Physical Chemistry Cumulative Exam Nov. 7, 2019

Don't Panic

Electrons! (20%)

1. This doesn't get more simple- let's say that the universe *only* consists of an electron at rest, i.e. kinetic energy (K.E.) = 0 J and momentum (p) = 0 kg·m/s, and a 500 nm photon. (Equations and constants are provided on the last page!)

a) What is the energy of the 500 nm photon?
b) What is the electron's kinetic energy if it absorbs the photon?
c) What is the electron's momentum after absorbing the photon?
d) What is the momentum of a 500 nm photon?

2. A free electron in space cannot absorb light. Why not? Hint: look at your answers to questions 1 c & d.

Hydrogen Atom Wavefunctions! (35%)

3. The hydrogen atom's Hamiltonian is:

$$\frac{-\hbar^2}{2\cdot\mathrm{mass}}\left\{\frac{1}{\mathrm{r}}\frac{\partial^2}{\partial \mathrm{r}^2}\mathrm{r}+\frac{1}{\mathrm{r}^2}\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right)\right\}-\frac{\mathrm{e}^2}{4\pi\mathcal{E}_0\mathrm{r}}$$

There are three "mini-Hamiltonians" that depend on different variable (r,ϕ,θ) that you can derive using the separability property of the Schrodinger equation. They are:

(1) $\frac{1}{\Psi(\phi)}\frac{\partial^2}{\partial\phi^2}\Psi(\phi)$, (2) $\frac{1}{\Psi(\theta)}\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\Psi(\theta)-\mathrm{m}^2$,

and: (3) $\frac{1}{\Psi(\mathrm{r})}\frac{-\hbar^2}{2\cdot\mathrm{mass}}\frac{1}{\mathrm{r}}\frac{\partial^2}{\partial\mathrm{r}^2}\mathrm{r}\cdot\Psi(\mathrm{r})+\frac{\hbar^2 l(l+1)}{2\cdot\mathrm{mass}\cdot\mathrm{r}^2}-\frac{\mathrm{e}^2}{4\pi\mathcal{E}_0\mathrm{r}}$

a) Which ones (1, 2 or 3) generate quantum numbers m, l and n? Big hint: they aren't the ones with m, l, or n in them.
b) What is m? How does m manifest itself in a hydrogen atom's wavefunction?
c) What is l? Can you describe l=0 vs. l=1 or l=2?
d) What does the n quantum number describe? Can you perhaps use the periodic table to answer this question?
e) Which of the "mini-Hamiltonians" actually determines the energy of the hydrogen atom?

4. Let's say that we can separate the electron's spin wavefunction from the spatial wavefunction as so: $\Psi(\mathrm{r},\phi,\theta)|\alpha\rangle$, where Ψ represents the spatial location of the electron and $|\alpha\rangle$ is for "spin-up" (and $|\beta\rangle$ is for spin down).

a) What is the mathematical behavior of spin wavefunctions? For example, I know $\Psi(\mathrm{r}, \phi, \theta)$ for the 2p$_z$ state of hydrogen is $\sim N \cdot \mathrm{r} \cdot \mathrm{e}^{-\mathrm{r}/\mathrm{a}_0} \cdot \cos(\theta)$. Can you mathematically express a spin wavefunction such as $\langle \mathrm{x}|\alpha\rangle$ in the same way?

b) Please evaluate the following:

1) $\langle\alpha|\alpha\rangle$ 2) $\langle\beta|\beta\rangle$ 3) $\langle\alpha|\beta\rangle$ 4) $\langle\beta|\alpha\rangle$

c) Calculate the expectation value of the spin operator $\hat{\mathbf{S}}$:

1) $\langle\alpha| \cdot \hat{S}_Z \cdot |\alpha\rangle$ 2) $\langle\alpha| \cdot \hat{S}_Z \cdot |\beta\rangle$ (obviously show your work!)

5. Electrons are magnetic, this is the basis of EPR spectroscopy. Nuclei may be magnetic, this is the basis of NMR. Now, tell me what is responsible for refrigerator magnets (electrons or protons, and please justify your answer).

Spin and Symmetry! (35%)

6. Do electrons follow Fermi or Bose statistics in terms of their occupancy of electronic states and why (and describe what Fermi and Bose statistics are as well for full credit)?

7. Since electrons can't be in the same state at the same time, they have to be ***antisymmetric to interchange***. This means that you can't say the wavefunction of a 1s^2 state of the hydrogen anion is: $\Psi_{1s}(1)\alpha(1) \cdot \Psi_{1s}(2)\beta(2)$ because:

$$\Psi_{1s}(1)\alpha(1) \cdot \Psi_{1s}(2)\beta(2) = \Psi_{1s}(2)\alpha(2) \cdot \Psi_{1s}(1)\beta(1)$$

However, you can use this: $\Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$ because:

$$\Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} = -\Psi_{1s}(2)\Psi_{1s}(1)\{\alpha(2)\beta(1) - \alpha(1)\beta(2)\}$$

It turns out that you should actually write it as:

$$\{\Psi_{1s}(1)\Psi_{1s}(2) + \Psi_{1s}(2)\Psi_{1s}(1)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

(the "space" part is the sum of the wavefunctions with the electrons interchanged)
This isn't necessary for the proper anti-symmetry with respect to interchange. Thus, why are we doing this to the space wavefunctions?

8. Now when I Googled the possible wavefunctions for the hydrogen anion in the 2p^2 state, I found four answers! They are:

$$\{\Psi_{2p}(1)\Psi_{2p}(2) + \Psi_{2p}(2)\Psi_{2p}(1)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

$$\{\Psi_{2p}(1)\Psi_{2p}(2) - \Psi_{2p}(2)\Psi_{2p}(1)\}\{\alpha(1)\alpha(2)\}$$

$$\{\Psi_{2p}(1)\Psi_{2p}(2) - \Psi_{2p}(2)\Psi_{2p}(1)\}\{\beta(1)\beta(2)\}$$

$$\{\Psi_{2p}(1)\Psi_{2p}(2) - \Psi_{2p}(2)\Psi_{2p}(1)\}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$$

Why are there four wavefunctions and not just one?

9. It turns out that the antisymmetry with respect to interchange prevents you from creating a wavefunction with two electrons in the same state. To convince yourself, show me what happens if you take the singlet wavefunction of the 1s^2 hydrogen anion:

$$\{\Psi_{1s}(1)\Psi_{1s}(2) + \Psi_{1s}(2)\Psi_{1s}(1)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

and make the two electrons spin-up (α). What do you get?

10. Fermionic particles must have total wavefunctions that are antisymmetric with respect to interchange of the particles' coordinates; how does this lead to exchange energy? Can you name a physical phenomenon described by exchange?

Safety! Answer just two! (10%)

11. **a**. What is a Chemical Hygiene Plan? **b**. Do you know where your lab's chemical hygiene plan is? (yes or no only!)
12. What is an MSDS?
13. Which is more dangerous, a class I or a class IV laser and why?
14. Describe the difference between energy and power.
15. Which blinds you, the energy of a laser's pulse or the power of that same laser pulse?

This is all you need for the test.

Conservation Laws of Nature: 1) The speed of light is constant. 2) The mass-energy of the universe is constant. 3) Linear momentum is conserved. 4) Angular momentum is conserved.

Joule (J) = $kg \cdot m^2/s^2$
Speed of light (c) = 3.0×10^{8} m/s
Plank's constant (h) = 6.626×10^{-34} J·s
$h/2\pi$ ($\hbar$) = 1.05×10^{-34} J·s
electron mass = 9.11×10^{-31} kg
proton mass = 1.67×10^{-27} kg
neutron mass = 1.67×10^{-27} kg
photon mass = 0.00 kg
photon momentum = h/λ
photon energy = $h\nu = h\cdot c/\lambda$
frequency of light (ν) = c/λ

Gyromagentic ratios ($rad\cdot s^{-1}\cdot T^{-1}$):
electron: 1.76×10^{11}
proton: 2.68×10^{8}
neutron: -1.83×10^{8}

General Equations:
Kinetic energy (K. E.) = ½ $m\cdot v^2$
Fermion Wavefunction: $\Psi_1(1)\Psi_2(2) = -\Psi_1(2)\Psi_2(1)$
Momentum (p) = $m\cdot v$
Boson Wavefunction: $\Psi_1(1)\Psi_2(2) = \Psi_1(2)\Psi_2(1)$
Spin operator $\hat{S}^2|\alpha,\beta\rangle = \hbar^2 \cdot s(s+1)|\alpha,\beta\rangle$ $\hat{S}_Z|\alpha\rangle = 0.5\hbar|\alpha\rangle$ $\hat{S}_Z|\beta\rangle = -0.5\hbar|\beta\rangle$
$\int \alpha\cdot\alpha = 1$ $\int \alpha\cdot\beta = 0$

Picture of a pig wearing boots:
(because this is *important*)