Chemistry 332 **Problem Set #3** due* Tuesday February 27, in class

*(this assignment is optional, happy Study Week)

1. In the treatment of the H_2^+ molecule ion, the expressions

$$S = e^{-R}(1+R+\frac{R^2}{3}) \qquad J = e^{-2R}(1+\frac{1}{R}) \qquad K = \frac{S}{R} - e^{-R}(1+R)$$

[12] for the overlap (S), Coulomb (J) and exchange (K) integrals were used to calculate the energy (in atomic units) as a function of internuclear distance R

$$E_+ = -\frac{1}{2} + \frac{J+K}{1+S}$$

Use this information to find **a)** the minimum value of the energy (in units of Joules)

b) the bond length (in nm)

c) the force constant of the bond (in N m^{-1})

d) the fundamental vibration frequency (in Hz).

Note: The atomic unit of energy is the Hartree, equivalent to 27.20 eV. The atomic unit of length is the Bohr radius (0.05292 nm).

Hint for part **c**: In cases where function $f(x)$ is too complicated to differentiate analytically, accurate derivatives can be evaluated numerically by using the following finite-difference formulas (and sufficiently small values of Δx).

at $x = x_i$: $$\frac{d\,f(x)}{d\,x} \cong \frac{f(x_i+\Delta x) - f(x_i-\Delta x)}{2\Delta x} \qquad \frac{d^2 f(x)}{d\,x^2} \cong \frac{f(x_i+\Delta x) - 2f(x_i) + f(x_i-\Delta x)}{(\Delta x)^2}$$

2. The **bond order** of a diatomic molecule can be defined as $(N - N^*)/2$, where N is the number of electrons in bonding molecular orbitals and N^* is the number of electrons in antibonding orbitals.

[3] Calculate the bond orders of H_2^+, N_2^+, N_2, O_2^-, O_2, and O_2^+ molecules.

3. Would you predict Mg_2 to be a stable diatomic molecule? Use molecular orbital theory to justify your

[1] answer.

Chemistry 332

1) a) Plotting E_+ against R shows that a minimum exists near $R = 2.5$. Plotting in the narrow range from $R = 2.45$ to $R = 2.55$ indicates the minimum energy:

a) $E_+ = -0.5648309923$ Hartrees (or, examine a Table of calculated E_+ values)

dissociation energy $= E_{1s} - E_+$

$$= -\frac{1}{2} - (-0.5648309923) = 0.0648309923$$

$$= (0.0648309923 \text{ Hartrees})\left(\frac{4.359744 \times 10^{-18}\,\text{J}}{\text{Hartree}}\right) = \boxed{2.8263 \times 10^{-19}\,\text{J}}$$

($170.2\ \text{kJ mol}^{-1}$)

b) the minimum energy occurs at $R = 2.4928$ au (equilibrium bond length in Bohr radii)

$$R_0 = 2.4928\,(5.29167 \times 10^{-11}\,\text{m})$$
$$= 1.3191 \times 10^{-10}\,\text{m}$$
$$= \boxed{0.13191\ \text{nm}}$$

c) $-\left.\frac{dE_+}{dR}\right|_{R_0} = 0$ zero restoring force at $R = R_0$

Hookes Law: $\text{Force} = -k(R - R_0)$

$$\frac{d\,\text{Force}}{dR} = -k = \frac{d}{dR}\left(-\frac{dE_+}{dR}\right)$$

$$k = \left.\frac{d^2E_+}{dR^2}\right|_{R_0}$$

(1 cont.)

R	E_+
2.4918	−.5648309590
2.4928	−.5648309923
2.4938	−.5648309629

using $\Delta R = 0.001$

$$\frac{d^2E_+}{dR^2} = \frac{-0.5648309590 + 2(.5648309923) - 0.5648309629}{(0.001)^2}$$

$$= 0.0627$$

R	E_+
2.4828	−.5648278091
2.4928	−.5648309923
2.5028	−.5648278917

using $\Delta R = 0.01$

$$\frac{d^2E_+}{dR^2} = 0.062838$$

smaller values of ΔR yield more accurate values of $\frac{d^2E_+}{dR^2}$ using

$$\frac{d^2E_+}{dR^2} \approx \frac{E_+(R+\Delta R) - 2E_+(R) + E(R-\Delta R)}{(\Delta R)^2}$$

use $\frac{d^2E_+}{dR^2} = 0.0627 \frac{\text{au energy}}{(\text{au length})^2}$

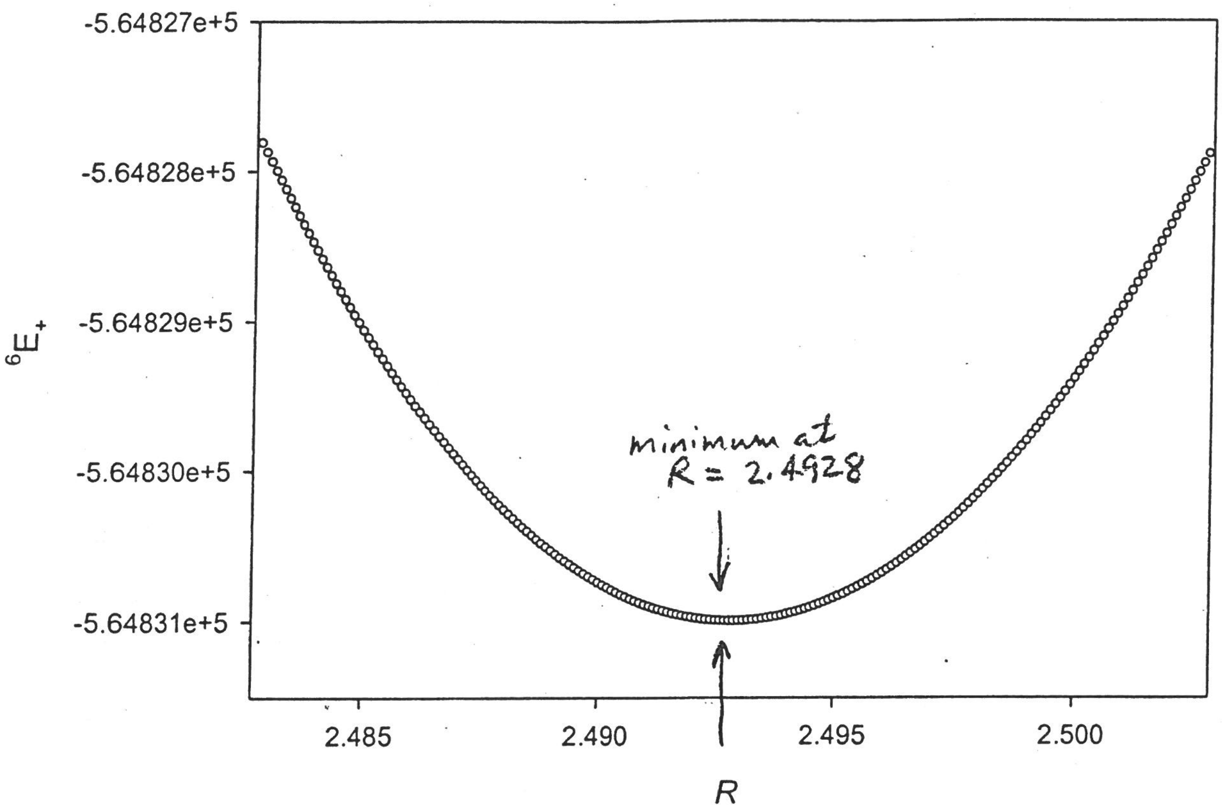
$$= 0.0627 \frac{4.35944 \times 10^{-18}\,J}{(5.29167 \times 10^{-11}\,m)^2}$$

$$\boxed{k = 97.6 \frac{N}{m}}$$

always plot calculations – in case there is an error

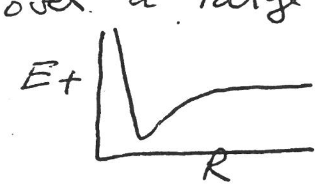
question 1 a, b

Plot of $10^6 E_+$ against R



* notice that E_+ is parabolic in R over small increments near the minimum

not parabolic over a large range of R values:



(1 cont.)

d) $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $k = \frac{m_p m_p}{m_p + m_p} = \frac{m_p}{2}$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{2k}{m_p}} = \frac{1}{2\pi}\sqrt{\frac{2(97.6)}{1.673\times10^{-27}}} = \boxed{5.436\times10^{13}\ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998\times10^{8}}{5.436\times10^{13}} = 5.514\times10^{-6}\ m$$

$$= 5514\ nm$$

(Q2) $\text{Bond Order} = \dfrac{\text{No. of electrons in bonding orbitals} - \text{No. of electrons in nonbonding orbitals}}{2}$

one electron: (H---H)

H_2^+ $(\sigma 1s)^1$ Bond Order $= \dfrac{1-0}{2} = \dfrac{1}{2}$

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zero Bond Order ... decides bond order

N_2^+ $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^1$

(13 electrons)

$\pi 2p$: $\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$

$\dfrac{4+1}{2} = 2.5$ (N≡N)

N_2 $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$

(14 electrons)

$\dfrac{4+2}{2} = 3$ (N≡N)

O_2^- $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^3$

$\dfrac{4+2-3}{2} = 1.5$ (17 electrons) (O=O)

O_2 (") $(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^2$ (O=O)

$\dfrac{4+2-2}{2} = 2$ (16 electrons)

O_2^+ (") $(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$ (O≡O)

$\dfrac{4+2-1}{2} = 2.5$ (15 electrons)

(Q3) Is Mg_2 a stable molecule?

$\left[\begin{array}{ll} \text{Mg atom} & 1s^2 2s^2 2p^6 3s^2 \\ (Z = 12) & \end{array} \right]$

Mg_2 24 electrons :

$$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4 (\sigma 2p_z)^2 (\pi^* 2p)^4 (\sigma^* 2p_z)^2 (\sigma 3s)^2 (\sigma^* 3s)^2$$

Bond Order = 0

Mg_2 is predicted to be unstable

(and is not observed spectroscopically)