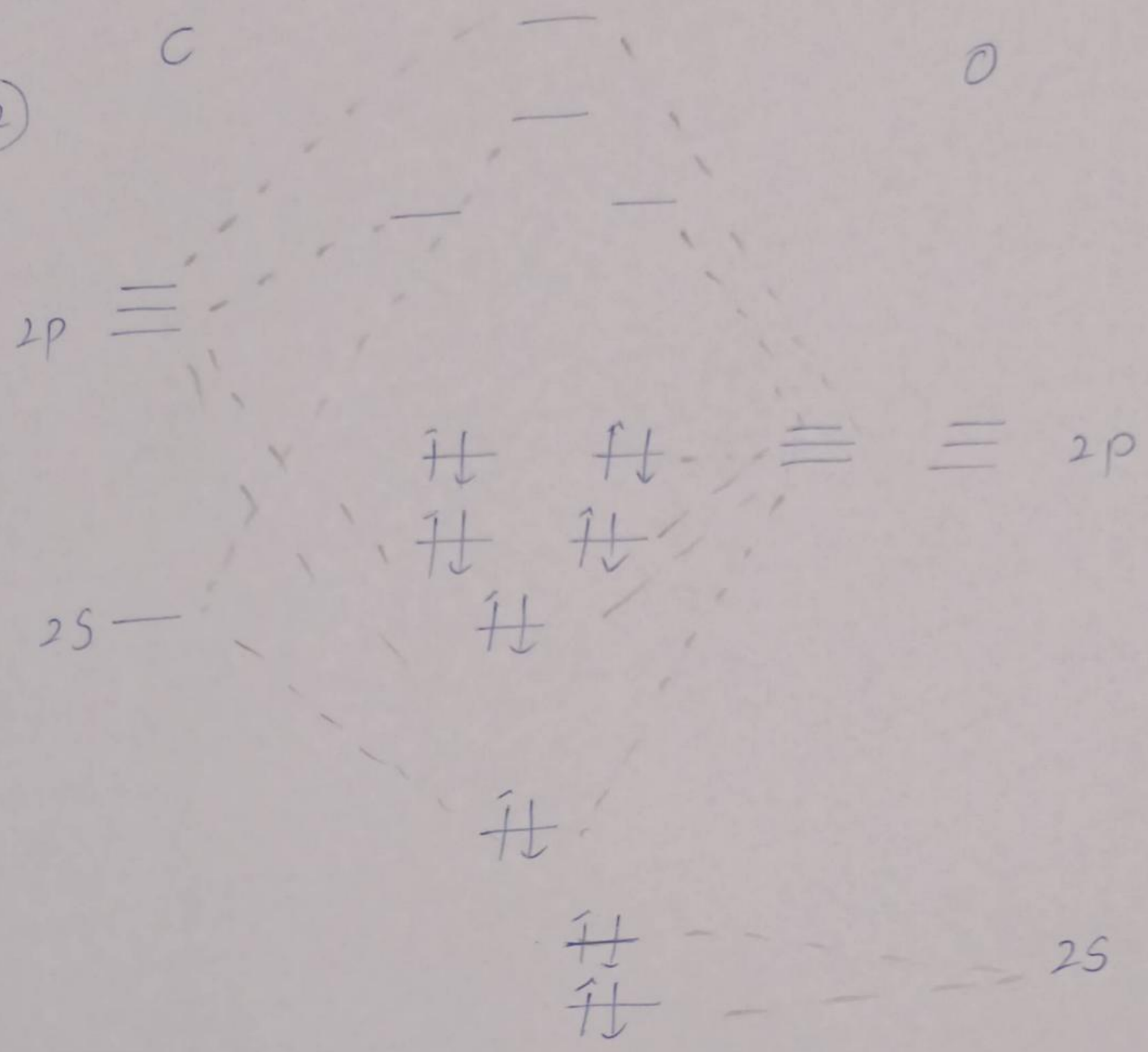
MM5003 - Assignment - 2

MM19B027 - Bhuvanesh. P

2)



Total orbital = 8 + 3 C (corresponding to 1s)

= 11 orbitals

Note :- Questions are Jumbled. Kindly Go through all

4)

a) For simple cubic

The reciprocal lattice vectors are

$$b_1 = 2\pi \times \frac{a \times a}{a^3} \qquad b_2 = \frac{2\pi}{a} \qquad b_3 = \frac{2\pi}{a}$$

Volume of first brillouin zone = $\frac{(2\pi)^3}{(a^3)}$

$(\vec{b_1} \cdot (\vec{b_2} \times \vec{b_3}))$

here $a = 2\,A^\circ$ so $V = \pi^3 \times 10^{-30}\ m^3$

b) For Bcc

$V_{BZ} = \frac{(2\pi)^3}{V_c}$ -> Primitive cell

$V_c = \vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})$

$\vec{a_1} = \frac{1}{2} a\,(-1, 1, 1)$

$\vec{a_2} = \frac{1}{2} a\,(1, -1, 1)$

$\vec{a_3} = \frac{1}{2} a\,(1, 1, -1)$

$V_{primitive\ bcc} = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{1}{2} a3$

$V_{BZ} = \frac{(2\pi)^3}{\frac{1}{2}(a^3)} = 2\pi^3 \times 10^{-30}\ m^3$

c) For FCC

Primitive Lattice vectors

$\vec{a}_1 = \frac{1}{2} a\,(1,0,1)$

$\vec{a}_2 = \frac{1}{2} a\,(1,1,0)$

$\vec{a}_3 = \frac{1}{2} a\,(0,1,1)$

$V_{primitive\ FCC} = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

$= \frac{1}{4} a^3$

$V_{BZ} = \frac{(2\pi)^3}{V_{primitive\ FCC}} = \frac{(2\pi)^3}{\frac{1}{4} a3}$

$= 4\pi^3 \times 10^{-30}\ m^3$

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8) Schrodinger Hamiltonian

$$H = -\sum \frac{\hbar^2}{2M_\nu} \nabla_\nu^2 - \sum \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum\sum \frac{e^2}{|r_i - r_j|}$$

$$- \sum\sum \frac{Z_\nu e^2}{|R_\nu - r_i|} + \frac{1}{2} \sum\sum \frac{Z_\nu Z_\mu e^2}{|R_\nu - R_\mu|}$$

Nuclear Kinetic Energy $= -\sum \frac{\hbar^2}{2M_\nu} \nabla_\nu^2$

Electronic Kinetic Energy $= -\sum \frac{\hbar^2}{2m} \nabla_i^2$

Nuclear - Nuclear Repulsion $= \frac{1}{2} \sum\sum \frac{Z_\nu Z_\mu e^2}{|R_\nu - R_\mu|}$

Electron - Electron Repulsion $= \frac{1}{2} \sum\sum \frac{e^2}{|r_i - r_j|}$

Electron - Nuclear Attraction $= -\sum \frac{Z_\nu e^2}{|R_\nu - r_i|}$

→ Hartee - Fock Hamiltonian

$$H = -\sum_{i=1}^{N} \frac{\hbar}{2m} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z_{n\nu} e^2}{|R_{n\nu} - r_i|} + \sum_{j+1}^{N} e^2 \int \frac{n_j(r_j)}{|r_i - r_j|} d^3 r_{ij}$$

Electronic Kinetic Energy $= -\sum_{i=1}^{N} \frac{\hbar}{2m} \nabla_i^2$

Electron Electron Repulsion $= \sum_{j+1}^{N} e^2 \int \frac{n_j(r_j)}{|r_i - r_j|} d^3 r_j$

Electron Nucleus Attraction $= -\sum_{i=1}^{N} \frac{Z_{n\nu} e^2}{|R_{n\nu} - r_i|}$

→ Hohenberg - Kohn Hamiltonian

$$H = -\frac{\hbar}{2m} \nabla^2 + \sum_{i=1}^{N} \frac{Z_{n\nu} e^2}{|R_{n\nu} - R_i|} + e^2 \int \frac{n(r_1)}{|r - r_1|} d^3 r_1$$

$$+ \frac{\partial E_{nc}[n(r)]}{\partial n(r)}$$

- Electronic Kinetic Energy $= -\frac{\hbar^2}{2m}\nabla^2$

- Electron Electron repulsion $= e^2 \int \frac{n(r')}{|r-r'|} d^3r'$

- Electron nucleus interaction $= \sum_{i=0}^{N} \frac{Z_\nu e^2}{|R_\nu - R_i|}$

- Quantum effects $= \frac{\partial E_{nc}[n(r)]}{\partial n(r)}$

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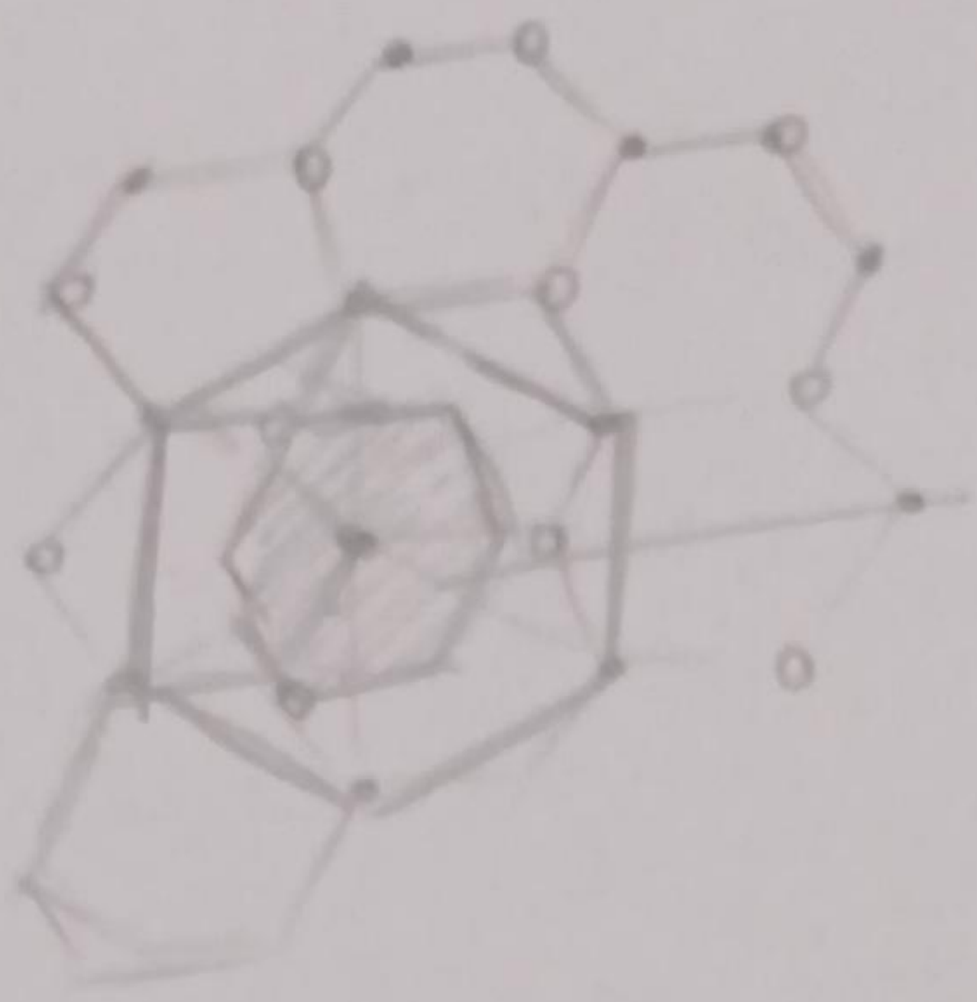
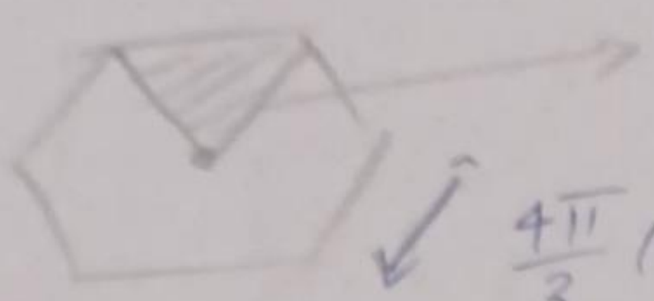
(9) Exchange - Co-relational functionals

- LDA - Local Density approximation
- GGA - Generalized Gradient approximation
- Hybrid Density functionals
- Meta generalized gradient approximation

5)



First Brillouin zone



$\frac{4\pi}{3}$ (A^{-1})

Irreducible Brillouin zone

Brillouin zone

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1) Only 1. Schrodinger equation will give analytical solution only if there no electron - electron interaction

11) $E_{cutoff} = \frac{\hbar^2 (\pi N)^2}{2m}$

$$250 \times 1.6 \times 10^{-19} = \left(\frac{6.625 \times 10^{-31}}{4\pi^2}\right)^2 \left((4\pi^2)/(2 \times 10^{-10})^2\right) \times N^2$$

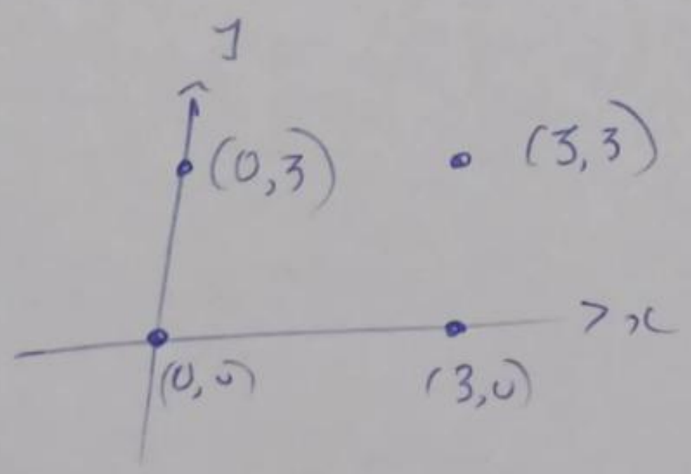
$$\times 9.1 \times 10^{-31}$$

$$N^2 = \frac{500 \times 1.6 \times 9.1 \times 10^{-50}}{(6.625 \times 2)^2 \times 10^{-48}}$$

$$= 6.6346$$

$$N \simeq 3$$

~~12~~)



Na = 11 protons

$$E_{NU} = \frac{1}{2} \sum\sum \frac{Z_i Z_2 e^2}{|r_i - r_j|}$$

$$V = \sum\sum \frac{Ze}{|r_i - r_j|}$$

$$= 1/e \left(\frac{1}{\sqrt{x^2+y^2}} + \frac{1}{\sqrt{(x-3)^2+y^2}} + \frac{1}{\sqrt{(x-3)^2+(y-3)^2}} + \frac{1}{\sqrt{(0)^2+(y-3)^2}} \right)$$

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b) The wave - particle duality forms the basis of the solution for electrons

- For explicit solution, the ~~depth~~ length of the well which corresponds to wavelength is necessary

- And of course fundamentally most of e^- is required

12) a) Yes - can be calculated

b) We optimize ($n^{(1)}$) before going for force ~~calculation~~ calculation, but still we can calculate, but not correct - Yes

c) No since its only for ground state - No

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10) ~~Yes, but~~ No, but it is advised ~~to use~~

Yes, it might lead to different pseudo potential, if some exchange co-relation is not used through-out

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3) We need a total of 6 equations, 1 for each electron No more than that.

14) Alternatives to DFT.

- Moller - Plesset Perturbation Theory
- Quadratic Configuration Interadim approach

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15) $\vec{a_1} = (3.2891030312, 0, 0)$

$\vec{b_2} = (-1.6445515156, 2.8484461806, 0)$

$\vec{b_3} = (0, 0, 5.3068203926)$

$b_1 = 2\pi \frac{(\vec{a_2} \times \vec{a_3})}{V}$ $b_2 = 2\pi \frac{(\vec{a_1} \times \vec{a_3})}{V}$ $b_3 = 2\pi \frac{(\vec{a_2} \times \vec{a_1})}{V}$

$V = \vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})$

$b_1 = 2\pi (1.905, 0, 0)$
$b_2 = 2\pi (0, 2.206, 0)$
$b_3 = 2\pi (0, 0, 1.184)$

} Final Answer

18) Since the no of atoms is more, the no of K points required will be reduced

$5 \times 3 \times 2$ → K points

13) The electron - electron interaction term would be absent in He^+ since it has only 1 electron, while it will be present in He as it has both the electrons