Accurate molecular energies by extrapolation of atomic energies using an analytic quantum mechanical model

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Using a new analytic quantum mechanical method based on Slater’s Xα method, we show that a fairly accurate estimate of the total energy of a molecule can be obtained from the exact energies of its constituent atoms. The mean absolute error in the total energies thus determined for the G2 set of 56 molecules is about 16 kcal/mol, comparable to or better than some popular pure and hybrid density functional models.

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The total electronic energy is the central quantity in quantum mechanical models that compute the ground state properties of many-electron systems. These methods rely on the variational principle and can be broadly classified into two categories. The first category is formed by ab initio quantum chemical methods which permit systematic improvement in accuracy and analytic computation of quantum mechanical matrix elements to machine precision. The high computational cost of these methods restricts their application to those systems with a few atoms. Density-functional-based computational models form the second category. These models are based on the Kohn-Sham formulation of density functional theory (DFT) which offers an alternative way to determine ground state properties. Today DFT based models have become the most popular choice for calculating these properties as they provide results of sufficient accuracy at reduced computational costs. Unlike ab initio quantum chemical methods, however, the computational implementation of almost all DFT models require the use of numerical grids making calculation of matrix elements at machine precision practically impossible. Round-off error, which grows as the square root of the number of points, is eliminated by analytic methods.

The desirable attribute of analytic computation, which is accurate to machine precision, is also possible within DFT. This approach is based on variational and robust fits to the orbitals and the effective one-body Kohn-Sham potential using Gaussian basis sets. This procedure does not alter the density-functional one-particle equations, but makes its analytic solution possible. The model has its roots in the early density-functional model of Slater wherein the exchange potential \( v_x \) is proportional to the one-third power of the electron density \( \rho \):

\[
v_x[\rho] = -\alpha \frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \rho^{1/3}(\vec{r}),
\]

where \( \alpha \) is called the Slater exchange parameter. We extended this analytic density-functional model so that an atom-dependent exchange parameter \( \alpha \), which scales the exchange potential differently for each element, can be used in heteratomic molecules or solids. Early numerical attempts to use atom dependent \( \alpha \) values had a mathematically undefined total energy that results from the discontinuity in the potential at the boundary of the muffin-tin sphere that enclosed atoms or ions, in the Multiple-Scattering Xα method. In our method the total energy is both well defined and stationary with respect to variations of all linear combination of atomic-orbital (LCAO) and Kohn-Sham-potential fitting coefficients. The energy is a function of basis sets and Slater’s \( \alpha \) for each element,

\[
E(\{\alpha_i\}) = \sum_i <\phi_i|f_1|\phi_i> + 2\langle\rho|\overline{\rho}\rangle - \langle\rho|\overline{\rho}\rangle
\]

\[
-\sum_{\sigma=\uparrow,\downarrow} \left[ \frac{4}{3} \langle g_{\sigma}\overline{\rho}_{\sigma}\rangle - \frac{2}{3} \langle \overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\rangle + \frac{1}{3} \langle \overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\overline{\rho}_{\sigma}\rangle \right].
\]

Here, \( f_1 \) is the one-electron part of the Hamiltonian, \( \rho_{\sigma} \) is the spin density and an overbar represents an LCAO fit, and \( g_{\sigma} \), the partitioned 3/4 power of the exchange energy density:

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

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

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

contains \( \alpha_i \), the \( \alpha \) within the muffin-tin in the Xα method, for the atom on which the atomic orbital \( i \) is centered. This unique expression for the total energy is obtained by adding different fitted expressions for the same components of the energy so as to cancel all first-order errors in the energy due to all fits. All orbitals and fits are determined through variation of Eq. 1.
TABLE I: The optimal $\alpha$ values that yield the exact atomic energies in the highest symmetry for which the solutions have integral occupation numbers for the analytic DFT calculations. The exact atomic energies given in the last column are from Ref. [16]. The basis sets are I: 6-311G**/RI-J, II: DZVP/A2.

|        | Basis I | Basis II | Numerical | $E$ (a.u.) |
|--------|---------|----------|-----------|-----------|
| H      | 0.77739 | 0.78124  | 0.77679   | -0.500    |
| Li     | 0.79169 | 0.79211  | 0.79118   | -7.478    |
| Be     | 0.79574 | 0.79614  | 0.79526   | -14.667   |
| B      | 0.78675 | 0.78677  | 0.78744   | -24.654   |
| C      | 0.77677 | 0.77665  | 0.77657   | -37.845   |
| N      | 0.76747 | 0.76726  | 0.76654   | -54.590   |
| O      | 0.76500 | 0.76448  | 0.76454   | -75.067   |
| F      | 0.76066 | 0.76001  | 0.75954   | -99.731   |
| Na     | 0.75204 | 0.75287  | 0.75110   | -162.260  |
| Mg     | 0.74994 | 0.75120  | 0.74942   | -200.060  |
| Al     | 0.74822 | 0.74869  | 0.74797   | -242.370  |
| Si     | 0.74539 | 0.74602  | 0.74521   | -289.370  |
| P      | 0.74324 | 0.74397  | 0.74309   | -341.270  |
| S      | 0.74262 | 0.74350  | 0.74270   | -398.140  |
| Cl     | 0.74197 | 0.74272  | 0.74183   | -460.200  |

This method inherits from Slater’s $X\alpha$ method the physically appealing advantage, which it had over all other quantum-chemical methods, that atoms dissociate correctly. For these molecules and this range of $\alpha$ values all dissociated atoms turn out to be neutral in spin-polarized (high-spin), broken-symmetry (the highest symmetry that gives integral occupation numbers in fractional-occupation-number) calculations. Using Eq. 1 and atomic $\alpha$ values is a single approximation, like the local density approximation is a single approximation and not a different parameterization for each range of densities. In particular, we determine a set of atomic $\alpha$ values that yield the exact atomic (EA) energies and use them to compute total energies of the G2 set\textsuperscript{[11]} of 56 molecules.

Our calculations use Gaussian basis sets to fit both the orbitals and the Kohn-Sham potential. Here, we choose two different combinations of basis sets. For orbitals, we use the valence triple-$\zeta$ (TZ) 6-311G** basis\textsuperscript{[13]} and the DGAuss valence double-$\zeta$ basis\textsuperscript{[14]} set (DZVP2). The s-type fitting bases are obtained by scaling the exponents of the s part of the orbital basis, by two to fit $\overline{p}_s$, by $2/3$ to fit $\overline{p}_p$, and by $4/3$ to fit $\overline{p}_d$. For the non-zero angular-momentum components the resolution-of-the-identity-J (RI-J)\textsuperscript{[15]} and A\textsuperscript{[16]} basis sets are used without scaling to fit the Coulomb potential as well as the exchange-correlation part of the Kohn-Sham potential. Thus, two combination sets 6-311G**/RI-J and DZVP/A2 of bases were used for obtaining the atomic $\alpha$ values. The $\alpha$ optimization was performed using the PERL scripts.

We determine of $\alpha$ values that give the exact total electronic energy for each atom in the molecule. That set of $\alpha$ values is given in Table I for each basis set. The “exact” atomic energies\textsuperscript{[17]} that these values of $\alpha$ reproduce are also included in the same table. These $\alpha$ values are obtained by the Newton-Raphson procedure to zero the function $f(\alpha) = E(\alpha) - E_{\text{exact}}$, where $E(\alpha)$ and $E_{\text{exact}}$ are the self-consistent atomic energy for each value of $\alpha$ and the exact total energies, respectively. The optimal $\alpha$ values are obtained for exact atomic energies in the highest symmetry for which the solutions have integral occupation numbers. The third set of $\alpha$ values is obtained from a spherically-symmetric, numerical electronic-structure code for atoms. The $\alpha$ values for the DZVP2/A2 basis are usually larger than those for the 6-311G**/RI-J as the orbital variational principle requires lower energy from a larger basis set and increasing $\alpha$ lowers the total energy. The fitting basis has a smaller effect on the total energies than the orbital basis\textsuperscript{[18]}.

The second step consists of computing total energy of molecules using Eq. 1 and these $\alpha$ values, which in effect extrapolates the atomic energies. All molecules belonging to the G2 set are optimized and the absolute errors in the total energies of these molecules are computed. These are given in Table III. We choose the G2 set as accurate experimental atomization energies and thus total energies for these molecules are well known. We used the zero-point corrected atomization energies from Ref. [15] and the atomic energies from Table I to synthesize an experimental total energy. The G2 set is routinely used for performance appraisal of density functional models. While our energy is not obviously a density-functional, it shares a common root\textsuperscript{[5]} with DFT. Of all methods with this common root, only one other\textsuperscript{[5]} has been treated analytically in these fifty years. The errors in the total energies computed in our model are compared with the popular density functional and hybrid models in Table III. These density functional models are certainly more sophisticated intrinsically than either the Gáspar-Kohn-Sham (GKS) or $X\alpha$ methods. The total energies corresponding to these sophisticated functionals, however, are not obtained in particularly sophisticated fashion. It is necessary to use a numerical grid for these more sophisticated functionals. Consequently the energies are dependent on how one (here GAUSSIAN03)\textsuperscript{[22]} chooses to orient each molecule relative to that necessary grid. On the other hand, energies obtained in our model use a less sophisticated functional, but are independent of molecular orientation, and thus could be obtained to whatever accuracy is needed to judge between analytic DFT models. The sophisticated pure and hybrid density functional models that we compare with are: the parameter-free PBE\textsuperscript{[19]} and the three-parameter hybrid density functional B3LYP, which mixes Hartree-Fock (HF) exchange with the local exchange functional and Becke’s generalized gradient exchange functional\textsuperscript{[20]} along with local correlation\textsuperscript{[20]} and the LYP\textsuperscript{[20]} correlation functionals. The mixing coefficients were empirically determined to minimize atomization energies, not total (less zero-point) energies addressed in this work. We also computed the total energies for several other density functional models. These include the local density approximation (LDA)\textsuperscript{[17]} BLYP-GGA\textsuperscript{[11,20]} Perdew-
Table II: Absolute Error in total molecular energies with respect to its exact value for the G2 set of molecules. The computational models are: M1: present/6311G**/RI-J, M2: PBE/6311G** M3: B3LYP/6311G*. The absolute errors are at the optimized geometries in the respective model. Last column contains "exact" total energy. The errors and mean absolute error (MAE) are in kcal/mol. (See text for more details).

| Molecule | M1 | M2 | M3 | Exact (a.u.) |
|----------|----|----|----|-------------|
| H₂       | 1.83 | 0.44 | 0.20 | -1.71530    |
| LiH      | 1.44 | 1.17 | 0.75 | -8.06995    |
| BeH      | 0.64 | 1.43 | 0.88 | -15.24604   |
| CH       | 1.23 | 2.48 | 0.63 | -38.4738    |
| CH₂⁺(²P₁) | 0.40 | 2.20 | 0.78 | -39.1474    |
| CH₂⁻(³A₁) | 1.64 | 2.75 | 0.54 | -39.1326    |
| CH₃      | 0.53 | 2.32 | 0.94 | -39.8328    |
| CH₄      | 0.87 | 2.46 | 0.96 | -40.5128    |
| NH       | 1.20 | 2.76 | 0.65 | -55.2229    |
| NH₂      | 1.79 | 2.78 | 0.73 | -55.8792    |
| NH₃      | 1.87 | 3.03 | 0.57 | -56.5637    |
| OH       | 0.56 | 3.19 | 0.84 | -75.7364    |
| H₂O      | 0.30 | 3.53 | 0.49 | -76.4368    |
| HF       | 0.30 | 3.96 | 0.67 | -100.4552   |
| Li₂      | 1.31 | 1.96 | 0.96 | -14.9488    |
| LiF      | 0.65 | 4.65 | 1.30 | -107.4301   |
| C₂H₂     | 1.29 | 4.34 | 0.87 | -77.3358    |
| C₂H₄     | 0.67 | 4.38 | 1.28 | -78.5824    |
| C₂H₆     | 0.98 | 4.56 | 1.55 | -79.8225    |
| CN       | 0.84 | 4.13 | 0.77 | -92.7202    |
| HCN      | 0.10 | 4.79 | 0.60 | -93.4390    |
| CO       | 1.77 | 4.93 | 0.98 | -113.3250   |
| HCO      | 2.14 | 4.49 | 1.43 | -113.8555   |
| H₂CO     | 1.55 | 4.85 | 1.35 | -114.5070   |
| H₂COH    | 0.75 | 5.36 | 1.39 | -115.7279   |
| N₂       | 0.99 | 5.02 | 0.54 | -109.5441   |
| N₂H₄     | 1.78 | 5.34 | 1.10 | -111.8776   |
| NO       | 0.76 | 4.85 | 1.20 | -129.9006   |
| O₂       | 2.73 | 4.73 | 1.80 | -150.3287   |
| H₂O₂     | 1.08 | 5.79 | 1.38 | -151.5620   |
| F₂       | 3.16 | 6.38 | 1.83 | -199.5235   |
| CO₂      | 1.97 | 6.81 | 1.96 | -188.5987   |
| SiH₂⁻(³A₁) | 1.91 | 7.13 | 1.32 | -290.6112   |
| SiH₂⁺(³B₁) | 0.70 | 6.76 | 1.37 | -290.5728   |
| SiH₄      | 2.35 | 7.20 | 1.38 | -291.2312   |
| PH₂      | 1.96 | 7.76 | 0.95 | -342.5135   |
| PH₃      | 2.84 | 8.13 | 0.79 | -343.1586   |
| H₂S      | 1.37 | 9.56 | 0.39 | -399.4305   |
| HCl      | 0.36 | 11.31 | 1.65 | -460.8692   |
| Na₂      | 0.87 | 9.52 | 2.47 | -324.5467   |
| Si₂      | 0.19 | 13.29 | 1.82 | -578.8590   |
| P₂       | 1.70 | 15.59 | 0.33 | -682.7267   |
| S₂       | 0.63 | 18.37 | 1.35 | -796.4419   |
| Cl₂      | 0.48 | 22.60 | 4.00 | -920.4922   |
| NaCl     | 0.66 | 16.28 | 0.72 | -622.6158   |
| SiO      | 0.57 | 10.02 | 1.10 | -634.7417   |
| CS       | 0.59 | 11.42 | 0.54 | -436.2578   |
| SO      | 1.28 | 12.18 | 0.32 | -473.4063   |
| ClO      | 1.12 | 14.00 | 1.39 | -535.3694   |
| CIF      | 1.41 | 14.74 | 1.25 | -560.0285   |
| SiH₆      | 3.98 | 14.51 | 2.52 | -582.5831   |
| CH₃Cl    | 0.50 | 13.37 | 0.99 | -500.1722   |
| H₃CSH    | 0.36 | 11.65 | 0.20 | -438.7383   |
| HClO     | 0.75 | 14.24 | 1.35 | -536.0288   |
| SO₂      | 1.68 | 16.03 | 1.38 | -548.6859   |

Table III: Mean absolute error (MAE) and mean error (ME) in total energies of G2 set of 56 molecules for different models. The errors are in kcal/mol and are at optimized geometries in respective model. M1: present/6-311G**/RI-J, M2: present/DGDZVP2/A2 (see text for more details).

| Model          | MAE  | ME  |
|----------------|------|-----|
| present (M1)   | 17.3 | -0.4 |
| present (M2)   | 16.0 | -0.5 |
| LDA            | 532  | 20.0 |
| PBE-GGA        | 101  | 3.9 |
| BLYP-GGA       | 13.4 | 0.4 |
| PW91-GGA       | 19.3 | 3.8 |
| PBE-GGA (NRLMOL) | 87   | 3.1 |
| HCTH407-GGA    | 14.0 | 0.3 |
| VSXC-meta GGA  | 60.0 | -1.7 |
| B3LYP-hybrid GGA | 15   | 0.3 |
| PBE1PBE-hybrid GGA |       | 9.1 |

Wang (PW91) GGA is the meta-GGA functional containing kinetic densities due to Voorhis and Scuseria (VSXC) is the empirical GGA due to Handy and Cohen (HCTH407) and the hybrid PBE1PBE (also called PBE0) functional. The HCTH407 functional contains 15 parameters that are fitted to a database of 407 properties including total energies. The PBE1PBE model is a hybrid functional of PBE and 25% of HF exchange. The total energies used for comparison are computed with the 6-311G** basis set by the GAUSSIAN03 code at fully optimized geometries within each respective model. The default fine mesh is used in all calculation.

It is well known that Gaussian are not ideal for computing atomic energies, and therefore larger Gaussian basis sets must be used. Thus we also calculated total energies for the PBE models at the geometries optimized by the NRLMOL code using the NRLMOL basis. The NRLMOL Gaussian basis set is optimized for the PBE density functional model and is much larger than the 6-311G** basis. These results are also included in Table III. The mean G2-set errors are also tabulated as a test for this, and potentially other, systematic errors. As the mean errors are small, Gaussian basis set incompleteness in computing atomic energies is not an important consideration.

In this study of extrapolating atomic energies only the MAE in total energy for the density functional models in Table III is of concern. The zero-point energy is not included in total energies as the analytic second derivative calculation required for vibrational frequencies is not yet available in our model. Correcting for zero-point motion can introduce a small error particularly for polyatomic systems. The MAE in total energy obtained by our method is 16.2 kcal/mol for the DZVP2/A2 and 17.3 kcal/mol for the 6-311G**/RI-J basis. The comparison of our MAE with that obtained from the most widely used pure and hybrid density-functional models is favorable. This simple way of determining total energies of molecules by extrapolation is remarkably accurate. It is
also likely to be significantly more accurate than the \textit{ab initio} methods that can treat the largest G2 molecules today because the HF energy bounds the exact energy from above.

Our model gives total energies comparable to the B3LYP, which is widely accepted as the most accurate hybrid density-functional model, because it gives the best atomization energies. The B3LYP/6-311G** MAE in atomization energy (for the G2 set) is about 4.5 kcal/mol. Using the larger 6-311+G(3df,2p) basis set the B3LYP MAE in atomization energy drops to 2.27 kcal/mol. As the error in the total atomic energies in the present model is zero by construction, its error in atomization energy is the same as its error in the total energy. For B3LYP, and perhaps other models, this essentially single experimental quantity, may be computed in ways that can differ by almost an order of magnitude in accuracy. Perhaps, density-functional models must benefit from cancellation of errors in total energies of atoms and molecules to give atomization energies comparable to or better than \textit{ab initio} methods. Unexpectedly, these models provide quite accurate total energies as well as atomization energies.

The mixing parameters in the hybrid B3LYP method are empirically obtained by minimizing the errors in atomization energies. Like B3LYP, our method can also be parameterized for atomization energies by optimizing the MAE in atomization energies of the G2 set of molecules. Such an optimized parametrization gives MAE in atomization energy that is intermediate between the PBE-GGA and B3LYP. The calculations could be further improved in several ways. A larger basis also lowers the B3LYP error. A larger basis might lower our MAE, but the basis-set effect is largely canceled by adjusting $\alpha$ to get exact atomic energies, and high angular-momentum functions are less important for HF-less functionals. Perhaps the $\alpha$ should be adjusted towards the GKS value for valence or open-shell electrons. That seems algorithmically possible, but departs from Slater’s original model for the binding of atoms in molecules and solids.

In conclusion, we have shown that fairly accurate estimates of the total energy of molecules can be obtained by extrapolation using experimental atomic energies and an analytic quantum mechanical model. The computational model is illustrated by computing the geometry-optimized total electronic energy of the G2 set of 56 molecules, without grids and thus with machine-precision matrix elements. It is shown to perform as well as or better than some widely used pure and hybrid density-functional models in computing total molecular electronic energies simply by extrapolating atomic energies quantum mechanically, according to Slater’s prescription. The Office of Naval Research, directly and through the Naval Research Laboratory, and the Department of Defense’s High Performance Computing Modernization Program, through the CHSSI Project MBD-5, supported this work. The calculations were performed at the Army Research Laboratory Major Shared Resource Center (ARL MSRC).

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