Supporting Information: Economical Models for Electron Densities

Ellena K. G. Black and Peter M. W. Gill*

School of Chemistry, University of Sydney, Camperdown, NSW 2006, Australia

E-mail: p.gill@sydney.edu.au

Phone: +61 2 8627 9486

1 Supporting Information : The Golub-Welsch algorithm

In the modeling methodology discussed in this paper, we use Gauss-Christoffel quadrature theory to construct initial guesses for exponents (β_i) and initial guesses for the centers (B_i). In each case, we must construct the m Gauss-Christoffel roots x_i and weights w_i from the first $2m+1$ moments

$$\mu_l = \int_a^b x^l w(x)\, dx \qquad (l = 0, 1, \ldots, 2m) \tag{1}$$

of the relevant weight function $w(x)$. Here, for the reader's convenience, we summarize the Golub-Welsch algorithm[?] for this task. To illustrate the algorithm, we apply it to the case where $w(x) = -\ln x$ on $[0, 1]$ and $m = 3$ and obtain results that agree with those in Table I of the 1965 paper by Anderson.[?]

Step 1: Use the moments $\mu_0, \mu_1, \ldots, \mu_{2m}$ to form an $(m+1) \times (m+1)$ Hankel matrix

$$\mathbf{H} = \begin{pmatrix} 1 & 1/4 & 1/9 & 1/16 \\ 1/4 & 1/9 & 1/16 & 1/25 \\ 1/9 & 1/16 & 1/25 & 1/36 \\ 1/16 & 1/25 & 1/36 & 1/49 \end{pmatrix} \tag{2}$$

Step 2: Form the diagonal and sub-diagonals of the Cholesky triangle of $\mathbf{H}$

$$\mathbf{L} = \begin{pmatrix} 1.000\,000 & 0 & 0 & 0 \\ 0.250\,000 & 0.220\,479 & 0 & 0 \\ - & 0.157\,485 & 0.053\,411 & 0 \\ - & - & 0.064\,081 & 0.013\,162 \end{pmatrix} \tag{3}$$

Step 3: Form a symmetric $m \times m$ tridiagonal matrix with diagonal elements equal to the differences of the ratios $L_{i+1,i}/L_{i,i}$ and subdiagonal elements equal to the ratios $L_{i+1,i+1}/L_{i,i}$

$$\mathbf{T} = \begin{pmatrix} 0.250\,000 & 0.220\,479 & 0 \\ 0.220\,479 & 0.464\,286 & 0.242\,249 \\ 0 & 0.242\,249 & 0.485\,482 \end{pmatrix} \tag{4}$$

Step 4: The eigenvalues of $\mathbf{T}$ are the roots x_i. The squares of the first components of the normalized eigenvectors of $\mathbf{T}$, scaled by μ_0, are the weights w_i.

$$\{x_1, x_2, x_3\} = \{0.063\,891\ ,\ 0.368\,997\ ,\ 0.766\,880\} \tag{5}$$

$$\{w_1, w_2, w_3\} = \{0.513\,405\ ,\ 0.391\,980\ ,\ 0.094\,615\} \tag{6}$$

The Cholesky decomposition of a symmetric, positive definite matrix normally requires $m^3/3$ floating-point operations (flops).[?] However, Step 2 involves a Hankel matrix and Phillips has devised an algorithm that decomposes such a matrix in only $4m^2$ flops.[?]

Calculating the eigenvalues of a real symmetric matrix normally requires $4m^3/3$ flops.[?] However, Step 4 involves a tridiagonal matrix and Dhillon has devised an algorithm that diagonalizes such a matrix in only $O(m^2)$ flops.[?]

In a thorough analysis of the problem of finding roots and weights for quadrature,[?] Gautschi has concluded that the use of the moments of the weight function $w(x)$ can produce devastating numerical instabilities for large m. However, we have not observed any significant instabilities in the present work, because we are interested in only modest values of m.

We note that, if one attempts to model $\widehat{\rho}(k)$ by a sum of $m \geq n$ gaussians, the Hankel matrix of moments is singular and the initial guess algorithm breaks down. In practice, of course, this is not very important.