

## Homework solutions Postulates of quantum mechanics - Chapter 1

**Homework problem Q1.1:** Try out the spectrum analyzer yourself - make an interesting sound, take a screenshot of the result, and submit the screenshot and once sentence about why you think the soundwave and its spectrum look the way they do.



**Sample solution** (you must have a different waveform): Animal roar. The roar covered a wide range of frequencies, but had ‘formants’ where the frequencies peaked.

**Homework problem Q1.2:** Apply the ‘frequency squared’ operator to the function  $y = \sin(2\pi 5t) - \cos(2\pi 7t)$ . Is  $y$  an eigenfunction of this operator? Why or why not?

**Solution:**  $\hat{v}^2 \Psi = \frac{-1}{4\pi^2} \frac{\partial^2}{\partial t^2} [\sin(2\pi 5t) - \cos(2\pi 7t)] = 5^2 \sin(2\pi 5t) - 7^2 \cos(2\pi 7t)$

$y$  is not an eigenfunction of the operator because the function obtained on the right is not a multiple of the original function. [Note that each of the two terms in  $y$  individually would have been an eigenfunction, with frequencies 5 and 7, respectively.]

**Homework problem Q1.3:** One of the weird things in quantum mechanics is that the order of things makes a difference even though it does not in classical mechanics. Consider for example the product  $xp$ . Classically, this is the same as  $px$ . But in quantum mechanics, the order in which you do things matters! Using  $\hat{x} = x$  and  $\hat{p} = \frac{h}{2\pi i} \frac{\partial}{\partial x}$ , the conjugate coordinate and momentum, show that  $\hat{x}\hat{p} \neq \hat{p}\hat{x}$ , and give the difference  $\hat{x}\hat{p} - \hat{p}\hat{x}$ . What if we had calculated  $\hat{x}\hat{y}$  and  $\hat{y}\hat{x}$ , where  $x$  and  $y$  are just two different coordinates?

**Solution:** One way to see what happens, is to imagine the operator  $x\hat{p} - \hat{p}x$  acting on a function ‘ $f$ ’, to see that the result is not zero like in classical mechanics, where  $xp - px = 0$  and therefore  $[xp - px]f = 0$  as well when you apply it to a function. Doing the same thing in quantum mechanics, let’s apply  $x\hat{p} - \hat{p}x$  to the function  $f$  and see if we get 0 or not:

$$\begin{aligned}
[x\hat{p} - \hat{p}x]f &= \left[ x \frac{\hbar}{i} \frac{\partial}{\partial x} - \frac{\hbar}{i} \frac{\partial}{\partial x} x \right] f, \text{ by using } \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \\
&= \frac{\hbar}{i} \left[ x \frac{\partial f}{\partial x} - \frac{\partial}{\partial x} x f \right], \text{ by pulling out } \frac{\hbar}{i}, \text{ pulling in } f \text{ since } \frac{\partial}{\partial x} f = \frac{\partial f}{\partial x} \\
&= \frac{\hbar}{i} \left[ x \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial x} - f \frac{\partial x}{\partial x} \right], \text{ by using the chain rule}
\end{aligned}$$

from calculus that  $\frac{\partial}{\partial x}(ab) = b \frac{\partial a}{\partial x} + a \frac{\partial b}{\partial x}$  in the last step. The first two terms in square brackets on the right hand side cancel, but the blue one is left over and  $\frac{\partial x}{\partial x} = 1$ , so we obtain

$$[x\hat{p} - \hat{p}x]f = i\hbar f,$$

by realizing that  $-1/i = i$ . Thus,

$$x\hat{p} - \hat{p}x = i\hbar \neq 0.$$

As a different example, if  $x$  and  $y$  are just two different coordinates,  $[xy-yx]f(x,y) = 0$ . So in that case, quantum mechanics agrees with classical mechanics.

[Note: there are also classical operations where the order matters; for example, rotating a book around its ‘long’ axis, then its ‘flat’ axis is not the same as ‘flat,’ then ‘long.’ Same for molecules. We say that such operations do ‘not commute’ or are ‘non-abelian.’]

## Homework solutions A vibrating molecule - Chapter 2

**Homework problem Q2.1:** Plug in that guess, and show that the Schrödinger equation can only be satisfied (the  $x^2\Psi_n$  gets canceled) if  $a = \frac{\sqrt{mk}}{2\hbar}$ , in which case the equation becomes  $\hat{H}\Psi_0 = \frac{\hbar}{2}\sqrt{k/m}\Psi_0$ , or the energy is  $E_0 = \frac{\hbar}{2}\sqrt{k/m}$ .

**Solution:** Leaving out the normalization constant ‘C’, which is just a multiplying factor,

$$\left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \right\} e^{-ax^2} = \left\{ \frac{\hbar^2 a}{m} - 2 \frac{\hbar^2 a^2 x^2}{m} + \frac{1}{2} kx^2 \right\} e^{-ax^2},$$

Note that this is not an eigenfunction for just any value of  $a$  because the function on the right side is not necessarily a multiple of the Gaussian  $e^{-ax^2}$ , the function we put in on the left side. However, if the second and third terms in the curly brackets, which contain an ‘extra’  $x^2$ , were to cancel, then we would have an eigenfunction. Picking the specific value for  $a = \frac{\sqrt{mk}}{2\hbar}$  to make these two terms cancel, we get

$$\left\{ \frac{\hbar}{2} \sqrt{\frac{k}{m}} - \frac{kx^2}{2} + \frac{1}{2} kx^2 \right\} e^{-ax^2} = \frac{\hbar\omega}{2} e^{-\frac{\sqrt{mk}}{2\hbar}x^2}.$$

So the Gaussian solves the Schrödinger equation for the vibrating molecule, with energy exactly equal to  $\frac{\hbar\omega}{2} = \frac{h\nu}{2}$ , where  $\omega = \sqrt{k/m}$  is the angular frequency of the spring, or equivalently  $\nu = \frac{1}{2\pi}\sqrt{k/m}$  is the ‘regular’ frequency of oscillation. The Gaussian is an ‘eigenfunction’ of the Schrödinger equation, and the energy is an ‘eigenvalue’ of the Schrödinger equation.

**Homework problem Q2.2:** Plug that guess into the Schrödinger equation with  $a = \frac{\sqrt{mk}}{2\hbar}$  and show that it also satisfies the equation, this time with a higher energy  $E_1 = 3h\nu/2$ .

**Solution:** If you proceed like in the previous problem,

$$\left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \right\} xe^{-ax^2} = \left\{ \frac{\hbar^2}{2m} 2a + \frac{\hbar^2}{2m} 4a - \frac{\hbar^2}{2m} 4a^2 x^2 + \frac{1}{2} kx^2 \right\} xe^{-ax^2},$$

where we used the chain rule, e.g.  $\frac{\partial}{\partial x} [xe^{-ax^2}] = (1e^{-ax^2} - 2ax^2 e^{-ax^2}) = (1 - 2ax^2)e^{-ax^2}$  for the first derivative, and similarly again for the second derivative.

Just like before, if we pick  $a = \frac{\sqrt{mk}}{2\hbar}$ , the last two terms in the curly brackets cancel, and we have  $\frac{\hbar^2}{2m} 6 \frac{\sqrt{mk}}{2\hbar} xe^{-ax^2}$  left over. So,

$$\hat{H}xe^{-ax^2} = \frac{3}{2} \hbar\omega xe^{-\frac{\sqrt{mk}}{2\hbar}x^2}.$$

Thus,  $xe^{-\frac{\sqrt{mk}}{2\hbar}x^2}$  is also an eigenfunction of the Schrödinger equation for a vibrating molecule, but this time with a higher eigenvalue  $E = \frac{3}{2} \hbar\omega$ .

[Note: lower-energy eigenfunction from the previous problem has only one wiggle, whereas the higher-energy eigenfunction here has two wiggles. More wiggles = bigger second derivative = more momentum and kinetic energy. Note that we can write the first two energies we found as  $E_0 = \hbar\omega \left(0 + \frac{1}{2}\right)$  and  $E_1 = \hbar\omega \left(1 + \frac{1}{2}\right)$ , and in general, other energy levels we can find obey the rule  $E_n = \hbar\omega \left(n + \frac{1}{2}\right)$ , where  $n=0, 1, 2, 3, \dots$ . We call  $n$  the ‘quantum number,’ and the energy is ‘quantized,’ i.e. only certain specific values of the energy can occur. This is different from classical mechanics, where a spring can vibrate with any energy starting from  $E=0$  (spring sits still) on up.]

**Homework problem Q2.3:** The square displacement of the vibrating molecule from equilibrium is  $x^2$  because the extension  $x_e=0$  for a spring at rest. Similarly, the square deviation of momentum from the average value is  $p^2$  because  $p$  on average is zero (the molecule vibrates ‘back’ and ‘forth’, switching from +p to -p). Use postulate 3,  $\bar{y} = \int dx \Psi^*(x) y(x) \Psi(x)$  to calculate the averages of the square displacement  $\Delta x^2$  and  $\Delta p^2$ , for the ground state of the vibrating molecule,  $\Psi_0 = \left(\frac{\sqrt{km}}{\pi\hbar}\right)^{1/4} e^{-\frac{\sqrt{mk}}{2\hbar}x^2}$ . I added the normalization factor out in front of  $\Psi_0$  such that  $\int dx |\Psi_0(x)|^2 = \int dx P(x) = 1$ . Multiply  $\Delta x^2 \Delta p^2$  together and take the square root - what do you get? You just proved Fourier’s principle, known in quantum mechanics also as the “Heisenberg uncertainty principle.” This is incorrect English; there is no ‘uncertainty,’ the variables  $x$  and  $p$  are conjugate, so they can’t be known simultaneously; just like there’s nothing wrong with your ears if you can’t hear the exact pitch of a snare drum beat - it has no exact pitch.

**Solution:** The average value of a function or operator  $y(x)$  is given by postulate 3. Let’s start with the average value of the square displacement from equilibrium,  $\Delta x^2$ , of the vibrating molecule,

$$\int_{-\infty}^{\infty} dx \Psi_0^* x^2 \Psi_0 = \int_{-\infty}^{\infty} dx \left(\frac{\sqrt{km}}{\pi\hbar}\right)^{1/4} e^{-\frac{\sqrt{mk}}{2\hbar}x^2} x^2 \left(\frac{\sqrt{km}}{\pi\hbar}\right)^{1/4} e^{-\frac{\sqrt{mk}}{2\hbar}x^2}, \text{ or}$$

$$\Delta x^2 = \int_{-\infty}^{\infty} dx x^2 \left(\frac{\sqrt{km}}{\pi\hbar}\right)^{1/2} e^{-\frac{\sqrt{mk}}{\hbar}x^2}.$$

Note that here we can just combine  $\Psi^*\Psi = P(x)$  because  $x^2$  is just a multiplicative function.

Renaming  $\frac{\sqrt{mk}}{\hbar} = a$  for simplicity, type this integral into Wolfram Integrator at

<https://www.wolframalpha.com/calculators/integral-calculator/>

like so, you get

The screenshot shows the WolframAlpha interface. The input field contains the integral  $\int x^2 \cdot \sqrt{\frac{a}{\pi}} \exp(-a \cdot x^2) dx$ . Below the input, there are buttons for "NATURAL LANGUAGE" and "MATH INPUT". The result is displayed as:
 
$$\int x^2 \sqrt{\frac{a}{\pi}} \exp(-a \cdot x^2) dx = \frac{\operatorname{erf}(\sqrt{a} x) - \frac{2\sqrt{a} x e^{-a x^2}}{\sqrt{\pi}}}{4 a} + \text{constant}$$
 At the bottom right, it says "erf(x) is the error function".

When we evaluate at  $x=\pm\infty$ , the constant cancels out, as does the middle term because it is an odd function of  $x$ . The error function  $\operatorname{erf}(x)=1$  at  $x=\infty$  and  $-1$  at  $x=-\infty$ . You can check this for yourself by clicking “erf(x) is the error function” at the bottom right, then click “Evaluation,” and type in

some large positive or negative values of  $x$ . Make sure to try this, you may need to do it on the exam!

So our integral simplifies to

$$\Delta x^2 = \frac{\text{erf}(\sqrt{ax})}{4a} \Big|_{-\infty}^{\infty} = \frac{1}{4a}(1 - (-1)) = \frac{1}{2a}.$$

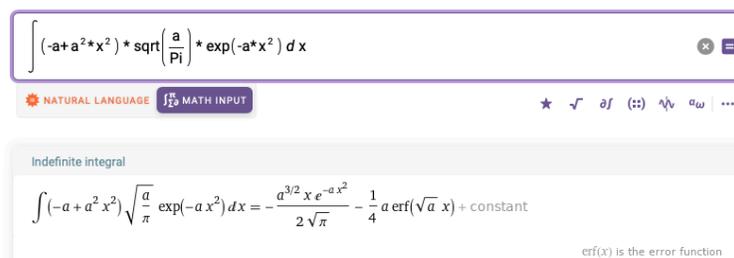
OK, now on to the  $\Delta p^2$  part. Instead of inserting  $x^2$  into the integral to calculate its average, we insert  $\hat{p}^2 = -\hbar^2 \partial^2 / \partial x^2$  to calculate the

$$\Delta p^2 = -\hbar^2 \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2} \frac{\partial^2}{\partial x^2} e^{-\frac{a}{2}x^2}.$$

Note that this time, we could not combine  $\Psi^* \Psi$  together and need to leave  $\Psi^*$  on the left: the operator  $\partial^2 / \partial x^2$  from the momentum-squared is not a simple multiplicative operator. Taking the second derivative, the integral becomes

$$\Delta p^2 = -\hbar^2 \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2} (-a + a^2 x^2) e^{-\frac{a}{2}x^2} = -\hbar^2 \int_{-\infty}^{\infty} dx (-a + a^2 x^2) \left(\frac{a}{\pi}\right)^{1/2} e^{-ax^2}.$$

You can enter this again in Wolfram Integrator,



The constant at the end and the middle term again cancel when the integral is evaluated from  $-\infty$  to  $\infty$ . The error function again comes out to  $\pm 1$ , so we get

$$\Delta p^2 = \hbar^2 \frac{a}{4} (1 - (-1)) = \hbar^2 \frac{a}{2}.$$

Multiplying the two results together, we get

$$\Delta x^2 \Delta p^2 = \frac{\hbar^2}{4}.$$

Note that then answer does not depend on  $a$ , so the answer does not depend on the properties of the molecule, or the spring, at all! It is universal. Taking the square root of this equation, we obtain

$$\Delta x \Delta p = \frac{\hbar}{2}.$$

The spread of momentum for a vibrating molecule and the spread of position are not independent. You have just proved the Heisenberg Principle or Uncertainty Principle for the ground state of a vibrating molecule (or spring), which is a special case of the Fourier Principle for any pair of conjugate variables that we discussed in class. In classical mechanics, you could determine precise values of  $x$  and  $p$  simultaneously, so  $\Delta x \Delta p = 0$ , but in quantum mechanics, this is not possible.

This is the reason why the lowest energy state of the spring cannot be  $E=0$ , but has to be  $E_0 = \frac{\hbar\omega}{2}$ , also known as the ‘zero point energy,’ ‘ground state energy’ or ‘minimal energy’ allowed for a quantum spring.

### Homework problem Q2.4:

a. Given the ground state energy  $E_0 = \frac{\hbar\nu}{2}$ , at what values of  $x_{\max} = -x_{\min}$  in  $\text{\AA}$  is  $E_0 = V(x) = kx^2/2$  for HCl?

b. Let's calculate the probability of being in the "forbidden region" where kinetic energy is negative. To make things simple, let's assume  $x_{\max}=1$ , in which case the ground state wavefunction becomes the Gaussian  $\Psi(x) = (\pi)^{-1/4} e^{-x^2/2}$ . Calculate the probability that the molecule will be in the "classically forbidden region" either at  $x > x_{\max}$  or  $x < x_{\min}$ . Tip: to save yourself a lot of hassles, you can go to a site like <https://www.integral-calculator.com>, enter the function (e.g.  $1/\sqrt{\pi}$ ) is  $(\pi)^{-1/2}$ , and  $\exp(-x^2)$  is  $e^{-x^2}$ ) and the integration limits (e.g.  $x=1$  for the lower limit,  $\infty$  for the upper limit). Remember: you need to integrate  $P(x) = |\Psi(x)|^2$ , not the wavefunction itself!

c. Also verify that if you just integrate from  $-\infty$  to  $\infty$ , i.e. over all values of  $x$ , the probability is 1: you have to find the particle somewhere. That's the reason a " $(\pi)^{-1/4}$ " is hanging out in front of the Gaussian: the wavefunction is normalized so the integrated probability adds up to 100% or 1.

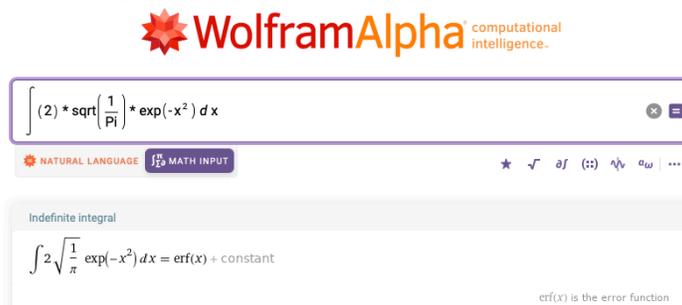
**Solution:**

a.  $\frac{\hbar\omega}{2} = \frac{1}{2} kx^2$  or  $x = \pm \sqrt{\frac{\hbar\omega}{k}}$ , so  $x_{\min} = -\sqrt{\frac{\hbar\omega}{k}}$  and  $x_{\max} = \sqrt{\frac{\hbar\omega}{k}}$ . Using  $k \approx 490$  N/m, and  $h\nu \approx 6.62 \cdot 10^{-34}$  J·s  $\cdot 8.65 \cdot 10^{13}$  Hz we get  $x_{\max} \approx 1.08 \cdot 10^{-11}$  m or 0.11 Å. So the molecule vibrates back and forth by about a tenth of an Ångstrom, or about 0.01 nanometers.

b. The Gaussian is symmetric, so to get the area under the forbidden region we can just integrate from  $x_{\max}$  to  $\infty$  and multiply by two, instead of doing the integral for  $x_{\min}$  as well:

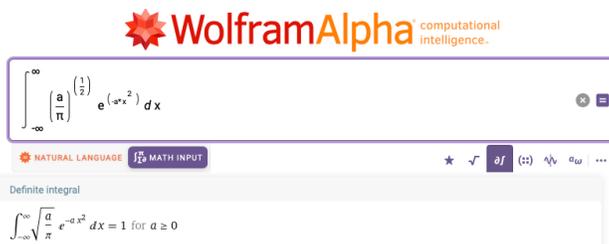
$$P_{\text{forbidden}} = 2 \int_{x_{\max}}^{\infty} dx |\Psi(x)|^2 = 2 \int_1^{\infty} dx \pi^{-1/2} e^{-x^2}.$$

Note that you would get the same result by variable substitution even in the most general case where  $x_{\max} \neq 1$ . Typing this integral into Wolfram Integrator, we obtain



and  $\text{erf}(\infty) - \text{erf}(1) \approx (1 - 0.84) = 0.16$ . Thus there is a 16% chance that a vibrating molecule in the ground state is tunneling into the "forbidden" region where the kinetic energy has a negative average. In classical mechanics, the bond would never stretch beyond  $x_{\max}$ .

c.  $P_{\text{total}} = \int_{-\infty}^{\infty} dx (1/\pi)^{1/2} e^{-x^2} = 1$ , or in the most general case when  $x_{\max} \neq 1$  then still  $P_{\text{total}} = \int_{-\infty}^{\infty} dx (a/\pi)^{1/2} e^{-ax^2} = 1$ , as you get from the Wolfram Alpha answer below:



(Note that in the most general case,  $a$  is given by  $a = 1/x_{\max}^2$ , so when  $x_{\max} = 1$ ,  $a = 1$ .)

## Homework solutions

### Other models interesting for chemistry - Chapter 3

**Homework problem Q3.1:** The meaning of “visible”: Retinal, the pigment in human eyes, has 12 conjugated oxygen and carbon atoms. What is its color? [Hint: first, use the same ‘box’ formula as shown above, but fill in 12 electrons up to  $n=6$ , so the HOMO to LUMO transition goes from orbital #6 to orbital #7, and use the “L” for retinal, about twice as long as benzene]. Remember, the color of a substance is complementary to the wavelength it absorbs, e.g. something that absorbs violet/blue light will look orange.

**Solution: Plugging into**

$$E_n = \frac{h^2 n^2}{8mL^2}$$

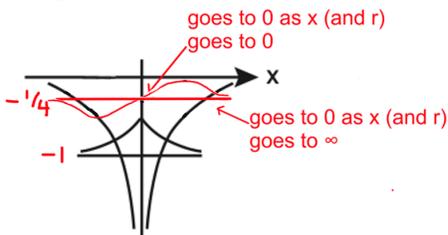
with  $n=6$  (filling 12 electrons into 6 orbitals according to Postulate 4) and  $n=7$  (first excited state when an electron from  $n=6$  moves up in energy after absorbing light energy,  $m \approx 9.11 \cdot 10^{-31}$  kg (electron mass) and  $L \approx 15 \text{ \AA} = 1.5 \cdot 10^{-9}$  m (from Figure on the first page of Chapter 3),  $E_6 = 9.64 \cdot 10^{-19}$  J and  $E_7 = 1.31 \cdot 10^{-18}$  J. Thus  $\Delta E = h\nu = (1.31 \cdot 10^{-18} - 9.64 \cdot 10^{-19}) \text{ J} = 3.46 \cdot 10^{-19}$  J and  $\nu = 5.23 \cdot 10^{14}$  Hz. Using  $\lambda = c/\nu$  and  $c \approx 2.99 \cdot 10^8$  m/s, we get  $\lambda \approx 574$  nm. Retinal in our simple box model absorbs yellow light. This is the wavelength that’s gone, so retinal’s color is the *complementary* color (what’s left over to be seen after light is absorbed). Looking at the color wheel in the notes, or at a table such as

<http://dept.harpercollege.edu/chemistry/chm/100/dgodambe/thedisk/spec/complem.htm> after searching Google for “complementary color,” we find it’s purple. Of course, take that answer with a grain of salt: we did not do an accurate quantum calculation of the whole molecule in the protein - but our model is certainly telling us that retinal absorbs visible light, which is why we call such light “visible” in the first place!

**Homework problem Q3.2:** Start with the figure at the beginning of section “2. The simplest atom”, showing the Coulomb potential along the x-axis and the  $n=1$  energy level. Draw in the  $n=2$  energy level to scale (read the figure caption to the end!) and sketch the profile of the  $\Psi_{n=2, l=1} \sim r e^{-r/2a_0} \sin\theta \cos\phi$  function, called ‘ $2p_x$  orbital.’ Note that unlike the 1s orbital already sketched,  $2p_x$  flips sign between the positive and negative x-axis (where  $\phi = 180^\circ$ ) because  $\cos(180^\circ) = -1 = -\cos(0^\circ)$ . So the  $2p_x$  orbital wiggles more than the 1s orbital, as we would expect: it has more energy, thus more kinetic energy, thus more momentum, and thus more curvature.

**Solution:** If the  $n=1$  state has an energy  $\sim -1/n^2 = -1$ , then the  $n=2$  state has an energy  $\sim -1/2^2 = 1/4$ . Now to the plot. The effect of the three variables  $r$ ,  $\theta$ , and  $\phi$  is:

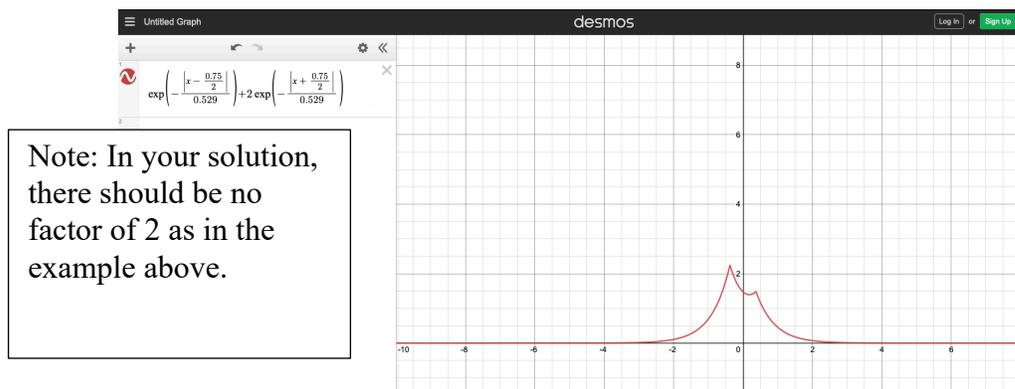
- For  $z=0$  (along the x-axis),  $\theta = 90^\circ$ , so  $\sin\theta = 1$ .
- Along the positive x-axis, the azimuthal angle  $\phi = 0$ , so  $\cos\phi = 1$ ; but along the negative x-axis,  $\phi = 180^\circ$ , so  $\cos\phi = -1$ , and the function will be negative.
- $r e^{r/a_0}$  starts out at 0 when  $x=0$  ( $r=0$ ), increases, then drops off as  $x$  (and  $r$ ) goes to  $\infty$  because the exponential  $e^{-r/a_0}$  goes to 0.



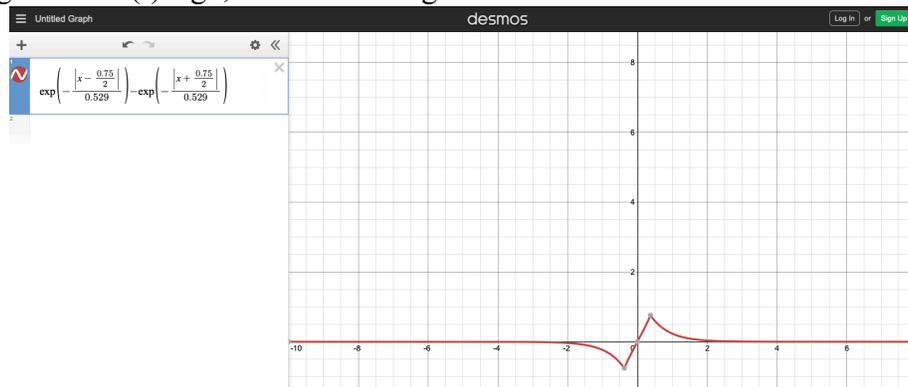
## Homework solutions Making molecules - Chapter 4

**Homework problem Q4.1:** Remember the formula for a 1s orbital along the x-axis:  $\Psi_{1s} \sim \exp(-|x|/a_0)$ . To make a molecule of bond distance  $R$ , put one atom at  $x=R/2$  and the other at  $x=-R/2$ , similar to the Figure above. Given  $\Psi_{\sigma} \sim \exp(-|x-R/2|/a_0) + \exp(-|x+R/2|/a_0)$ , use a graphing program to plot the  $\sigma$  wavefunction for a bond distance  $R=0.75 \text{ \AA}$  and using the Bohr length  $a_0=0.529 \text{ \AA}$  from the last chapter. Plot  $\Psi_{\sigma^*} \sim \exp(-|x-R/2|/a_0) - \exp(-|x+R/2|/a_0)$  as well. Compare to the Figure above. [Tip:  $|x|$  is the absolute value of  $x$ ].

**Solution:** There are many graphing calculators online, I used <https://www.desmos.com/calculator> for this:



Note that I made the left exponential bigger because it is multiplied by '2' in the formula at the top left. Make sure to plot your own, multiplied by '1'. In desmos, e-to-the-power is  $\exp()$ , sine-of-x is  $\sin(x)$ , etc. Absolute value bars are just the  $|$  on your keyboard, or use the  $\text{abs}()$  function. Below is what you get with a  $(-)$  sign, the antibonding wavefunction:

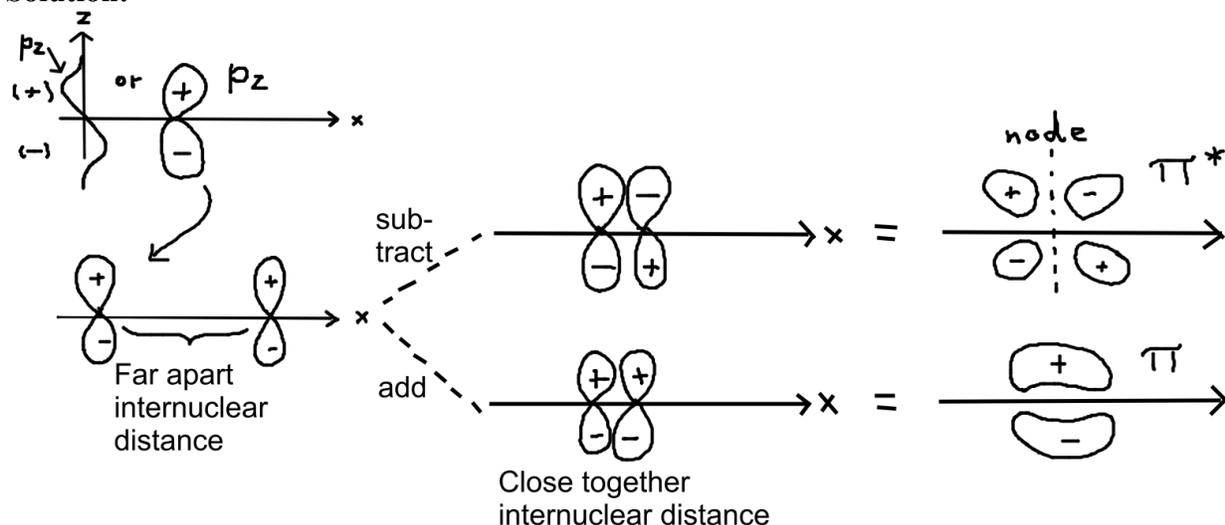


If you have a little time, play around, and plot a few other functions, like  $x \cdot \exp(-x^2)$ , which is the  $n=1$  state of the vibrating molecule, if you remember. Or  $x \cdot (\exp(-\text{abs}(x)/a))$ , which is the radial part of a p orbital. desmos even lets you add a 'slider,' so if you copy the above formula, make a slider for 'a,' and see how the function changes when you increase or decrease a!

**Homework problem Q4.2:** Draw two p orbitals far apart and perpendicular to the internuclear axis, keeping in mind the + and - signs of the two lobes. Now draw them together in both  $\pm$  combination - sketch what a bonding and an antibonding  $\pi$  orbital looks like. Adding increases

probability, subtracting decreases probability, and we generally call this effect ‘quantum interference,’ which can be constructive (add) or destructive (subtract).

**Solution:**



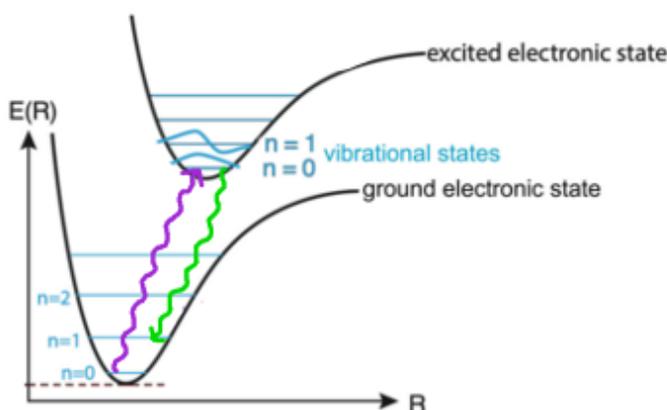
**Homework problem Q4.3:** Writing the wavefunction a bit shorter as  $(\sigma_{1+} \sigma_{2-} - \sigma_{2+} \sigma_{1-})/\sqrt{2}$ , show that indeed switching the particles #1 and #2 gives you the negative of the function, satisfying Postulate 4.

**Solution:** Switching particles 1 and 2, we get the function  $(\sigma_{2+} \sigma_{1-} - \sigma_{1+} \sigma_{2-})/\sqrt{2} = -(\sigma_{1+} \sigma_{2-} - \sigma_{2+} \sigma_{1-})/\sqrt{2}$ , where we pulled out a minus sign in the second step. So indeed, this wavefunction is an antisymmetric (minus sign) combination of ‘electron 1 being in sigma orbital with spin up’, and ‘electron 2 being in sigma orbital with spin down’ with ‘electron 2 being in sigma orbital with spin up’, and ‘electron 1 being in sigma orbital with spin down.’ We say that the two electrons are in a superposition state because each has spin up and spin down at the same time in this wavefunction. This is not possible in classical mechanics of course. The two electrons are like a Schrödinger’s cat, up and down at the same time (better than dead and alive at the same time!)

**Homework solutions**  
**Potential surfaces: Spectroscopy and chemical reactions - Chapter 5**

**Homework Problem Q5.1:** In the above figure, a molecule absorbs  $\lambda=480$  nm light and goes from the ground electronic state and ground vibrational state ( $n=0$ ) to the excited electronic state, also no vibrational excitation ( $n=0$  again). When the molecule emits light, the wavelength instead is 520 nm because it went to the  $n=1$  vibrational state in the ground electronic state. What is the vibrational frequency in  $\text{cm}^{-1}$ ? We call the 40 nm red-shift in wavelength the ‘Stokes shift.’

**Solution:**



The diagram above has the  $\lambda_1=480$  nm light (purple arrow going up) going from  $n=0$  in the ground electronic state to  $n=0$  in the excited electronic state drawn in and the  $\lambda_2=520$  nm light (green arrow going down) going from  $n=0$  in the excited electronic state to  $n=1$  in the ground state. The difference in energies is the difference between the  $n=1$  and  $n=0$  vibrational states in the ground electronic state, which is  $\Delta E=E_1-E_2=h\nu_1-h\nu_2=h\nu_{vib}$ , where  $\nu_{vib}$  is the vibrational frequency we are looking for. So we need to convert the wavelengths into energies using  $\nu\lambda=c$ :

$$E_i = h\nu_i = \frac{hc}{\lambda_i}$$

Solving for  $\nu$  in Hz,

$$\nu_1 - \nu_2 = \frac{c}{\lambda_1} - \frac{c}{\lambda_2} = \nu_{vib}$$

But we want frequency in number of waves per cm, i.e. units of  $\text{cm}^{-1}$ , not in Hz. To get this, we divide by  $c$  to go from units of oscillations per second (Hz) to oscillations per meter ( $\text{m}^{-1}$ ), and multiply by 0.01 because a cm is 1/100 of a meter:

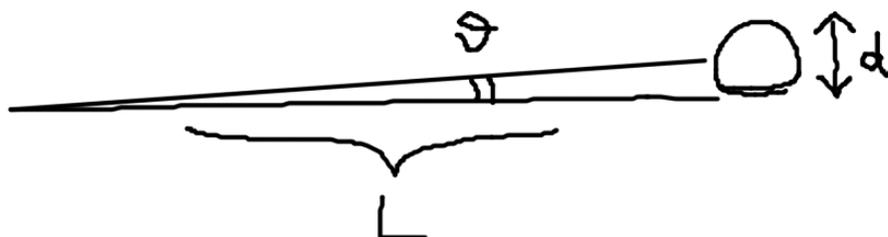
$$\begin{aligned} \tilde{\nu}_{vib}(\text{cm}^{-1}) &= \left\{ \frac{1}{\lambda_1(\text{m})} - \frac{1}{\lambda_2(\text{m})} \right\} \cdot 0.01 \left( \frac{\text{m}}{\text{cm}} \right) = \left\{ \frac{1}{480 \cdot 10^{-9} \text{ m}} - \frac{1}{520 \cdot 10^{-9} \text{ m}} \right\} \cdot 0.01 \left( \frac{\text{m}}{\text{cm}} \right) \\ &\approx 1600 \text{ cm}^{-1} \end{aligned}$$

This is a typical frequency for a molecular vibration in the mid-infrared, close to the bending vibration of water vapor, which causes a greenhouse effect. In fact, water accounts for about 70% of the greenhouse effect on Earth, while  $\text{CO}_2$  accounts only for about 25%. The greenhouse effect is not necessarily bad: it's what keeps Earth's surface reasonably warm on average, vs. a planet like Mars, which could be much warmer if it had more water vapor, and unlike Venus, which has too many greenhouse gases and is very hot. The temperature differences between planetary

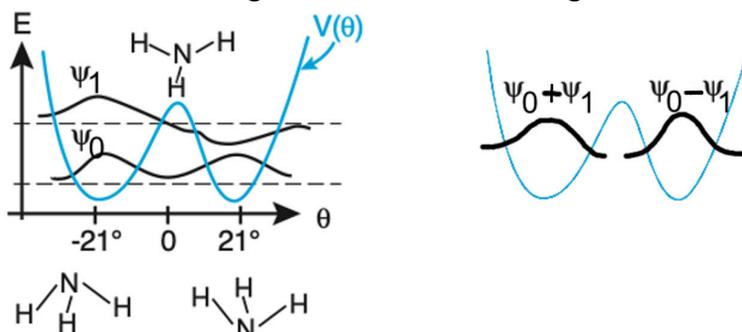
surfaces are not just due to the distance from the sun, but also depend on the balance of gases in the planetary atmospheres.

**Homework problem Q5.2:** If I wanted to resolve a ‘continent’ from an ‘ocean’ on an Earth-size planet 10 light years away to spectroscopically distinguish silicates from water, what fraction of a degree angle would I need to be able to resolve?

**Solution:** The sketch shows the problem we need to solve.



The Earth’s diameter is about 12000 km or  $d=1.2 \cdot 10^7$  m. Let’s say a typical ocean covers half the surface, then that’s  $r = 6 \cdot 10^6$  m. A light year is  $\approx 3 \cdot 10^8$  m/s  $\cdot 3 \cdot 10^7$  s  $\approx 9 \cdot 10^{15}$  m, so 10 light years is  $L \approx 9 \cdot 10^{16}$  m. The angle  $h$  we want is  $\tan^{-1}(r/L) \approx 4 \cdot 10^{-9}$  degrees or 0.004 microdegrees. The human eye has a resolution of about 0.02 degrees, so a telescope would have to magnify the image 5,000,000 times for us to make out the ocean. More to the point, the telescope would have to be a very large diameter so it can resolve the image limited by diffraction of light. The James Webb space telescope has a resolution of about  $2 \cdot 10^{-5}$  degrees, which is still 5000 times worse than what is needed. However, that does not mean we cannot detect oceans on a planet: water has a very specific spectroscopic signature, and if a large fraction of a planetary surface is covered with water, we will be able to tell even if the surface cannot be fully resolved. The real difficulty is suppressing the light of its sun,, which is much brighter than the reflected light from the exoplanet’s surface.



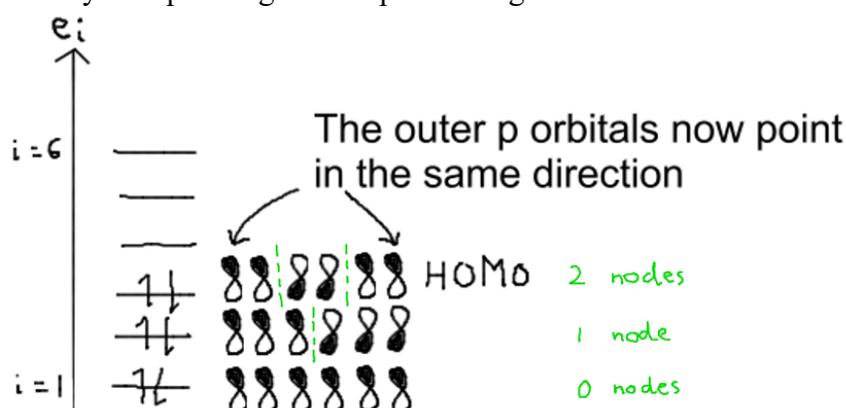
**Homework problem Q5.3:** Sketch what the functions  $\Psi_0 + \Psi_1$  and  $\Psi_0 - \Psi_1$  based on the above figure look like. If the splitting is  $\Delta E=2 \cdot 10^{-23}$  J, use the uncertainty principle to estimate how long the time  $\Delta t$  is for ammonia to ‘tunnel’ from one side of the potential energy barrier to the other.

**Solution:** The sketch on the right above shows the sum and difference between  $\Psi_0$  and  $\Psi_1$ , drawn next to each other because they have the same average energy: the left and right wells look the same. Note that these new wavefunctions are much more ‘classical’ than the eigenstates of ammonia: one is a hump on the left side of the barrier, the other is a hump on the right side of the barrier. So one corresponds to the hydrogen atoms pointing down only, and the other to them pointing up only. No Schrödinger’s cat! But if ammonia is in its lowest energy state, then it is pointing up and down and measurements will yield both results even though the molecules is in an eigenstate!

The uncertainty principle for energy and time is  $\Delta E \Delta t = \hbar/2$ , and plugging in  $\hbar \approx 1.05 \cdot 10^{-34} \text{ Js}$  and  $\Delta E = 2 \cdot 10^{-23} \text{ J}$ , we solve for  $\Delta t \approx 2.6 \cdot 10^{-12} \text{ s}$ , or about 2.6 picoseconds. So ammonia goes about its ‘forbidden’ business very quickly, but look at it this way: a modern microprocessor runs at about 3 GHz, or the inverse is a period of 300 ps. So the electronics in your iPhone is not that far off from switching as fast as ammonia tunnels through the barrier to get from one side to the other.

**Homework problem Q5.4:** What would happen to the above reaction, if I had added two more carbons to the hexadiene, making it octatriene? To show what happens with heat vs. light, draw six energy levels (6 p orbitals for the 6 pi-bonded carbon atoms), fill with electrons and sketch what happens when the  $\pi$  orbitals at the ends twist ‘con-’ vs. ‘dis’ rotatory.

**Solution:** If you had added two more carbons, you would fill 6 electrons pairwise into the three lowest orbitals. Thus you flip the sign of the p orbital again:



So the opposite will happen: when heated, to make a ring, the outer orbitals have to rotate in opposite direction for their ‘black’ or ‘+’ lobes to overlap. Thus both  $\text{CH}_3$  groups end up on the same side, not on opposite sides.

When you apply light, you put an electron into the  $i=4$  orbital (next one up, which has 3 nodes). To show what happens, **draw its p orbitals with 3 nodes as part of your homework solution** (the exact location of nodes is actually not that important, only that there are 3 nodes), and explain why now, when light is used to start the reaction, the methyl groups are on opposite sides.

So hexatriene behaves in the opposite way as butadiene: it has  $\text{CH}_3$  groups on the same side when heated, and on opposite sides when excited by light. This kind of control allows chemists to make stereoisomers of molecules, which is very important when making drugs: drugs generally fit onto protein molecules to stop them from doing something, or ‘fix them up’ if they are faulty (e.g. a mutation) so they can do their job again. This fitting depends on the exact geometry and handedness of all the atoms in the drug molecule, just like a left-side hand has a tough time fitting into a right-side glove.

By the way, when a property depends not on exactly where things are located, but on their general arrangement in space (e.g. the 3 nodes can be after atoms 1, 2 and 3, or after atoms 1, 3 and 5, and the outer p orbitals will still point in opposite directions), mathematicians call it a ‘topological’ property. These are very powerful because they do not depend on the exact placement of things, but are much more generally valid.

**You’ve made it through the quantum homework!**