

Chapter 9
Ab Initio and Density Functional Methods
Homework Solutions

1. Please see the PowerPoint slides and class notes for answers to these qualitative questions.
2.
 - (a) STO-3G: PH_2F
H: 2 STOs (1s) [one on each H]
F: 5 STOs: 1s + 2s + 2p (3)
P: 9 STOs: 1s + 2s + 2p (3) + 3s + 3p(3)
Total: $2 + 5 + 9 = 16$ atomic orbitals
 - (b) PH_2F has a total of: $15 + 2 \times 1 + 9 = 26$ electrons
Because 16 atomic orbitals are used, 16 MOs will be formed
13 of these orbitals are occupied (containing the 26 electrons). 3 orbitals are unoccupied.
 - (c) 3-21G
The "3" means that core electrons are characterized by a single STO of each type, comprised by a fixed linear combination of 3 GTOs
The 21 means that 2 STOs of each type are used to characterize valence shell electrons.
The inner STO is a combination of 2 GTOs. The outer STO is a single GTO.
 - (d) PH_3 : 6-31G(2d,p)
H: 2 1s STOs (doubly split valence)
1 x 3 2p STOs (one set of polarization functions)
Total H: $3 \times (2 + 3) = 15$ basis functions

P: 1 1s STO (core)
1 2s STO (core)
3 2p STO (core)
2 x 3s STO (doubly split valence)
2 x 3 3p STO (doubly split valence)
2 x 5 3d STO (two sets of polarization functions)
Total P: $1 + 1 + 3 + 2 + 6 + 10 = 23$ basis functions

(e) PH₃: 6-311++G

H: 3 1s STOs (triply split valence)

1 s (diffuse orbital)

Total H: 3 x (3+1) = 12 basis functions

P: 1 1s STO (core)

1 2s STO (core)

3 2p STO (core)

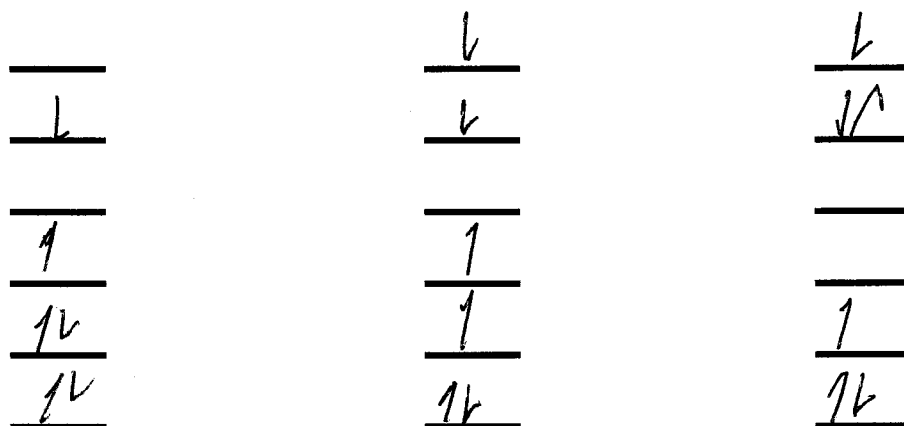
3 x 3s STO (triply split valence)

3 x 3 3p STO (triply split valence)

1 s + 3 p STO (diffuse orbitals)

Total P: 1 + 1 + 3 + 3 + 9 + 4 = 21 basis functions

3. (a) Singly Excited Config. (b) Doubly Excited Config. (c) Triply Excited Config.



(d) CISD represents Configuration Interaction with Single and Double Excited Configurations. Therefore, the Triply Excited Configuration above would **not** be used in the calculation.

4. N₂(g) + 3 H₂(g) ⇌ 2 NH₃(g)

(a) Entropy change, ΔS°

$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= 2(233.3 \text{ J / mol} \cdot \text{K}) - [(215.1 \text{ J / mol} \cdot \text{K} + 3(153.7 \text{ J / mol} \cdot \text{K})] \\ &= -209.6 \text{ J / mol} \cdot \text{K}\end{aligned}$$

(b) Enthalpy Change, ΔH°

Let's convert E_{el} to $H^\circ(673K)$ for reactants and products.

$$\begin{aligned} N_2 : H^\circ(N_2, 673K) &= E_{el} + E_{ZPE}(vib) + E_{therm}(673K) + PV(673K) \\ &= -109.372 + 0.006 + 0.005 + 0.002 = -109.359 a.u. \end{aligned}$$

$$\begin{aligned} H_2 : H^\circ(H_2, 673K) &= E_{el} + E_{ZPE}(vib) + E_{therm}(673K) + PV(673K) \\ &= -1.171 + 0.009 + 0.005 + 0.002 = -1.155 a.u. \end{aligned}$$

$$\begin{aligned} NH_3 : H^\circ(NH_3, 673K) &= E_{el} + E_{ZPE}(vib) + E_{therm}(673K) + PV(673K) \\ &= -56.471 + 0.033 + 0.005 + 0.002 = -56.429 a.u. \end{aligned}$$

$$\begin{aligned} \Delta H^\circ &= 2H^\circ(NH_3) - [H^\circ(N_2) + 3H^\circ(H_2)] \\ &= 2(-56.429 a.u.) - [(-109.359 a.u.) + 3(-1.155 a.u.)] \\ &= -0.034 a.u. \cdot \frac{2625 kJ / mol}{1 a.u.} = -89.25 kJ / mol = -8.925 \times 10^4 kJ / mol \end{aligned}$$

Note that ΔH° is significantly different from ΔE_{el} , which is the energy difference without corrections for ZPE, thermal energy and conversion from energy to enthalpy.

$$\begin{aligned} \Delta E_{el} &= 2E_{el}(NH_3) - [E_{el}(N_2) + 3E_{el}(H_2)] \\ &= 2(-56.471 a.u.) - [(-109.372 a.u.) + 3(-1.171 a.u.)] \\ &= -0.057 a.u. \cdot \frac{2625 kJ / mol}{1 a.u.} = -149.6 kJ / mol \end{aligned}$$

(c) Equilibrium Constant, K_{eq}

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -8.925 \times 10^4 J / mol - (673K)(-209.6 J / mol \cdot K) \\ &= +5.181 \times 10^4 J / mol \end{aligned}$$

$$\Delta G^\circ = -RT \ln K_{eq} \rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT} = -\frac{5.181 \times 10^4 J / mol}{(8.31 J / mol \cdot K)(673K)} = -9.26$$

$$\text{Therefore: } K_{eq} = e^{-9.26} = 9.5 \times 10^{-5}$$