Molecules

Initial questions: What are the new aspects of molecules compared to atoms? What part of the electromagnetic spectrum can we probe? What can we learn from molecular spectra? How large a molecule could we identify?

We now turn from atoms to molecules. For our purposes, a molecule is two or more separate nuclei that are bonded together by an electron cloud. This introduces interesting new effects but also some complications, so after a general overview we'll stick to molecules with just two nuclei.

First, **Ask class:** what are some qualitatively new effects introduced with molecules vis a vis atoms, in terms of energy levels and transitions? With more than one nucleus, there are new degrees of freedom. Unlike an atom, a molecule can vibrate (distance between nuclei changes periodically) and rotate (distance remains same, but orientation changes). In addition to the electronic transitions that still occur, this may seem to leave an irreducible mess. **Ask class:** can they think of any simplifications that might help? One is an approximation we've seen several times. The nuclei are much more massive than the electrons. Therefore, if we consider rotation or vibration as motion of the nuclei, we will assume that the electron cloud adjusts to the new positions rapidly, meaning that the electronic configuration is always close to equilibrium during vibration or rotation. This is called the Born-Oppenheimer approximation.

We can quantify this a bit, and in the process show that the energies of electronic, vibrational, and rotational transitions are well separated from each other. The byproduct is that these can be treated independently in perturbation theory, which saves a lot of effort!

Let's first consider vibration. As we've done rather often, we can get an order of magnitude idea about vibrational energies using a semiclassical model. In this case, we imagine that the nuclei vibrate by moving back and forth in a potential, which we can treat as a harmonic oscillator. In a classical harmonic oscillator we can figure out the frequency $\omega = \sqrt{k/M}$ if we know the spring constant k and the mass M. **Ask class:** what is the mass in our case? It's roughly the mass of a nucleus. We can estimate the spring constant if we know a typical energy E at a typical distance x; then $E = \frac{1}{2}kx^2$. **Ask class:** what typical energy and distance do we have in this case? Our rough estimate could be that the energy is the binding energy $E = m_e e^4/2\hbar^2$ of hydrogen, and the distance is the Bohr radius $a_0 = \hbar^2/(m_e e^2)$. Solving, $k = m_e^3 e^8/\hbar^6$, so the vibrational energy is

$$E_{\rm vib} = \hbar\omega = \hbar\sqrt{k/M} \sim (m_e/M)^{1/2} m_e e^4/\hbar^2 \sim (m_e/M)^{1/2} E_{\rm elect}\ . \tag{1}$$

Since $m_e/M \sim 1/(1800A)$, where A is the atomic weight of the nucleus, these energies are a few percent to a few tenths of a percent of the electronic transition energies, or tenths to hundredths of an eV compared with a few eV for electronic transitions. Vibrational transitions are therefore in the infrared.

What about rotation? When you think about rotation, you think about angular momentum. **Ask class:** what is the minimum change in angular momentum something can have? Roughly $\hbar$. **Ask class:** how can we use this to estimate rotational transition energies? We can do it by estimating the rotational energy that corresponds to an angular momentum of $\hbar$ for a given molecule. If the molecule has a moment of inertia I and rotational frequency Ω, then its angular momentum is $L = I\Omega$ and its rotational energy is $\frac{1}{2}I\Omega^2 = L^2/(2I)$. The moment of inertia of a molecule of mass M and dimension a is $\sim Ma^2$, so the energy is of order $E_{\rm rot} = \hbar^2/(Ma^2)$. If $a \sim a_0$, we then find

$$E_{\rm rot} \sim (m_e/M)E_{\rm elect}\ . \tag{2}$$

These are usually in the 10^{-3} eV range, putting the transitions in the radio.

We are therefore fortunate in that there is a clear hierarchy of energies:

$$E_{\rm elect} : E_{\rm vib} : E_{\rm rot} = 1 : \left(\frac{m_e}{M}\right)^{1/2} : \left(\frac{m_e}{M}\right)\ . \tag{3}$$

Such a hierarchy allows accurate treatment with perturbation theory. We'll start out with electronic binding of nuclei, then in the next class will consider vibrational and rotational states.

To get a handle on electronic binding of nuclei, we need a simple approximation of the potential as a function of separation of nuclei. We'll start with the simplest molecule: H_2^+, which is two protons held together by one electron. To simplify things, we'll write the Hamiltonian in "atomic units" in which the unit of length is the Bohr radius $a_0 = \hbar^2/(m_e e^2)$ and the unit of energy is *twice* the hydrogen ground state binding energy: $e^2/a_0 = 27.2$ eV. Suppose that the location of the first nucleus is $\mathbf{R}_A$, of the second nucleus is $\mathbf{R}_B$, and of the electron is $\mathbf{r}$. **Ask class:** what is the Hamiltonian? It's

$$H = -\frac{\nabla^2}{2} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|} - \frac{1}{|\mathbf{R}_A-\mathbf{R}_B|}\ . \tag{4}$$

Note that, consistent with the Born-Oppenheimer approximation, we have ignored the kinetic energy of the nuclei and have kept their positions fixed.

What next? We can try a variational approach, in which we consider a class of wavefunctions and then minimize the energy. We'll assume that the electron is in a superposition of the one-particle states around each proton individually:

$$\psi(\mathbf{r}) = \alpha\psi_A(\mathbf{r}) + \beta\psi_B(\mathbf{r}) \tag{5}$$

where we assume that ψ_A and ψ_B are ground states:

$$\begin{aligned} \psi_A(\mathbf{r}) &= \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{R}_A|} \\ \psi_B(\mathbf{r}) &= \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{R}_B|}\ . \end{aligned} \tag{6}$$

The $\pi^{-1/2}$ factors in front are to ensure that the squares of the wavefunctions integrate to 1: $\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr \psi_A^*(\mathbf{r})\psi_A(\mathbf{r}) = 1$, where in this case the wavefunctions are real so we don't actually need to take a complex conjugate.

To restrict things further, we can consider symmetries. **Ask class:** from the setup of the problem, can we say that the total wavefunction has any particular symmetries? Since the two protons are identical, the wavefunction must be symmetric about the midpoint of the molecule $(\mathbf{R}_A + \mathbf{R}_B)/2$. **Ask class:** what does this imply about the possible relative values of α and β? There are only two possibilities: either $\alpha = \beta$ or $\alpha = -\beta$. The wavefunction is then

$$\psi_\pm(\mathbf{r}) = C_\pm[\psi_A(\mathbf{r}) \pm \psi_B(\mathbf{r})] \ . \tag{7}$$

The normalization constants $C_\pm$ are determined by the condition that $|\psi_\pm|^2$ integrates to 1 over all space. Note that in general $C_\pm$ could be complex, but that since we have the freedom to choose a global phase factor $\exp(i\phi)$ to multiply $C_\pm$ we can choose $C_\pm$ to be real. Rybicki and Lightman do this integral in the solution to their Problem 11.2, but let's fill in some of the steps they skip. We'll take $\psi_+(\mathbf{r})$ as our example; ψ_- proceeds in the same way.

We want to find C_+ so that

$$C_+^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr [\psi_A(\mathbf{r}) + \psi_B(\mathbf{r})]^*[\psi_A(\mathbf{r}) + \psi_B(\mathbf{r})] = 1 \ . \tag{8}$$

Expanding out the brackets (and recognizing that the wavefunctions are real) we get

$$C_+^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr [\psi_A^2 + \psi_B^2 + 2\psi_A(\mathbf{r})\psi_B(\mathbf{r})] = 1 \ . \tag{9}$$

But ψ_A^2 and ψ_B^2 integrate to 1. Substituting in the expressions for the wavefunctions, we have

$$2C_+^2 + 2C_+^2\pi^{-1} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr e^{-|\mathbf{r}-\mathbf{R_A}|} e^{-|\mathbf{r}-\mathbf{R_B}|} = 1 \ . \tag{10}$$

Now let's define $\mathbf{R} \equiv \mathbf{R}_A - \mathbf{R}_B$ and $y \equiv |\mathbf{r} - \mathbf{R_A}|/R$, where $R = |\mathbf{R}|$. In addition, we can take advantage of our freedom in coordinate definitions to decide that θ will be the angle between $\mathbf{R}$ and $\mathbf{r} - \mathbf{R_A}$ (it should be clear that we could make our definitions with respect to $\mathbf{R_B}$ instead if we wished). Then we define $x \equiv \cos\theta$. We can also shift the origin of our coordinates to $\mathbf{R_A}$, which means that $r^2 dr$ becomes $R^3 y^2 dy$. Finally, we note that $|\mathbf{r} - \mathbf{R_B}| = \sqrt{(\mathbf{r} - \mathbf{R_B}) \cdot (\mathbf{r} - \mathbf{R_B})} = \sqrt{(\mathbf{r} - \mathbf{R_A} + \mathbf{R}) \cdot (\mathbf{r} - \mathbf{R_A} + \mathbf{R})} = \sqrt{(\mathbf{r} - \mathbf{R_A}) \cdot (\mathbf{r} - \mathbf{R_A}) + 2\mathbf{R} \cdot (\mathbf{r} - \mathbf{R_A}) + R^2} = \sqrt{R^2y^2 + 2R^2yx + R^2}$. Thus normalization implies

$$C_+^2(2 + 2S(R)) = 1 \tag{11}$$

where

$$S(R) = 2R^3 \int_{-1}^{1} dx \int_0^{\infty} y^2 dy e^{-R(y+\sqrt{y^2+2yx+1}} \ . \tag{12}$$

This still isn't an easy integral, but in their solution to problem 11.2, Rybicki and Lightman indicate the needed transformations. We then find that

$$C_\pm = [2 \pm 2S(R)]^{-1/2} \tag{13}$$

where

$$S(R) = (1 + R + \frac{1}{3}R^2)e^{-R} \ . \tag{14}$$

We now need to minimize the energy over our class of trial wavefunctions, meaning that we minimize the energy over R. **Ask class:** in quantum mechanics, how do we find the expectation value of the energy for a given wavefunction? The expectation value of the energy is the expectation value of the Hamiltonian

$$\langle H_\pm \rangle = \langle \psi_\pm | H | \psi_\pm \rangle = \int \psi_\pm^* H \psi_\pm \, d^3\mathbf{r} \ . \tag{15}$$

Let's write the result out in its fully gory glory, to make a point about looking for limits.

$$\langle H_\pm \rangle = \frac{-1 + 2(1 + 1/R)e^{-2R} \pm 2[(-1/2 + 1/R)(1 + R + R^2/3)e^{-R} - (1 + R)e^{-R}]}{2[1 \pm (1 + R + R^2/3)e^{-R}]} \ . \tag{16}$$

Yuck! Let's approach this one step at a time by looking at limits. **Ask class:** what is the limit of this expression as $R \rightarrow \infty$? It's $H_\pm = -1/2$. **Ask class:** what does that mean? It means that when the nuclei are separated by a great distance, the problem reduces to a single electron around either proton, so the energy is the binding energy of a single hydrogen atom. This makes sense. **Ask class:** what about the limit $R \rightarrow 0$, for the + parity? Here the $1/R$ terms dominate, giving $\langle H_+ \rangle \rightarrow 1/R$. It's less obvious, but an expansion of $\exp(-R)$ and $\exp(-2R)$ to order R^2 also gives $\langle H_- \rangle \rightarrow 1/R$ for the – parity. **Ask class:** what does this mean, physically? It means that there is strong Coulomb repulsion between the nuclei as they come close together.

We can plot the energy expectation values for the even (+) and odd (–) parities, and look for an energy minimum. The odd parity has no energy minimum; it goes to $+\infty$ for $R \rightarrow 0$, and asymptotes from above to $-1/2$ (i.e., -13.6 eV) for $R \rightarrow \infty$. The even parity, however, does have a minimum at $R = 1.3$Å, for which the energy in normal units is -15.4 eV, for a relative binding of about 1.8 eV. The real values are 1.03Åand a relative binding of about 2.8 eV. Thus, qualitatively we got it right that there is a minimum for the even but not the odd parity, but quantitatively we missed. Note that the true energy is less than the minimum we found with our particular trial wavefunctions, as required in variational theory.

Why is there a minimum only for the even parity? The electron serves as a bond between the two nuclei. For the odd parity, there is zero probability of the electron being on the midplane between the nuclei, so it can't do any bonding. For the even parity, its probability is maximal between the two, so bonding can happen. One reason that we didn't get the energy right is that in using hydrogen wavefunctions, we assume a functional form that goes like $\exp(-|\mathbf{r}-\mathbf{R}|)$, whereas for He^+ (i.e., one electron around two protons) it should be $\exp(-2|\mathbf{r}-\mathbf{R}|)$. We can take this into account by allowing $\psi_A(r) \rightarrow \psi_A(\eta r)$ where η is some constant, and minimize the energy with respect to both R and η. With this extra functional freedom, we can get closer to the correct value. Remember, this is the magic of variational calculations: the true ground state wavefunction will have a lower energy expectation value than any other wavefunction, so you can feel free to choose trial wavefunctions any way you like.

Now let's consider two electrons, specifically in the molecule H_2. **Ask class:** what major new principle arises when two, instead of one, electrons are considered? The Pauli principle, which says that no two identical fermions may occupy the same state. This means that the total wavefunctions of the two electrons must be antisymmetric with respect to each other. If the spatial part of the wavefunction is symmetric (as it is in the + parity), the spin part must be antisymmetric. Let's use trial wavefunctions derived from the H_2^+ orbitals, so that

$$\psi_s(1,2) = \frac{1}{2[1+S(r)]}\left[\psi_A(\mathbf{r}_1)+\psi_B(\mathbf{r}_1)\right]\left[\psi_A(\mathbf{r}_2)+\psi_B(\mathbf{r}_2)\right]\chi_s \tag{17}$$

where χ_s is the singlet spin wavefunction, where singlet means that the electron spins are antialigned (hence the total spin angular momentum is zero). Let's expand out the spatial wavefunction and explore its meaning as $r \rightarrow \infty$. We have

$$\psi_s \propto \left[\psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2)+\psi_B(\mathbf{r}_1)\psi_B(\mathbf{r}_2)\right]+\left[\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)+\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)\right] \; . \tag{18}$$

Examine the first term. **Ask class:** as $r \rightarrow \infty$, what does this mean? It means that both electrons are around a single proton (either A or B), so we have a lone proton plus an H^- ion. The H^- ion is loosely bound, by about 0.75 eV, so we don't expect this term to play much of a role. We can therefore ignore this first term; this is called the *valence bond* or *London-Heitler* method, which gives

$$\psi_2(1,2) = \frac{1}{\sqrt{2(1+S^2)}}\left[\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)+\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)\right]\chi_s \; . \tag{19}$$

A similar result holds for triplet states, where the electron spins are parallel to each other. **Ask class:** for this triplet state, what is the parity of the spatial wavefunction? It must be odd, so that the parity of the spatial+spin wavefunction is odd.

The full calculation is apparently ghastly, but it is found that the full binding energy is somewhat greater than 27.2 eV, so the H_2 molecule has net binding. In the case of this molecule, it's the singlet state that gives the greatest binding, because the electrons can play the role of exchange particles between the protons. This is opposite to the case for atoms, where when it's allowed the lowest energy state is one in which the electrons have *aligned* spins. The reason in that case is that the mutual electrostatic potential energy of electrons is positive, so to lower the energy as much as possible they need to be well-separated. The Pauli principle means that electrons with the same spin tend to avoid each other, which lowers the positive electrostatic energy. In the molecular case, however, it's the binding role electrons play between nuclei that matters most. The difference in energy is tiny, though. Incidentally, a spin 1 state (ortho) has three possible orientations. A spin 0 state (para) has only one orientation. Thus, in thermodynamic equilibrium one expect ortho H_2 states to be three times as abundant as para H_2 states, but the energy difference is so tiny that the transition rates are small and there often is not time to reach this equilibrium.

I'll conclude with some interesting thoughts Shu mentioned about the relation of electronic binding with other ideas. When neutrons were discovered various people (including Heisenberg) wondered what might keep them bound to the protons in nuclei. He considered an analogy with electronic binding in molecules: maybe, he thought, the protons and neutrons exchanged particles, and this kept them bound together. Now, if these exchange particles ("gauge bosons") have finite mass, this implies a force that decreases exponentially with distance. One can see this by considering quantum tunneling; a particle with finite mass can exist virtually, but the probability of its reaching some point decreases like $\exp(-r/\lambda_C)$, where λ_C is its Compton wavelength (in contrast, zero-rest-mass gauge bosons such as photons have infinite range). From the range $\sim 10^{-13}$ cm of the strong force, Yukawa suggested that a "meson" of mass 100-200 times the mass of an electron might be the exchange particle. Such a particle was indeed found: the π meson. Unfortunately, this idea as such is no longer considered the basis of the strong force, which is now understood as a "leftover" of quantum chromodynamics, the interactions between quarks and gluons. Still, it's an interesting road from molecular binding to the strong force!

Recommended Rybicki and Lightman problem: 11.1