Physical Chemistry Cumulative Examination

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1. (60 pts) For this problem you must show your work. For full credit you must get the right answers by valid methods The H atom wavefunctions, $\psi_{n,l,m}(r,\theta,\varphi)$, can be factored into a radial part, $R_{n,l}(r)$, and an angular part, $Y_{l,m}(\theta,\varphi)$, also known as a spherical harmonic. For n = 4, there are sixteen different wavefunctions for the H atom: 4s, $4p_{-1}$, $4p_0$, $4p_{+1}$, $4d_{-2}$, $4d_{-1}$, $4d_0$, $4d_{+1}$, $4d_{+2}$, $4f_{-3}$, $4f_{-2}$, $4f_{-1}$, $4f_0$, $4f_{+1}$, $4f_{+2}$, and $4f_{+3}$ (Tables of the $R_{n,l}(r)$ and $Y_{l,m}(\theta,\varphi)$ functions are attached). Explicit forms for the $\psi_{n,l,m}(r,\theta,\varphi)$ functions can be obtained by combining the appropriate radial functions with the appropriate spherical harmonic. This problem concerns the rms (root mean square) distance of the electron from the nucleus, $\{\langle r^2\rangle\}^{1/2}$, for an electron in one of the sixteen n = 4 orbitals.

   a)(15 pts) Choose one of the sixteen n = 4 functions. Without doing any calculations and based on qualitative reasoning only, indicate if $\{\langle r^2\rangle\}^{½}$ for the orbital you chose will be less than, greater than, or equal to $\langle r\rangle$ for that orbital. Briefly explain your reasoning.

   b)(30 pts) For the orbital you chose in part a, calculate the rms distance of the electron from the nucleus, $\{\langle r^2\rangle\}^{1/2}$. Your answer should equal: (unitless number)(a_0), Hint: pick the function for which the integration is easiest. The only integration formula you should need is given below.

   c) (15 pts) For the function you chose in parts a) and b), determine the expectation value, $\langle \ell_z \rangle$, of the z component of the orbital angular momentum. The operator is given by $\ell_z = (\hbar/i)\partial/\partial\varphi$. Clearly indicate the method you used to get your answer.

2. (40 pts) A student uses a pH meter to measure the pH of pure water at 25 °C and obtains a value of 7.00. He then heats the water to 50 °C and measures a pH of 6.63. What is ΔH^0 for the reaction

$$2H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq) \text{ ?}$$

Miscellaneous Information

$$\int_0^\infty r^n e^{-br} dr = \frac{n!}{b^{n+1}}$$

$\exp(ax) = 1+(ax)+½(ax)^2+... = \sum(1/n!)(ax)^n$

SI units: mass: kilograms (kg), distance: meters (m), time: seconds (s), energy: Joules (J)

$i = \sqrt{-1}$ c = speed of light = 2.998×10^8 ms^{-1}, h = 6.626×10^{-34} J s, k = Boltzmann's constant = 1.38×10^{-23} J K^{-1}, R= the gas constant = 8.3 J mol^{-1} K^{-1}.

<u>Hydrogen atom n = 4 wavefunctions</u>

$$R_{4,0} = \frac{1}{96 a_0^{3/2}}(24 - 36\rho + 12\rho^2 - \rho^3)e^{-\rho/2}, \ \rho = \frac{r}{2a_0}$$

$$R_{4,1} = \frac{1}{32\sqrt{15} a_0^{3/2}}(20 - 10\rho + \rho^2)\rho e^{-\rho/2}$$

$$R_{4,2} = \frac{1}{96\sqrt{5} a_0^{3/2}}(6 - \rho)\rho^2 e^{-\rho/2}$$

$$R_{4,3} = \frac{1}{96\sqrt{35} a_0^{3/2}}\rho^3 e^{-\rho/2}$$

$$Y_{3,0} = \frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$$

$$Y_{3,1} = -\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{i\phi}$$

$$Y_{3,-1} = \frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{-i\phi}$$

$$Y_{3,2} = -\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta(\cos\theta)e^{2i\phi}$$

$$Y_{3,-2} = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta(\cos\theta)e^{-2i\phi}$$

$$Y_{3,3} = -\frac{1}{8}\sqrt{\frac{35}{\pi}}(\sin^3\theta)e^{3i\phi}$$

$$Y_{3,-3} = \frac{1}{8}\sqrt{\frac{35}{\pi}}(\sin^3\theta)e^{-3i\phi}$$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,0} = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$$Y_{1,1} = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}$$

$$Y_{1,-1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi}$$

$$Y_{2,0} = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

$$Y_{2,1} = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta e^{i\phi}$$

$$Y_{2,-1} = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta e^{-i\phi}$$

$$Y_{2,2} = -\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\phi}$$

$$Y_{2,-2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{-2i\phi}$$