Name_____   Student #_____

Quiz 10
CHEM 3PA3; Fall 2018

This quiz has 2 problems worth 50 points each. There are 10 bonus points….

1.   **(a) Sketch the occupied orbitals in the BF$_3$ molecule. (b) Write (approximate) forms for the molecular orbitals as linear combinations of atomic orbitals.** BF$_3$ is a planar molecule where the Fluorine atoms occupy the corners of an equilateral triangle and the Boron atom occupies the center of the triangle. (If you cannot figure this one out, I will give partial credit for the BH$_3$ molecule, which has the same geometry but with Hydrogens instead of Fluorines at the corners of the triangle.)

2. **(a) Write the electron configuration of the _lowest triplet excited state_ of the Nitrogen dimer, N₂. (b) Write the forms for the molecular orbitals as linear combinations of atomic orbitals.**

BONUS. The force constant for Hydrogen Chloride (with the ^{35}Cl isotope; $H^{35}Cl$) is $482 \; \frac{N}{m}$ and the equilibrium bond length is 127.46 picometers ($1.2746 \cdot 10^{-10}$ m). When the hydrogen is replaced by a tritium atom and the ^{37}Cl isotope is used (i.e., the $^{3}H^{37}Cl$ molecule) the rotational and vibrational energy levels change. Recall that 1 atomic mass unit is $1.66 \cdot 10^{-27}$ kg and that Planck's constant is $h = 6.626 \cdot 10^{-34} \, J \cdot s = 6.626 \cdot 10^{-34} \, \frac{kg \cdot m^2}{s} = 6.626 \cdot 10^{-34} \, N \cdot m \cdot s$. Now, consider the lowest allowed rotational excitation ($J = 0$ to $J = 1$) and the lowest allowed vibrational excitation ($k = 0$ to $k = 1$).

Is the rotational spectrum or the vibrational spectrum most sensitive to the changes in the isotopes in the molecule? (You do not really need to work through the problem to answer this!)
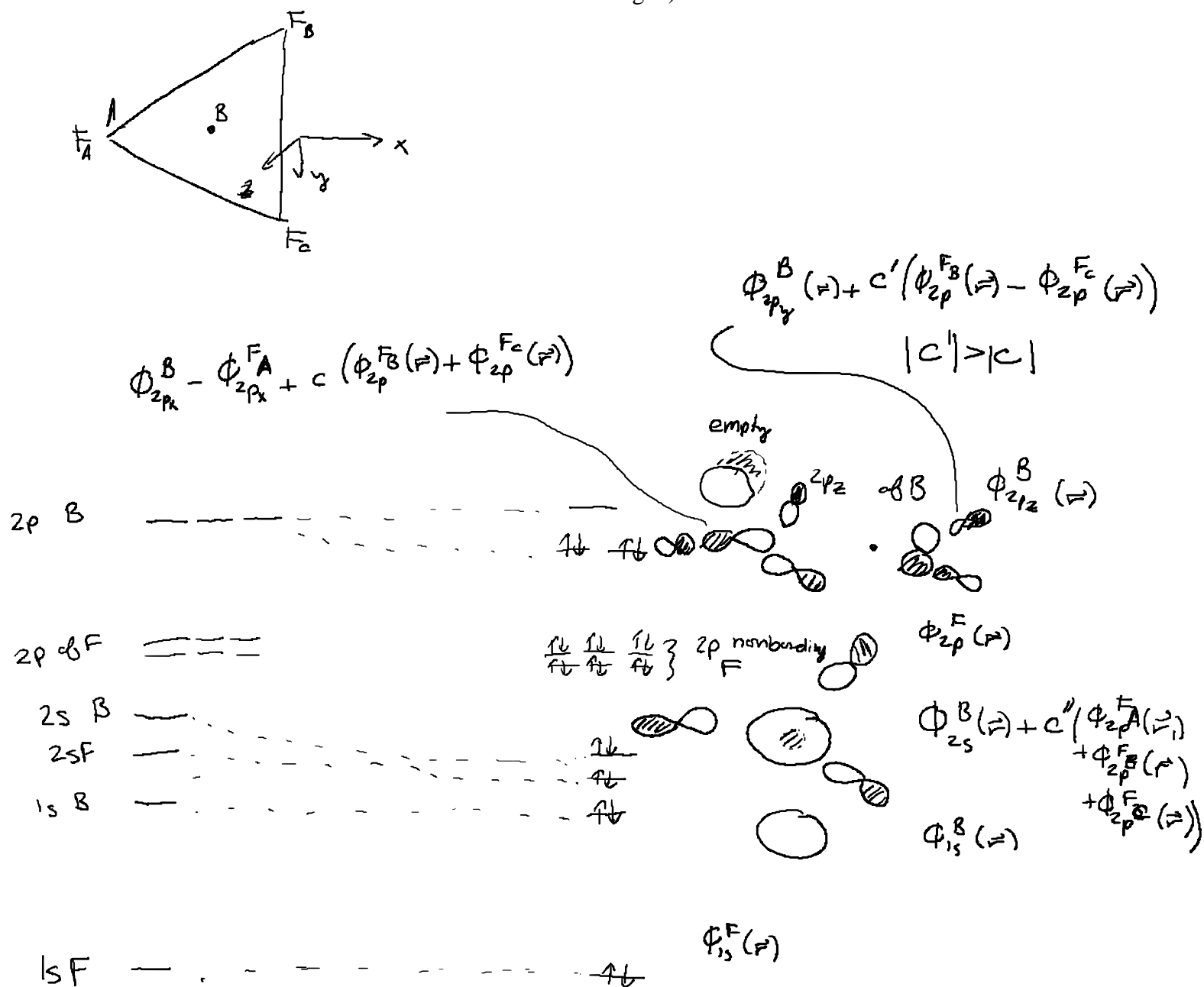   **(a) rotational spectrum**   **(b) vibrational spectrum**

Quiz 10
CHEM 3PA3; Fall 2018

This quiz has 2 problems worth 50 points each. There are 30 bonus points….

1. **(a) Sketch the occupied orbitals in the BF$_3$ molecule. (b) Write (approximate) forms for the molecular orbitals as linear combinations of atomic orbitals.** BF$_3$ is a planar molecule where the Fluorine atoms occupy the corners of an equilateral triangle and the Boron atom occupies the center of the triangle. (If you cannot figure this one out, I will give partial credit for the BH$_3$ molecule, which has the same geometry but with Hydrogens instead of Fluorines at the corners of the triangle.)

$$\phi_{2p_y}^B (\vec{r}) + c' \left(\psi_{2p}^{F_B}(\vec{r}) - \phi_{2p}^{F_C}(\vec{r}) \right)$$

$$\phi_{2p_x}^B - \phi_{2p_x}^{F_A} + c \left(\phi_{2p}^{F_B}(\vec{r}) + \phi_{2p}^{F_C}(\vec{r}) \right)$$

$$|c'| > |c|$$

empty

$2p \ \ B$

$2p \ \alpha\beta F$

$2s \ B$
$2s F$
$1s \ B$

$2p_z$ $\alpha\beta B$

$\phi_{2p_z}^B (\vec{r})$

$2p$ nonbonding F

$\phi_{2p}^F (\vec{r})$

$$\phi_{2s}^B(\vec{r}) + c'' \left(\phi_{2p}^{F_A}(\vec{r}) + \phi_{2p}^{F_B}(\vec{r}) + \phi_{2p}^{F_C}(\vec{r}) \right)$$

$$\phi_{1s}^B(\vec{r})$$

$1s F$

$$\phi_{1s}^F(\vec{r})$$

2. **(a) Write the electron configuration of the _lowest triplet excited state_ of the Nitrogen dimer, N₂. (b) Write the forms for the molecular orbitals as linear combinations of atomic orbitals.**

$$\left(1\sigma_g^+\right)^2\left(1\sigma_u^+\right)^2\left(2\sigma_g^+\right)^2\left(2\sigma_u^+\right)^2\left(3\sigma_g^+\right)^2\left(1\pi_u^+\right)^2\left(1\pi_u^-\right)^{\uparrow}\left(1\pi_g^-\right)^{\uparrow}$$

The idea here is that you would like to maximize the amount of angular momentum around the z axis for a low-lying triplet state.

$$\phi_{1\sigma_g^+}(\mathbf{r})\propto\phi_{1s}^N(\mathbf{r})+\phi_{1s}^N(\mathbf{r})$$

$$\phi_{1\sigma_u^+}(\mathbf{r})\propto\phi_{1s}^N(\mathbf{r})-\phi_{1s}^N(\mathbf{r})$$

$$\phi_{2\sigma_g^+}(\mathbf{r})\propto\phi_{2s}^N(\mathbf{r})+\phi_{2s}^N(\mathbf{r})$$

$$\phi_{2\sigma_u^+}(\mathbf{r})\propto\phi_{2s}^N(\mathbf{r})-\phi_{2s}^N(\mathbf{r})$$

$$\phi_{3\sigma_g^+}(\mathbf{r})\propto\phi_{2p_z}^N(\mathbf{r})-\phi_{2p_z}^N(\mathbf{r})$$

$$\phi_{1\pi_u^+}(\mathbf{r})\propto\phi_{2p_{+1}}^N(\mathbf{r})+\phi_{2p_{+1}}^N(\mathbf{r})\sim\phi_{2p_x}^N(\mathbf{r})+\phi_{2p_x}^N(\mathbf{r})$$

$$\phi_{1\pi_u^-}(\mathbf{r})\propto\phi_{2p_{-1}}^N(\mathbf{r})+\phi_{2p_{-1}}^N(\mathbf{r})\sim\phi_{2p_y}^N(\mathbf{r})+\phi_{2p_y}^N(\mathbf{r})$$

$$\phi_{1\pi_g^-}(\mathbf{r})\propto\phi_{2p_{-1}}^N(\mathbf{r})-\phi_{2p_{-1}}^N(\mathbf{r})\sim\phi_{2p_y}^N(\mathbf{r})-\phi_{2p_y}^N(\mathbf{r})$$

BONUS. The force constant for Hydrogen Chloride (with the ^{35}Cl isotope; H^{35}Cl) is $482\ \frac{N}{m}$ and the equilibrium bond length is 127.46 picometers ($1.2746\cdot10^{-10}$ m). When the hydrogen is replaced by a tritium atom and the ^{37}Cl isotope is used (i.e., the ^{3}H^{37}Cl molecule) the rotational and vibrational energy levels change. Recall that 1 atomic mass unit is $1.66\cdot10^{-27}$ kg and that Planck's constant is $h=6.626\cdot10^{-34}$ J·s $=6.626\cdot10^{-34}\ \frac{\text{kg·m}^2}{\text{s}}=6.626\cdot10^{-34}$ N·m·s. Now, consider the lowest allowed rotational excitation ($J=0$ to $J=1$) and the lowest allowed vibrational excitation ($n=0$ to $n=1$).
Is the rotational spectrum or the vibrational spectrum most sensitive to the changes in the isotopes in the molecule? (You do not really need to work through the problem to answer this!)

     (a) **rotational spectrum**   (b) vibrational spectrum

I will work through the problem but it isn't really necessary. At the level of the rigid-rotor harmonic oscillator approximation, the nuclear Schrödinger equation after separation of the center of mass and rewriting in spherical coordinates in terms of the internuclear distance is

$$\left(-\frac{\hbar^2}{2m_{\text{total}}}\nabla^2_{\mathbf{R}_{\substack{\text{center}\\\text{of mass}}}}-\frac{\hbar^2}{2\mu}\left(\frac{1}{u^2}\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u}\right)+\frac{\hat{L}^2}{2\mu u^2}+\frac{1}{2}k\left(u-r_e\right)^2\right)\chi\left(\mathbf{R}_{\text{c.o.m.}},u,\theta,\phi\right)=E_{\text{nuclear}}\chi\left(\mathbf{R}_{\text{c.o.m.}},u,\theta,\phi\right)$$

The center-of-mass motion is merely translation of the entire molecule and if the molecule is not confined, we safely neglect its quantum aspect. The eigenfunctions of the angular momentum squared operator are

$$\hat{L}^2Y_J^{M_J}(\theta,\phi)=\hbar^2J(J+1)Y_J^{M_J}(\theta,\phi)$$

and if we assume that the rotation of the molecule does not stretch the bond (very much) then we can safely write the harmonic oscillator Hamiltonian for a given rotational state as

$$\left(-\frac{\hbar^2}{2\mu}\left(\frac{1}{u^2}\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u}\right)+\frac{\hbar^2 J(J+1)}{2\mu r_e^2}+\frac{1}{2}k_e\left(u-r_e\right)^2\right)\chi_{\text{vib}}\left(u\right)=E_{\text{rovib}}\chi_{\text{vib}}\left(u\right)$$

The rotational energy is a constant for a given vibrational state in this approximation, so the rovibrational energy is the sum of the harmonic-oscillator energies and the rigid rotor energies,

$$E_{\text{rovib}}=\frac{\hbar^2 J(J+1)}{2\mu r_e^2}+\left(n+\tfrac{1}{2}\right)\hbar\omega \qquad\qquad J=0,1,2\ldots;n=0,1,2,\ldots$$

$$\omega=\sqrt{\frac{k}{\mu}}$$

So I have

$$E_{\text{rovib}}=\frac{\hbar^2 J(J+1)}{2\mu r_e^2}+\hbar\left(n+\tfrac{1}{2}\right)\sqrt{\frac{k_e}{\mu}} \qquad\qquad J=0,1,2\ldots;k=0,1,2,\ldots$$

Now I can tell that the rotations depend on μ^{-1} and the vibrations depend on $\mu^{-\frac{1}{2}}$. So the rotations are more sensitive to changes in mass than the vibrations.

To quantify this we can compute the actual transitions. The reduced masses in question are:

$$\mu_{{}^1\text{H}^{35}\text{H}}=\tfrac{1\cdot 35}{36}\cdot 1.66\cdot 10^{-27}\ \text{kg}=1.61\cdot 10^{-27}\text{kg}$$

$$\mu_{{}^3\text{H}^{37}\text{H}}=\tfrac{3\cdot 37}{40}\cdot 1.66\cdot 10^{-27}\ \text{kg}=4.61\cdot 10^{-27}\text{kg}$$

The lowest-energy rotational excitation has energy

$$E(J=1)-E(J=0)=\frac{\hbar^2 1\cdot 2}{2\mu r_e^2}=\frac{\hbar^2}{\mu r_e^2}$$

and the frequency associated with this transition, remembering $E=h\nu$, will be $\nu=\frac{\hbar}{2\pi\mu r_e^2}$, with the corresponding wavelength $\lambda=\frac{c}{\nu}=\frac{2\pi\mu c r_e^2}{h}$. Let's consider the ratio of absorption wavelengths for the two cases; one has (for rotation)

$$\frac{\lambda_{{}^3\text{H}^{37}\text{Cl}}}{\lambda_{{}^1\text{H}^{35}\text{Cl}}}=\frac{4.61\cdot 10^{-27}}{1.61\cdot 10^{-27}}=2.86$$

Similarly, the lowest-energy vibrational transition has energy

$$E(n=1)-E(n=0)=\hbar\omega=\hbar\sqrt{\frac{k_e}{\mu}}$$

and the frequency of the transition is $\nu=\frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}}$ and the wavelength of the transition is $\frac{2\pi c\sqrt{\mu}}{\sqrt{k_e}}$. The ratio of the absorption wavelengths in the two cases is (for vibration)

$$\frac{\lambda_{{}^3\text{H}^{37}\text{Cl}}}{\lambda_{{}^1\text{H}^{35}\text{Cl}}}=\sqrt{\frac{4.61\cdot 10^{-27}}{1.61\cdot 10^{-27}}}=1.69$$

So the wavelength (and frequencies) of absorption are less affected by the mass for vibrations than for rotations.

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