The limitations of Slater’s element-dependent exchange functional from analytic density functional theory

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Abstract

Our recent formulation of the analytic and variational Slater-Roothaan (SR) method, which uses Gaussian basis sets to variationally express the molecular orbitals, electron density and the one body effective potential of density functional theory, is reviewed. Variational fitting can be extended to the resolution of identity method, where variationality then refers to the error in each two electron integral and not to the total energy. However, a Taylor series analysis shows that all analytic ab initio energies calculated with variational fits to two-electron integrals are stationary. It is proposed that the appropriate fitting functions be charge neutral and that all ab initio energies be evaluated using two-center fits of the two-electron integrals. The SR method has its root in the Slater’s Xα method and permits an arbitrary scaling of the Slater-Gáspár-Kohn-Sham exchange-correlation potential around each atom in the system. The scaling factors are the Slater’s exchange parameters α. Of several ways of choosing these parameters, two most obvious are the Hartree-Fock (HF) αHF values and the exact atomic αEA values. The former are obtained by equating the self-consistent Xα energy and the HF energies, while the latter set reproduce exact atomic energies. In this work, we examine the performance of the SR method for predicting atomization energies, bond distances, and ionization potentials using the two sets of α parameters. The atomization energies are calculated for the extended G2 set of 148 molecules for different basis set combinations. The mean error (ME) and mean absolute error (MAE) in atomization energies are about 25 and 33 kcal/mol, respectively for the exact atomic, αEA, values. The HF values of exchange parameters, αHF, give somewhat better performance for the atomization energies with ME and MAE being about 15 and 26 kcal/mol, respectively. While both sets give performance better than the local density approximation or the HF theory, the errors in atomization energy are larger than the target chemical accuracy. To further improve the performance of the SR method for atomization energies, a new set of α values is determined by minimizing the MAE in atomization energies of 148 molecules. This new set gives atomization energies half as large (MAE ∼ 14.5 kcal/mol) and that are slightly better than those obtained by one of the most widely used generalized gradient approximations. Further improvements in atomization energies require going beyond Slater’s element-dependent functional form for exchange employed in this work to allow exchange-correlation interactions between electrons of different spin. The MAE in ionization potentials of 49 atoms and molecules is about 0.5 eV and that in bond distances of 27 molecules is about 0.02 Å. The overall good performance of the computationally efficient SR method using any reasonable set of α values makes it a promising method for study of large systems.

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Theoretical methods for electronic structure calculations in practice today can be broadly classified into two categories. From the perspective of density functional theory (DFT), these two classes of models differ from each other only in the way the unknown exact exchange-correlation (XC) energy functional is approximated. The first class of methods are the traditional quantum chemical methods such as Hartree-Fock (HF) theory and beyond [1]. These methods are generally implemented using Gaussian basis sets. The molecular orbitals are analytically expressed as linear combinations of atomic orbitals (LCAO). The atomic orbitals are contracted sets of primitive Gaussian basis functions. One advantage of the Gaussian basis set is that it permits computation of matrix elements of the energy and a number of other properties completely analytically, which allow them to be computed to whatever precision is desired. Another advantage of Gaussians is that they are very localized in real and momentum space resulting in sparse matrices. The primary disadvantage of Gaussian-based HF is that it formally scales as \( N^4 \), where \( N \) is the number of atomic orbital basis functions. Despite that single disadvantage HF is often the choice of users for geometry-optimization of molecules because usually some combination of basis-set choice, cutoff and other approximations define HF calculations that are the fastest all-electron calculations using current, commercial, quantum chemistry computer packages. HF-based methods can always be systematically improved towards the exact results.

Density functional (DF) based models [2, 3] form the second class of methods for studying the ground-state properties of materials. The most important aspect of density functional theory is relative computational simplicity which leads to better scaling and the ability to optimize the functional form of the Kohn-Sham (KS) multiplicative potential. Today, KS density functional models are the predominant choice for pure electronic structure calculations. DFT formally scales as \( N^3 \). Various implementations of the DF models that use a variety of different type basis sets as well as those that are fully numerical (use no basis sets) have been reported. Most of these implementations including those that use analytic Gaussian basis sets require use of numerical mesh to compute the contribution from the XC term. The complexity of the functional forms, particularly for all-electron calculations using the gradient-corrected functionals can require a very sophisticated numerical grid of points to integrate the XC energy density to get the total energy accurately. The use of grids makes calculations of matrix elements that are accurate to arbitrary precision (as in the Hartree-Fock method) practically impossible and leads to number of problems such as steps or kinks in the potential energy surface, spurious negative frequencies, etc. Also, a numerical total energy incorrectly depends on how the molecule is oriented with respect to the
orientation of the numerical grid. Consequently, the total energy is not exactly rotationally
invariant \cite{4, 5}. Some of these problems can be eliminated by using very refined numerical
grids which, needless to say, leads to reduction in computational speed that compromises
the inherent efficiency of the DF models. DF implementations that are fully analytic are
obviously desirable.

While translating the Slater-type-orbital DF method of Baerends, Ellis and Ros \cite{6} for
Gaussian-type-orbitals, Sambe and Felton \cite{7} proposed treating the KS equation completely
analytically, which was a significant first step towards analytic DFT, however a numerical
grid was needed to fit the XC potential. This works quite well for the subset of DF theory in
which the same fits can be used in the KS equations and the energy thereby almost preserving
the variational principle; i.e. preserving the variation principle when a complete basis set is
used to fit the XC potential \cite{8}. These efforts greatly improved upon the muffin-tin (MT)
approach to DFT, which spherically averaged the KS potential introducing a discontinuity
in the potential at the surface of the spheres. Direct integration of the potential in the
MT approximation leads to an undefinable energy. Instead, as is common even today with
diverse formulations of DFT, one simply makes the same approximations in evaluating the
energy that one makes in computing the potential \cite{9, 10, 11, 12}. In such cases today one
argues, where possible, that the energy and the KS potential are computed exactly, therefore
the calculation is variational. In this work the calculation of the energy and potential is
inexact due to incomplete basis sets, but the calculations are to machine-precision explicitly
variational.

Our variational solution \cite{8} to the problem of fitting any charge distribution has become
quite popular, particularly for simplifying MP2. While adding second derivatives \cite{14}
to a descendant of our code, DGauss \cite{15}, a different fit was used to simplify the MP2 energy
expression. That new fit was called Resolution of the Identity (RI) \cite{16}. In a later application
of their RI method, one of the definers of RI showed empirically that our fitting method
was better than the original approach \cite{17}. Many have attributed this improvement to some
unknown \cite{17, 18} or not clearly relevant \cite{19} properties of the Coulomb norm and have
told us that others \cite{20, 21} used the Coulomb norm before our work. Our work concerns
variational fitting, whereas RI, which if it is not precisely our method, requires a complete
basis set.

The fits used in the later RI work are precisely the variational solutions that maximize
the unique robust (no first-order error due to fitting) Coulomb self-energy of the fitted
charge distributions. Furthermore, with these fits, the RI energy calculated using three-
center approximations to the two-electron integrals is identical to the same expression using the two-center approximations to the two-electron integrals that are obtained using fits to both charge distributions [22]. In the following, we examine a Taylor-series expansion in the error made in fitting two-electron integrals in all \textit{ab initio} energies. We define good (but not perfect) fits to have negligible quadratic and higher errors. All XC-related, robust and variational fits used in this work do not involve the Coulomb norm.

Chemists are beginning to say that our method does not work in RI applications to large systems [23, 24, 25]. The physics problem is that an unbalanced charge, no matter how small or how far separated, when arranged on an infinite, periodic lattice has an infinite Coulomb self-energy. A way to handle this fact is to constrain the fits to have the right charge [6, 26, 27, 28]. If this is done, then by Gauss’ law the electrostatic potentials of the fitted and exact charge distributions become identical as soon as they possibly can, outside the two distributions. Our code uses both constrained and unconstrained fits. The fits are robust, and if they are good (but not perfect) then the constrained and unconstrained energy are the same within typical quantum chemical tolerances.

This work also uses robust and variational fits of the XC potential. A set of DFT models that have the same functional form in the energy density and the KS potentials,

\[ E_{xc}[\rho] = \frac{3}{4} \rho(\vec{r}) v_x[\rho(\vec{r}), \vec{r}] d^3r, \]

with

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

where \( \alpha \) is the Slater exchange parameter (which was found to be 1 by Slater [29] and 2/3 by Gàspàr [30] and Kohn and Sham [3] (GKS)), is easiest to treat analytically. The difference in the two values of \( \alpha \) has roots in the averaging process employed in the simplification of the HF exchange potential. Slater obtained \( \alpha = 1 \) while simplifying the nonlocal exchange potential of the Hartree-Fock approximation by averaging exchange potential over the entire Fermi sphere of radius \( k_f = (3\pi^2 \rho(\vec{r})) \). The GKS value of 2/3 is obtained by applying the variational method to the statistical total energy expression, and only uses an average over surface of the Fermi sphere \( k = k_f(\vec{r})^{1/3} \). Later, Kohn and Sham also set \( \alpha \) to be 2/3 for general energy functionals through the construct of the non-interacting electron gas. Most DF models that are in practice today use the GKS value of \( \alpha \). Recently, overall improvement in performance of some of these DF models has been noted if \( \alpha \) is allowed to vary [31, 32, 33].

In the \( X\alpha \) method, the form of the exchange potential is given by Eq. [1] and the \( \alpha \) are the scaling parameters. The \( X\alpha \) method is the outcome of simplifying the Hartree-Fock method.
It was suggested that the scaling parameters $\alpha$ could be obtained by ensuring that the self-consistent $X\alpha$ energy for atoms matches the Hartree-Fock energy. Such set of $\alpha$ parameters was determined by Schwarz [34]. Subsequently, several other ways to determine the $\alpha$ parameters were proposed [35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47]. The muffin-tin implementation of the X$\alpha$ method allowed the use of atom-dependent $\alpha$ values. The unique advantage of this quantum-chemical method was that the model smoothly dissociates into atoms as it was pulled apart, independent of the basis-set (partial waves in the muffin-tin method). With the ability to choose the atomic energies however one wanted, it is a way to extrapolate atomic properties to all homogeneous and heterogeneous materials, or alternatively the properties of all elemental molecules or crystals to all heterogeneous materials.

A fully analytic method that allows arbitrary scaling of exchange potential around each type of atom in the heteroatomic system was recently formulated and implemented [5]. It is called Slater-Roothaan (SR) method. It is free from the problematic energy of the multiple scattering X$\alpha$ model but retains all its advantages. It is computational very efficient and has been successfully applied to study boron and aluminum nitride nanotubes contains about two hundred atoms [48, 49].

The accuracy of the SR method ultimately depends on the choice of scaling parameters, $\alpha$’s, used in calculations. Two obvious choices for choosing $\alpha$ are: (1) the $\alpha = \alpha_{HF}$ values that give the HF energy for atoms, and (2) the $\alpha = \alpha_{EA}$ values that give the exact atomic energies. The use of later set is appealing because when used in molecular calculations, as the molecule dissociates the corresponding sum of the exact atomic energies can be obtained. Our early calculations on the total energies of molecules shows that remarkably accurate total molecular energies can be obtained using the second set [50]. These molecular energies of the G2 set of 56 molecules are better than or comparable to most pure or hybrid density functional models (such as PBE [51], B3LYP [52] etc, see Ref. 50 for details). In the present work, we examine the overall performance of the Slater-Roothaan method for the atomization energies, bond distances, and ionization potentials when the above sets of $\alpha$ values are used. We use the extended G2 set of 148 molecules for the benchmark. This set is routinely used to examine the performance of various density functional and related models. As we shall see, the performance for atomization energies with these two combinations of Gaussian basis sets, though better than the local density approximation or the Hartree-Fock method, is inferior to that of the DFT models with generalized-gradient approximations (GGA). Many density functional models are parametrized to give better
atomization energy. Following this practice, we explore the possibility of improving the performance of Slater-Roothaan method for atomization energies. This is accomplished by determining a new set of $\alpha$ values that minimize the mean absolute error (MAE) in the atomization energies of 148 molecules. This parametrization gives accuracy comparable to some of widely used gradient-corrected density functional models.

I. THEORETICAL METHOD

A. Variation and the Eigenvalue Problem

Our interest is in the development of analytic DFT through robust and variational fitting. The total electronic energy in Hohenberg-Kohn-Sham [2, 3] DFT for an $N$-electron system is a functional of electron density $\rho$. The electron density is given by

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

(2)

where, $\phi_{i,\sigma}(\vec{r})$ are single particle orbitals, and $n_{i,\sigma}$, the occupation numbers for both spins. The total electron density $\rho$ is the sum of spin densities $\rho_{\uparrow}$ and $\rho_{\downarrow}$. In chemistry, the orbitals are still usually expressed in LCAO form,

$$\phi_{i,\sigma}(\vec{r}) = \sum_{j} C_{ij} u_{j}(\vec{r})$$

(3)

The energy is determined by constrained variation of the energy with respect to orthonormal orbitals,

$$\frac{dE}{dC_{ij}} = \epsilon_{ik} \langle \phi_{k} u_{j} \rangle,$$

(4)

where the angular braces indicate the overlap integral and the $\epsilon$ matrix is all the Lagrange multipliers needed to allow the orbitals to be made orthonormal while minimizing the energy. In DFT a unitary transformation can always be found to diagonalize this matrix to generate a conventional molecular-orbital eigenvalue problem. This eigenvalue problem is called the Kohn-Sham (KS) equations. We approximate these equations by fitting in uniques ways to make them less computationally challenging while preserving the full variational principle.

The first robust and variational fit was to the self-Coulomb energy of a charge distribution,

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

(5)
This energy is approximated by expressing the charge density as a fit to a set of Gaussian functions,
\[ \rho(\vec{r}) \approx \bar{\rho}(\vec{r}) = \sum_i d_i G_i(\vec{r}), \] (6)
where, \( \bar{\rho}(\vec{r}) \) is the fitted density, \( d_i \) 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 the unique robust expression for the self-Coulomb energy \[ E_{ee} \simeq E_{ee} = 2\langle \bar{\rho} || \rho \rangle - \langle \bar{\rho} || \bar{\rho} \rangle = \langle \bar{\rho} || \rho \rangle + \langle \Delta \rho || \rho \rangle, \] (7)
where, \( \Delta \rho = \rho - \bar{\rho} \). Unconstrained variation of this energy gives \[ \bar{d} = \langle \bar{G} || \bar{G} \rangle^{-1} \cdot \langle \bar{G} || \rho \rangle. \] (8)

In this work, an overline represents any approximation, good, bad or exact. Thus the identity is not necessarily resolved, and we do not use the RI method \[16, 17\]. Hopefully we and others can generate basis sets that deliver good fits.

In any event we single out fitted energies that contain no first-order error and call them robust, because mathematically speaking, it makes no sense to include non-robust, approximate energies in any eigenvalue problem. The fit, if it is good, will change if the original charge distribution does; the derivatives of good fitting coefficients with respect to LCAO orbital coefficients are not zero. In the derivative of the total energy, however, this derivative is multiplied by zero if the fit is obtained by variation of a robust energy. It is easy to obtain atomic density-fitting bases for which the first-order error is small and approximately equal to the square root of the total (quadratic) error made in this approximation \[53\]. (Of course, variational fits only have a first-order error if they are constrained.)

With the advent of fitting basis sets that are individually optimized for corresponding orbital basis sets \[54, 55\], it is appropriate to define a stronger definition of good fit. If we can use basis sets that are accurate to one part in \(10^{-5}\) then a robust fitted energy is accurate to is about one part in \(10^{-10}\), which is a appropriate number to be used for molecular integral cutoffs, defining convergence, etc., in \textit{ab initio} quantum chemistry codes and can probably be safely neglected in most of quantum chemistry. We call a fit this good or better a good fit. Such a fit is only a good fit, we do not claim it to be exact. This is our target, which at this point we cannot guarantee.

One could, of course, use a non-robust expression for the fitted energy and then correct the effects of that error on the orbital variational problem by taking the total derivative of
the energy, as written in Eq. 3. In that case the corresponding Fock matrix or KS equations differ from what would be obtained by inserting the non-robust fit where appropriate in the fit-free eigenvalue or KS equations. The potential of the eigenvalue problem cannot be made independent of the energy. If the dependence of the energy on the orbitals is not treated variationally, then the forces are not accurate \[56\]. This fundamental problem probably means that the proposal of Sambe and Felton \[7\] to fit the exchange-correlation (XC) potential of DFT to LCAO form by numerical sampling (or direct numerical integration) must be abandoned. Now almost all DFT codes treat the XC potential by direct numerical integration, despite the fact that exact forces arising from using an auxiliary basis to numerically fit the XC potential are known \[57\] and have been implemented precisely for gradient corrected functionals \[58\]. The exact partitioning scheme of Becke \[59\] together with adaptive grids that vary with the orbital basis set \[60\] are now overwhelmingly popular with LCAO approaches to DFT \[61\]. Intermediate in the trade-off between accuracy and efficiency between the Sambe-Felton and Becke approaches is one in which the variationally-fitted density (Eq. \[6\] ) replaces the two-center exact density in the numerical construction of the XC matrix elements \[62\].

B. Robust Fitting and the Resolution of the Identity

The post-HF \textit{ab initio} energies are functions of the two-electron integrals

\[
\langle \phi_i \phi_j || \phi_k \phi_l \rangle \equiv \langle ij || kl \rangle. \tag{9}
\]

RI energies are defined to be functions of \( \langle ij || kl \rangle \), where \( kl \) is the fit to the \( kl \) orbital pair. The post-HF \textit{ab initio} energies can be expanded in a Taylor series in the difference between an exact two-electron energy and any approximate two-electron energy,

\[
E(\langle ij || kl \rangle) - E(\langle ij || kl \rangle) = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n E}{\partial (ij || kl)^n} \Delta_{ijkl}^n, \tag{10}
\]

where

\[
\Delta_{ijkl} = \langle ij || kl \rangle - \langle ij || kl \rangle. \tag{11}
\]

The unique robust two-electron energy

\[
\langle ij || kl \rangle \approx \langle ij || kl \rangle_{rob} = \langle ij || kl \rangle + \langle ij || kl \rangle - \langle ij || kl \rangle, \tag{12}
\]

where both fits are separately determined by Eq. \[8\], is beginning to be used directly in \textit{ab initio} quantum chemistry \[63\]. No matter how both fits are obtained there is no first-order
error,
\[ \langle ij||kl \rangle - \langle ij||kl \rangle_{rob} = \langle \Delta_{ij}||\Delta_{kl} \rangle. \] (13)

If Eq. (8) is used then all approximations are exactly equal \[64\],
\[ \langle ij||kl \rangle = \langle ij||kl \rangle = \langle ij||kl \rangle, \] (14)
and the RI and robust (Eq. (12)) approximations to the two electron integral are identical.

The Coulomb norm is not magical. Coulomb potentials from charge distributions can
be approximated robustly by fitting the potential due to a charge distribution rather than
fitting the charge distribution itself \[53\]. Obtaining good basis sets, however, is more of a
problem than in the charge distribution fitting case \[65\], which is being overcome \[66\]. For
\textit{ab initio} energies,
\[ E(\langle ij||kl \rangle) - E(\langle ij||kl \rangle_{rob}) = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n E}{\partial \langle ij||kl \rangle^n} \langle \Delta_{ij}||\Delta_{kl} \rangle_{ijkl}^n. \] (15)

If both fits are good, then this equation practically equals zero, i.e., \( \langle \Delta_{ij}||\Delta_{kl} \rangle \), being
quadratic in errors, is expected to be accurate to one part in \( 10^{10} \). Thus, for good RI
fits, the fitted energy is practically identical to the original energy
\[ E(\langle ij||kl \rangle) \simeq E(\langle ij||kl \rangle_{rob}) = E(\langle ij||kl \rangle) = E(\langle ij||kl \rangle) = E(\langle ij||kl \rangle), \] (16)
where the last three equalities hold only if the fits are obtained using Eq. (8).

These simplest, global fits are problematical for large clusters \[23, 24\]. They could be
constrained, in which the case the robust, rather than either of these two approximate,
two-electron energies that involve a single fit must be used to obtain robust energies, independent
of whether or not the Coulomb metric is used. It might be better to consider changing the
fitting basis. The amount of charge in the product of two molecular orbitals is either zero or
one depending on whether or not the orbitals are the same. If the orbitals are the same, then
our methods are sufficient \[8, 53\]. If the orbitals differ, as is the case in MP2, then all fitting
basis functions should contain no charge, and a similar \( p \) RI basis for atoms corresponding
to our \( s \)-type density-fitting basis, would include all the atomic \( p \) exponents in the orbital
basis, but rather than doubled simply incremented by the smallest \( s \) exponent. This picks
up the smallest \( p \)-type contribution possible from the product of primitive \( p \) and \( s \) orbital
functions and this basis has a flexibility equal to that of the \( p \) orbital basis. For most basis
sets this is smaller than the correspond \( s \)-type charge-density fitting basis. Since the basis
is neutral and the product of different orbitals pairs to be fit is neutral, then all interactions
die off as fast as possible by Gauss’ law. All non-s fitting functions have no charge, therefore the $L > 1$ charge-density fitting functions are probably a good basis sets for fitting both the diagonal and non-diagonal products of two molecular orbitals. This is obviously a better basis than any currently used for studies of large systems. If the RI fitting basis behaves well asymptotically, then the Coulomb norm is likely to be proved best again for standard RI approximations to the MP2 energy of infinite systems [67]. A zero-charge basis will likely to be effective in density functional perturbation theory as well, if the resolution of the identity [68, 69] or ideally robust and variational fitting is used. With such a basis we envision keeping constrained fits as a simple option to test the stability of the calculation even for large systems.

C. Variational Fitting

We take the full variation of the energy with respect to the orbitals before solving the eigenvalue problem in order to obtain precise forces. If we modify the energy by adding any number of robust fits,

$$f[a_i(\vec{r})] = f[\overline{a}_i(\vec{r})] + \text{Order}[(a_i - \overline{a}_i)^2], \quad (17)$$

$$\overline{a}_i(\vec{r}) = \sum_{ij} a_{ij} A_i(\vec{r}), \quad (18)$$

where $A_i(\vec{r})$ is an appropriate LCAO basis for the $i$th fit, to approximate troublesome terms in the energy, then the Fock matrix for the corresponding eigenvalue equation is obtained by the chain rule of differentiation,

$$\frac{dE}{dC_{ij}} = \sum_{kl} \frac{dE}{da_{kl}} \frac{da_{kl}}{dC_{ij}}. \quad (19)$$

If robust fits are available, then we can improve upon them by obtaining the fits through a variation of our robust energy, exactly as orbitals are obtained. If and only if the fits are variational can the same fits be present in both the energy and the corresponding eigenvalue problem for the orbitals.
D. Analytic formulation of the Gàspàr-Kohn-Sham-Slater density functional model

The KS energy is given by

\[ E^{KS}[\rho] = \sum_{i}^{N} \langle \phi_i | f_1 | \phi_i \rangle + E_{ee} + E_{xc}[\rho^\uparrow, \rho^\downarrow] \]  (20)

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

\[ f_1 = -\frac{\nabla^2}{2} - \sum_{A} M \frac{Z_A}{|\vec{r} - \vec{R}_A|}. \]  (21)

The second term in Eq. (20) represents the classical Coulomb interaction energy of electrons discussed above. It is approximated robustly through Eqs. (7) and (8). The last term \( E_{xc} \) in Eq. (20) is the exchange energy,

\[ E_{xc}[\rho^\uparrow, \rho^\downarrow] = -\frac{9}{8} \alpha \left[ \frac{6}{\pi} \right]^{1/3} \int d^3r \left[ \frac{\rho^\uparrow}{4} (\vec{r}) + \frac{\rho^\downarrow}{4} (\vec{r}) \right]. \]  (22)

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 expanded in Gaussian basis sets:

\[ \rho^{1/3}(\vec{r}) \approx \rho^{1/3} = \sum_i e_i E_i \]  (23)

\[ \rho^{2/3}(\vec{r}) \approx \rho^{2/3} = \sum_i f_i F_i. \]  (24)

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

\[ E_{xc} = C_{\alpha} \left[ \frac{4}{3} \langle \rho^{1/3} \rangle - \frac{2}{3} \langle \rho^{1/3} \rho^{1/3} \rangle + \frac{1}{3} \langle \rho^{2/3} \rho^{2/3} \rangle \right], \]  (25)

where \( C_{\alpha} = -9\alpha \left[ \frac{3}{\pi} \right]^{1/3} \). 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 \( \mathbf{d}, \mathbf{e}, \) and \( \mathbf{f} \) are found by constrained variation.
E. Slater-Roothaan method

The expression for the total electronic energy in the Slater-Roothaan method has the following form:

\[ E^{SR} = \sum_i \langle \phi_i | f_1 | \phi_i \rangle + 2 \langle \rho | \bar{\rho} \rangle - \langle \bar{\rho} | \bar{\rho} \rangle - \sum_{\sigma=\uparrow,\downarrow} C_x \left[ \frac{4}{3} \langle g_\sigma \bar{g}_\sigma \rangle + \frac{2}{3} \langle g_\sigma \bar{g}_\sigma \rangle \right] \]

(26)

Here, \( C_x = C_\alpha / \alpha \); the partitioned 3/4 power of the exchange energy density,

\[ g_\sigma (\vec{r}) = \sum_{ij} \alpha(i) \alpha(j) D_{ij}^\sigma (\vec{r}) \]

(27)

where \( D_{ij}^\sigma (\vec{r}) \) is the diagonal part of the spin density matrix, and the function,

\[ \alpha(i) = \alpha_i^{3/8} \]

(28)

contains the \( \alpha_i \), the \( \alpha \) in the X\( \alpha \) for the atom on which the atomic orbital \( i \) is the centered. The fits to powers of \( g_\sigma \) corresponding to Eq. 23-24 are obtained variationally from Eq. 26.

II. COMPUTATIONAL DETAILS

The analytic SR method requires four Gaussian basis sets. One for the orbital expansion and others to fit different powers of electron density, which we obtain from literature. We choose Pople’s triple-\( \zeta \) (TZ) 6-311G** basis\cite{75,76} and the DGAuss\cite{15} valence double-\( \zeta \) (DZ) basis set\cite{54} called DZVP2 for orbitals basis sets. The \( s \)-type fitting bases are obtained by scaling and uncontracting the \( s \) part of the orbital basis. The scaling factors are 2 for the density, \( \frac{2}{3} \) for \( \rho^\frac{1}{4} \) and \( \frac{4}{3} \) for \( \rho^\frac{2}{4} \). These scaled bases are used for all \( s \)-type fitting bases. Ahlrichs’ group has generated a RI-J basis for fitting the charge density of a valence triple-\( \zeta \) orbital basis set used in the TURBOMOLE program\cite{55}. The non-\( s \) parts of Ahlrich’s fitting bases are used in combination with the 6-311G** orbital basis sets. Hereafter, we shall refer to this combination of basis sets as basis set I or 6-311G**/RIJ. In combination with DZVP2 orbital basis, we use the \( pd \) part of the A2 charge density fitting basis. This will be referred to as basis set II or DZVP2/A2. The geometries of molecules were optimized using
the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm \[74, 78, 79, 80, 81\]. The forces on atoms are rapidly computed non-recursively using the 4-j generalized Gaunt coefficients \[82, 83\]. The atomic energies are obtained in the highest symmetry for which the self-consistent solutions have integral occupation numbers. The atomization energy is computed from the total energy difference of optimized molecule and its constituent atoms. The open shell atoms are treated in lower than spherical symmetry so that they could have integrals occupation numbers. Thus, following point group symmetries were chosen: \(C_{2v}\) for C, O, Si and S atoms, \(D_{6h}\) for atoms F, Al, and Cl, \(D_{3h}\) for B, and \(I_h\) for Li, N, Na and P.

A database of geometries of set of 148 molecules, known in literature as the extended G2 set, was built. The molecules were built with appropriate symmetries to expedite their structure optimization. A new set of \(\alpha\) values was optimized by minimizing the mean absolute error in the atomization energies of the 148 molecules:

\[
\{\alpha_{OPT}\} = \min \left[ \frac{1}{148} \sum_{i} |D_e^i(\{\alpha_j\}) - D_e^i(\text{exact})| \right],
\]

where, \(D_e^i(\{\alpha_j\})\) is the atomization energy of the \(i^{th}\) molecule with \(j^{th}\) set of alpha values. The \(\{\alpha_j\}\) optimization was repeated by starting with two different sets of alpha values: \(\alpha_{HF}\) and \(\alpha_{EA}\). We used the simplex method \[81\] and during each iteration of \(\{\alpha_i\}\) optimization procedure, all 148 molecules were reoptimized. The \(\{\alpha_i\}\) optimization process all together involved about 10000 optimization of molecules, which was accomplished by the use of PERL scripts. The final optimal set gives the best atomization energies for the simple element dependent Slater’s exchange functional employed in the present model. It is called \(\alpha_{OPT}\) hereafter.

III. RESULTS AND DISCUSSION

A. Atomization energies

The two sets of \(\alpha\) values used calculations in these calculations are given in Table I. The last column in this table is a new set of \(\alpha\) values, which as noted earlier, is parametrized to give the best atomization energies. The computed atomization energies for the G2 set of 148 molecules are given in Table II. The point group symmetries of molecules are also listed in the Table III. The last two rows in Table III give the mean absolute error (MAE) and the mean error (ME) in the atomization energies of the 148 molecules. It is apparent from the MAE and ME that the basis sets effects are marginal. The errors with smaller
basis DZVP2/A2 are of similar magnitude to those obtained by the larger 6-311G**/RIJ basis set. For the exact atomic alpha, $\alpha_{EA}$, values the MAE is about 34 kcal/mol which is larger than that for the atomic Hartree-Fock, $\alpha_{HF}$, values ($\sim$ 26 kcal/mol). In the former case, the atomic energies by construction have zero error. In the case of $\alpha_{HF}$, the atomic energies are equal to the Hartree-Fock energies. So error in atomic energies is roughly the correlation energies of these atoms [84]. As the $\alpha_{EA}$ values give exact total energies of atoms, it was expected that their use in molecular calculations will result in overall improvement in molecular properties. This expectation is not unreasonable as atomic energies are exact by construction and the molecules in the dissociation limit would give sum of exact atomic energies. It is therefore surprising that the $\alpha_{HF}$ set performs better than the $\alpha_{EA}$ set. The better performance for the former set is clearly a consequence of error cancellation of total energies of molecules and atoms. On the other hand, the MAE in atomization energies is the same as error in total energies when $\alpha_{EA}$ values of used. No error cancellation occurs in this case. Note that performance of many density functional models for atomization of energies is due to such cancellations of errors in total atomic and molecular energies [50]. Many of these sophisticated functionals perform poorly for the total energies. The ME reflect that use of $\alpha_{EA}$ and $\alpha_{HF}$ values lead to an overall overestimation of the atomization energies. The largest deviation of about 146 kcal/mol occurs for the C$_2$F$_4$ molecule. There are about 6 molecules with absolute errors larger than 100 kcal/mol. These are CF$_4$, CF$_3$CN, C$_6$H$_6$, C$_4$H$_4$O, C$_5$H$_5$N, and C$_2$F$_4$.

Optimizing the SR method for atomization energies significantly improves its performance as can be seen from the Table II. The MAE and ME in atomization energies are reduced to 14.5 kcal/mol and -4.5 kcal/mol. The optimization process varies most the $\alpha$ values of atoms on the left of periodic table and those on the right side. The $\alpha$ values of N, O, and F are reduced with respect to the $\alpha_{HF}$ and $\alpha_{EA}$ values. The maximum absolute error is also reduced significantly. Overall performance of $\alpha_{OPT}$ set for atomization energies is comparable to that of the Perdew-Burke-Ernzerhof [51] generalized gradient approximation (PBE-GGA)[86].

B. Bond distances

The bond distances of 27 selected diatomic molecules [87] are compared in Table III with their exact counterparts. The MAE and ME in bond distances are in the last two rows of the same table. The maximum MAE is about 0.02 Å. Except for the larger basis with $\alpha_{HF}$
the ME are negative. Unlike LDA or GGA, there is no consistent trend of overestimation or underestimation. On the whole the bond distances are smaller than the experimental bond distances. This trend is different from that of the local density approximation (Slater exchange + Vosko-Wilk-Nusair correlation, called sometimes as SVWN) and GGA functionals[4, 88] which either overestimate or underestimate bond distances. The slight underestimation of bond distances, on average seems consistent with the on the whole over-estimation of atomization energies. In particular, the $\alpha_{EA}$ bond distances are shorter and the atomization energies higher. The present value of MAE (Table III) can be reduced if molecules containing Li and Na are omitted. The largest deviation of 0.09 Å occurs for the Na$_2$. Also, F$_2$ is another molecule which is difficult for the present models. Indeed, our study on these diatomics show that even a very small value of $\alpha$ leads to binding of the F$_2$ molecule[43]. Overall the bond distances are fairly accurately predicted for both the $\alpha$ values are used, with $\alpha_{HF}$ values giving somewhat better performance. The bond distances with new $\alpha_{OPT}$ set are not given in Table III. Using this set, the MAE in bond distances of 27 molecules increases to 0.04 Å.

C. Ionization potentials

The ionization potentials of 49 atoms and molecules[89] computed for the $\alpha_{HF}$ and $\alpha_{EA}$ values are compared with their experimental counterparts in Table IV. In computing the ionization potential (IP) the energy of the cation was calculated at the geometry of the neutral molecule. Also, the symmetry of the neutral system was assumed for the cation. This choice of convenience will tend to exaggerate the errors in IP for some systems. For example, the IP of nitrogen atom and methane molecule, are overestimated. For N atom, broken-symmetry calculation will give lower energy for cation. Similarly, Jahn-Teller distortion will lower the energy of methane cation and will reduce the error in the (adiabatic) IP. The MAE in IP for two sets of $\alpha$ values are about 0.5 eV. Both, MAE and ME are of roughly similar magnitude for both basis sets combinations indicating that the basis set effects are negligible. The sign of deviations do not show any consistent trend of overestimation or underestimation. The electron affinities could be similarly computed from the energy difference of the neutral molecule and its anion. However, we did not compute the electron affinities as the computation of electron affinities within the most density functional models (including the present one) is problematic as these quantities are sensitive to the self-interaction of electrons. The presence of self-interaction error leads to exponential decay of
the effective potential in the asymptotic region as opposed to the correct $-1/r$ asymptote. The additional electron in the anion therefore experiences shallower potential than it otherwise should. This sometimes leads to the positive eigenvalue for this electron although the total energy may be lowered. For this reason we did not compute electron affinities but we expect that accuracy of the present method for electron affinity will be similar to that of the local density approximation.

IV. SUMMARY

Analytic quantum mechanics using Gaussian basis sets has been extended. RI \textit{ab-initio} energies evaluated using two electron integrals in which both charge distributions are variationally fitted are themselves variational with respect to the fitting parameters. The performance of fully analytic density functional model called the Slater-Roothaan method, is examined for various properties, using two different sets of $\alpha$ values, for two different basis sets. The comparison of two sets of $\alpha$ values used in this work show that $\alpha$ values obtained by matching atomic Hartree-Fock energies ($\alpha_{HF}$) give better performance that those obtained by equating atomic energy to the exact atomic energies ($\alpha_{EA}$). The basis set effects as judged from the comparison of results obtained with two sets of bases show that smaller DZVP2/A2 basis provides accuracy comparable to the larger 6-311G**/RIJ basis. The MAE in atomization energies of the SR method with $\alpha_{HF}$ and $\alpha_{EA}$ sets are about 26 and 34 kcal/mol, respectively. In comparison with the local density approximation or the Hartree-Fock method, the SR method with $\alpha_{HF}$ and $\alpha_{EA}$ sets performs quite well for atomization energies, bond distances and ionization potentials. Further improvement in performance of the Slater-Roothan method for atomization energies is obtained by parameterizing it for atomization energies. A new set of $\alpha$ parameters ($\alpha_{OPT}$), is determined by minimizing the MAE in atomization energies of a set of 148 molecules. With this set of $\alpha_{OPT}$ parameters, the mean and mean absolute errors in atomization energies of 148 molecules are -4.5 kcal/mol and 14.5 kcal/mol. This makes its performance for atomization energies comparable to that of the PBE-GGA. This is remarkable considering it is perhaps the simplest of the density functional models and it is certainly the oldest such model. The hybrid and even more complex functionals like B3LYP or the PBE0 perform better than the PBE-GGA. To further improve the performance of the SR method for the atomization energy it is necessary to go beyond the simple element dependent Slater’s exchange functional form employed in this work. Considering the overall performance of SR method, it is a good starting point.
for optimization of large systems. Many calculations employ Hartree-Fock method to optimize geometries or to explore potential energy surfaces, and then compute properties of interest at a more sophisticated level. The analytic SR model scales better than the HF method and being analytic it is necessarily computationally efficient. One could use the $\alpha$ value used in this work to optimize structures and then perform single point calculations, if feasible, using more sophisticated models. The ability of density functional models to perform large scale calculations is well known. Of the plethora of density functional models of different accuracy, choosing the simpler ones like the local density approximation further enhances one’s ability to study large systems and/or to perform longer molecular dynamics simulations. Indeed, several recent large scale simulations are performed using local density approximation. In a recent work, the local density approximation (SVWN) was shown to be about 55% faster than the B3LYP and 40% faster than the BLYP for a calculation on 9-alanine system. The analytic implementation like the present one, being free from grids, will perform even better and is a promising alternative for large scale calculations at modest accuracy.

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TABLE I: The set of $\alpha$ values used in the present work. The $\alpha_{HF}$ values are due to Schwarz [34] (spin-polarized by Connolly [11]) and the $\alpha_{EA}$ values are from Ref. [43]. The $\alpha_{OPT}$ values in the last column are obtained by minimizing the mean absolute error in atomization energy of 148 molecules (see text for more details).

| Molecule | $\alpha_{HF}$ | $\alpha_{EA}(6-311G^{**}/RIJ)$ | $\alpha_{EA}$(DZVP2/A2) | $\alpha_{OPT}$ |
|----------|---------------|---------------------------------|--------------------------|----------------|
| H        | 0.77627       | 0.777390                        | 0.781240                 | 0.753703       |
| Li       | 0.77157       | 0.791690                        | 0.792110                 | 0.839295       |
| Be       | 0.76823       | 0.795740                        | 0.796140                 | 0.557058       |
| B        | 0.76206       | 0.786750                        | 0.786770                 | 0.674430       |
| C        | 0.75331       | 0.776770                        | 0.776650                 | 0.675039       |
| N        | 0.74522       | 0.767470                        | 0.767260                 | 0.645482       |
| O        | 0.74188       | 0.765000                        | 0.764480                 | 0.657869       |
| F        | 0.73587       | 0.760660                        | 0.760010                 | 0.575118       |
| Na       | 0.73115       | 0.752040                        | 0.752870                 | 0.823779       |
| Mg       | 0.72918       | 0.749940                        | 0.751200                 | 0.768385       |
| Al       | 0.72853       | 0.748220                        | 0.748690                 | 0.743690       |
| Si       | 0.72751       | 0.745390                        | 0.746020                 | 0.767716       |
| P        | 0.72620       | 0.743240                        | 0.743970                 | 0.860982       |
| S        | 0.72475       | 0.742620                        | 0.743500                 | 0.743745       |
| Cl       | 0.72325       | 0.741970                        | 0.742720                 | 0.662447       |
TABLE II: The deviation in atomization energies for the set of 148 (extended G2 set) of molecules within different computational models- M1: SR-$\alpha_{EA}$/6311G**/RIJ, M2: SR-$\alpha_{EA}$/DGDZVP2/A2, M3: SR-$\alpha_{HF}$/6311G**/RIJ, M4: SR-$\alpha_{HF}$/DGDZVP2/A2, M5: SR-$\alpha_{Opt}$/DGDZVP2/A2, All energies are in kcal/mol and are calculated at the optimized geometries of molecules in the respective model. The exact atomization energies are from Ref.

| Molecule       | Symmetry | M1    | M2    | M3    | M4    | M5    | Exact |
|----------------|----------|-------|-------|-------|-------|-------|-------|
| H₂             | D$_{6h}$ | -24.9 | -22.7 | -24.9 | -22.8 | -23.4 | 110.0 |
| LiH            | C$_{6v}$ | -19.6 | -23.9 | -20.1 | -24.4 | -19.6 | 57.7  |
| BeH            | C$_{6v}$ |  8.6  | -16.9 |   6.3 | -18.5 |   1.7 | 49.6  |
| CH             | C$_{6v}$ | -16.7 | -15.5 | -17.1 | -16.2 | -16.2 | 83.7  |
| CH$_2$(³B₁)   | C$_{2v}$ |  5.5  |   7.2 |   1.8 |   2.6 |  -7.4 | 189.8 |
| CH$_2$(₁A₁)   | C$_{2v}$ | -22.4 | -19.1 | -24.3 | -21.7 | -25.6 | 180.5 |
| CH₃            | D$_{3h}$ | -7.2  |  -4.0 | -11.5 |  -9.4 | -19.5 | 306.4 |
| CH₄            | Td      | -11.8 |  -7.3 | -16.9 | -13.9 | -23.4 | 419.1 |
| NH             | C$_{6v}$ | -16.3 | -14.6 | -16.7 | -15.4 | -15.1 | 83.4  |
| NH$_2$         | C$_{2v}$ | -24.4 |  -20.0 | -25.5 | -22.0 | -22.9 | 181.5 |
| NH$_3$         | C$_{3v}$ | -25.5 | -18.9 | -27.6 | -22.6 | -25.8 | 297.3 |
| OH             | C$_{6v}$ | -7.7  |  -6.2 |  -8.7 |  -7.8 | -11.2 | 106.3 |
| H$_2$O         | C$_{2v}$ | -4.1  |   0.7 |  -6.9 |  -3.5 | -13.9 | 232.1 |
| HF             | C$_{6v}$ |  4.1  |   7.7 |   1.5 |  -4.3 | -10.7 | 140.7 |
| Li₂            | D$_{6h}$ | -17.8 | -18.8 | -17.8 | -18.8 | -18.7 |  24.4 |
| LiF            | C$_{6v}$ |  8.9  |  -2.4 |   4.2 |  -7.3 | -26.1 | 138.8 |
| C$_2$H$_2$     | D$_{6h}$ | 17.5  |   8.9 |  11.7 |   1.1 | -13.1 | 405.3 |
| C$_2$H$_4$     | D$_{2h}$ |  9.2  |  11.1 |   0.6 |   1.0 | -17.3 | 562.4 |
| C$_2$H$_6$     | D$_{3d}$ |  1.0  |   7.4 |  -9.3 |  -4.6 | -19.8 | 710.7 |
| CN             | C$_{6v}$ | 11.5  |   2.4 |   8.3 |  -0.3 |  -8.0 | 179.0 |
| HCN            | C$_{6v}$ |  1.4  |  -8.5 |  -3.3 | -13.3 | -24.7 | 316.3 |
| CO             | C$_{6v}$ | 24.0  |  11.3 |  19.6 |   7.4 |  -6.1 | 259.2 |
| HCO            | C$_{1h}$ | 29.1  |  23.1 |  23.4 |  17.4 |   0.8 | 278.3 |
| Compound            | Symmetry | C     | H     | O     | N     | Si    | P     | Cl    | Na    | C     | S     | F     |
|---------------------|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| H₂CO (formaldehyde) | C₂ᵥ      | 21.0  | 17.8  | 14.5  | 10.6  | -8.3  | 373.4 |
| H₃COH               | C₁₇h     | 10.3  | 15.4  | 2.2   | 5.7   | -13.5 | 511.6 |
| N₂                  | D₆h      | -13.5 | -24.9 | -15.3 | -26.2 | -32.6 | 228.5 |
| N₂H₄                | C₂       | -24.2 | -12.9 | -29.3 | -18.8 | -15.2 | 437.8 |
| NO                  | C₂ᵥ      | 10.3  | 2.4   | 8.2   | 0.6   | -6.3  | 152.9 |
| O₂                  | D₆h      | 37.1  | 33.6  | 34.1  | 30.7  | 20.1  | 120.4 |
| H₂O₂                | C₂ᵥ      | 14.7  | 20.4  | 9.8   | 14.5  | -1.0  | 268.6 |
| F₂                  | D₆h      | 28.0  | 29.8  | 26.5  | 27.8  | 13.7  | 38.5  |
| CO₂                 | D₆h      | 67.6  | 49.0  | 58.1  | 40.4  | 10.7  | 388.9 |
| SiH₂(¹A₁)           | C₂ᵥ      | -26.0 | -23.4 | -25.1 | -23.5 | -24.6 | 151.4 |
| SiH₂(³B₁)           | C₂ᵥ      | -9.5  | -8.1  | -9.9  | -9.5  | -6.9  | 130.7 |
| SiH₃                | D₃h      | -32.0 | -30.4 | -32.0 | -31.9 | -29.0 | 226.7 |
| SiH₄                | Td       | -39.7 | -37.3 | -39.0 | -38.5 | -37.4 | 321.4 |
| PH₂                 | C₂ᵥ      | -26.7 | -22.4 | -26.2 | -22.3 | -10.2 | 152.8 |
| PH₃                 | C₃ᵥ      | -38.6 | -32.0 | -38.1 | -31.8 | 0.6   | 242.0 |
| H₂S                 | C₂ᵥ      | -18.7 | -13.0 | -19.3 | -14.0 | -14.4 | 182.3 |
| HCl                 | C₆ᵥ      | -4.8  | -3.7  | -5.7  | -4.9  | -8.0  | 106.2 |
| Na₂                 | D₆h      | -11.9 | -11.6 | -11.8 | -11.5 | -11.9 | 16.8  |
| Si₂                 | D₆h      | -2.7  | -2.5  | -3.6  | -3.6  | -1.2  | 74.7  |
| P₂                  | D₆h      | -23.1 | -22.7 | -23.6 | -23.2 | -18.7 | 117.2 |
| S₂                  | D₆h      | 8.6   | 10.1  | 6.8   | 8.1   | 10.2  | 101.6 |
| Cl₂                 | D₆h      | 6.5   | 8.0   | 4.7   | 6.0   | 0.3   | 57.9  |
| NaCl                | C₆ᵥ      | -9.0  | -7.2  | -11.0 | -9.7  | -7.9  | 97.8  |
| SiO                 | C₆ᵥ      | 7.8   | 7.3   | 4.0   | 3.5   | -2.5  | 191.2 |
| CS                  | C₆ᵥ      | 8.0   | 7.2   | 4.8   | 4.1   | -0.9  | 171.2 |
| SO                  | C₆ᵥ      | 17.5  | 22.7  | 14.1  | 19.3  | 8.8   | 125.1 |
| ClO                 | C₆ᵥ      | 15.2  | 21.3  | 12.8  | 18.7  | 9.7   | 64.3  |
| ClF                 | C₆ᵥ      | 19.1  | 24.3  | 16.2  | 21.2  | 1.5   | 61.4  |
| Si₂H₆               | D₃d      | -54.1 | -49.2 | -54.4 | -52.3 | -47.4 | 529.5 |
| CH₃Cl               | C₃ᵥ      | 6.9   | 11.2  | -0.2  | 3.3   | -12.6 | 393.6 |
| H₃CSH (?)           | C₁₇h     | -4.9  | 3.1   | -11.9 | -4.9  | -13.4 | 472.7 |
| HOCl                | C₁₇h     | 10.2  | 17.8  | 6.6   | 13.4  | 0.6   | 164.3 |
| Chemical   | Symmetry | C<sub>2v</sub> | C<sub>2h</sub> | C<sub>3v</sub> | C<sub>3h</sub> | C<sub>4v</sub> | C<sub>4v</sub> | C<sub>6v</sub> | C<sub>6h</sub> | C<sub>1h</sub> | C<sub>1h</sub> | C<sub>2h</sub> | C<sub>1h</sub> |
|------------|----------|---------------|----------------|---------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| SO<sub>2</sub> | C<sub>2v</sub> | 22.9 | 27.9 | 15.4 | 20.5 | -3.8 | 258.5 |
| BF<sub>3</sub> | D<sub>3h</sub> | 93.7 | 83.5 | 79.2 | 69.3 | 9.9 | 470.0 |
| BCl<sub>3</sub> | D<sub>3h</sub> | 43.7 | 59.1 | 33.9 | 48.3 | 13.1 | 325.0 |
| AlF<sub>3</sub> | D<sub>3h</sub> | 43.1 | 39.4 | 30.1 | 26.4 | -17.7 | 425.0 |
| AlCl<sub>3</sub> | D<sub>3h</sub> | 3.1 | 13.0 | -3.2 | 5.5 | 3.3 | 309.0 |
| CF<sub>4</sub> | Td | 118.0 | 105.9 | 102.3 | 90.1 | 17.2 | 482.0 |
| CCl<sub>4</sub> | Td | 68.9 | 73.5 | 58.0 | 62.2 | 26.9 | 316.0 |
| COS | C<sub>6v</sub> | 49.7 | 40.7 | 41.4 | 32.9 | 17.3 | 336.0 |
| CS<sub>2</sub> | D<sub>6h</sub> | 39.0 | 35.8 | 30.9 | 28.5 | 23.3 | 280.0 |
| COF<sub>2</sub> | C<sub>2v</sub> | 92.2 | 79.3 | 79.7 | 67.3 | 17.4 | 423.0 |
| SiF<sub>4</sub> | Td | 61.2 | 63.7 | 44.3 | 46.6 | 1.0 | 566.0 |
| SiCl<sub>4</sub> | Td | 11.3 | 12.3 | 3.0 | 3.2 | 15.9 | 387.0 |
| N<sub>2</sub>O | C<sub>6v</sub> | 34.0 | 17.4 | 28.7 | 13.0 | -4.6 | 270.0 |
| C<sub>2</sub>Cl<sub>4</sub> | D<sub>2h</sub> | 94.2 | 101.0 | 77.7 | 84.7 | 32.8 | 471.0 |
| CF<sub>3</sub>CN | C<sub>3v</sub> | 115.6 | 98.7 | 97.7 | 81.4 | 14.0 | 645.0 |
| CH<sub>3</sub>CCH (propyne) | C<sub>3v</sub> | 35.0 | 27.6 | 22.9 | 13.5 | -15.0 | 703.0 |
| CH<sub>2</sub>CCH<sub>2</sub> (allene) | D<sub>2d</sub> | 38.3 | 33.4 | 24.8 | 18.8 | -13.6 | 702.0 |
| C<sub>3</sub>H<sub>4</sub> (cyclopropyne) | C<sub>2v</sub> | 42.8 | 39.1 | 30.0 | 25.0 | -2.5 | 679.0 |
| CH<sub>3</sub>CHCH<sub>2</sub> (propene) | C<sub>1h</sub> | 23.7 | 27.6 | 9.8 | 12.0 | -12.5 | 859.0 |
| C<sub>3</sub>H<sub>6</sub> | D<sub>3h</sub> | 31.9 | 36.8 | 16.2 | 19.8 | -11.4 | 851.0 |
| C<sub>3</sub>H<sub>8</sub> (propane) | C<sub>2v</sub> | 13.6 | 22.0 | -1.9 | 4.6 | -16.1 | 1005.0 |
| CH<sub>2</sub>CHCHCH<sub>2</sub> (butidene) | C<sub>2v</sub> | 48.6 | 50.6 | 31.5 | 31.5 | 1.9 | 1009.0 |
| C<sub>4</sub>H<sub>6</sub> (butyne) | D<sub>3d</sub> | 50.7 | 44.3 | 31.5 | 24.5 | -8.8 | 1001.0 |
| C<sub>4</sub>H<sub>6</sub> (methylene cyclopropane) | C<sub>2v</sub> | 58.3 | 58.3 | 38.8 | 37.1 | -7.5 | 990.0 |
| C<sub>4</sub>H<sub>6</sub> (bicyclobutane) | C<sub>2v</sub> | 63.3 | 65.3 | 43.8 | 44.6 | 9.4 | 983.0 |
| C<sub>4</sub>H<sub>6</sub> (cyclobutene) | C<sub>2v</sub> | 57.9 | 61.0 | 39.1 | 41.2 | 9.2 | 998.0 |
| C<sub>4</sub>H<sub>8</sub> (Cyclobutane) | D<sub>4h</sub> | 43.9 | 52.7 | 25.0 | 30.9 | 5.4 | 1147.0 |
| C<sub>4</sub>H<sub>8</sub> (isobutene) | C<sub>2v</sub> | 38.0 | 44.4 | 18.7 | 22.7 | -13.5 | 1156.0 |
| C<sub>4</sub>H<sub>10</sub> (butane) | C<sub>2h</sub> | 26.5 | 36.8 | 5.8 | 14.2 | -1.7 | 1299.0 |
| C<sub>4</sub>H<sub>10</sub> (isobutane) | C<sub>3v</sub> | 28.4 | 37.2 | 7.7 | 14.7 | -9.0 | 1301.0 |
| C<sub>5</sub>H<sub>8</sub> (spiropropane) | D<sub>2d</sub> | 79.0 | 84.3 | 53.2 | 57.1 | 8.1 | 1281.0 |
| C<sub>6</sub>H<sub>6</sub> (benzene) | D<sub>6h</sub> | 116.4 | 116.3 | 90.6 | 89.5 | 54.2 | 1362.0 |
| Compound                  | Symmetry | C1  | C2  | C3  | C4  | C5  | C6  |
|--------------------------|----------|-----|-----|-----|-----|-----|-----|
| CH₂F₂ (difluromethylene) | C₂ᵥ      | 47.0| 36.9| 35.8| 10.9| 439.0|
| CHF₃ (trifluromethane)   | C₃ᵥ      | 81.8| 68.9| 62.3| 0.4 | 462.0|
| CH₂Cl₂ (trichloromethane)| C₂ᵥ      | 26.3| 17.6| 21.8| 0.0 | 370.0|
| CHCl₃ (chloroform)       | C₃ᵥ      | 47.7| 37.7| 42.2| 15.1| 344.0|
| CH₃NH₂ (methylamine)     | C₁₉      | -11.9| -3.9| -19.5| -13.1| -23.1| 581.0|
| CH₃CN (methyl cyanaide)  | C₃ᵥ      | 21.3| 9.9 | 2.1 | -25.0| 615.0|
| CH₃NO₂ (nitromethane)    | C₁₉      | 59.0| 55.5| 45.7| 5.5 | 603.0|
| CH₃ONO (methyl nitrite)  | C₁₉      | 47.8| 36.1| 33.1| 4.4 | 601.0|
| CH₃SiH₃ (methyl silane)  | C₁₉      | -27.6| -23.1| -33.5| -30.7| -34.8| 627.0|
| CH₂OH (formic acid)      | C₁₉      | 51.4| 40.7| 33.8| 3.8 | 503.0|
| CH₃OOH (methyl formate)  | C₁₉      | 61.7| 45.4| 41.7| 1.3 | 788.0|
| CH₃CH₉ (acetaldehyde)    | C₁₉      | 46.9| 29.4| 30.4| 22.9| 867.0|
| C₂H₄NH (aziridine)       | C₂ᵥ      | 5.1 | 10.2| -8.0| -3.2| -9.2 | 719.0|
| CNVN (cyanoen)           | D₆h      | 42.3| 32.1| 9.7 | -18.2| 501.0|
| (CH₃)₂NH (dimethylamine) | C₁₉      | -3.6| -16.7| -9.0| -23.4| 869.0|
| CH₃CH₂NH₂ (trans ethyalmine) | C₁₉    | -0.3| -13.4| -5.4| -20.1| 877.0|
| CH₂CO (ketene)           | C₂ᵥ      | 53.2| 41.6| 30.0| -1.2 | 533.0|
| C₂H₄O (oxirane)          | C₂ᵥ      | 38.7| 25.6| 27.4| -4.5 | 651.0|
| CH₃CHO (acetaldehyde)    | C₁₉      | 34.4| 21.7| 20.5| -8.5 | 677.0|
| HCOOCH₃ (methyl formate) | C₁₉      | 67.2| 53.6| 45.3| 8.6 | 636.0|
| CH₃CH₉ (ethanol)         | C₁₉      | 23.0| 9.5 | 14.0| -12.2| 810.0|
| (CH₃)₂O (dimethylether)  | C₂ᵥ      | 16.7| 3.3 | 8.2 | -18.5| 799.0|
| C₂H₄S (thioxirane)       | C₂ᵥ      | 25.8| 13.1| 18.5| -0.0 | 624.0|
| (CH₃)₂SO (dimethyl sulfoxide) | C₁₉    | 17.2| 0.8 | 12.0| -16.0| 853.0|
| CH₃CH₂SH (ethanethiol)   | C₁₉      | 8.6 | -3.7| 5.3 | -10.3| 767.0|
| (CH₃)₂S (dimethyl sulphide) | C₂ᵥ      | 5.3 | -8.2| 0.2 | -11.1| 766.0|
| CH₂CHF (vinyl fluride)   | C₁₉      | 44.0| 32.6| 32.5| -2.5 | 573.0|
| CH₃CH₂Cl (ethyl chloride)| C₁₉      | 19.4| 6.8 | 12.1| -12.0| 691.0|
| CH₂CHCl (vinyl chloride) | C₁₉      | 31.0| 20.6| 22.3| -1.2 | 542.0|
| CH₃CHCN (acrylonitrile)  | C₁₉      | 44.2| 29.7| 18.8| -12.9| 761.0|
| (CH₃)₂CO (acetone)       | C₂ᵥ      | 47.9| 31.1| -6.0| 978.0|
| CH₃COOH (acetic acid)    | C₁₉      | 65.7| 48.9| 45.0| 0.6 | 804.0|
| Chemical Structure                  | Symmetry | MAE  | ME  | 71.0  | 67.8  | 55.1  | 51.6  | 2.6   | 707.0  |
|------------------------------------|----------|------|-----|-------|-------|-------|-------|-------|--------|
| CH₃COF (acetyl fluoride)           | C₁h      | 57.2 | 32.5| 40.8  | 21.8  | -5.4  | 707.0 | 669.0 |
| CH₃COCl (acetyl chloride)         | C₁h      | 40.0 | 32.5| 14.6  | 21.8  | 2.8   | 1108.0| 985.0 |
| CH₃CH₂CH₂Cl (propyl chloride)     | C₁h      | 32.5 | 32.5| 14.6  | 21.8  | -5.4  | -7.6  | 1096.0|        |
| (CH₃)₂CHOH (isopropanol)          | C₁h      | 32.5 | 32.5| 14.6  | 21.8  | -5.4  | -7.6  | 1096.0|        |
| CH₃CH₂OCH₃ (methyl ethylether)     | C₁h      | 32.5 | 32.5| 14.6  | 21.8  | -5.4  | -7.6  | 1096.0|        |
| (CH₃)₃N (trimethylamine)           | C₃v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| C₄H₄O (furan)                     | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| C₄H₄S (thiophene)                 | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| C₄H₄NH (pyrole)                   | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| C₅H₅N (pyridine)                  | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| HS                                 | C₆v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CCH (ethynyl radical)              | C₆v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₂CH (vinyl radical)              | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₃CO                                | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₂OH (hydroxymethyl)              | C₁      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| ClNO                                | C₆v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| NF₃                                 | C₃v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| PF₃                                 | C₃v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| O₃                                  | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| F₂O                                 | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| ClF₃                                | C₃v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| C₂F₄                                | D₂h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₃O (methoxy radical)             | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₃CH₂O                              | C₁      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₃S (methylsulfide radical)        | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| CH₃CH₂ (ethyl radical)              | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| (CH₃)₂CH (isopropanyl radical)      | C₁h      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| (CH₃)₃C (isobutanyl radical)        | C₃v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |
| NO₂ (nitrogen dioxide)              | C₂v      | 15.8 | 15.8| 25.6  | -3.0  | 4.6   | -24.4 | 1160.0|        |

MAE: 33.9 33.7 26.4 25.4 14.5 -
ME: 25.0 25.6 15.5 15.4 -4.8 -
TABLE III: The comparison of bond distances of selected molecules from the G2-148 set, calculated within different computational models- M1: SR-$\alpha_{EA}/6311G^{**}/RIJ$, M2: SR-$\alpha_{EA}/$DGZVP2/A2, M3: SR-$\alpha_{HF}/6311G^{**}/RIJ$, M4: SR-$\alpha_{HF}/$DGZVP2/A2, All distances are in Å. The mean absolute error (MAE) and mean error are given in last two rows. The experimental bond lengths are from Ref. 87.

| Molecule | M1       | M2       | M3       | M4       | Exact   |
|----------|----------|----------|----------|----------|---------|
| H₂       | 0.746    | 0.742    | 0.747    | 0.743    | 0.741   |
| LiH      | 1.562    | 1.628    | 1.573    | 1.631    | 1.595   |
| BeH      | 1.309    | 1.412    | 1.320    | 1.425    | 1.343   |
| CH       | 1.113    | 1.117    | 1.117    | 1.125    | 1.120   |
| NH       | 1.033    | 1.037    | 1.035    | 1.042    | 1.036   |
| OH       | 0.960    | 0.967    | 0.961    | 0.970    | 0.971   |
| HF       | 0.905    | 0.912    | 0.903    | 0.914    | 0.917   |
| Li₂      | 2.666    | 2.722    | 2.690    | 2.750    | 2.673   |
| LiF      | 1.513    | 1.596    | 1.520    | 1.610    | 1.564   |
| CN       | 1.142    | 1.159    | 1.150    | 1.167    | 1.172   |
| CO       | 1.105    | 1.127    | 1.112    | 1.134    | 1.128   |
| N₂       | 1.077    | 1.097    | 1.084    | 1.103    | 1.098   |
| NO       | 1.125    | 1.148    | 1.133    | 1.156    | 1.151   |
| O₂       | 1.175    | 1.197    | 1.186    | 1.207    | 1.208   |
| F₂       | 1.356    | 1.362    | 1.371    | 1.376    | 1.412   |
| HCl      | 1.269    | 1.266    | 1.269    | 1.269    | 1.275   |
| ClF      | 1.628    | 1.611    | 1.643    | 1.626    | 1.628   |
| ClO      | 1.559    | 1.550    | 1.575    | 1.565    | 1.570   |
| ClO₂     | 1.559    | 1.550    | 1.575    | 1.565    | 1.570   |
| Na₂      | 2.990    | 3.000    | 3.015    | 3.024    | 3.079   |
| NaCl     | 2.366    | 2.324    | 2.383    | 2.338    | 2.361   |
| NH       | 1.033    | 1.037    | 1.035    | 1.042    | 1.036   |
| P₂       | 1.876    | 1.886    | 1.886    | 1.896    | 1.893   |
| S₂       | 1.893    | 1.897    | 1.905    | 1.909    | 1.889   |
|    |    |    |    |    |
|----|----|----|----|----|
| CS | 1.511 | 1.518 | 1.523 | 1.529 | 1.535 |
| SiO | 1.501 | 1.507 | 1.510 | 1.516 | 1.510 |
| SO | 1.487 | 1.486 | 1.498 | 1.496 | 1.481 |
| MAE: | 0.020 | 0.018 | 0.016 | 0.017 | - |
| MEAN: | -0.018 | -0.004 | -0.009 | 0.006 | - |
TABLE IV: The deviation in the first vertical ionization energies with respect to experimental ionization potentials for the subsets G2 set of molecules (49 in total) within different computational models- M1: SR-α_{EA}/6311G**/RIJ. M2: SR-α_{EA}/DGDZVP2/A2, M3: SR-α_{HF}/6311G**/RIJ, M4: SR-α_{HF}/DGDZVP2/A2, All energies are in eV and are calculated at the optimized geometries of molecules in the respective model. The last column contains exact ionization potentials; these are obtained from tabulation in Ref. 89.

| Molecule | M1 | M2 | M3 | M4 | Exact |
|----------|----|----|----|----|-------|
| B        | 0.6| 0.6| 0.3| 0.4| 8.3   |
| Be       | 0.1| 0.1| -0.1| -0.1| 9.3   |
| C        | 0.8| 1.0| 0.5| 0.6| 11.3  |
| N        | 1.2| 1.2| 0.8| 0.8| 14.5  |
| O        | -0.5| -0.4| -0.8| -0.7| 13.6  |
| f        | 0.2| 0.3| -0.2| -0.1| 17.4  |
| Na       | 0.1| 0.1| 0.0| 0.0| 5.1   |
| Mg       | -0.0| 0.0| -0.1| -0.1| 7.7   |
| Al       | -0.2| -0.2| -0.4| -0.3| 6.0   |
| Si       | -0.1| -0.1| -0.3| -0.2| 8.2   |
| P        | 0.0| 0.1| -0.2| -0.1| 10.5  |
| S        | -0.9| -0.8| -1.1| -1.0| 10.4  |
| Cl       | -0.6| -0.4| -0.9| -0.7| 13.0  |
| CH₄      | 1.5| 1.5| 1.4| 1.4| 12.6  |
| NH₃      | 0.4| 0.5| 0.2| 0.3| 10.2  |
| OH       | -0.4| -0.2| -0.6| -0.5| 13.0  |
| H₂O      | -0.0| 0.2| -0.2| -0.1| 12.6  |
| HF       | 0.4| 0.6| 0.1| 0.3| 16.0  |
| SiH₄     | 1.0| 1.0| 1.0| 0.9| 11.0  |
| PH₂      | -0.0| 0.0| -0.2| -0.1| 9.8   |
| PH₃      | 0.4| 0.4| 0.3| 0.3| 9.9   |
| Compound             | MAE | Mean |     |     |     |
|----------------------|-----|------|-----|-----|-----|
| HS                   | -0.7| -0.6 | -0.9| -0.8| 10.4|
| HCl                  | -0.4| -0.3 | -0.6| -0.5| 12.8|
| CO                   | -0.5| -0.3 | -0.7| -0.6| 14.0|
| O₂                   | 1.0 | 0.9  | 0.5 | 0.5 | 12.1|
| P₂                   | -0.3| -0.2 | -0.5| -0.4| 10.5|
| S₂                   | -0.2| -0.0 | -0.4| -0.3| 9.4 |
| Cl₂                  | -0.9| -0.6 | -1.1| -0.9| 11.5|
| ClF                  | -0.5| -0.3 | -0.8| -0.6| 12.7|
| CS                   | -0.7| -0.6 | -0.9| -0.8| 11.3|
| BF₃                  | -0.4| -0.2 | -0.9| -0.7| 15.6|
| BCl₃                 | -1.0| -0.9 | -1.2| -1.2| 11.6|
| CO₂                  | 0.3 | 0.4  | -0.1| 0.0 | 13.8|
| CS₂                  | -0.1| -0.0 | -0.3| -0.2| 10.1|
| CH₃                  | 0.4 | 0.4  | 0.3 | 0.3 | 9.8 |
| CN                   | 0.9 | 1.0  | 0.6 | 0.7 | 13.6|
| CH₃O (methoxy radical)| 0.2 | 0.3  | 0.0 | 0.1 | 10.7|
| H₃COH                | -0.2| -0.2 | -0.4| -0.3| 10.8|
| CH₂OH (hydroxymethyl)| 0.4 | 0.5  | 0.2 | 0.2 | 7.5 |
| CH₂(¹A₁)             | 0.7 | 0.8  | 0.6 | 0.6 | 9.4 |
| CH₃Cl                | -0.4| -0.3 | -0.5| -0.5| 11.2|
| CNCN (cyanogen)      | 0.4 | 0.4  | 0.0 | 0.1 | 13.4|
| C₄H₄O (furan)        | 0.6 | 0.6  | 0.4 | 0.4 | 8.8 |
| NH                   | -0.8| -0.8 | -1.0| -0.9| 13.5|
| NH₂                  | 0.3 | 0.3  | 0.1 | 0.2 | 11.1|
| SiH₃                 | -0.2| -0.2 | -0.3| -0.3| 8.1 |
| C₆H₆ (benzene)       | 0.4 | 0.4  | 0.3 | 0.2 | 9.2 |
| Si₂H₆                | 0.5 | 0.4  | 0.4 | 0.3 | 9.7 |
| PH₂                  | -0.0| 0.0  | -0.2| -0.1| 9.8 |

MAE: 0.5  0.5  0.5  0.5  -  
Mean: 0.0  0.1 -0.2 -0.1 -