

Modeling the potential of a charge distribution

Peter M. W. Gill, Benny G. Johnson, and John A. Pople
Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Stephen W. Taylor
School of Mathematics, University of Minnesota, Minneapolis, Minnesota 55455

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Suppose that we wish to approximate a charge distribution $\rho(\mathbf{r})$ by a model charge distribution $\rho^*(\mathbf{r})$ such that

(a) the difference between their *potentials* is least-squares minimal; and (b) the distributions contain the same total charge.

The obvious formulation of this potential-matching problem begins by defining

$$\epsilon(\mathbf{r}) = \rho(\mathbf{r}) - \rho^*(\mathbf{r}), \quad (1)$$

$$V(\mathbf{x}) = \int \frac{\epsilon(\mathbf{r})}{|\mathbf{r}-\mathbf{x}|} d\mathbf{r} \quad (2)$$

and then seeks the function $\rho^*(\mathbf{r})$ which minimizes

$$Z = \int [V(\mathbf{x})]^2 d\mathbf{x} \quad (3)$$

subject to the constraint

$$\int \epsilon(\mathbf{r}) d\mathbf{r} = 0. \quad (4)$$

(Throughout this Letter, unless otherwise noted, we will follow the convention that integrals are over all space.) Minimizing Eq. (3) subject to Eq. (4), however, poses some irritating numerical difficulties which have been discussed by Hall and co-workers.¹ Most of these difficulties arise because the integral in Eq. (3) *diverges* for all $\rho^*(\mathbf{r})$ except those which satisfy Eq. (4) exactly. Recently, in the context of computing the two-electron repulsion integrals which arise in *ab initio* quantum chemical calculations, Fortunelli and Salvetti have outlined an *approximate* procedure which avoids some of these difficulties, but their method cannot be applied universally and is undesirably dependent on the geometry of the molecule under investigation.² We now demonstrate that, under the constraint (4), we can transform Z to a form which is ideal for numerical work and in which all needed integrals can be computed by minor modifications of existing computer codes.

We achieve the transformation of Z by recognizing that, if $\epsilon(\mathbf{r})$ satisfies certain conditions³ (given by Fubini's theorem⁴), the integrations implicit in Eq. (3) can be re-ordered and we can then invoke Eq. (4) and integrate over \mathbf{x} , thus

$$\begin{aligned} Z &= \int [V(\mathbf{x})]^2 d\mathbf{x} \\ &= \int \left[\int \frac{\epsilon(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{x}|} d\mathbf{r}_1 \right] \left[\int \frac{\epsilon(\mathbf{r}_2)}{|\mathbf{r}_2-\mathbf{x}|} d\mathbf{r}_2 \right] d\mathbf{x} \\ &= \iiint \epsilon(\mathbf{r}_1)\epsilon(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1-\mathbf{x}| |\mathbf{r}_2-\mathbf{x}|} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{x} \\ &= -\frac{1}{2} \iiint \epsilon(\mathbf{r}_1)\epsilon(\mathbf{r}_2) \left[\frac{1}{|\mathbf{r}_1-\mathbf{x}|} - \frac{1}{|\mathbf{r}_2-\mathbf{x}|} \right]^2 d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{x} \\ &= -2\pi \iint \epsilon(\mathbf{r}_1)|\mathbf{r}_1-\mathbf{r}_2|\epsilon(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5)$$

The integration over \mathbf{x} can be achieved by placing \mathbf{r}_1 at the origin and \mathbf{r}_2 on the z axis and then using the Legendre expansion to express $|\mathbf{r}_2-\mathbf{x}|^{-1}$ as an infinite series. The square of this series is easily integrated term by term and then summed to yield $4\pi|\mathbf{r}_1-\mathbf{r}_2|$. Equation (5) shows that, under the constraint (4), the least-squares minimization of the potential of a distribution $\epsilon(\mathbf{r})$ is equivalent to the maximization of the self-interaction of $\epsilon(\mathbf{r})$ over the distance operator

$$\hat{D}(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 - \mathbf{r}_2|. \quad (6)$$

Thus, we can transform the problem of minimizing Eq. (3) subject to Eq. (4) into the problem of maximizing

$$Z' = \iint \epsilon(\mathbf{r}_1)|\mathbf{r}_1-\mathbf{r}_2|\epsilon(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (7)$$

subject to the same constraint.

If $\epsilon(\mathbf{r})$ is a sum of Gaussian functions, Z' can be computed efficiently using our recently developed PRISM algorithm.⁵ the $[0]^{(m)}$ integrals must be redefined to account for the fact that we are using \hat{D} (instead of the Coulomb operator $1/D$) but the rest of the algorithm remains unchanged. We will develop these ideas further in a future paper.⁶

As a simple demonstration of the use of \hat{D} to solve a potential-matching problem, we will set up the equations to model the sum of N Gaussian functions

$$\rho(\mathbf{r}) = \sum_i^N b_i(\pi\beta_i)^{-3/2} \exp(-r^2/\beta_i) \quad (8)$$

by a sum of $M \leq N$ Gaussian functions

$$\rho^*(\mathbf{r}) = \sum_i^M a_i (\pi\alpha_i)^{-3/2} \exp(-r^2/\alpha_i), \quad (9)$$

where all $(M + N)$ functions share the same origin. Fortunelli and Salvetti have studied this problem^{2(a)} but, instead of maximizing Eq. (7), they minimized

$$Z'' = \iint \epsilon(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \epsilon(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (10)$$

which, as Hall *et al.* have argued,¹ results in a fit of the electric fields of $\rho(\mathbf{r})$ and $\rho^*(\mathbf{r})$, not their potentials. However, the integrals over \hat{D} are easily computed and, upon dropping irrelevant terms and factors, we obtain

$$Z' = \sum_i^M \sum_j^M a_i a_j (\alpha_i + \alpha_j)^{+1/2} - 2 \sum_i^M \sum_j^N a_i b_j (\alpha_i + \beta_j)^{+1/2}, \quad (11)$$

$$\sum_i^M a_i - \sum_j^N b_j = 0. \quad (12)$$

Thus, the task of determining the optimal amplitudes and reciprocal exponents reduces to the purely algebraic, and remarkably simple, problem of maximizing Eq. (11) within the constraint (12).

The example above, which involves only one center, is a relatively simple one but our methodology is very general and easily extends to more complicated cases. We are currently investigating applications of this modeling procedure to various problems in conventional and density func-

tional quantum chemistry and we will present detailed accounts of our results in a forthcoming paper.⁶ We have found, as did Fortunelli and Salvetti,² that the two-electron repulsion integrals $(\mu\nu|\lambda\sigma)$, whose computation is the most expensive step in the direct SCF method,⁷ can be computed significantly more efficiently if the two overlap distributions $(\mu\nu|$ and $|\lambda\sigma)$ are first replaced by concise, potential-matched models. We are also exploring the usefulness of modifying the popular method⁸ of Dunlap *et al.* by using \hat{D} , instead of $1/\hat{D}$, to project the molecular electron density onto a finite basis set. We hope that this will enhance those density functional procedures⁹ which use this technique.

¹ (a) G. G. Hall and D. Martin, *Isr. J. Chem.* **19**, 255 (1980); (b) G. G. Hall, *Theor. Chim. Acta* **63**, 357 (1983); (c) G. G. Hall and C. M. Smith, *Int. J. Quantum Chem.* **25**, 881 (1984); (d) C. M. Smith and G. G. Hall, *Theor. Chim. Acta* **69**, 63 (1986).

² (a) A. Fortunelli and O. Salvetti, *J. Comput. Chem.* **12**, 36 (1991); (b) A. Fortunelli and O. Salvetti, *Chem. Phys. Lett.* **186**, 372 (1991).

³ A sufficient condition for the order of integration to be changed is that ϵ be measurable and continuous and that all integrals arising in Eqs. (4) and (5) be absolutely convergent.

⁴ A. N. Kolmogorov and S. V. Fomin, *Introductory Real Analysis* (Dover, New York, 1970).

⁵ P. M. W. Gill and J. A. Pople, *Int. J. Quantum Chem.* **40**, 753 (1991).

⁶ P. M. W. Gill, B. G. Johnson, and J. A. Pople, *J. Chem. Phys.* (in preparation).

⁷ J. Almlöf, K. Faegri, and K. Korsell, *J. Comput. Chem.* **3**, 385 (1982).

⁸ B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, *J. Chem. Phys.* **71**, 3396 (1979); **71**, 4993 (1979).

⁹ See, e.g., J. Andzelm and E. Wimmer, *J. Chem. Phys.* **96**, 1280 (1992), and references therein.