1 a. $[x, \frac{d^2}{dx^2}]\psi = (x\frac{d^2}{dx^2}\psi - \frac{d^2}{dx^2}x\psi) =$

$= x\frac{d^2}{dx^2}\psi - \frac{d}{dx}\frac{d}{dx}(x\psi) = x\frac{d^2}{dx^2}\psi - \frac{d}{dx}(\psi + x\frac{d\psi}{dx}) =$

$= x\frac{d^2}{dx^2}\psi - \frac{d\psi}{dx} - \frac{d\psi}{dx} - x\frac{d^2}{dx^2}\psi = -2\frac{d\psi}{dx}$

$[x, \frac{d^2}{dx^2}] = -2\frac{d}{dx}$

b. i $f(x) = ax + b$

$\frac{d f(x)}{dx} = a \neq c \cdot f(x)$ not an eigenfunction!

ii $g(x) = e^{ax}$

$\frac{d g(x)}{dx} = a e^{ax} = c \cdot g(x)$ eigenfunction, eigenvalue a.

iii. $h(x) = e^{ax^2}$

$\frac{d h(x)}{dx} = 2x \cdot e^{ax^2} \neq c \cdot h(x)$ not an eigenfunction.

c. $f(\varphi) = Ne^{i\varphi}$

$$1 = N^2 \int_0^{2\pi} (e^{i\varphi})^* (e^{i\varphi}) d\varphi = N^2 \int_0^{2\pi} \underbrace{e^{-i\varphi} \cdot e^{i\varphi}}_{1} d\varphi = N^2 \int_0^{2\pi} d\varphi =$$

$$1 = N^2 \cdot 2\pi$$

$$N^2 = \frac{1}{2\pi} \qquad N = \frac{1}{\sqrt{2\pi}}$$

$$f(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i\varphi}$$

d. the probability that the particle will be found in a volume element $d\tau$ is proportional to

$$|\Psi(r)|^2 d\tau$$

i) $\psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1$

$$\Psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{L}\right)$$

$$|\Psi(x)|^2 = \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) dx$$

ii) $x = \frac{L}{2} \qquad \psi\left(\frac{L}{2}\right) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin \frac{\pi \cdot \cancel{L}}{2\cancel{L}} = \left(\frac{2}{L}\right)^{\frac{1}{2}} \underbrace{\sin\left(\frac{\pi}{2}\right)}_{1} =$

$$= \left(\frac{2}{L}\right)^{\frac{1}{2}}$$

$$\left|\Psi\left(\frac{L}{2}\right)\right|^2 = \frac{2}{L} dx$$

2 a) He

$$\hat{H} = -\frac{1}{2}\vec{\nabla}_1^2 - \frac{1}{2}\nabla_2^2 - \underbrace{\frac{2}{r_1}}_{Z=2} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

$$\quad (1) \qquad (2) \qquad (3) \qquad (4) \qquad (5)$$

1, 2 - kinetic energy of electrons 1 and 2

3, 4 - attractive potential between electrons 1 and 2 and the nucleus ($Z=2$)

5 - repulsion between the electrons.

b). $\hat{H}^0 = -\frac{1}{2}\vec{\nabla}_1^2 - \frac{1}{2}\vec{\nabla}_2^2 - \frac{2}{r_1} - \frac{2}{r_2} = h(1) + h(2)$

$V = +\frac{1}{r_{12}}$

~~the~~ H^0 describes 2 non interacting electrons in the field of helium nucleus. V is the repulsion between the electrons. ~~Then~~ $h(1)$ and $h(2)$ describe He^+ ions.

c) $\epsilon^1 = \langle \Psi_0 | V | \Psi_0 \rangle$

3.

a).

$$\begin{vmatrix} H_{11} - WS_{11} & H_{12} - WS_{12} \\ H_{21} - WS_{21} & H_{22} - WS_{22} \end{vmatrix} = 0$$

$\varphi_1 = p_z(O)$

$\varphi_2 = p_z(C)$

4

$H_{11} = \langle \varphi_1 | H | \varphi_1 \rangle$

$H_{12} = \langle \varphi_1 | H | \varphi_2 \rangle = H_{12}$

$H_{22} = \langle \varphi_2 | H | \varphi_2 \rangle = H_{22}$

$S_{11} = \langle \varphi_1 | \varphi_1 \rangle$

etc.

~~b)~~.

b. $H_{11} = -1$ eV $\qquad S_{ij} = \delta_{ij}$

$H_{22} = 0$

$H_{12} = H_{21} = -0{,}5$ eV

$$\begin{vmatrix} -1 - W & -0{,}5 \\ -0{,}5 & -W \end{vmatrix} = 0$$

$-w(-1-w) - 0{,}5^2 = 0$

$w + w^2 - 0{,}5^2 = 0$

$w^2 + w - 0{,}5^2 = 0$

$$w = \frac{-1 \pm \sqrt{1 + 4 \cdot 1 \cdot 0{,}5^2}}{2 \cdot 1} = \frac{-1 \pm \sqrt{1+1}}{2} = \frac{-1 \pm \sqrt{2}}{2}$$

$$W_{ground} = \frac{-1 - \sqrt{2}}{2} = -1{,}21 \text{ eV}$$

This energy should be <u>higher</u> than the true ground state energy.

3 c.

$$\begin{pmatrix} -1+1{,}21 & -0{,}5 \\ -0{,}5 & +1{,}21 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$0{,}21\, c_1 - 0{,}5\, c_2 = 0$ $\quad$ $0{,}21\, c_1 = 0{,}5\, c_2$ $\quad$ $\boxed{c_2 = 0{,}42\, c_1}$

$-0{,}5\, c_1 + 1{,}21\, c_2 = 0$

From normalization:

$c_1^2 + c_2^2 = 1$ $\quad$ $c_1^2 + 0{,}42^2 c_1^2 = 1$

$\cancel{4{,}4}$ $1{,}18\, c_1^2 = 1$

$c_1^2 = 0{,}85$

$c_1 = 0{,}92$

$c_2 = 0{,}387$

$$\psi = 0{,}92\, \varphi_1 + 0{,}39\, \varphi_2 = 0{,}92\, p_z(O) + 0{,}39\, p_z(C)$$

(4). a). STO-3G minimal basis set

C: 1s, 2s, 2px, 2py, 2pz => 5

H: 1s => 1

$5 \cdot 2 + 6 \cdot 1 = 16$ orbitals.

b) 8 atoms

number of vib. modes: $3N-6$

$3 \cdot 8 - 6 = 24 - 6 = 18$

c). $\Delta E = (-78{,}3016 + 0{,}08931) - (-78{,}3062 + 0{,}0897) =$

$= 0.00418$ a.u.

1 au = 627,52 kcal/mol

$\Delta E = 2{,}626$ kcal/mol.

d.) 6-31G*

C: 1s, 2s, 2s'', 2px, 2py, 2pz, 2px', 2py', 2pz,

3d×5 = 14

H: 1s, 1s' = 2

$2 \cdot 14 + 6 \cdot 2 = 40$

Fb

e). $2e^-$ - integrals: $\frac{m^4}{8}$

STO-3G: $\frac{18^4}{8} = 13122$

6-31G** $\frac{40^4}{8} = 320000$

Factor of 25!

5. a. H - 1 $\bar{e}$

F - 9 $\bar{e}$

1+9 = 10e 2e per orbital - 5 occupied spatial orbitals:

$$\Psi_{HF}(HF) = |a\bar{a}\, b\bar{b}\, c\bar{c}\, d\bar{d}\, e\bar{e}|$$

b. h_{ii} - 1 electron part: kinetic energy + nucleus-electron attraction.

$$\cancel{h_{ii}}\ h_{ab} = \int a^*(1)\, h(1)\, b(1)\, d\tau_1$$

$$h_{ii} = \int i^*(1)\, h(1)\, i(1)\, d\tau_1$$

$(ii|jj)$ - 2 electron Coulomb integral: $\bar{e} - \bar{e}$ repulsion.

$$(ab|cd) = \iint a^*(1) b(1) \frac{1}{r_{12}} c^*(2) d(2) d\tau_1 d\tau_2$$

$$(ii|jj) = \iint i^*(1) i(1) \frac{1}{r_{12}} j^*(2) j(2) d\tau_1 d\tau_2$$

$(ij|ji)$ - 2 electron repulsion - exchange integral.

$$(ij|ji) = \iint i^*(1) j(1) \frac{1}{r_{12}} j^*(2) i(2) d\tau_1 d\tau_2 .$$

The summation runs over all the occupied orbitals (spatial orbitals), in this case 5.

c. For closed shells, the energy needed to remove an electron from orbital i is equal to the orbital energy:

$$IP_i = -\varepsilon_i = -(h_{ii} + \sum_j [2(ii|jj) - (ij|ji)]$$

d. We would not expect HF to perform well for dissociation of ~~the molecules~~ a closed-shell molecule. This is due to the fact that we start out with a single determinant, which is not appropriate for description of two open shell atoms at dissociation limit.

e.

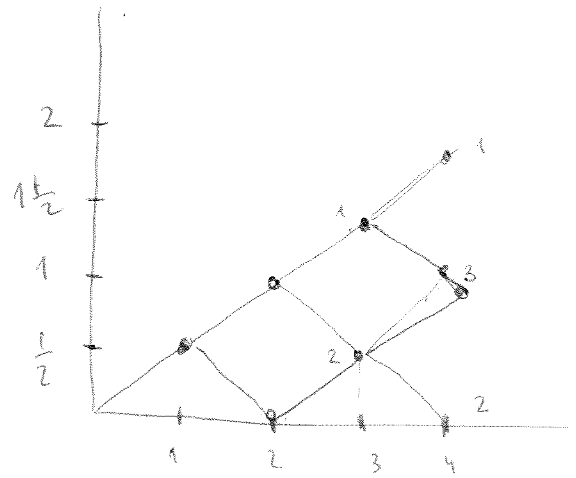
---

6. a $2^4 = 16$

(Or, explicitly: $\alpha\alpha\alpha\alpha$, $\beta\beta\beta\beta$ etc.. should still give 16.

$S^2 = S(S+1)$, $S_z = -S, \ldots +S$

b.



1 quintet $(S=2)$

$S^2 = 2(2+1) = 6$

~~M_S~~ $= -2, -1, 0, 1, 2$

3 triplets

$S^2 = 1(1+1) = 2$

~~M_S~~ ~~S_z~~ $M_S = -1, 1, 0$

2 singlets

$S^2 = 0$

$M_S = 0$

c. Highest multiplet: $S=2$

Start with $M_S = 2$, $\sigma = \alpha\alpha\alpha\alpha$

$$S_-(1,2,3,4)\,\alpha\alpha\alpha\alpha = \beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta$$

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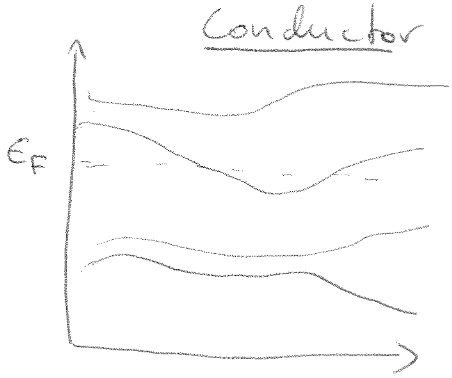
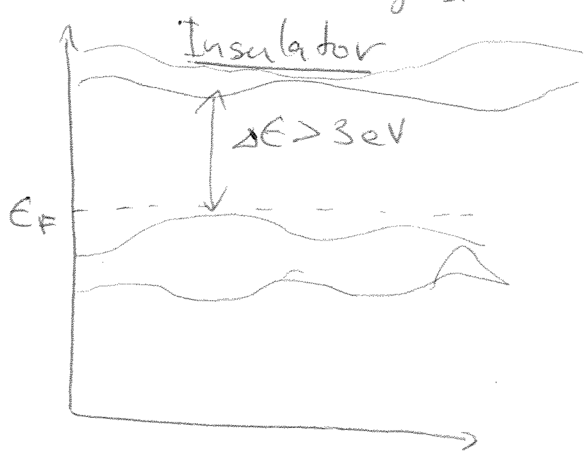
7. a) On the x-axis we have the k-vector, and in particular special symmetry points in the Brillouin zone (i.e. Γ - center of BZ, etc)
On the y axis we have the orbital energies.

b).





c. 2 atom × 10 = 20 bands

Na - 11 $\bar{e}$
Cl - 17 $\bar{e}$ } $28\bar{e}$ ~~[illegible]~~

2 electrons per band - 14 bands below the Fermi level.