Chem 442
Fall 2016

Exam 1 ANSWER KEY

1. (10 pts) **Calculate** the energy separation (in Joules) between the n = 2 and n = 3 levels of a fluorine molecule confined in a one-dimensional box of length 1 cm. The energy levels for the particle in a box are given by

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

Answer: One fluorine atom is 18.998 amu, one fluorine molecule would then be 37.996 amu. One mole, 6.626×10^{23} molecules, of fluorine molecules would be 0.037 kg implying a single fluorine molecule is 6.31×10^{-26} kg (5 pts)

$$\Delta E = \frac{(6.626 \times 10^{-34})^2}{8(6.31 \times 10^{-26})(0.01)^2}(9-4) = 4.35 \times 10^{-38}\ J$$ (5 pts)

2. (10 pts) The Lennard-Jones potential for argon is given by the formula:

$$V(r) = 502.8\left[\left(\frac{3.34}{r}\right)^{12} - \left(\frac{3.34}{r}\right)^{6}\right]$$

where r is in Ångströms. **Calculate** the force between two atoms, $F(r)=-\partial V/\partial r$. **Show** that F approaches 0 as r approaches ∞. **Does** F equal 0 at any other value of r? If so, **at what value** of r?

Answer:

$$F(r) = -\frac{\partial V}{\partial r} = -502.8\left[(-12)\left(\frac{3.34^{12}}{r^{13}}\right) - (-6)\left(\frac{3.34^{6}}{r^{7}}\right)\right] = 3016.8\left[2\left(\frac{3.34^{12}}{r^{13}}\right) - \left(\frac{3.34^{6}}{r^{7}}\right)\right]$$ (5 pts)

$\lim_{r\to\infty} 2\left(\frac{3.34^{12}}{r^{13}}\right) = 0$ and $\lim_{r\to\infty}\left(\frac{3.34^{6}}{r^{7}}\right) = 0$ implies that $\lim_{r\to\infty} F(r) = 0$ (3 pts)

$F = 0$ when $2\left(\frac{3.34^{12}}{r^{13}}\right) = \left(\frac{3.34^{6}}{r^{7}}\right)$ or $2 \cdot 3.34^6 = r^6$. Then $r = 3.34 \cdot 2^{1/6}$ Å.

at any other r value. As two argon atoms move further away, the force each exerts on the other decreases. (2 pts)

3. (15 pts) An electron has mass $m_e \approx 9.1 \times 10^{-31}$ kg.

a. Its velocity has a range of Δv = 5 m/s. What is the range of positions that will be measured?

b. In a helium atom, the range of velocities for an electron is closer to two million meters/second (2×10^6 m/s). What is the range of positions, Δx, that will be measured in meters? In Ångstroms? In nanometers?

c. How does the length in (b) compare to the Bohr radius: 5.29×10^{-11} m? What is the significance of that comparison?

Answer:
a. Starting with the Heisenberg uncertainty principle

Chem 442
Fall 2016

$$\Delta x \Delta p = \frac{\hbar}{2}, \text{ we have the relationship } \Delta x = \frac{\hbar}{2\Delta p} \text{ and } \Delta p = m_e \Delta v.$$

If $\Delta v = 5$ m/s and $m_e \approx 9.1\times10^{-31}$ kg, $\Delta p = 4.55\times10^{-30}$ kg*m/s and $\Delta x = 1.16\times10^{-5}$ m. (5 pts)

b. Same work as above, but this time $\Delta v = 2.0\times10^{6}$ m/s making $\Delta p = 1.82\times10^{-24}$ kg·m/s and $\Delta x = 2.90\times10^{-11}$ meters $= 2.90\times10^{-1}$ Å $= 2.90\times10^{-2}$ nm (5 pts)
c. The length in (b) is a little more than half (0.547 factor difference) of the Bohr radius. This suggests that the most probable size of the 1s orbital of a helium atom is smaller than that of hydrogen. (5 pts)

4. (20 pts) Consider the sound wavefunction

$$\Psi(t) = \exp[-(t/2\Delta t)^2] \exp[i\omega t]$$

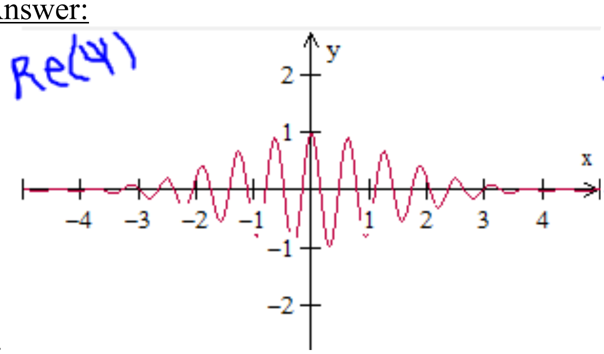
a. **Make two separate sketches** of the real and of the imaginary parts of $\Psi(t)$ where $\Delta t = 1$ s and $\omega = 10$ s^{-1}, from $t = -5$ to 5 s. Remember even/oddness of the sin and cos functions.

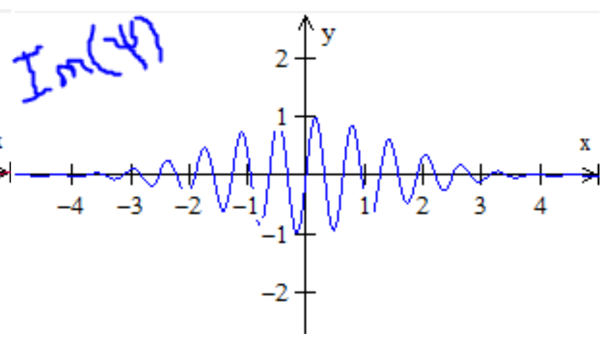
b. Consider only the real part of Ψ(t), and **create another sketch** of what would happen if Δt was increased to 2 s.

c. Now **sketch** what would happen to the real part if Δt remains 1 s, but the frequency is inreased to $\omega = 20$ s^{-1}.

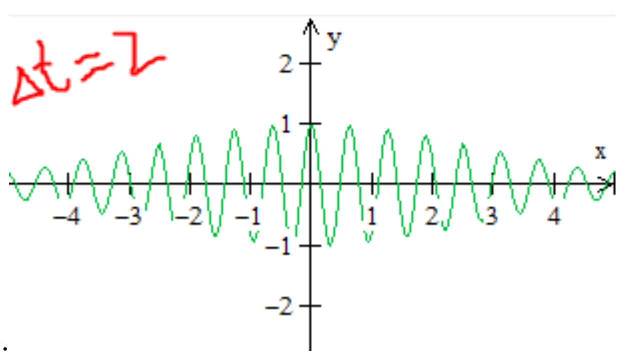
d. **Does** taking the complex conjugate of Ψ(t) change either of your sketches from part (a)? If so, **how**? (You can state the answer in words – no sketch required.)

Answer:



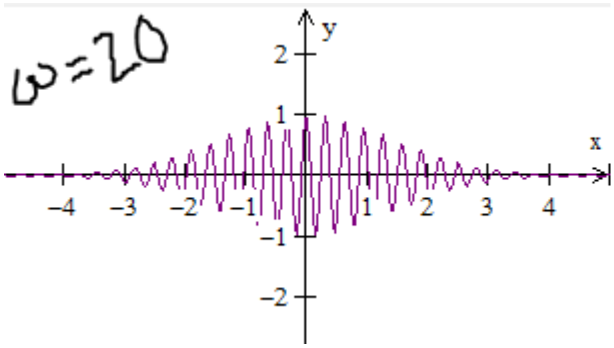


a.
(5 pts)



b. (5 pts)

Chem 442
Fall 2016

c. 

(5 pts)

d. Taking the complex conjugate of the wavefunction only changes the imaginary part. The imaginary part of the wavefunction is now negated (sin(x) → -sin(x)). (5 pts)

5. (20 pts) Let a quantum particle be in state $\Psi(x,t)$. In this question, we will use postulate 4 to show step-by-step that the average value $\langle A\rangle = \bar{A}$ of observable A is given by

$$\bar{A} = \int_{-\infty}^{\infty} dx \Psi^*(x,t)\hat{A}\Psi(x,t),$$

where $\hat{A}$ is the operator for observable A.

a. Recall from the $ bills homework that $\bar{A} = \Sigma a_n P(A = a_n)$, and from postulate 4 that $P(A = a_n) = \left|\int_{-\infty}^{\infty} dx \varphi_n^*(x)\Psi(x,t)\right|^2$. **Combine these two equations** to write an expression for $\bar{A}$ in terms of the eigenvalues and eigenfunctions of $\hat{A}$.

b. Now **write down** the same expression for $\bar{A}$, but multiply out the $|\ |^2$ square modulus containing the integral explicitly. Something like

$$\int_{-\infty}^{\infty} dx \Psi^*(x,t)\varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x')\Psi(x',t)$$

should appear in your expression (the integral times its complex conjugate). It's always a good idea to give your integration variables <u>different</u> names (here x and x') when you have several integrals in an expression!

c. Your expression for $\bar{A}$ has an "a_n" outside the first integral. You can stick it inside the integral in front of $\varphi_n(x)$, and play the reverse of a trick we have done in class several times: since $\hat{A}\varphi_n(x) = a_n\varphi_n(x)$, you can replace "$a_n$" **by what** in the integral? **Write down** the formula for $\bar{A}$ again.

d. Remember that any function can be expanded as a linear combination of a complete set of functions. For example, $\Psi(x,t) = \Sigma c_m\, \varphi_n(x)$, where $c_m = \int_{-\infty}^{\infty} dx' \varphi_n^*(x')\Psi(x',t)$ is the "overlap integral" between φ_n and Ψ. Look at your expression from c., and you should be able to **replace one of the integrals** by c_m, and then **do the sum** $\Sigma c_m\, \varphi_n(x)$, which equals $\Psi(x,t)$**.** If all went right, you should now have the expression

$$\bar{A} = \int_{-\infty}^{\infty} dx \Psi^*(x,t)\hat{A}\Psi(x,t)$$

that you were supposed to prove. Congrats, in 1926 you would have won a Nobel Prize!

Chem 442
Fall 2016

Answer:

a. (5 pts)

$$\bar{A} = \sum_n a_n \left| \int_{-\infty}^{\infty} dx \varphi_n^*(x) \Psi(x,t) \right|^2$$

b. (5 pts)

$$\bar{A} = \sum_n a_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

c. (5 pts)

$$\bar{A} = \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) a_n \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$
$$= \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{A} \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$

d. (5 pts)

$$\bar{A} = \sum_n \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{A} \varphi_n(x) \int_{-\infty}^{\infty} dx' \varphi_n^*(x') \Psi(x',t)$$
$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{A} \sum_n \varphi_n(x) \cdot c_n = \int_{-\infty}^{\infty} dx \Psi^*(x,t) \hat{A} \Psi(x,t)$$