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Q1 a) $[y^2, \frac{\partial}{\partial y}]$

$$y^2 \frac{\partial}{\partial y} f - \frac{\partial}{\partial y} y^2 f = y^2 f' - (2yf + y^2 f') =$$

$$-2yf$$

$$[y^2, \frac{\partial}{\partial y}] = -2y$$

b) $Af = af$ and $Ag = ag$

$Ah = A(c_1 f + c_2 g) = c_1 Af + c_2 Ag = c_1 af + c_2 ag = a(c_1 f + c_2 g)$

Yes, h is an eigenfunction of A with eigen value a.

c) $\psi = \phi_1 + 2\phi_2$ $\langle \phi_1 | \phi_1 \rangle = \langle \phi_2 | \phi_2 \rangle = 1$ and $\langle \phi_1 | \phi_2 \rangle = 0.3$

$$\langle \phi_1 + 2\phi_2 | \phi_1 + 2\phi_2 \rangle = \langle \phi_1 | \phi_1 \rangle + 4 \langle \phi_2 | \phi_2 \rangle + 4 \langle \phi_1 | \phi_2 \rangle =$$

$$1 + 4 \cdot 1 + 4 \cdot 0.3 = 6.2$$

No, it is not normalized to 1.

$$N^2 \langle \psi | \psi \rangle = N^2 \cdot 6.2 = 1 \rightarrow N = \frac{1}{\sqrt{6.2}} = 0.4$$

$$\psi = 0.4\phi_1 + 0.8\phi_2 .$$

d) $\psi = \sin(3x)$ $P_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$

$P_x \psi = \frac{\hbar}{i} \frac{\partial}{\partial x} \sin(3x) = \frac{\hbar}{i} 3 \cos 3x$.   Not eigenfunction.

$$e^{ikx} = \cos(kx) + i \sin(kx)$$

$$e^{i3x} = \cos(3x) + i\sin(3x)$$

$$e^{-i3x} = \cos(+3x) \cancel{+} i \sin(3x)$$

$$e^{i3x} - e^{-i3x} = 2i\sin(3x) \rightarrow \sin(3x) = (e^{i3x} - e^{-3x}) \cdot \frac{1}{2i}$$

e^{i3x} and e^{-i3x} are eigenfunctions of P_x:

$$\frac{\hbar}{i}\frac{\partial}{\partial x} e^{i3x} = 3\hbar\, e^{i3x}$$

and

$$\frac{\hbar}{i}\frac{\partial}{\partial x} e^{-i3x} = -\cancel{k}3\hbar\, e^{-i3x}$$

In a measurement you would measure $3\hbar$ or $-3\hbar$.

The average is $\langle\psi|P_x|\psi\rangle = 0$.

Q2

a) $H^0 = -\frac{1}{2}\nabla^2 - \frac{1}{r}$

$V = \frac{1}{2}L_z B$

b) The is function.

c) $E^{(1)} = \langle\psi^0|V|\psi^{(0)}\rangle = \langle 1s|\frac{1}{2}L_z B|1s\rangle$

d) The other eigenfunctions of H^0: 2s, 2p, 3s, 3p, 3d etc.

Q3

a) $\psi = a\varphi_1 + b\varphi_2$ $\quad \langle\varphi_i|\varphi_j\rangle = \delta_{ij}$

$$\begin{vmatrix} -1.5-E & -0.25 \\ -0.25 & -1.0-E \end{vmatrix} = 0$$

$(-1.5-E)(-1.0-E) - (-0.25)^2 = 0 \iff$

$E^2 + 2.5E + \cancel{1.5} 1.4375 = 0 \iff$

$(E+1.25)^2 - 0.125 = 0 \iff$

$$(E+1.25)^2-(0.354)^2=0$$

$$(E+1.25-0.354)(E+1.25+0.354)=0$$

~~E= 0.896 V E=~~

$$E=-0.896 \quad \vee \quad E=-1.604$$

ground state.

b) $E=-1.604$

$$\begin{pmatrix} -1.5-(-1.604) & -0.25 \\ -0.25 & -1.0-(-1.604) \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}=0$$

$$\begin{pmatrix} 0.104 & -0.25 \\ -0.25 & 0.604 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}=0$$

$$\left.\begin{array}{l} 0.104c_1-0.25c_2=0 \\ -0.25c_1+0.604c_2=0 \end{array}\right\} \Rightarrow \begin{array}{l} c_1=2.404c_2 \\ c_1=2.4c_2 \end{array}$$

Normalise: $c_1^2+c_2^2=1 \rightarrow 5.78c_2^2+c_2^2=1 \rightarrow c_2=0.38$

$c_1=0.92$

$$\psi=0.92\,\phi_1+0.38\,\phi_2$$

Q4/

a)

	r (Å)	α (°)
1)	1.0	132
2)	1.8	140
3)	2.95	98
4)	2.5	85
TS1)	1.5	140
TS2)	2.8	90
TS3)	2.5	120
TS4)	1.5	90

~~Q~~

Answer sheet Question 4.

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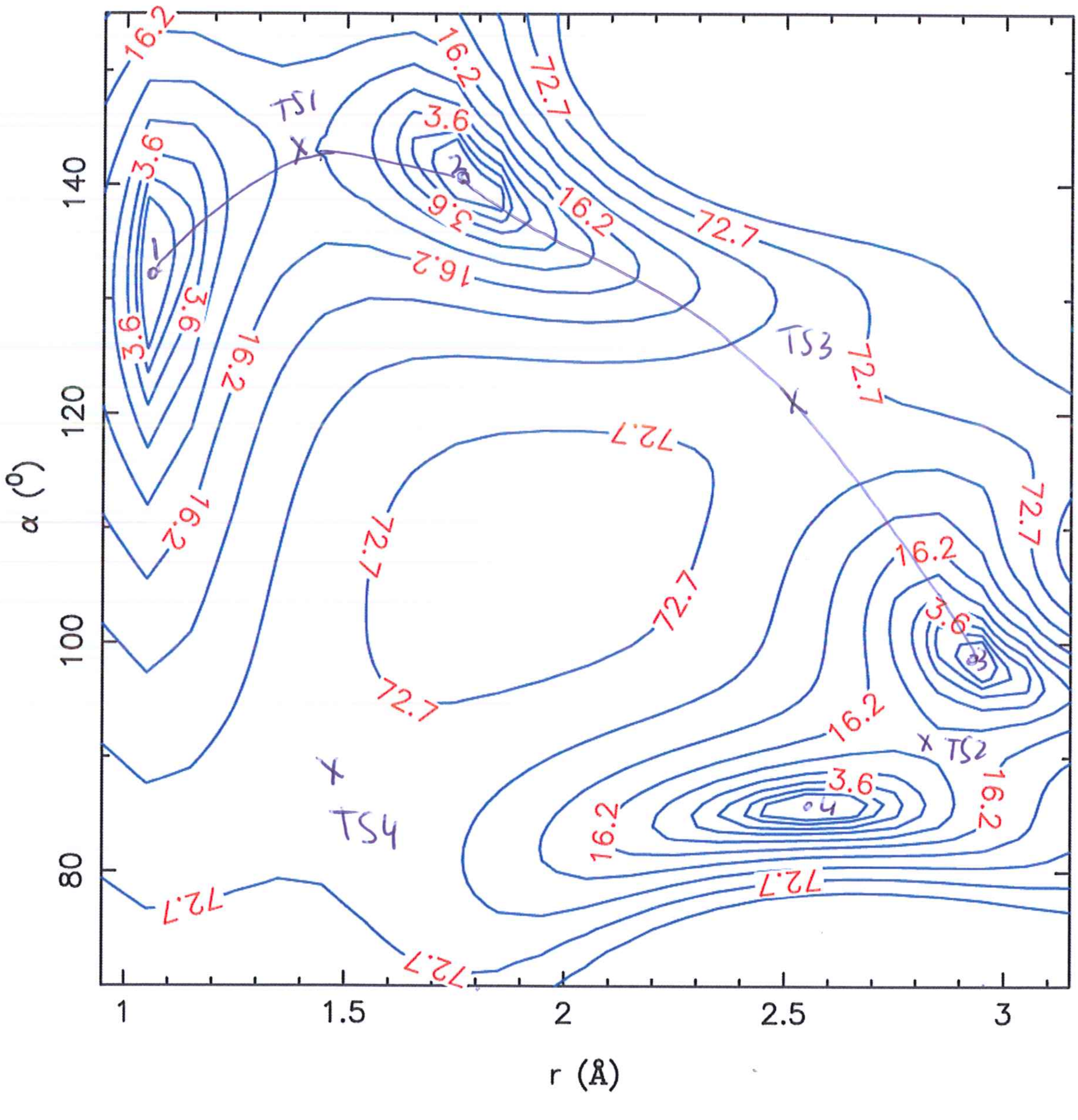
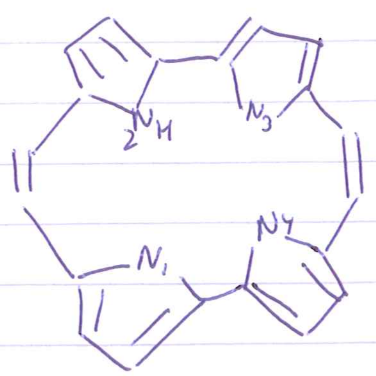
PES Porphycene(−1)



b) Intermediate



c) + Include correlation (MP2, DFT, SDCI)
+ Bigger basis set (6-31G** ~~*~~, etc.)

Q5/a) STO-3G minimal basis set, each shell only 1 function.
6-311G* Triple zeta basis; has polarization functions.
6-311G* is larger, gives a lower HF energy.

b) C/O: 1s 2s* 2s' 2s'' ~~*~~ 4
2p 2p' 2p'' 9
d 5 +
18 x 2 = 36 functions.

c) Sums go over the occupied ~~spin~~ spatial orbitals ($6+8=14/2=7$ in this case).

h_{ii} = 1-electron part: kinetic energy + nuclear-electron attraction
$(ii|jj)$: 2 electron integral: Coulomb integral: $e^- - e^-$ repulsion
$(ij|ji)$: 2 electron repulsion: Exchange integral.

d) $6+8 = 14/2 = 7$ occupied spatial orbitals:
$\Psi_{HF} = |a\bar{a}\, b\bar{b}\, c\bar{c}\, d\bar{d}\, e\bar{e}\, f\bar{f}\, g\bar{g}|$

e) Ψ_{HF} is not an eigenfunction of H. The orbitals are eigenfunctions of F. The eigenvalues are the orbital energies.

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f) P is the density matrix : $P_{\mu\nu} = \sum_i^{occ} 2 c_{i\mu} c_{i\nu}$

$$\sum_n 2(nn|ij) - (in|nj) = 2 \sum_n (nn|ij) - \frac{1}{2}(in|nj)$$

$$= \sum_{\mu\nu} P_{\mu\nu}[(\mu\nu|ij) - \frac{1}{2}(i\mu|\nu j).$$

Q6

a) $2^3 = 8$.

$\langle S^2 \rangle = S(S+1)$

b) $\alpha\alpha\alpha$ — $S = \frac{3}{2} \rightarrow S^2 = \frac{15}{4}$ $S_z = \frac{3}{2}$ * Quartet

$\alpha\alpha\beta$	$S^2 = \frac{15}{4}$	$S_z = \frac{1}{2}$	1 quartet comp.
$\alpha\beta\alpha$	$S^2 = \frac{3}{4}$	$S_z = \frac{1}{2}$	1 doublet
$\beta\alpha\alpha$	$S^2 = \frac{3}{4}$	$S_z = \frac{1}{2}$	1 doublet
$\alpha\beta\beta$	$S^2 = \frac{15}{4}$	$S_z = -\frac{1}{2}$	1 quartet comp
$\beta\alpha\beta$	$S^2 = \frac{3}{4}$	$S_z = -\frac{1}{2}$	1 doublet
$\beta\beta\alpha$	$S^2 = 3/4$	$S_z = -\frac{1}{2}$	1 doublet

$\beta\beta\beta$ — $S = \frac{3}{2} \rightarrow S^2 = \frac{15}{4}$ $S_z = -\frac{3}{2}$ * Quartet

1 Quartet : $S^2 = \frac{15}{4}$ $S_z : \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

2 doublets : $S^2 = \frac{3}{4}$ $S_z = \frac{1}{2}, -\frac{1}{2}$.

c) $M_s : \frac{1}{2}$ for quartet : start with $\alpha\alpha\alpha$

$S_-(1,2,3)\,\alpha\alpha\alpha = \alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha.$

Q7)

a) Insulator: large band gap.

b) For C: 5 functions
H: 1 function.

$Z=4$: $C_{18}H_{12}$: $4 \times 18 = 72$ C atoms $\times 5 = 360$
$4 \times 12 = 48$ H atoms $\times 1 = 48$ +
408 functions in unit cell.

So in total 408 bands.
All the other bands ~~flat~~ are not within the energy range of the plot.

c) No interaction → flat bands