Modern Quantum Chemistry, Szabo & Ostlund

HW

wsr

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Ex C.1

(a)

$$\begin{aligned}\mathbf{H} &= \begin{pmatrix} \dfrac{\partial^2 E}{\partial x^2} & \dfrac{\partial^2 E}{\partial x \partial y} \\ \dfrac{\partial^2 E}{\partial y \partial x} & \dfrac{\partial^2 E}{\partial y^2} \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \end{aligned} \tag{C.5.1}$$

$$\begin{aligned}\mathbf{f}(\mathbf{X}) &= \begin{pmatrix} \dfrac{\partial E}{\partial x} \\ \dfrac{\partial E}{\partial y} \end{pmatrix} \\ &= \begin{pmatrix} K(x-a) + K''y \\ K'(y-b) + K''x \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} - \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \mathbf{X} - \begin{pmatrix} Ka \\ K'b \end{pmatrix} \end{aligned} \tag{C.5.2}$$

$$\begin{aligned}\mathbf{q} &= -\mathbf{H}^{-1}\mathbf{f} \\ &= -\mathbf{X} + \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}^{-1} \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2} \begin{pmatrix} K' & -K'' \\ -K'' & K \end{pmatrix} \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2} \begin{pmatrix} KK'a - K'K''b \\ -KK''a + KK'b \end{pmatrix} \\ &= -\mathbf{X} + \frac{1}{KK' - K''^2} \begin{pmatrix} KK' & -K'K'' \\ -KK'' & KK' \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \end{aligned} \tag{C.5.3}$$

(b) Since $\mathbf{q} = \mathbf{X}_e - \mathbf{X}$,

$$\begin{aligned}\mathbf{X}_e &= \frac{1}{KK' - K''^2} \begin{pmatrix} KK' & -K'K'' \\ -KK'' & KK' \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \\ &= \frac{1}{0.1 - K''^2} \begin{pmatrix} 0.1 & -0.1K'' \\ -K'' & 0.1 \end{pmatrix} \begin{pmatrix} 3 \\ 2 \end{pmatrix} \end{aligned} \tag{C.5.4}$$

K''	$\mathbf{X}_e = (x_e, y_e)$
0	(3.000, 2.000)
0.010	(2.983, 1.702)
0.030	(2.967, 1.110)

Ex C.2

$$\begin{aligned}\mathbf{H} &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix} \\ &= \begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix}\end{aligned} \tag{C.5.5}$$

$$\begin{aligned}\mathbf{f} &= \begin{pmatrix} K & K'' \\ K'' & K' \end{pmatrix}\mathbf{X} - \begin{pmatrix} Ka \\ K'b \end{pmatrix} \\ &= \begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix}\begin{pmatrix} 3.3 \\ 1.8 \end{pmatrix} - \begin{pmatrix} 1.000 \times 3.00 \\ 0.100 \times 2.00 \end{pmatrix} \\ &= \begin{pmatrix} 0.354 \\ 0.079 \end{pmatrix}\end{aligned} \tag{C.5.6}$$

$$\begin{aligned}\mathbf{q} &= -\mathbf{H}^{-1}\mathbf{f} \\ &= -\begin{pmatrix} 1.000 & 0.030 \\ 0.030 & 0.100 \end{pmatrix}^{-1}\begin{pmatrix} 0.354 \\ 0.079 \end{pmatrix} \\ &= \big(-0.333, -0.690\big)\end{aligned} \tag{C.5.7}$$

thus

$$\begin{aligned}\mathbf{X}_e &= \mathbf{q} + \mathbf{X} \\ &= \big(2.967, 1.110\big)\end{aligned} \tag{C.5.8}$$

which agrees with the result in Ex C.1(b).

Ex C.3 A program is written to solve this problem, which is `C-3.py`.
For example, run the program by `python C-3.py 0.03`, and the Nelder-Mead optimization steps will be printed for $K'' = 0.03$.

Ex C.4 A program is written to solve this problem, which is `C-4.py`.
For example, run the program by `python C-4.py`, and the MS optimization steps will be printed.

C.6 Transition States

C.7 Constrained Variation

D Molecular Integrals for H_2 as a Function of Bond Length