

Lecture 14, February 20, 2006

Solved Homework

We are given that the lowest microwave absorption of carbon monoxide (CO, with ^{12}C and ^{16}O specified) is $115,271,000,000 \text{ s}^{-1}$ (115.271 GHz). We are asked first to compute the moment of inertia of CO.

Remember that the first absorption corresponds to the $0 \rightarrow 1$ rotational transition, and the energy separation between these two levels is $\Delta E = h\nu = 2B$ where

$$B = \frac{\hbar^2}{2I}$$

Rearranging, we have

$$\begin{aligned} I &= \frac{\hbar^2}{2B} \\ &= \frac{\hbar^2}{h\nu} \\ &= \frac{(1.0545 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})^2}{(6.6256 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})(115,271,000,000 \text{ s}^{-1})} \\ &= 1.456 \times 10^{-46} \text{ kg m}^2 \end{aligned}$$

We may compute the reduced mass for this system from the atomic masses for ^{12}C and ^{16}O

$$\begin{aligned} \mu &= \frac{m_{^{12}\text{C}} m_{^{16}\text{O}}}{m_{^{12}\text{C}} + m_{^{16}\text{O}}} \\ &= \frac{(12 \times 1.66 \times 10^{-27} \text{ kg})(15.9949 \times 1.66 \times 10^{-27} \text{ kg})}{(12 \times 1.66 \times 10^{-27} \text{ kg}) + (15.9949 \times 1.66 \times 10^{-27} \text{ kg})} \\ &= 1.138 \times 10^{-26} \text{ kg} \end{aligned}$$

Recalling that

$$I = \mu R^2$$

where R is the bond length, we have

$$\begin{aligned} R &= \sqrt{\frac{I}{\mu}} \\ &= \sqrt{\frac{1.456 \times 10^{-46} \text{ kg m}^2}{1.138 \times 10^{-26} \text{ kg}}} \\ &= 1.131 \times 10^{-10} \text{ m} \\ &= 1.131 \text{ \AA} \end{aligned}$$

The standard tabulated value is 1.128 Å. The difference reflects the very small correction that is associated with CO *not* being a rigid rotator (it vibrates while it rotates).

Finally, we are asked to predict the frequency at which the $1 \rightarrow 2$ rotational transition occurs. Recall that the spacing between adjacent transitions in the frequency spectrum is precisely equal to the frequency of the $0 \rightarrow 1$ transition, we may estimate a value of twice the ground state absorption, or $230,542,000,000 \text{ s}^{-1}$. If you refer back to the DIB website we visited that had the rotational spectrum for CO, you will see that this is about right. In cm^{-1} units, which are gotten simply by dividing ν by the speed of light c (which is $3 \times 10^{10} \text{ cm s}^{-1}$), this is 7.7 cm^{-1} .

The Hydrogen Atom (again)

It's time to return to our old friend, the H atom. Bohr found a quantum relationship useful for rationalizing the spectra of H, but it violated classical physics by having one charged particle orbiting about another with no loss of energy through radiation. de Broglie made the suggestion that the angular momentum quantization invoked by Bohr was suggestive of wave-particle duality for the electron. We are finally in a position to look at these waves more carefully.

Consider a proton and an electron bound together in some way. As these are quantum particles, they may not be still (that would violate the uncertainty principle); instead, they must be in motion. Just as for a rigid rotator, we may divide the total motion into a center of mass motion and a rotational motion about the center of mass. The wave function associated with center of mass motion is boring: it is that for a free particle having a mass equal to the sum of the masses of the proton and the electron. We'll take that as a given and focus on the remaining motion in the proton/electron system. The Hamiltonian, as for any system, is given by

$$H = T + V \tag{14-1}$$

In this case, the potential energy is the Coulomb interaction between the proton and the electron, given by

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad (14-2)$$

where the negative sign reflects the attractive nature of the potential, e is the charge on an electron (and also on a proton but having opposite sign), ϵ_0 is the dielectric permittivity of free space, and r is the interparticle distance.

The radial form of the potential energy function suggests that it will be most convenient to work in spherical polar coordinates. In that coordinate system, with the center of mass at the origin, the kinetic energy operator is

$$T = -\frac{\hbar^2}{2\mu}\nabla^2(r,\theta,\phi) = -\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2}\right) \quad (14-3)$$

where μ is the reduced mass (given the enormous mass difference between the proton and the electron—about a factor of 1800—this is *almost* equal to the mass of the proton, but not exactly), r is the interparticle distance, and L^2 is the total angular momentum squared operator. Thus, the full kinetic energy includes the angular kinetic energy associated with rotation at a fixed value of r , plus a term we've not considered before associated with contraction or lengthening of r .

So, the time independent Schrödinger equation for the H atom is

$$\left[-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \quad (14-4)$$

If we assume that the wave function is a separable product of a radial function depending only on r and a remaining function depending on θ and ϕ , we may write

$$\left[-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right]R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi) \quad (14-5)$$

This can be rearranged to

$$Y(\theta,\phi)\left[\left(\frac{d}{dr}r^2\frac{d}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right)\right]R(r) = R(r)\frac{L^2}{\hbar^2}Y(\theta,\phi) \quad (14-6)$$

If we now divide both sides by $R(r)Y(\theta,\phi)$, we have

$$\frac{1}{R(r)} \left[\left(\frac{d}{dr} r^2 \frac{d}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \right] R(r) = \frac{1}{Y(\theta, \phi)} \frac{L^2}{\hbar^2} Y(\theta, \phi) \quad (14-7)$$

This is the usual separation of variables game. Since the l.h.s. depends only on r and the r.h.s. depends only on θ and ϕ , both sides must be equal to a constant.

Fortunately, we know the constant (let's temporarily call it K) because we can solve for it from the r.h.s. using

$$\begin{aligned} K &= \frac{1}{Y(\theta, \phi)} \frac{L^2}{\hbar^2} Y(\theta, \phi) \\ &= \frac{1}{Y(\theta, \phi)} \frac{l(l+1)\hbar^2}{\hbar^2} Y(\theta, \phi) \\ &= l(l+1) \end{aligned} \quad (14-8)$$

This works because we already know the eigenfunctions of the total angular momentum operator: they are our old friends the spherical harmonics. All that's left for us to finish, then, in developing the full H-atom wave function is to figure out the radial part R that depends on r .

Since we now know the constant both sides of eq. 14-7 are equal to, we may use it with the l.h.s. of eq. 14-7 to write

$$\frac{1}{R(r)} \left[\left(\frac{d}{dr} r^2 \frac{d}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \right] R(r) = l(l+1) \quad (14-9)$$

or, in a (slightly) nicer form

$$\left[\left(\frac{d}{dr} r^2 \frac{d}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - l(l+1) \right] R(r) = 0 \quad (14-10)$$

This is one *nasty* looking differential equation. To clean up the notation, we introduce some new symbols defined by

$$\alpha^2 = -\frac{2\mu E}{\hbar^2} \quad \text{and} \quad \beta = \frac{\mu e^2}{4\pi\epsilon_0 \alpha \hbar^2} \quad \text{and} \quad \rho = 2\alpha r \quad (14-11)$$

Note that α is a real number, because we are considering only bound states of H, in which case E is negative, so α^2 is positive. Note that α has units of m^{-1} , so ρ is dimensionless. Physicists usually like to work in dimensionless quantities.

In any case, with these newly defined symbols, eq. 14-10 can be rewritten

$$\left\{ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \left[\frac{1}{\rho^2} l(l+1) - \frac{1}{\rho} \beta + \frac{1}{4} \right] \right\} P(\rho) = 0 \quad (14-12)$$

This is finally starting to look slightly tractable. As with most differential equations, we attack it from various angles. We consider first solutions appropriate for large values of ρ (i.e., the electron far from the nucleus). In that case, the only terms surviving in eq. 14-12 are those not preceded by ρ^{-1} or ρ^{-2} , i.e.,

$$\left(\frac{d^2}{d\rho^2} - \frac{1}{4} \right) P(\rho) = 0 \quad (14-13)$$

That's a nice easy differential equation, with one reasonable looking solution being $P(\rho) = e^{-\rho/2}$. Since we know that in general our wave functions must go to zero as ρ goes to infinity, this seems like a good place to start. Of course, this is only a good solution at large ρ , so the more general formulation of $P(\rho)$ is

$$P(\rho) = S(\rho)e^{-\rho/2} \quad (14-14)$$

where $S(\rho)$ is the "short-range" part of $P(\rho)$, which must not overwhelm the exponential at large ρ . If we take this new form for $P(\rho)$, we have the derivative relationships

$$\begin{aligned} \frac{d}{d\rho} [S(\rho)e^{-\rho/2}] &= \frac{dS(\rho)}{d\rho} e^{-\rho/2} - \frac{1}{2} S(\rho) e^{-\rho/2} \\ \frac{d^2}{d\rho^2} [S(\rho)e^{-\rho/2}] &= \frac{d}{d\rho} \left[\frac{dS(\rho)}{d\rho} e^{-\rho/2} - \frac{1}{2} S(\rho) e^{-\rho/2} \right] \\ &= \frac{d^2 S(\rho)}{d\rho^2} e^{-\rho/2} - \frac{1}{2} \frac{dS(\rho)}{d\rho} e^{-\rho/2} \\ &\quad - \frac{1}{2} \frac{dS(\rho)}{d\rho} e^{-\rho/2} + \frac{1}{4} S(\rho) e^{-\rho/2} \end{aligned} \quad (14-15)$$

that we can use in eq. 14-12 to get (after collecting terms and multiplying through by $\rho^2 e^{\rho/2}$)

$$\left\{ \rho^2 \frac{d^2}{d\rho^2} + \rho(2-\rho) \frac{d}{d\rho} + [\rho(\beta-1) - l(l+1)] \right\} S(\rho) = 0 \quad (14-16)$$

This represents some progress. If we consider $\rho=0$, then eq. 14-16 gives

$$l(l+1)S(0) = 0 \quad (14-17)$$

Since we are interested in wave functions that work for all values of l , it would appear that a good choice for S will be a polynomial series in ρ that must start with a higher power of ρ than ρ^0 (otherwise $S(0)$ would not be equal to zero and eq. 14-17 would not be satisfied for all values of l). Put mathematically, we consider

$$S(\rho) = \rho^k \sum_{j=0}^{\infty} a_j \rho^j \quad (14-18)$$

where k is the smallest integer greater than zero that makes a_0 be non-zero. For notational convenience, let us represent the sum in eq. 14-18 as the function $\Sigma(\rho)$. That is

$$S(\rho) = \rho^k \Sigma(\rho) \quad (14-19)$$

again, we note that

$$\begin{aligned} \frac{d}{d\rho} [\rho^k \Sigma(\rho)] &= k\rho^{k-1} \Sigma(\rho) + \rho^k \frac{d\Sigma(\rho)}{d\rho} \\ \frac{d^2}{d\rho^2} [\rho^k \Sigma(\rho)] &= \frac{d}{d\rho} \left[k\rho^{k-1} \Sigma(\rho) + \rho^k \frac{d\Sigma(\rho)}{d\rho} \right] \\ &= k(k-1)\rho^{k-2} \Sigma(\rho) + k\rho^{k-1} \frac{d\Sigma(\rho)}{d\rho} \\ &\quad + k\rho^{k-1} \frac{d\Sigma(\rho)}{d\rho} + \rho^k \frac{d^2 \Sigma(\rho)}{d\rho^2} \end{aligned} \quad (14-20)$$

We plug this all back into eq. 14-16 and collect terms to arrive at

$$\begin{aligned} \rho^2 \left[k(k-1)\rho^{k-2} \Sigma(\rho) + 2k\rho^{k-1} \frac{d\Sigma(\rho)}{d\rho} + \rho^k \frac{d^2 \Sigma(\rho)}{d\rho^2} \right] \\ + \rho(2-\rho) \left[k\rho^{k-1} \Sigma(\rho) + \rho^k \frac{d\Sigma(\rho)}{d\rho} \right] + [\rho(\beta-1) - l(l+1)] \rho^k \Sigma(\rho) = 0 \end{aligned} \quad (14-21)$$

Now, we rearrange this after collecting up all the terms having common powers of ρ to

$$\begin{aligned} \rho^{k+2} \left[\frac{d^2 \Sigma(\rho)}{d\rho^2} - \frac{d\Sigma(\rho)}{d\rho} \right] + \rho^{k+1} \left[2(k+1) \frac{d\Sigma(\rho)}{d\rho} - (k-\beta+1) \Sigma(\rho) \right] \\ + \rho^k [k(k+1) - l(l+1)] \Sigma(\rho) = 0 \end{aligned} \quad (14-22)$$

For this to work for all values of ρ , it must be true that in a full polynomial expansion every coefficient for every power of ρ vanishes (i.e., is equal to zero) *individually*!

In eq. 14-22, the smallest power of ρ that can appear is k , and its coefficient will be $[k(k+1)-l(l+1)]a_0$. Since we earlier specified that a_0 was non-zero, it is apparent that a first requirement is $k = l$ (remember that l is the quantum number for the total angular momentum which depends on which angular momentum eigenfunction Y_{l,m_l} we are using).

Now, note that

$$\begin{aligned}\frac{d\Sigma(\rho)}{d\rho} &= \sum_{m=0}^{\infty} m a_m \rho^{m-1} \\ \frac{d^2\Sigma(\rho)}{d\rho^2} &= \sum_{m=0}^{\infty} m(m-1) a_m \rho^{m-2}\end{aligned}\tag{14-23}$$

(the first term in the first-derivative expression is zero, and the first two terms in the second derivative expression are zero, so there really are *not* terms in negative powers of ρ ; writing the expansions this way simply makes a bit more clear how to form a single sum below...) If for the remaining two terms on the l.h.s. of eq. 14-22 we insert these expressions and we use our above result to set $k = l$ (the last term is zero by this choice), and finally we divide both sides by ρ^{l+1} , we find we can write

$$\sum_{m=0}^{\infty} \left\{ [m(m-1) + 2m(l+1)] a_m \rho^{m-1} + (\beta - l - m - 1) a_m \rho^m \right\} = 0\tag{14-24}$$

Again, such an equation can only be satisfied for all values of ρ if every coefficient of ρ vanishes separately. This requirement for the coefficient of ρ^m is in general

$$[(m+1)(m+2l+2)] a_{m+1} + (\beta - l - m - 1) a_m = 0\tag{14-25}$$

This defines a recursion relationship like those we've seen previously. The recursion is question is

$$\frac{a_{m+1}}{a_m} = -\frac{(\beta - l - m - 1)}{(m+1)(m+2l+2)}\tag{14-26}$$

In the limit as $m \rightarrow \infty$, the ratio of successive coefficients can be seen from eq. 14-26 to go to m^{-1} .

This limiting relationship between successive coefficients is exactly that for the power series expansion of e^x , where you'll recall

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \dots \quad (14-27)$$

so, the function $\Sigma(\rho)$ (remember, at this stage what we are doing is trying to determine that function!) resembles e^ρ , at least for $\rho > 1$. That means from eq. 14-19 that

$$S(\rho) \approx \rho^l e^\rho \quad (14-28)$$

and from eq. 14-14

$$\begin{aligned} P(\rho) &= \rho^l e^\rho e^{-\rho/2} \\ &= \rho^l e^{\rho/2} \end{aligned} \quad (14-29)$$

However, this function for $P(\rho)$ diverges for large ρ . That's bad, since a good wave function must go to zero as $\rho \rightarrow \infty$. The only way to ensure that this happens *is to require the power series expansion $\Sigma(\rho)$ to terminate after a finite number of terms*. Looking at eq. 14-26, we see that this requires that

$$l + m + 1 - \beta = 0 \quad (14-30)$$

where, let us pause a moment to remember, l is the quantum number for the total angular momentum spherical harmonic eigenfunction we are using (a non-negative integer, possibly zero), m is the term in the series expansion for $\Sigma(\rho)$ that we are requiring to be the last one (another non-negative integer, possibly zero since our sum starts at zero), and β is a function of the energy (because it is a function of α) as defined by eq. 14-11. So, we may write

$$n - \beta = 0 \quad (14-31)$$

or $\beta = n$ where $n = 1, 2, 3, \dots$ and n must be greater than or equal to $l+1$, the total angular momentum quantum number. If we now re-expand β using eq. 14-11 and solve for E , we at last arrive at (fanfare!)

$$E_n = -\frac{e^4 \mu}{32\pi^2 \epsilon_0^2 n^2 \hbar^2} \quad (14-32)$$

Notice that this is exactly equal to eq. 3-16 from lecture 3 that Bohr derived classically ($Z = 1$ for H and $\mu = m_e$ if one ignores the slight displacement of the center of mass for H from the proton nucleus).

The above derivation works for *any* one-electron atom, except that the generalization of eq. 14-2 for the Coulomb potential between the electron and an arbitrary nucleus of atomic number Z is

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (14-33)$$

The appearance of the constant Z in our above derivations has no effect on the process itself, but modifies the final result to the more general

$$E_n = -\frac{Z^2 e^4 \mu}{32\pi^2 \epsilon_0^2 n^2 \hbar^2} \quad (14-34)$$

The form of eq. 14-34 makes clear that the lowest (most negative) energy wave function corresponds to $n = 1$, while the energy is zero for infinite n . An energy of zero also corresponds to ionization of the H atom. That is, the zero of energy refers to complete separation of the proton and the electron with both particles at rest. So, E_1 is also the ionization potential.

Homework

To be solved in class:

What is the minimum energy required to remove the final electron from Be^{3+} ? (The ionization potential of the H atom is -13.6 eV. With this datum, there is a clever way to do this problem in under a minute...) (Also, it is a subtle point, but the problem is deliberately poorly worded; how could it be better worded?)

To be turned in for possible grading Feb. 24:

What is the error introduced in the ionization potential of the H atom if the mass of the electron is used in place of the reduced mass of the H atom?