Chem 30324, Spring 2024, Homework 6

Due March 18, 2024

The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for stable molecule. It acts as a signaling molecule in the body, helping to regulate blood pressure, is a primary pollutant from combustion, and is a key constituent of smog. It exists in several isotopic forms, but the most common, ^{14}N=^{16}O, has a bond length of 1.15077 Å and harmonic vibrational frequency of 1904 cm^{-1}.

Spin the NO.

1. Calculate the moment of inertia of ^{14}N=^{16}O, in amu Å^2, the rotational energy constant, $B=\hbar^2/2I$, in kJ mol^{-1}, and the rotational spectral constant, $\tilde{B}=B/hc$, in cm^{-1}.

2. Imagine that the NO molecule is adsorbed flat on a surface upon which it is free to rotate. Plot out the energies of the four lowest-energy rotational quantum states, in units of $\tilde{B}$, being sure to include appropriate quantum numbers and degeneracies. Also indicate the total rotational angular moment of each state, in units of $\hbar$.

3. Whether light can induce an NO to jump from some rotational level m_l to some other one $m_l^\prime$ is determined by whether the transition dipole moment integral $\langle\psi_{m_l}\lvert x\rvert\psi_{m_l'}\rangle$ is zero or non-zero. Find the *selection rule* on Δm_l that make the integral non-zero. Recall that x can be written $r \cos\phi=r(e^{i\phi}+e^{-i\phi})/2$ in polar coordinates.

4. Use your selection rule to determine the frequencies, in wavenumbers, of the four lowest-energy rotational transitions of an ^{14}N=^{16}O adsorbed flat on a surface.

5. Use your selection rule to determine the change in angular momentum of the ^{14}N=^{16}O in each allowed transition. Compare your result to the angular momentum of a photon, $\hbar$.

5. Now imagine the NO molecule is free to rotate in three-dimensional space. As in Question 2 above, plot out the energies of the four lowest-energy rotational quantum states, in units of $\tilde{B}$, being sure to include appropriate quantum numbers and degeneracies.

6. Predict the populations of the second, third, and fourth quantum states relative to the first, at 298 K. Do you expect one or all of these states to potentially contribute to the rotational spectrum of NO?

Quantum mechanics of an H atom:

Consider an excited hydrogen atom with a 2s^1 electron configuration. The 2s radial wavefunction is given by $$R_{2,0} = \frac{1}{\sqrt{2a_0^3}}(1-\rho/2)e^{-\rho/2}, \rho = r/a_0$$ where a_0 = bohr radius. (*Hint:* It's easiest to solve the following using a_0 as the unit of length.)

6. Provide a complete set of possible quantum numbers for an electron with the 2s wavefunction.

7. Provide a hand sketch of the 3-D shape of a 2s wavefunction ("orbital"). Be sure to indicate the *sign* of the wavefunction in each region and the location(s) of nodes. How many radial and how many angular nodes does a 2s wavefunction have?

8. Plot the radial probability function $P_{20}(r) = r^2\lvert R_{2,0}(r)\rvert^2$. Be sure to label both axes appropriately. (*Hint:* Stick with a_0 as the length unit.)

9. Determine and indicate on your plot $\langle r\rangle$, the expectation value of the distance of the electron from the nucleus. (*Hint*: the course outline gives an expression for this expectation value.)

10. Determine and indicate on your plot r_{MP}, the most probable distance of the electron from the nucleus.

11. Determine and indicate on your plot the maximum classical distance of the electron from the nucleus in this orbital.

12. (*Extra credit*) What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)

13. Can a 2s electron undergo an allowed transition to a lower energy electronic state? If so, what frequency (in cm^{-1}) of light would be emitted?

Variations on the hydrogen atom:

The *variational principle* guarantees that the expectation value of the energy of a guessed wavefunction is always greater than that of the true lowest energy solution. Here you will apply the variational principle to the H atom. For this problem it is easiest to work in atomic units. In these units, $\hbar$, a_0, and $4\pi\epsilon_0$ are all equal to 1 and the unit of energy is the Hartree, equivalent to 27.212 eV. In atomic units the H atom Schrödinger equation is written:

$$\left \{-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr}-\frac{1}{r}+\frac{l(l+1)}{2r^2} \right \}R(r) = ER(r)$$

14. Suppose in a fit of panic you forget the 1s radial function when asked on an exam. Not wanting to leave the answer blank, you decide to guess something, and liking bell-shaped curves, you guess $R_{10}(r) = e^{-r^2}$. Normalize this guess. Do not forget to include the r^2 Jacobian integration factor.

15. Calculate the expectation value of the energy of your normalized guess. Is it greater or less than the true value?

16. What does the variational principle say about the expectation value of the energy of your guess as you vary a parameter γ in your guess, $R_{10}=e^{-\gamma r^2}$? Suggest a strategy for determining the "best" γ.

17. (*Extra credit*) Determine the best value of γ. Show and carefully justify your work to receive credit.

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