Chem 155
Quantum Chemistry
Midterm Exam
November 13, 2002

Name KEY Dirac

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a closed book and closed notes exam, and you are responsible to be sure that your exam has no missing pages(5 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

But surely this is an old tale you tell, they say;
But surly this is a new tale you tell, other say.
Tell it once again, they say;
Or, do not tell it yet again, others say.
But I have heard all this before, say some;
Or, but this is not how it was before, say the rest

Naqshbandi recital, from The Way of the Sufi, by Idries Shah

Honor Statement

I have neither give nor received aid in this examination.

Full signature _____

Problem 1 (20 points)

Light with a wavelength of 400 nm strikes the surfaces of cesium in a photocell, and the maximum kinetic energy of the electron ejected is 1..54 x 10^{-19} J. Calculate the longest wavelength of light in nanometers that is capable of ejecting electrons from that metal.

$$K = h\nu - h\nu_0$$

$$K = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

$$\frac{hc}{\lambda_0} = \frac{hc}{\lambda} - K$$

$$\frac{1}{\lambda_0} = \frac{1}{\lambda} - \frac{K}{hc} = \frac{hc - \lambda K}{\lambda hc}$$

$$\boxed{\lambda_0 = \frac{\lambda hc}{hc - \lambda K} = \frac{\lambda}{1 - \frac{K}{hc}\lambda}}$$

$$\frac{K}{hc} = \frac{1.54 \times 10^{-19}\ \cancel{J}}{6.62 \times 10^{-34}\ \cancel{J s}\ 2.99 \times 10^{8}\ m\ \cancel{s^{-1}}} = 7.78 \times 10^{5}\ m^{-1}$$

$$\frac{K\lambda}{hc} = 7.78 \times 10^{5} \cdot 4 \times 10^{-7} = 3.11 \times 10^{-1}$$

$$\boxed{\lambda_0 = \frac{\lambda}{1 - 0.311} = \frac{400\ nm}{0.689} = 581\ nm}$$

Problem 2 (20 points)
Give an argument and predict which atom or ion in each of the following pairs should be larger:
a) Kr or Rb
b) Y or Cd
c) F^- or Br^-

a) Rb SHOULD BE LARGER BECAUSE IT HAS AN EXTRA e^- IN A 5S ORBITAL BEYOND THE Kr

b) Y SHOULD BE LARGER BECAOSE THE EFFECTIVE NUCLEAR CHARGE INCREASES THROUGH THE TRANSITION SERIES FROM Y → Cd

c) Br^- SHOULD BE LARGER BECAUSE THE THE EXTRA ELECTRONS ARE FILLING THE 4P SHELL. F^- FILLS THE 2p SHELL

Problem 3 (20 points)
The motion of an electron in a carbon-carbon double bond C=C can be treated very crudely as a motion in a one-dimensional box of length 1.34 A. Calculate the wavelength in nm of light necessary to excite the electron from the ground state to the first excited state.

$$E_n = \frac{h^2}{8mL^2} n^2$$

$$h\nu = |E_2 - E_1| = \frac{3h^2}{8mL^2} = \frac{hc}{\lambda}$$

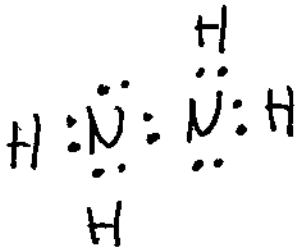
$$\lambda = hc \frac{8mL^2}{3h^2} = c \frac{8mL^2}{3h}$$

$$\lambda = \frac{2.99 \times 10^8 \, m s^{-1} \cdot 8 \cdot 9.11 \times 10^{-31} kg \, (1.34 \times 10^{-10} m)^2}{3 \cdot 6.626 \times 10^{-34} J s}$$

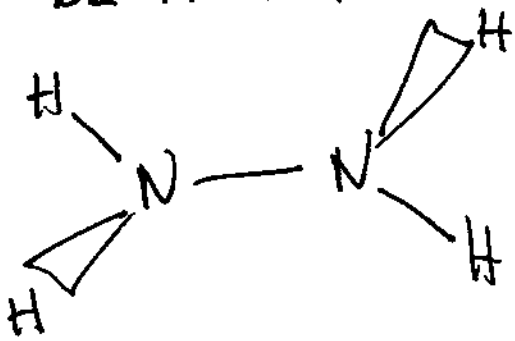
$$\boxed{\lambda = 19.7 \times 10^{-9} m = 19.7 \text{ nm}}$$

Problem 4 (20 points)
Predict the structure of hydrazine (H_2NNH_2) by writing down its Lewis structure first and using VSEPR theory. What is the hybridization of the two nitrogen atoms?

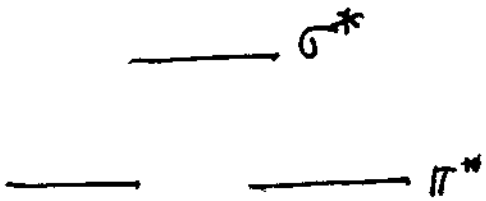
THE LEWIS DIAGRAM IS

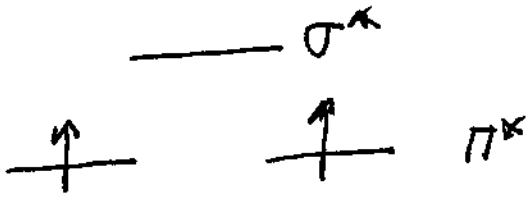


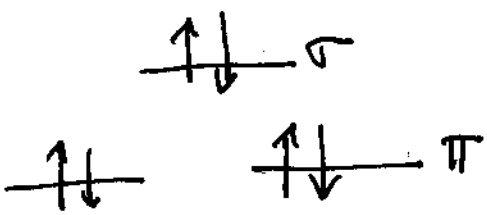
BOTH NITROGENS ATOMS HAVE STERIC # 4 AND ARE sp^3 HYBRIDIZED WITH H–N–H AND H–N–N ANGLES OF APPROX. 109.5°, THE EXTENT OF ROTATION ABOUT THE N–N BOND CANNOT BE PREDICTED FROM VSEPR THEORY.

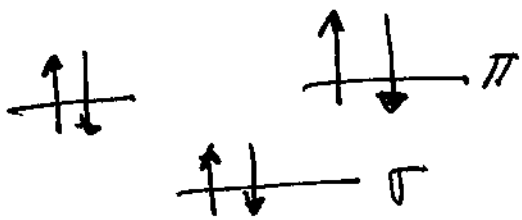


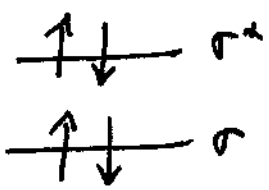
Problem 5 (20 points)
Using MO theory, determine why the dissociation energy of N_2 is greater than N_2^+ but for O_2^+ the dissociation energy is greater than O_2.











N_2

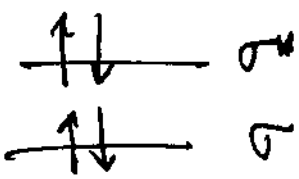
$10\ e^-$

N_2 BO 3

N_2^+ BO $2\frac{1}{2}$

DISS E

$N_2 > N_2^+$



O_2

$12\ e^-$

O_2 BO 2

O_2^+ BO $2\frac{1}{2}$

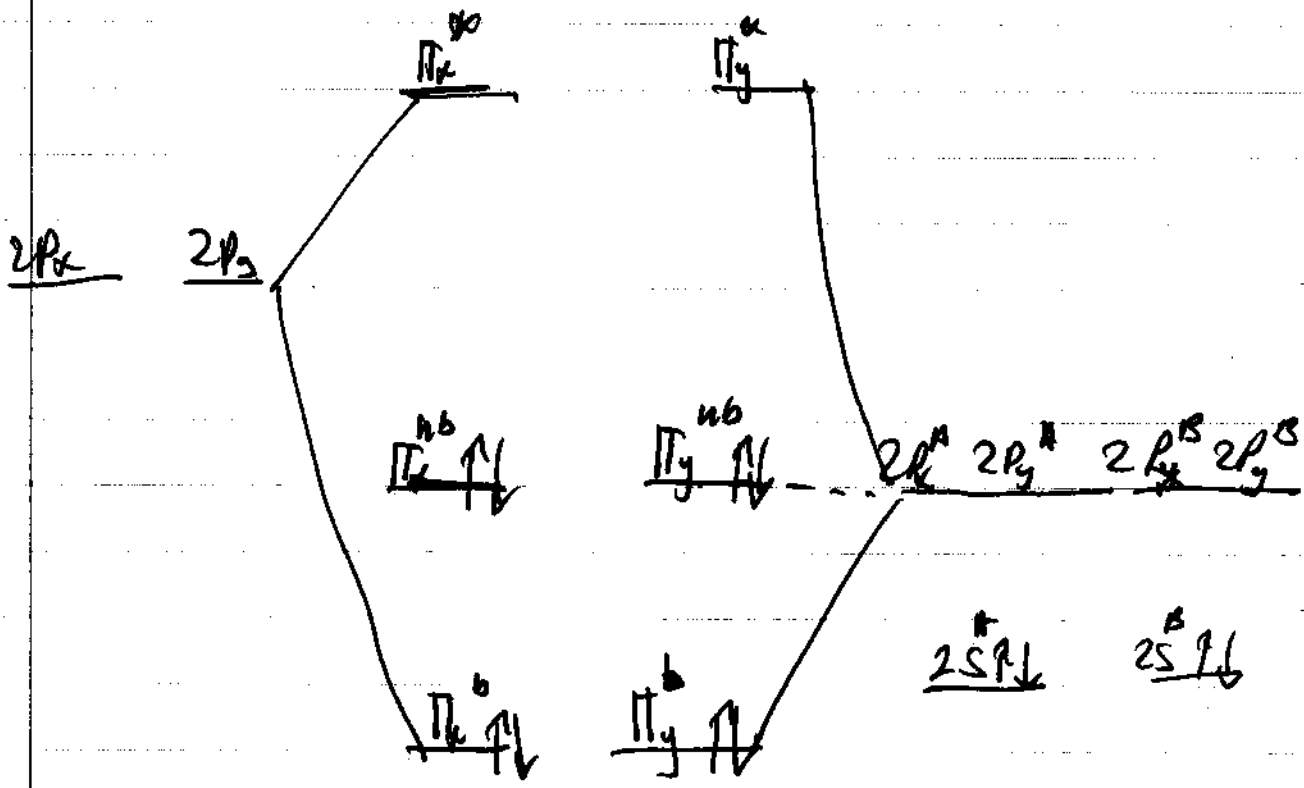
DISS E

$O_2 < O_2^+$

NO_2^+ 16 e⁻ LINEAR

HYBRIDIZE SP_z FOR THE CENTRAL ATOM

WE COMBINE THE P_x AND P_y TO FORM 6 DELOCALIZED MO

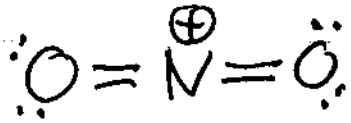


4 e⁻ FORM 2 σ BONDS ($SP + P_z$)

4 e⁻ ARE PLACED IN THE 2S ORBITAL OF THE OUTER ATOMS

8 e⁻ ARE PLACED IN THE π ORBITALS

$BO = 2\sigma + 2\pi = 4$

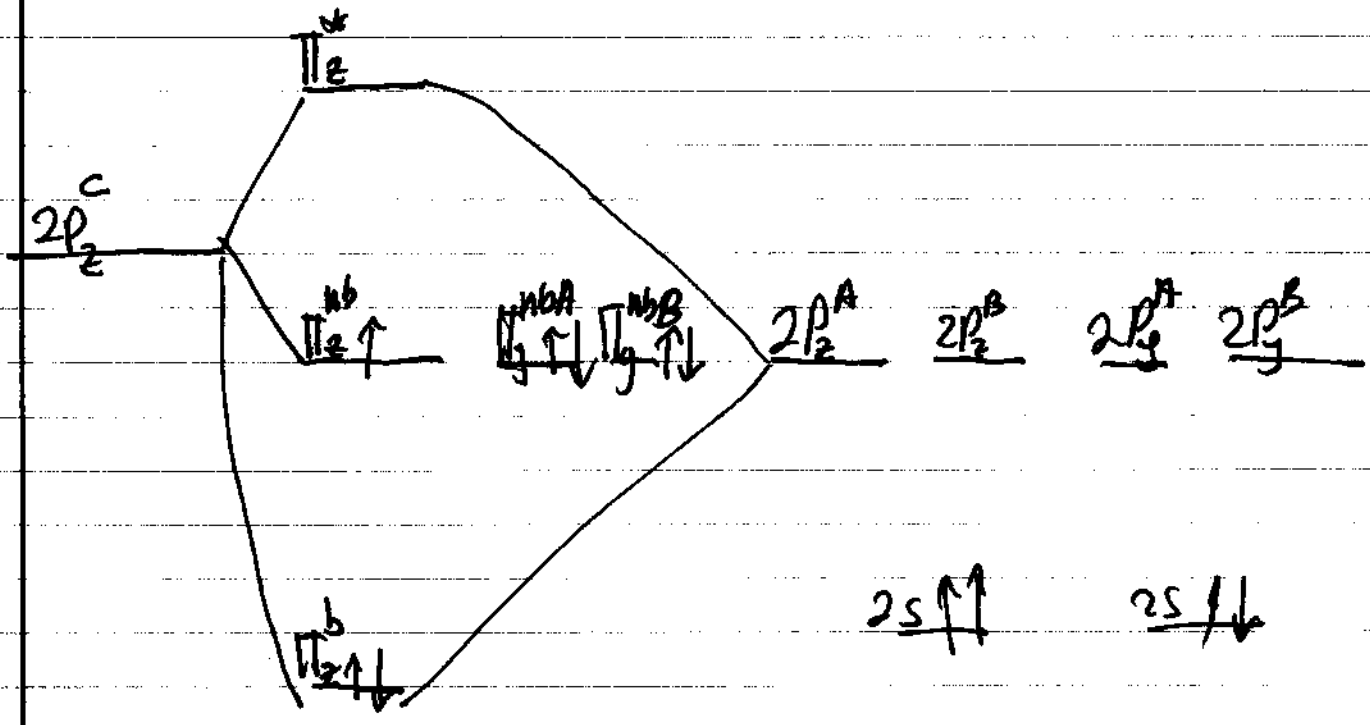


NO_2 $17e^-$ bent

WE USE THE p_x AND p_y AO OF THE CENTRAL ATOM AND THE S TO FORM sp^2 MO.

$4e^- \rightarrow 2\sigma$ bonds $\Big\}$ 3 sp^2 MO
$2e^- \rightarrow$ LONE PAIR $\Big\}$

WE ARE LEFT WITH A p_z FROM THE CENTRAL ATOM, WHICH WE COMBINE WITH p_z^A AND p_z^B TO GET 3 DELOCALIZED MO



$4e^-$ IN THE OUTER AO 2S.
$7e^-$ IN THE π MO
$BO = 2\sigma + 1\pi = 3$