CH107 IIT Bombay 2020-21

Answer keys and model solutions to end-semester exam

(Page number corresponds to question number)

Q1. Considering Pauli exclusion principle to hold for 4 non-interacting electrons confined in a 1D infinite potential well of length L (V(x) = 0, 0<x<L), the total ground state energy of the system will be   [1 mark]

A. $10h^2/8mL^2$
B. $4h^2/8mL^2$
C. $20h^2/8mL^2$
D. $30h^2/8mL^2$
E. I won't answer this question

Q1. 4 non-interacting electrons assumed confined in a 1D-potential well of length L $\left(v(x) = 0, 0<x<L \right)$ while satisfying the Pauli exclusion principle would have total energy :-

$$E_{total} = 2\left[\frac{1^2 h^2}{8mL^2}\right] + 2\left[\frac{2^2 h^2}{8mL^2}\right]$$

$$= \frac{10 h^2}{8mL^2}$$

⇅ $E_2 = \frac{2^2 h^2}{8mL^2}$

⇅ $E_1 = \frac{1^2 h^2}{8mL^2}$

Q2. Consider the following two electron slater determinant.

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

In the absence of any external field, the energy degeneracy of the state is:
[1 mark]

A. 1
B. 2
C. 3
D. 4
E. I won't answer this question

2. The given Slater Determinant
has antisymmetric spatial part and
symmetric spin part.

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}}\left[1s(1)\,2s(2) - 2s(1)\,1s(2)\right]\alpha(1)\alpha(2).$$

Since the spatial part is antisym,
the corresponding spin fns need to be
symmetric, which has three distinct
possibilities $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$ and
$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$.

Hence energy degeneracy is 3.

**Q3.** Suppose a quantum state of a Hydrogenic system is denoted by

$\psi = -\frac{\sqrt{5}}{3}\phi_{4,2,-1}(x,y,z) + \frac{2}{3}\phi_{3,2,1}(x,y,z)$, where $\phi_{n,l,m}$'s are eigenfunctions

of H, L^2, and L_z. Here, ψ is an eigenfunction of   [1 mark]

A. *H* only
B. *L²* only
C. L_z only
D. L_z and L^2 only
E. I won't answer this question

3. If two fn.s ϕ_1 and ϕ_2 are eigenfns of an operator $\hat{O}$, then their linear combination $\psi = c_1\phi_1 + c_2\phi_2$ is also an eigenf. of $\hat{O}$ if ϕ_1 and ϕ_2 have degenerate eigenvalue spectra.

Since $\phi_{4,2,-1}$ and $\phi_{3,2,1}$ have same $l = 2$, which is the quantum # associated with L^2 operator. Hence ψ is an eigenf. of L^2 only.

Q4. Photoelectron spectrum of a diatomic molecule is shown below. Excitation light of wavelength (λ) 50 nm can eject one electron from each molecular orbital. The ratio of the ionization energies corresponding to peaks A and B is _____.
Given, (E in eV) = 1250/(λ in nm).   **[1 mark]**
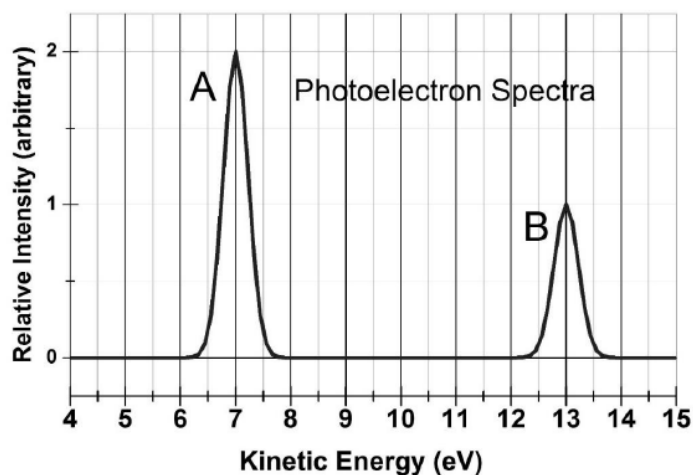
A. **3:2**
B. 2:1
C. 3:4
D. 43:37
E. I won't answer this question

Q4. E (in ev) $= \dfrac{1250}{50} = 25\,ev$

K.E. peak A (from graph) $= 7\,ev$

K.E. peak B (from graph) $= 13\,ev$

I.E. peak A $= 25\,ev - 7\,ev = 18\,ev$

I.E. peak B $= (25 - 13)\,ev = 12\,ev$

$\therefore \quad \dfrac{I.E. \text{ peak A}}{I.E. \text{ peak B}} = \dfrac{18}{12} = \boxed{3:2} \qquad \text{option A}$

Q5. Which of the following is the correct electronic Hamiltonian for carbon atom?   **[1 mark]**

A. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1 \\ j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

B. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 + \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1 \\ j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

C. $\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} - \sum_{i=1}^{6}\sum_{\substack{j=1 \\ j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

D. $\hat{H} = +\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{6}\sum_{\substack{j=1 \\ j>i}}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

E. I won't answer this question

Q5.   The   correct   electronic   Hamiltonian   for   Carbon   atom   is

A. $\hat{H} = -\frac{\hbar^2}{2me}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\frac{6e^2}{4\pi\varepsilon_0 r_i} + \sum_{\substack{i=1 \\ j>i}}^{6}\sum_{j=1}^{6}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$

The second term is for nuclear - electron   attraction ,
and should be negative.

The third term is for electron- electron   repulsion ,
and should be positive.

The first term is K.E.   and should be -ve.

Q6. A hybrid atomic orbital is expressed as:

$$\phi_h = 0.5\ 4s + 0.707\ 4p_x + 0.5\ d_{x^2-y^2}.$$

ϕ_h is _____ hybrid: [1 mark]

A. sp^3d
B. spd
C. sp^3d^2
D. sp^2d
E. I won't answer this question

6. The hybrid orbital is normalized.
The $4s$-contribution is $(0.5)^2 \times 100\%$.
$= 25\%$.

$4p_x$-contribution is $\sim (0.707)^2 \times 100\%$.
$= 50\%$.

$4d_{x^2-y^2}$ contribution is $(0.5)^2 \times 100\% = 25$

Hence it is sp^2d hybrid.

Q7. For a polyatomic system, if you do not consider the formation of non-bonding MOs, the coefficients of individual AOs in the normalized linear combination of AOs can be (select all that apply): **[1 mark]**

   A. non-zero integer
   B. rational number
   C. irrational number
   D. zero
   E. I won't answer this question

Q7) $\Psi_{MO} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$

c_1 can be   zero

rational (like $\frac{1}{2}$)

irrational (like $\frac{1}{\sqrt{2}}$)

non-zero integer → Consider Antibonding MO

$$\Psi = \frac{1}{\sqrt{2-2S}} [\phi_A - \phi_B]$$

If $S = 0.5$, $\frac{1}{\sqrt{2-2S}} = 1$ integer.

Correct answer

(a), (b), (c), (d) all

Q8. Consider the excited states of H_2 molecule where the two nuclei are separated by $2a_0$, formed by the promotion of 1 electron from HOMO (1σ) to LUMO ($1\sigma^*$). Which of the following statement(s) is/are correct?   **[1 mark]**

A. The singlet excited state corresponds to an ionic form
B. The triplet excited state corresponds to an ionic form
C. The singlet excited state corresponds to a covalent form
D. The triplet excited state corresponds to a covalent form
E. I won't answer this question

$$\sigma_H(1) = N\left[1s_A(1) + 1s_B(1)\right]$$

$$\sigma_L^*(2) = N'\left[1s_A(2) - 1s_B(2)\right]$$

$$\sigma(1)\,\sigma^*(2) = N\cdot N'\left[1s_A(1)\,1s_A(2) - 1s_B(1)\,1s_B(2) - 1s_A(1)\,1s_B(2) + 1s_B(1)\,1s_A(2)\right]$$

$$\sigma(2)\,\sigma^*(1) = N N'\left[1s_A(2)\,1s_A(1) - 1s_B(2)\,1s_B(1) - 1s_A(2)\,1s_B(1) + 1s_B(2)\,1s_A(1)\right]$$

$$\psi_{sing.} = \sigma(1)\sigma^*(2) = 2NN'\left[1s_A(1)\,1s_A(2) - 1s_B(1)\,1s_B(2)\right]$$
$$\quad + \sigma(2)\sigma^*(1)$$
$$\longrightarrow \text{Ionic}$$

$$\psi_{triplet} = \sigma(1)\sigma^*(2) = 2NN'\left[1s_B(1)\,1s_A(2) - 1s_A(1)\,1s_B(2)\right]$$
$$\quad - \sigma(2)\sigma^*(1)$$
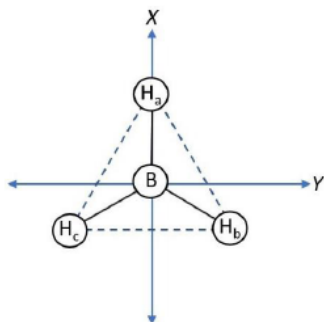$$\longrightarrow \text{Covalent}$$

Correct ans: (A) singlet excited state corresponds to ionic
(D) Triplet excited state corresponds to covalent

Q9. The linear combination of two $3d_{xz}$ atomic orbitals on two different atoms can form: (select all that apply)   **[1 mark]**

   A. π bonding and anti-bonding MOs if 2 atoms approach along z-direction
   B. π bonding and anti-bonding MOs if 2 atoms approach along x-direction
   C. π bonding and anti-bonding MOs if 2 atoms approach along y-direction
   D. δ bonding and anti-bonding MOs if 2 atoms approach along y-direction
   E. δ bonding and anti-bonding MOs if 2 atoms approach along x-direction
   F. δ bonding and anti-bonding MOs if 2 atoms approach along z-direction
   G. I won't answer this question
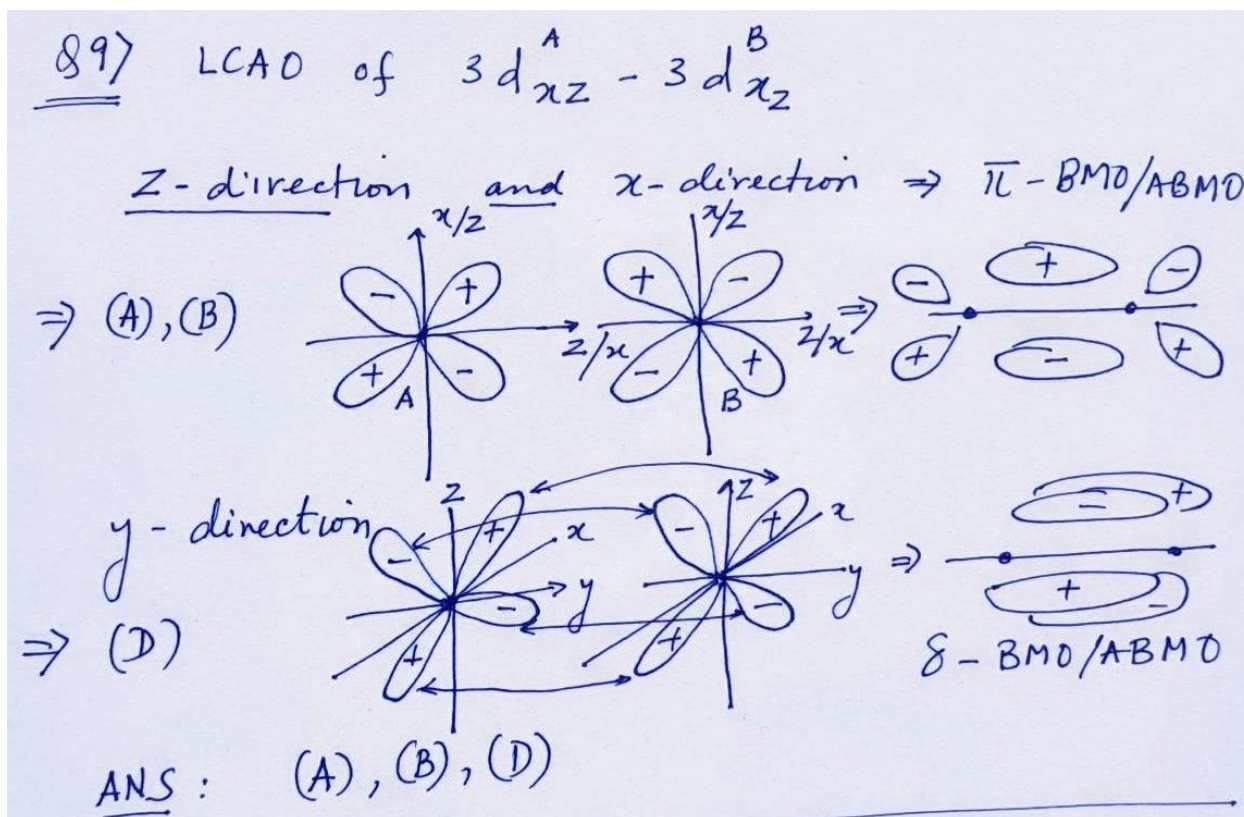
Q10. Consider BH_3 molecule in the xy-plane, as shown below. A linear combination of H 1s orbitals $(c_1 1s_a + c_2 1s_b + c_3 1s_c)$ forms a bonding/antibonding MO with $2p_x$ orbital of B. The allowed values of coefficients c_1, c_2 and c_3 is/are: **[1 mark]**

A. $c_1 = \sqrt{\frac{2}{3}}; c_2 = -\sqrt{\frac{1}{6}}, c_3 = -\sqrt{\frac{1}{6}}$

B. $c_1 = \sqrt{\frac{1}{6}}; c_2 = -\sqrt{\frac{2}{3}}, c_3 = \sqrt{\frac{2}{3}}$

C. $c_1 = -\sqrt{\frac{2}{3}}; c_2 = \sqrt{\frac{1}{6}}, c_3 = \sqrt{\frac{1}{6}}$

D. $c_1 = -\sqrt{\frac{2}{3}}; c_2 = \sqrt{\frac{1}{6}}, c_3 = -\sqrt{\frac{1}{6}}$

E. I won't answer this question
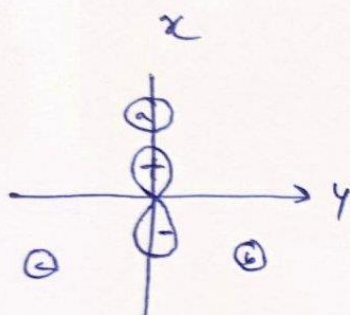
Q11. Solution END-SEM.

$$\langle F \rangle = \langle \psi_{1s} | F | \psi_{1s} \rangle$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0) \quad \text{consider. } e, \varepsilon_0, a_0 = 1.$$

$$F = \frac{-Ze^2}{4\pi\varepsilon_0 r^2}$$

$$\langle F \rangle = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(\frac{-Zr}{a_0} \right) \cdot \left(\frac{-Ze^2}{4\pi\varepsilon_0 r^2} \right)$$

$$\cdot \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(\frac{-Zr}{a_0} \right)$$

$$\times r^2 \, dr \cdot \sin\theta \cdot d\theta \cdot d\phi.$$

$$= \frac{-Z^4 e^2}{4\pi^2 \varepsilon_0 a_0^3} \int_{r=0}^{\infty} \exp\left(\frac{-Zr}{a_0} \right)^2 dr \int_{\theta=0}^{\pi} \sin\theta \cdot d\theta \int_{\phi=0}^{2\pi} d\phi$$

$$= \frac{-Z^4 e^2}{4\pi^2 \varepsilon_0 a_0^3} \times 4\pi \int_{r=0}^{\infty} \exp\left(\frac{-Zr}{a_0} \right)^2 dr.$$

$$= \frac{-Z^4 e^2}{\pi \varepsilon_0 a_0^3} \int_{r=0}^{\infty} \exp\left(-\frac{Zr}{a_0} \right)^2 dr.$$

$$\left. \begin{array}{c} e=1, \ a_0=1 \\ \varepsilon_0 = 1 \end{array} \right\} \quad = \frac{-Z^4 e}{\pi} \int_{r=0}^{\infty} \exp\left(-Zr \right)^2 dr.$$

$$= -\frac{1}{2} \frac{Z^3}{\pi}$$

For $Z=2 \quad \langle F \rangle = -1.27$

$\quad Z=3 \quad \langle F \rangle = -4.3$

$\quad Z=4 \quad \langle F \rangle = -10.19.$

Q12. Calculate the electronic energy (in eV) of the Li$^+$ atom in ground state within the orbital approximation. Use $E_{1s} = -122.4\ eV$ and

$$\left\langle 1s(1)1s(2)\left|\frac{e^2}{4\pi\epsilon_0 r_{12}}\right|1s(1)1s(2)\right\rangle = 57.0\ eV.$$ **[2 marks]**

(Write "99999" if you do not want to answer this question.)

2 12.

Assuming non-interacting electrons, the electronic energy of of Li$^+$ is

$$\left(-122.4\right)\times 2\ eV = -244.8\ eV.$$

Inclusion of e$^-$-e$^-$ repulsion

$\left\langle 1s(1)1s(2)\left|\frac{e^2}{4\pi\epsilon_0 r_{12}}\right|1s(1)1s(2)\right\rangle$ destabilises the system by 57.0 eV.

Hence the total energy of Li$^+$ would be $\left(-244.8 + 57.0\right)eV = -187.8\ eV.$

13

Q13. For H_2 molecule, assume that the normalized VBT wavefunction of the ground state is given by $\psi(1,2) = 0.95\phi_{covalent} + 0.1\phi_{ionic}$. If $\phi_{covalent}$ and ϕ_{ionic} are normalized covalent and ionic wavefunctions, respectively, the atomic overlap integral S= _____. **Important: Write your answer to 2 decimal places.** [2 marks]
(Write "99999" if you do not want to answer this question.)

13) $\psi = c_1\phi_{cov.} + c_2\phi_{ION}$

$\langle \psi | \psi \rangle = 1 = c_1^2 \underbrace{\langle\phi_{cov}|\phi_{cov}\rangle}_{1} + c_2^2 \underbrace{\langle\phi_{ION}|\phi_{ION}\rangle}_{1} + 2c_1c_2\langle\phi_{cov}|\phi_{ION}\rangle \quad -\textcircled{1}$

$\phi_{cov} = \frac{1}{\sqrt{2+2S^2}}[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)]$

$\phi_{ION} = \frac{1}{\sqrt{2+2S^2}}[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]$

$\langle\phi_{cov}|\phi_{ION}\rangle = \frac{1}{2+2S^2}\Big[\underbrace{\langle\psi_A(1)|\psi_A(1)\rangle}_{1}\underbrace{\langle\psi_B(2)|\psi_A(2)\rangle}_{S} + \underbrace{\langle\psi_A(2)|\psi_B(2)\rangle}_{S}\underbrace{\langle\psi_B(1)|\psi_B(1)\rangle}_{1}$
$+ \underbrace{\langle\psi_A(1)|\psi_B(1)\rangle}_{S}\underbrace{\langle\psi_B(2)|\psi_B(2)\rangle}_{1} + \underbrace{\langle\psi_A(2)|\psi_A(2)\rangle}_{1}\underbrace{\langle\psi_B(1)|\psi_A(1)\rangle}_{S}\Big]$

$= \frac{4S}{2+2S^2} = \frac{2S}{1+S^2}$

Eq $\textcircled{1}$ $\Rightarrow 1 = c_1^2 + c_2^2 + 2c_1c_2 \cdot \frac{2S}{1+S^2}$

$\frac{S}{1+S^2} = \frac{1-c_1^2-c_2^2}{4c_1c_2}$ $c_1 = 0.95$, $c_2 = 0.1$

$\frac{S}{1+S^2} = 0.23$

$S^2 - 4.34S + 1 = 0$

$S = \frac{4.34 \pm \sqrt{(4.34)^2 - 4}}{2}$

$= 0.24, \quad 4.096$

Since $S<1$, $\boxed{S = 0.24}$

Q14. Consider the H_2^+ molecule. If the overlap integral is 0.1, the magnitude of energy difference (in eV, correct up to 1st place of decimal) between the bonding and antibonding MOs generated by linear combination of two 2s AOs, is _____.
Given, $\langle\psi_{2sA}|H|\psi_{2sA}\rangle = -4\ eV$,

$\langle\psi_{2sA}|H|\psi_{2sB}\rangle = 15\langle\psi_{2sA}|\psi_{2sB}\rangle\langle\psi_{2sA}|H|\psi_{2sA}\rangle$.   **[2 marks]**
(Write "99999" if you do not want to answer this question.)

14) $E_+ = \dfrac{H_{aa} + H_{ab}}{1 + S}$

$E_- = \dfrac{H_{aa} - H_{ab}}{1 - S}$

$H_{aa} = \langle\psi_{2s_A}|H|\psi_{2s_A}\rangle = -4\ e.V.$

$S = 0.1$

$H_{ab} = \langle\psi_{2s_A}|H|\psi_{2s_B}\rangle = 15.(0.1)(-4)$
$= -6\ e.V.$

$E_+ = \dfrac{-4-6}{1+0.1} = -9.09\ e.V.$

$E_- = \dfrac{-4+6}{1-0.1} = 2.22\ e.V.$

$|E_- - E_+| = 11.31\ eV$

Q15. For the molecule CH_2Cl_2, the central carbon atom forms two non-equivalent sets of hybrid orbitals using 2s and 2p AOs. The expressions of the two normalized hybrids which bond with 1s orbitals of the H atoms are: (*Note: for your calculations, make sure you go up to 3rd place of decimal for coefficients*).

$$\phi^C_{H_A} = 0.522\psi_s - 0.477\psi_{p_x} - 0.707\psi_{p_y}$$

$$\phi^C_{H_B} = 0.522\psi_s - 0.477\psi_{p_x} + 0.707\psi_{p_y}$$

The Cl-C-Cl angle (*in degrees, correct to the 2nd place of decimal*) is _____.
(Write "99999" if you do not want to answer this question.)   [2 marks]

Note: symmetry arguments are used – coefficeints of s, px and pz are going to be same for both the hybrid orbitals which will bon to Cl AOs

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$$C_3^2 = 0.5 \quad \text{or} \quad \boxed{C_3 = 0.707}$$

$$C_1^2 = 0.5 (1 - 0.545) = 0.5 \times 0.455 = 0.2275$$

$$C_2^2 = 0.5 (1 - 2 \times 0.227) = 0.5(1 - 0.455) = 0.545/2$$
$$= 0.272$$

$$\Rightarrow \boxed{C_1 = 0.477} \qquad \boxed{C_2 = 0.522}$$

$$\therefore \quad c\text{-}Cl_A : \phi_{C_A}^C = 0.477 \, \psi_s + 0.522 \, \psi_{p_x} + 0.707 \, \psi_{p_z}$$

$$c\text{-}Cl_B : \phi_{C_B}^C = 0.477 \psi_s + 0.522 \, \psi_{p_x} - 0.707 \, \psi_{p_z}$$

NEGLECT ψ_s (coefficients)

$$\phi_{C_A}^C \Rightarrow 0.522 \, \psi_{p_x} + 0.707 \, \psi_{p_z}$$

$$\phi_{C_B}^C \Rightarrow 0.522 \, \psi_{p_x} - 0.707 \, \psi_{p_z}$$

$$\cos\theta = \frac{\vec{r_1} \, \vec{r_2}}{|r_1| |r_2|} = \frac{(0.522)^2 - (0.707)^2}{(0.522)^2 + (0.707)^2}$$

$$= \frac{0.272 - 0.499}{0.272 + 0.499} = -\frac{0.227}{0.771} = -0.294$$

$$\therefore \quad \theta = \cos^{-1}(-0.294) = 107.1°$$

$$\therefore \quad Cl\text{-}c\text{-}Cl \quad \text{in } CH_2Cl_2 \text{ is } 107°1°$$