100/ Avg = 60

ATOMS, MOLECULES AND RESEARCH

QUANTUM MECHANIC (SPRING) MID-TERM EXAMINATION, 2004

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STUDENT NAME _____

ANSWER ALL THE QUESTIONS.

1. Give short answers to the following questions.

(a) State the Born-Oppenheimer approximation

2 The mass of the nuclei are much higher than that of the electrons. Therefore the kinetic energy of the nuclei can be ignored when writing the Hamiltonian.

(b) What is a basis set?

2 a set of functions selected to represent a system.

(c) If you are given two wavefunctions ϕ_1 and ϕ_2 and the Hamiltonian of the system ~~is~~ is $\hat{H}$, define the following.

- an overlap integral

2 $\int \phi_1^* \phi_1 d\tau$ or $\int \phi_2^* \phi_2 d\tau$

- a Coulomb integral

2 $\int \phi_1^* \hat{\mathcal{H}} \phi_1 d\tau$ or $\int \phi_2^* \hat{\mathcal{H}} \phi_2 d\tau$

- a resonance integral

2 $\int \phi_1^* \hat{\mathcal{H}} \phi_2 d\tau$ or $\int \phi_2^* \hat{\mathcal{H}} \phi_1 d\tau$

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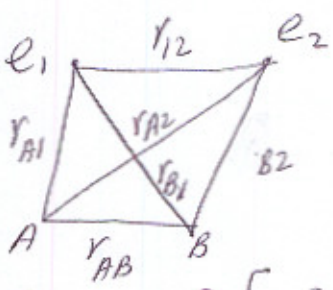
2. Write the Hamiltonian for the H_2 molecule. Clearly identify each of the terms in the Hamiltonian. State any of the assumptions you made in writing the Hamiltonian.

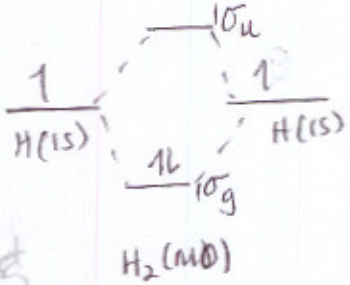


Assumption –
Ignore the kinetic energy of the nuclei, because it is too small relative to the other terms.

$$\hat{\mathcal{H}} = \underbrace{-\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2\right]}_{\text{K.E. of electrons}} \underbrace{- \frac{Z_A e^2}{(4\pi\varepsilon_0) r_{A1}} - \frac{Z_A e^2}{(4\pi\varepsilon_0) r_{A2}} - \frac{Z_B e^2}{(4\pi\varepsilon_0) r_{B1}} - \frac{Z_B e^2}{(4\pi\varepsilon_0) r_{B2}}}_{\text{electron – nuclei attraction}} \underbrace{+ \frac{e^2}{(4\pi\varepsilon_0) r_{12}}}_{\text{electron – electron repulsion}}$$

$$+ \frac{Z_A Z_B e^2}{(4\pi\varepsilon_0) r_{AB}} \leftarrow \text{nuclear–nuclear repulsion}$$

b) Using a Slater determinant, write a wave function (first approximation only) for the ground state of the H_2 molecule.



$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix}$$

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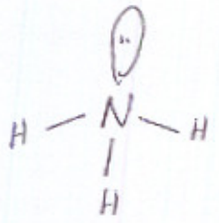
3. Use the hybridization model (only) to describe the bonding in the following molecules.

- NH_3



The N atom is sp^3 hybridized. The four sp^3 hybrid orbitals are at 109° to each other forming a tetrahedral geometry. Three of these overlap with the 1S orbitals of H atoms. The other contains the lone pair electrons.

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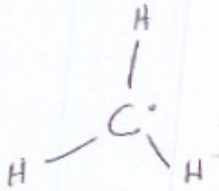
- Methyl radical (CH_3), which has a planar geometry



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C is sp^2 hybridized. The three sp^2 hybrid orbitals are planar, at 120° to each other, forming a trigonal planar geometry. The three H atom 1S orbitals overlap with these hybrid orbitals. The unhybridized p orbital is perpendicular to the plane of CH_3 and contains an unpaired electron.

- MgH_2

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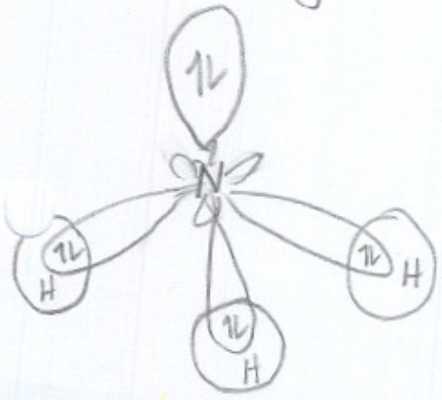
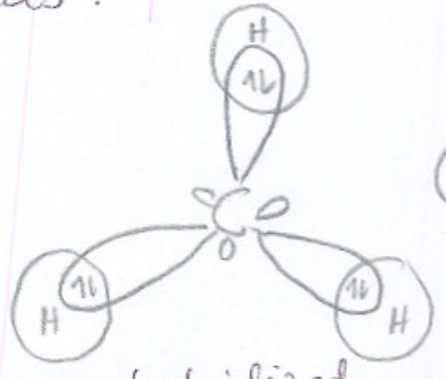
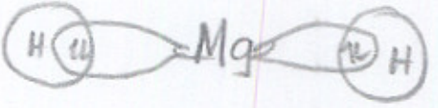
Mg is sp hybridized. The two sp hybrid orbitals are at 180° to each other, forming a linear geometry. The 1S orbitals of the two H atoms overlap with these two hybrid orbitals.





unhybridized orbital is not shown (⊥ to the CH_3 molecular plane)



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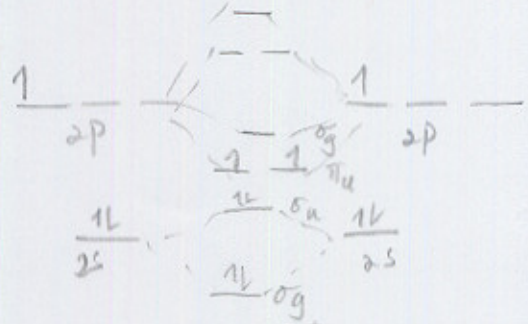
ground state

4. What are the term symbols of the following molecular species? Show all work.

- B_2

electron configuration $1\sigma_g^2\ 1\sigma_u^2\ 1\pi_u^2$

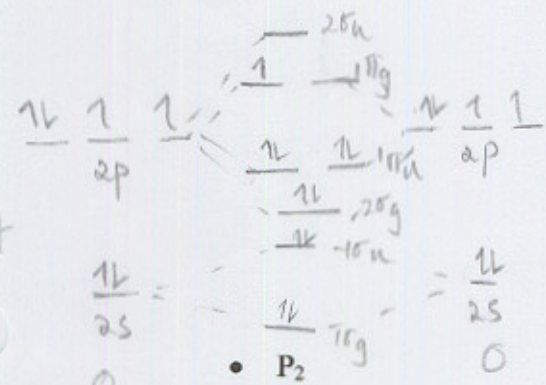


π_u^2 configuration $\Rightarrow$ $^3\Sigma_g^-$ $^1\Sigma_g^+$

Ground state = $^3\Sigma_g^-$

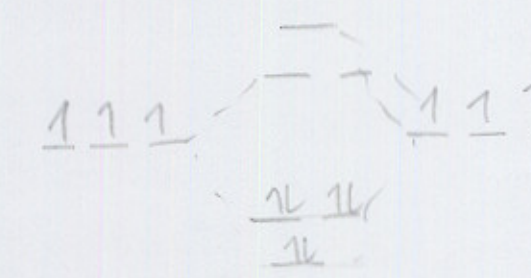
- O_2^+

Config. $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 1\pi_u^4\ 1\pi_g^1$



π_g^1 configuration $^2\Pi_g$

- P_2

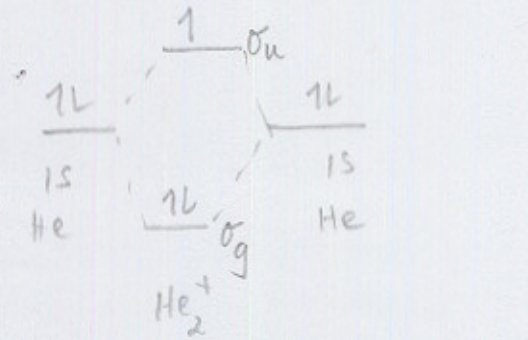


$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 1\pi_u^4$

closed shell $^1\Sigma_g^+$

- He_2^+

$1\sigma_g^2\ 1\sigma_u^1$



$^2\Sigma_u^+$

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5. If a molecule has a $^2\Delta_g$ term symbol, what do you know about the following of the molecule?

- Magnetic properties when placed in an external magnetic field (explain)

$2S+1 = 2 \Rightarrow S = 1/2$

3 $\therefore$ There are unpaired electrons

$\Rightarrow$ paramagnetic behavior.

- Spin quantum number (explain)

$2S+1 = 2$ (spin multiplicity)

2 $\therefore$ $S = 1/2$

- Component of the total orbital angular momentum about the inter-nuclear axis (explain)

Since this is a Δ term; $\Lambda = 2$

2 $M_L = \pm 2$

- Absence/presence of a center of inversion (explain)

The molecule must have a center of inversion

3 since the term symbol contains a "g" as a subscript.

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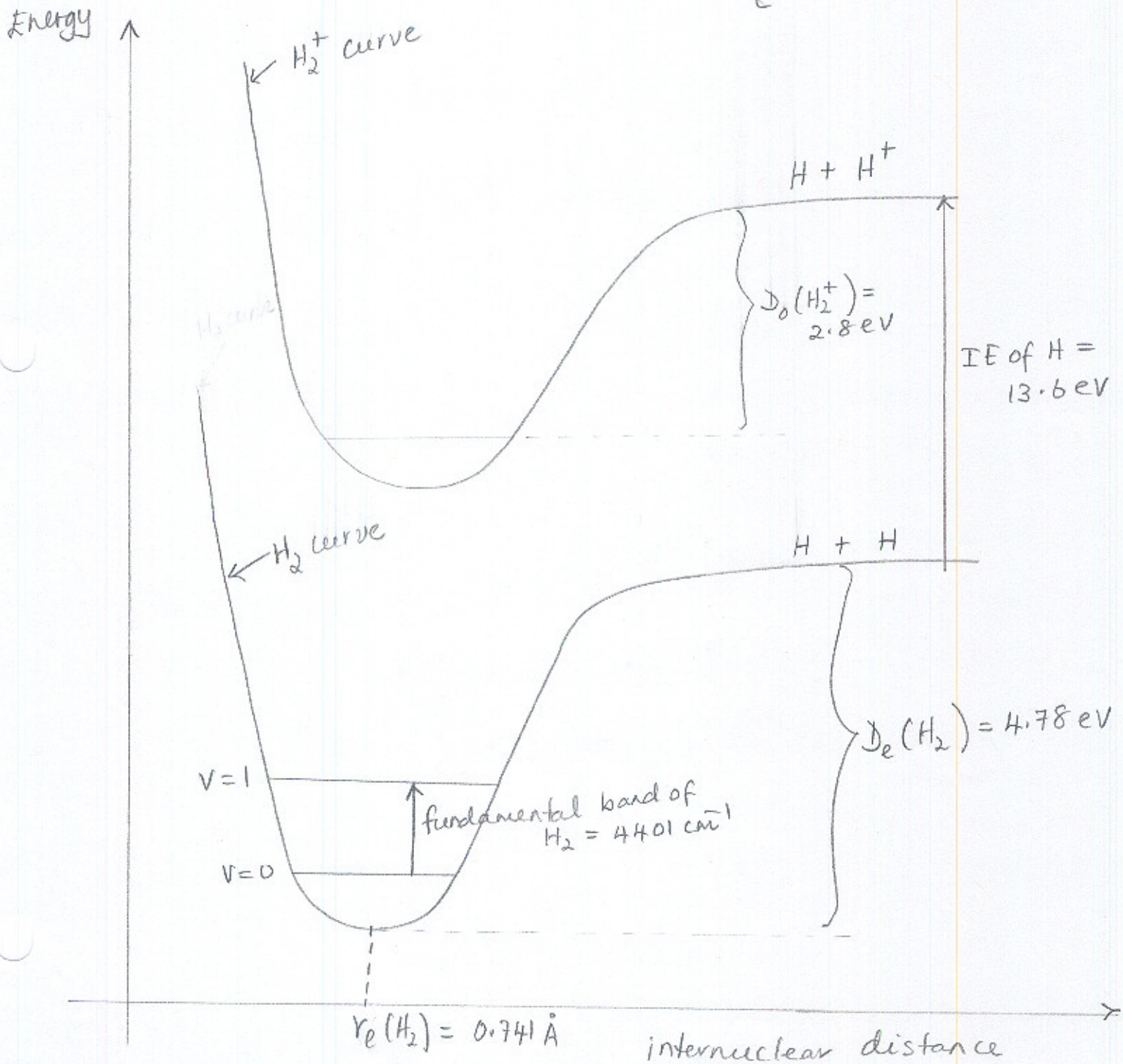
6. Draw the total energy of H_2 and H_2^+ as a function of the inter-nuclear distance. Clearly label the axes. Be sure to draw both energy curves on the same axis system (one diagram containing both curves). Clearly label the curves for identification of H_2 and H_2^+.

b) Clearly label the following in your diagram.

- Ionization energy of the H atom is 13.6 eV (IE of H)
- Spectroscopic dissociation energy of H_2^+ is 2.8 eV [$D_0(H_2^+)$]
- Equilibrium bond dissociation energy of H_2 is 4.78 eV [$D_e(H_2)$]
- The fundamental band of H_2 is observed at 4401 cm^{-1}
- The equilibrium bond distance of H_2 is 0.741 Å [$r_e(H_2)$]



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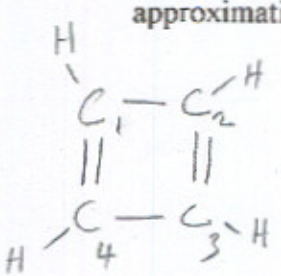
secular

7. Write the ~~Slater~~ determinant for the π electron system of the cyclobutadiene (C_4H_4) molecule. Then use Huckel approximations to simplify this determinant. State the approximations clearly. **You do not have to solve the determinant.**



$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

Hückel's approximations:

(a) $S_{ij} = \delta_{ij}$ (b) $H_{ii} = \alpha$

(c) $H_{ij} = \beta$ if atoms i and j are adjecent

$H_{ij} = 0$ if the atoms i and j are not adjacent

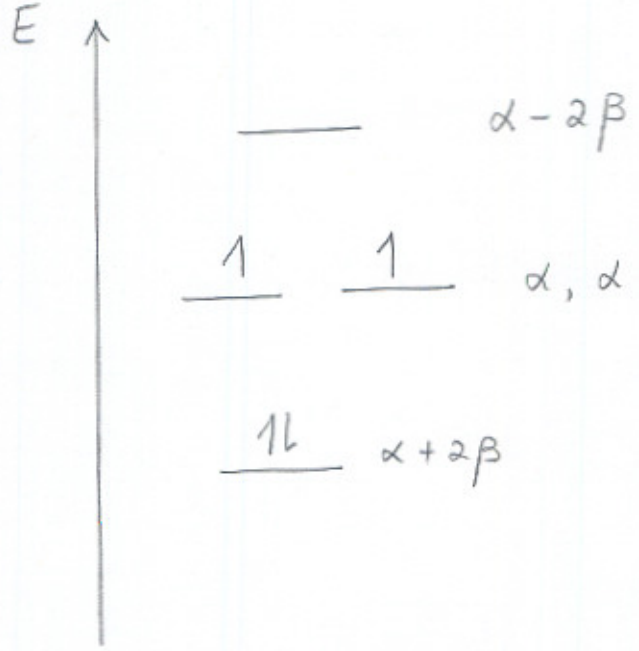
∴ The secular determinant simplifies to;

$$\begin{vmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

following energies.

$E = \alpha + 2\beta$, $E = \alpha$, $E = \alpha$, $E = \alpha - 2\beta$

Draw an energy level diagram to show the energy levels for the π electron system of the cyclobutadiene (C_4H_4) molecule and add the correct number of electrons to this diagram.



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c) Based on your diagram decide whether the ground state of cyclobutadiene (C_4H_4) would be stable or unstable. State your reasoning clearly.

5 The ground state has 2 unpaired electrons Therefore C_4H_4 is a radical, and is unstable in the ground state.

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