Chem 30324, Spring 2020, Homework 6

Due March 4, 2020

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}.

```
In [0]: import numpy as np
        N = 14.0067   # amu
        O = 15.999   # amu
        mu = N*O/(N+O)   # amu
        r = 1.15077   # bond length (angstrom)
        h = 6.62607E-34   # J*s
        hbar = 1.05457E-34   # J*s
        NA = 6.02214E23 #molecules/mol
        c = 299792458   # m/s

        I = mu*r**2 #amu * anstrom^2
        print('The moment of inertia is',round(I,2),'amu*angstrom^2.')

        B = hbar**2/2/I*6.022e26*(1e10)**2*NA/1000 #kJ/mol
        print('The rotational energy constant is', round(B,5),' kJ/mol.')

        Btilde = B/h/c*1000/NA/100 #1/cm
        print('The rotational spectral constant is', round(Btilde,3),' cm^-1.')
```

```
The moment of inertia is 9.89 amu*angstrom^2.
The rotational energy constant is 0.02039  kJ/mol.
The rotational spectral constant is 1.704  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 $\hbar$.

Since we are looking at a molecule adsorbed flat on a surface, we will use the 2-D rigid rotor model.

$$E_{ml} = \frac{\hbar^2}{2I} m_l^2$$

The four lowest-energy rotational quantum states are: $m_l = \pm0, \pm1, \pm2, \pm3$

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 $r \cos \phi$ in polar coordinates.

Wave Function for 2-D rotor model: $\Psi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im_l\phi}, m_l = 0, \pm1, \pm2, etc$

Transition dipole moment integral: $< \psi_{m_l} | x | \psi_{m_l'} > = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im_l\phi} x e^{-im_l'\phi} = \frac{r}{2\pi} \int_0^{2\pi} e^{i\Delta m_l\phi} d\phi$

$cos\phi = \frac{1}{2}(e^{-i\phi} + e^{\phi})$

$< \psi_{m_l} | x | \psi_{m_l'} > = \int_0^{2\pi} \frac{r}{4\pi} e^{i(\Delta m_l - 1)\phi} e^{i(\Delta m_l + 1)\phi} d\phi$

For an integer n, we can have $\int_0^{2\pi} e^{ni\phi} d\phi \neq 0$ when n = 0

We can have $< \psi_{m_l} | x | \psi_{m_l'} > \neq 0$ only when $\Delta m_l = \pm1$

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.

$$\Delta E_{m_{l0} \to m_{l1}} = B$$

$$\Delta E_{m_{l1} \to m_{l2}} = 3B$$

$$\Delta E_{m_{l2} \to m_{l3}} = 5B$$

$$\Delta E_{m_{l3} \to m_{l4}} = 7B$$

Wavenumber

$$\tilde{v}_{m_{l0} \to m_{l1}} = \frac{B}{hc}$$

$$\tilde{v}_{m_{l1} \to m_{l2}} = \frac{3B}{hc}$$

$$\tilde{v}_{m_{l2} \to m_{l3}} = \frac{5B}{hc}$$

$$\tilde{v}_{m_{l3} \to m_{l4}} = \frac{7B}{hc}$$

```
In [0]: print('From problem 1, we know that B =',round(B,5), 'kJ/mol.')
        h = 6.62607E-34  # J*s
        c = 299792458  # m/s
        NA = 6.02214E23 #molecules/mol

        v = []
        for l in [1,3,5,7]:
          v.append(B*l/h/c*1000/100/NA)

        print('0 to 1:',round(v[0],3),'cm^-1')
        print('1 to 2:',round(v[1],3),'cm^-1')
        print('2 to 3:',round(v[2],3),'cm^-1')
        print('3 to 4:',round(v[3],3),'cm^-1')
```

```
From problem 1, we know that B = 0.02039 kJ/mol.
0 to 1: 1.704 cm^-1
1 to 2: 5.113 cm^-1
2 to 3: 8.522 cm^-1
3 to 4: 11.931 cm^-1
```

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, $\hbar$.

Absolute change in angular momentum $|\Delta l_z| = \hbar$, identical to angular momentum of a photon.

NO flips

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 relative populations of the first four rotational quantum states at 298 K. Do you expect one or all of these states to potentially contribute to the rotational spectrum of NO?

```python
In [0]:  import numpy as np

         kB = 1.3806e-23 #J/K
         T = 298 #K

         P = []
         for i in [0,1,2,3]:
             p = (2*i+1)*np.exp(-B*i*(i+1)/kB/T*1000/6.022e23)
             P.append(p)

         total = np.sum(P)
         print('When l = 0, relative population =',round(P[0]/total,4))
         print('When l = 1, relative population =',round(P[1]/total,4))
         print('When l = 2, relative population =',round(P[2]/total,4))
         print('When l = 3, relative population =',round(P[3]/total,4))

         print('At 298 K, all of these states potentially contribute to the rotat
         ional spectrum of NO.')
```

```
When l = 0, relative population = 0.0664
When l = 1, relative population = 0.1961
When l = 2, relative population = 0.3162
When l = 3, relative population = 0.4213
At 298 K, all of these states 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.)

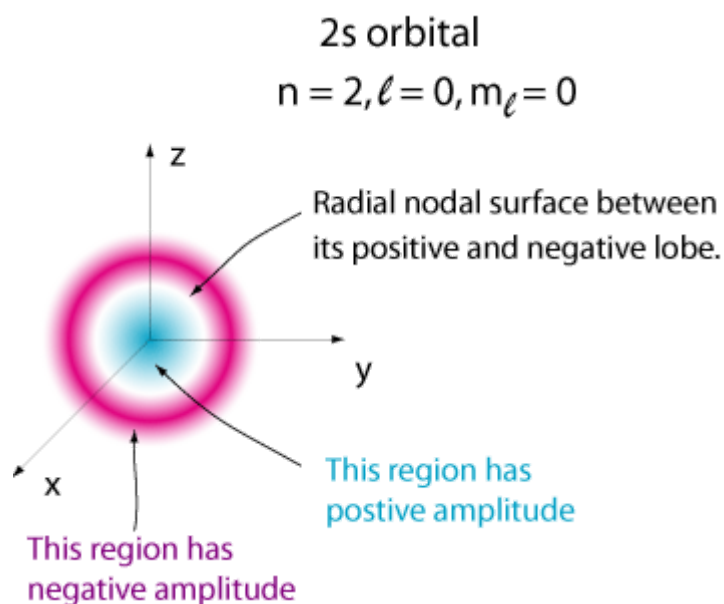## 7. Provide a complete set of possible quantum numbers for an electron with the 2s wavefunction.

Principle Quantum Number: $n = 2$

Angular Quantum Number: $m_\ell = 0$

Azimuthal Quantum Number: $\ell = 0$

Spin Quantum Number: $m_s = \pm 1/2$

8. 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?


2s orbital
$n = 2, \ell = 0, m_\ell = 0$

Radial nodal surface between its positive and negative lobe.

This region has postive amplitude

This region has negative amplitude

9. 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.)

$P_{20}(r) = r^2|R_{2,0}(r)|^2 = \rho^2 a_0^2 [\frac{1}{\sqrt{2a_0^3}}(1 - \rho/2)e^{-\rho/2}]^2 = \frac{\rho^2}{2}(1 - \rho/2)^2 e^{-\rho}\frac{1}{a_0}$. Plot $\frac{\rho^2}{2}(1 - \rho/2)^2 e^{-\rho}$ vs ρ, the

unit of P is $\frac{1}{a_0}$.

```
In [0]:  import numpy as np
         import matplotlib.pyplot as plt

         rho = np.linspace(0,16,100)
         a = 1
         R20 = 1/(np.sqrt(2*a**3))*(1-rho/2)*np.exp(-rho/2)
         P20 = a**2*rho**2*R20**2

         plt.plot(rho,P20)
         plt.xlabel('Length Ratio ($r/a_0$)')
         plt.ylabel('Probability ($1/a_0$)')
         plt.axvline(x = 6, color = 'r', linestyle = '--', label = 'Expected')
         plt.axvline(x = 3 + np.sqrt(5), color = 'g', linestyle = '--', label =
         'Most Probable')
         plt.axvline(x = 8, color = 'k', linestyle = '--', label = 'Classical Lim
         it')
         plt.legend()
         plt.show()
```
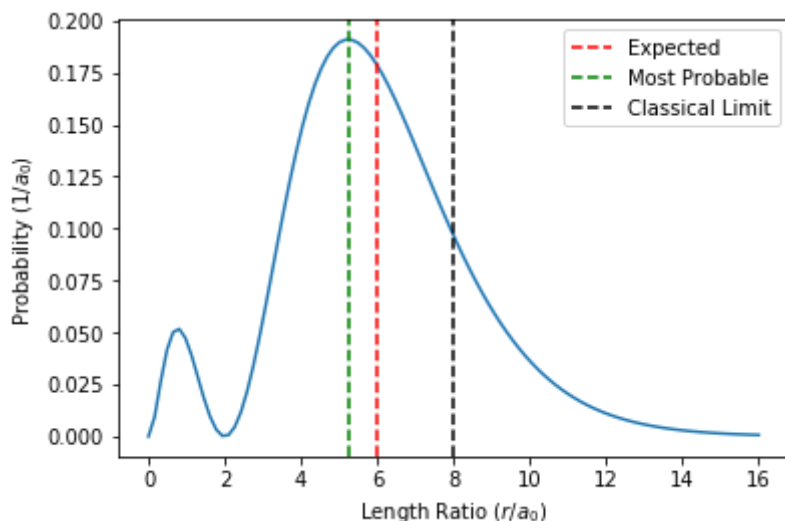

10. Determine and indicate on your plot $\langle r \rangle$, the expectation value of the distance of the electron from the nucleus.

$\langle r \rangle = \int_0^\infty rP_{20}dr = \int_0^\infty \frac{\rho^3}{2}(1 - \rho/2)^2 e^{-\rho} dr = a_0 \int_0^\infty \frac{\rho^3}{2}(1 - \rho/2)^2 e^{-\rho} d\rho$

```
In [0]: from sympy import *
        rho = symbols('rho')
        I = integrate(rho**3/2*(1-rho/2)**2*exp(-rho),(rho,0,oo))
        print('The expectation value of the distance of the electron from the nu
        cleus is',I,"* a0.")
```

```
The expectation value of the distance of the electron from the nucleus
is 6 * a0.
```

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

```
In [0]: print("Possible solutions are ", solve(diff(rho**2/2*(1-rho/2)**2*exp(-r
        ho),rho),rho))
        print('Comparing these solutions, the universal maximum occurs at sqrt
        (5) + 3')
```

```
Possible solutions are  [0, 2, -sqrt(5) + 3, sqrt(5) + 3]
Comparing these solutions, the universal maximum occurs at sqrt(5) + 3
```

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

Classical theory states that orbitals energy must equals to Coulombic energy:

$$-\frac{\hbar^2}{2m_e a_o^2}\frac{1}{N^2} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, where \quad N = 2 \quad and \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

$$r_{max,classic} = 8a_0$$

13. What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)

```
In [0]: rho_ = symbols('rho_')
        I = integrate(rho_**2/2*(1-rho_/2)**2*exp(-rho_),(rho_,8,oo)) #intrgrate
        from 8 to infinity
        print("Prob = %f"%I)
```

```
Prob = 0.185511
```

14. 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?

NO! Quantum number (n, l, m_l) of 2s = 2,0,0 while 1s = 1,0,0. Since $\Delta l \neq \pm 1$, the transition is not allowed.