Fitting the Coulomb potential variationally in
linear-combination-of-atomic-orbitals density-functional calculations

J. W. Mintmire*

Quantum Theory Project, Williamson Hall, University of Florida, Gainesville, Florida 32611

B. I. Dunlap

Naval Research Laboratory, Code 6170, Washington, D.C. 20375

A previously developed method for self-consistent-field density-functional calculations involving a variational fit to the charge density is generalized to the case in which the total (electronic plus nuclear) Coulomb potential is fit. Previously the total energy $E(\rho,\tilde{\rho})$ was viewed as a functional of the exact ρ and fitted $\tilde{\rho}$ charge density. The energy expression was modified to be correct when $\tilde{\rho}=\rho$ while at the same time allowing $\tilde{\rho}$ to be obtained variationally through $\partial E(\rho,\tilde{\rho})/\partial\tilde{\rho}=0$. Herein an expression for $E(\rho,\tilde{V})$, where $\tilde{V}$ is the fit to the Coulomb potential, is derived with similar properties. In particular, $\tilde{V}$ can be determined variationally through $\partial E(\rho,\tilde{V})/\partial\tilde{V}=0$. In various linear-combination-of-atomic-orbitals calculations on atomic neon, the superiority of variational over conventional least-squares-fitting methods is demonstrated.

I. INTRODUCTION

Due to the nonanalytic nature of the dependence[1-3] of the exchange correlation energy functional on the electronic density in all density-functional (DF) methods, at least this part of the electronic potential is fit to analytic functions in all linear-combination-of-atomic-orbitals (LCAO) DF calculations on molecules and solids. Furthermore, for computational advantages, the entire potential (Coulomb plus exchange and correlation) is fit, except where Hartree-Fock methodology is used.[4,5] In fact, the most widely used DF method for molecules, the multiple scattering (MS) $X\alpha$,[6] and solids, the augmented plane wave (APW),[7] can be viewed as involving a fit to the total potential, where that fit is obtained by muffin-tin averaging the potential.

Recently, a molecular DF method has been developed based on the method of Sambe and Felton[8] but in which the fit to the electronic charge density, and consequently, to the electronic Coulomb potential, is determined variationally.[9] As a result, the error introduced by fitting in the computation of the total energy appears only in second order. Thus, total energy and related quantities such as dissociation energies can be obtained reliably within the $X\alpha$ approximation.[9-13] Herein,

we extend this work to the cases in which the total Coulomb potential, electronic plus nuclear, is fit. Fitting the entire Coulomb potential rather than just the electronic part is a much more widely used approach, particularly in treating solids. The advantage is that the potential generated by a neutral charge distribution is short-ranged, whereas for a charge distribution with a net charge the potential decays as the reciprocal of the distance.

Our approach is to examine the functional form of the proposed fit to the potential and in order to deal with nonsingular potentials subtract off the nuclear contribution. We then use Poisson's equation to fit variationally the charge density to a fitted charge distribution which generates the desired form of the fitted potential. The resulting equations can then be rearranged to preserve the short-range nature of the various integrals. In Sec. II we review the LCAO approach to Slater's $X\alpha$ equations. In Sec. III we discuss several variational and nonvariational methods for fitting the potential. These various fitting procedures are compared in Sec. IV for various LCAO basis sets used in calculations on atomic neon.

II. THE $X\alpha$ MODEL

In the $X\alpha$ model[14] the one-electron orbitals $\phi_i(r)$ are determined by variationally minimizing the to-

tal energy given by the expression

$$E_{X\alpha} = \sum_i n_i \left[-\tfrac{1}{2} \int \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) d\vec{r} \right] - [\rho_e \,|\, \rho_N]$$

$$+ \tfrac{1}{2} [\rho_e \,|\, \rho_e] - \tfrac{3}{4}\alpha \left[\frac{81}{8\pi} \right]^{1/3} \int \rho_e^{4/3}(\vec{r}) d\vec{r}$$

$$+ \tfrac{1}{2} [\rho_N \,|\, \rho_N] \,, \tag{2.1}$$

where ρ_N is the nuclear charge density (represented as a sum of Dirac delta functions) and $\rho_e(\vec{r})$ is the electronic density,

$$\rho_e(\vec{r}) = \sum_i n_i \phi_i^*(\vec{r}) \phi_i(\vec{r}) \,, \tag{2.2}$$

with n_i being the occupation of th ith orbital ϕ_i. We use the notation $[\rho_1 \,|\, \rho_2]$ to represent the classical interaction of two charge distributions, $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$: viz.,

$$[\rho_1 \,|\, \rho_2] = \int d\vec{r}_1 \int d\vec{r}_2 \rho_1(\vec{r}_1) \rho_2(\vec{r}_2) / r_{12} \,, \tag{2.3}$$

with the understanding that the self-interaction of point nuclear charges is not to be included.

The resulting one-electron equations are thus of the form

$$\epsilon_i \phi_i(\vec{r}_1) = \left[-\tfrac{1}{2} \nabla^2 \right.$$

$$- \int d\vec{r}_2 [\rho_N(r_2) - \rho_e(r_2)] / r_{12}$$

$$\left. -\alpha \left[\frac{81}{8\pi} \right]^{1/3} \rho^{1/3}(\vec{r}_1) \right] \phi_i(\vec{r}_1) \,, \tag{2.4}$$

and are normally solved using a self-consistent field (SCF) iterative scheme.

We note several points about this model. First, for atoms the solutions of Eq. (2.4) can be reduced to a one-dimensional problem and the resulting equations solved numerically using the Herman-Skillman program.[15] For molecules and solids, however, the numerical solution of this equation will in general require the use of a three-dimensional numerical integration except where the muffin-tin approximation is used. Such a procedure can become prohibitive due to the large number of points involved, necessitating additional approximations such as the use of analytic basis sets. The use of such basis sets enables smooth interpolation between the three-dimensional grid points (in particular with respect to the kinetic energy terms). This is the basic approach introduced in the discrete variational (DV) method[16] which

determines the integrals needed for the usual secular equation via a numerical integration procedure.

Several authors[4,5,8] have introduced methods for solving the $X\alpha$ equations using an LCAO approach, where the orbitals $\phi_i(\vec{r})$ are expressed using an analytic basis set of functions $U_n(\vec{r})$,

$$\phi_i(\vec{r}) = \sum_n c_{ni} U_n(\vec{r}) \,, \tag{2.5}$$

which leads to the secular equation

$$\sum_n H_{mn} c_{ni} = \epsilon_i \sum_n S_{mn} c_{ni} \,, \tag{2.6}$$

where S_{mn} and H_{mn} are the overlap and effective Hamiltonian matrix elements, respectively:

$$S_{mn} = \int d\vec{r} \, U_m^*(\vec{r}) U_n(\vec{r}) \,, \tag{2.7}$$

$$H_{mn} = T_{mn} + Z_{mn} + V_{mn} + X_{mn} \,, \tag{2.8}$$

where T_{mn} is the kinetic energy matrix elements

$$T_{mn} = -\tfrac{1}{2} \int d\vec{r} \, U_m^*(\vec{r}) \nabla^2 U_n(\vec{r}) \,. \tag{2.9}$$

The matrix elements Z_{mn} and V_{mn} are the nuclear attraction and electron repulsion Coulomb integrals, respectively:

$$Z_{mn} = -[U_m^* U_n \,|\, \rho_N] \,, \tag{2.10}$$

$$V_{mn} = [U_m^* U_n \,|\, \rho_e] \,, \tag{2.11}$$

and the matrix elements X_{mn} are exchange terms of the form

$$X_{mn} = \int d^3r \, U_m^*(\vec{r}) U_n(\vec{r}) \rho^{1/3}(\vec{r}) \,. \tag{2.12}$$

It can be easily demonstrated that all terms in the effective Hamiltonian matrix elements may be calculated using integrals in the analytic form except for the exchange integrals X_{mn} in Eq. (2.12). Sambe and Felton[8] have suggested that $\rho^{1/3}$ be fit to a linear combination of auxiliary basis functions $G_i(\vec{r})$,

$$\rho^{1/3}(\vec{r}) \simeq \overline{\rho^{1/3}}(\vec{r}) = \sum_i g_i G_i(\vec{r}) \,, \tag{2.13}$$

in order to treat this difficulty. In addition, Sambe and Felton suggested fitting the charge density using least-squares-fitting techniques to a different auxiliary basis set,

$$\rho(\vec{r}) \simeq \widetilde{\rho}(\vec{r}) = \sum_i f_i F_i(\vec{r}) \,. \tag{2.14}$$

The rationale for fitting the charge density is that of reducing the total number of analytic integrals that must be evaluated, thus saving computational

time. It is to be noted that $\overline{\rho^{1/3}}$ does not equal $[\tilde{\rho}]^{1/3}$ since these are determined independently using separate basis sets.

Recently, a method which is variational in the electrostatic repulsion energy, and thus the total energy, has been introduced[9] for fitting the charge density to a linear combination of Gaussian-type orbitals (GTO's). Due to the positive definite nature of the mathematical expression for the

Coulomb interaction, the following inequality holds:

$$[\rho_e \mid \rho_e] \ge 2[\rho_e \mid \tilde{\rho}_e] - [\tilde{\rho}_e \mid \tilde{\rho}_e] , \qquad (2.15)$$

with the equality holding only for $\tilde{\rho}_e$ equal to ρ_e. We may then define a new energy functional $\tilde{E}_{X\alpha}$ as an approximation to the original functional $E_{X\alpha}$ where $\tilde{E}_{X\alpha}$ is a functional of both the one-electron orbitals ϕ_i and the approximate electron density $\tilde{\rho}_e$:

$$\tilde{E}_{X\alpha}(\rho_e,\tilde{\rho}_e) = \left[-\tfrac{1}{2} \sum_i n_i \int \phi_i^*(\vec{r})\nabla^2\phi_i(\vec{r})d\vec{r} \right] - [\rho_e \mid \rho_N] + \left[[\rho_e \mid \tilde{\rho}_e] - \tfrac{1}{2}[\tilde{\rho}_e \mid \tilde{\rho}_e] \right]$$

$$- \frac{3}{4}\alpha \left[\frac{81}{8\pi} \right]^{1/3} \int \rho_e(\vec{r})\overline{\rho_e^{1/3}}(\vec{r})d\vec{r} + \tfrac{1}{2}[\rho_N \mid \rho_N] . \qquad (2.16)$$

This approach allows a certain consistency in the manner in which orbital coefficients c_{ni} and the fitting coefficients f_i are determined. The orbital coefficients are chosen by requiring the variation of $\tilde{E}_{X\alpha}$ with respect to variations of the orbital coefficients equal zero; in the same way the fitting coefficients are chosen by requiring that the variation of $\tilde{E}_{X\alpha}$ with respect to variations in the fitting coefficients also equal zero. That is, the ϕ_i are defined implicitly by

$$\frac{\partial E(\rho,\tilde{\rho})}{\partial \phi_i} = \frac{\partial E(\rho,\tilde{\rho})}{\partial \rho} \frac{\partial \rho}{\partial \phi_i} = 0$$

and $\tilde{\rho}$ is defined implicitly by

$$\frac{\partial E(\rho,\tilde{\rho})}{\partial \tilde{\rho}} = 0 .$$

(Throughout this work we neglect the small errors that arise due to the inadequacy of the basis set and numerical procedures used to obtain the fit $\overline{\rho_e^{1/3}}$ and thus the exchange energy.[9])

Thus we see at least two alternative methods which may be used to choose the fitting coefficients f_i in Eq. (2.14), one method being variational in the total energy. Other authors have suggested fitting the total (electronic plus nuclear) potential instead of fitting just the electronic charge density, to an expansion of the form (for the atomic case)

$$\tilde{V}(\vec{r}) = \sum_i f_i F_i(\vec{r}) - \frac{Z}{r}e^{-\delta r^2} , \qquad (2.17)$$

where Z is the nuclear charge and the functions

$F_i(\vec{r})$ are some well-behaved and usually exponentially decreasing functions such as Gaussian functions. We may express the potential resulting from merely the electrons, if the expansion in Eq. (2.17) is taken to be that of the total nuclear and electronic potential, to be

$$\tilde{V}_e(\vec{r}) = \sum_i f_i F_i(\vec{r}) + \frac{Z}{r}(1 - e^{-\delta r^2}) . \qquad (2.18)$$

Appelbaum, Hamann, and co-workers[17-19] use a method similar to the above in their calculations on surface systems, where the fitting procedure used to choose the fitting coefficients f_i in Eqs. (2.17) and (2.18) is a least-squares-fitting (LSF) procedure. In the following section we introduce a new approach to fitting this form of the potential extending the energy variational approach described above.

III. FITTING METHODS

We wish to review briefly some of the basic techniques available for approximating the Coulomb potential using fitting methods. We shall first describe two methods which fit the electron density to an expansion of the form given in Eq. (2.14). One method results from minimizing the quantity

$$\int [\rho_e(\vec{r}) - \tilde{\rho}_e(\vec{r})]^2 d\vec{r} , \qquad (3.1)$$

while requiring the charge conserving constraint condition

$$\int \rho_e(\vec{r})d\vec{r} = \int \widetilde{\rho}_e(\vec{r})d\vec{r} \ . \tag{3.2}$$

This procedure is the conventional LSF method and yields the algebraic equations

$$\sum_j \theta_{ij} f_j = \sum_k n_k \sum_{m,n} c_{mk}^* c_{nk} S_{imn} + \lambda P_i \ , \tag{3.3}$$

which must be solved subject to the constraint equation

$$\sum_i f_i P_i = N \ , \tag{3.4}$$

where N is the total number of electrons, n_k are the orbital occupation numbers from Eq. (2.2), and c_{mk} and c_{nk} are the orbital expansion coefficients defined in Eq. (2.5). The assorted algebraic terms in Eqs. (3.3) and (3.4) are

$$\theta_{ij} = \int F_i(\vec{r}) F_j(\vec{r}) d\vec{r} \ , \tag{3.5}$$

$$S_{imn} = \int F_i(\vec{r}) U_m^*(\vec{r}) U_n(\vec{r}) d\vec{r} \ , \tag{3.6}$$

and

$$P_i = \int F_i(\vec{r}) d\vec{r} \ . \tag{3.7}$$

The variational fitting techniques are based on minimizing the quantity

$$E_2 = [\rho_e - \widetilde{\rho}_e \,|\, \rho_e - \widetilde{\rho}_e] \ . \tag{3.8}$$

This procedure yields the algebraic equations

$$\sum_j D_{ij} f_j = \sum_k n_k \sum_{m,n} c_{mk}^* c_{nk} R_{imn} + \lambda P_i \ , \tag{3.9}$$

if the charge conserving constraint condition defined in Eq. (3.4) is invoked. Both sets of equations may also be solved without invoking the constraint condition by deleting the last term in Eq. (3.9) which contains the undetermined Lagrange multiplier λ. The new algebraic terms contained in Eq. (3.9) are defined

$$D_{ij} = [F_i \,|\, F_j] \tag{3.10}$$

and

$$R_{imn} = [F_i \,|\, U_m^* U_n] \ . \tag{3.11}$$

We see that the electron repulsion energy terms contained in Eq. (2.16) may thus be expressed as

$$[\rho_e \,|\, \widetilde{\rho}_e] - \tfrac{1}{2}[\widetilde{\rho}_e \,|\, \widetilde{\rho}_e] = \sum_i f_i \sum_k n_k \sum_{m,n} c_{mk}^* c_{nk} R_{imn}$$
$$- \tfrac{1}{2} \sum_{i,j} f_i f_j D_{ij} \ , \tag{3.12}$$

which contains the same analytic integrals required for the fitting process, Eq. (3.9).

We can likewise fit the electrostatic potential due to the electronic charge density to an expansion of the form given in Eq. (2.18). Using the LSF technique where the quantity

$$\int \,|\, V_e(\vec{r}) - \widetilde{V}_e(\vec{r}) \,|^2 d\vec{r} \tag{3.13}$$

is minimized results in the algebraic equations

$$\sum_j \theta_{ij} f_i = \sum_k n_k \sum_{m,n} c_{mk}^* c_{nk} R_{imn} - V_i \ , \tag{3.14}$$

where

$$V_i = Z \int [F_i(\vec{r})(1 - e^{-\delta r^2})/r] d\vec{r} \ . \tag{3.15}$$

However, we may consider any potential fitting techniques using the expansion in Eq. (2.18) to be a charge-density-fitting technique. This may be seen by using Poisson's equation,

$$\nabla^2 V_e(\vec{r}) = -4\pi \rho_e(\vec{r}) \ . \tag{3.16}$$

Thus, Eq. (2.18) can be reinterpreted

$$\widetilde{E}_{X\alpha}(\rho_e, \widetilde{\rho}_e) = \widetilde{E}_{X\alpha}[\rho_e, \widetilde{V}_e(\widetilde{\rho}_e)] = \widetilde{E}_{X\alpha}(\rho_e, \widetilde{V}_e) \ ,$$

and a variational $\widetilde{V}_e$ is obtained via

$$\frac{\partial \widetilde{E}_{X\alpha}(\rho_e, \widetilde{V}_e)}{\partial \widetilde{V}_e} = 0 \ .$$

As in the case of the fit to the charge density this $\widetilde{V}_e$ also minimized E_2 (Eq. 3.8). However, this minimization is over all allowed variations of $\widetilde{V}_e$. Specifically,

$$\rho_e(\vec{r}) \simeq \widetilde{\rho}_e(\vec{r}) = \sum_i f_i \widehat{F}_i(\vec{r}) + \rho_0(\vec{r}) \ , \tag{3.17}$$

where

$$\widehat{F}_i(\vec{r}) = -\frac{1}{4\pi} \nabla^2 F_i(\vec{r}) \tag{3.18}$$

and

$$\rho_0(\vec{r}) = -\frac{Z}{4\pi} \nabla^2 \left[\frac{1 - e^{-\delta r^2}}{r} \right] \ . \tag{3.19}$$

We may use our previous variational fitting methods to select a set of coefficients f_i which is the solution of the algebraic equations

$$\sum_j Q_{ij} f_j = \sum_k n_k \sum_{m,n} c_{mk}^* c_{nk} G_{imn} - W_i \ , \tag{3.20}$$

where

$$Q_{ij} = [\widehat{F}_i \,|\, F_j] \ , \tag{3.21}$$

$$G_{imn} = [\widehat{F}_i \,|\, U_m^* U_n] \ , \tag{3.22}$$

and

$$W_i = [\rho_0 \mid \hat{F}_i] \ . \qquad (3.23)$$

Whenever $V_e(\vec{r})$ is fit, exponentially decaying $F_i(\vec{r})$ are used. The corresponding charge distribution $\hat{F}_i(\vec{r})$ [c.f. Eq. (3.18)] is neutral:

$$\int \hat{F}_i(\vec{r}) d\vec{r} = -\frac{1}{4\pi} \int \nabla^2 F_i(\vec{r}) d\vec{r} = 0 \ . \qquad (3.24)$$

Thus, the condition that $\tilde{V}$ be generated by a neutral charge distribution is automatically satisfied, and there is no need to impose such a constraint in fitting V.

IV. DISCUSSION

In LCAO calculations on atomic neon, we have tested the following four methods for fitting the Coulomb potential described above.

(1) Least-squares fit (LSF) to ρ using Eq. (3.3) and the charge preserving constraint Eq. (3.4).

(2) Variational fit to ρ using Eq. (3.9) and the constraint Eq. (3.4).

(3) LSF to V Eq. (3.14). [Actually in this work we use the essentially equivalent and much more practical method of Ref. 17 in which first the density is fit via Eqs. (3.3) and (3.4) and the result fit via Eq. (3.14) using a common set of fitting functions. The advantage of this procedure is that a common set of integrals is used in the construction of the Hamiltonian matrix and in the fitting process.]

(4) Variational fit to V Eq. (3.20).

These tests are compared with each other and the exact results of a Herman-Skillman calculation in Tables I—III. These calculations used three dif-

ferent Gaussian basis sets—the $5s/3p$, $11s/6p$, and $14s/9s$ basis sets for neon given by van Duijneveldt.[20]

The most direct method of testing these various fitting methods is to simply fit some given electronic density. We chose instead to perform complete SCF calculations using various bases exactly as they would be used in practical calculations. This has the disadvantage of introducing second-order errors due to the fact that inexact fits introduce errors into the SCF orbitals. However, from these calculations we find that Eq. (4.4) (below) is always satisfied. Thus, even in full SCF calculations E_2 is minimized over the appropriate variational space when either variational method is employed and we conclude this will be the case in all SCF calculations.

The Coulomb potential fitting basis sets were chosen so that each s-type orbital function generated an s-type fitting function with an exponent twice that of the orbital function; each p-type orbital function generated a fitting function of the form $r^2 \exp[-\beta r^2]$ where β is twice the orbital exponent. In both cases in which V is fit an additional exponent is needed for the term

$$\frac{Z}{r}(1 - e^{-\delta r^2})$$

in Eq. (2.18) describing the variation of the field near the origin. That exponent was chosen to be 1.0 bohr^{-2}.

For fitting $\rho^{1/3}$, Eq. (2.13), in the exchange energy we use the same basis set as above but with exponents reduced by $\frac{1}{3}$. The fit is performed by numerical LSF procedures using every point of the Herman-Skillman grid. We chose $\alpha = 0.7$ for this work. The exchange potential is quite a smooth function of r and the particular methods used to

TABLE I. Comparison of Herman-Skillman (HS) results with various LCAO energies (in hartrees) using van Duijneveldt's $5s/3p$ Gaussian basis set for atomic neon.

	Variational $\tilde{\rho}$	LSF $\tilde{\rho}$	Variational $\tilde{V}$	LSF $\tilde{V}$	HS
E_0	−127.486 234	−127.420 902	−127.746 884	−127.417 525	−128.038 676
E_1	−0.019 708	−0.076 154	0.018 808	−0.713 211	
E_2	0.000 247	0.000 445	0.235 225	0.634 267	
Error					
$(E_0 + E_1 + E_2 - E_{HS})$	0.541 981	0.542 064	0.545 024	0.542 207	
ϵ_{1s}	−30.230 417	−30.220 894	−30.419 647	−30.206 875	−30.351 150
ϵ_{2s}	−1.122 596	−1.114 430	−1.114 235	−1.107 363	−1.291 325
ϵ_{2p}	−0.331 321	−0.323 940	−0.347 766	−0.322 096	−0.465 110

TABLE II. Comparison of Herman-Skillman (HS) results with various LCAO energies (in hartrees) using van Duijneveldt's $11s/6p$ Gaussian basis set for atomic neon.

	Variational $\tilde{\rho}$	LSF $\tilde{\rho}$	Variational $\tilde{V}$	LSF $\tilde{V}$	HS
E_0	$-128.031\,412\,64$	$-128.017\,113\,36$	$-128.043\,930\,55$	$-128.017\,146\,55$	$-128.038\,675\,75$
E_1	$-0.001\,652\,34$	$-0.015\,966\,04$	$0.010\,675\,54$	$0.016\,811\,41$	
E_2	$0.000\,003\,50$	$0.000\,018\,56$	$0.000\,193\,53$	$0.000\,897\,11$	
Error					
$(E_0+E_1+E_2-E_{HS})$	$0.005\,614$	$0.005\,615$	$0.005\,614$	$0.005\,615$	
ϵ_{1s}	$-30.343\,769$	$-30.341\,687$	$-30.346\,278$	$-30.341\,690$	$-30.351\,150$
ϵ_{2s}	$-1.284\,919$	$-1.282\,608$	$-1.287\,406$	$-1.282\,608$	$-1.291\,325$
ϵ_{2p}	$-0.458\,272$	$-0.456\,024$	$-0.460\,758$	$-0.456\,030$	$-0.465\,110$

treat it are irrelevant to the following discussion.

In the tables E_0 is the total energy without corrections for fitting the Coulombic energy, i.e., the interelectronic Coulombic energy is approximated by

$$E_0 = \tfrac{1}{2} \int \rho_e(\vec{r})\tilde{V}_e(\vec{r})d\vec{r} = \tfrac{1}{2}[\rho_e \,|\, \tilde{\rho}_e] . \qquad (4.1)$$

The first-order, in $\rho_e - \tilde{\rho}_e$, correction energy is

$$E_1 = \tfrac{1}{2}[\tilde{\rho}_e \,|\, \rho_e - \tilde{\rho}_e]$$

$$= \tfrac{1}{2}\left[\int \tilde{V}_e(\vec{r})\rho_e(\vec{r})d\vec{r} \right.$$

$$\left. + \frac{1}{4\pi} \int \tilde{V}_e(\vec{r})\nabla^2\tilde{V}_e(\vec{r})d\vec{r} \right] . \qquad (4.2)$$

The second-order correction is

$$E_2 = \tfrac{1}{2}[\rho_e - \tilde{\rho}_e \,|\, \rho_e - \tilde{\rho}_e]$$

$$= \tfrac{1}{2} \int \rho_e(\vec{r})V_e(\vec{r})d\vec{r} - \int \rho(\vec{r})\tilde{V}_e(\vec{r})d\vec{r}$$

$$- \frac{1}{8\pi} \int \tilde{V}_e(\vec{r})\nabla^2\tilde{V}_e(\vec{r})d\vec{r} . \qquad (4.3)$$

In calculations on atoms and molecules, the computation of the second-order correction would involve four center terms, and thus its direct computation would defeat the purpose of fitting. However, we compute it in this work to compare its magnitude with that of the first-order correction and to facilitate comparison with the exact Herman-Skillman results. The error, $\Delta E = E_0 + E_1 + E_2 - E_{HS}$, where E_{HS} is the Herman-Skillman total energy, is exclusively due to orbital basis set incompleteness and the indirect effect which is that the errors in fitting the potential induce slight variations in the SCF orbitals. This latter effect is quite small as shown by the near independence of ΔE on the fitting method for a given orbital basis set. (A multiple precision computer code was developed to eliminate any numerical errors.) Also included in the tables are the one-electron orbital eigenvalues, ϵ_i.

One caveat must be mentioned. We did not optimize the fitting basis sets. Our prescription for choosing these sets is most appropriate to fitting the charge density—it allows an exact fit to the di-

TABLE III. Comparison of Herman-Skillman (HS) results with various LCAO energies (in hartrees) using van Duijneveldt's $14s/9p$ Gaussian basis set for atomic neon.

	Variational $\tilde{\rho}$	LSF $\tilde{\rho}$	Variational $\tilde{V}$	LSF $\tilde{V}$	HS
E_0	$-128.038\,699\,21$	$-128.040\,406\,09$	$-128.037\,965\,04$	$-128.040\,410\,59$	$-128.038\,675\,75$
E_1	$0.000\,307\,30$	$0.002\,183\,95$	$-0.000\,428\,87$	$0.002\,117\,09$	
E_2	$0.000\,000\,12$	$0.000\,000\,36$	$0.000\,002\,15$	$0.000\,007\,09$	
Error					
$(E_0+E_1+E_2-E_{HS})$	$0.000\,284$	$0.000\,284$	$0.000\,284$	$0.000\,284$	
ϵ_{1s}	$-30.350\,949$	$-30.351\,230$	$-30.350\,800$	$-30.351\,230$	$-30.351\,150$
ϵ_{2s}	$-1.291\,142$	$-1.291\,441$	$-1.290\,994$	$-1.291\,442$	$-1.291\,325$
ϵ_{2p}	$-0.464\,929$	$-0.465\,223$	$-0.464\,780$	$-0.465\,223$	$-0.465\,110$

agonal, in the orbital basis set, terms in ρ_e. Thus, there is a slight bias in favor of charge-density fitting relative to fitting the potential directly, particularly for the $5s/3p$ basis. However, for the two

larger basis sets we expect the results of optimization to be insignificant. Thus, we focus on the results of the calculation involving the larger basis sets. For our neon results the relationships,

$$|E_1(\text{ Variational } \rho)| \; < \; |E_1(\text{ Variational } \tilde{V})| \; < \; |E_1(\text{ LSF } \rho)| \; < \; |E_1(\text{ LSF } \tilde{V})| \qquad (4.4)$$

and

$$0 < E_2(\text{ Variational } \tilde{\rho}) < E_2(\text{ LSF } \tilde{\rho}) < E_2(\text{ Variational } \tilde{V}) < E_2(\text{ LSF } \tilde{V}) , \qquad (4.5)$$

are usually obeyed. We suspect that for optimized basis sets of equivalent sizes these inequalities always hold. Furthermore, the variational fitting procedures use a common set of integrals in both the computation of the total energy and of the fit to the potential. However, this latter advantage of variational over LSF methodologies is lost if the two-step process of fitting first the charge density and then the potential to a common set of fitting functions is used.[17] Nevertheless, we recommend variational fitting methods.

In any truly variational LCAO calculation the total energy will be higher than the total energy of an exact calculation. Thus, one of our goals in using variational fitting procedures is that the errors in the energy due to the fitting procedure are negligible compared to the energy difference mentioned above due to using a finite orbital basis. As shown in Eq. (4.5) and our data we find the variational methods are superior to their corresponding LSF methods in this respect. For the simple atomic calculations reported here the differences in E_2 between the variational $\tilde{\rho}$ fit and the LSF $\tilde{\rho}$ fit are small in magnitude. We have noted in molecular calculations that the differences between these two methods are more pronounced and are manifested directly in a slower rate of convergence of the SCF procedure for the LSF $\tilde{\rho}$ fitting procedure. We suspect these differences (in E_2 and convergence behavior) between the variational and LSF $\tilde{V}$ fitting techniques will also be more pronounced in

the more complicated molecular applications.

A final point that we wish to make is that unless a grossly inadequate basis set is used (such as we used to fit $\tilde{V}$ in our $5s/3p$ calculations) E_2 will be of order E_1^2. Thus, without computing E_2, one still has an excellent estimate of its magnitude provided E_1 is computed. We feel that a further argument for computing E_1 (a computationally economical proposition) is that its magnitude cannot be predicted *a priori* and in our earlier calculations on molecules we find that it can often be a significant fraction of the binding energy. Furthermore, in molecular potential-energy curve calculations using fixed basis sets it invariably changes sign as the internuclear distance is varied.

V. CONCLUSION

We have extended earlier work that introduced variational fitting methods in density-functional calculations to include the more prevalent case in which the potential rather than the charge density is fit. The variational fitting methods have been shown to be more accurate and more economical than nonvariational fitting methods in various LCAO calculations on atomic neon.

*Present address: Naval Research Laboratory, Code 6170, Washington, D.C. 20375.

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