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1a) $[x, x\frac{\partial}{\partial x}] = x^2\frac{\partial}{\partial x} f - x\frac{\partial}{\partial x} xf = x^2\frac{\partial f}{\partial x} - \left[xf + x^2\frac{\partial f}{\partial x}\right] =$

$-xf$

$[x, x\frac{\partial}{\partial x}] = -\hat{x}$

b) $[A, B] = 0$

$Af = af$

$Bf = f + g$

$ABf = BAf$

$\downarrow = Baf = aBf$

$A(f+g) = Af + Ag = af + Ag = aBf$

$aBf = a(f+g) = af + ag = af + Ag \longrightarrow Ag = ag.$

Yes, g is an eigenfunction of A with eigenvalue a.

c) $\psi = \phi_1 + 2\phi_2$ $\quad \langle\phi_1|\phi_1\rangle = \langle\phi_2|\phi_2\rangle = 1$ and $\langle\phi_1|\phi_2\rangle = 0$

$\langle\psi|\psi\rangle = \langle\phi_1 + 2\phi_2 | \phi_1 + 2\phi_2\rangle = \langle\phi_1|\phi_1\rangle + 4\langle\phi_2|\phi_1\rangle + 4\langle\phi_2|\phi_2\rangle = 1 + 0 + 4 = 5$

No, ψ is not normalised.

$N^2\langle\psi|\psi\rangle = 1 \longrightarrow N^2 \cdot 5 = 1 \rightarrow N = \frac{1}{\sqrt{5}}$

$\frac{1}{5}\sqrt{5}(\phi_1 + 2\phi_2) = \frac{1}{5}\sqrt{5}\,\phi_1 + \frac{2}{5}\sqrt{5}\,\phi_2.$

d) $\psi = e^{i2x}$

$P_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$ $\qquad P_x\psi = \frac{\hbar}{i}\frac{\partial}{\partial x} e^{i2x} = i2\frac{\hbar}{i} e^{i2x} =$

$2\hbar e^{i2x}$

You would measure $2\hbar$.

$\langle P_x\rangle = \langle e^{-i2x} | \frac{\hbar}{i}\frac{\partial}{\partial x} e^{i2x}\rangle / \langle e^{-i2x}|e^{i2x}\rangle = 2\hbar.$

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

$V = 2L_2 F$

b) ψ_0 is the 1s function.

c) $E^{(1)} = \langle \psi_0 | V | \psi_0 \rangle = \langle \psi_0 | 2L_2 F | \psi_0 \rangle = \langle 1s | 2L_2 F | 1s \rangle$

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

3a) $\psi = a\phi_1 + b\phi_2 \quad \langle \phi_1 | \phi_1 \rangle = \langle \phi_2 | \phi_2 \rangle = 1 \quad \langle \phi_1 | \phi_2 \rangle = 0$

$$\begin{vmatrix} -1-E & -1 \\ -1 & -E \end{vmatrix} = 0$$

$$-E(-1-E) - (-1)^2 = 0$$

$$E^2 + E - 1 = 0$$

$$(E+\tfrac{1}{2})^2 - \tfrac{1}{4} - \tfrac{4}{4} = 0$$

$$(E+\tfrac{1}{2})^2 - (\tfrac{1}{2}\sqrt{5})^2 = 0$$

$$(E + \tfrac{1}{2} - \tfrac{1}{2}\sqrt{5})(E + \tfrac{1}{2} + \tfrac{1}{2}\sqrt{5}) = 0$$

$E = -\frac{1}{2} - \frac{1}{2}\sqrt{5}$ V $E = -\frac{1}{2} + \frac{1}{2}\sqrt{5}$

$E = -1.62$ V $E = 0.62$

ground state.

b) $\begin{pmatrix} -1 - -1.62 & -1 \\ -1 & - -1.62 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$

$\begin{pmatrix} 0.62 & -1 \\ -1 & 1.62 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$

$0.62c_1 - c_2 = 0 \longrightarrow c_2 = 0.62c_1$

$-c_1 + 1.62c_2 = 0$

$c_1^2 + c_2^2 = 1$

$c_1^2 + (0.62c_1)^2 = 1 \longrightarrow c_1 = 0.85$

$c_2 = 0.53$

$\psi = 0.85\phi_1 + 0.53\phi_2$

4a) Line A : HF : does not dissociate properly to the atoms
Line B : CI : proper dissociation curve.

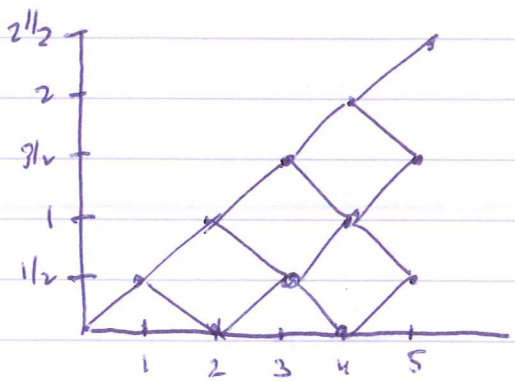
b) ~ 100 kcal/mol (read from Figure).

c) - Better basis set
- Include zero-point vibrational energy.

d) The CI gives a lower total energy because electron correlation is included.

5a) $2^5 = 32$.

b).



1 sextet : 6

4x quartet : 4x4 = 16

5x doublet : 5x2 = 10

+

32.

c) $M_S = -3/2$. highest multiplet sextet: $\beta\beta\beta\beta\beta$ $M_S = -\frac{5}{2}$

So $S_+(1,2,3,4,5)\,\beta\beta\beta\beta\beta = \alpha\beta\beta\beta\beta + \beta\alpha\beta\beta\beta + \beta\beta\alpha\beta\beta +$

$\beta\beta\beta\alpha\beta + \beta\beta\beta\beta\alpha$.

6) a) 6-31G has no polarization functions while 6-31G* has polarization functions (a d function on both atoms)

~~b)~~ The 6-31G* has more functions → lower energy.

b) 1S : 1
2S : 1
2S' : 1
2P : 3
2P' : 3
d : 5
+
14 functions per atom : 2 atoms 2×14 = 28.

c). h_{II} is the one-electron integral that contains the kinetic energy and the electron-nuclear attraction energy for an electron in spinorbital I.
(II|JJ) : electron-electron repulsion (coulomb) between electrons in orbital I and J.
(IJ|JI) : $e^- - e^-$ repulsion (exchange)

the summations go over all occupied spinorbitals.

a). N: 7 electrons, O 8 electrons → 15 electrons.
7 doubly occupied levels + 1 singly occupied orbital.

$\Psi_{HF} = |a\bar{a}\, b\bar{b}\, c\bar{c}\, d\bar{d}\, e\bar{e}\, f\bar{f}\, g\bar{g}\, h|$.

e). A lower energy as spin polarization is included.

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7a). A conductor. There is no band gap.

b). 4 bands are all valence bands.
For one atom we expect to see 5 bands, one of those bands corresponds to the 1s ((core)). So 4 valence band per atom ⇒ 1 atom in the unit cell.
The 1s is so low in energy that it is not shown in the energy range plotted on the figure.