The performance of a family of density functional methods

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(Received 5 November 1992; accepted 16 December 1992)

The results of a systematic study of molecular properties by density functional theory (DFT) are presented and discussed. Equilibrium geometries, dipole moments, harmonic vibrational frequencies, and atomization energies were calculated for a set of 32 small neutral molecules by six different local and gradient-corrected DFT methods, and also by the *ab initio* methods Hartree–Fock, second-order Møller–Plesset, and quadratic configuration interaction with single and double substitutions (QCISD). The standard 6-31G* basis set was used for orbital expansion, and self-consistent Kohn–Sham orbitals were obtained by all DFT methods, without employing any auxiliary fitting techniques. Comparison with experimental results shows the density functional geometries and dipole moments to be generally no better than or inferior to those predicted by the conventional *ab initio* methods with this particular basis set. The density functional vibrational frequencies compare favorably with the *ab initio* results, while for atomization energies, two of the DFT methods give excellent agreement with experiment and are clearly superior to all other methods considered.

I. INTRODUCTION

Density functional theory[1–6] (DFT) is developing rapidly as a cost-effective general procedure for studying physical properties of molecules. In its common practical forms, DFT replaces the exchange-correlation (XC) energy by a one-electron integral involving the local electron spin densities ρ_α, ρ_β (LSD methods) or, more recently, by an integral involving ρ_α, ρ_β and their gradients $\nabla\rho_\alpha$, $\nabla\rho_\beta$ (gradient-corrected or GCLSD methods). Many such functionals have been proposed.[7–21] When used in conjunction with the self-consistent Kohn–Sham (KS) procedure[2] and an expansion of molecular orbitals in terms of an orbital basis, the techniques become analogous to conventional Hartree–Fock (HF) theories, with the additional feature that a description of electron correlation is included.

There is a growing literature[22–31] on systematic comparisons of DFT theories with experiment and also with HF and Møller–Plesset (MP2) treatments. Perhaps the most comprehensive is that of Andzelm and Wimmer,[24] who have studied structures, frequencies, energies, and dipole moments for a number of molecules using the DGAUSS program.[32] In this approach, a particular functional was used (Becke–Perdew[15,17] or B–P) and additional basis sets were employed for expansion of the density and the exchange-correlation potential, following the work of Dunlap, Connolly, and Sabin.[33] Further, the self-consistent KS procedure was only carried out at the LSD level, the final energy being obtained by a single application of the B-P functional to the LSD density. These authors found that their results compared favorably with standard HF and MP2 results from the literature, using a different orbital basis. In other work, Becke[25] was able to obtain excellent agreement (better than 4 kcal/mol) with experimental total atomization energies with the fully numerical NUMOL program,[34] using his own exchange functional[17] and a free-electron (LSD) functional[11] for correlation. Again, the self-consistent procedure and geometry determinations were carried out only at the LSD level. Since no basis expansion is used in NUMOL, direct comparison with other conventional methods is difficult.

The objective of this paper is to systematically test a related set of functionals, with a given orbital basis, so that a more direct comparison with HF and MP2 is possible. The basis employed is 6-31G*,[35] already widely used in studies of moderately large organic molecules. (This basis has polarization functions on nonhydrogen atoms and is comparable to DZP bases used elsewhere.) To facilitate such direct comparisons, our work has the following features:

1. The functionals used are separated into exchange and correlation parts. The exchange part is either Slater[9] (S), corresponding to the free-electron gas, or Becke[17] (B), which includes a gradient correction. The correlation part is either ignored (null), treated by LSD theory using the Vosko, Wilk, and Nusair (VWN) parametrization[11] of exact uniform gas results,[36] or treated using the gradient-corrected functional of Lee, Yang, and Parr[19] (LYP), as transformed by Miehlich *et al.*[37] These are combined to give the six functionals S-null (corresponding to Hartree–Fock–Slater or $X\alpha$ theory, $\alpha=2/3$), B-null, S-VWN (corresponding to regular LSD theory), B-VWN, S-LYP, and B-LYP (with gradient corrections for both exchange and correlation). The relation between these functionals is illustrated in Fig. 1.
2. As noted above, the 6-31G* basis is used for orbital expansion. No additional expansion of the density or the XC potential is employed. The results are therefore more directly comparable to HF/6-31G* and MP2/6-31G* work in the literature.
3. The self-consistent KS equations are properly solved for gradient-corrected functionals, rather than applying a single calculation after LSD iterations, as is done in the work cited above.

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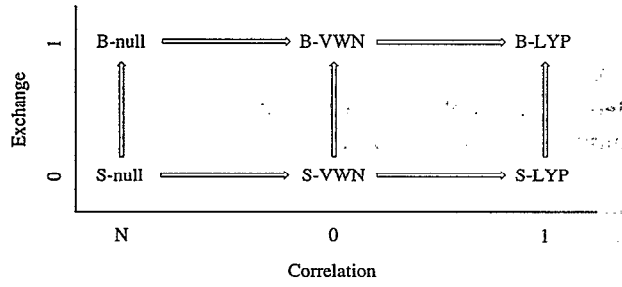

FIG. 1. Density functional methods used in the present study, classified by treatment of exchange and correlation. Moving upward along the vertical axis replaces a zeroth-order exchange functional with a gradient-corrected one. Moving along the horizontal axis corresponds to increasing the sophistication of the correlation treatment, from none, to zeroth order, to first order.

4. A sufficiently large integration grid is used such that sensitivity to grid size is minimized. It may be that coarser grids are required for large molecules, but in this study our emphasis is on testing the functionals without the complication of numerical quadrature error.
5. The set of compounds studied is a subset of the G2 data set,[38] including all neutral molecules with only first-row atoms, plus H_2. These compounds have all been studied in the past at the HF/6-31G* and MP2/6-31G* levels. To further the comparison, we have also employed the more elaborate QCISD/6-31G* model. Equilibrium geometries, dipole moments, harmonic vibrational frequencies, and total atomization energies are reported for the six DFT methods and these three *ab initio* methods, and the results are compared with experiment.

II. METHOD

We have modified the GAUSSIAN 92 quantum chemistry software package[39] to incorporate the above DFT methods. Our DFT package currently has the following capabilities, each available with all six methods:

1. Calculation of the XC energy from an arbitrary density.
2. Calculation of self-consistent spin-restricted (RKS) and spin-unrestricted (UKS) orbitals and densities (analogous to the RHF and UHF procedures, respectively).
3. Calculation of analytic first derivatives of the self-consistent KS total energy.
4. Calculation of properties of the one-electron KS density such as multipole moments and electrostatic potential.

To discuss our DFT implementation, it is convenient to express the general first-order functional[40] f as

$$f=f(\rho_\alpha,\rho_\beta,\gamma_{\alpha\alpha},\gamma_{\alpha\beta},\gamma_{\beta\beta}), \tag{1}$$

where the γ's are the gradient invariants

$$\gamma_{\alpha\alpha}=\nabla\rho_\alpha\cdot\nabla\rho_\alpha,\quad \gamma_{\alpha\beta}=\nabla\rho_\alpha\cdot\nabla\rho_\beta,\quad \gamma_{\beta\beta}=\nabla\rho_\beta\cdot\nabla\rho_\beta. \tag{2}$$

Then, the exchange-correlation energy E_{XC} is given by the three-dimensional integral

$$E_{XC}=\int f(\rho_\alpha,\rho_\beta,\gamma_{\alpha\alpha},\gamma_{\alpha\beta},\gamma_{\beta\beta})d\mathbf{r}. \tag{3}$$

In practice, this integral and others which arise are generally too complicated to be evaluated analytically, and numerical quadrature must be used. In particular, we employ an atomic partitioning scheme, proposed by Satoko[41] and subsequently developed by Becke,[42] which rigorously separates the molecular integral into atomic contributions which may then be individually treated by standard single-center techniques. (We have not, however, adopted Becke's suggested "atomic size adjustments" in the Appendix of Ref. 42.) Thus, in our implementation we have replaced the definition of the XC energy by

$$E_{XC}\equiv\sum_A\sum_i w_{Ai}f(\rho_\alpha,\rho_\beta,\gamma_{\alpha\alpha},\gamma_{\alpha\beta},\gamma_{\beta\beta};\mathbf{r}_{Ai}), \tag{4}$$

where the first summation is over the atoms and the second is over the numerical quadrature grid points for the current atom. The w_{Ai} are the quadrature weights, and the grid points $\mathbf{r}_{Ai}$ are given by

$$\mathbf{r}_{Ai}=\mathbf{R}_A+\mathbf{r}_i, \tag{5}$$

where $\mathbf{R}_A$ is the position of nucleus A, with the $\mathbf{r}_i$ defining a suitable one-center integration grid, which is independent of the nuclear configuration.

The single-center integrations are further separated into radial and angular integrations. The radial part is treated by the Euler–Maclaurin scheme suggested by Murray, Handy, and Laming,[43] which supports an arbitrary number of radial integration points. Radial scaling factors, or "atomic radii," are applied to the Euler–Maclaurin formula as described in Ref. 26.

The angular part is treated by various formulas from the mathematical literature for quadrature on the surface of a sphere; most of the ones we use are due to Lebedev.[44,45] The Lebedev grids, whose base points are invariant under the octahedral group with inversion, are highly efficient in terms of the number of surface harmonics integrated per degree of freedom in the formula; efficiencies near unity are typical, with unit efficiency surpassed in certain cases. The largest Lebedev grid in our program has 302 points and is 29th degree, where nth degree indicates that all surface harmonics of degree n or less are exactly integrated. As a check on our implementation, we have explicitly verified the degrees of the Lebedev grids by numerically integrating the required surface harmonics. Gauss–Legendre spherical product angular quadrature of general degree is also available. We do not recommend this for practical computations, though others do.[43] Such grids are less effective than Lebedev grids of comparable size, having efficiency of only 2/3.[46] However, Gauss–Legendre is useful as a mechanism of attaining arbitrary accuracy in the angular quadrature when desired, which is trivial to implement compared with the general Lebedev procedure. All the angular grids are oriented according to the "standard orientation" conventions of the GAUSSIAN program.[47]

In the present work, atomic grids consisting of 50 radial points and 194 angular points (23rd-degree Lebedev formula) were used throughout. In practice, not all of the 9700 points per atom are explicitly considered; dynamic cutoff schemes are used which prescreen many grid points which would not yield a significant contribution.[48]

As mentioned previously, it is convenient to view the KS self-consistent procedure as strictly analogous to HF, except that the HF exchange potential is replaced by a local DFT XC potential. We have recently presented[49] an efficient formulation of KS self-consistant-field (SCF) and gradient theory within a finite basis set for the general first-order functional. The resulting orbital equations have the same form as the Roothaan–Hall[50,51] (closed-shell) or Pople–Nesbet[52] (unrestricted open-shell) equations in HF theory, with a differently defined Fock matrix

$$F^{\alpha}=H+J+F^{\mathrm{XC}\alpha}, \tag{6}$$

where H is the one-electron Hamiltonian matrix and J is the usual Coulomb matrix. The elements of the alpha XC matrix $F^{\mathrm{XC}\alpha}$ are given by

$$F_{\mu\nu}^{\mathrm{XC}\alpha}=\int\left\{\frac{\partial f}{\partial\rho_\alpha}\phi_\mu\phi_\nu+\left[2\frac{\partial f}{\partial\gamma_{\alpha\alpha}}\nabla\rho_\alpha+\frac{\partial f}{\partial\gamma_{\alpha\beta}}\nabla\rho_\beta\right]\cdot\nabla(\phi_\mu\phi_\nu)\right\}d\mathbf{r}, \tag{7}$$

where the ϕ_μ are the atomic orbital basis functions. The beta Fock matrix is similarly defined. Note that Eq. (7) does *not* require evaluation of the spin density second derivatives as is necessary in many other formulations, a major computational advantage.[48] The fact that these can be avoided has been previously noted by Kobayashi *et al.*[53] We also stress that our formulation involves no auxiliary fitting[33] of the Coulomb or XC potentials usually done in KS implementations.

Some relevant points about our KS implementation are as follows. The integral in Eq. (7) is implemented as a double sum over atoms and grid points as in Eq. (4). The first derivatives of the functional, which are the various XC potentials, are straightforward to obtain, but can be tedious as some functionals have quite complicated forms. Therefore, for convenience we list in Appendix A the formulas for the functionals and their first derivatives as we have implemented them. Some of the functionals we have coded are special cases of the first-order functional; S and VWN are functionals only of ρ_α and ρ_β (zeroth-order functionals), and B is a functional only of ρ_α, ρ_β, $\gamma_{\alpha\alpha}$, and $\gamma_{\beta\beta}$. LYP is of the fully general form. For maximum efficiency, separate code treats each special case so that terms unnecessary to the functional at hand are not evaluated. Special-case closed-shell code also exists to take advantage of the simplification in that case. The same code in GAUSSIAN 92 controls both HF and KS SCF iterations, so the various features already present for aiding HF convergence, such as DIIS extrapolation, are equally available for KS as well.

Once self-consistency is achieved, the KS electronic total energy is

$$E=\sum_{\mu\nu}P_{\mu\nu}H_{\mu\nu}+\frac{1}{2}\sum_{\mu\nu\lambda\sigma}P_{\mu\nu}P_{\lambda\sigma}(\mu\nu|\lambda\sigma)+E_{\mathrm{XC}}. \tag{8}$$

Here $P_{\mu\nu}$ is an element of the total density matrix, and a conventional notation is used for the two-electron repulsion integrals. Note that this formula is the same as the HF energy, except the HF exchange energy has been replaced by E_{XC}.

Differentiation of E with respect to the displacement of nucleus A formally yields[49]

$$\begin{aligned}\nabla_A E=&\sum_{\mu\nu}P_{\mu\nu}(\nabla_A H_{\mu\nu})+\frac{1}{2}\sum_{\mu\nu\lambda\sigma}P_{\mu\nu}P_{\lambda\sigma}\nabla_A(\mu\nu|\lambda\sigma)\\&-\sum_{\mu\nu}W_{\mu\nu}(\nabla_A S_{\mu\nu})-2\sum_{\mu}{}'\sum_{\nu}P_{\mu\nu}^{\alpha}\int\left\{\frac{\partial f}{\partial\rho_\alpha}\phi_\nu\nabla\phi_\mu\right.\\&\left.+X_{\mu\nu}\left[2\frac{\partial f}{\partial\gamma_{\alpha\alpha}}\nabla\rho_\alpha+\frac{\partial f}{\partial\gamma_{\alpha\beta}}\nabla\rho_\beta\right]\right\}d\mathbf{r}-2\sum_{\mu}{}'\sum_{\nu}P_{\mu\nu}^{\beta}\\&\times\int\left\{\frac{\partial f}{\partial\rho_\beta}\phi_\nu\nabla\phi_\mu+X_{\mu\nu}\left[\frac{\partial f}{\partial\gamma_{\alpha\beta}}\nabla\rho_\alpha+2\frac{\partial f}{\partial\gamma_{\beta\beta}}\nabla\rho_\beta\right]\right\}d\mathbf{r},\end{aligned} \tag{9}$$

where the restricted sums over μ run only over the basis functions centered on A. $W_{\mu\nu}$ is the energy-weighted density matrix, as appears in HF gradient theory, and $S_{\mu\nu}$ is the overlap matrix. $X_{\mu\nu}$ is given by

$$X_{\mu\nu}=\phi_\nu\nabla(\nabla\phi_\mu)^T+(\nabla\phi_\mu)(\nabla\phi_\nu)^T. \tag{10}$$

The implementation of the energy gradient with numerical quadrature is not as straightforward as with previous equations, because the quadrature weights depend on the nuclear configuration and hence have a nonzero gradient with respect to nuclear displacements. Therefore, in practice there are two parts to the gradient of E_{XC} as defined in Eq (4):

$$\nabla_A E_{\mathrm{XC}}=\sum_{B}\sum_{i}[w_{Bi}\nabla_A f(\mathbf{r}_{Bi})+(\nabla_A w_{Bi})f(\mathbf{r}_{Bi})]. \tag{11}$$

Although the first term appears to be the numerical integral of the XC contribution to the total energy gradient, it is stressed that *both* terms are required for consistency with the implementation of E_{XC}. Our gradient implementation is the only one of which we are aware which properly includes both terms. While it is true that the error in neglecting the weight derivatives can be made insignificant by taking a large enough number of grid points (as is the case with the grids in the present study), for smaller grids their omission is not justified.[54] It is ultimately desirable to use a grid which is as small as possible but does not sacrifice the quality of the results, and this is a topic currently under investigation.[47] There exist relatively modest grids which have practical utility, yet require evaluation of the weight derivative term to avoid significant errors in the gradient. A derivation of the weight first derivatives is given in Appendix B.

The first term in Eq. (11) merits further elaboration. It should be made clear that the positions of the grid points are a central feature in the definition of the numerical XC energy. Therefore, differentiation of Eq. (4) to produce Eq. (11) requires explicit consideration of the grid points in the process, to be contrasted with first taking the gradient of Eq. (3) to yield the analytic XC integrals in Eq. (9), followed by the application of numerical quadrature to these. As a result, the atomic contribution of A to this term is quite different from that of the other atomic grids. The atomic grids are defined such that an atom's grid "moves with" a displacement of its nucleus, exactly as do the basis functions situated on the atom. As a result, there is a contribution on A's grid to the gradient with respect to A from *all* basis functions *except* those centered on A. The formula for the gradient with respect to A on other atomic grids, however, carries over straightforwardly from Eq. (9). [This is easily seen, e.g., by substituting Eq. (5) into the expansion of the density in products of the atom-centered basis functions and then differentiating.] For this reason, and others particular to the nature of the atomic weighting scheme which shall soon become apparent, the gradient of an atomic contribution to E_{XC} with respect to its own nuclear center is never explicitly worked out; instead, it is more conveniently obtained at the end of the atomic computation by the translational invariance relationship

$$\sum_A \nabla_A = 0. \tag{12}$$

And now, some comments on program efficiency. The literature is teeming with assertions to the effect that the computational cost of HF is $O(N^4)$ while the cost of DFT methods is $O(N^3)$, where N is the number of basis functions. Such statements are strictly misleading, for a variety of reasons. It is true that the cost of a HF calculation is proportional to N^4 for small systems; however, to assign an asymptotic scaling behavior of $O(N^4)$ assumes a naive implementation in which no account is taken of the fact that, for large systems, most of the $O(N^4)$ two-electron repulsion integrals are negligible due to insufficient basis function overlap. Sophisticated cutoff schemes[55] exist for estimating in advance which integrals are insignificant and can be avoided; this reduces the cost of the HF integral processing to $O(N^2)$, and for practical computations this is the rate-determining step. The statement that the cost of a KS calculation is $O(N^3)$, on the other hand, is deceptive for two reasons. Again, it assumes an inefficient implementation, in which all of the $O(N^2)$ XC matrix elements must be represented on a grid of size $O(N)$. In our implementation, however, the calculation of these scales only as $O(N)$, with a small quadratic cost which is insignificant for practical purposes. Details of this scheme will be presented in a future publication.[48] Furthermore, it ignores the fact that in conventional KS calculations treatment of the Coulomb interactions (without fitting) requires the same two-electron integrals as in HF (though once they have been constructed they contribute to fewer Fock matrix elements), the cost of which is $O(N^2)$ in the best case by conventional algorithms. Both HF and KS contain an $O(N^3)$ step, namely, diagonalization of the Fock matrix, but for presently feasible calculations ($N<2000$) this is not dominant. Thus, not only can the XC portion of a KS calculation be made to cost less than $O(N^3)$, for well-implemented KS the XC cost is insignificant for large systems.

Finally, it should also be noted that, due to the modular structure of our program, the addition of new functionals which are of the form of Eq. (1) requires that only one new subroutine be written, to evaluate the functional and its appropriate derivatives. Once this is done, all features present for previous functionals are immediately available with the new functional as well, with the full benefit of efficiency measures.

III. RESULTS AND DISCUSSION

The full set of results is presented in Tables I–V. Table I lists atomic total energies for the DFT and *ab initio* methods, all with the 6-31G* basis. For MP2 and QCISD, it should be noted that full correlation is used, i.e., the frozen-core approximation is not applied. The best available set of atomic energies[56] is included for comparison.

Table II presents equilibrium geometries for all of the molecules studied, together with a mean error analysis at the end. The experimental data are subject to considerable uncertainty for many of the molecules because distances and angles properly corrected for zero-point and anharmonic effects are often unavailable. The dipole moment data are presented in a similar format in Table III. Here we should note that the comparisons are all based on the (positive) magnitude of the dipole moment and no attempt is made to compare dipole directions with experiment. Table IV contains the complete list of computed harmonic frequencies together with corresponding experimental data. Again, we note that the experimental numbers are generally not harmonic frequencies, since anharmonic corrections usually have not been applied. Finally, Table V lists the atomization eenergies, which we have previously summarized,[28] and compares with experimental values already discussed in the G1[57] and G2[38] manuscripts. We now discuss these tables in turn.

A. Atomic energies

The HF, MP2, and QCISD total atomic energies fall somewhat short of the most accurate values listed. This is primarily due to the limitations of the 6-31G* basis, which leads to HF energies significantly above the HF limit and which also recovers only a limited part of the correlation energy. In particular, very little account is taken of correlation energy involving the 1*s* core.

Density functional methods do purport to compute the whole correlation energy. It is worth pointing out, however, that KS energies are *not* variational with respect to the Schrödinger Hamiltonian, and hence are not guaranteed to lie above the exact values. (There does of course exist an analogous variational principle for the true KS eigenfunctions.)

TABLE I. Absolute total energies of neutral atoms (hartrees). Theoretical values were obtained with the 6-31G* basis.

Atom	HF	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	MP2	QCISD	Exact[a]
H	0.4982	0.4540	0.4760	0.4540	0.4954	0.5178	0.4954	0.4982	0.4982	0.5000
He	2.8552	2.7146	2.8267	2.7582	2.8540	2.9671	2.8978	2.8664	2.8702	2.9037
Li	7.4314	7.1896	7.3410	7.2433	7.4264	7.5781	7.4801	7.4319	7.4319	7.4781
Be	14.5669	14.2164	14.4420	14.3119	14.5606	14.7869	14.6563	14.5964	14.6165	14.6674
B	24.5220	24.0532	24.3441	24.1798	24.5145	24.8061	24.6413	24.5625	24.5826	24.6539
C	37.6809	37.0950	37.4537	37.2527	37.6723	38.0318	37.8320	37.7365	37.7552	37.8450
N	54.3854	53.6840	54.1125	53.8760	54.3761	54.8053	54.5684	54.4595	54.4754	54.5893
O	74.7839	73.9544	74.4884	74.2105	74.7890	75.3238	75.0470	74.8820	74.8977	75.067
F	99.3650	98.4097	99.0490	98.7290	99.3803	100.0220	99.7021	99.4890	99.4995	99.734
Ne	128.4744	127.3950	128.1419	127.7777	128.4964	129.2442	128.8796	128.6262	128.6285	128.939

[a]From Ref. 56.

The B-LYP energies do approach the estimated precise values quite well. Errors, relative to the best values, range from 5 mhartree (H) to 57 mhartree (Ne). However, this is partly due to error cancellation. For the Ne atom, the HF limit is approximately -128.5471 hartrees,[56] so that the 6-31G* value is 73 mhartree too positive; the B-LYP correlation energy (-405 mhartree), on the other hand, is 15 mhartree too negative.

The other functionals tested do not give satisfactory total energies. S-null fails to reproduce atomic energies of sufficient magnitude. B-null, which adds a gradient correction to S-null exchange, gives energies which are generally within a few mhartree of HF. B-VWN, while giving reasonable exchange energies, overestimates the correlation energy by using the free-electron gas approximation and hence gives total energies which are far too negative for every atom listed, illustrating the nonvariational character mentioned above. These functional deficiencies are well known.

B. Bond lengths

It has long been recognized that HF theory frequently gives bond lengths which are too short, while MP2, the simplest perturbation correlation theory, often gives values which are too long. Mean deviations for our data set are -0.011 and $+0.010$ Å, respectively. The performance of QCISD theory is comparable to MP2 within this basis. The bond lengths by the various DFT methods are mostly too long, with some methods always giving long bond lengths. The mean deviations vary from $+0.012$ Å for the S-VWN (LSD) functional to $+0.036$ Å for B-null (HF exchange replaced by the Becke-88 functional). The simplest density functional (S-null or Hartree–Fock–Slater theory) gives long bond lengths with a mean error of $+0.032$ Å. All three functionals with gradient-corrected exchange (B-null, B-VWN, and B-LYP) give bond lengths which are consistently long, while S-LYP is similar to S-VWN.

Some of our results parallel others already in the literature. Andzelm and Wimmer[24] (AW) have published an extensive study of equilibrium geometries with the S-VWN functional, using an orbital basis comparable to ours. (They also use additional basis sets to represent the density and exchange-correlation potentials.) They find, as we do, that single bonds between nonhydrogen atoms are too short, double bonds are approximately correct, and triple bonds are too long. This is true for C–C, C=C, and C≡C, as also noted by Salahub *et al.*[58] Our further results show that proceeding to the gradient-corrected B-LYP functional (the most complete in our study) leads to carbon–carbon lengths which are too long by about 0.01 Å.

In common with AW, we find that bonds to hydrogen are usually too long at the S-VWN level by 0.01 to 0.02 Å. This trend is apparently unaltered with the more elaborate gradient-corrected functionals such as B-LYP.

Carbon–oxygen bonds behave similarly to carbon–carbon. At the S-VWN level, single bonds are short, double bonds are good, and carbon monoxide is long, in agreement with AW. With the B-LYP functional, all become too long by 0.01 to 0.02 Å. A similar pattern is shown by carbon–nitrogen bonds. Thus it appears that the B-LYP functional is fairly systematic in predicting bond lengths which are too long by a mean of 0.018 Å at the 6-31G* basis level. However, we should note that a very recent study on a smaller molecular set by Handy and coworkers[29] indicates that this overestimation is reduced if a larger orbital basis is employed.

C. Bond angles

Some general trends can also be discerned for bond angles, particularly the HOH angle in water, which is sensitive to the level of theory used. We find that all of the density functionals give values in the range 102.2°–103.6°, somewhat below the HF value of 105.5° (AW report an S-VWN value of 105.2°, which differs significantly from our result, even though a comparable orbital basis was used; the reason for this discrepancy is not clear). Similar trends are found with singlet methylene, but other bond angles are fairly close to the HF values. This also applies to the dihedral twist angles in hydrazine and hydrogen peroxide.

D. Dipole moments

The dipole moments calculated with the various density functionals are often significantly in error, by amounts comparable to the errors for the conventional procedures HF, MP2, and QCISD. These discrepancies are most probably due to the deficiencies in the 6-31G* orbital basis set.

TABLE II. Theoretical and experimental geometries. Bond distances in angstroms, bond and dihedral angles in degrees. Theoretical values were obtained with the 6-31G* basis.

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt.[a]
H_2										
r(HH)	0.781	0.765	0.774	0.755	0.740	0.748	0.730	0.738	0.746	0.741
LiH										
r(LiH)	1.683	1.640	1.646	1.663	1.624	1.628	1.636	1.640	1.653	1.595
BeH										
r(BeH)	1.392	1.370	1.377	1.371	1.349	1.355	1.348	1.348	1.357	1.343
CH										
r(CH)	1.175	1.152	1.159	1.162	1.140	1.146	1.108	1.120	1.131	1.120
$CH_2(^3B_1)$										
r(CH)	1.110	1.093	1.097	1.101	1.085	1.089	1.071	1.077	1.082	1.078
a(HCH)	132.9	134.8	135.3	131.7	133.1	133.5	130.7	131.6	132.2	136.0
$CH_2(^1A_1)$										
r(CH)	1.158	1.135	1.141	1.148	1.127	1.132	1.097	1.109	1.117	1.111
a(HCH)	98.3	99.1	98.7	98.7	99.5	99.1	103.0	102.1	101.5	102.4
CH_3										
r(CH)	1.109	1.093	1.097	1.102	1.086	1.090	1.073	1.078	1.083	1.079
CH_4										
r(CH)	1.118	1.101	1.105	1.114	1.097	1.100	1.084	1.090	1.094	1.086
NH										
r(NH)	1.083	1.063	1.068	1.074	1.055	1.060	1.024	1.039	1.048	1.045
NH_2										
r(NH)	1.064	1.045	1.050	1.060	1.042	1.046	1.013	1.028	1.034	1.024
a(HNH)	100.9	101.7	101.4	100.6	101.4	101.1	104.4	103.4	102.9	103.4
NH_3										
r(NH)	1.044	1.027	1.031	1.043	1.026	1.030	1.002	1.017	1.020	1.012
a(HNH)	104.9	106.0	105.8	104.0	105.0	104.8	107.2	106.4	106.0	106.0
OH										
r(OH)	1.008	0.993	0.997	1.006	0.991	0.995	0.959	0.979	0.984	0.971
OH_2										
r(OH)	0.991	0.976	0.980	0.991	0.976	0.980	0.947	0.969	0.970	0.959
a(HOH)	102.9	103.6	103.4	102.2	102.9	102.7	105.5	104.0	104.0	103.9
FH										
r(FH)	0.953	0.940	0.944	0.954	0.941	0.945	0.911	0.934	0.934	0.917
Li_2										
r(LiLi)	2.849	2.750	2.750	2.826	2.728	2.728	2.807	2.773	2.725	2.67
LiF										
r(LiF)	1.559	1.544	1.534	1.588	1.571	1.561	1.555	1.567	1.567	1.564
HCCH										
r(CC)	1.225	1.212	1.214	1.226	1.213	1.215	1.185	1.216	1.211	1.203
r(CH)	1.093	1.078	1.082	1.083	1.069	1.073	1.057	1.066	1.069	1.061
H_2CCH_2										
r(CC)	1.346	1.331	1.331	1.356	1.341	1.341	1.317	1.335	1.337	1.339
r(CH)	1.115	1.098	1.102	1.107	1.091	1.095	1.076	1.085	1.088	1.085
a(HCH)	116.3	116.4	116.5	116.0	116.1	116.2	116.4	116.6	116.3	117.8
H_3CCH_3										
r(CC)	1.534	1.513	1.509	1.569	1.546	1.541	1.527	1.524	1.528	1.526
r(CH)	1.123	1.105	1.109	1.117	1.100	1.104	1.086	1.093	1.097	1.088
a(HCH)	107.2	107.2	107.2	107.6	107.6	107.5	107.7	107.7	107.7	107.4
CN										
r(CN)	1.191	1.179	1.181	1.198	1.186	1.187	1.162	1.135	1.180	1.172[b]
HCN										
r(CN)	1.175	1.163	1.165	1.180	1.168	1.169	1.133	1.176	1.165	1.153
r(CH)	1.098	1.083	1.087	1.088	1.073	1.077	1.059	1.069	1.072	1.065
CO										
r(CO)	1.153	1.142	1.143	1.161	1.150	1.150	1.114	1.150	1.145	1.128
HCO										
r(CO)	1.196	1.185	1.185	1.207	1.196	1.196	1.159	1.191	1.191	1.117[c]
r(CH)	1.167	1.143	1.150	1.157	1.134	1.141	1.106	1.123	1.125	1.110
a(HCO)	123.3	123.1	122.9	123.4	123.1	122.9	126.3	123.4	124.3	127.4
H_2CO										
r(CO)	1.218	1.206	1.207	1.230	1.218	1.218	1.184	1.220	1.216	1.208
r(CH)	1.145	1.125	1.131	1.135	1.116	1.121	1.092	1.104	1.107	1.116
a(HCH)	114.9	115.1	115.2	114.7	114.9	114.9	115.7	115.6	115.7	116.5
H_3COH (H_a in-plane, H_b out-of-plane)										
r(CO)	1.419	1.400	1.397	1.462	1.440	1.435	1.400	1.423	1.423	1.421
r(CH$_a$)	1.121	1.104	1.109	1.113	1.097	1.101	1.081	1.090	1.093	1.093

TABLE II. (*Continued.*)

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt.[a]
$r(CH_b)$	1.132	1.114	1.119	1.123	1.105	1.110	1.087	1.097	1.100	1.093
$r(OH)$	0.992	0.977	0.981	0.991	0.976	0.980	0.946	0.970	0.970	0.963
$a(OCH_a)$	106.8	107.0	107.0	106.1	106.3	106.4	107.2	106.3	106.4	107.0
$a(COH)$	107.2	107.7	107.6	106.3	106.9	106.8	109.4	107.4	107.6	108.0
$a(H_bCH_b)$	107.7	107.8	107.6	108.4	108.5	108.3	108.7	108.8	108.8	108.5
N_2										
$r(NN)$	1.122	1.111	1.113	1.128	1.117	1.118	1.078	1.130	1.114	1.098
H_2NNH_2										
$r(NN)$	1.434	1.406	1.401	1.507	1.470	1.463	1.413	1.438	1.443	1.447
$r(NH_b)$	1.048	1.031	1.035	1.047	1.029	1.033	1.003	1.020	1.022	1.008
$r(NH_a)$	1.042	1.026	1.029	1.041	1.024	1.028	0.999	1.016	1.018	1.008
$a(NNH_b)$	112.8	113.6	113.9	109.8	110.7	111.1	112.2	111.5	111.1	109.2
$a(NNH_a)$	107.0	108.3	108.5	103.9	105.3	105.5	107.9	106.4	106.1	109.2
$a(H_aNH_b)$	106.4	107.6	107.7	104.5	105.7	105.7	108.1	107.0	106.6	113.3
$d(H_aNNH_b)$	89.6	90.2	90.0	90.7	90.9	90.4	90.4	90.6	90.9	88.9
NO										
$r(NO)$	1.174	1.161	1.162	1.189	1.176	1.176	1.127	1.143	1.174	1.151[b]
O_2										
$r(OO)$	1.230	1.215	1.215	1.257	1.240	1.240	1.168	1.246	1.221	1.207
HOOH										
$r(OO)$	1.461	1.436	1.430	1.532	1.502	1.494	1.397	1.468	1.464	1.475
$r(OH)$	0.998	0.983	0.988	0.996	0.982	0.986	0.949	0.976	0.975	0.950
$a(OOH)$	99.4	99.9	100.0	97.9	98.3	98.5	102.1	98.7	99.4	94.8
$d(HOOH)$	117.0	117.1	116.1	122.0	121.8	120.5	116.0	121.2	119.3	120.0
F_2										
$r(FF)$	1.407	1.389	1.383	1.462	1.442	1.434	1.345	1.421	1.425	1.417
CO_2										
$r(CO)$	1.185	1.173	1.173	1.195	1.182	1.183	1.143	1.179	1.172	1.162[d]
Bond distances:										
Mean deviation	0.033	0.014	0.016	0.037	0.018	0.020	−0.010	0.010	0.012	
Mean absolute deviation	0.035	0.021	0.025	0.037	0.018	0.020	0.020	0.014	0.013	
Bond angles:										
Mean deviation	−1.37	−0.74	−0.76	−2.19	−1.59	−1.61	0.11	−0.87	−0.89	
Mean absolute deviation	2.39	1.93	1.99	2.68	2.24	2.33	1.99	1.78	1.79	

[a]From Ref. 63 unless otherwise noted.
[b]From Ref. 64.
[c]From Ref. 65.
[d]From Ref. 35.

For the lone-pair molecules NH_3, H_2O, and HF, theoretical dipole moments are too long by almost all methods. The theoretical values for ammonia, for example, are all in the narrow range 1.885–1.980 D, far above the experimental value of 1.47 D. On the other hand, for the more polar ionic species such as LiH and LiF, the theoretical values are all too small, both *ab initio* and DFT. This can probably be attributed to the failure of the 6-31G* basis to provide a satisfactory description of the incipient anions H^- and F^-. We note that Krijn and Feil[59] have obtained a good S-VWN dipole moment for water using a large basis.

The density functional theories have some success in computing the sign of dipole moments with values close to zero, as already noted in the case of CO.[59] HF theory gives incorrect directions for both CO and NO. The proper dipole direction is predicted by all of the DFT calculations, as it is by MP2 for both of these and by QCISD for NO.

E. Vibrational frequencies

As noted earlier, the computed frequencies are *harmonic* and should properly be compared with *harmonic* experimental frequencies, deduced, where possible, from appropriate fundamentals and anharmonic corrections. Such data, where available, are displayed in the final column of Table IV. The observed fundamentals (usually lower frequencies) are listed for all of the molecules considered.

All of the density functionals are remarkably successful in reproducing the known fundamental frequencies. The HF results are well known to be systematically large, and the same is clearly true for MP2 and QCISD. However, the very precise agreement with observed fundamentals is somewhat fortuitous, since comparison with known harmonic frequencies shows that the DFT values are generally too low. QCISD gives results closest to the experi-

TABLE III. Theoretical and experimental dipole moments (debye). Theoretical values were obtained with the 6-31G* basis.

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt.[a]
LiH	5.357	5.514	5.346	5.521	5.662	5.501	5.981	5.776	5.563	5.88
BeH	0.222	0.216	0.194	0.298	0.293	0.273	0.337	0.218	0.167	
CH	1.285	1.368	1.349	1.234	1.314	1.296	1.582	1.507	1.371	1.46[b]
$CH_2(^1A_1)$	1.814	1.903	1.895	1.702	1.789	1.783	2.016	1.965	1.802	
$CH_2(^3B_1)$	0.610	0.689	0.694	0.547	0.631	0.638	0.582	0.636	0.635	
NH	1.522	1.599	1.580	1.458	1.529	1.511	1.750	1.709	1.658	1.389[c]
NH_2	1.999	2.067	2.057	1.875	1.945	1.937	2.135	2.120	2.080	
NH_3	1.979	1.969	1.980	1.885	1.893	1.902	1.920	1.965	1.959	1.47
OH	1.745	1.793	1.784	1.652	1.701	1.693	1.884	1.862	1.833	1.66
OH_2	2.109	2.146	2.141	2.000	2.042	2.037	2.199	2.200	2.179	1.85
FH	1.860	1.894	1.886	1.776	1.812	1.805	1.972	1.948	1.934	1.82
LiF	5.216	5.386	5.239	5.330	5.510	5.359	6.173	5.850	5.864	6.33
CN	1.168	1.048	1.025	1.149	1.031	1.009	2.182	2.113	1.378	1.15[b]
HCN	2.827	2.873	2.860	2.762	2.808	2.796	3.209	2.949	2.976	2.98
CO[d]	0.214	0.189	0.209	0.148	0.122	0.145	−0.264	0.192	−0.011	0.112
HCO	1.349	1.436	1.401	1.355	1.438	1.401	2.083	1.584	1.665	
H_2CO	1.932	2.039	1.994	1.964	2.069	2.022	2.666	2.275	2.333	2.33
H_3COH	1.592	1.643	1.619	1.601	1.651	1.622	1.867	1.834	1.830	1.70
H_2NNH_2	2.196	2.148	2.129	2.214	2.206	2.200	2.243	2.312	2.302	1.75
NO[d]	0.195	0.201	0.217	0.121	0.130	0.147	−0.210	0.078	0.057	0.153
HOOH	1.826	1.858	1.878	1.608	1.650	1.680	1.951	1.796	1.825	2.2
Mean deviation	−0.076	−0.035	−0.062	−0.113	−0.069	−0.094	0.239	0.133	0.052	
Mean absolute deviation	0.280	0.252	0.278	0.255	0.227	0.251	0.289	0.277	0.233	

[a]From Ref. 66 unless otherwise noted.
[b]From Ref. 67.
[c]From Ref. 68.
[d]Negative value means the dipole vector points away from the O atom.

TABLE IV. Theoretical and experimental vibrational frequencies (cm^{-1}). Theoretical values were obtained with the 6-31G* basis.

										Expt.	
Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Obs.[a]	Harm.[b]
H_2 ($D_{\infty h}$)											
Σ_g	4035	4207	4119	4286	4461	4373	4646	4534	4367	4160	4401
LiH ($C_{\infty v}$)											
Σ	1270	1353	1338	1304	1385	1373	1416	1392	1331	1360	1406
BeH ($C_{\infty v}$)											
Σ	1919	1984	1958	1981	2049	2023	2151	2135	2059	1986	2059
CH ($C_{\infty v}$)											
Σ	2534	2682	2647	2569	2718	2684	3058	2944	2818	2733	2862
CH_2 ($^3B_1$) (C_{2v})											
A_1	2961	3078	3048	2989	3102	3073	3325	3250	3186		
	1015	1010	985	1089	1093	1069	1239	1192	1149	963[c]	
B_2	3173	3311	3284	3192	3327	3301	3525	3471	3398	3190	
CH_2 ($^1A_1$) (C_{2v})											
A_1	2614	2757	2726	2639	2784	2754	3129	3001	2903	2806[c]	
	1363	1392	1374	1425	1457	1437	1564	1499	1470	1353	
B_2	2694	2844	2814	2695	2847	2819	3192	3085	2980	2865	
CH_3 (D_{3h})											
A_1'	2950	3069	3044	2971	3092	3068	3285	3220	3159	3005[c]	
A_2''	396	488	492	346	449	456	308	406	434	606	
E'	3123	3252	3227	3129	3260	3237	3461	3409	3336	3161	
	1320	1356	1337	1378	1416	1395	1540	1481	1454	1396	
CH_4 (T_d)											
A_1	2879	2988	2969	2887	2999	2980	3197	3112	3066	2917	3137
E	1487	1526	1508	1535	1576	1557	1703	1626	1603	1534	1567
T_2	3000	3121	3104	2974	3098	3083	3302	3250	3188	3019	3158
	1260	1293	1272	1327	1362	1339	1488	1414	1400	1306	1357
NH ($C_{\infty v}$)											
Σ	2941	3116	3080	2966	3135	3099	3528	3366	3225		3300

TABLE IV. (*Continued.*)

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. Obs.[a]	Expt. Harm.[b]
NH_2 (C_{2v})											
A_1	3058	3216	3183	3039	3199	3169	3607	3423	3332	3219[c]	
	1501	1530	1513	1557	1589	1570	1711	1632	1625	1497	
B_2	3172	3337	3303	3135	3302	3272	3708	3545	3441	3301	
NH_3 (C_{3v})											
A_1	3218	3372	3342	3174	3332	3305	3689	3504	3457	3337	3506
	1060	1045	1036	1151	1140	1128	1209	1161	1178	950	1022
E	3359	3520	3490	3294	3459	3433	3822	3660	3596	3444	3577
	1622	1654	1636	1674	1710	1690	1849	1756	1751	1627	1691
OH ($C_{\infty v}$)											
Σ	3402	3556	3522	3359	3516	3485	3997	3740	3652	3570	3735
OH_2 (C_{2v})											
A_1	3504	3657	3625	3439	3597	3568	4070	3776	3751	3657	3832
	1623	1646	1631	1672	1698	1682	1827	1735	1745	1595	1648
B_2	3632	3789	3755	3558	3721	3690	4189	3918	3878	3756	3943
FH ($C_{\infty v}$)											
Σ	3772	3912	3877	3696	3841	3810	4358	4041	4020	3962	4139
Li_2 ($D_{\infty h}$)											
Σ_g	301	331	325	305	338	333	340	339	340	346	351
LiF ($C_{\infty v}$)											
Σ	981	1014	1034	933	966	984	1031	1002	1002	898[b]	914
HCCH ($D_{\infty h}$)											
Σ_g	3338	3452	3425	3370	3486	3460	3719	3570	3541	3374	3497
	1985	2041	2035	1967	2025	2019	2247	2005	2056	1974	2011
Σ_u	3236	3349	3320	3277	3392	3364	3607	3482	3444	3289	3415
Π_g	420	475	455	376	439	420	794	394	435	612	624
Π_u	711	730	723	729	750	743	883	752	754	730	747
H_2CCH_2 (D_{2h})											
A_g	2971	3089	3065	2985	3104	3082	3344	3231	3189	3026	3153
	1634	1685	1682	1621	1672	1664	1856	1721	1719	1623	1655
	1311	1345	1330	1334	1371	1360	1497	1415	1403	1342	1370
A_u	1007	1036	1028	1018	1047	1040	1155	1085	1059	1023	1044
B_{3g}	3026	3151	3128	3028	3155	3134	3395	3300	3247	3103	3232
	1162	1187	1173	1205	1232	1217	1352	1266	1260	1236	1245
B_{3u}	902	926	916	925	950	940	1095	990	979	949	969
B_{2g}	877	910	900	880	915	907	1099	942	939	943	959
B_{2u}	3052	3175	3152	3057	3182	3160	3421	3323	3270	3106	3234
	782	800	790	806	825	814	897	851	847	826	843
B_{1u}	2956	3073	3050	2971	3091	3069	3321	3214	3170	2989	3147
	1383	1417	1397	1443	1479	1458	1610	1521	1511	1444	1473
H_3CCH_3 (D_{3d})											
A_{1g}	2863	2978	2956	2871	2987	2967	3206	3113	3068	2954	3043
	1351	1390	1374	1394	1433	1414	1580	1493	1484	1388	1449
	997	1038	1047	921	964	975	1061	1051	1040	995	1016
A_{1u}	312	317	321	298	304	307	326	332	323	289	303
A_{2u}	2868	2982	2962	2871	2988	2969	3200	3114	3066	2986	3061
	1326	1360	1341	1381	1419	1398	1548	1466	1457	1379	1438
E_g	2922	3045	3025	2906	3032	3014	3249	3189	3129	2969	3175
	1424	1463	1443	1475	1516	1495	1644	1569	1552	1468	1552
	1149	1178	1163	1186	1217	1203	1338	1271	1261	1190	1246
E_u	2947	3069	3049	2933	3057	3039	3274	3209	3150	2985	3140
	1428	1466	1447	1482	1522	1502	1650	1573	1557	1469	1526
	780	800	788	803	825	813	889	850	844	822	822
CN ($C_{\infty v}$)											
Σ	2079	2143	2143	2009	2074	2075	1982	2869	2181	2042	2069
HCN ($C_{\infty v}$)											
Σ	3265	3381	3352	3296	3415	3387	3680	3514	3489	3311	3442
	2097	2163	2158	2057	2123	2119	2438	2046	2172	2097	2129
Π	711	732	727	709	732	727	889	730	738	712	727
CO ($C_{\infty v}$)											
Σ	2105	2169	2169	2040	2105	2105	2439	2125	2176	2143	2170
HCO (C_s)											
A'	2386	2570	2519	2390	2580	2528	2918	2752	2715	2434[c]	
	1872	1928	1932	1789	1846	1852	2144	2021	1896	1868	
	1059	1087	1073	1082	1112	1098	1251	1136	1160	1081	

TABLE IV. (*Continued.*)

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. Obs.[a]	Expt. Harm.[b]
H_2CO (C_{2v})											
A_1	2672	2801	2773	2702	2833	2806	3160	3014	2976	2783	2944
	1786	1838	1841	1719	1773	1774	2028	1792	1823	1746	1764
	1464	1502	1486	1495	1537	1522	1680	1585	1575	1500	1563
B_2	2704	2842	2816	2727	2867	2841	3232	3085	3039	2843	3009
	1199	1232	1219	1220	1254	1242	1383	1297	1293	1249	1287
B_1	1112	1143	1132	1128	1162	1151	1336	1213	1202	1167	1191
H_3COH (C_s)											
A'	3522	3676	3642	3459	3618	3589	4118	3796	3777	3681	
	2929	3051	3025	2949	3072	3046	3305	3223	3166	3000	
	2780	2899	2874	2811	2931	2905	3185	3077	3034	2844	
	1437	1476	1459	1479	1521	1502	1663	1579	1562	1477	
	1408	1446	1428	1448	1489	1470	1638	1540	1528	1455	
	1320	1344	1331	1352	1378	1366	1508	1418	1423	1345	
	1075	1124	1137	1040	1069	1061	1189	1114	1110	1060	
	1017	1045	1034	945	998	1012	1164	1085	1085	1033	
A''	2815	2943	2917	2838	2966	2940	3231	3144	3088	2960	
	1411	1452	1432	1462	1504	1483	1652	1566	1548	1477	
	1110	1143	1131	1120	1157	1145	1290	1205	1198	1165	
	356	356	359	342	343	347	348	351	345	250	
N_2 ($D_{\infty h}$)											
Σ_g	2332	2401	2398	2269	2340	2337	2758	2180	2400	2331	2360
H_2NNH_2 (C_2)											
A	3305	3459	3429	3258	3419	3392	3819	3617	3565	3325[b]	
	3180	3334	3303	3148	3305	3277	3718	3494	3456	3280	
	1621	1663	1645	1645	1694	1675	1871	1751	1749	1587	
	1283	1311	1301	1303	1332	1320	1468	1383	1383	1275	
	1117	1167	1174	1083	1105	1103	1226	1170	1161	1098	
	756	760	745	730	779	780	979	893	903	780	
	443	489	498	328	377	388	474	430	413	377	
B	3314	3465	3435	3267	3426	3400	3826	3621	3569	3350	
	3164	3327	3297	3119	3284	3256	3706	3488	3443	3314	
	1605	1649	1631	1629	1678	1660	1854	1738	1735	1628	
	1243	1275	1261	1263	1296	1283	1436	1345	1347	1275	
	963	942	924	1060	1056	1040	1112	1081	1090	966	
$NO(C_{\infty v})$											
Σ	1891	1960	1963	1784	1855	1859	2221	3895	1949	1876	1904
O_2 ($D_{\infty h}$)											
Σ_g	1581	1642	1652	1444	1505	1518	1998	1413	1639	1556	1580
$HOOH$ (C_2)											
A	3453	3602	3563	3425	3577	3543	4091	3738	3726	3618[c]	
	1383	1428	1416	1363	1412	1400	1635	1465	1477	1394	
	927	975	991	810	853	872	1151	929	931	864	
	354	371	379	289	307	318	399	338	350	371	
B	3457	3605	3567	3429	3579	3546	4093	3741	3729	3619	
	1253	1295	1284	1220	1266	1259	1493	1324	1338	1274	
F_2 ($D_{\infty h}$)											
Σ_g	1052	1087	1110	928	962	987	1245	1008	969	923	891
CO_2 ($D_{\infty h}$)											
Σ_g	1312	1354	1355	1258	1303	1304	1518	1336	1368	1333	
Σ_u	2371	2450	2452	2260	2342	2345	2585	2455	2425	2349	
Π_u	603	623	619	585	607	602	746	642	658	667	
Observed:											
Mean deviation	−46	28	12	−49	28	13	243	138	95		
Mean absolute deviation	63	46	47	69	51	45	250	153	103		
Harmonic:											
Mean deviation	−126	−51	−68	−123	−47	−63	165	69	12		
Mean absolute deviation	135	75	93	130	61	73	168	99	42		

[a]Diatomic values from Ref. 64 and polyatomic values from Ref. 69 unless otherwise noted.
[b]From Ref. 35.
[c]From Ref. 70.

TABLE V. Theoretical and experimental atomization energies (kcal/mol). Theoretical values were obtained with the 6-31G* basis.

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt.[a]
H_2	76.8	107.5	100.2	79.5	110.8	103.2	75.9	86.6	91.2	103.3
LiH	31.4	57.5	52.5	33.6	60.3	54.9	30.4	39.8	44.1	56.0
BeH	46.4	57.7	54.4	46.1	57.6	53.9	48.8	45.3	38.3	46.9
CH	61.0	86.7	85.4	56.6	82.4	79.9	50.0	63.6	66.6	79.9
$CH_2(^3B_1)$	163.8	201.0	198.1	144.7	181.8	177.7	142.9	161.7	160.7	179.6
$CH_2(^1A_1)$	135.6	185.1	181.7	121.0	170.8	166.1	112.3	141.2	145.0	170.6
CH_3	255.2	320.5	316.7	227.2	292.5	287.3	223.3	259.4	259.4	289.2
CH_4	347.5	436.8	432.1	306.6	396.0	389.9	300.4	354.2	353.9	392.5
NH	58.8	87.7	86.2	54.4	83.3	81.8	43.0	60.6	62.5	79.0
NH_2	133.2	189.1	186.6	117.6	173.4	170.8	98.8	137.8	139.0	170.0
NH_3	224.9	306.0	302.6	192.7	273.5	270.1	170.2	232.4	230.7	276.7
OH	85.5	112.9	112.8	72.4	99.7	98.6	57.7	84.7	83.9	101.3
OH_2	188.1	240.8	239.9	156.6	209.1	207.3	131.7	188.8	183.7	219.3
FH	119.3	146.2	145.6	99.5	125.3	124.4	82.1	118.2	114.0	135.2
Li_2	5.6	22.5	21.8	3.4	20.5	19.8	2.2	14.1	20.9	24.0
LiF	125.9	151.3	152.6	110.5	134.9	135.6	85.2	129.5	123.5	137.6
HCCH	363.9	438.6	444.0	305.5	380.1	383.4	271.9	365.6	351.2	388.9
H_2CCH_2	489.8	600.9	603.0	417.5	528.5	528.1	394.2	489.4	481.7	531.9
H_3CCH_3	604.7	752.1	751.2	517.7	664.9	660.9	506.0	608.5	603.1	666.3
CN	172.9	213.5	221.5	138.8	179.1	186.0	84.4	150.6	155.4	176.6
HCN	281.6	346.5	352.6	236.5	301.2	306.2	184.9	287.3	269.7	301.8
CO	258.2	293.4	301.9	215.9	250.9	257.4	168.3	254.3	237.4	256.2
HCO	273.1	323.4	331.4	222.4	272.4	278.3	170.6	258.0	243.6	270.3
H_2CO	345.1	417.6	423.3	286.0	358.4	361.8	237.8	335.5	321.9	357.2
H_3COH	441.4	551.2	554.2	365.7	475.0	475.3	331.5	434.8	425.3	480.8
N_2	202.6	257.3	264.3	169.9	224.3	231.3	105.1	212.1	192.3	225.1
H_2NNH_2	340.8	470.6	472.7	272.4	400.9	402.4	222.0	339.9	332.5	405.4
NO	153.5	193.8	202.8	114.9	154.8	162.8	46.4	134.8	124.8	150.1
O_2	149.0	174.6	185.8	102.7	127.6	136.8	28.9	117.6	99.0	118.0
HOOH	240.6	310.4	317.3	179.6	248.2	252.8	109.4	219.6	206.8	252.3
F_2	68.8	83.6	91.8	35.3	47.4	54.4	−34.3	36.8	27.9	36.9
CO_2	406.3	464.3	481.0	321.8	379.2	392.9	234.7	381.0	347.8	381.9
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	

[a]From Ref. 38.

mental harmonic frequencies. The DFT results are still quite good, with S-VWN, B-VWN, and B-LYP giving mean absolute errors less than MP2. The mean absolute error of S-LYP is essentially the same as that of MP2, while those of S-null and B-null are between HF and MP2.

Certain particular failures should be noted. The frequency of the out-of-plane symmetric vibration of CH_3 is found to be too low for all the DFT methods. The same is true for the three *ab initio* methods as well. For the umbrella motion of NH_3, too high a value is found by all theoretical methods. For the Π_g vibration of C_2H_2, all of the theoretical values except HF are too low.

Finally, we note that some of our results (for N_2, F_2, and CO) have been obtained independently by Murray *et al.*[29] They have also used a larger basis for these molecules but found only small changes in the calculated frequencies.

F. Atomization energies

The atomization energies listed in Table V show a large variation with the theoretical method. The *ab initio* methods HF, MP2, and QCISD all give binding energies which are too low, primarily because of inadequate treatment of electron correlation. The functionals S-null and B-null also give binding energies which are generally too low. B-null, with a mean absolute error of 54.2 kcal/mol, is the worst performer among the DFT methods, better only than HF. The S-VWN and S-LYP functionals give binding energies which are almost always too large. The two functionals B-VWN and B-LYP, on the other hand, perform very well and give binding energies with a mean error (relative to experiment) close to zero.

The B-VWN functional is that used by Becke[25] in his important recent paper on density functional thermochemistry. His numerical program (no orbital basis) actually uses the S-VWN density for a single calculation at the B-VWN level. This hybrid method is denoted B-VWN/S-VWN. He gave results for all of these compounds and others. He achieved an overall mean absolute error of 3.7 kcal/mol with a general tendency for the magnitudes to be too large. In general, our self-consistent B-VWN results show somewhat less binding than this, probably because of the limitations of the 6-31G* orbital basis.

The B-LYP binding energies listed in Table V are gen-

erally satisfactory, particularly when it is noted that they are associated with excellent total energies (Table I). The mean error is 1.0 kcal/mol and the mean absolute error is 5.6 kcal/mol. The molecules which are underbound at this theoretical level are the simple hydrides with lone-pair electrons (H_2O and NH_3, for example). Molecules with multiple bonds, together with H_2O_2 and F_2, on the other hand, tend to be overbound. Taken together, these two tendencies lead to a low mean error. It should be noted, however, that this is partly due to the fairly small basis set used. In other studies, we have examined the same set of molecules with a large basis [6-311+G(3*df*,2*p*)] and have found, not surprisingly, that almost all theoretical bindings become larger whether the DFT energies are calculated post-HF[30] or KS energies are used.[60] The mean error in the latter case becomes 4.1 kcal/mol and the mean absolute error 5.2 kcal/mol. Thus, the overall conclusion is that B-LYP theory leads to some overbinding with a large basis, but the effect is ameliorated in this study by the use of 6-31G*.

In summary, we have presented the results of a systematic study of properties of small neutral molecules by a variety of DFT and *ab initio* methods. Since fully self-consistent KS densities were obtained for all the DFT methods, local and gradient-corrected, without auxiliary fitting, direct comparison of the DFT and *ab initio* results is facilitated. Within the 6-31G* basis, the DFT geometries generally compare slightly less favorably with experiment than do the *ab initio* values. The theoretical dipole moments are in error by roughly comparable amounts by all nine methods, and are not satisfactory. DFT harmonic vibrational frequencies agree quite well with experimental fundamentals, and also with experimental harmonic frequencies for the systems where they are known. For atomization energies, the B-VWN and B-LYP methods gave excellent agreement with experiment and were in fact the only acceptable theoretical methods. For the various properties studied here, the B-LYP method is the DFT method with the best overall performance.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHEM-8918623. B.G.J. thanks the Mellon College of Science for a Graduate Fellowship. An account of this work was presented at the 11th Canadian Symposium on Theoretical Chemistry held at McGill University in Montreal. Professor N. C. Handy is kindly acknowledged for preprints of Refs. 29 and 43.

APPENDIX A: FIRST DERIVATIVES OF THE FUNCTIONALS

The simplest exchange functional is the Slater ($X\alpha$) functional:[9]

$$S=-\frac{9}{4}\alpha\left(\frac{3}{4\pi}\right)^{1/3}(\rho_\alpha^{4/3}+\rho_\beta^{4/3}), \tag{A1}$$

where the constant α is taken as a parameter (not to be confused with α spin). Its derivatives are trivial, but for completeness we include them:

$$\frac{\partial S}{\partial\rho_\alpha}=-3\alpha\left(\frac{3}{4\pi}\right)^{1/3}\rho_\alpha^{1/3},\quad \frac{\partial S}{\partial\rho_\beta}=-3\alpha\left(\frac{3}{4\pi}\right)^{1/3}\rho_\beta^{1/3}. \tag{A2}$$

The Becke gradient-corrected exchange functional[17] has the form

$$B=\rho_\alpha^{4/3}g(x_\alpha)+\rho_\beta^{4/3}g(x_\beta), \tag{A3}$$

where

$$g(x)=-\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}-\frac{bx^2}{1+6bx\sinh^{-1}x}, \tag{A4}$$

with

$$x_\alpha=\frac{\gamma_{\alpha\alpha}}{\rho_\alpha^{4/3}},\quad x_\beta=\frac{\gamma_{\beta\beta}}{\rho_\beta^{4/3}}, \tag{A5}$$

and b being an empirical parameter. The relevant derivatives are

$$\frac{\partial B}{\partial\rho_\alpha}=\frac{4}{3}\rho_\alpha^{4/3}[g(x_\alpha)-x_\alpha g'(x_\alpha)], \tag{A6}$$

$$\frac{\partial B}{\partial\gamma_{\alpha\alpha}}=\frac{1}{2}\gamma_{\alpha\alpha}^{-1/2}g'(x_\alpha), \tag{A7}$$

$$g'(x)=\frac{6b^2x^2[x/(x^2+1)^{1/2}-\sinh^{-1}x]-2bx}{(1+6bx\sinh^{-1}x)^2}, \tag{A8}$$

and similarly for the β derivatives.

The version of the Vosko–Wilk–Nusair correlation functional[11] we have implemented is

$$\mathrm{VWN}=\rho\epsilon_c(x,\zeta), \tag{A9}$$

where

$$\rho=\rho_\alpha+\rho_\beta,\quad x=\left(\frac{3}{4\pi\rho}\right)^{1/6},\quad \zeta=\frac{\rho_\alpha-\rho_\beta}{\rho}. \tag{A10}$$

The correlation potential is

$$\epsilon_c(x,\zeta)=\epsilon_c^P(x)+\epsilon_c^A(x)g(\zeta)\times\left\{1+\left[\frac{4}{9(2^{1/3}-1)}\frac{\epsilon_c^F(x)-\epsilon_c^P(x)}{\epsilon_c^A(x)}-1\right]\zeta^4\right\}, \tag{A11}$$

where

$$g(\zeta)=\tfrac{9}{8}[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2], \tag{A12}$$

and the various ϵ_c have the form

$$\epsilon_c(x)=A\left\{\ln\frac{x^2}{X(x)}+\frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b}-\frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)}+\frac{2(2x_0+b)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\right\}, \tag{A13}$$

where

$$X(x)=x^2+bx+c, \quad Q=(4c-b^2)^{1/2}, \tag{A14}$$

and A, b, c, and x_0 are parameters assuming different values for each individual ϵ_c. Introducing

$$h(x)=\frac{4}{9(2^{1/3}-1)}\frac{\epsilon_c^F(x)-\epsilon_c^P(x)}{\epsilon_c^A(x)}-1, \tag{A15}$$

the derivatives are expressible as

$$\frac{\partial \mathrm{VWN}}{\partial \rho_i}=\epsilon_c(x,\zeta)+\rho\frac{\partial \epsilon_c(x,\zeta)}{\partial \rho_i}, \quad i=\alpha,\beta, \tag{A16}$$

$$\frac{\partial \epsilon_c(x,\zeta)}{\partial \rho_i}=-\frac{x}{6\rho}\{\epsilon_c^{P\prime}(x)+\epsilon_c^{A\prime}(x)g(\zeta)[1+h(x)\zeta^4]+\epsilon_c^A(x)g(\zeta)h'(x)\zeta^4\}+\epsilon_c^A(x)\{g'(\zeta)\times[1+h(x)\zeta^4]+4g(\zeta)h(x)\zeta^3\}\frac{\partial\zeta}{\partial\rho_i}, \tag{A17}$$

$$\epsilon_c'(x)=A\left\{\frac{2}{x}-\frac{2x+b}{X(x)}-\frac{4b}{(2x+b)^2+Q^2}-\frac{bx_0}{X(x_0)}\left[\frac{2}{x-x_0}-\frac{2x+b}{X(x)}-\frac{4(2x_0+b)}{(2x+b)^2+Q^2}\right]\right\}, \tag{A18}$$

$$h'(x)=\frac{4}{9(2^{1/3}-1)\epsilon_c^A(x)}\left[\epsilon_c^{F\prime}(x)-\epsilon_c^{P\prime}(x)-\frac{\epsilon_c^F(x)-\epsilon_c^P(x)}{\epsilon_c^A(x)}\epsilon_c^{A\prime}(x)\right], \tag{A19}$$

$$g'(\zeta)=\tfrac{3}{2}[(1+\zeta)^{1/3}-(1-\zeta)^{1/3}], \tag{A20}$$

$$\frac{\partial\zeta}{\partial\rho_\alpha}=\frac{1}{\rho}(1-\zeta), \quad \frac{\partial\zeta}{\partial\rho_\beta}=-\frac{1}{\rho}(1+\zeta). \tag{A21}$$

As previously mentioned, we use a transformed[37] version of the Lee–Yang–Parr correlation functional.[19] The first-order arguments γ are linear in this functional, so it may be written as

$$\mathrm{LYP}=-\frac{4a}{1+d\rho^{-1/3}}\frac{\rho_\alpha\rho_\beta}{\rho}-2^{11/3}\tfrac{3}{10}(3\pi^2)^{2/3}ab\omega(\rho)\rho_\alpha\rho_\beta(\rho_\alpha^{8/3}+\rho_\beta^{8/3})+\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\alpha}}\gamma_{\alpha\alpha}+\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\beta}}\gamma_{\alpha\beta}+\frac{\partial \mathrm{LYP}}{\partial\gamma_{\beta\beta}}\gamma_{\beta\beta}, \tag{A22}$$

where

$$\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\alpha}}=-ab\omega(\rho)\left[\frac{1}{9}\rho_\alpha\rho_\beta\left\{1-3\delta(\rho)-[\delta(\rho)-11]\frac{\rho_\alpha}{\rho}\right\}-\rho_\beta^2\right], \tag{A23}$$

$$\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\beta}}=-ab\omega(\rho)\left\{\frac{1}{9}\rho_\alpha\rho_\beta[47-7\delta(\rho)]-\frac{4}{3}\rho^2\right\}, \tag{A24}$$

$$\frac{\partial \mathrm{LYP}}{\partial\gamma_{\beta\beta}}=-ab\omega(\rho)\left[\frac{1}{9}\rho_\alpha\rho_\beta\left\{1-3\delta(\rho)-[\delta(\rho)-11]\frac{\rho_\beta}{\rho}\right\}-\rho_\alpha^2\right], \tag{A25}$$

$$\omega(\rho)=\frac{e^{-c\rho^{-1/3}}}{1+d\rho^{-1/3}}\rho^{-11/3}, \tag{A26}$$

$$\delta(\rho)=c\rho^{-1/3}+\frac{d\rho^{-1/3}}{1+d\rho^{-1/3}}, \tag{A27}$$

with a, b, c, d constants. It now remains only to find the derivative with respect to ρ_α (the ρ_β derivative is obtained by simply interchanging α and β):

$$\frac{\partial \mathrm{LYP}}{\partial\rho_\alpha}=-\frac{4a}{1+d\rho^{-1/3}}\frac{\rho_\alpha\rho_\beta}{\rho}\left[\frac{1}{3}\frac{d\rho^{-4/3}}{1+d\rho^{-1/3}}+\rho_\alpha^{-1}-\rho^{-1}\right]-2^{11/3}\frac{3}{10}(3\pi^2)^{2/3}ab\left[\omega'(\rho)\rho_\alpha\rho_\beta(\rho_\alpha^{8/3}+\rho_\beta^{8/3})+\omega(\rho)\rho_\beta\left(\frac{11}{3}\rho_\alpha^{8/3}+\rho_\beta^{8/3}\right)\right]+\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\alpha\alpha}}\gamma_{\alpha\alpha}+\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\alpha\beta}}\gamma_{\alpha\beta}+\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\beta\beta}}\gamma_{\beta\beta}, \tag{A28}$$

$$\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\alpha\alpha}}=\frac{\omega'(\rho)}{\omega(\rho)}\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\alpha}}-ab\omega(\rho)\left[\frac{1}{9}\rho_\beta\left\{1-3\delta(\rho)-[\delta(\rho)-11]\frac{\rho_\alpha}{\rho}\right\}-\frac{1}{9}\rho_\alpha\rho_\beta\left\{\left(3+\frac{\rho_\alpha}{\rho}\right)\times\delta'(\rho)+[\delta(\rho)-11]\frac{\rho_\beta}{\rho^2}\right\}\right], \tag{A29}$$

$$\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\alpha\beta}}=\frac{\omega'(\rho)}{\omega(\rho)}\frac{\partial \mathrm{LYP}}{\partial\gamma_{\alpha\beta}}-ab\omega(\rho)\times[\tfrac{1}{9}\rho_\beta[47-7\delta(\rho)]-\tfrac{7}{9}\rho_\alpha\rho_\beta\delta'(\rho)-\tfrac{8}{3}\rho], \tag{A30}$$

$$\frac{\partial^2 \mathrm{LYP}}{\partial\rho_\alpha\partial\gamma_{\beta\beta}}=\frac{\omega'(\rho)}{\omega(\rho)}\frac{\partial \mathrm{LYP}}{\partial\gamma_{\beta\beta}}-ab\omega(\rho)\times\left[\frac{1}{9}\rho_\beta\left\{1-3\delta(\rho)-[\delta(\rho)-11]\frac{\rho_\beta}{\rho}\right\}-\frac{1}{9}\rho_\alpha\rho_\beta\left\{\left(3+\frac{\rho_\beta}{\rho}\right)\delta'(\rho)-[\delta(\rho)-11]\frac{\rho_\beta}{\rho^2}\right\}-2\rho_\alpha\right], \tag{A31}$$

$$\omega'(\rho)=-\frac{1}{3}\rho^{-4/3}\omega(\rho)\left(11\rho^{1/3}-c-\frac{d}{1+d\rho^{-1/3}}\right), \tag{A32}$$

$$\delta'(\rho)=\frac{1}{3}\left[\frac{d^2\rho^{-5/3}}{(1+d\rho^{-1/3})^2}-\rho^{-1}\delta(\rho)\right]. \tag{A33}$$

Note that the ρ_α correlation potential requires three of the second partial derivatives of the functional, Eqs. (A29)–(A31). These are necessary when computing such properties as molecular polarizabilities and harmonic vibrational frequencies analytically by DFT methods.[61] This illustrates the convenience of the way the LYP functional is written in Eq. (A22).

APPENDIX B: FIRST DERIVATIVES OF THE QUADRATURE WEIGHTS

The weights w_{Ai} may be expressed as

$$w_{Ai}=w_i w_A(\mathbf{r}_{Ai}). \tag{B1}$$

The w_i are simply the weights of the one-center quadrature formula and are independent of the nuclear configuration. The w_A, as indicated, contain the explicit nuclear dependence. The definition of these is due to Becke,[42] who gives a thorough discussion of the theory of the atomic partitioning scheme and a derivation of the weights; accordingly, we merely present the formulas we have implemented. Again, we point out that we have not considered Becke's proposed "atomic size adjustments."

The Becke weight of a point $\mathbf{r}$ with respect to nucleus A is

$$w_A(\mathbf{r})=\frac{P_A(\mathbf{r})}{\Sigma_B P_B(\mathbf{r})}=\frac{P_A(\mathbf{r})}{Z(\mathbf{r})}, \tag{B2}$$

where the P's are unnormalized "cell functions" and Z serves as a normalization factor to ensure the relative nuclear weights sum to unity. The cell functions are composed of independent pairwise contributions as follows:

$$P_A(\mathbf{r})=\prod_{B\neq A} s(\mu_{AB}), \tag{B3}$$

with

$$s(\mu)=\tfrac{1}{2}[1-p_3(\mu)], \tag{B4}$$

where $p_n(\mu)$ is an iterated function defined by

$$p_{n+1}(\mu)=p[p_n(\mu)], \quad p_1(\mu)\equiv p(\mu)=\tfrac{3}{2}\mu-\tfrac{1}{2}\mu^3. \tag{B5}$$

The arguments μ_{AB} are the hyperbolic coordinates

$$\mu_{AB}=\frac{r_A-r_B}{R_{AB}}, \tag{B6}$$

where r_A and r_B are the respective distances from $\mathbf{r}$ to nuclei A and B, and R_{AB} is the A–B internuclear distance. In Eqs. (B2)–(B6), P and μ should not be confused with the prior usage of these for the density matrix and as a basis function index, respectively. We have closely followed Becke's notation[42] here for consistency.

Having defined the Becke weights, we are now ready to differentiate them. The gradient of a weight w_A with respect to its own nuclear center A has the most complicated form, since the grid points depend on $\mathbf{R}_A$ through Eq. (5) and thus every individual $s(\mu)$ in w_A has a nonzero gradient. So, as when differentiating the functional values on the grid, these are avoided through use of translational invariance. In the following formulas, therefore, this special case has not been considered.

The result is

$$\nabla_B w_A=\frac{\nabla_B P_A}{Z}-P_A\frac{\nabla_B Z}{Z^2}, \tag{B7}$$

which requires the gradients of the cell functions

$$\nabla_A P_A=P_A\sum_{B\neq A} t(\mu_{AB})\nabla_A\mu_{AB},$$

$$\nabla_B P_A=-P_A t(\mu_{AB})\nabla_B\mu_{BA}, \quad B\neq A, \tag{B8}$$

where we have introduced the auxiliary function $t(\mu)$,[62] defined by

$$t(\mu)=\frac{1}{s(\mu)}\frac{ds}{d\mu}=-\frac{27}{16}\frac{[1-p_2^2(\mu)][1-p_1^2(\mu)][1-\mu^2]}{s(\mu)}. \tag{B9}$$

Finally, the gradient of the arguments completes the first derivative evaluation.

$$\nabla_A\mu_{AB}=\frac{1}{R_{AB}}\mathbf{u}_A-\frac{(r_A-r_B)}{R_{AB}^2}\mathbf{u}_{AB}, \tag{B10}$$

where $\mathbf{u}_A$ is a unit vector in the direction from the grid point to $\mathbf{R}_A$, and $\mathbf{u}_{AB}$ is a unit vector in the direction from $\mathbf{R}_B$ to $\mathbf{R}_A$.

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