Modern Quantum Chemistry, Szabo & Ostlund
HW

wsr

May 15, 2020

Contents

A Integral Evaluation with 1s Primitive Gaussians

B 2-Electron Self-consistent-field Program

C Analytic Derivative Methods and Geometry Optimization

C.1 Introduction

C.2 General Considerations

C.3 Analytic Derivatives

C.4 Optimization Techniques

C.5 Some Optimization Algorithms

Ex C.1

(a)

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

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

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

Ex C.2

Ex C.3

Ex C.4