

HW6

March 3, 2024

1 Chem 30324, Spring 2024, Homework 6

2 Due March 18, 2024

2.0.1 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, $^{14}\text{N}^{16}\text{O}$, has a bond length of 1.15077 Å and harmonic vibrational frequency of 1904 cm^{-1} .

2.1 Spin the NO.

2.1.1 1. Calculate the moment of inertia of $^{14}\text{N}^{16}\text{O}$, 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} .

2.1.2 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 momentum of each state, in units of \hbar .

2.1.3 3. Whether light can induce an NO to jump from some rotational level m_l to some other one m'_l is determined by whether the transition dipole moment integral $\langle \psi_{m_l} | x | \psi_{m'_l} \rangle$ 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.

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

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

2.2 Quantum mechanics of an H atom:

2.2.1 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 $a_0 = \text{bohr radius}$. (*Hint:* It's easiest to solve the following using a_0 as the unit of length.)

- 2.2.2 6. Provide a complete set of possible quantum numbers for an electron with the 2s wavefunction.
- 2.2.3 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?
- 2.2.4 8. Plot the radial probability function $P_{20}(r) = r^2 |R_{2,0}(r)|^2$. Be sure to label both axes appropriately. (*Hint:* Stick with a_0 as the length unit.)
- 2.2.5 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.)
- 2.2.6 10. Determine and indicate on your plot r_{MP} , the most probable distance of the electron from the nucleus.
- 2.2.7 11. Determine and indicate on your plot the maximum classical distance of the electron from the nucleus in this orbital.
- 2.2.8 12. (*Extra credit*) What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)
- 2.2.9 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?

2.3 Variations on the hydrogen atom:

- 2.3.1 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:

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

- 2.3.2 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.
- 2.3.3 15. Calculate the expectation value of the energy of your normalized guess. Is it greater or less than the true value?
- 2.3.4 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 .
- 2.3.5 17. (*Extra credit*) Determine the best value of γ . Show and carefully justify your work to receive credit.

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