman problem: 9.1