Preliminary results on the performance of a family of density functional methods

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In the quest for accurate molecular energies, the vehicle most often taken for the first leg of the journey is Hartree–Fock (HF) theory.[1] This method generally yields more than 99% of the true (Born–Oppenheimer) energy, but the path for recovering the remaining one percent or so, the correlation energy, is much less clear. A wide variety of techniques are available for predicting the correlation energy, but most are quite computationally expensive relative to HF. In the LCAO approach, the cost of HF formally increases as $O(N^4)$, where N is the number of atomic orbital basis functions. However, the formal cost of a second-order perturbation theory, or MP2,[2] correlation calculation is $O(N^5)$, and for more sophisticated methods such as MP4,[3] QCISD(T),[4] and CCSD(T),[5] the cost is formally $O(N^7)$. In practice, the cost scaling can be diminished for large systems through efficient implementation. For example, cutoff schemes reduce the cost of integral handling in HF to $O(N^2)$, and for practical computations this is the rate-limiting step. Nonetheless, the expense of many traditional correlated methods soon becomes prohibitive as N increases.

Density functional theory (DFT)[6] is an alternative approach, which uses general functionals of the electron density (and possibly its derivatives) to model exchange and correlation. DFT is an exception to most correlated methods, such as the ones mentioned above, in that it provides an estimate of the correlation energy at a relatively modest cost, formally $O(N^3)$, which is reduced to $O(N)$ by efficient implementation.[7] Therefore, for large systems the DFT cost scales only as $O(N^2)$, as in HF (due to Coulomb integral handling). Such computational inexpense is, of course, a necessary prerequisite for correlated studies of large systems, and hence the investigation of the quality of density functional methods deserves attention.

This Communication gives a preliminary report of a study comparing the performance of a family of six DFT methods with HF and the correlated *ab initio* methods MP2 and QCISD.[4] The set of 32 molecules studied[8] is a subset of that used in the validation of G2 theory,[9] consisting of all the neutral systems having first-row atoms only, plus H_2. Equilibrium geometries, dipole moments, harmonic vibrational frequencies, and total atomization energies were calculated for each system by each theoretical method and compared with experimental data. Complete results of these calculations and a full discussion will be given in a future publication;[10] here, however, we merely summarize the results for atomization energies.

Two exchange and two correlation functionals are used in the present study. The simplest exchange functional is the familiar zeroth-order[11] Slater (S), or Xα functional.[12] We have adopted throughout the value $\alpha=2/3$, from the theory of the uniform electron gas. Attempts to improve the quality of zeroth-order functionals generally involve the introduction of gradient-correction (first-order) terms. We have chosen the first-order exchange functional of Becke (B).[13] The correlation functionals are the Vosko, Wilk, and Nusair (VWN) parameterization (Recipe V)[14] of exact uniform electron gas results,[15] and the first-order functional of Lee, Yang, and Parr (LYP),[16] as transformed by Miehlich *et al.*[17] This leads to a total of six different DFT methods, illustrated diagrammatically in Fig. 1. The vertical axis represents the type of exchange functional (zeroth order or first order), while the horizontal axis classifies the correlation treatment (null, zeroth order, or first order).

At this point we introduce a general notation for DFT methods, which is used in Fig. 1. We propose the name X–C for a method that uses exchange functional X and correlation functional C. Thus, for example, Becke exchange paired with Lee, Yang, and Parr correlation is abbreviated B–LYP. For methods which do not employ either an exchange or a correlation functional, the label "null" is used for X or C to indicate the "null functional." Note that S-null is the method commonly referred to in the literature as HFS (Hartree–Fock–Slater), and that S–VWN is also known as LSDA (local spin-density approximation).

We have implemented the Kohn–Sham (KS) equations[18] for each of the DFT methods in Fig. 1 in a modified version of the GAUSSIAN 92 quantum chemistry package.[19] The DFT densities are therefore obtained in a self-consistent manner strictly analogous to the HF SCF procedure. Projection techniques, such as those of Dunlap

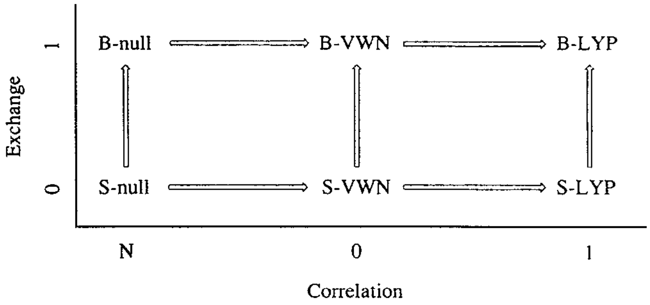

FIG. 1. Density functional methods used in the present study, classified by type of exchange and correlation functional. N = null, 0 = zeroth order, 1 = first order.

et al.,[20] are not employed. Our method for numerical integration of the functionals[21] uses the atomic decomposition scheme of Becke,[22] the 50-point Euler–Maclaurin scheme described by Murray *et al.*[23] for the radial integrations, and the 194-point formula of Lebedev[24] for the angular integrations. A complete description of our implementation will be given in future publications.[7,10,25]

It should be noted that the use of KS densities is in contrast to the DFT studies published by our research group to date,[21,26] in which the HF density was substituted directly into the functionals. Such hybrid methods are denoted by DFT/HF.

Before summarizing the atomization energy results, we give some details of these calculations. We have previously shown[21] that the B–LYP/HF method is quite successful in reproducing experimental atomization energies, ionization potentials, and proton affinities for neutral systems, even with the relatively modest 6-31G* basis set, and so the 6-31G* basis was adopted for all calculations here. The atomic reference energies were calculated by a spin-unrestricted KS procedure strictly analogous to the UHF procedure, i.e., a spherical atom approximation was not employed. For the zero-point vibrational corrections, harmonic frequencies by the appropriate method at the optimized geometry were used. In the case of HF, the recommended empirical scale factor of 0.8929[27] was applied to the frequencies first. The MP2 frequencies were also scaled, by a factor of 0.93. The energy second derivatives required for the frequency calculations were obtained analytically for HF and MP2, and by finite-difference of analytic first derivatives for the DFT methods and QCISD.

Table I compares the theoretical atomization energies with experimental data[9] as mean deviations and mean absolute deviations across the molecular data set. Many interesting observations can be made from these numbers. First of all, the B–VWN and B–LYP methods, with respective mean absolute deviations of only 4.4 and 5.6 kcal/mol, are clearly superior to all other methods considered, including the correlated *ab initio* methods. None of the others could be considered to perform acceptably, but it should be noted that all six DFT methods performed significantly better than HF.

The following trends are observed: S–VWN and S–LYP consistently overestimate the atomization energies, while B-null, HF, MP2, and QCISD consistently underestimate. S-null tends to underestimate as well, but not as predictably. The character of the S-null and S-VWN results is in general accord with bond dissociation energy results reported by Tschinke and Ziegler,[28] and atomization energy results of Becke,[29] respectively.

No significant systematic error is observed for B–VWN and B–LYP. The high accuracy of these two methods is to a degree fortuitous, because of the small basis set employed. Increasing the size of the basis set will generally increase binding and raise the atomization energies; hence, B–VWN and B–LYP will eventually tend to exceed experiment on average. However, the infinite basis limit is approached relatively rapidly and such an effect is expected to be small. Becke has recently performed a fully numerical study of B–VWN/S–VWN atomization energies.[29] This work is significant in that it gives the infinite basis B–VWN results, apart from the error introduced by using the S–VWN rather than the self-consistent B–VWN density. On the same set of molecules, he obtained an average deviation from experiment of 3.6 kcal/mol and an average absolute deviation of 4.2 kcal/mol. These results will be discussed in more detail in the full presentation of our work to follow.[10] From our previous work on B–LYP/HF atomization energies,[21,26] in which very large basis sets were used, it is estimated that the average increase for B–LYP would be similar.

The B–LYP/6-31G* mean absolute deviation of 5.6 kcal/mol can be compared with 7.1 kcal/mol for B–LYP/HF/6-31G*.[21] The better agreement in the present work is mainly attributed to the use of proper KS rather than HF densities. This tends to increase the atomization energies, which are generally too low by B–LYP/HF.

Comparing the S–VWN results with S–LYP, and likewise B–VWN with B–LYP, reveals that the VWN and LYP functionals yield quite similar atomization energies. This is interesting since VWN is a zeroth-order functional while LYP is the first-order, and since the actual correlation energies given by the two functionals are vastly different. Also, it is noteworthy that the mean deviations for S-null, the simplest DFT method, are similar to those for MP2, and that both these methods are superior to QCISD. The poor quality of the QCISD results is attributed to the small basis set used. It is expected that QCISD would be superior to MP2 for large basis sets.

In summary, these initial results indicate that DFT is a promising means of obtaining quantum mechanical atomization energies; here, the DFT methods B–VWN and B–LYP outperformed correlated *ab initio* methods, which are computationally more expensive. Good agreement with experiment was obtained with a small basis set. A more in-

TABLE I. Deviation (kcal/mol) from experiment of DFT and *ab initio* 6-31G* atomization energies, for 32 neutral molecular systems.

	Method								
	S-null	S–VWN	S–LYP	B-null	B–VWN	B–LYP	HF	MP2	QCISD
Mean deviation	−19.1	35.6	37.7	−54.2	0.1	1.0	−85.8	−22.4	−28.8
Mean absolute deviation	25.0	35.7	38.3	54.2	4.4	5.6	85.9	22.4	28.8

depth look at these results, as well as results for other molecular properties, will be reported shortly.[10]

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