

Week 6 Worksheet

Chem 11200-2: Section 33

Feb. 15, 2022

The following might be useful

1. $c = 3 \times 10^8$ m/s
2. $h = 6.63 \times 10^{-34}$ Js
3. $1 \text{ J} = 6.242 \times 10^{18}$ eV

Problem 1: If a wavelength can be associated with every moving particle, then why are we not forcibly made aware of this property in our everyday life? Calculate the de Broglie wavelength

$$\lambda = \frac{h}{p}$$

for each of the following ‘particles’

- a) An automobile of mass 200 kg traveling at a speed of 50 mph (22 m/s)
- b) A marble of mass 10 g moving with a speed of 10 cm/s
- c) A smoke particle of diameter 100 nm and a mass of 1fg being jostled about by air molecules at room temperature ($T=300\text{K}$) (assume that the particle has the same translational kinetic energy as the thermal average of the air molecules, $KE = \frac{3}{2}k_B T$)

Problem 2: A photon of green light with a wavelength of 486 nm was emitted when an e^- in a hydrogen atom fell to the $n = 2$ level. From what higher level n did the electron fall? *Useful information* $E = -2.18 \times 10^{-18} \text{ J } \frac{1}{n^2}$

Problem 3: The longest wavelength of light with enough energy to break one C-C bond is 346 nm.

1. Calculate the energy (in Joules) involved in breaking 6.02×10^{23} C-C bonds with 346 nm light.
2. When a bond like C-C is broken, what forces between the C atoms are being disrupted?
3. To completely break both bonds in one C=C double bond, must you use light of a larger or smaller wavelength than 346 nm? Why?

Problem 4:

- a) Let an electron be described by the normalized wavefunction $\Psi(\mathbf{x})$. Describe the physical interpretation of

$$|\Psi(\mathbf{x})|^2 d\mathbf{x}$$

- b) Based on your previous answer, compute what

$$\int_{\mathbb{R}} |\Psi(\mathbf{x})|^2 d\mathbf{x}$$

should be for the interpretation to make sense. *Hint: you don't actually need to do an integral.*

The following problems are written by Professor Mcleod or Head TA Miah Turke. They may mimic homework problems closely, but will be highly beneficial for the midterms and final.

Problem 5: You might find the following information useful: $m_e = 9.11 \times 10^{-31}$ kg, 1 Rydberg = 2.18×10^{-18} J

- a) Define the term “work function” and how it differs from ionization energy.
- b) Consider a hydrogen atom that undergoes a transition from a higher energy state, described by the quantum number n , to the lower energy state $n = 2$ ($6 \rightarrow 2$, $5 \rightarrow 2$, etc). The photon emitted from this electronic transition hits a solid lithium surface. What is the maximum initial quantum number required to emit a photocurrent from the lithium metal? The work function of Li is 2.93 eV.
- c) For all valid n values that generate a photocurrent from part b, calculate the maximum speed of the photoelectron from the lithium.

Problem 6: Consider an electron in a 13.5\AA 1D box, with a potential energy $V(x) = 0$ inside the box, and $V(x) = \infty$ outside ($x \leq 0$ and $x \geq 13.5\text{\AA}$)

1. Qualitatively draw the wavefunction $\psi_n(x)$ and the probability density $|\psi_n(x)|^2$ for $n = 1, 2, 3, 4, 5$.
2. How many nodes will be in $\psi_{12}(x)$? Would it be possible to find electron density at $13.5/2$ \AA ?
3. What wavelength of light (in nm) is required to excite the electron from its ground state to $n = 3$? What frequency (in Hz) does this correspond to?
4. Describe at what position in the box you would expect this transition to take place (you don't need to do a calculation, but a drawing would help your description).

The following questions go a bit beyond what would be expected of you on an exam and can be skipped. They are provided for those that are interested...

Problem 7: Having solved for the 1D infinite well potential, lets try solving for the 2D infinite well potential. Say the box is of side-length $a \times b$, that is goes from 0 to a along the x -direction and 0 to b along the y -direction. That is we want to find $\psi(x, y)$ such that

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x, y) = E\psi(x, y)$$

In general partial differential equations can be quite tricky to solve, however, a common trick is to use the ansatz that

$$\psi(x, y) = \phi(x)\eta(y)$$

This is called separation of variables. That is, ϕ only depends on x and η only depends on y .

- a) Show that using the separation of variables ansatz, we can rewrite the Schrodinger equation as

$$\frac{d\phi(x)}{dx} + \frac{d\eta(y)}{dy} = -\frac{2mE}{\hbar^2}$$

- b) Convince yourself that we must have that

$$\frac{d^2\phi(x)}{dx^2} = -A$$

and

$$\frac{d^2\eta(y)}{dy^2} = -B$$

where A, B are constants such that $A + B = \frac{2mE}{\hbar^2}$. We have therefore reduced the problem to a (relatively simple) second order ordinary differential equation!

- c) By substitution, show that

$$\begin{aligned} \phi(x) &= \alpha \sin(\sqrt{A}x) + \beta \cos(\sqrt{A}x) \\ \eta(x) &= \gamma \sin(\sqrt{B}y) + \delta \cos(\sqrt{B}y) \end{aligned}$$

satisfy the ordinary differential equations, for some constants $\alpha, \beta, \gamma, \delta$.

- d) Apply the boundary conditions to deduce that $\beta = \delta = 0$ and

$$\begin{aligned} \sqrt{A} &= \frac{n\pi}{a} \\ \sqrt{B} &= \frac{m\pi}{b} \end{aligned}$$

for $n, m = 1, 2, 3, \dots$. Show that

$$E_{n,m} = \frac{\hbar^2\pi^2}{2m} \left[\frac{n^2}{a} + \frac{m^2}{b^2} \right]$$

The wavefunction (normalized) is therefore

$$\psi(x, y) = \frac{2}{\sqrt{ab}} \sin\left(\frac{2\pi}{a}x\right) \sin\left(\frac{m\pi}{b}y\right)$$

I have taken the special case of $a = b = 1$ and plotted the first 3 energy states. Note that $E_{2,1} = E_{1,2}$ and there is degeneracy in the energies! That is 2 different physical states give the same energy (this is due to the symmetry present in the problem)

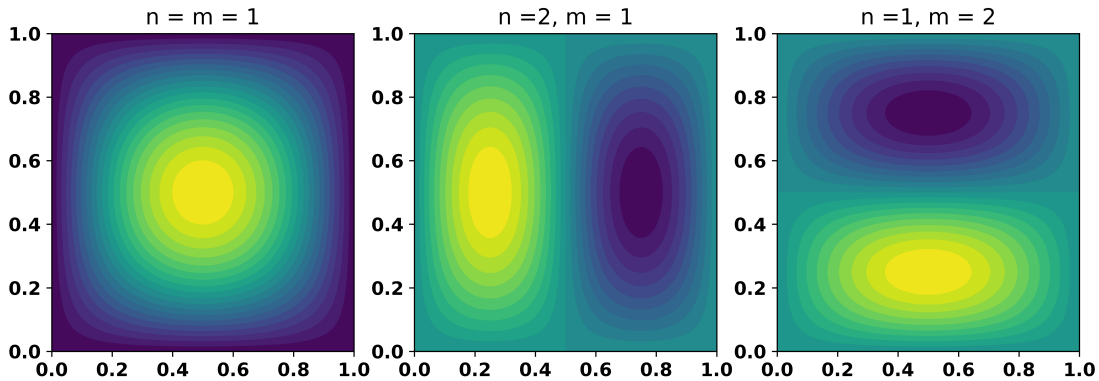


Figure 1: Wavefunctions for the particle in a 2D box. Green regions are > 0 and blue regions are < 0 . Notice the degeneracy of $n = 2, m = 1$ and $n = 1, m = 2$, as well as the nodal lines that separate the 2 regions.

Problem 8: Consider a wavefunction that behaves as follows

$$\psi(x) = \begin{cases} 0 & \text{if } x < 0 \\ 2 & \text{if } 0 \leq x \leq x' \\ 0 & \text{if } x > x' \end{cases}$$

- What is the probability density that the particle can be found at $x = x'/2$?
- Interestingly, it is sometimes useful to consider the momentum space wavefunction $\psi(p)$. Conversion state space to momentum space occurs via a Fourier transform given as

$$\psi(p) = \int_{-\infty}^{+\infty} dx \frac{1}{\sqrt{2\pi\hbar}} \exp\left\{-\frac{ip}{\hbar}x\right\} \psi(x)$$

Find the momentum space wavefunction $\psi(p)$ for the wavefunction given above.

- From what you know, give a physical interpretation of

$$|\psi(p)|^2 dp$$

Problem 9: *A bit of Quantum Dynamics...* Time evolution in quantum mechanics is governed by the unitary operator $U(t, t_0)$ which satisfies the partial differential equation

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = HU(t, t_0)$$

For time-independent hamiltonians, we can solve this exactly and find that

$$U(t, t_0) = e^{-\frac{i}{\hbar}H(t-t_0)}$$

In general if we know the state of the system at time t_0 is $\Psi(x, t_0)$, then we can determine what it will be at some later time $t > t_0$ by

$$\Psi(x, t) = U(t, t_0)\Psi(x, t_0)$$

- a) Write the power series expression for $e^{\lambda x}$ where λ is a constant.
- b) What is $\frac{d}{dx}e^{\lambda x}$? Show how this is true by differentiating the power series term by term. *In this case, we are able to differentiate term by term since the power series expansion of $e^{\lambda x}$ is uniformly convergent everywhere.*
- c) Verify that U given above satisfied the differential equation when H has no time dependence. *Hint: expand U in a power series and differentiate term by term.*
- d) Suppose that $\psi_n(x, t_0)$ is an energy eigenstate of H with energy E_n . Show that the state at some later time, t , is the same, but has only rotated with some complex phase. More precisely, show that

$$\psi_n(x, t) = e^{-\frac{i}{\hbar}E_n(t-t_0)}\psi_n(x, t_0)$$

- e) Show that

$$|\psi_n(x, t)|^2 = |\psi_n(x, t_0)|^2$$

- f) Recalling the probabilistic interpretation of $\psi(x, t)$, can you give a physical justification for why $|\psi_n(x, t)|^2 = |\psi_n(x, t_0)|^2$. *Hint: what would be the implications if $|\psi_n(x, t)| > |\psi_n(x, t_0)|$?*