JCTC Journal of Chemical Theory and Computation

Slater's Exchange Parameters α for Analytic and Variational Xα Calculations

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Abstract: Recently, we formulated a fully analytical and variational implementation of a subset of density functional theory using Gaussian basis sets to express orbital and the one-body effective potential. The implementation, called the Slater-Roothaan (SR) method, is an extension of Slater's Xα method, which allows arbitrary scaling of the exchange potential around each type of atom in a heteroatomic system. The scaling parameter is Slater's exchange parameter, α, which can be determined for each type of atom by choosing various criteria depending on the nature of problem undertaken. Here, we determine these scaling parameters for atoms H through Cl by constraining some physical quantity obtained from the self-consistent solution of the SR method to be equal to its *exact* value. Thus, the sets of α values that reproduce the *exact* atomic energies have been determined for four different combinations of basis sets. A similar set of α values that is independent of a basis set is obtained from numerical calculations. These sets of α parameters are subsequently used in the SR method to compute atomization energies of the G2 set of molecules. The mean absolute error in atomization energies is about 17 kcal/mol and is smaller than that of the Hartree−Fock theory (78 kcal/mol) and the local density approximation (40 kcal/mol) but larger than that of a typical generalized gradient approximation (∼8 kcal/mol). A second set of α values is determined by matching the highest occupied eigenvalue of the SR method to the negative of the first ionization potential. Finally, the possibility of obtaining α values from the exact atomization energy of homonuclear diatomic molecules is explored. We find that the molecular α values show much larger deviation than what is observed for the atomic α values. The α values obtained for atoms in combination with an analytic SR method allow elemental properties to be extrapolated to heterogeneous molecules. In general, the sets of different α values might be useful for calculations of different properties using the analytic and variational SR method.

The Hohenberg−Kohn−Sham (HKS) formulation of density functional theory is by far the choice for today's electronic structure calculation.[1−4] Prior to the HKS formulation of the density functional theory (DFT), Slater formulated its basis

in an attempt to reduce the computational complexity of the Hartree−Fock (HF) method.[3] Unlike the HF method, this Xα method has an exchange potential v_x that is local and proportional to the one-third power of the electron density ρ. It is given by

$$v_x[\rho] = -\alpha \frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\vec{r})$$

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where α is called Slater's exchange parameter and was originally equal to one. Gáspár[6] and Kohn−Sham[2] obtained a similar expression on other rigorous grounds. They variationally minimized the total energy functional and determined α to be 2/3, in contrast to Slater's value. The difference in the two values is rooted in the averaging process employed in the simplification of the HF exchange potential. Slater, taking a cue from Dirac's earlier work,[5] averaged the exchange potential over the entire Fermi sphere of radius $k_f = (3\pi^2\rho(\vec{r}))^{1/3}$, while in the Gáspár and Kohn−Sham procedure the value of the exchange potential at $k = k_f(\vec{r})$ is used. It was suggested that the α parameter in Slater's method could be treated as an adjustable parameter.[7] The set of α parameters for atoms that make self-consistent Xα energy match the HF energy was determined by Schwarz.[8] The α values he obtained typically range from 0.77 for light atoms to 0.69 for heavy atoms. He also noted that different atomic configurations lead to only slight changes in the α values, suggesting that the Xα method can also be applied to the molecules or solids. Several other ways to determine the α parameters have been put forth.[9−16]

Early implementations of the Xα method for molecules with atom-dependent α parameters employed the muffin tin (MT) approximation.[17−21] In this scheme, atoms or ions are enclosed by the atomic spheres in which the potential is approximated to be spherically symmetric, while, in the interstitial region, the potential is constant. The effective one body potential in the MT implementation is discontinuous at the surface of the MT sphere, and therefore the energy was mathematically undefined. This method, however, had an advantage over all the other quantum-chemical methods which was that the molecules dissociated correctly. At infinite interatomic distances a sum of atomic energies could be reproduced. When the MT model was discarded due to difficulties in geometry optimization, a single value of α (= 0.7) had to be chosen for all types of atoms.[22] There are, however, some attempts to obtain good thermochemistry from the Xα calculations by correcting or improving the uniform α calculations in a secondary calculation.[23−26]

Electronic structure calculations using traditional quantum chemical methods such as the HF theory, and beyond, generally employ basis sets to expand molecular orbitals. In these methods, calculations of matrix elements and other quantities of interests are analytic. On the other hand, almost all implementations of density functional models, until recently, required use of numerical grids to compute contributions to matrix elements from the exchange-correlation terms. Cook and co-workers[27−31] successfully demonstrated fully analytic implementation of a density functional model. His variational implementation used Gaussian basis sets to express molecular orbitals, the one-body effective potential,[27] and the uniform α Xα exchange potential.[28,29] The advantages of analytic calculations are obvious. The calculations are fast and accurate to machine precision (within the limitations of the model and basis set). Round-off error, which grows as the square root of the number of points and other numerical problems are eliminated.[32] Consequently, smooth potential energy surfaces are obtained.[28,29] Unfortunately, modern sophisticated exchange-correlation functionals are too complex to

allow a fully analytic solution at this time. Analytic DFT, at this stage, is restricted to Slater's exchange-type functionals. We have recently proposed an algorithm that permits fully analytic solutions and also allows for atom dependent values of Slater's exchange parameter α for heteroatomic systems.[33] This method, called the Slater-Roothaan (SR) method, is based on robust and variational fitting and requires four sets of Gaussian bases. It can have the advantage of MT Xα that molecules dissociate correctly as interatomic distances tend to infinity.[34] Intuitively, it is natural to expect that when molecules dissociate the constituent atoms would have *exact* atomic energies at infinite separation. This important physical requirement is satisfied within the SR method if α parameters that reproduce exact atomic energies are used in molecular calculations, although one might want to use other sets of α's for other molecular properties.

In this work, we report different sets of α parameters that could be used in the SR method. The first such a set is determined by requiring that the self-consistent atomic SR atomic energy be equal to the *exact* atomic energies. The α values in this set will be hereafter referred to as atomic alpha values. We have recently used some of the α values from this set to calculate the *total* energies for the G2 set[35] of molecules and found that these α values give remarkably good total energies.[36] Here, we use them to compute the *atomization* energies for the G2 set of molecules and compare them with other models. Further, we also obtain two additional sets of α based on other criteria for possible use in the SR method. The second set of atomic α values is determined to provide the negative of the eigenvalue of the highest occupied molecular orbital (HOMO), ϵ_{HOMO}, that matches with the *exact* value of the first ionization potential determined.[37−42] The third set of α is determined to provide the *exact* atomization energy for the selected homonuclear diatomic molecules of the first and second rows of the periodic table. All calculations are repeated for four different combinations of analytic Gaussian basis sets.

It is apparent that the analytic Slater-Roothaan method is empirical in nature as it uses adjustable α values. It, however, differs from the semiempirical[43−45] methods which use a minimal basis set, or empirical[46−49] models which do not compute electronic structure, and the minimal-basis tight binding methods[50] reported in the literature. It is a variant of density functional models that is also computationally very efficient because it is fully analytic and requires *no* numerical integration. We have successfully used it for studying the heterogeneous systems such as boron and aluminum nitride nanotubes containing up to 200 atoms.[51,52] Furthermore, it also provides the flexibility of being tuned, through the α parameters, according to the need of the problem. The sets of α parameters reported in this work will be useful starting points in this regard. In the following section we outline the analytic SR method used in this work. In section II, we describe computational details which are followed by results and discussion in section III.

I. Theoretical Method

The total electronic energy in the DFT for an *N*-electron system is a functional of electronic density ρ and is given

by

$$E^{KS}[\rho] = \sum_i^N < \phi_i| f_1 |\phi_i > + E_{ee} + E_{xc}[\rho_\uparrow, \rho_\downarrow] \qquad (1)$$

where the first term contains the kinetic energy operator and the nuclear attractive potential due to the M nuclei

$$f_1 = -\frac{\nabla^2}{2} - \sum_A^M \frac{Z_A}{|\vec{r} - \vec{R}_A|} \qquad (2)$$

The total electron density is expressed in terms of the Kohn−Sham orbitals $\phi_{i,\sigma}$ as

$$\rho(\vec{r}) = \rho_\uparrow + \rho_\downarrow \qquad (3)$$

with

$$\rho_\sigma(\vec{r}) = \sum_i n_{i,\sigma} \phi_{i,\sigma}^* \phi_{i,\sigma}(\vec{r}) \qquad (4)$$

where $n_{i,\sigma}$ is the occupation number for the $\phi_{i,\sigma}$ orbital. The second term in eq 1 represents the classical Coulombic interaction energy of electrons

$$E_{ee} = \langle \rho || \rho \rangle = \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}|} d^3r \, d^3r' \qquad (5)$$

This energy is approximated by expressing the charge density as a fit to a set of Gaussian functions

$$\rho(\vec{r}) \approx \bar{\rho}(\vec{r}) = \sum_i d_i G_i(\vec{r}) \qquad (6)$$

where $\bar{\rho}(\vec{r})$ is the fitted density and d_i is the expansion coefficient of the charge density Gaussian basis function G_i. The elimination of the first-order error in the total energy due to the fit leads to[27]

$$E_{ee} = 2\langle \bar{\rho} || \rho \rangle - \langle \bar{\rho} || \bar{\rho} \rangle \qquad (7)$$

The expansion coefficients $\{d_i\}$ are determined by variationally minimizing this energy with respect to $\{d_i\}$. The last term E_{xc} in eq 1 is the exchange energy

$$E_{xc}[\rho_\uparrow, \rho_\downarrow] = -\frac{9}{8}\alpha\left(\frac{6}{\pi}\right)^{1/3} \int d^3r[\rho_\uparrow^{4/3}(\vec{r}) + \rho_\downarrow^{4/3}(\vec{r})] \qquad (8)$$

The form of above functional allows analytic calculations with the Gaussian basis to be performed. For this purpose the one-third and two-third powers of the electron density are also expanded in Gaussian basis sets

$$\rho^{1/3}(\vec{r}) \approx \bar{\rho}^{1/3} = \sum_i e_i E_i(\vec{r}) \qquad (9)$$

$$\rho^{2/3}(\vec{r}) \approx \bar{\rho}^{2/3} = \sum_i f_i F_i(\vec{r}) \qquad (10)$$

Here, $\{E_i\}$ and $\{F_i\}$ are independent Gaussian basis functions, while e_i and f_i are expansion coefficients. The exchange energy is then given by[28−31,53]

$$E_{xc} = C_\alpha\left[\frac{4}{3}\langle \rho\bar{\rho}^{1/3}\rangle - \frac{2}{3}\langle \bar{\rho}^{1/3}\,\rho\,\bar{\rho}^{2/3}\rangle + \frac{1}{3}\langle \bar{\rho}^{2/3}\,\bar{\rho}^{2/3}\rangle\right] \qquad (11)$$

where $C_\alpha = -(9/8)\alpha(6/\pi)^{1/3}$. Thus, using the four LCGO basis sets (one for orbital expansion and three fitting basis sets) the total energy is calculated analytically. The LCAO orbital coefficients and the vectors **d**, **e**, and **f** are found by (constrained if desired) variation.

Slater-Roothaan Method. The expression for the total electronic energy in the Slater-Roothaan method has the following form:[33]

$$E^{SR} = \sum_i < \phi_i| f_1 |\phi_i > + 2\langle\rho||\bar{\rho}\rangle - \langle\bar{\rho}||\bar{\rho}\rangle +$$

$$\sum_{\sigma=\uparrow,\downarrow}\left[\frac{4}{3}\langle g_\sigma\,\bar{g}_\sigma^{1/3}\rangle - \frac{2}{3}\langle \bar{g}^{1/3}{}_\sigma\,\bar{g}^{1/3}{}_\sigma\,\bar{g}^{2/3}{}_\sigma\rangle + \frac{1}{3}\langle \bar{g}^{2/3}{}_\sigma\,\bar{g}^{2/3}{}_\sigma\rangle\right] \qquad (12)$$

Here, the partitioned 3/4 power of the exchange energy density

$$g_\sigma(\vec{r}) = C_x\sum_{ij}\alpha(i)\,\alpha(j)\,D_{ij}^\sigma(\vec{r}) \qquad (13)$$

where $C_x = C_\alpha/\alpha$ and $D_{ij}^\sigma(\vec{r})$ is the diagonal part of the spin density matrix, and the function

$$\alpha(i) = \alpha_i^{3/8} \qquad (14)$$

contains the α_i, the α in the Xα, for the atom on which the atomic orbital i is centered.

II. Computational Details

The α values are calculated for the atoms that occur in a standard set of (Becke's)[54] 56 molecules. These atoms are H, Be through F, and Na through Cl. Magnesium and aluminum atoms do not occur in the Becke's set but have been included in the present work. The set of 56 molecules actually consist of 54 molecules with two molecules in two different electronic states. The SR method requires four basis sets, of which one is the orbital basis. The remaining three basis sets are required for fitting of the Kohn−Sham potential (see ref 33 for more details). For the orbital basis sets, our choices are the triple-ζ (TZ) 6-311G** basis[55,56] and the DGauss[57] valence double-ζ (DZ) basis set[58] called DZVP2. The most reliable and thus best s-type fitting bases are those that are scaled from the s-part of the orbital basis.[27] The scaling factors are two for the density, (2/3) for $\bar{\rho}^{1/3}$ and (4/3) for $\bar{\rho}^{2/3}$. These scaled bases are used for all s-type fitting bases. A complete package of basis sets has been optimized[58] for use with DGauss.[57] In addition to the valence double-ζ orbital basis, called DGDZVP2 herein, we use the *pd* part of the (4,3;4,3) for Be−F (A2) charge density fitting basis. Ahlrichs' group has generated a RI-J basis for fitting the charge density of a valence triple-ζ orbital basis set used in the TURBOMOLE program.[59] These fitting bases are used in combination with the 6-311G** and DGDZVP2 basis sets. The α are obtained for the different combination of above basis sets. The molecule geometries were optimized using the Broyden−Fletcher−Goldfarb−Shanno (BFGS) algorithm.[60−64] Forces on ions are rapidly computed nonrecursively using the 4-j generalized Gaunt coefficients.[65,66] The calculations are spin-polarized for open-shell systems.

III. Results and Discussion

The optimal α values that give the exact atomic energies can be obtained by the Newton−Raphson procedure that

Table 1. Optimal α Values for the Different Basis Sets that Yield the *Exact* Atomic Energies in the Highest Symmetry for Which the Solutions Have Integral Occupation Numbers[a]

	basis I	basis II	basis III	basis IV	numerical	E (au)
H	0.77739	0.77739	0.78124	0.78124	0.77679	−0.500
Li	0.79169	0.79169	0.79211	0.79211	0.79118	−7.478
Be	0.79574	0.79574	0.79614	0.79614	0.79526	−14.667
B	0.78675	0.78668	0.78684	0.78677	0.78744	−24.654
C	0.77677	0.77672	0.77670	0.77665	0.77657	−37.845
N	0.76747	0.76747	0.76726	0.76726	0.76654	−54.590
O	0.76500	0.76495	0.76454	0.76448	0.76454	−75.067
F	0.76066	0.76067	0.76002	0.76001	0.75954	−99.731
Na	0.75204	0.75204	0.75287	0.75287	0.75110	−162.260
Mg	0.74994	0.74994	0.75120	0.75120	0.74942	−200.060
Al	0.74822	0.74819	0.74872	0.74869	0.74797	−242.370
Si	0.74539	0.74540	0.74600	0.74602	0.74521	−289.370
P	0.74324	0.74324	0.74397	0.74397	0.74309	−341.270
S	0.74262	0.74260	0.74352	0.74350	0.74270	−398.140
Cl	0.74197	0.74196	0.74273	0.74272	0.74183	−460.200

[a] The numerical values are for the spherically symmetric atoms and are obtained by the numerical atomic structure code. The *exact* atomic energies given in the last column are from ref 67. The basis sets are I: 6-311G**/RI-J, II: 6-311G**/A2, III: DGDZVP2/RI-J, and IV: DGDZVP2/A2.

finds zeros of the function $f(\alpha) = E^{SR}(\alpha) - E_{exact} = 0$, where E and E_{exact} are the self-consistent Xα (SR) and the *exact* total energies, respectively. Finding zero of this function requires frequent calculation of this function and its derivative. Determination of the derivative, $f'(\alpha)$, is straightforward. Only the exchange term in the energy functional $E^{SR}(\alpha)$ depends explicitly on the α parameter. The derivative obtained as the exchange-energy divided by the α parameter provides sufficiently accurate approximation to the actual derivative. The LCAO fits depend weakly on α. The Newton−Raphson procedure was implemented using PERL scripts, and the energy and its derivative with respect to α were obtained from the FORTRAN90 SR code. The sets of α values obtained using this procedure are given in Table 1. It is evident from the table that the choice of fitting basis does not significantly affect the α values. The α values do show some dependence on the orbital basis set. However, the changes in alpha values are small with the α values for the 6-311G** basis set being consistently smaller than those for the DGDZVP2 basis set for the same fitting basis set. For the same choice of fitting basis sets, the 6-311G** orbital basis set will give lower energy than the DGDZVP2 basis. Therefore, the α values for the DGDZVP2 basis should be larger than the 6-311G** basis to provide the more negative (or binding) potential required to give the energy equal to the *exact* energy. Except for H, which has no correlation energy, these α values are larger than the reported HF values[8] which is expected as these values are obtained for the exact energy (bounded from above by the HF energy). The HF α values show systematic monotonic decrease with the atomic number.[19] The current α values show overall decrease with the atomic number except for peaks at Li and Be. The peak at Li is caused by the fact that H has no correlation energy, while the peak for Be is caused by electron pairing and correlation in the outer orbital.

Table 2. Optimal α Values for the Different Basis Sets for Which the Eigenvalue of the Highest Occupied Molecular Orbital Is Exactly Equal to the *Exact* Ionization Potential (IP)[a]

	basis I	basis II	basis III	basis IV	IP[68]
H	1.1901	1.1901	1.1877	1.1877	13.60
Li	1.1246	1.1246	1.1152	1.1152	5.39
Be	1.2749	1.2749	1.2581	1.2581	9.32
B	1.1227	1.1220	1.0993	1.0989	8.30
C	1.1006	1.1000	1.0775	1.0770	11.26
N	1.0832	1.0832	1.0629	1.0629	14.52
O	1.2360	1.2345	1.1958	1.1946	13.61
F	1.1696	1.1694	1.1501	1.1498	17.42
Na	1.1181	1.1181	1.1221	1.1221	5.14
Mg	1.2256	1.2256	1.2311	1.2311	7.64
Al	1.1113	1.1112	1.1074	1.1067	5.98
Si	1.0864	1.0836	1.0875	1.0844	8.15
P	1.0501	1.0501	1.0662	1.0662	10.49
S	1.1543	1.1562	1.1759	1.1770	10.35
Cl	1.1211	1.1218	1.1344	1.1347	12.96

[a] The experimental values of the first ionization potentials (in eV) are also included in the last column. The basis sets are I: 6-311G**/RI-J, II: 6-311G**/A2, III: DGDZVP2/RI-J, and IV: DGDZVP2/A2.

The atomic α values can also be determined by different criteria. In the KS DFT it has been argued that the negative of the eigenvalue of the highest occupied orbital $-\epsilon_{max}$ equals the first ionization potential.[37−42] Although such an interpretation of the $-\epsilon_{max}$ is not yet settled, it gives us another way to determine set of α parameters. Such a such set of α's might be useful in future for calculations of polarizability or optical spectra. These α values are given in Table 2 for the four combinations of basis set. All the values presented are larger than those obtained from the total energy matching criteria. This is not surprising as the $-\epsilon_{max}$ for the local density type (α = 2/3) functionals typically underestimate the ionization potential by as much as 30−50%. It is known that this occurs due to the incorrect asymptotic behavior of the effective potential. The asymptotic behavior of the effective potential is governed by the exchange potential. In the present Xα method, the exchange potential decays exponentially in the asymptotic region, due to which the valence electrons experience shallower long-range potential than they otherwise should. In the present work, we, however, treat α as purely a fitting parameter to get the right ϵ_{max}. These α values do not decrease left to right across the periodic table and are rather close to Slater's value of α. The removal of self-interaction of an electron also leads to a better asymptotic description.[69] We think that the self-interaction correction can also be implemented in the present analytic SR method. Orbital densities are non-negative.

Finally, we explore the possibility of obtaining exact atomization energy (AE) within the present SR method, for selected diatomic molecules. For this purpose we use the Newton−Raphson procedure to obtain the zero of the following function: $f(\alpha) = E^{SR}_{mol}(\alpha) - 2E^{SR}_{atom}(\alpha) - AE = 0$. Here, E^{SR}_{mol} is the self-consistent total energy of the optimized molecules for a given α, and E^{SR}_{atom} is the self-consistent total atomic energy for a given alpha. The bond length of the molecule is optimized during each Newton−Raphson step. These calculations were performed using

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Table 3. Optimal α Values for the Selected Homonuclear Dimers that Yield the *Exact* Atomization Energies for the 6-311G**/RI-J Basis Set[a]

	α	D_0 (kcal/mol)	R_e present	R_e expt[76]
H_2	1.39172	−103.5	0.59	0.74
Li_2	1.45747	−24.0	2.12	2.67
Be_2	0.56596	−2.4	2.82	2.46
C_2	0.81530	−148.7	1.21	1.24
N_2	0.88901	−225.1	1.04	1.10
O_2	0.42790	−118.0	1.36	1.21
F_2	0.29685	−36.9	1.67	1.41
Na_2	1.61278	−16.6	2.27	3.08
Si_2	0.78366	−74.0	2.10	2.24
P_2	1.43361	−116.1	1.58	1.89
S_2	0.64867	−100.7	1.96	1.89
Cl_2	0.66335	−57.2	2.06	1.99

[a] The *exact* bond lengths (in Å) are also included in the last column.

PERL scripts, and the calculated set of α values is presented in Table 3. These values show a large variation as a function of the atomic number. The general trend is that the α values for the dimers of atom on the left of the periodic table are larger than 1.0 and smaller than 1.0 for the atoms on the right. For the exact values of the atomization energies the bond lengths of these dimers show the general trend that the atoms on the left side of the periodic table are larger and those on the right are smaller. The exception are the Be_2 and N_2 dimers, perhaps due to their weak and very strong bonding, respectively. Another noteworthy observation is that these dimers with exception of Be_2 are still bound for vanishingly small value of α. This is interesting as no molecules are bound in the Thomas-Fermi model.[70] It seems the bonding therefore occurs due to the exact treatment of kinetic energy in the present Xα method. Here, it should be noted that the 6-311G** basis sets used in this work may not provide a satisfactory description for very small α values as the electrons then will experience a very shallow potential and will be rather delocalized leading thereby to the artifacts like positive eigenvalues for the outermost electrons. For this reason the α for the F_2 dimer should be used cautiously. Further, these α values when viewed relative to the Kohn−Sham's value of 2/3 provide some hints on how the corrections to the Kohn−Sham exchange should energetically contribute for an accurate determination of atomization energies. The molecules with molecular α values larger than the Kohn−Sham value of 2/3 will be underbound in the exchange only KS scheme and those with α lower will be overbound. Any universal correction to the KS exchange functional should be such that it simultaneously reduces overbinding in some molecules and underbinding in others.

The atomization energies for the set of 54 molecules in 56 of the electronic states are presented in Table 4. These are calculated by the SR (EA) method using the set of α values given in Table 1. The calculations are performed for the two sets of basis sets. These molecules in the dissociation limit will give the *exact* atomized energies. It is evident from Table 4 that the Xα underbinds some molecules, while it overbinds others. This trend is in contrast with the local density approximation and the HF theory. The former

Table 4. Atomization Energies D_0 (kcal/mol) for the 56 Set of Molecules Calculated Using the Two Sets of α Values Given in Table 1 for the Two Basis Sets that Reproduce the *Exact* Atomic Energies[a]

	basis I	basis II	exact
H_2	85.1	87.3	110.0
LiH	38.1	33.8	57.7
BeH	58.2	32.7	49.6
CH	67.0	68.2	83.7
$CH_2(^3B_1)$	195.3	197.0	189.8
$CH_2(^1A_1)$	158.1	161.4	180.5
CH_3	299.2	302.4	306.4
CH_4	407.3	411.8	419.1
NH	67.1	68.8	83.4
NH_2	157.1	161.5	181.5
NH_3	271.8	278.4	297.3
OH	98.6	100.0	106.3
H_2O	228.0	232.8	232.1
HF	144.8	148.4	140.7
Li_2	6.6	5.6	24.4
LiF	147.7	136.4	138.8
C_2H_2	422.8	414.2	405.3
C_2H_4	571.6	573.5	562.4
C_2H_6	711.7	718.1	710.7
CN	190.5	181.4	179.0
HCN	317.7	307.8	316.3
CO	283.2	270.5	259.2
HCO	307.4	301.4	278.3
H_2CO (formaldehyde)	394.4	391.2	373.4
H_3COH	521.9	527.0	511.6
N_2	215.0	203.6	228.5
N_2H_4	413.6	424.9	437.8
NO	163.2	155.3	152.9
O_2	157.5	154.0	120.4
H_2O_2	283.3	289.0	268.6
F_2	66.5	68.3	38.5
CO_2	456.5	437.9	388.9
$SiH_2(^1A_1)$	125.4	128.0	151.4
$SiH_2(^3B_1)$	121.2	122.6	130.7
SiH_3	194.7	196.3	226.7
SiH_4	281.7	284.1	321.4
PH_2	126.1	130.4	152.8
PH_3	203.4	210.0	242.0
H_2S	163.6	169.3	182.3
HCl	101.4	102.5	106.2
Na_2	4.9	5.2	16.8
Si_2	72.0	72.2	74.7
P_2	94.1	94.5	117.2
S_2	110.2	111.7	101.6
Cl_2	64.4	65.9	57.9
NaCl	88.8	90.6	97.8
SiO	199.0	198.5	191.2
CS	179.2	178.4	171.2
SO	142.6	147.8	125.1
ClO	79.5	85.6	64.3
ClF	80.5	85.7	61.4
Si_2H_6	475.4	480.3	529.5
CH_3Cl	400.5	404.8	393.6
H_3CSH	467.8	475.8	472.7
HOCl	174.5	182.1	164.3
SO_2	281.4	286.4	258.5

[a] The two basis sets are I: 6311G**/RIJ, II: DZVP2/A2. The last column contains the *exact* values.

Table 5. Mean and Mean Absolute Error (kcal/mol) in the Calculated *Atomization* Energy of 56 Molecules (Cf. Table 4) Relative to Their Experimental Values for Different Basis Sets[a]

OB	FB	SR (EA) mean	SR (EA) absolute	SR (HF) mean	SR (HF) absolute
6-311G**	RI-J	−1.9	17.3	−5.1	16.4
DGDZVP2	A2	−1.6	16.2	−4.8	16.1

[a] The SR (EA) are present calculations, while SR (HF) are SR calculation with α_{HF} values. The SR (HF) results are from ref 33. The mean absolute error for the standard Hartree−Fock theory and the local density approximation is 78 and 40 kcal/mol,[54,84] respectively. Abbreviations: OB, orbital basis; FB, fitting basis (pdfg-type).

uniformly overbinds, while the latter uniformly underbinds. A similar trend has been found when the HF values of α are used.[33] In general, the error in atomization energy is smaller when the molecules consist of atoms on the opposite sides of the periodic table, for example, HCl, H_2S, NaCl, HO, etc. The best agreement is observed for the NH_3 with the DGDZVP2 basis and OH with all basis. The mean and mean absolute errors in the atomization energies of these molecules calculated with respect to their experimental values is given in Table 5. These errors are somewhat larger than those obtained when the HF α values are used. We note here that the HF values of α, α_{HF}, are those that when used in the Xα model reproduce the HF exchange energies for atoms.

The α values obtained from the ϵ_{max} matching criteria can be used to obtain the first ionization energy of a molecule from its highest occupied eigenvalue. Here, we demonstrate their use for calculations of the first ionization potential of N_2 and CO molecules. For the N_2 molecule, using the α values from Table 2 for basis sets I−IV, the ionization potential is 15.38, 15.34, 15.40, and 15.20 eV, respectively. These values are in good agreement with the experimental value of 15.58 eV.[71] For the CO molecule, the ionization potential is 14.83, 14.83, 14.53, and 14.53 eV for the basis sets I−IV. These values are also in very good agreement with CO's experimental ionization energy (14.01 eV).[72] We expect that the use of these α values gives better eigenspectra, which could be used in the polarizability calculations by the sum over states method.[73] The atomic or Hartree−Fock α values could be used to optimize the geometry of a molecule and then to calculate the matrix elements required in the sum over states expression. The eigenvalues required in the sum over states method can be obtained by performing one more self-consistent calculation using the α values from Table 2. The use of the improved eigenspectrum in the sum over states method has been found to give good estimates of polarizability.[73] Calculations for the set of 54 molecules using molecular α values (cf. Table 3) are not performed because the SR method as implemented now[33] cannot handle a wide variation in the molecular α values. Moreover for the reasons mentioned earlier these α values (particularly for the molecules containing *F*) necessitate bigger orbital basis sets. The trend in the bond lengths in Table 3 suggests that for these dimers better values of α may be obtained by minimizing the deviation of both the dissociation energy and the bond length, from their experimental values. There are several other possibilities for determination of α which may be useful in improving the performance of the SR method.

As mentioned earlier the differences in the Slater and the Gáspár−Kohn−Sham value of α are the result of a different averaging process employed in the derivation of exchange potential. This suggests the possibility that different α values for the description of the core (say α_c) and valence (α_v) electrons may provide a better description of the exchange correlations. The additional parameter in this case will provide greater flexibility in the fitting procedure. Alternatively, the Xα exchange functional can be augmented with suitable functional forms that allows the analytic solution of the problem. The local functional form by Liu and co-workers that consists of the sum of 0, 1, 1/3, and 2/3 powers of electron density and originates from the adiabatic connection formulation appears to be particularly suitable for this purpose.[74,75] We are currently exploring these possibilities.

To summarize three sets of α values are obtained on the different criteria for the use in the analytic SR method. The first set of α values is determined by equating the self-consistent total energy of atoms to the "exact" atomic energy. Two other sets are determined using different constraints such as equating the negative of the eigenvalue of the highest occupied orbital to the first ionization potential and reproduction of exact atomization energies for the diatomic molecules. The examination of the performance of the SR method for the atomization energies of 56 molecules with the first set of α values gives the mean absolute error to be about 17 kcal/mol. This value is far larger than the generally accepted chemical accuracy of 2 kcal/mol. The tabulation of the MAE for the G2 set and extended G2 set for more sophisticated functionals is given in ref 77. The MAE is within 4−9 eV for the parametrizations at the level of the generalized-gradient approximation (GGA).[78−81] The meta-GGA[82] or hybrid GGA functionals[54,83] perform even better with MAE of about 3 eV. The MAE is 37−40 kcal/mol for the local spin density approximation.[84] The SR method's performance is intermediate between the local spin density approximation and the GGA. We note that we have not optimized the method to give an accurate estimate of any particular property. The α parameters could be chosen to minimize the MAE in atomization energies such as the other density functional models, including the GGA, do. Such an optimization process would necessarily lower the error in Table 5. Our goal in this work is to examine simple schemes for extrapolating elemental properties to heterogeneous molecules, without any additional massaging of the results. For example, the set of α values from Table 1 can be used to extrapolate atomic energies to molecular energies by the SR method. Indeed, such an extrapolation gives remarkably accurate total energies (see Table 6), that are comparable to or better than those obtained by some popular, sophisticated pure and hybrid density functional models.[36] By construction, using the α values of this table, the MAE in total energies is the same as that in atomization energy. This is in contrast to many popular density functional models which seem to give better atomization energies due to cancellations of errors in total energies of atoms and molecules. Also, the SR method is unique in that molecules dissociate correctly in the separated atom limit. It is therefore not unreasonable to use α values adjusted for atoms. The present work shows

Table 6. Mean Absolute Error (MAE) in Calculated *Total* Energies of G2 Set of 56 Molecules for Different Models[a]

model	MAE
M1	17.3
M2	16.2
LDA	532
PBE-GGA	101
B3LYP-hybrid GGA	15

[a] The errors are in kcal/mol and are at optimized geometries in the respective model. M1: SR(EA)/6-311G**/RI-J, M2: SR(EA)/DGDZVP2/A2, LDA: local density approximation (see ref 36 for more details).

that fitting perhaps any molecular property can be done quantum mechanically through density functional theory. If the calculations are analytic and variational, then small basis sets can be used to generate unique, stable, and reliable energies using minimal computer time. Thus one can envision embedding quantum-mechanical calculations, with full geometry optimization where appropriate, to optimize very sophisticated quantum-mechanical calculations of molecular properties over the G2 and larger sets of molecules using PERL scripts to control the optimization on a single processor or to farm out independent suboptimizations on multiple processors. Our toolbox of functionals that can be treated analytically contains more[85] than the cube-root functional used in this work. Thus one can expect that as more experience is gained in analytic DFT we can better approximate the best exchange and correlation functionals that currently require limited-precision numerical integration. The process of driving MAEs lower and lower through better and better analytic functionals need never end, short of perfect agreement.

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