Chem 442
Fall 2016

Exam 1

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

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

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?

3. (15 pts) An electron has mass $m_e \approx 9.1\times10^{-31}$ kg.

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

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 **Ångstrons**? 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?

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 Ψ(t) where Δt = 1 s and ω = 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 ω = 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.)

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!

<u>Useful numbers:</u>
1 atomic mass unit = 1.66×10^{-27} kg
Fluorine atom mass: 18..998 amu
Planck's constant = 6.626×10^{-34} Js
1 m = 100 cm