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Analytic and Variational Xα in the Slater−Roothaan Method

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An analytic and mathematically variational linear-combination-of-atomic-orbitals density-functional method that allows arbitrary scaling of the Slater−Gáspár−Kohn−Sham exchange-correlation potential about each atom is described. The method can be made exact in the separated-atom limit. It is based on robust and variational fitting, which is reviewed and extended to fast-multipole methods. The Slater−Roothaan method requires four basis sets and delivers a total energy that is independent of all fitting errors through first order. A database of atomic Gaussian basis sets is used to construct inputs for a standard set of 56 molecules. That database contains our basis sets as well as the DGauss DZVP2 double-ζ and 6-311G triple-ζ polarized Gaussian basis sets for fitting molecular orbitals. Another two subdatabases contain the s- and non-s-type basis sets for fitting the charge density and the exchange-correlation potentials, which are related to the cube root of a partitioned density and its square. A bond-centered basis function can be added to all fitting bases via software. Eight different fitting basis sets are studied. Using the Hartree−Fock values of α, these molecules are overbound on average, but using a uniform $\alpha = 0.7$, these molecules are underbound on average, independent of fitting basis. Mixing exact exchange will not obviously improve the method.

Introduction

Traditional ab initio physical chemists use the word variational to describe energies that rigorously bound the exact energy from above. One good thing that can be said about the Hartree−Fock (HF) energy is that it bounds the nonrelativistic, Born−Oppenheimer energy from above. Because of the vastly influential work of Peter Pulay,[1] the word variational now almost never appears in the physical chemistry literature in a meaningful context, because all physical chemical computer codes are mathematically variational with respect to orbital coefficients. With Gaussian orbitals, the energy must be variational in order to have reliable forces. This development means that if no part of the electronic energy is approximated then the code gives a completely mathematically variational energy. It also means that if any part of the electronic energy is fitted then the code delivers an energy that is not mathematically variational unless the fit is variational as defined in this work.

Approximate Kohn−Sham[2] energies must differ from the Schrödinger energy if the Schrödinger energy is the exact Kohn−Sham (KS) energy. A variational result for one energy does not necessarily provide an upper bound to another energy. This work considers energies that differ, but differ only in second order in a fitted quantity. Such fitted energies are called robust.

Gaussian-based ab initio quantum chemistry (AIQC) has embraced KS density-functional theory (DFT). The strength of AIQC has been that the theory involves no three-dimensional (3-D) numerical integration, i.e., is analytic. The energy of the most popular AIQC method B3LYP,[3] which mixes HF and DFT, however, can only be computed using 3-D numerical integration. The problems associated with numerical integration in AIQC are well-known.[4−9] This work extends the purview of analytic AIQC to a method that has asymptotic properties similar to Xα,[10] but avoids the muffin-tin approximation and preserves the variational principle.

If there were no problem with numerical integration in quantum chemistry, then the preferred basis might become numerical atomic orbitals, which are the product of spherical harmonics and numeric radial functions about each atom. Such basis functions are used in the DMOL approach to DFT.[11] These basis functions ensure an exact solution to the DFT equations in the separated-atom limit. Because molecular orbitals decay exponentially with distance far from a molecule and have cusps at the nuclei, one can probably achieve an equally satisfactory solution of the numerical DFT equations using a slightly larger basis of Slater-type-orbitals (STO's) as in the ADF code,[12] Gaussian type orbitals are correct neither close to the nuclei nor far from any nucleus. Thus, an accurate solution of Schrödinger's equation or any of its various simplifications requires a very large number of Gaussian-type-orbital (GTO) basis functions. Fortunately GTO's are much more localized than STO's or numerical wave functions, and one can readily use a very large GTO basis set. In practice, however, one uses rather small GTO basis sets together with the variational principle, which ensures that the computed energy is accurate through first order in the error made by using a small number of GTO's to fit the molecular orbitals. The variational principle is essential to the current success of Gaussian-based quantum chemistry and likely to be essential to any future that Gaussians might have in quantum chemistry. This work extends variational use of rather small GTO basis sets to fit both the molecular orbitals and the electronic potential. The atomic potentials are independently variable through a parameter, α, for each element, which could be adjusted to give exact separated-atom limits. These parameters are not optimized in this work. Instead traditional values are used and the mathematical stability of this new nonlinear method demonstrated.

Slater invented the precursor[13] to DFT as a method that is computationally faster than HF. The significant computational difference between DFT and HF is that in the former all electrons see the same local, KS potential, whereas in the latter

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every electron sees a differential potential due to the other $N-1$ electrons. It is both efficient and natural to fit the KS potential to linear-combination-of-atomic-orbitals (LCAO) form in any LCAO DFT method.[14-16] One can, however, defeat Slater's purpose by treating the KS potential using the N^4 methods that are efficient and natural in GTO approaches to HF.[17-20] Fitting all of the KS potential except the long-ranged Coulomb terms to LCAO Gaussian form ensures that that part of the potential dies off rapidly with distance from any atom just like the corresponding atomic component of a molecular orbital does.

A large and growing number of quantum mechanical operators can be treated analytically using robust and variational fitting[7,21-24] This work defines a new analytic and variational density-functional method called the Slater−Roothaan (SR) method. The names are chosen because it is based on Slater's Xα method,[10] but it is also analytic and variational via extension of the methods of Roothaan.[25]

The next section describes fitting charge distributions robustly and variationally. The method is applied to fitting multipole moments of charge distributions. The third section describes fitting the $^4/_3$ power of a function robustly and variationally. The following section describes the origin of the Xα method and modern applications. The fifth section combines these fitting methods into the SR method, which is completely analytic and variational in all fitting basis sets. The density is partitioned according to atomic center. The geometric mean of the atomic α's multiply each two-center part of the density. Preliminary work suggests that the SR method is acceptably insensitive to choice of fitting bases[26] and that it is stable enough to follow DFT chemical dynamics at identically zero electronic temperature.[27] It approximates as close as possible the old nonvariational multiple-scattering Xα method. That section also describes all the major fitting basis sets that have been published and uses them in double-ζ and triple-ζ calculations on a standard test set of molecules. A final section discusses the results obtained using the SR method.

Robust and Variational Fitting of Charge Densities

In KS DFT the electronic energy,

$$E = \sum_i n_i \langle u_i | f_1 | u_i \rangle + \langle \rho || \rho \rangle + E_{\mathrm{xc}}(\rho_\uparrow,\rho_\downarrow) \qquad (1)$$

is (apart from the kinetic energy) a functional of the total density, $\rho(\mathbf{r})$, which is in turn the sum of both spin densities,

$$\rho_{\mathrm{s}}(\mathbf{r}) = \sum_i n_{i\mathrm{s}} u^*_{i\mathrm{s}}(\mathbf{r}) u_{i\mathrm{s}}(\mathbf{r}) \qquad (2)$$

where $n_{i\mathrm{s}}$ is the occupation of the ith molecular orbital, $u_{i\mathrm{s}}(\mathbf{r})$, of spin s. It also depends on the standard one-electron part, f_1, of electronic structure theory (kinetic energy, nuclear attraction, and applied electric field in the Born−Oppenheimer, nonrelativistic limit), the self-Coulomb repulsion of the density, and the spin-dependent exchange and correlation functional, E_{xc}. The notation, $\langle a||b\rangle$, represents half of the Coulomb energy of charge distribution $a(\mathbf{r})$ in the electric field of another charge distribution $b(\mathbf{r})$. Variation of this energy with respect to an orbital, u_i, constrained by Lagrange multipliers, ϵ_{ij}, to be orthogonal to the remaining orbitals yields the KS equations,

$$\langle u_i | f_1 | \delta u_i \rangle + 2\langle \mathrm{r} || u_i^* \delta u_i \rangle - \langle v_{\mathrm{xc}} | u_i^* \delta u_i \rangle = \epsilon_i \langle u_i | \delta u_i \rangle \qquad (3)$$

in variational form, where $v_{\mathrm{xc}}$is the functional derivative of E_{xc} with respect to $n_i u_i^* u_i$. In this expression the eigenvalue matrix, ϵ_{ij}, has been diagonalized by a unitary transformation of the orbitals, which is always possible in DFT because the Kohn−Sham potential is local or multiplicative.

This work concerns fitting the KS potential to GTO's analytically. In the following an overbar represents a fitted quantity, and Δ indicates the difference between exact and fitted quantities. One way to fit the KS potential is to fit separately the charge density, $\bar{\rho}$, and the exchange-correlation potential, $\bar{v}_{\mathrm{xc}}$.

No matter how the charge density is fit, one can compute the Coulomb energy of the electronic charge distribution that is accurate through first order in the error made due to fitting. A unique robust Coulomb energy is generated using only the exact and fitted charge densities,[21]

$$\langle \rho || \rho \rangle \approx \overline{\langle \rho || \rho \rangle} \equiv 2\langle \bar{\rho} || \rho \rangle - \langle \bar{\rho} || \bar{\rho} \rangle. = \langle \rho || \rho \rangle - \langle \Delta\rho || \Delta\rho \rangle \qquad (4)$$

Thus, the error in making this approximation for the Coulomb energy is the self-Coulomb energy of the difference between the exact and fitted charge density, $\Delta\rho = \rho - \bar{\rho}$. The error is nonnegative because it is an energy,[25] and it will decrease as the quality of the fit increases. For use in quantum chemistry, one must take a complete variation of this robust Coulomb energy,

$$\delta\overline{\langle \rho || \rho \rangle} = 2\langle \bar{\rho} || \delta\rho \rangle + 2\langle \delta\bar{\rho} || \rho - \bar{\rho} \rangle \qquad (5)$$

If the fitting basis has full variational freedom, then the last term vanishes and one can freely interchange the exact and fitted quantities, which are ρ and $\bar{\rho}$ in this case. If the fitting basis is incomplete, however, then a stationary fitted energy requires that the full variation, the right-hand side of eq 5, be used to generate the corresponding Fock matrix. Alternatively, the energy also remains variational if the Fock matrix is unchanged, but the fit is determined by setting the variation of the energy with respect to the fit (last term) in eq 5 to zero. This latter approach is taken throughout this work, except for the case of multipole moments, which have independent definition. If this second, minimalist strategy is used to ensure variationality, then the fit is said to be variational.

Herein i, j, k, etc. label basis functions, and subscripts indicate the basis set when necessary. Zeroing the variation of the robustly fitted Coulomb energy with respect to the LCAO coefficients gives the simplest variational fit,

$$\langle i || \rho - \bar{\rho} \rangle = \langle i || \rho \rangle - \sum_j c_j \langle i || j \rangle = 0 \Rightarrow c_i = \sum_j \langle i || j \rangle^{-1} \langle j || \rho \rangle \qquad (6)$$

This expression contains the inverse of the Coulomb repulsion matrix, which by definition satisfies $\delta_{ik} = \sum_j \langle i||j\rangle^{-1} \langle j||k\rangle$. This robust and variational fit of a charge distribution is called by others the resolution of the identity (RI) method.[28,29] As will be shown, this terminology incorrectly suggests the need for complete basis sets and high precision arithmetic.

An unconstrained fit, such as eq 6 is seldom used in traditional DFT calculations. Instead codes typically allow the user to constrain the fit to contain the proper amount of charge, $N = c_i\langle i\rangle$, where N is the number of electrons and $\langle i\rangle$ is the charge of i^{th} fitting basis function. The fit is obtained using a Lagrange multiplier λ[14-16]

$$c_i = \sum_j \langle i || j \rangle^{-1} [\langle j || \rho \rangle + \lambda \langle j \rangle] \qquad (7)$$

where satisfying the constraint implicitly gives λ.

So far nothing has been said about the functional form to which the charge density is robust and variationally fit. Gaussians are used in quantum chemistry because the product of two Gaussians is a third Gaussian centered on the line joining the original two,

$$\exp(-\alpha(\mathbf{r}-\mathbf{a})^2-\beta(\mathbf{r}-\mathbf{b})^2) = \exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2-(\alpha+\beta)\left(\mathbf{r}-\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta}\right)^2\right] \quad (8)$$

If both centers are the same, then the exponent of the final Gaussian is the sum of the exponents of the original two. If $\alpha = \beta$ then the exponent is doubled. Thus, it is natural to fit the charge density to atom-centered Gaussians that have exponents between twice the smallest and twice the largest s-type exponents in the orbital basis for each atom. An s-type charge-density-fitting basis, which has roughly the same flexibility as the orbital basis, is obtained by simply scaling all the exponents by a factor of 2.[21] This basis will be called the scaled s-type $\bar{\rho}$ basis in the following.

Because of the long-range nature of the Coulomb force, the Coulomb potential, rather than the charge density, can be fit to Fourier series[30,31] and/or multipole fields[9,32,33] in periodic crystals and for large molecules.[34,35] Equations 4 and 7 deliver robust and variation fits if the Coulomb potential is fit to short-ranged Gaussians and a few long-range functions.[36−39] One can optimize both the long-ranged[37] and short-ranged[39] parts of these mixed basis sets. For calculations on small or compact systems, the same accuracy requires more fitting functions if the potential is fit than if the charge density is fit.[36,37] Obviously, potential fitting wins over charge density fitting for large enough systems described by a single global fitting basis.[39] It is better still to use multiple fitting basis sets rather than one large global fitting basis to fit the Coulomb interactions of large systems.

The Coulomb interaction between two charge distributions can be recast to include a quadratic error term involving both fits,[23,24]

$$\langle\rho_a||\rho_b\rangle = \langle\rho_a||\bar{\rho}_b\rangle + \langle\bar{\rho}_a||\rho_b\rangle - \langle\bar{\rho}_a||\bar{\rho}_b\rangle + \langle\Delta\rho_a||\Delta\rho_b\rangle \quad (9)$$

Ignoring only the quadratic error yields an interaction energy that is symmetric and robust,

$$\overline{\langle\rho_a||\rho_b\rangle} = \langle\rho_a||\bar{\rho}_b\rangle + \langle\bar{\rho}_a||\rho_b\rangle - \langle\bar{\rho}_a||\bar{\rho}_b\rangle \quad (10)$$

If the two charge distributions are sufficiently removed that they do not overlap, then the smallest number of terms arise if the Coulomb interaction is treated using the Gaussian or continuous fast multipole method.[40−43] It is convenient to define the interaction energy of approximations to two charge densities through multipole-moment cutoffs L_1 and L_2,

$$\langle\rho_a||\rho_b\rangle \approx \langle{\bar{\rho}_a}^{L_1}||{\bar{\rho}_b}^{L_2}\rangle = \sum_{l_1=0}^{L_1}\sum_{m_1=-l_1}^{l_1} a_{l_1m_1}\sum_{l_2=0}^{L_2} N_{l_1l_2}\sum_{m_2=-l_2}^{l_2} \times b_{l_2m_2}\hat{Y}_{l_1,m_1}(\nabla_{\mathbf{a}})\hat{Y}_{l_2,m_2}(\nabla_{\mathbf{b}})\frac{1}{|\mathbf{a}-\mathbf{b}|} \quad (11)$$

where the $N_{l_1l_2}$ are normalization constants, $\hat{Y}_{l,m}(\mathbf{a}) = a^lY_{lm}(\hat{\mathbf{a}})/\sqrt{(l+m)!(l-m)!}$ is a solid harmonic, and $a_{l_1m_1} = \langle\hat{Y}_{l_1m_1}\rho_a\rangle$ and $b_{l_2m_2} = \langle\hat{Y}_{l_2m_2}\rho_b\rangle$ are the strengths of each multipole. For the evaluation of these derivatives see refs 44 and 45. In this case, the fit can either be considered to be of the charge density, in which case the two fits are the two multipole moments, or of the field, in which case the fits are of the multipole fields. The robust fit,

$$\langle\rho_a||\rho_b\rangle \approx \langle\rho_a||{\bar{\rho}_b}^{L_2}\rangle + \langle{\rho_a}^{L_1}||\rho_b\rangle - \langle{\rho_a}^{L}{}_1||{\bar{\rho}_b}^{L_2}\rangle \quad (12)$$

contains more multipole interactions than either of the first two terms on the right-hand side of this equation because each entire density feels the multipole fields of the other. The third term removes double counted terms.

Three changes are necessary to a fast-multipole code to make it robust and give variational energy. First, make certain that all expressions involving multipoles were treated symmetrically. Second, add to the energy the easily computed Coulomb energy of the multipoles interacting with each other. Third, all of eq 5 must be used to construct the Fock matrix; i.e., it must be reflected in a fitting-modified KS potential.

The Robust and Variational LCAO Three-Fourths-Power Functional

One can take the cube root (and other roots[23]) of a function, $f(\mathbf{r})$, using robust and variational fitting. Let $x(\mathbf{r})$ be an LCAO approximation to the cube root of the function and let $y(\mathbf{r})$ be an LCAO approximation to the square of x or equivalently an LCAO approximation to the $^2/_3$ power of f. For any such fits, the associated errors can be defined,

$$\begin{aligned} f^{1/3}(\mathbf{r}) &= x(\mathbf{r}) + \Delta x(\mathbf{r}) \\ f^{2/3}(\mathbf{r}) &= y(\mathbf{r}) + \Delta y(\mathbf{r}) \end{aligned} \quad (13)$$

The robust approximation to the $^4/_3$ power of $f(\mathbf{r})$ using these two fits,

$$3\mathrm{f}^{4/3}(\mathbf{r}) = 4\mathrm{f}(\mathbf{r})x(\mathbf{r}) - 2x^2(\mathbf{r})y(\mathbf{r}) + y^2(\mathbf{r}) + \mathrm{order}(\Delta^2) \quad (14)$$

is unique, however. If x and y approximate the cube root and cube root squared of f, then one-third of this equation less the quadratic terms will yield a better, i.e., robust approximation to the $^4/_3$ power of f.[7,22]

Setting the variation of the $^4/_3$ power functional with respect to $x(\mathbf{r})$ to zero, i.e., making it variational,

$$0 = \langle\delta x\,|\,f - xy\rangle \quad (15)$$

determines x in the absence of constraint. If the x basis is complete, then its solution,

$$f(\mathbf{r}) = x(\mathbf{r})y(\mathbf{r}) \quad (16)$$

implicitly gives x. If, on the other hand, the x basis is incomplete, then this equation is only an approximation. It becomes exact when projected against any of the x basis functions, which is eq 15, if that variation is taken with respect to an x LCAO coefficient. We use the constraint that the integral of f and xy be the same. Setting the variation of the $^4/_3$-power functional with respect to $y(\mathbf{r})$ to zero, i.e., making it, too, variational implicitly determines y,

$$0 = \langle\delta y\,|\,x^2 - y\rangle \quad (17)$$

If the y basis is complete, then its solution,

$$y(\mathbf{r}) = x^2(\mathbf{r}) \quad (18)$$

gives $y(\mathbf{r})$. If the y basis is incomplete, then this equation is only an approximation. It becomes exact when projected against any of the y basis functions, which is eq 17 if the variation is taken with respect to a y LCAO coefficient. Solving that equation eliminates y,

$$y_i = \sum_{j_y} \langle i_y j_y \rangle^{-1} \langle j_y xx \rangle \tag{19}$$

Also, given x, one can define a scalar,

$$X = \sum_{i_y j_y} \langle xx i_y \rangle \langle i_y j_y \rangle^{-1} \langle j_y xx \rangle \tag{20}$$

and from it a vector by variation,

$$X_i = \delta X = 4 \sum_{j_y k_y} \langle i_x x j_y \rangle \langle j_y k_y \rangle^{-1} \langle k_y xx \rangle \tag{21}$$

and from that a matrix by another variation,

$$X_{ij} = \frac{1}{2} \delta X_i = \sum_{k_y l_y} 2 \langle i_x j_x k_y \rangle \langle k_y l_y \rangle^{-1} \langle l_y xx \rangle + 4 \langle k_y i_x x \rangle \langle k_y l_y \rangle^{-1} \langle l_y j_x x \rangle \tag{22}$$

Thus, one can solve the constrained LCAO $^4/_3$-power problem using Newton−Raphson, if a scalar and vector are defined toward satisfying the constraint

$$n = \langle f \rangle \text{ and } N_i = \sum_{j_y k_y} \langle i_x j_y \rangle \langle j_y k_y \rangle^{-1} \langle k_y xx \rangle \tag{23}$$

A Newton−Raphson step is simply

$$\Delta x_i = \sum_j X_{ij}^{-1} (\langle j_x f \rangle - X_j + \lambda N_j) \tag{24}$$

where the Lagrange undetermined multiplier is implicitly determined by satisfying the constraint

$$\sum_i \Delta x_i N_i = n - \sum_i x_i N_i \tag{25}$$

Gradients of this functional for the special case of f being the density are given in refs 46 and 47.

This problem is nonlinear, but the self-consistent-field (SCF) method was developed to solve nonlinear problems. Thus, there is no additional problem with including this functional in any quantum-chemical method that requires SCF solution. Of course, all SCF calculations do not converge at times, a problem that has no solution other than trying a different starting point or adjusting mixing parameters. We start from superposed atomic potentials as approximate KS potentials. That gives the density and orbitals, which in turn allow us to determine a new f and thus a new KS potential. In the calculations described below the new KS potential is mixed with roughly half of the old SCF potential. Toward the end of the SCF process the DIIS procedure[48] is begun to speed convergence.

Slater−Gáspár−Kohn−Sham Exchange Functional and Xα

In a homogeneous electron gas the electronic quantum numbers are linear momentum and spin.[49] Dirac-averaged HF exchange for each spin over all momentum up to the highest occupied orbitals, which due to the isotropic nature of the approximation, form a spherical Fermi surface in momentum space. Integrating the average exchange energy yields the total exchange energy

$$E_{\langle \mathrm{HF}x \rangle} = -\frac{9}{4}\left(\frac{3}{8\pi}\right)^{1/3} \langle \rho^{4/3} \rangle \tag{26}$$

Slater realized that this density-functional approximation for exchange would greatly simplify HF because every electron would see the same potential.[13]

HF spin-unrestricted calculations are suspect because they favor high spin. For crystals spin-unrestricted calculations are quite important, however, as they provide a quantitative theory of magnetism, which is caused by an excess number of electrons of one spin due to electronic exchange interactions. For properties that are dependent on the electronic structure in the vicinity of the Fermi energy (average of the HOMO and LUMO energy levels), a variational approach is superior to a complete averaging. Gáspár[50] and later Kohn−Sham[2] used a variational approach to determine the density-functional exchange energy. They obtained two-thirds of Dirac's exchange energy. Thus, a parameter α has been introduced to define the Xα exchange energy for up spin,

$$E_{x\uparrow} = -\alpha \frac{9}{4}\left(\frac{3}{4\pi}\right)^{1/3} \langle \rho_\uparrow^{4/3} \rangle \tag{27}$$

Xα energies are obtained by replacing E_{xc} in eq 1 with this expression and minimizing this energy in an SCF calculation. Schwarz fixed α by equating the Xα and HF energies for atoms in a spin-restricted calculation.[51] The HF α varies monotonically from 0.97804 for H to 0.70383 for Nb. The corresponding α's for spin-unrestricted calculations vary from 0.77627 for H to 0.69248 for Rn.[52] HF theory is exact for H, and for heavier atoms, the difference between the HF α and the values of α that would give the exact total electronic energy are quite small. This is because correlation energies are much smaller than exchange energies, which in DFT include the self-Coulomb interaction of all orbitals.

Thus, the theory has widest applicability if each element is allowed to have its own α, which is the case in the original applications.[10] This was accomplished via the muffin-tin approximation,[52] in which the potential is approximated as being spherically symmetric near each atom and constant in between. That model dissociates correctly if the muffin-tin spheres grow in size with distance between atoms. In the separated-atom limit, the calculation could reproduce the atomic calculation. That is not the case with HF.

In HF theory, the separated-atom limits lie artificially very high in energy due to the inclusion of ionic character in the HF wave function.[53] Thus, HF binding energies are much too low and HF vibrational frequencies are too high. Thus, nonDFT ab initio frequencies are scaled by a factor less than one. In a study of 1066 frequencies, all ab initio scaling factors are less than all DFT scaling factors, even allowing hybrid functionals to be included in either set, and all are less than one.[54] The revolutionary advantage of the Xα method[10] was that it was fast, it was based on first-principles, and it allowed molecules to dissociate correctly. The disadvantage was that its KS potential was discontinuous. Thus, the energy was hard to define and evaluate,[55] and no variational principles were developed. Thus, the muffin-tin approximation has been abandoned in quantum chemistry, and the first nonmuffin-tin DFT codes adopted the compromise value of 0.7.[14] If a single value of α can be used, then variational calculations are possible using the Gaussian basis set to fit the orbitals and the KS potential.[21]

Xα energies in which the values of α vary from atom to atom can be estimated from uniform α calculations.[56] The approach of correcting a uniform α calculation can be extended to generate good thermochemistry with a small computation effort.[57−59] It should be useful to develop an analytic and variational Xα-like method that precisely recovers the total energy of atomized molecules. The SR method is such a method, but this work will not address optimizing α.

The Slater−Roothaan Method and Basis Sets

In any LCAO approach the density, eq 2, may be expanded in terms of an LCAO density matrix P_{ij} multiplying products of atomic orbitals,

$$\rho(\mathbf{r}) = \sum_{ij} P_{ij}\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \tag{28}$$

By definition the atomic orbitals, ϕ, are centered on atoms, so LCAO quantum chemistry is replete with methods that associate density with individual atoms. Mulliken population analysis is one. In it, each density matrix element is associated with two atoms equally, half to the atom of the first index and the other half to the atom of the second index. In this work it is simpler computationally to use the geometric mean of the two α's to define f,

$$f_{\mathrm{s}}(\mathbf{r}) = \sum_{ij} \alpha(i)\alpha(j)P^{\mathrm{s}}_{ij}\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \tag{29}$$

where s indicates spin, and the function,

$$\alpha(i) = \left[3\alpha_i\left(\frac{3}{4\pi}\right)^{1/3}\right]^{3/8} \tag{30}$$

includes α_i, the value of α of the atom on which atomic orbital i is centered. For a single center eq 29 squares this quantity and determining x and y variationally raise that to the $^4/_3$ power to give the constant of eq 27. In this, one of many full and variational implementations of analytic Xα, the α associated with cross terms in the density matrix is the geometric mean of the two atomic α's. In the separated-atom limit no part of the density matrix is on two different atoms. Thus, SR separates into atoms, with independent values of α in that limit.

The full SR energy is written,

$$E = \sum_i n_i\langle u_i|f_1|u_i\rangle + 2\langle\rho||\bar{\rho}\rangle - \langle\bar{\rho}||\bar{\rho}\rangle - \sum_{\mathrm{s}=\uparrow,\downarrow}\frac{4}{3}\langle f_{\mathrm{s}}x_{\mathrm{s}}\rangle - ({}^1/_3)\langle {x_{\mathrm{s}}}^2 y_{\mathrm{s}}\rangle + \frac{2}{3}\langle y_{\mathrm{s}}y_{\mathrm{s}}\rangle \tag{31}$$

where the orbitals, $\bar{\rho}$,and x and y for both spins are to be determined variationally. This work considers the only the smallest of molecules. Thus, it is appropriate to make each LCAO fit global. All fits, including the two exchange-correlation fits, are constrained in these calculations. The functional form of f can be quite general and thus enable a wide variety of different LCAO Xα-like density-functional methods.

Computational Methods and Basis Sets

The SR method is implemented by storing in code the atomic values of α and loading the three-eighths power of the appropriate value into an extension of the array that stores the nuclear charges. That array is used to multiply the two orbitals in the integral of f and the three-center overlap integrals $\langle i_x j_\phi k_\phi\rangle$. The gradient code[47,60,61] needs a similar change in the evaluation of the gradients of the three-center overlap integrals. The variational process takes care of the rest.

TABLE 1: Spin-Polarized HF α Values[52] for the Atoms Used in This Study[51]

element	α	element	α
H	0.776 27	F	0.735 87
Li	0.771 57	Na	0.73
Be	0.768 23	Si	0.727 51
B	0.762 06	P	0.726 13
C	0.753 31	S	0.724 75
N	0.745 22	Cl	0.723 26
O	0.741 88		

Our gradients are precise for fractional-occupation-number solutions,[62] but DFT is problematical in cases of degeneracy. Thus, all calculations have been performed in the highest symmetry for which the Kohn−Sham equations have integral-occupation-number, unrestricted solutions. All geometries have been optimized using the Broyden−Fletcher−Goldfarb−Shanno method,[63] which sometimes does not converge for a diatomic molecules because it hops back and forth between two separations. Other than that, SCF convergence and geometry optimization was never a problem.

Unfortunately, the derivative code is quite slow, and optimization of large fullerenes such as C_{240}[64] or carbon nanotube segments using polarized basis sets is not practical at this time; however, better derivative methods are known[65] but not yet optimally implemented.[66]

A standard set of molecules containing first- and second-row atoms[67] includes 54 molecules in 56 electronic states. The geometry of these molecules are all optimized in about an hour on a PC, and are easily used for a simple test of the feasibility of SR calculations. Table 1 gives the spin-polarized values of α linearly interpolated, where necessary, from ref 52. Our code uses solid-harmonic Gaussians.[68] Thus, the smallest standard orbital basis set with polarization functions that it can readily use is 6-311G**,[69,70] which was downloaded from PNNL.[71] These were entered into an orbital database for use with our code via the UNIX operating system. Our orbital basis sets, which tend to be bigger due to less contraction, are also entered into that database.

Our work has spawned a number of research efforts. Fitting is being established in quantum chemistry and there are several choices for fitting basis sets. A package of orbital, $\bar{\rho}$, and exchange-correlation basis (for fitting the VWN local-density functional[72]) was optimized[73] for use with DGauss.[74] The DGauss valence double-ζ (DZ) orbital basis set DZVP2 has been added to our orbital database and is used for comparison with valence triple-ζ (TZ) 6-311G**. Ahlrichs' group has generated another valence TZ orbital basis set and a matched RI-*J* basis for fitting the charge density in the Turbomole program.[75,76] These bases have been downloaded. The orbital basis set is not used, and the RI-*J* fitting bases are labeled "RIJ" in the following.

An SR calculation requires three fitting basis sets $\bar{\rho}$, x and y. This work examines only eight different combinations chosen to span the space from large to small basis sets. The errors in an SR calculation correlate with the amount of energy that that basis set affects. The biggest error is due to orbital-basis-set incompleteness. The second biggest error is due to an incomplete $\bar{\rho}$ basis. That error is always positive; and we will see that for a fixed orbital basis the atomization energy is always higher for the smallest fitting basis sets. The easiest way to improve any basis set is to add bond-centered s-type functions. These practical functions cut down on the need for high-angular momentum functions to fit these nodeless quantities. If one bond-centered function is used for each fitting basis set, then it is best to choose the exponent 1.0 au for the $\bar{\rho}$ basis and 0.3 au for the other two bases. The use of these bond-centered functions will be indicated by yes in the "Bond" column of the following tables.

The next choice concerns atom-centered fitting functions that have zero angular momentum, i.e., s-type functions. This type of basis function is special because our calculations start from overlapping atomic potential. Starting coefficients are needed only for this type of fitting function, which must be input. We can get s-type bases from any orbital basis set by scaling:[21] by two to fit the charge density, by $^2/_3$ to generate the s-type x basis, and by $^4/_3$ to generate the s-type y basis. This we do and attach the atomic $\bar{\rho}$ and x fitting coefficients (without exponents, which are generated by software) to all orbital basis sets. This basis and coefficients are overridden if some other s-type basis is input. Such alternative s-type fitting basis sets require the input of exponents as well as a set of $\bar{\rho}$ atomic coefficients and a set of x fitting coefficients for two spins. (Only y exponents are used in the SR method.)

In this work the s-type basis set choice is between scaled orbital exponents and the s-type part of the Turbomole RI-*J* basis. This choice is labeled by "Scaled" and "RIJ" in the following, and it only affects the $\bar{\rho}$ basis. All calculations use scaled x and y s-type bases. The RIJ basis is the smaller of these two bases. As optimized, the RIJ bases are contracted, but they were optimized for a different orbital basis than that used in this work. Thus, all s-type fitting functions are uncontracted in this work.

The final choice of fitting functions is potentially quite significant because it represents different philosophies between the developers of DGauss and Turbomole. Each exponent of angular momentum L actually represents $2L + 1$ fitting functions that allow the angular momentum to point in arbitrary directions. If an even-tempered set of exponents were chosen based on representative bond distances, then the number of fitting functions would rapidly get out of hand as the maximum angular momentum increased. Consequently, the DGauss basis functions are arbitrarily limited to $L < 3$. In the following these basis set are labeled "A2", because they are so named in a file called BASIS originally distributed with the DGauss[74] and deMon[77] codes. These basis sets have different exponents for different basis sets. To keep things simple and show that SR calculations are reliable, however, the DGauss charge-density exponents are used in all fitting basis sets. There is a basis called "A2" downloadable from PNNL. It is larger, and is called "A3" in BASIS for first-row atoms. The A2 basis set is efficient like the early Gaussian basis sets in using the same exponents for the s, p, and d basis sets, but unlike the early Gaussian basis sets it does not use contractions.

The entire RI-*J* basis used with a Turbomole TZ orbital basis is expected to be accurate to 0.02 mH for nonspherically symmetric atoms, which cannot be achieved without higher angular-momentum fitting functions, and the total fitting error less than one mH for small molecules.[76] For atoms that have open shell electrons of angular momentum L, the density must have components of angular momentum $2L$. Therefore, for second-row atoms with polarized orbital basis functions, the RI-*J* fitting basis has g functions. The basis is made manageable by reducing the total number of fitting functions through contraction for p and d bases. These basis set are labeled "RIJ" in the following. Specifically, the number of functions for stretches of the periodic table for A2 followed by RIJ in parentheses, with contractions in square brackets, are: H 1p (2p1d); Li 2p1d (2p2d1f); Be 3p3d (2p2d1f); C−F 3p3d (3p3d1f), Na 4p4d (4p4d1f[2p2d1f]); and Si−Cl 4p4d (6p5d1f1g[3p2d1f1g]). Thus, the ratio of basis size A2:RIJ for the elements used in this work are as follows: H, 3:11; Li, 11:23; Be, 24:23; C−F, 24:31; Na, 32:23; Si−Cl, 32:35. In total, eight fitting bases are used in this work.

Becke[67] compellingly demonstrated both theoretically, through the adiabatic connection formula that relates the electron−electron interactions of KS noninteracting and interacting densities, and numerically, through a study of 54 molecules in 56 electronic states, that mixing HF and local density functional (LDF) calculations would cure LDF overbinding. Overbinding had been known to be a serious problem with LDF calculations for a long time, but Xα does not share the problem.[21] This fact is demonstrated in Table 2, which compares atomization energies using the biggest fitting bases (bond-centered and scaled s-type and RIJ non-s-type fitting functions). Becke did not list his LDF results. They have been reconstructed in the third column by multiplying his half-and-half results by two and subtracting his exact (HF) exchange results. The trend for all these molecules is apparent in the average (last row). The half-and-half model (not Becke's best) has an average absolute error of 6.5 kcal/mol,[67] and it will be taken as close enough to be treated as exact in analyzing this table. On average, HF underbinds by 70 kcal/mol and LDF overbinds by as much. The table also includes three analytic and variational Xα calculations. The fifth column uses the 6-311G** basis and HF values of α. The last column is identical except for using the DGauss DZ basis. The biggest difference between the last two columns is for BeH. The range in BeH DZ dissociation energies using the eight fitting bases is 0.046−0.053 H. The TZ range is 0.089−0.093 H. Perhaps this difference is due to the fact that the TZ basis has five p exponents compared to one for the DZ basis. In comparison to Becke's work, the last three columns of Table 2 are quite similar. As a rule they correlate better to the half-and-half method then to the two extremes. Exceptions to this rule are H_2, LiH, and H_2, which are very close to HF, and F_2, which is closer to LDF.

Discussion

Table 3 globally compares the eight fitting bases when used with the 6-311G** orbital basis and if α is 0.7 everywhere. The mean and mean absolute errors relative to experiment[78] are compared. The biggest spreads in mean atomization error occur if there is either no bond functions, 2.2 kcal/mol, or if the A2 basis set is used, 1.9 kcal/mol. The total spread in atomization energy error is 2.6 kcal/mol. Treating the choice of fitting basis as introducing uncertainty, then these calculations underbind by 4.2 ± 0.9 kcal/mol. The spread in mean absolute energies, 0.5 kcal/mol, is relatively small.

Table 4 considers using the HF values of α with two orbital basis sets. Now all calculations indicate overbinding. 6-311G** overbinds by 5.8 ± 1.1 kcal/mol and the DGauss DZVP2 basis overbinds by 3.2 ± 0.8 kcal/mol. All spreads are larger than if a uniform α value is used. The biggest spreads occur if no bond-centered function is used or if the A2 basis is used. The mean absolute variation is reduced significantly, from almost 5 to 1 kcal/mol if the TZ orbital basis, rather than DZ orbital basis is used.

Xα overbinds some molecules and underbinds others, both if $\alpha = 0.7$ and if the HF values of α are used. This contrasts with the LDA, which uniformly overbinds, and HF, which uniformly underbinds. From the signs of the mean errors in

TABLE 2: Comparing Becke's Numerical Atomization Energies,[67] D_0 (kcal/mol), with Our Analytic Xα Values for 56 Molecules[a]

	exact	Becke's half and half	LDF	Xα (6-311G**)	α = 0.7 (6-311G**)	Xα (DZ)
H_2	78.4	101.8	125.2	85.1	82.8	86.8
LiH	32.2	53.1	74.0	37.6	34.7	33.2
BeH	46.1	55.9	65.7	55.9	49.7	29.1
CH	51.4	78.1	104.8	66.6	64.4	66.5
CH_2 ($^3B_1$)	143.1	185.0	226.9	191.5	179.9	191.4
CH_2 ($^1A_1$)	115.4	167.7	220.0	156.2	148.6	156.7
CH_3	224.8	294.1	363.4	294.9	279.4	295.4
CH_4	300.9	396.6	492.3	402.2	381.8	403.5
NH	44.3	76.8	109.3	66.7	64.1	66.8
NH_2	103.6	167.9	232.2	156.0	148.9	157.7
NH_3	179.0	273.6	368.2	269.8	256.1	272.3
OH	62.0	99.4	136.8	97.6	93.8	98.3
H_2O	142.4	215.0	287.6	225.2	213.4	227.9
HF	91.0	132.2	173.4	142.1	135.4	144.3
Li_2	2.8	17.0	31.2	6.6	6.7	5.4
LiF	85.9	128.6	171.3	142.9	134.7	132.5
C_2H_2	275.6	384.7	493.8	416.9	394.3	405.9
C_2H_4	395.0	534.8	674.6	563.0	533.1	559.4
C_2H_6	503.8	674.4	845.0	701.3	663.6	702.6
CN	68.6	157.4	246.2	187.2	180.5	178.0
HCN	185.8	290.6	395.4	312.9	300.3	302.6
CO	167.9	245.0	322.1	278.7	269.8	265.7
HCO	168.2	264.2	360.2	301.5	288.3	293.9
H_2CO	235.8	351.4	467.0	387.8	369.4	382.1
CH_3OH	334.2	481.0	627.8	513.6	486.1	515.0
N_2	108.0	205.2	302.4	213.1	209.4	200.6
N_2H_4	230.3	399.2	568.1	408.7	386.6	411.5
NO	43.9	134.5	225.1	160.9	158.7	152.0
O_2	23.7	107.9	192.1	155.5	150.5	149.9
H_2O_2	113.5	239.7	365.9	278.6	265.3	279.4
F_2	−41.8	22.8	87.4	65.2	63.2	66.0
CO_2	227.7	368.9	510.1	447.0	428.0	430.1
SiH_2 ($^1A_1$)	100.9	144.0	187.1	125.8	118.9	125.8
SiH_2 ($^3B_1$)	95.2	128.1	161.0	120.4	113.9	120.1
SiH_3	163.4	216.8	270.2	194.4	184.9	193.6
SiH_4	233.3	305.9	378.5	281.0	266.3	281.7
PH_2	96.0	146.0	196.0	125.1	120.1	127.6
PH_3	152.8	226.0	299.2	202.1	193.8	206.6
H_2S	120.0	173.1	226.2	160.9	156.0	165.2
HCl	74.2	102.4	130.6	99.4	97.2	99.7
Na_2	−2.2	12.3	26.8	5.1	5.3	5.2
Si_2	38.0	71.7	105.4	70.8	69.4	70.2
P_2	32.0	101.5	171.0	91.6	90.9	92.3
S_2	45.8	98.1	150.4	105.0	102.7	106.4
Cl_2	16.5	54.7	92.9	61.4	59.4	60.0
NaCl	69.3	92.5	115.7	87.8	85.3	85.9
SiO	104.3	175.5	246.7	195.1	188.6	195.1
CS	91.4	156.8	222.2	174.6	167.9	174.5
SO	45.8	115.4	185.0	137.9	131.9	141.6
ClO	−10.6	54.5	119.6	76.6	72.2	79.5
ClF	2.0	53.7	105.4	77.1	73.1	80.6
Si_2H_6	379.4	506.1	632.8	473.1	449.8	474.5
CH_3Cl	272.3	374.9	477.5	392.6	373.9	394.0
H_3CSH	320.1	448.2	576.3	458.0	435.5	462.9
HOCl	66.5	149.3	232.1	169.8	161.7	173.5
SO_2	90.2	231.5	372.8	272.7	259.5	275.3
average	131.1	204.3	277.6	213.3	203.6	211.7

[a] After the molecule/state, the next three columns use Becke's exact exchange, his half-and-half model and, from those two, his LDF calculations. The fifth and sixth columns use the 6-311G** basis, while the last uses the DGauss DZVP2 basis. The sixth column uses a constant value of α of 0.7 everywhere. The two neighboring columns (sixth and eighth) use instead the HF values of α for each element.

Tables 3 and 4, on average a uniform value of α set to 0.7 is too low and the HF values of α are too high. (Chemical bonds are characterized by the buildup of charge between atoms. Thus, the superlinear Xα exchange and correlation functional increases the binding energy as α is increased.) For this set of molecules, where the molecules are dominated by hydrogen compounds, the difference between using HF and α = 0.7 is substantial.

TABLE 3: Mean and Mean Absolute Error Relative to Experiment (kcal/mol)[78] in the Atomization Energy of the Set of Molecules Listed in the Previous Table for a Uniform α Equal to 0.7 Using the 6-311G Orbital Basis Set and Different Fitting Basis Sets[a]**

fitting basis			6-311G**	
bond	s-type	pdfg-type	mean	absolute
no	RIJ	A2	3.1	13.2
no	RIJ	RIJ	4.8	13.2
no	scaled	A2	2.6	13.4
no	scaled	RIJ	4.7	13.5
yes	RIJ	A2	4.0	13.3
yes	RIJ	RIJ	4.6	13.4
yes	scaled	A2	4.5	13.4
yes	scaled	RIJ	5.2	13.7

[a] The rows test different fitting options as indicated by the first three columns. The fitting-basis-set types and names are discussed in the text. Note that the mean absolute error is quite independent of fitting basis set to 0.5 kcal/mol.

TABLE 4: Mean and Mean Absolute Error Relative to Experiment (kcal/mol) in the Atomization Energy of the Molecules of Table 1 for the 6-311G and DGauss DZ Orbital Basis Set Using the HF Value of α for Each Atom Using Different Fitting Basis Sets[a]**

fitting basis			6-311G**		DGauss DZ	
bond	s-type	pdfg-type	mean	absolute	mean	absolute
no	RIJ	A2	−7.1	16.7	−3.9	20.1
no	RIJ	RIJ	−5.1	16.2	−2.7	15.4
no	scaled	A2	−7.6	17.0	−4.8	16.1
no	scaled	RIJ	−5.1	16.4	−2.8	15.4
yes	RIJ	A2	−6.1	16.3	−2.5	19.2
yes	RIJ	RIJ	−5.2	16.4	−2.3	19.0
yes	scaled	A2	−5.5	16.3	−3.5	15.5
yes	scaled	RIJ	−4.6	16.4	−3.0	15.6

[a] The eight fitting-basis-set options are described in the text.

This work shows that the conventional ab initio SCF process can support some imposed changes in the potential from atom to atom. The spread in absolute mean deviation going from Table 3 to Table 4 suggests that as the variation of α from atom to atom increases, bigger basis sets should be used.

The concepts of robust and variational fitting have been reviewed and the definitions applied to fitting the charge density and its $^4/_3$ power. Any LCAO density can be associated with atoms and pairs of atoms, naturally partitioning the density. A partitioned density allows scaling, by atom-specific α values, the Slater−Gáspár−Kohn−Sham exchange functional for each atom. The final method, called the Slater−Roothaan method, is quite well behaved computationally for small molecules containing first- and second-row atoms. The comparison of Xα treated variationally with other DFT methods for these molecules is far from complete. In particular, a meaningful comparison requires at least the optimization of the atomic α's, which might require that the total energy in all atomized limits be exact for each basis set. This work tested these robust and variational nonlinear fitting methods for a large number of heterogeneous molecules and orbital, fitting, and bond-centered basis sets. Analytic DFT is reliable. Now the physical chemistry can be meaningfully optimized.

These tests must also be extended to heavy-atoms and large molecules. For heavy-atom molecules the calculations scale as N^3. For large molecules a robust and variational fast-multipole method should be used, which in order to eliminate all first-order errors must be modified, eq 12. A Department of Defense Common High Performance Software Support Initiative has begun to make the SR method scalable and enable calculations on very large molecules.

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