Ground-State Enthalpies: Evaluation of Electronic Structure Approaches with Emphasis on the Density Functional Method

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Ground-state enthalpies, calculated by various electronic structure methods, are compared with experimentally well-established values across a sizable data base of 577 molecules and 15 atoms. With the diversity of species and bonding types available in this compilation it is possible to detect deficiencies that may escape with smaller test sets. The present analysis relying on DAtEF (Data base optimized Atomic Enthalpies of Formation) yields error statistics which relate to reaction enthalpies among the species much more directly than extrapolations based on atomization enthalpies. The evaluation is applied to methods ranging from high level first principles wavefunction calculations to density functionals and to semiempirical approaches. It is found that computationally efficient and broadly applicable density functional methods with relatively small but adequate numerical basis sets can provide ground-state enthalpies within ∼20 kJ/mol rms (∼4.8 kcal/mol). This must be considered an excellent result, as presently only the heaviest available methods appear to provide about a factor of 2 more accuracy as inferred from a subset of the data base used here.

I. Introduction

Accurate energy predictions for molecular binding are a theorist's nightmare. There are no simple rules that allow predictions with uniform accuracy across a range of molecules. Rather, the type of atoms, the type of bonding, electron correlation, and other concerns are significant for accurate prediction of energy differences between compounds. It is clear that quantum mechanics is required at some level for even a qualitative understanding about what happens in some reactions and what are the differences between reactants and products. For a more quantitative account of energies, not only simple quantum mechanics but also electronic correlations play a significant role. Furthermore, energy contributions due to vibrations and to relativistic effects may be far from negligible. In this field, the introduction and fundamental justification of density functional theory (DFT) has been a most significant step toward simplification. Density functional theory as put forward by Kohn and Sham[1] keeps the essentials of quantum mechanics, by keeping wavefunctions at the level of orbitals. From the orbitals on, correlation effects on ground state energetics may indeed be hidden away and approximated by relatively simple functionals. During the past two decades, significant progress has been made modeling the fine points of energetics by exchange correlation functionals. This progress continues.

With this background we are interested in finding out what levels of accuracy are currently achievable. It is clear that this needs a sufficiently large data base of molecules with well-established, accurately determined experimental energies, which also are accessible for various theoretical methods.

In section II various aspects of the methods used here are briefly reviewed. Our interest is to put the performance of relatively simple exchange correlation functionals, which depend only on the electron density and its gradient, into perspective with heavier as well as with faster methods.

The quality of variational basis sets is relevant for accurate energy predictions. For the Gaussian based methods, we rely on work done by others. The calculations done specifically for this work are done with numerical local orbital basis sets.

Enthalpies of formation from the thermodynamic reference state of each element are useful to calculate enthalpies of arbitrary reactions from experimental data. Often, enthalpies of formation are calculated from "first principles" by actually combining calculated atomization enthalpies with experimental enthalpies of atom formation. This approach overemphasizes atomic dissociation reactions, and leads to statistics mostly reflecting errors for this particular reaction type. Here we develop a method to minimize such errors and derive statistics which are relevant for the theoretical prediction of reaction enthalpies in general. We are led to introduce data base optimized enthalpies of atom formation.

The quality and size of the data base is of importance. With almost 600 enthalpy data for a wide variety of bonding types, we expect statistically significant statements, which are not biased by a serendipitous selection of species.

It is found that simple functionals, depending only on density and density gradients or spin density and gradients, can lead to results which rival much more demanding methods in the accuracy of energy predictions.

II. Methods

A. Density Functionals. The simplest class of density functionals is the local density functional approximation (LDA). We consider LDA to be the generic term covering also the local spin density functional (LSD or LSDA). In the case of spin paired electrons, the LSDA involves a vanishing net spin density and is identical to a spin restricted LDA. As a representative of this class the PWC[2] functional was chosen. This functional is derived from an interpolation of the most accurate available first principles correlation data for the homogeneous electron system.

Several functionals which depend on electron density and gradients are investigated in the present study. In the case of

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open shell systems this class of functionals also involves explicit dependence on spin density and its gradients. The functional PBE[3] involves both an exchange and a correlation part and is constructed to satisfy various limiting and scaling properties of exchange and correlation, which are known from first principles for ideal model systems. PBE contains a parameter controlling the large gradient limit. The functional P91[4] is a correlation functional constructed earlier along similar lines as PBE. The exchange functional originally proposed for P91 has not become very popular, so it is not used for this work. We would refer to that exchange plus correlation functional as "generalized gradient approximation" GGA. The exchange functionals B86[5] and B88[6] contain semiempirical parameters obtained by optimizing dissociation energies for a small molecular training set. P91 correlation is often combined with B88 exchange (we abbreviate B88−P91 as BP), and sometimes P91 is combined with B86. Several functionals which are similar to BP and PBE are also in use: revPBE[7] and RPBE.[8] Several functionals with parameters determined from a molecular training set have been proposed by Handy and co-workers, the one from a training set of 147 molecules, HCTH147,[9] is used in the present study. The functional LYP[10] is a correlation functional modeled after first principles data for the helium atom. It is often combined with B88 exchange and termed BLYP. The functional B3LYP is mostly used with Gaussian based methods, it is an implementation of Becke's[11] adiabatic connection model. In the homogeneous electron gas limit, the B3 family of functionals recovers the electron gas correlation as modeled by the PWC local density functional. The LDA exchange part is partly replaced by Hartree−Fock exchange. Dependence of exchange on spin-density gradients is introduced via the B88 gradient part with an adjusted parameter. Similarly, gradient dependence for correlation is of LYP form with a third adjusted parameter. This functional is significantly more computationally demanding than the functionals mentioned before, because of the Hartree−Fock term.

B. Numerical Basis Sets. For this class of methods, calculations were done with with the DMol^3 code.[12−14] This code uses numerically defined local orbital functions as variational basis sets. The numerical approach to the generation of basis functions consists of a recipe rather than defining a fixed set of functions. The idea is to solve the free atom exactly for the given functional, and then use variation functions to cover the response of the atom to various molecular or other environments. The recipe consists of building the entire atomic basis set from three subsets of basis functions. Subset 1 is the minimal set of atomic orbitals for the spin-restricted atom calculated self-consistently with the functional to be used. Subset 2 usually contains a duplicate set of valence functions for that atom, again with the functional in question, calculated for a positive ionic charge. The charge is predefined, in accordance with results from energy minimizations of test molecules. Subset 3 contains polarization functions again derived from an atomic ion. It is expected that the charge parameters for the radial functional in subsets 2 and 3 are transferable from one functional to another, while the actual radial functions depend slightly on the functional. Therefore, the charge values for subsets 2 and 3 are part of the basis set construction recipe. Polarization functions in DMol^3 are formed by using spherical harmonics Y_{lm} for the angular part. Thus d-functions involve sets of 5 functions and f-functions involve sets of 7 functions, etc. The recipes for "double numerical set plus polarization" (DNP) and "double numerical set plus d-functions" (DND) basis sets have been obtained by optimizing the variational approximation to the atomic response. DND contains a single set of d-polarization functions for elements starting with B. DNP contains a set of p-polarization functions for H. DND is the default basis set for DMol^3. A larger basis set "TNP" is used here too. It includes up to a triplicate set of valence functions in subset 2, and subset 3 involves a duplicate set of d-polarization functions and a set of f-polarization functions for elements beyond hydrogen. The number of radial functions in TNP is the same as there are contracted radial functions in cc-pVTZ.[15] Specifications for the numerical TNP basis sets used in this work are given in the Supporting Information. The recipe defines subsets 2 and 3 which describe the atomic responses to the molecular environments. The method is quite fast for large systems because of the efficient basis set and efficient evaluations of the matrix elements. An important advantage of these numerical basis sets is the property of being equally well adapted to any particular functional, as the radial functions are generated on the fly by using the functional in question.

A further parameter defining the basis set is the atomic localization radius, an important issue with respect to the computation time of larger size molecules or solid cells. In the present work the atom radial cutoff was chosen conservatively large ($14a_o = 741$ pm) as to become unimportant, since our principal aim is to work out limitations due to the functional. For larger molecules than considered here, it is computationally expedient to push the localized basis function method to shorter cutoff radius. This cutoff can be made element dependent, to balance accuracy and computational speed. Further down, examples are given, indicated by an additional label "-m", illustrating the effect of reasonable shorter cutoffs for faster calculations.

Harmonic frequencies calculated by using the same numerical basis set and functional as for the geometry optimization and final energy are used for the vibrational contribution to the integrated heat capacity.

Energies of free atoms can be calculated according to Hund's rule occupations. In the case of partially filled p-shells with 1, 2, 4, or 5 electrons this leads to a representative of the degenerate ground state with a nonspherical density. The total energy for such Hund's rule atomic densities often, but not always, yield the lowest DFT energy for a given functional. We consider the lowest atomic electronic energy as the relevant one, when atomic dissociation is involved in enthalpy calculations. In calculations of reaction enthalpies or enthalpies of formation, the energies of isolated atoms drop out unless the reactants or products contain single atoms.

For some molecules it may be difficult to reach SCF convergence maintaining Fermi occupations. This happens particularly as a consequence of level crossing when using the zero temperature Fermi function. In this study C_2 and SiC are potentially such cases. Here these molecules are treated within the spin restricted method, with thermal occupations characterized by an electron temperature of 0.001 hartree $= 27$ meV $\approx$ 300 K. This is sufficient to ensure convergence. With thermal occupations, electronic free energy[16,17] is used instead of total energy. The electronic free energy differs slightly from the total energy by a small entropy term. These details do not noticeably influence the results presented below.

C. Gaussian Based Calculations. Here results, using Gaussian basis sets, calculated by Johnson et al.[18] are analyzed by the method of section D. For self-containedness of this article a short summary of these methods is given. One of the Gaussian basis sets in this study is the 6-31G**.[19] This basis set includes a valence double-ζ set plus 6 d-polarization functions. The 6-th d-function is the s-like polynomial $x^2 + y^2 + z^2$. The second asterisk denotes a set of p-polarization functions on hydrogen. This is a popular medium-sized basis set that is used in many applications where the size of the molecules demands a compromise trading off accuracy against improved speed of calculation.

Larger basis sets are needed for correlated methods in order not to mask the improved description of correlation energy with deficiencies of the basis set. In the tables also results from cc-pVTZ[15] basis sets are shown.

G1, G2, and G3 theories[20] are Gaussian based methodologies, where levels of correlation treatment and levels of basis sets judiciously combine the theoretical levels required for the parts of the enthalpy calculations: single point energy with high level correlation corrections, geometry, and vibrations at a more expedient level of approximation, to obtain an accurate result efficiently. MP2 is Moller Plesset order 2 treatment of correlation, a very popular first principles wave function method. For the Gaussian MP2, B3LYP, and BLYP methods, final energy, optimization, and vibrational analysis were done with exactly the same method in each case. Frequencies were scaled by factors of 0.94, 0.96, and 0.99, respectively, for the calculation of the integrated heat capacity. AM1 is “Austin model 1”,[21] one of the most popular semiempirical methods, where minimal basis sets are predefined, and hard to obtain matrix elements are estimated by using experimental atomic and molecular data. PM3 is the “Modified Neglect of Diatomic Overlap, Parametric Method Number 3”, another popular semiempirical method. Gaussian-based calculations shown here are all from ref 18.

D. Enthalpies of Formation. Enthalpies of formation are defined as the reaction enthalpy for forming a compound from the elemental thermodynamic reference states. The reference states have been chosen with considerations of experimental practicability.

Calculations for the thermodynamic reference states for the elements should be done at a consistent level of theory for a purely theoretical calculation of the enthalpy of formation of a molecule. This is obviously possible for elemental reference states that are gas-phase molecules. Some molecular orbital methods like DMol^3 are equally well suited for molecular and crystalline solid-state studies. In this case it is possible to also calculate the reference states for C, Si, and S, which are crystalline solids, as has been done in ref 13. However, these and the reference states for some other elements are not very accessible for most quantum chemical methods. Approximations to atomic ground states are accessible for all molecular quantum methods. As a consequence, one may be led to compare calculated enthalpies of atomization with experiment. Experimental data of atomization enthalpy of a molecule can be compiled from its enthalpy of formation and the enthalpies of formation for the atoms occurring in the molecule. However, since the atomic energy is involved in every molecular enthalpy of atomization, such enthalpies are susceptible to a statistical bias not relevant for most reaction enthalpies! As a consequence, enthalpies of atomization are a mediocre predictor for the statistics to be expected for reaction enthalpies.

It should be observed that often calculations of molecular enthalpies of formation use experimental enthalpies of atom formation.[22] The errors of such assembled enthalpies of formation as compared to experimental enthalpies of formation amount to a hidden comparison of calculated and assembled experimental atomization energies as described above. As a consequence the error characteristics are the same as for atomization enthalpies.

A much better predictor for the errors to be expected in calculations of reaction enthalpy can be obtained with a sufficiently large data base. The acronym DAtEF (Data base optimized Atomic Enthalpies of Formation) is proposed for the approach presented here. In this method, the enthalpy of formation of an isolated atom from the reference state is taken as an element dependent parameter $H_d(a,T)$. Here a stands for the atomic species, and T for the temperature. We will use $T = 298.15$ K in the following calculations. Since the present data base involves only 15 elements, there are 15 such parameters to be determined by the requirement

$$\sum_m (H_{th}(m,T) + \sum_a n_{a,m} H_d(a,T) - H_{fg}(m,T))^2 = \min \quad (1)$$

where the index m runs across the species of the data base. $n_{a,m}$ is the number of occurrences of element a in molecule m, and $H_{fg}(m,T)$ is the experimentally known enthalpy of formation for molecule m from the elemental thermodynamic reference states. $H_{th}(m,T)$ is the calculated molecular enthalpy of formation in the electronic ground state from gas-phase atoms

$$H_{th}(m) = E(m) + H_{\text{gas}}(m) - \sum_a n_{a,m}\{E(a) + H_{\text{gas}}(a)\} \quad (2)$$

where E is the total energy and H_{gas} involves the zero point and thermal vibrational energy and classical approximations for the translational, rotational, and ideal gas pressure−volume term. The temperature dependence of the enthalpy terms is not shown again to lighten the notation from eq 2 on. The parameters $H_d(a,T)$ that minimize the sample variance for the data base can be interpreted as estimates of the enthalpy of formation of an atom in its ground state. The values $H_d(a,T)$ are optimal for the given data base. The theoretical enthalpy of formation of a molecule from the thermodynamic reference state is $H_{fg,th}(m,T) = H_{th}(m,T) + \sum_a n_{a,m} H_d(a,T)$ within this approach. This applies also for the case of formation of an isolated atom from the reference state: $H_{fg,th}(a,T) = H_d(a,T)$, since $H_{th}(a,T) = 0$ by the definition of eq 2. The $H_d(a,T)$ can be compared with the experimental enthalpy of atom formation: $H_{fg}(a,T)$. For the DMol^3 calculations, we have included the numbers $H_{fg}(a,T)$ as part of the data base. This scheme is similar to “atom equivalents schemes” which have been introduced by Dewar and Storch[23] and Ibrahim and Schleyer[24] and have been used by several authors.[25−31] Atom equivalents schemes parametrize the molecular enthalpy terms, in particular the vibrational enthalpy term, into the element dependent parameters by making the hypothesis that thermal and zero point energies are additive functions of the atoms in the molecule. Here no additivity hypothesis is used and vibrations have to be calculated as a consequence.

The values of $H_d(a,T)$ cancel out for a calculation of an enthalpy for any specific reaction, as the number of atoms for each element is preserved through the reaction. The calculated enthalpy of reaction depends only on the $H_{th}(m,T)$ of the species involved in the reaction. A realistic statistical expectation for the size of errors of reaction enthalpies can be derived from DAtEF performance. If alternatively the error estimate for reaction enthalpies is based on the statistics of atomization enthalpies, unrealistic error terms are included. For a more detailed discussion of the statistics of error terms, a general chemical reaction with n_r distinct reactants and n_p product molecules is considered. The reaction enthalpy can be calculated from the enthalpies of formation of the species involved:

$$\Delta H = \sum_{m_p} H_{fg}(m_p) - \sum_{m_r} H_{fg}(m_r) \tag{3}$$

Experimental and theoretical enthalpies are related via a deviation $u(m)$, a random variable, which is specific for the molecule m and the approximations of the particular theoretical model: $H_{fg}(m) = H_{th}(m) + u(m)$. The random distribution can be characterized by the root mean square (rms) deviation for a sample of n values $u(m)$, rms $= \sqrt{\sum_m u(m)^2/(n-1)}$ or in compact notation rms $= \sqrt{\langle u^2 \rangle}$. Since the DAtEF method leads to a very small mean deviation, small terms involving $\langle u \rangle$ are neglected in the following discussion. The deviation for a specific reaction involving reactant species m_r and product species m_p is $U_{\text{reac}} = \sum_{m_p} u(m_p) - \sum_{m_r} u(m_r)$. With the assumption that $u(m)$ obeys a Gaussian normal distribution and that the $u(m)$ are statistically uncorrelated among the species for the reactions of interest, the deviations for reactions are expected to be

$$\text{rms}(U_{\text{reac}}, n_r, n_p) = \text{rms}(u_{\text{DAtEF}}) \sqrt{(n_r + n_p)/2} \tag{4}$$

The divisor 2 is introduced by counting the reference state in the DAtEF ensemble as one reactant and the species m as the single product molecule. Equation 4 is valid for reactions which are first order for each reactant or product. This is easily generalized for the statistics of reaction classes involving higher orders o_m for some species m:

$$\text{rms}(U_{\text{reac}}) = \text{rms}(u_{\text{DAtEF}}) \sqrt{\left(\sum_{i}^{n_r} o_i^{\,2} + \sum_{j}^{n_p} o_j^{\,2}\right)/2} \tag{4a}$$

The assumption of statistical independence of reactants and products leads to slightly exagerated estimates of rms for reaction enthalpies. The larger the molecules in the data base are, the larger is the remainder of the molecule that is not changed much in the reaction. This may be significant for data bases involving substantially larger species than the present one.

In calculating theoretical reaction enthalpies the $H_d(a,T)$ terms cancel out and are not used. For comparison the statistics of atomization enthalpies are analyzed now:

$$H_A(m) = \sum_a n_{a,m} H_{fg}(a) - H_{fg}(m) \tag{5}$$

with an error term $U_A(m) = \sum_a n_{a,m} u(a) - u(m)$. By the arguments of the previous paragraph, this leads to statistical expectations:

$$\langle U_A^{\,2} \rangle = \langle u^2 \rangle + \langle (\sum_a n_{a,m} u(a))^2 \rangle \tag{6}$$

The rms(U_A) deviation can be significanly larger than the rms(DAtEF), because it is enhanced by the extra term, which depends on the deviations of the enthalpies of atom formation $u(a)$ for the 15 elements under consideration here and their occurrence $n_{a,m}$ in the data base. This second term does not occur on estimation of the statistics of reactions in general. This second term is consistent with the general considerations of eqs 4 and 4a. This paragraph shows that the statistics of atomization reactions follow from eq 4a applied to the special case of reactions with as many product entities as the sum formula of molecule m indicates.

The automatic inclusion of the $\langle (\sum_a n_{a,m} u(a))^2 \rangle$ term in the statistics of atomization enthalpies, or equivalently when using experimental enthalpies of atom formation in tables of theoretical enthalpies, leads to unjustified pessimistic expectations for the error statistics of reaction enthalpies. The DAtEF analysis on the other hand should give realistic unbiased expectations according to eqs 4 and 4a for the error statistics of calculated reaction enthalpies.

E. Data Base. For this study we use a data base consisting of data for 577 molecular entities with well-established enthalpies of formation. The data base has been limited to molecules involving not more than 6 non-hydrogen atoms and not more than 20 atoms total for the sake of expedient calculations with computationally demanding methods. A table with all species and the experimental enthalpies $H_{fg}(m,T{=}298.15\text{K})$ is given as Supporting Information. The data base is taken from the NIST CCCBDB data collection.[18] References to original data are given there.

Each species is characterized by a formula, by a chemical abstract service (CAS) registry number, and a molecule name.

The full data base including atom formation enthalpies finally used for the results section includes 577 molecular entities plus 15 atom formation enthalpies. Among these enthalpy data there are 293 with an estimated uncertainty of 3 kJ/mol or less.

III. Results

A. Enthalpies of Formation. In this section the deviations of the enthalpies of formation as obtained with the DAtEF approach are discussed. The methods are ranked according to the performance in terms of the mean absolute deviation (MAD). This is shown in Table 1. The computationally very demanding wave function methods G1−G3 and CCSD(T) are leading in terms of accuracy. CCSD(T) stands for single point coupled cluster energies, combined with MP2 geometries and frequencies all using the relatively large cc-pVTZ basis set. Using MP2 also for the energies yields only a slightly inferior result. Unfortunately, only results for less than half of the data base are available for these two methods, which makes the results statistically less significant than for the other methods. The root-mean-square (rms) deviations for G3 are similar to the ones for the best DFT methods because of a few cases with large errors. The cases with large errors for G3 include Al_2, Be_2, and C_5H_6. Results for these molecules are missing for the G1, G2, CCSD(T) and MP2 calculations. At least for Be_2 it is known that the correlation energy is difficult to obtain with wave function methods, while DFT methods give a fair value.[32,33] The present statistics for G1, G2 for the incomplete dataset as available[18] may therefore be fortouitously good.

The DFT calculations with numerical basis sets shown here cover all species in the dataset. The statistical performance therefore risks no revision because of incompleteness. For molecules with elements not represented in this datatset, obviouosly no statement can be made on the basis of this investigation. Sporadic evidence from other DFT applications suggests that errors of similar size, but not dramatically larger, are to be expected in compounds containing other elements. (For elements much heavier than investigated here, an appropriate relativistic treatment is needed[34,35] to avoid systematic errors.)

Among the DFT methods the B3-family functionals rank top, when large basis sets, like cc-pVTZ, are used. The best of the “fast” density functional methods, the ones not involving a Hartree−Fock term, rank only a few percent less well than the B3-type ones. The good performance can already be reached by a numerical basis set of double numerical valence plus polarization type, such as “DNP”. On the other hand the particularly good performance of B3LYP is lost when using

TABLE 1: Errors for Molecular and Atomic Enthalpies of Formation [kJ/mol] with DAtEF Approach[a]

method	freq	*e*	*n*	rms	MAD	MIN	MAX	cas-min	mol-min	cas-max	mol-max
G2	I	7	525	11.2	7.8	−58	35	627510	C_4H_6S	157404	C5H8
G1	I	7	408	11.8	7.9	−54	39	627510	C_4H_6S	14989323	SCl
G3	I	7	569	19.5	9.1	−219	195	32752946	Al_2	5164352	C5H6
CCSD(T)/cc-pVTZ	m	7	253	18.6	12.5	−115	52	14452643	BH_2	14989323	SCl
B3PW91/cc-pVTZ	s	5	514	19.2	13.0	−120	62	12070154	C_2	10544726	N2O4
MP2/cc-pVTZ	s	6	234	21.1	13.2	−99	35	15499237	FO_2	10024972	N2O
B3LYP/cc-pVTZ	s	5	512	19.8	13.9	−106	72	7616946	$ClFO_3$	14989323	SCl
PBE/TNP	S	3	592	20.3	14.0	−95	86	616455	C_4H_7NO	10544726	N2O4
PBE/DNP	S	2	592	21.9	15.0	−97	97	616455	C_4H_7NO	10544726	N2O4
PBE/cc-pVTZ	s	3	543	23.4	15.4	−110	118	7783611	SiF_4	10544726	N2O4
B86P91/DNP	S	2	592	22.7	16.0	−111	98	7647190	PF_5	10544726	N2O4
revPBE/DNP	S	2	592	23.0	16.2	−111	103	7647190	PF_5	10544726	N2O4
PBE/DNP[a]	S	2	592	24.1	16.2	−104	114	7664939	H_2SO_4	10544726	N2O4
B88P91/DNP	S	2	592	22.9	16.5	−108	109	7647190	PF_5	2231574	CH6N4S
PBE/DNP[m]	r	2	592	24.2	16.5	−99	119	7664939	H_2SO_4	10544726	N2O4
HCTH147/DNP	S	2	592	23.1	16.6	−105	115	616455	C_4H_7NO	10544726	N2O4
RPBE/DNP	S	2	592	24.8	17.8	−123	105	7647190	PF_5	10544726	N2O4
B3LYP/6-31G**	s	4	574	27.5	17.9	−190	72	7616946	$ClFO_3$	7789266	FNO3
PBE/DND[m]	S	2	592	26.0	18.1	−110	131	7664939	H2SO4	10544726	N2O4
BLYP/DNP	S	2	592	25.6	19.0	−119	121	616455	C_4H_7NO	2231574	CH6N4S
PBE/DND[m]	x	1	592	27.1	19.4	−105	133	7664939	H_2SO_4	10544726	N2O4
MP2/6-31G**	s	5	571	35.4	20.5	−449	101	2231574	CH_6N_4S	151188	C3H6N2
PWC/DNP	S	2	592	31.4	22.9	−136	94	12070154	C_2	10544726	N2O4
PM3	I	0	536	72.9	34.2	−801	740	1163313	BH_3	13701672	B2Cl4
AM1	I	0	543	108.6	65.1	−896	266	7616946	$ClFO_3$	7646697	NaH

[a] See text for details. Freq: type of zero point vibrational energies used—I, defined as intrinsic part of the method; S, at same level of method, non-scaled; s, same method with scaling factor; r, from PBE/DNP calculation; m, from MP2 calculation; x, no vibrations calculated, see text; *e*, relative order of magnitude of computational effort (time ~10^e); *n*, number of entities; rms, root-mean-square error; MAD, mean average deviation; MIN and MAX, deviation and corresponding species with CAS number.

smaller basis sets of 6-31G** type. The aug-cc-pVDZ performs similarly for the present ranking as the 6-31G** basis set, which is clearly not better than many other, faster to evaluate, density functional implementations.

Not too surprisingly, the LDA receives among the lowest rankings within the DFT methods. However, LDA relative enthalpy predictions have only about 50% larger errors than the most accurate DFT methods. This is in stark contrast to the poor performance of LDA for atomic dissociation, which is dominated by the well-known systematic over-binding by LDA. The good performance of LDA enthalpies with DAtEF is consistent with the fact that LDA gets quite good results for geometries and vibrational frequencies, indicating that the energy surface is well-described around the local minima.

The lowest ranks among the quantum chemical methods investigated here go to semiempirical methods PM3 and AM1, which are clearly in a different accuracy league. The strong point of these methods is that for the largest molecules where a quantum method is feasible, results of often acceptable accuracy can be obtained with 2 orders of magnitude lower computational effort than with the fastest DFT methods.

A few calculations with significant speedup potential for large clusters were investigated in order to study the tradeoff of accuracy versus computing time. A first step is to sharpen the localization of the orbital basis set, which requires element dependent radial cutoffs. A moderate cutoff, labeled as "m", still performs well and falls near the middle in Table 1. A second question is whether computationally intensive vibrational calculations for the zero point energy can be spared. Within the DAtEF approach this implies that an element-dependent estimate of the zero point energy per atom and thermal correction are built into the atom formation energies. As a comparison of the method without vibrational data (freq = "x") with the corresponding ones with vibrational data shows, only a marginal down-ranking results from this significant reduction of computations. For some calculations here, the computation of the vibrational spectrum was skipped and the one from the PBE/DNP method was used. In view of the minor impact that the freq = "x" has on DAtEF enthalpy errors, it can be safely assumed that this replacement has negligible impact in practice. Table 1 shows one such example.

The MIN, MAX deviations remain uncomfortably large for all methods. A silver lining is that the gradient-dependent DFT methods, where results for the entire set were done, robustly show MIN, MAX values which are among the more favorable ones for this table.

The order of magnitude estimate in column *e* is meant as a rough order of magnitude indicator of relative computation time: e.g. 2 means 10^2 times more calculation time needed as compared to semiempirical methods for the largest molecules in this set.

The column "*n* entities" should have 592 successful calculations for the entire data set including the atoms. If the atoms are omitted there should be 577 species. Whether the 15 enthalpies of isolated atom formation are included in the data base or not makes no difference for the ranking here. The number of missing successful calculations may give hints at difficulties performing the calculations with a particular method.

The distributions of enthalpy deviations from experiment for all the methods presented appear to be consistent with a Gaussian (normal) distribution. The rms deviation for the subset of molecules with experimental quoted errors of 3 kJ/mol or less is typically 2 to 4 kJ/mol smaller than for the other half of the molecules.

It is interesting to compare the error characteristics of different methods by scatter plots. Figure 1a shows such a plot for the CCSD(T)/MP2/MP2/cc-pVTZ versus the G2 method. It is clear from the figure that the error characteristics of these very high quality methods are only moderately similar. This can be quantified by its Pearson's correlation coefficient of $P = 0.703$ (based on 213 species common to both data sets). Not surprisingly less similarity is found between B3LYP/cc-pVTZ

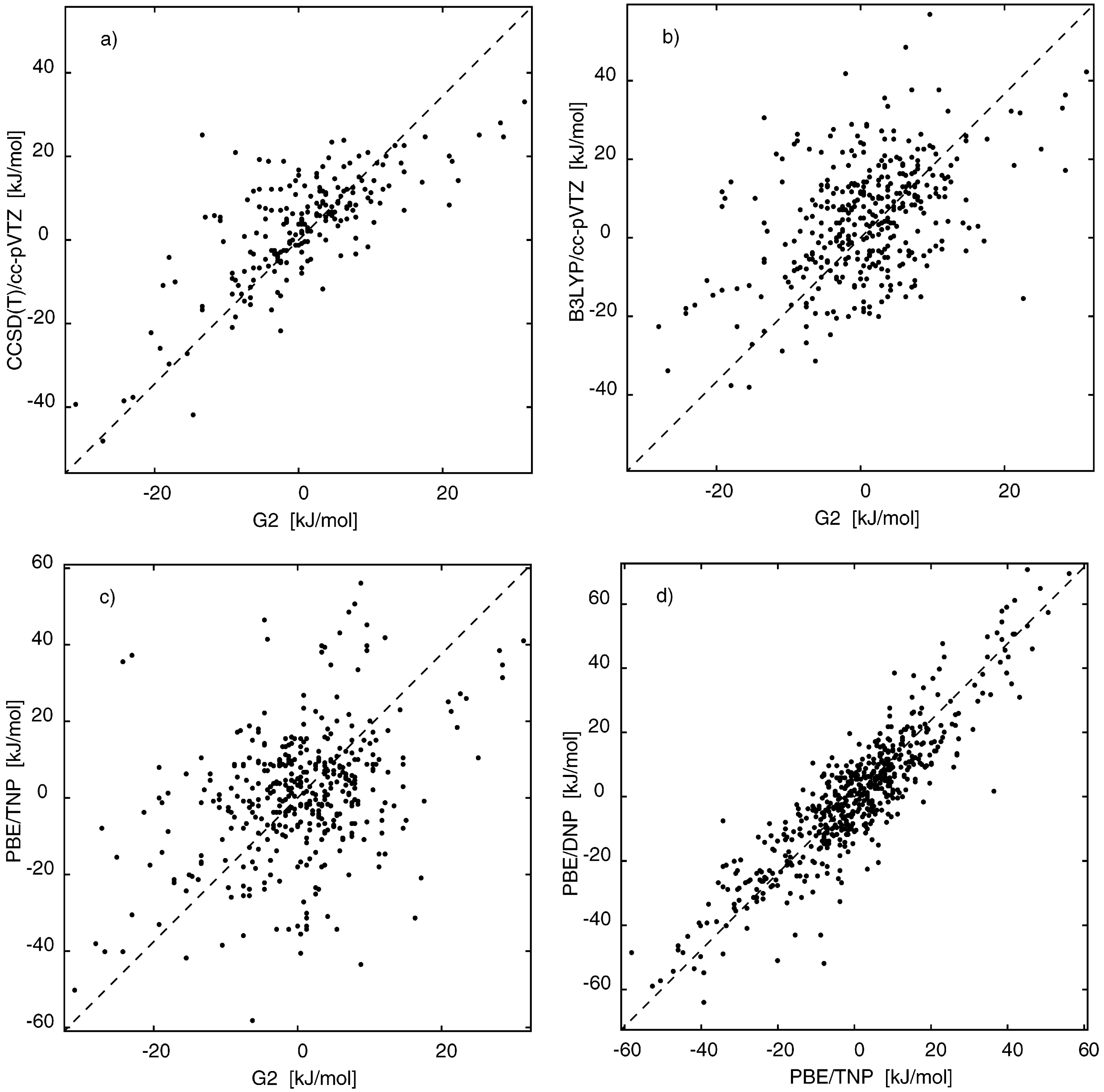

Figure 1. Scatter plots: deviations (theory 1 − experiment) versus (theory 2 − experiment): (a) CCSD(T) cc-pVTZ vs G2, (b) B3LYP cc-pVTZ vs G2, (c) PBE TNP vs G2, and (d) PBE DNP vs PBE TNP. Units [kJ/mol], figure window ±3 × rms for each theory.

and G2 Figure 1b, $P = 0.558$ (387), and even less between PBE/TNP and G2 with $P = 0.381$ (412) in Figure 1c. The correlation coefficient for B3LYP calculations with the 6-31G** basis set versus cc-pVTZ is $P = 0.622$ (511) suggesting moderate similarity. The deviations due to the limitations of the 6-31G** basis set are of similar importance as the shortcomings of the functional. For the pure DFT calculations, the DNP basis is already fairly well converged; this is illustrated in Figure 1d showing a scatter plot of PBE/DNP versus PBE/TNP and by $P = 0.914$ (592) suggesting that the properties of the functional are reproduced with high confidence at the DNP basis set level already. A similar, very high, correlation is found between PBE calculations with DNP (also with TNP) and the cc-pVTZ basis set.

In the past years B3LYP has acquired a strong reputation especially as a particularly accurate method for enthalpy calculations. Part of the support for B3LYP is coming from a purely theoretical argument: the adiabatic connection.[11,36] Practical evidence and support stems mostly from tests with the G2 data base of 147 molecules for enthalpy of formation. This test[22] used experimental values for the enthalpy of atom formation. It is thus equivalent to a test on atomization enthalpies, as discussed in section II.D. The present results show only marginal superiority of B3LYP over PBE when large basis sets are used. For molecules with a hundred and more atoms or a surface model with adsorbed molecule(s) one would resort today to basis sets of DNP or 6-31G** size. Table 1 shows that at this basis set level PBE/DNP is superior to B3LYP/6-31G** for reaction enthalpy calculations.

It is instructive to compare DAtEF values for different methods with experimental enthalpies of formation of an atom in the ground state, Table 2. The deviations that occur for these

TABLE 2: Experimental Enthalpies of Formation of an Atom in Its Ground State from the Standard State of the Element, and DAtEF [kJ/mol] for Various Methods, All at Standard Temperature

elem	exp	G2	B3LYP/ cc-pVTZ	B3LYP/ 6-31G**	PBE/ TNP	PBE/ DNP	PWC/ DNP
H	218.0	218.1	217.0	222.8	208.1	208.2	241.4
Li	159.3	161.8		149.3	146.6	146.4	147.9
Be	324.0	301.4		339.4	333.1	333.4	336.4
B	565.0	567.0	573.9	584.2	574.5	574.4	611.7
C	716.7	715.7	713.1	711.3	751.1	747.9	825.1
N	472.7	471.2	483.6	477.2	524.2	519.2	593.3
O	249.2	245.4	241.1	233.1	285.6	282.6	371.2
F	79.4	77.1	74.2	77.1	99.1	94.5	164.3
Na	107.5	111.2		90.1	85.7	87.2	84.5
Mg	147.1	137.9		131.2	140.2	138.1	133.2
Al	330.0	339.8	316.2	313.4	316.0	314.8	321.9
Si	450.0	444.6	441.1	420.4	436.5	428.6	447.3
P	316.5	313.1	299.5	282.6	322.7	310.5	359.6
S	277.2	270.3	254.4	238.7	297.6	288.0	343.6
Cl	121.3	119.0	105.8	97.2	134.3	129.8	170.0
deviations:							
AVG		−2.7	−5.1	−11.1	8.1	4.7	41.2
MAD		5.1	7.7	16.9	18.6	17.3	49.1
rms		7.7	10.8	20.6	23.2	21.3	65.9
MIN		−22.6	−22.8	−38.5	−21.8	−21.4	−23.0
MAX		9.8	10.9	19.2	51.6	46.5	122.0

15 monoatomic species fit well into the error distribution for each method according to Table 1. For G2 and B3LYP/cc-pVTZ the rms deviations of Table 2 are about half as big as the overall value in Table 1, while for PWC the atom formation rms is about twice as large as the overall one. In that sense no particularly large deviations occur for any of the 15 elements here with any of the methods. However, for some methods only relatively small deviations occur for the "important" elements. For example, the largest deviation for G2 occurs with Be. In the present data base this element only occurs 10 times (for Be2 two occurrences are counted). Since the G2 DAtEF deviations are quite small, 7 kJ/mol rms, the atomization enthalpy deviations for the dataset is rms 12.6 kJ/mol, which is only about 15% larger than the present rms deviations from DAtEF analysis. It is also true that the deviations in Table 2 for the important elements, H, C, O, and N, are favorably small for B3LYP, especially with the larger cc-pVTZ basis set, while these deviations are clearly unfavorable for the PWC functional. As a consequence atomization enthalpies significantly underestimate the predictive power of a method for reaction enthalpies. The present DAtEF analysis suggests that PWC predicts reaction enthalpies with only 50% larger deviation than the very best DFT methods. PWC predictions for reaction enthalpies are by a factor 2 better than the PM3 semiempirical method as judged by the rms deviations, and by a larger factor when MIN/MAX deviations are considered.

IV. Summary and Conclusions

The accuracy of predictions for enthalpies of formation by a representative set of electronic structure methods was studied for a challenging and sizable molecular data set of 577 molecules. A method of data base optimized atomic enthalpies of formation (DAtEF) was introduced to avoid over-counting deviations arising from energy errors with isolated atoms. Because of the internal consistency of the present procedure, much smaller deviations are found for all methods than when using experimental enthalpies of atom formation. The enthalpies of atom formation from the reference state become a subset of the verifiable experimental data. It was found that the errors for this subset fall into the general range of deviations to be expected for each of the methods considered here.

The DAtEF analysis sets the correct expectation for the error statistics of reaction enthalpy calculations.

The theoretical deviations of the methods studied here remain larger than the error estimates for the experimental enthalpies in the data set. The magnitude of the maximum deviations remains unsettlingly large. The total spread between the extreme errors goes down from 263 kJ/mol for PWC to about 180 kJ/mol for the best DFT methods shown here. That spread appears to be similar for PBE and B3LYP, B3PW91 functionals when using good basis sets. The about a factor of 2 smaller errors as suggested by the partial data available for the best performing wave function methods help to set realistic expectations for future more sophisticated density functionals. However, the full data base used here contains a number of difficult molecules which have not entered the statistics for the shining high level methods yet. With the inclusion of these molecules it remains to be seen if a wave function treatment at the level of the G1−G3 methods can deliver substantially better enthalpy predictions across the present data base. For G3, where calculations are still missing for 8 molecules of the data base, rms only marginally superior and more substantial MIN/MAX deviations are found as compared to DFT methods.

The present study shows that relatively simple functionals, depending on (spin) densities and their gradients, perform only marginally less well than computationally much more demanding methods. This fact has not been generally known until now. It is gratifying to know that these DFT methods, which are well suited for the study of much larger molecules than studied here, are among the more accurate electronic structure methods applicable to the energetics of bonding. For metallic solids and their surfaces with chemisorbed species, these DFT methods remain as the most accurate theoretical method to study bonding energetics.

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Supporting Information Available: Numerical basis sets (numerical basis sets for DMol^3 were presented in ref 12, here detailed specifications for the previously unpublished TNP basis sets are given; the light elements DNP basis sets of the revised set, used for most of this work, and of the commonly used DNP V3.5 are shown for comparison; basis-subset 1 is the set of occupied functions of the self-consistent spin-restricted solution for the spherical atom and the functional in question; a table showing the construction recipe for the response s,p functions and polarization functions from subsets 2 and 3 as described in section IIB is given; the basis set atoms are confined within a conservatively large radius; where indicated by superscript *m* in Table 1, the "medium" confinement radii given in the supplement are used); data base: a second table containing details about the data base of 577 molecular and 15 atomic species (for each species: electron number, CAS number, chemical formula, a common name for the species, enthalpy of formation in the ground state at normal conditions, experimental uncertainty of enthalpy when avaliable; the data are taken from the NIST CCCBDB data base, which also contains the references to the original work; as the CCCBDB data base gets expanded from time to time, the purpose of the duplication in the Supporting Information here is to precisely define the data used in this study). This material is available free of charge via the Internet at http://pubs.acs.org.

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