Chemistry 332 **Problem Set #6** (due Monday, March 08, in class)

Q1. The ground-state energy and equilibrium bond length of H_2^+ are 2.78 eV and 0.106 nm. Use this information to calculate the percentage of the energy of H_2^+ from

[3]

i) the electron kinetic energy

ii) the proton – proton electric potential energy

iii) the electron – proton electric potential energy.

Hint: $E = -\langle T \rangle = \langle V \rangle/2$ from the virial theorem

Q2. Accurate quantum mechanical treatments give −3.42 eV for the ground-state energy (D_e) of the H_2 molecule. But the measured dissociation energy (D_0) of H_2 is 3.15 eV! Explain.
[2] *Hint*: The fundamental vibration frequency of H_2 is $1.32 \times 10^{14}\ s^{-1}$.

Q3. The dissociation energies (D_0) of H_2 and H_2^+ are 4.47 eV and 2.65 eV. Calculate the first ionization energy of H_2 (the energy required to remove one electron from a ground-state H_2
[2] molecule). *Hint*: The ionization energy of a ground-state hydrogen atom is 13.60 eV.

Q4. How many electrons are involved in σ and π bonding in:

[3] **i)** ethane **ii)** ethylene **iii)** benzene

Q5. Chemists are fond of using linear combinations of s and p atomic hydrogen orbitals to give qualitative (but very useful) descriptions of valence bonding in terms of sp, sp2 and sp3 hybrid molecular orbitals.

What gives chemists the right to do this?

[2] From CHEM 331, we know ns, np_x, np_y and np_z atomic hydrogen orbitals with principal quantum number n are degenerate (*i.e.*, have the same energy E_n). Show that any hybrid wave function

$$\psi = c_1 ns + c_2 np_x + c_3 np_y + c_4 np_z$$

is therefore a valid solution of Schrodinger's equation $\hat{H}\psi = E_n\psi$ with energy E_n.

…page 2

Q6. Show the sp hybrid orbitals $\varphi_{\mathrm{sp(i)}} = \dfrac{2s + 2p_z}{\sqrt{2}}$ $\varphi_{\mathrm{sp(ii)}} = \dfrac{2s - 2p_z}{\sqrt{2}}$ are:

[2] **a)** normalized

b) orthogonal.

Q7. Calorimetry shows the standard enthalpy change for the hydrogenation of cyclohexene

$$\text{cyclohexene} + H_2 = \text{cyclohexane}$$

is -121 kJ mol^{-1}, compared to -209 kJ mol^{-1} for the hydrogenation of benzene

$$\text{benzene} + 3H_2 = \text{cyclohexane}$$

a) Use this data to estimate the delocalization energy stabilizing the formation of benzene.

[3] **b)** Organic chemists tell us the extra stability of conjugated molecules is caused by "delocalization" of π electrons. But why does delocalization of π electrons reduce the energy? Give a quantum mechanical explanation, in words.

Q8. Use simple MO theory to

a) predict the relative stabilities of N_2^-, N_2 and N_2^+

[3] **b)** determine the bond order of the cyanide ion (CN^-).

Chem 332 Assignment #6

Ⓠ① The energy and bond length of H_2^+ are:

$E \quad -2.78 \text{ eV} \qquad 0.106 \times 10^{-9} \text{ m}$

a) $\approx$ all of the kinetic energy is due to the motion of the electron

$$\langle T \rangle = -E = \boxed{2.78 \text{ eV}} \qquad (100\% \text{ of } E)$$

b) proton-proton electric potential energy

$$= \frac{e^2}{4\pi\varepsilon_0 r} = \frac{(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(0.106 \times 10^{-9})}$$

$$= 2.176 \times 10^{-18} \text{ J} = \boxed{13.58 \text{ eV}} \qquad (488\%)$$

c) total electric potential energy:

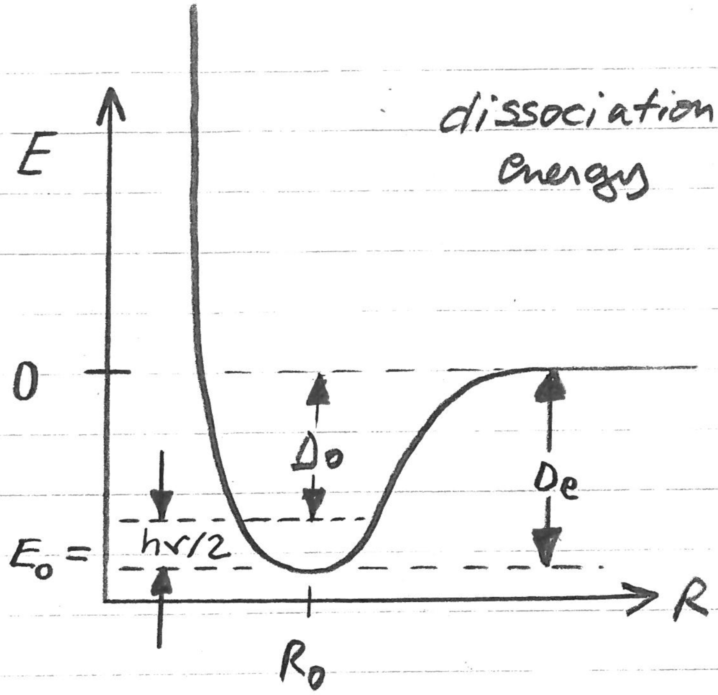
$$\langle V \rangle = 2E = 2(-2.78 \text{ eV}) = -5.56 \text{ eV}$$

$$\langle V \rangle = \langle \text{proton-proton } V \rangle + \langle \text{electron-protons } V \rangle$$

$$2(-2.78 \text{ eV}) = 13.58 \text{ eV} + \langle \text{electron-proton } V \rangle$$

$$\langle \text{electron-proton } V \rangle = \boxed{-19.14 \text{ eV}} \qquad (688\%)$$

Ⓠ2



dissociation energy $D_0 = D_e - \frac{h\nu}{2}$

zero-point vibrational energy $= h\nu/2 = E_0$

zero-point vibration energy

$$\frac{h\nu}{2} = 0.273 \text{ eV} = 4.37 \times 10^{-20} \text{ J}$$

$$D_0 = D_e - \frac{h\nu}{2} = 3.42 - 0.273 = 3.15 \text{ eV}$$

Ⓠ3

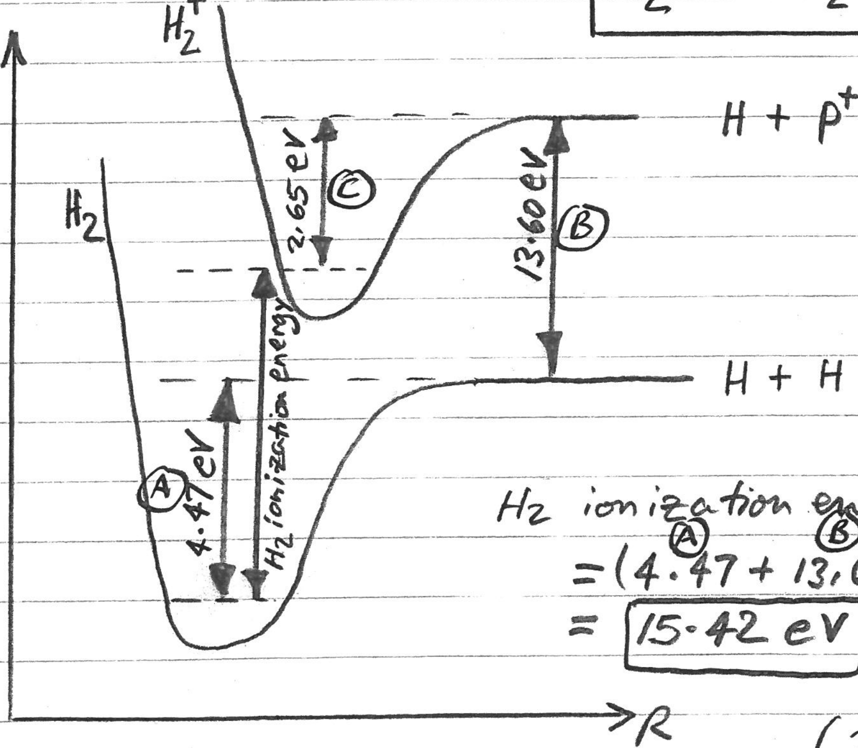
$$\boxed{H_2 \rightarrow H_2^+ + e^-}$$

3 steps:

Ⓐ dissociate H_2

Ⓑ ionize one H atom

Ⓒ re-associate to form H_2^+



H_2 ionization energy

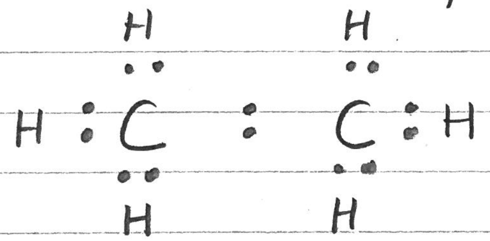
$$= (\overset{Ⓐ}{4.47} + \overset{Ⓑ}{13.60} - \overset{Ⓒ}{2.65}) \text{ eV}$$

$$= \boxed{15.42 \text{ eV}}$$

$$(2.470 \times 10^{-18} \text{ J})$$

Q4 a) bonding in ethane (H_3C-CH_3)

the carbon atoms are sp^3 hydridized (4 electrons each)

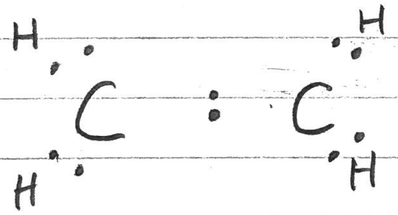


each H atom brings 1 electron

a total of 14 electrons are involved, all σ bonds

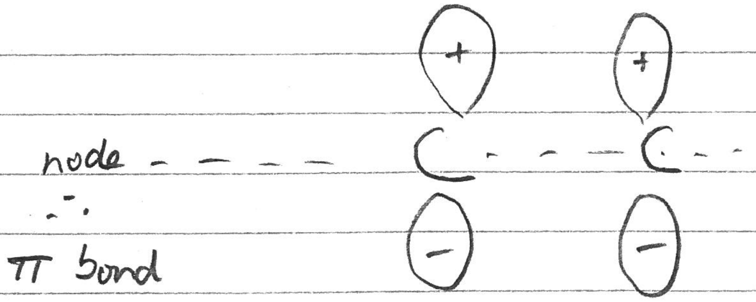
b) bonding in ethylene ($H_2C=CH_2$)

the carbon atoms are sp^2 hybridized to σ bond with 2 H atoms and the other C atom



five σ bonds (10 electrons)

the p_z orbitals on the C atoms form an addition π bond

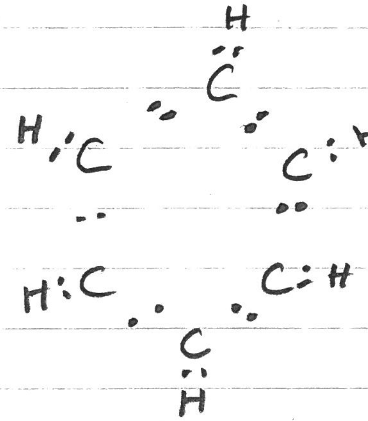


one π bond (2 electrons)

(Q4 cont.)

c) bonding in benzene (C_6H_6)

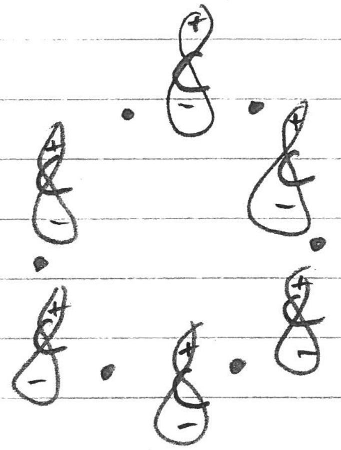
as in ethylene, the carbon atoms are sp^2 hybridized to form σ bonds



3 electrons per C atom, 1 electron per H atom involved

$3(6) + 6 = \boxed{\text{24 electrons in } \sigma \text{ bonds}}$

in addition, 6 electrons (one per C atom) form π bonds using p_z orbitals



$\boxed{\text{6 electrons in } \pi \text{ bonds}}$

Q5 For the hydrogen atom:

$$\left.\begin{aligned} \hat{H}\psi_{ns} &= E_n \psi_{ns} \\ \hat{H}\psi_{npx} &= E_n \psi_{npx} \\ \hat{H}\psi_{npy} &= E_n \psi_{npy} \\ \hat{H}\psi_{npz} &= E_n \psi_{npz} \end{aligned}\right\} \text{degenerate energy levels (identical principal quantum number } n\text{)}$$

for any linear combination of ψ_{ns}, ψ_{npx}, ψ_{npy}, ψ_{npz}:

$$\begin{aligned} \hat{H}\psi &= \hat{H}(c_1\psi_{ns} + c_2\psi_{npx} + c_3\psi_{npy} + c_4\psi_{npz}) \\ &= c_1\hat{H}\psi_{ns} + c_2\hat{H}\psi_{npx} + c_3\hat{H}\psi_{npy} + c_4\hat{H}\psi_{npz} \\ &= c_1E_n\psi_{ns} + c_2E_n\psi_{npx} + c_3E_n\psi_{npy} + c_4E_n\psi_{npz} \\ &= E_n(c_1\psi_{ns} + c_2\psi_{npx} + c_3\psi_{npy} + c_4\psi_{npz}) \end{aligned}$$

$$\hat{H}\psi = E_n\psi$$

Q6 a) are the sp_z hybrid wave functions normalized?

$$\int \varphi^*_{sp_z}\varphi_{sp_z}\,d\tau = \int\left(\frac{2s \pm 2p_z}{\sqrt{2}}\right)^*\left(\frac{2s \pm 2p_z}{\sqrt{2}}\right)d\tau$$

$$= \frac{1}{2}\left(\int \cancelto{1}{2s^*2s\,d\tau} \pm \int \cancelto{0}{2s^*2p_z\,d\tau} \pm \int \cancelto{0}{2p_z^*2s\,d\tau} + \int \cancelto{1}{2p_z^*2p_z\,d\tau}\right)$$

$= 1$ yes

b) are the sp_z wave functions orthogonal?

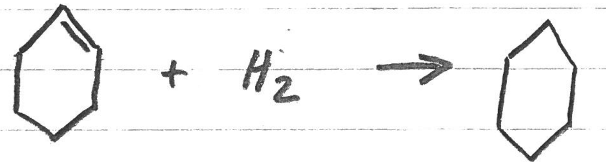
$$\int \varphi^*_{spi}\,\varphi_{spii}\,d\tau = \int\left(\frac{2s+2p_z}{\sqrt{2}}\right)^*\left(\frac{2s-2p_z}{\sqrt{2}}\right)d\tau$$

$$= \frac{1}{2}\left(\int \cancelto{1}{2s^*2s\,d\tau} - \int \cancelto{0}{2s^*2p_z\,d\tau} + \int \cancelto{0}{2p_z^*2s\,d\tau} - \int \cancelto{1}{2p_z^*2p_z\,d\tau}\right)$$

$$= \frac{1}{2}(1 - 0 + 0 - 1)$$

$= 0$ yes

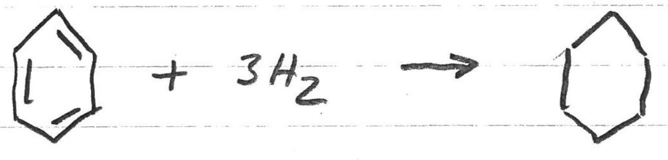
Q7



$\Delta H = -121\ \text{kJ mol}^{-1}$

If the π electrons in benzene are localized, then expect $\Delta H \simeq 3(-121)\ \text{kJ mol}^{-1}$
$= -363\ \text{kJ mol}^{-1}$
for the hydrogen of benzene

But



has $\Delta H = -209\ \text{kJ mol}^{-1}$

suggesting benzene has $\simeq (363-209)\ \text{kJ mol}^{-1}$
$\boxed{= 154\ \text{kJ mol}^{-1}}$

stabilization energy due to π electron delocalization.

Q8 a) electronic configurations of N_2^+, N_2, N_2^-:

N_2^+ $(\sigma 1s)^2(\sigma * 1s)^2(\sigma 2s)^2(\sigma * 2s)^2\overbrace{(\pi 2p_x)^2(\pi 2p_y)^2}^{\text{degenerate}}(\sigma 2p_z)^1$

N_2 ["] $(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

N_2^- ["] $(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\pi * 2p_{x \text{ or } y})^1$

anti-bonding

N_2^+	5 bonding electrons	bond order $2\frac{1}{2}$
N_2	6 " "	" " 3
N_2^-	$6-1=5$ " "	" " $2\frac{1}{2}$

anti-bonding electron

$\boxed{\text{stability} \quad N_2 > N_2^+ \simeq N_2^-}$

(Q8 cont.)

b) bond order of CN^- with electronic configuation

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2\underbrace{(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2}$$

6 bonding electrons
(3 pairs)

$\boxed{\text{bond order} = 3}$