Calculation of chemical reaction energies using the AM05 density functional

Richard P. Muller and Ann E. Mattsson Multiscale Dynamic Material Modeling, Sandia National Laboratories, Albuquerque, NM

Curtis L. Janssen

Scalable Computing Research and Development, Sandia National Laboratories, Livermore, CA (Dated: October 29, 2018)

Abstract

We present results that compare the accuracy of the AM05 density functional [1, 2] to a set of chemical reaction energies. The reactions were generated from the singlet species in the wellknown G2 test suite [3, 4]. Our results show that, in general, the AM05 functional performs nearly as well as the other "pure" density functionals, but none of these perform as well as the hybrid B3LYP functional. These results are nonetheless encouraging because the AM05 functional arises from very simple assumptions, and does not require the calculation of the Hartree-Fock exchange integrals.

I. INTRODUCTION

Density functional theory (DFT) [5, 6] has become a central method in computational chemistry for understanding the energetics involved in structural changes to molecules and clusters. Conventional wisdom in the field states that hybrid density functionals, that is, functionals that combine the traditional DFT exchange with some amount of Hartree-Fock (HF) exchange [7], are required to produce *chemical accuracy* in molecules. The use of hybrid functionals is often associated with Becke [7] and the B3LYP functional, which combines HF exchange with the Becke 88 exchange functional [8] and the Lee, Yang, and Parr [9] correlation functional, and is the most widely-used DFT functional in chemistry. However, the use of hybrid exchange is not limited to B3LYP, and has been included in many other functionals [10, 11, 12].

The difficulty with the inclusion of any amount of HF exchange is that its computation is substantially more expensive. In non-periodic systems, molecules and clusters, this expense is normally small compared to the overall cost of the calculation. In solids, however, computation of the HF exchange represents a substantial portion of the overall computational expense. The situation presents something of a conundrum for those interested in chemical reactions in the condensed phase: the inclusion of the exchange is necessary for chemical accuracy, but renders the calculation intractable. Proper treatment of, say, heterogeneous catalysis, with density functional theory requires that the functional perform equally well for both molecules and solids. We therefore seek a pure density functional (one without HF exchange) that is capable of describing both molecules and solids.

The AM05 density functional [1, 2] is one solution to this problem. AM05 is a simple density functional designed to describe electronic surfaces accurately. AM05 uses a subsystem functional approach [13, 14] to include the effect of electronic surfaces via the Airy gas [13], while still retaining the physical consistency arising from the uniform electron gas approximation in the LDA. In recent investigations [2] it has been shown to provide the same accuracy as hybrid functionals in calculations of bulk properties of solids, at a fraction of the computational cost. Our goal in the current paper is to understand how well this functional performs for chemical reactions.

As the spin-polarized version of AM05 is currently under development [15], we chose the subset of the G2 test suite [3, 4] having singlet ground states, computed the optimized structures for these compounds using the AM05, BLYP, PBE [16] and B3LYP density functionals. We then compute a wide range of chemical reaction energies using the total energies from these calculations. Our results suggest that, although none of the pure density functionals (i.e. BLYP, PBE, and AM05) perform as well as the hybrid functional we consider, AM05 performs roughly as well as the other two, suggesting that it can be used for accurate calculation of chemical reaction energetics is solids, where such numbers might otherwise be impossible to compute.

II. COMPUTATIONAL METHOD

The AM05 functional is described at length in reference [1]. The Massively Parallel Quantum Chemistry (MPQC) program [17] was used for the calculation of the electronic structure of all species considered for each of the functionals. We used the 6-31G^{**} double- ζ -plus-polarization basis set in all calculations, and computed optimized geometries for each structure. The total energy of each structure was used to compute the reaction energy for the range of reactions being considered. In the computation of DFT energies, we do not include corrections due to zero-point vibrational energy. From these energies, we compute the reaction energy, the total energy difference between reactants and products, for a series of reactions of general interest. In the results section, below, we report the relative errors for these reaction energies with respect to the G2 energies for the B3LYP [7, 8, 9], BLYP [8, 9], PBE [16], and AM05 [1, 2] functionals. It is also worth noting that throughout this study we are comparing pure DFT total energy values to G2 values that have additional corrections, such as zero-point vibrational energy, that can be substantial for some of the reactions we consider.

III. RESULTS

In this section we report the reaction energies for a variety of reactions constructed from the singlet molecules in the G2 test suite. Our aim in this comparison is to demonstrate that, although there can be quite substantial differences in the total energies that result from AM05 as compared to other density functionals, this functional can still be used to study the energy of a variety of chemical reactions. To facilitate the discussion in this section, we have grouped the reactions into broad categories related to the chemistry occurring in each case. Such a grouping is not intended to be canonical, as in some cases a reaction could be categorized in multiple groups, but rather as an aid to the discussion of the broad trends of the results. In each section we present the reactions and their energies with the different density functionals, with the results presented as mean absolute errors (MAE), with respect to the appropriate G2 energies.

A. Hydrogenation reactions

Reaction	B3LYP	BLYP	PBE	AM05
$C_2H_4 + H_2 \rightleftharpoons C_2H_6$	3.090	0.807	5.227	7.077
$C_2H_2 + 2 H_2 \rightleftharpoons C_2H_6$	8.557	1.252	12.744	16.046
$CO + H_2 \rightleftharpoons H_2CO$	4.717	3.295	8.944	11.333
$Li_2 + H_2 \rightleftharpoons 2 LiH$	2.169	2.605	1.633	1.346
$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$	1.217	10.118	2.194	8.040
${\sf SiH_6} + {\sf H_2} \rightleftharpoons 2 \; {\sf SiH_4}$	0.825	0.151	3.170	3.640
$N_2 + 2 H_2 \rightleftharpoons H_2NNH_2$	3.136	6.872	8.112	11.406
$C_{3}H_{6}~({\rm cyclopropene}) + H_{2} \rightleftharpoons C_{3}H_{8}$	1.283	3.828	2.242	3.956
$CH_2{=}C{=}CH_2 + H_2 \rightleftharpoons CH_3CH{=}CH_2$	0.447	5.228	0.378	1.547
$CH_3CH{=}CH_2{+}H_2\rightleftharpoons \mathrm{propane}$	1.845	2.226	3.687	5.225
$\text{2-butyne} + 2 \text{ H}_2 \rightleftharpoons \textit{trans-butane}$	2.509	5.174	6.013	8.882
butadiene + 2 $H_2 \rightleftharpoons \mathit{trans}$ -butane	2.270	6.426	5.706	9.024
$H_2 + CO_2 \rightleftharpoons HCOOH$	1.055	3.138	1.152	3.189
$(CH_3)_2CO + H_2 \rightleftharpoons (CH_3)_2CHOH$	2.680	7.267	1.663	0.268
MAE	2.557	4.170	4.490	6.498

TABLE I: Errors in hydrogenation reactions relative to the G2 reference energies, in kcal/mol.

Table I shows the errors in the various hydrogenation energies relative to the G2 reference energies. In general, the AM05 errors in the hydrogenation energies are similar to, but greater than, the errors produced by the other standard density functionals (BLYP and PBE), all of which are significantly greater than the errors produced by the hybrid functional B3LYP. For AM05, the most problematic reactions involve the hydrogenation of triple bonds such as in C_2H_2 or N_2 , a difficulty that is also reflected to a lesser degree in the other pure density functionals.

B. Oxygenation reactions

Reaction	B3LYP	BLYP	PBE	AM05
$CH_4 + H_2O \rightleftharpoons CH_3OH + H_2$	2.975	4.826	3.731	3.627
$HOOH + H_2 \rightleftharpoons 2 \; H_2O$	11.638	18.062	14.898	12.998
$CO + H_2O \rightleftharpoons CO_2 + H_2$	10.540	15.447	17.742	19.681
$C_2H_4 + HOOH \rightleftharpoons CHOCOH + 2 H_2$	0.598	4.033	0.465	1.606
$C_2H_6 + HOOH \rightleftharpoons CH_3CH_2OH + H_2O$	9.212	13.839	11.593	9.595
$C_2H_4 + HOOH \rightleftharpoons C_2H_4O + H_2O$	5.350	9.626	3.379	0.302
$CH_3SCH_3+HOOH\rightleftharpoons(CH_3)_2SO+H_2O$	18.618	19.367	16.493	14.979
$CH_3CHO + H_2O \rightleftharpoons CH_3COOH + H_2$	6.189	7.805	8.646	10.131
MAE	8.140	11.626	9.618	9.115

TABLE II: Errors in oxygenation reactions relative to the G2 reference energies, in kcal/mol.

Table II shows the errors in the various oxygenation energies relative to the G2 reference energies. Here the AM05 functional performs very well compared to the others, with a MAE of 9.115, close to the value of 8.140 achieved by B3LYP, and better than that of the other pure density functionals. The largest error for AM05 comes from the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$, which potentially continues the trend with triple bonds giving difficulties for the AM05 functional relative to other chemical moieties.

C. Nitrogen addition reactions

Table III shows the errors in the various nitrogen addition reactions, relative to the G2 reference energies. Here all functionals perform fairly well, with MAE values that span from 4.8–6.6 kcal/mol, with B3LYP being the best of these, and AM05 being the worst. It is difficult to draw too many conclusions about the trends in the AM05 behavior. The worst behavior is for the reaction $C_2H_2 + HCN \rightleftharpoons CH_2 = CHCN$, and one would be tempted

Reaction	B3LYP	BLYP	PBE	AM05
$CH_4 + NH_3 \rightleftharpoons CH_3NH_2 + H_2$	0.892	2.070	1.982	2.307
$3 CH_4 + NH_3 \rightleftharpoons (CH_3)_3 N + 3 H_2$	1.711	1.411	2.510	3.803
$NH_3 + 2 \ CH_4 \rightleftharpoons (CH_3)_2 NH + 2 \ H_2$	0.538	2.740	3.069	3.866
$CH_4 + HCN \rightleftharpoons CH_3CN + H_2$	0.665	1.212	2.401	3.311
$C_2H_6+NH_3\rightleftharpoonsCH_3CH_2NH_2+H_2$	0.379	1.656	1.853	2.308
$CH_2O + NH_3 + CH_3CHO \rightleftharpoons C_5H_5N + 3 H_2O + H_2$	12.639	16.967	11.807	6.942
$C_2H_2 + HCN \rightleftharpoons CH_2{=}CHCN$	7.551	5.480	11.990	14.283
$C_4H_4O + NH_3 \rightleftharpoons C_4H_5N + H_2O$	4.609	6.653	4.314	3.092
$CH_3CHO + NH_3 \rightleftharpoons CH_3CONH_2 + H_2$	16.451	15.435	14.546	13.549
$2 \text{ HCN} \rightleftharpoons \text{NCCN} + \text{H}_2$	4.610	7.855	8.476	8.972
$C_2H_4 + NH_3 \rightleftharpoons C_2H_4NH + H_2$	2.611	3.094	7.992	10.648
MAE	4.787	5.870	6.449	6.644

TABLE III: Errors in nitrogen addition reactions relative to the G2 reference energies, in kcal/mol.

to attribute the poor behavior to the triple bond, which is problematic in other reactions studied in this paper, but the reaction $CH_4 + HCN \rightleftharpoons CH_3CN + H_2$, also containing the HCN molecule, is one of the reactions on which AM05 performs best. AM05 also does poorly on the formation of acetamide, $CH_3CHO + NH_3 \rightleftharpoons CH_3CONH_2 + H_2$, but as the other functionals all do similarly poorly, this is not a fault of AM05 alone.

D. Halogenation reactions

Table IV shows the errors in the various halogenation energies, relative to the G2 reference energies. In general, this is another class of reactions in which the AM05 functional out performs the other pure density functionals, and performs nearly as well as the hybrid B3LYP functional. There are two important points to make for these reactions. First, although it is true that AM05 performs as well or better than the other density functionals for these reactions, in general the reaction energies for these reactions have larger errors than do the other reaction groups we consider here. Moreover, there are a number of systems, in particular those containing F atoms, which all of the functionals in general, and the AM05

Reaction	B3LYP	BLYP	PBE	AM05
$H_2 + CI_2 \rightleftharpoons 2 HCI$	0.580	4.481	1.480	0.360
$H_2 + F_2 \rightleftharpoons 2 FH$	23.405	33.663	28.971	25.092
$Li_2 + F_2 \rightleftharpoons 2 LiF$	9.105	13.410	19.087	20.025
$Na_2 + Cl_2 \rightleftharpoons 2 NaCl$	7.042	13.570	13.730	13.651
$CH_4 + HCI \rightleftharpoons H_2 + CH_3CI$	0.314	1.666	1.256	0.767
$BF_{3}{+}1.5~Cl_{2} \rightleftharpoons BCl_{3}{+}1.5~F2$	4.596	10.478	17.640	15.730
$AIF_3{+}1.5~Cl_2 \rightleftharpoons AICl_3{+}1.5~F_2$	9.264	12.460	20.075	19.923
$OF_2 + H_2 \rightleftharpoons H_2O + F_2$	10.376	18.948	16.657	15.702
$SiH_4 + 2 \ Cl_2 \rightleftharpoons SiCl_4 + 2 \ H_2$	19.143	25.110	16.551	14.393
$SiH_4 + 2 \; F_2 \rightleftharpoons SiF_4 + 2 \; H_2$	21.755	35.139	37.307	33.667
$NH_3 + 1.5 \; F_2 \rightleftharpoons NF_3 + 1.5 \; H_2$	1.436	6.433	7.725	11.038
$PH_3 + 1.5 \ F_2 \rightleftharpoons PF_3 + 1.5 \ H_2$	17.440	23.814	24.934	22.103
$0.5 \operatorname{Cl}_2 + 1.5 \operatorname{F}_2 \rightleftharpoons \operatorname{CIF}_3$	13.499	8.868	3.407	0.587
$C_2H_4 + 2 \; F_2 \rightleftharpoons C_2F_4 + 2 \; H_2$	6.814	13.234	8.701	0.732
$C_2H_4 + 2 \; Cl_2 \rightleftharpoons C_2Cl_4 + 2 \; H_2$	8.313	8.717	0.772	5.688
$CH_4 + F_2 \rightleftharpoons CH_2F_2 + H_2$	8.458	12.965	12.123	8.913
$CH_{4} + 1.5 \; F_2 \rightleftharpoons CHF_3 + 1.5 \; H_2$	9.812	16.821	14.100	8.001
$CH_4 + CI_2 \rightleftharpoons CH_2CI_2 + H_2$	1.777	2.353	0.347	1.555
$CH_4 + 1.5 Cl_2 \rightleftharpoons CHCl_3 + H_2$	5.393	5.569	0.897	1.248
$CH_3CN + 1.5 \; F_2 \rightleftharpoons CF_3CN + 1.5 \; H_2$	7.316	12.613	10.114	4.164
$C_2H_2 + HF \rightleftharpoons CH_2 {=} CHF$	14.903	15.049	19.056	20.759
$C_2H_4 + HCI \rightleftharpoons C_2H_5CI$	2.309	0.169	5.702	7.201
$C_2H_2 + HCI \rightleftharpoons CH_2 {=} CHCI$	5.646	3.971	9.986	11.702
$H_2O + CI_2 \rightleftharpoons HOCI + HCI$	4.894	6.023	6.145	6.190
$CH_3CH{=}CH_2+HCI\rightleftharpoonsCH_2CH$	0.759	1.920	3.869	5.057
$2 C_2H_4 + CCI_4 \rightleftharpoons C_5H_8 + 2 CI_2$	9.398	6.919	13.189	16.952
$H_2CO+F_2 \rightleftharpoons CF_2O+H_2$	2.352	6.475	2.348	3.367
$CH_3CHO+HF\rightleftharpoonsCH_3COF+H_2$	9.197	12.441	11.810	12.479
MAE	8.403	11.903	11.713	10.966

TABLE IV: Errors in halogenation reactions relative to the G2 reference energies, in kcal/mol.

in particular, have trouble with.

E. Sulfur addition reactions

Reaction	B3LYP	BLYP	PBE	AM05
$CH_4 + SH_2 \rightleftharpoons CH_3SH + H_2$	0.682	0.302	0.873	0.730
$CO_2 + CS_2 \rightleftharpoons 2 \ COS$	0.272	0.752	0.061	0.367
$C_2H_4+SH_2\rightleftharpoonsC_2H_4S+H_2$	0.449	0.526	5.266	7.418
$C_2H_6+SH_2\rightleftharpoonsCH_3CH_2SH+H_2$	2.203	1.238	0.348	0.395
$C_4H_4O+SH_2\rightleftharpoonsC_4H_4S+H_2O$	11.591	13.387	10.263	10.813
MAE	3.040	3.241	3.362	3.945

TABLE V: Errors in sulfur addition reactions relative to the G2 reference energies, in kcal/mol.

Table V shows the errors in the various sulfur addition reactions, relative to the G2 reference energies. There are too few reactions here to draw very extensive conclusions about trends in the energetics. In general all of the functionals perform well for these reactions, with the AM05 functional yielding slightly higher errors relative to the G2 reference energies than the other reactions. Notable is that AM05 shows a higher error for the formation of C_2H_4S , which has considerable ring strain, than do the other functionals. This might indicate a difficulty with ring strain, although the somewhat analogous reaction $C_2H_4 + HOOH \rightleftharpoons C_2H_4O + H_2O$ forming oxirane rather than tioxirane is a reaction that AM05 has a much smaller error relative to the G2 reference energies than do the other functionals.

F. Isomerization reactions

Table VI shows the errors in the various isomerization reactions, relative to the G2 reference energies. In general, the performance of all the functionals is quite good. Here the AM05 functional does worse than either of the other pure functionals. We note, in particular, that the trend of the errors being highest for reactions that either have ring strain or triple bonds continues with these reactions as well.

Reaction	B3LYP	BLYP	PBE	AM05
allene \rightleftharpoons propyne	4.109	5.354	5.265	5.341
$cyclopropene \rightleftharpoons propyne$	2.333	1.842	6.639	8.740
$trans$ -butane \rightleftharpoons isobutane	1.237	1.332	1.049	1.017
$propylene \rightleftharpoons cyclopropane$	0.046	2.112	3.238	5.807
2 -butyne \rightleftharpoons butadiene	0.238	1.253	0.307	0.142
2 -butyne \rightleftharpoons methylene cyclopropane	1.200	0.469	5.068	7.684
2 -butyne \rightleftharpoons bicylobutane	0.984	3.483	6.567	11.555
$2\text{-butyne} \rightleftharpoons \text{cyclobutene}$	0.048	1.442	4.091	6.940
nitrometh \rightleftharpoons meth nitrite	0.086	2.085	1.311	3.688
dimethamine \rightleftharpoons transethylamine	1.156	1.568	0.878	0.880
$\text{ethanol}\rightleftharpoons \text{dimethyl ether}$	2.782	4.017	2.314	1.804
$ethanethiol \rightleftharpoons dimethyl sulfide$	0.648	1.111	0.935	0.526
MAE	1.239	2.172	3.138	4.510

TABLE VI: Errors in isomerization reactions relative to the G2 reference energies, in kcal/mol.

G. Carbon or silicon addition reactions

Table VII shows the errors in the various carbon and silicon addition reactions, relative to the G2 reference energies. Several species in this category reveal problems for the AM05 functional. The reactions containing CO show the problem that AM05 has shown in other reactions with triple bonds. But of greatest concern is the results for benzene formation from acetylene, which shows a error in the reaction energy of 38.4 kcal/mol. The latter reaction also poses significant trouble for the PBE and B3LYP functionals. It is also worth restating that throughout this study we are comparing pure DFT total energy values to G2 values that have additional corrections, such as zero-point vibrational energy, that are substantial for some of these reactions.

IV. CONCLUSION

None of the pure density functionals achieves the accuracy, compared to the G2 data, that the hybrid B3LYP functional achieves. The data presented in tables I–VII are summarized in

Reaction		B3LYP	BLYP	PBE	AM05
$CH_4 + SiH_4 \rightleftharpoons CH_3SiH_3$	$+ H_2$	2.572	2.159	0.816	0.636
$HCOOH + CH_4 \rightleftharpoons HCOO$	$OCH_3 + H_2$	0.311	1.248	0.259	0.033
$CH_4 + CO \rightleftharpoons CH_2CO + \\$	H ₂	4.779	8.435	11.136	13.789
$CH_4 + CO \rightleftharpoons CH_3CHO$		3.829	2.969	9.871	13.148
$2 CH_3OH \rightleftharpoons CH_3OCH_3 + \\$	H ₂ O	1.739	1.897	1.504	1.369
$CH_3OH + CH_3CH_2OH \rightleftharpoons$	$C_2H_5OCH_3{+}H_2O$	2.039	2.182	1.791	1.655
$3 C_2 H_2 \rightleftharpoons C_6 H_6$		18.150	9.755	30.222	38.383
MAE		4.774	4.092	7.943	9.859

TABLE VII: Errors in carbon or silicon addition reactions relative to the G2 reference energies, in kcal/mol.

TABLE VIII: Summary of the results presented in tables I–VII. MAE, in kcal/mol, with respect to the G2 energies.

Reaction Class	B3LYP	BLYP	PBE	AM05
Hydrogenation Reactions	2.557	4.170	4.490	6.498
Oxygenation Reactions	8.140	11.626	9.618	9.115
Nitrogen Addition Reactions	4.787	5.870	6.449	6.644
Halogenation Reactions	8.403	11.903	11.713	10.966
Sulfur Addition Reactions	3.040	3.241	3.362	3.945
Isomerization Reactions	1.239	2.172	3.138	4.510
Carbon/Silicon Addition Reactions	4.774	4.092	7.943	9.859
All Reactions	5.322	7.296	7.633	8.081

table VIII. We find, for the set of chemistry we consider here, that the B3LYP functional has only 5.32 kcal/mol mean absolute error with respect to the G2 data. In contrast, the PBE functional has 7.63 kcal/mol, the BLYP functional 7.29 kcal/mol, and the AM05 functional has 8.08 kcal/mol mean absolute error as compared to the G2 data.

It is dangerous to draw too many conclusions from the grouped reaction energies as displayed in table VIII about why different functionals perform well in some cases and poorly in others. In general, the AM05 functional performs most poorly in systems with ring strain and triple bonds. Because the AM05 functional is based on two model systems that are infinite, the uniform electron gas and the Airy gas, there are problems in systems with confined densities, which will be addressed in the successors to the AM05 functional.

In spite of the fact that the AM05 functional performs slightly worse with respect to the G2 data than the PBE and BLYP functionals, we are heartened by the results here. In the derivation of the AM05 functional, no adjustable parameters, and no knowledge of chemistry or even molecules were used. The lack of adjustable parameters, and the lack of a need for the Hartree-Fock exchange to be computed are shared by the BLYP and PBE functionals. The superior performance of the AM05 functional in solids, which was one of the motivating factors in this study, coupled with the good performance in chemical reaction energies, suggests that AM05 is a good choice when considering reaction energies in the solid phase. Furthermore, the AM05 functional has been constructed in a very different way from other functionals, with no information about chemistry or molecules used in its design. The fact that this functional performs nearly as well as the standard functionals is encouraging, because it suggests new directions and new ideas that may be used for the development of further improved functionals.

V. ACKNOWLEDGMENTS

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