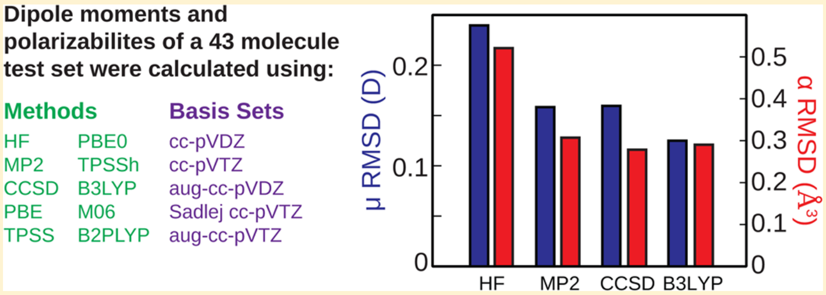
THE JOURNAL OF PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

Benchmarking Quantum Chemical Methods for the Calculation of Molecular Dipole Moments and Polarizabilities

A. Leif Hickey and Christopher N. Rowley*

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X7, Canada

Supporting Information



ABSTRACT: The calculation of molecular electric moments, polarizabilities, and electrostatic potentials is a widespread application of quantum chemistry. Although a range of wave function and density functional theory (DFT) methods have been applied in these calculations, combined with a variety of basis sets, there has not been a comprehensive evaluation of how accurate these methods are. To benchmark the accuracy of these methods, the dipole moments and polarizabilities of a set of 46 molecules were calculated using a broad set of quantum chemical methods and basis sets. Wave function methods Hartree−Fock (HF), second-order Møller−Plesset (MP2), and coupled cluster-singles and doubles (CCSD) were evaluated, along with the PBE, TPSS, TPSSh, PBE0, B3LYP, M06, and B2PLYP DFT functionals. The cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, aug-cc-pVTZ, and Sadlej cc-pVTZ basis sets were tested. The aug-cc-pVDZ, Sadlej cc-pVTZ, and aug-cc-pVTZ basis sets all yield results with comparable accuracy, with the aug-cc-pVTZ calculations being the most accurate. CCSD, MP2, or hybrid DFT methods using the aug-cc-pVTZ basis set are all able to predict dipole moments with RMSD errors in the 0.12−0.13 D range and polarizabilities with RMSD errors in the 0.30−0.38 Å^3 range. Calculations using Hartree−Fock theory systematically overestimated dipole moments and underestimate polarizabilities. The pure DFT functionals included in this study (PBE and TPSS) slightly underestimate dipole moments and overestimate polarizability. Polarization anisotropy and implications for charge fitting are discussed.

■ INTRODUCTION

The electric properties of molecules have importance across all the branches of chemistry. Features such as the dipole and higher electric moments are the basis for understanding and quantifying intermolecular interactions.[1,2] Polarizability is also an important parameter in molecular electronics.[3] Further, the electric properties of molecules provide one of the most direct relations between the electronic structure of molecules and spectroscopically observable quantities and are a means to assess the accuracy of a quantum chemical method.

Computational methods for calculating electric moments of molecules from the electronic structure are well-developed. Straightforward expressions for the molecular dipole moment have been derived for most wave function and density functional theory (DFT) methods. Molecular polarizabilities can be determined using the coupled-perturbed Hartree−Fock equations (CPHF).[4] For methods such as coupled cluster theory, where this method is not available, the polarizability can be computed using the linear response approximation.[5−7]

In addition to molecular electric moments and polarizabilities, quantum chemical methods are often used to calculate the electrostatic potential (ESP) on a surface around a molecule. This surface can be used to qualitatively identify sites of a molecule that will engage in intermolecular electrostatic interactions or chemical reactions, but perhaps its most successful application is in the assignment of partial atomic charges. Broadly, these methods determine the set of partial atomic charges that best reproduce the quantum chemical ESP in the space around the molecule. A method based on this strategy was originally proposed by Singh et al.[8] and was later refined by Breneman et al. in the CHELPG method.[9] This type of method has been used extensively to assign partial atomic charges within molecular mechanical force fields and a variety of quantum chemical methods have been used to compute the target ESP surfaces: HF/6-31G(d) was used to define charges for GAFF,[10] B3LYP/cc-pVTZ//HF/6-31G(d) was used to define charges for the AMBER ff03 force field,[11] B3LYP/aug-cc-pVDZ was used to fit charges and polarizabilities of the Drude force field,[12] and

Received: March 11, 2014
Revised: May 2, 2014
Published: May 5, 2014

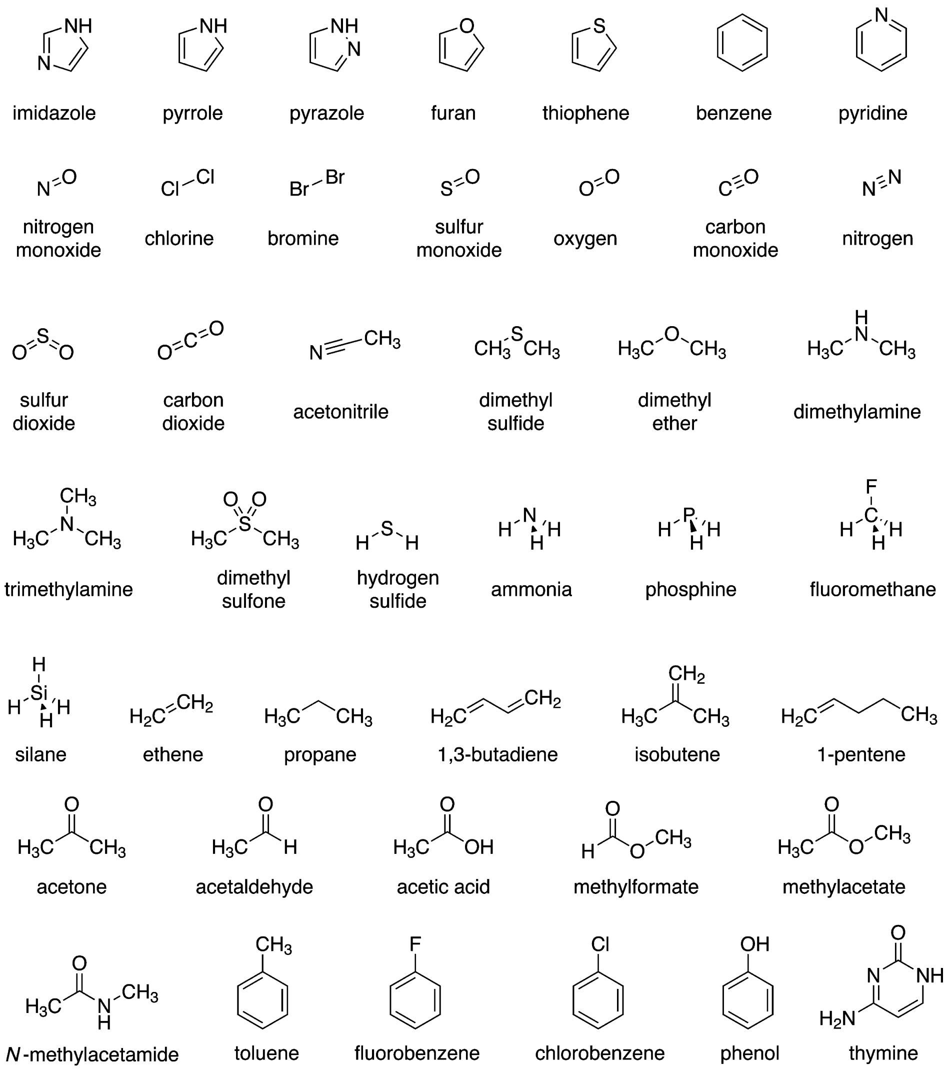


Figure 1. Molecular structures of the molecules included in the test set.

MP2/aug-cc-pVTZ has been used to fit the atomic electric moments of the AMOEBA force field.[13] There is no direct way to assess the accuracy of the ESP surface calculated using a given quantum chemical method with respect to experimental data; however, we can infer that a quantum chemical method that can accurately calculate observable electric properties, like molecular dipoles and polarizabilities, will also yield accurate ESP surfaces.

Beyond the isotropic polarizability, the calculation of the polarization anisotropy of a molecule is also of interest. The three-dimensional arrangement of atoms and the bonding between them causes the dipole of the molecule to respond to an electric field anisotropically. This is particularly significant in molecules with a π-bonding system, as these molecules tend to be much less polarizable along the axis normal to the molecular plane than along axes where the σ-bonding network is polarized. In recent years, these effects have also been incorporated into polarizable force fields, creating a need for accurate QM target data.[14]

The advent of more efficient quantum chemical algorithms and massively parallel computing codes has made it possible to employ more rigorous quantum chemical methods and larger basis sets in the calculation of molecular electric properties. Although there have been a number of studies that have tested the accuracy of individual quantum chemical methods for the calculation of the electric properties of small sets of molecules,[12,15−20] there has not been a comprehensive evaluation of how well the available wave function and DFT methods perform in the calculation of molecular electric properties for a large and diverse set of molecules. Using automated job submission and processing on supercomputing facilities, it is now possible to perform a more comprehensive analysis.

In this paper, we compare the results of 7 popular DFT functionals, Hartree−Fock (HF) theory, second-order Møller−Plesset (MP2) theory,[21] and the coupled clusters-singles and doubles (CCSD) method for the calculation of the dipole moments and polarizabilities of a set of small molecules composed of elements from the first two rows of the main group. Basis set convergence is also a significant issue in the calculation of molecular electric properties, so we also examined the effect of the basis set on the accuracy of these methods, including the effect of diffuse functions and double vs triple-ζ basis sets. Experimental values were taken from refs 22 and 23. As experimental data are most reliable and widely available for molecular dipole moments, we only report benchmarks of these moments, although quadrupole and higher moments can also be computed. Likewise, we only evaluate these methods for calculating the molecular polarizabilities, although higher order terms like the hyperpolarizability are also of interest.

THEORY AND METHODS

HF and MP2 calculations were performed using Gaussian 09 C.01.[24] The frozen core approximation was applied in the MP2 calculations. The geometry of each molecule was energy-minimized for each method/basis set combination. The dipole moment (μ) and isotropic polarizability (α) of each molecule was calculated at this optimized structure. The polarizability was calculated by solving the coupled-perturbed Hartree−Fock (CPHF) equations.[4]

Coupled cluster-singles and doubles (CCSD) calculations were performed at the MP2/aug-cc-pVTZ minimum-energy geometry using the tensor contractor engine (TCE) module of NWChem 6.1.[25] The frozen core approximation was used in all CCSD calculations. Polarizabilities were calculated using the linear response (LR) approximation.[5−7]

We also evaluated seven DFT functionals. As a very large number of DFT functionals have been formulated, we considered only some of the more popular functionals. We tested the PBE pure functional,[26] the TPSS meta functional,[27] the PBE0 hybrid functional,[28] the B3LYP hybrid functional,[29] the TPSSh hybrid meta functional,[27] the M06 empirical hybrid functional,[30] and the B2PLYP double-hybrid functional.[31] All DFT calculations were performed using Gaussian 09 C.01. DFT polarizabilities were calculated by solving the CPHF equations.

To provide an initial indication of basis set convergence, we calculated the dipole moments and polarizabilities of a small set of small molecules using the HF, MP2, B3LYP, and CCSD methods using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets. The test set was limited to hydrogen sulfide, ammonia, hydrogen fluoride, dinitrogen, dioxygen, and carbon monoxide. For each method, the dipole moments and polarizabilities converged when an aug-cc-pVTZ basis set was used and the calculations were only slightly more accurate when a aug-cc-pVQZ basis set was used. These data are included in the Supporting Information.

On the basis of these calculations, four Dunning-type basis sets were tested for each method: the double-ζ cc-pVDZ basis set, the triple-ζ cc-pVTZ basis set, and their diffuse function augmented variants, aug-cc-pVDZ and aug-cc-pVTZ.[32,33] We also evaluated the Sadlej basis set, which is the cc-pVTZ basis set augmented with additional basis functions specifically for the calculation of molecular polarizabilities.[34] HF/6-31G(d) was also evaluated because this method is used to calculate the target ESP for fitting atomic charges in the GAFF force field.[10]

We note that we have only calculated static dipole moments and polarizabilities. Experimentally, the static polarizability must be extrapolated from dynamic polarizabilities measured at a series of wavelengths of polarizing radiation, which introduces an additional source of uncertainty. For some nonvolatile molecules, the experimental measurements were made in solution, although all our calculations reflect gas phase conditions. Further, we make no correction for vibrational effects, because these effects are typically small unless the vibrations are strongly anharmonic. As these approximations limit the accuracy of our calculations, we generally only discuss general trends in the computed values.

We chose a broad selection of molecules composed of main group elements for which experimental dipole and polarizability data had been reported. These molecules were selected to include elements C, Cl, F, N, H, O, P, and S in a variety of hybridizations and topologies. The test set molecules were selected to include those relevant to chemical processing, pollution, biochemistry, and energy. The names and structures of these molecules are presented in Figure 1. Some highly conjugated molecules, like polyacetylenes, are challenging for conventional DFT functionals.[35] We have not included this type of molecule in this test set because we are primarily concerned with charge fitting for small organic molecules.

RESULTS AND DISCUSSION

A total of 240 method/basis set combinations were evaluated. The dipole moment and polarizability of the 46 molecules in the test set were calculated for each of these combinations. Tables of these data are presented as Tables S1−S53 in the Supporting Information. Using these data, we calculated the root-mean-square deviation (RMSD) and mean absolute error (MAE) of the dipole moments and polarizabilities for each method/basis set combination with respect to the experimental values. To identify systematic errors, we also performed a least-squares fit of the calculated data to the experimental data, determining the regression coefficient (m) and coefficient of determination (R^2) value. To provide another point of comparison, we also calculated the RMSDs with respect to the CCSD/aug-cc-pVTZ calculations. The aggregated data from these calculations are presented in the following sections.

Basis Set Convergence. Basis set convergence is known to be an important factor in the calculation of molecular electric properties, particularly for the calculation of polarizabilities. To examine this, we compare the RMSDs for the dipole moments and polarizabilities for the HF, MP2, CCSD, and B3LYP calculations using all five basis sets. These data are presented in Figure 2 and Table 1. Only the results for the B3LYP function are presented because the effect of the basis set was consistent for all the other DFT functionals evaluated in this study.

The trend in basis set convergence is apparent in the plots of the CCSD data vs experiment in Figure 3. Dipole moments and polarizabilities calculated using the cc-pVDZ basis set were the least accurate; the RMSDs were 0.22 D and 1.57 Å^3 for dipole moments and polarizabilities, respectively. The use of the triple-ζ Dunning basis set, cc-pVTZ, showed some improvement over the cc-pVDZ basis set for both properties; for CCSD, the RMSDs are reduced to 0.13 D and 0.91 Å^3 for dipole moments and polarizabilities, respectively. Augmentation of the basis sets with diffuse functions led to a large improvement, particularly for polarizabilities; the RMSDs for values calculated using the aug-cc-pVDZ basis were 0.12 D and 0.41 Å^3 for dipole moments and polarizabilities, respectively. The calculations using the aug-cc-pVTZ basis set are of comparable accuracy for polarizabilties, with RMSDs errors less than 0.38 Å^3, a small but significant improvement over the aug-cc-pVDZ basis set.

This error due to basis incompleteness is largely systematic. This is apparent in the least-squares fitting of the CCSD-calculated vs experimental values for the cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ basis sets, plotted in Figure 3. Although we only show plots for the CCSD data, the other methods show the same trend. The CCSD-calculated dipole moments using the cc-pVDZ basis set underestimate the experimental value (m = 0.94), whereas the cc-pVTZ and aug-cc-pVTZ basis sets have regression coefficients of m = 0.98 and m = 1.00, respectively. A stronger systematic effect is apparent in the calculated polarizabilities, which are significantly underestimated by the cc-pVDZ and cc-pVTZ basis sets (m = 0.78 and m = 0.88, respectively). The augmentation of the basis sets with diffuse

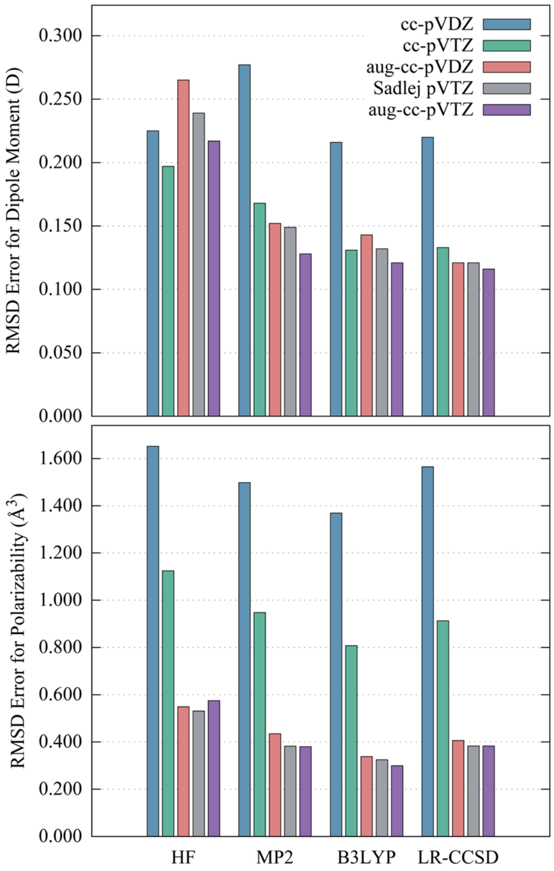


Figure 2. RMSD of the dipole moments and polarizabilities calculated using HF, MP2, B3LYP, and CCSD for the basis sets evaluated.

Table 1. RMSDs and MAEs of the Calculated Dipole Moments and Polarizabilities with Respect to the Experimental Values

	dipole moment		polarizability	
method/basis	RMSD	MAE	RMSD	MAE
HF/6-31G(d)	0.26	0.22	1.89	1.77
HF/cc-pVDZ	0.23	0.16	1.65	1.56
HF/cc-pVTZ	0.20	0.15	1.13	1.07
HF/aug-cc-pVDZ	0.27	0.19	0.55	0.48
HF/Sadlej pVTZ	0.24	0.17	0.53	0.45
HF/aug-cc-pVTZ	0.22	0.16	0.58	0.51
MP2/cc-pVDZ	0.28	0.19	1.50	1.41
MP2/cc-pVTZ	0.17	0.10	0.95	0.87
MP2/aug-cc-pVDZ	0.15	0.10	0.44	0.31
MP2/Sadlej pVTZ	0.15	0.09	0.38	0.25
MP2/aug-cc-pVTZ	0.13	0.08	0.38	0.27
CCSD/cc-pVDZ	0.22	0.15	1.57	1.47
CCSD/cc-pVTZ	0.13	0.08	0.91	0.84
CCSD/aug-cc-pVDZ	0.12	0.08	0.41	0.29
CCSD/Sadlej pVTZ	0.12	0.07	0.38	0.25
CCSD/aug-cc-pVTZ	0.12	0.07	0.38	0.27
PBE/cc-pVDZ	0.28	0.20	1.23	1.14
PBE/cc-pVTZ	0.19	0.12	0.66	0.60
PBE/aug-cc-pVDZ	0.13	0.10	0.46	0.31
PBE/Sadlej pVTZ	0.14	0.09	0.48	0.33
PBE/aug-cc-pVTZ	0.14	0.09	0.41	0.26
TPSS/cc-pVDZ	0.25	0.17	1.28	1.19
TPSS/cc-pVTZ	0.16	0.10	0.72	0.66
TPSS/aug-cc-pVDZ	0.12	0.08	0.41	0.25
TPSS/Sadlej pVTZ	0.13	0.08	0.40	0.24
TPSS/aug-cc-pVTZ	0.12	0.08	0.36	0.21
PBE0/cc-pVDZ	0.21	0.14	1.41	1.33
PBE0/cc-pVTZ	0.14	0.10	0.85	0.78
PBE0/aug-cc-pVDZ	0.14	0.10	0.33	0.23
PBE0/Sadlej pVTZ	0.13	0.10	0.30	0.19
PBE0/aug-cc-pVTZ	0.12	0.09	0.31	0.22
TPSSh/cc-pVDZ	0.22	0.15	1.35	1.26
TPSSh/cc-pVTZ	0.14	0.09	0.79	0.73
TPSSh/aug-cc-pVDZ	0.13	0.09	0.36	0.22
TPSSh/Sadlej pVTZ	0.12	0.09	0.33	0.19
TPSSh/aug-cc-pVTZ	0.12	0.08	0.32	0.19
B3LYP/cc-pVDZ	0.22	0.15	1.37	1.29
B3LYP/cc-pVTZ	0.13	0.09	0.81	0.74
B3LYP/aug-cc-pVDZ	0.14	0.10	0.34	0.21
B3LYP/Sadlej pVTZ	0.13	0.10	0.33	0.19
B3LYP/aug-cc-pVTZ	0.12	0.09	0.30	0.18
M06/cc-pVDZ	0.21	0.15	1.42	1.34
M06/cc-pVTZ	0.15	0.10	0.82	0.76
M06/aug-cc-pVDZ	0.16	0.12	0.34	0.25
M06/Sadlej pVTZ	0.14	0.11	0.32	0.20
M06/aug-cc-pVTZ	0.13	0.09	0.32	0.20
B2PLYP/cc-pVDZ	0.23	0.15	1.42	1.34
B2PLYP/cc-pVTZ	0.13	0.08	0.87	0.79
B2PLYP/aug-cc-pVDZ	0.14	0.09	0.36	0.24
B2PLYP/Sadlej pVTZ	0.13	0.08	0.34	0.21
B2PLYP/aug-cc-pVTZ	0.11	0.08	0.33	0.21

functions largely eliminates this error; the regression coefficient for the aug-cc-pVTZ basis set is $m = 0.98$. This effect can be interpreted by considering the definition of polarizability as a sum over electronic states; excited states are commonly more diffuse, so a basis set that lacks diffuse functions will underestimate the contribution of these states. This effect was noted by Ansimov et al.[12] and Kaminski et al.[36]

The Sadlej basis set yields results that are improved over the cc-pVTZ basis set and have effectively the same accuracy as the aug-cc-pVTZ basis set. For instance, for the CCSD calculations the RMSDs for dipoles and polarizabilities are 0.12 D and 0.38 Å^3 for both basis sets. As the Sadlej basis sets are of intermediate size, they provide an economical alternative in calculations where a fully augmented basis set is impractical. The improved accuracy of the calculations using the Sadlej basis set over the cc-pVTZ basis set shows that augmenting a basis set with functions specifically chosen to increase the accuracy of polarizability calculations is a sound strategy.

Relative Accuracies of Wave Function and DFT Methods. *Comparison to Experiment.* In this section, we compare the accuracy of the quantum chemical methods on the basis of their accuracy with respect to the experimental dipole moments and polarizabilities reported in the literature. The comparisons in this section refer to calculations performed using the aug-cc-pVTZ basis set, the most complete basis set evaluated in this study. The relative accuracy of these methods using the other basis sets generally show the same trends.

The RMSD of the dipole moments and polarizabilities calculated with HF, MP2, CCSD, and the DFT methods using the aug-cc-pVTZ basis set is presented in Figure 4. To determine if any of these methods show a systematic error, we performed linear regression analysis. The RMSDs, regression coefficients, and coefficients of determination are presented in Table 2.

The RMSDs for dipoles and polarizabilities calculated with HF/aug-cc-pVTZ are 0.22 D and 0.58 Å^3, respectively. These

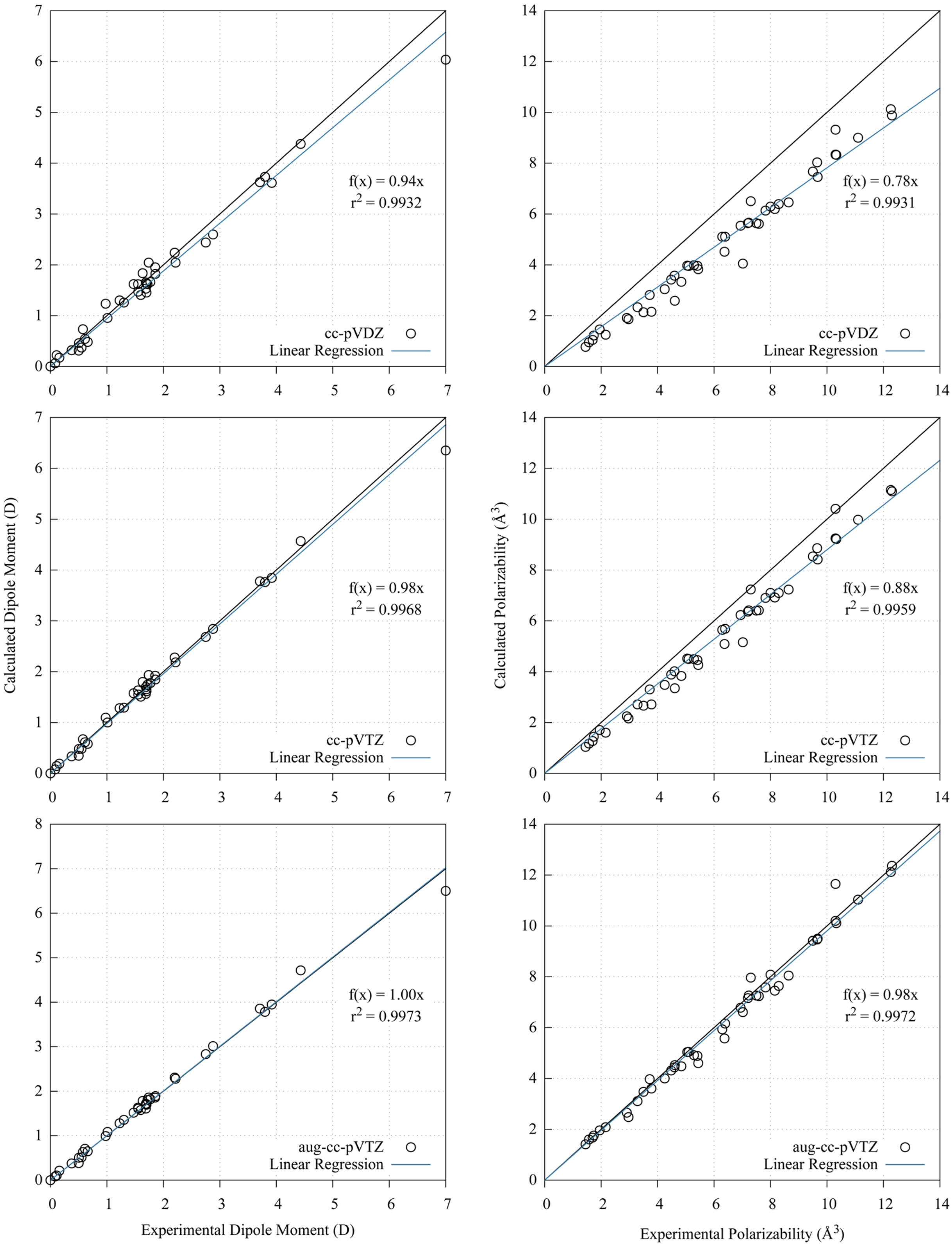


Figure 3. Plots of the molecular dipole moments (left) and polarizabilities (right) calculated using CCSD and the cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ basis sets vs the experimentally determined values.

errors are larger than those for any other method evaluated in this study. Linear regression analysis shows that the dipole moments are systematically overestimated by a factor of 1.07 and polarizabilities are systematically underestimated by a factor of 0.93. Significantly, RMSD for calculated dipole moments using a basis set like cc-pVTZ are actually smaller than those calculated using aug-cc-pVTZ, showing that this method actually becomes less accurate when larger basis sets are used. This indicates that the neglect of electron correlation leads to sizable errors in the calculation of electric properties.

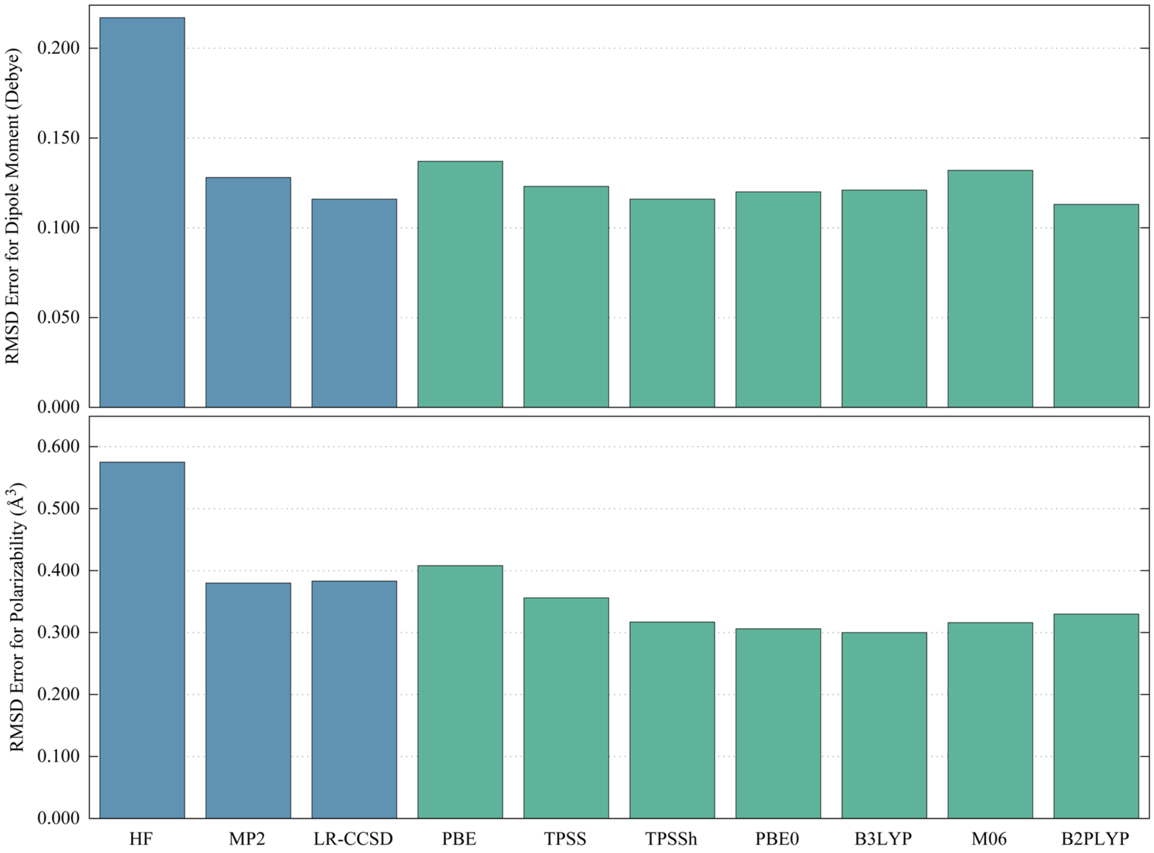


Figure 4. RMSD of dipole moments and polarizabilities calculated using various quantum chemical methods with respect to the experimental data. All calculations employ the aug-cc-pVTZ basis set.

Table 2. Linear Regression Coefficients (m) and Coefficient of Determination (R^2) for Dipole Moments and Polarizabilities Calculated with the Given Method and the aug-cc-pVTZ Basis Set with Respect to the Experimental Values

	dipole moment		polarizability	
method	m	R^2	m	R^2
HF	1.07	0.9960	0.93	0.9921
MP2	1.00	0.9967	0.98	0.9922
CCSD	1.00	0.9973	0.98	0.9914
PBE	0.98	0.9967	1.03	0.9924
TPSS	0.98	0.9972	1.02	0.9922
PBE0	1.00	0.9971	0.98	0.9927
TPSSh	0.99	0.9974	1.00	0.9924
B3LYP	1.01	0.9972	1.00	0.9925
M06	0.98	0.9967	0.99	0.9922
B2PLYP	1.00	0.9975	0.99	0.9922

The treatment of electron correlation using the MP2 method results in a large improvement in accuracy; the RMSDs are reduced to 0.13 D and 0.38 Å^3 for dipole moments and polarizabilities, respectively. Calculations using CCSD have an accuracy similar to that of MP2, with RMSDs of 0.12 D for dipole moments and 0.38 Å^3 for polarizablities.

The DFT methods show some variety in accuracy depending on the exchange−correlation functional. The PBE functional underperforms all other DFT methods for both dipole moments and polarizabilities, with RMSDs of 0.14 D for dipole moments and 0.41 Å^3 for polarizabilities. There is a small tendency for this functional to underestimate dipole moments (m = 0.98) and overestimate polarizabilities (m = 1.03). Some improvement was seen for the TPSS meta-functional, although this method still underperforms the other DFT functionals that were tested. Both of these functionals are "pure", as they do not include a component of exact exchange in the exchange functional. Hybrid functionals, which include a component of exact exchange in the exchange functional, generally show good performance; the B3LYP, TPSSh, M06, PBE0, and B2PLYP functionals have modest RMSDs for both dipoles and polarizabilities, ranging from 0.11 to 0.13 D for dipoles and from 0.30 to 0.32 Å^3 for polarizabilities. The regression coefficients calculated for these methods are near 1 (m = 0.98−1.02), indicating that there are no large systematic errors for these methods. This trend indicates that the inclusion of exact exchange in the exchange-correlation functional results in a significant increase in accuracy, particularly for polarizability. Generally, any of these hybrid functionals show comparable performance for the calculation of dipole moments and polarizabilities.

The calculated dipole moment and polarizability of cytosine was a notable outlier for most methods, which generally predict dipole moments of 6.3−6.6 D and polarizabilities of 11.3−12.1 Å^3, whereas the experimental values are 7.0 D and 10.3 Å^3, respectively. Even the most accurate method we tested, CCSD/aug-cc-pVTZ, predicts a dipole moment of 6.5 D and a polarizability of 11.7 Å^3. Errors of this magnitude did not occur for thymine, the other pyrimidine in the test set. Though this might reflect an inherent limitation of our computational methods, the experimental values deserve reexamination.

Comparison to CCSD. The neglect of vibrational quantum and solvent effects in our calculations and experimental

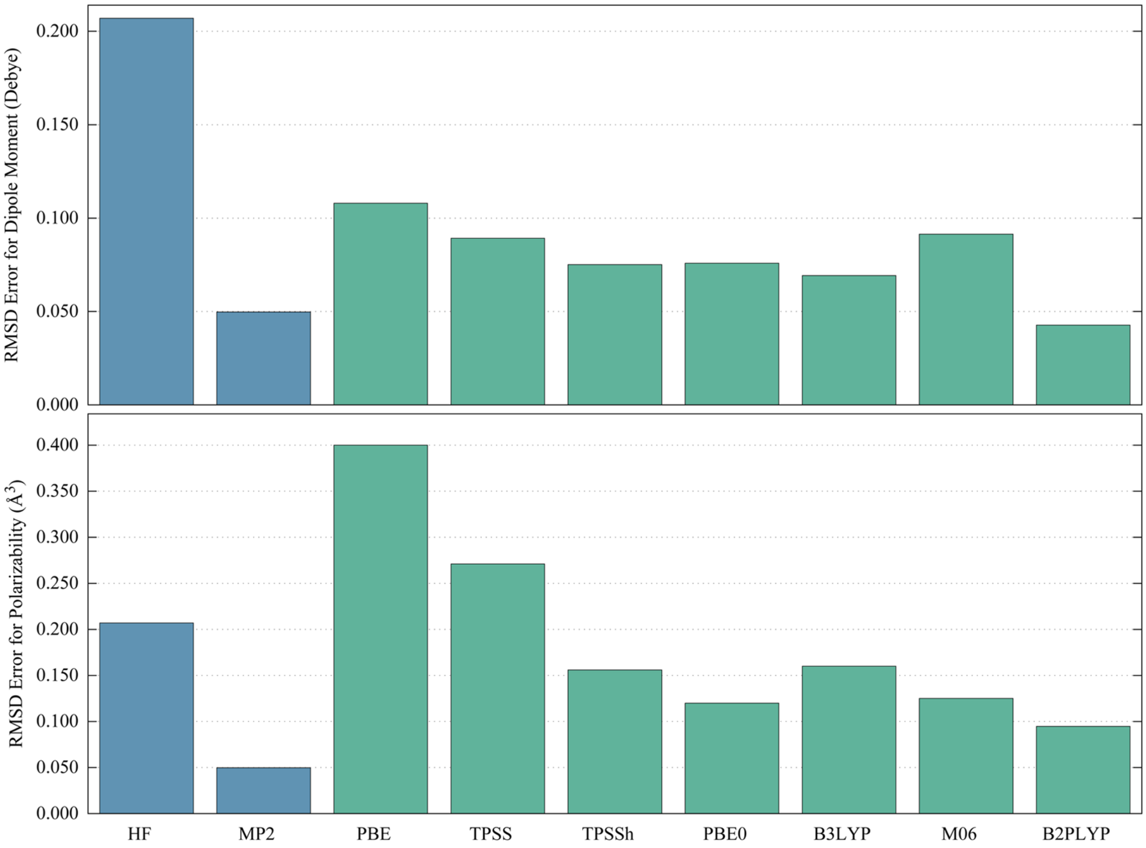


Figure 5. RMSD of dipole moments and polarizabilities calculated using various quantum chemical methods with respect to the CCSD-calculated data. All calculations employ the aug-cc-pVTZ basis set.

uncertainty creates a limit on how closely our calculations can match the experimental values; even CCSD/aug-cc-pVTZ, the most rigorous method we use, has RMSDs that are similar in magnitude to those of other methods. In an attempt to rank the accuracy of these methods more conclusively, we also calculated the RMSD of the values calculated with the DFT and wave function methods with respect to those calculated using CCSD/aug-cc-pVTZ (Figure 5).

The RMSDs for dipole moments and polarizabilities for this comparison to CCSD follow the same trends as RMSDs with respect to the experimental values, although we see a clearer distinction between the methods. We present this comparison only for the aug-cc-pVTZ basis set because the trend holds for all other basis sets. MP2 and B2PLYP are in close agreement with CCSD for both dipole moments and polarizabilities. HF underperforms all the other methods by a significant margin for dipole moments but outperforms the pure DFT functionals for the calculation of polarizabilities. The hybrid DFT functionals generally show a substantial improvement over the pure DFT functionals (PBE and TPSS), especially for polarizabilities. For example, the RMSD with respect to CCSD for the PBE functional is 0.4 Å^3 but it is only 0.3 Å^3 for PBE0, the hybrid variant of PBE. This illustrates the importance of the treatment of electron exchange in the calculation of polarizability. In general, MP2 or any of the hybrid DFT functionals tested here are good approximations to CCSD for the calculation of both dipole moments and polarizabilities.

The larger errors observed in the calculation of polarizabilities using the "pure" functionals PBE and TPSS are consistent with previous reports.[20,37] Calculations of the polarizability of highly conjugated linear molecules, such as polyacetylene, are a challenge for DFT methods.[35,37,38] Pure functionals overestimate the polarizabilities of these systems along the longitudinal axis, an error that is largely improved when hybrid functionals with a large component of exact exchange are used. This error has been attributed to the "locality" of conventional exchange−correlation functionals. For these functionals, the exchange−correlation energy at a point in space is a function of only the electron density and its derivatives at that point, so the influence of distant parts of the molecule is not always described accurately. These calculations are also affected by self-interaction error,[39] which results in more delocalized electron density distributions that reduce this spurious electron self-repulsion.[40−43] This error generally manifests itself as a systematic underestimation of polarizability because polarized electron density distributions tend to be more delocalized. It should be noted that the magnitude of this error is modest for the molecules included in this test set; the catastrophic failures for the calculation of polarizabilities of linear oligomers are not evident in any of the molecules studied here. Even a PBE, a pure DFT functional, can generally provide an estimate of molecular polarizability within 0.41 Å^3.

Polarization Anisotropy. In this section, we evaluate the accuracy of the quantum chemical methods for the calculation of polarization anisotropies for the molecules where an experimental polarization anisotropy has been reported. The isotropic polarizability can be calculated from the trace of the polarization tensor,

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

The polarization anisotropy (γ) is calculated using the equation,

$$\gamma = \frac{1}{\sqrt{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6({\alpha_{xy}}^2 + {\alpha_{yz}}^2 + {\alpha_{zx}}^2)]^{1/2} \qquad (2)$$

These molecules can be divided into two subsets: small molecules and aromatic molecules. The small molecule set is composed of water, hydrogen sulfide, carbon dioxide, and ethene. The aromatic set is composed of benzene, furan, thiophene, pyrrole, and pyridine. For simplicity, we present only the results of the calculations using B3LYP, MP2, and CCSD with the aug-cc-pVTZ basis set. The calculated and experimental polarization components, isotropic polarizabilities, and polarization anisotropies of the small molecule set are collected in Table 3, and the data for the aromatic set are collected in Table 4.

Table 3. Calculated and Experimental Polarization Anisotropies of Small Molecules[a]

method	α_{xx}	α_{yy}	α_{zz}	α	γ
		Water			
B3LYP	1.44	1.39	1.49	1.45	0.111
MP2	1.42	1.37	1.49	1.42	0.099
CCSD	1.40	1.35	1.49	1.41	0.121
exptl[49]	1.467	1.415	1.528	1.470	0.098
		Hydrogen Sulfide			
B3LYP	3.79	3.68	3.66	3.71	0.12
MP2	3.68	3.59	3.57	3.61	0.10
CCSD	3.65	3.57	3.59	3.60	0.08
exptl[50]	4.273	4.156	4.171	4.200	0.110
		Carbon Dioxide			
B3LYP	1.89	3.86	1.89	2.55	1.97
MP2	1.92	4.14	1.92	2.66	2.23
CCSD	1.90	4.16	1.90	2.65	2.25
exptl[51]	1.93	4.03	1.93	2.63	2.10
		Ethene			
B3LYP	3.77	3.37	5.31	4.15	1.78
MP2	3.70	3.33	5.07	4.03	1.59
CCSD	3.86	3.25	5.08	4.00	1.66
exptl[52]	3.86	3.40	5.40	4.22	1.81

[a] All calculations use the aug-cc-pVTZ basis set.

Generally, all the methods considered perform well for predicting the polarization anisotropy (γ) of small molecules, with errors ranging from 0.01 to 0.22 Å^3 for small molecules. The calculated polarization anisotropies of the aromatic molecules had greater deviations, with errors in the range 0.12−0.94 Å^3. All the methods we compare here have errors in similar ranges, so there is no clear advantage in terms of accuracy for any of them.

Implications for Atomic Charge and Polarizability Fitting. Under the assumption that quantum chemical methods that accurately predict dipole moments and polarizabilities will also provide more accurate ESP surfaces, we can make some inferences about the suitability of these methods for the assignment of atomic charges and polarizabilities. Basis sets that lack diffuse functions systematically underestimate molecular polarizabilities. The use of triple-ζ basis sets with diffuse functions yields improved accuracy. Calculations using hybrid DFT functionals (PBE0, B3LYP, TPSSh, and M06) were only incrementally less accurate than those calculated using MP2 theory. Short of computationally demanding CCSD/aug-cc-pVTZ calculations, we expect MP2/aug-cc-pVTZ to yield the most accurate ESP surfaces of the methods evaluated in this study.

Table 4. Calculated and Experimental Polarization Anisotropies of Aromatic and Heteroaromatic Molecules[a]

method	α_{xx}	α_{yy}	α_{zz}	α	γ
		Benzene			
B3LYP	12.09	12.09	6.64	10.27	5.42
MP2	12.02	12.02	6.67	10.24	5.31
CCSD	11.86	11.86	6.59	10.11	5.27
exptl[53]	11.73	11.73	6.54	10.0	5.19
		Thiophene			
B3LYP	11.51	10.56	6.62	9.56	4.46
MP2	11.30	10.50	6.64	9.48	4.32
CCSD	11.45	10.45	6.59	9.50	4.44
exptl[54]	13.1	11.7	7.28	10.7	5.26
		Furan			
B3LYP	7.91	8.67	5.19	7.26	3.10
MP2	7.78	8.52	5.18	7.16	2.97
CCSD	7.89	8.46	5.13	7.16	3.08
exptl[54]	8.79	9.76	5.75	8.10	3.62
		Pyrrole			
B3LYP	5.81	9.10	9.51	8.14	3.07
MP2	5.83	9.04	9.42	8.09	2.97
CCSD	5.77	9.11	9.37	8.08	3.48
exptl[55]	6.46	9.68	10.34	8.83	3.60
		Pyridine			
B3LYP	11.54	10.84	6.04	9.47	5.19
MP2	11.45	10.81	6.07	9.44	5.09
CCSD	11.41	10.78	6.05	9.42	5.07
exptl[56]	11.87	10.83	5.78	9.49	5.64

[a] All calculations use the aug-cc-pVTZ basis set.

The systematic error of HF/6-31G(d) is of particular interest, as it is widely used in the fitting of atomic charges with the RESP method. This was one of the least accurate methods we evaluated, with an RMSD of 0.26 D for dipole moments and 1.89 Å^3 for polarizabilities. The MAEs are particularly high as well; 0.22 D and 1.77 Å^3 for dipole moments and polarizabilities, respectively. This method systematically tends to overestimate the dipole moment of molecules, with a linear regression coefficient of $m = 1.08$. This exaggerated polarity appears to be an intrinsic feature of HF theory rather than a basis set effect because the regression coefficient for HF/aug-cc-pVTZ is $m = 1.07$. This systematic error mimics the effect of solvent-induced polarization, so this method has been used to assign charges for force fields intended to be used for molecules in aqueous solution, although this factor is not necessarily optimal. Polarizabilities are substantially underestimated by this method; the linear regression coefficient is $m = 0.73$.

Atomic polarizability parameters determined by empirical fitting of polarizable force fields tend to be lower than the corresponding experimental gas phase molecular polarizability.[44−46] Friesner and co-workers chose to use basis sets without diffuse functions expressly because these methods tended to predict lower molecular polarizabilities.[36,47] This was rationalized by noting that electron density occupying orbitals with diffuse character would experience Pauli repulsion with the electron density of neighboring molecules in condensed phases. Although using a basis set that does not include diffuse functions is effective in providing systematically lower polarizabilities, these polarizabilities do not necessarily correspond to the optimal effective "solution" polarizabilities; the regression coefficient for CCSD/cc-pVTZ-calculated vs experimental polarizabilities is 0.88, but optimal solution phase atomic polarizabilities in polarizable force fields are typically about 70% of the gas phase value.[45,46]

Although these data show the relative accuracy of these methods for the calculation of electric properties, it is not immediately clear if their use in charge fitting will result in more accurate force fields. Mobley et al. evaluated a large number of quantum chemical methods in charge fitting and found that fitting atomic charges to an ESP surface calculated with a more rigorous QM model did not result in more accurate computed solvation free energies.[48] It should be noted that intermolecular forces calculated using a molecular mechanical force field depend on both the atomic charges and the Lennard-Jones parameters. In particular, the Lennard-Jones radius, σ, largely determines the distance between the solute and solvent atomic charges, which has a large effect on solvation free energies. Ideally, the Lennard-Jones parameters of a force field should be reoptimized for each charge model. Determination of charges using one of the quantum chemical methods found to be accurate (e.g., MP2/aug-cc-pVTZ) combined with optimization of Lennard-Jones parameters is a potentially viable strategy for developing a more accurate force field.

CONCLUSION

The dipole moments and polarizabilities for set of 46 molecules containing elements C, Si, N, O, S, F, and Cl were calculated using a range of common quantum chemical methods. The effect of basis set and quantum chemical method on the accuracy of these calculations was evaluated.

The calculated electric properties are sensitive to the basis set used. The augmentation of the basis sets with diffuse functions led to a large improvement in accuracy, particularly in terms of polarizabilities. A triple-ζ basis set augmented with diffuse functions (i.e., aug-cc-pVTZ) provided the most accurate results.

The choice of quantum chemical method was also examined. CCSD/aug-cc-pVTZ was in good agreement with experiment for both properties; however, MP2/aug-cc-pVTZ was generally of comparable accuracy at a much lower computational cost. HF performs worse than any of the other methods. For the DFT methods, pure functionals were generally less accurate than the hybrid functionals. Among the hybrid functionals considered, none was decisively more accurate and all had accuracies comparable to those of CCSD and MP2. A more exact ranking of the DFT functionals is difficult because this type of calculation neglects effects vibrational effects and the uncertainty on the experimental data is of the order of the deviation, although a comparison to CCSD/aug-cc-pVTZ data was generally consistent.

For the purposes of charge/polarizability fitting, we expect that fitting charges to ESP surfaces calculated using HF theory should yield more polarized atomic charges and smaller atomic polarizabilities. When a sufficiently complete basis set is used, MP2 theory and hybrid DFT functionals should provide very accurate target data for this fitting.

ASSOCIATED CONTENT

Supporting Information

Tables of calculated dipole moments and polarizabilities for each combination of method and basis set and plot of the basis set convergence for the small molecule test set. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*C. N. Rowley: e-mail, crowley@mun.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Memorial University of Newfoundland, the Research and Development Corporation of Newfoundland and Labrador, and an NSERC of Canada Discovery Grant for funding. A.L.H. thanks the Dean of Science of Memorial University for a Summer Undergraduate Research Award. Computational resources were provided by Compute Canada (RAPI: djk-615-ab) through the ACEnet and SciNET consortia.

REFERENCES

(1) Israelachvili, J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: San Diego, 2010.

(2) Stone, A. *The Theory of Intermolecular Forces*, 2nd ed.; Oxford University Press: Oxford, U.K., 2013.

(3) Mirkin, C. A.; Ratner, M. A. Molecular Electronics. *Annu. Rev. Phys. Chem.* **1992**, *43*, 719−754.

(4) Cohen, H. D.; Roothaan, C. C. J. Electric Dipole Polarizability of Atoms by the Hartree−Fock Method. I. Theory for Closed-Shell Systems. *J. Chem. Phys.* **1965**, *43*, S34−S39.

(5) Monkhorst, H. J. Calculation of Properties with the Coupled-Cluster Method. *Int. J. Quantum Chem.* **1977**, *12*, 421−432.

(6) Dalgaard, E.; Monkhorst, H. J. Some Aspects of the Time-Dependent Coupled-Cluster Approach to Dynamic Response Functions. *Phys. Rev. A* **1983**, *28*, 1217−1222.

(7) Koch, H.; Jørgensen, P. Coupled Cluster Response Functions. *J. Chem. Phys.* **1990**, *93*, 3333−3344.

(8) Singh, U. C.; Kollman, P. A. An Approach to Computing Electrostatic Charges for Molecules. *J. Comput. Chem.* **1984**, *5*, 129−145.

(9) Breneman, C. M.; Wiberg, K. B. Determining Atom-Centered Monopoles from Molecular Electrostatic Potentials. The Need for High Sampling Density in Formamide Conformational Analysis. *J. Comput. Chem.* **1990**, *11*, 361−373.

(10) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157−1174.

(11) Duan, Y.; Wu, C.; Chowdhury, S.; Lee, M. C.; Xiong, G.; Zhang, W.; Yang, R.; Cieplak, P.; Luo, R.; Lee, T.; et al. A Point-Charge Force Field for Molecular Mechanics Simulations of Proteins Based on Condensed-Phase Quantum Mechanical Calculations. *J. Comput. Chem.* **2003**, *24*, 1999−2012.

(12) Anisimov, V. M.; Lamoureux, G.; Vorobyov, I. V.; Huang, N.; Roux, B.; MacKerell, A. D. Determination of Electrostatic Parameters for a Polarizable Force Field Based on the Classical Drude Oscillator. *J. Chem. Theory Comput.* **2005**, *1*, 153−168.

(13) Wu, J. C.; Chattree, G.; Ren, P. Automation of AMOEBA Polarizable Force Field Parameterization for Small Molecules. *Theor. Chem. Acc.* **2012**, *131*, 1−11.

(14) Harder, E.; Anisimov, V. M.; Vorobyov, I. V.; Lopes, P. E. M.; Noskov, S. Y.; MacKerell, A. D.; Roux, B. Atomic Level Anisotropy in the Electrostatic Modeling of Lone Pairs for a Polarizable Force Field Based on the Classical Drude Oscillator. *J. Chem. Theory Comput.* **2006**, *2*, 1587−1597.

(15) Dalskov, E. K.; Sauer, S. P. A. Correlated, Static and Dynamic Polarizabilities of Small Molecules. Comparison of Four "Black Box" Methods. *J. Phys. Chem. A* **1998**, *102*, 5269−5274.

(16) Guan, J.; Duffy, P.; Carter, J. T.; Chong, D. P.; Casida, K. C.; Casida, M. E.; Wrinn, M. Comparison of Local-Density and Hartree−Fock Calculations of Molecular Polarizabilities and Hyperpolarizabilities. *J. Chem. Phys.* **1993**, *98*, 4753−4765.

(17) Hinchliffe, A.; M, H. J. S. Ab Initio Studies of the Dipole Polarizabilities of Conjugated Molecules: Part 5. The Five-Membered Heterocyclics C_4H_4E (E = BH, AlH, CH2, SiH_2, NH, PH, O and S). *J. Mol. Struct. (THEOCHEM)* **1995**, *331*, 109−125.

(18) Adamo, C.; Cossi, M.; Scalmani, G.; Barone, V. Accurate Static Polarizabilities by Density Functional Theory: Assessment of the PBE0 Model. *Chem. Phys. Lett.* **1999**, *307*, 265−271.

(19) St-Amant, A.; Cornell, W. D.; Kollman, P. A.; Halgren, T. A. Calculation of Molecular Geometries, Relative Conformational Energies, Dipole Moments, and Molecular Electrostatic Potential Fitted Charges of Small Organic Molecules of Biochemical Interest by Density Functional Theory. *J. Comput. Chem.* **1995**, *16*, 1483−1506.

(20) Hammond, J. R.; Govind, N.; Kowalski, K.; Autschbach, J.; Xantheas, S. S. Accurate Dipole Polarizabilities for Water Clusters n=2−12 at the Coupled-Cluster Level of Theory and Benchmarking of Various Density Functionals. *J. Chem. Phys.* **2009**, *131*, 214103.

(21) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.

(22) *CRC Handbook of Chemistry and Physics*; CRC Press: Cleveland, OH, 2013.

(23) Miller, K. J. Additivity Methods in Molecular Polarizability. *J. Am. Chem. Soc.* **1990**, *112*, 8533−8542.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision A.01; Gaussian Inc.: Wallingford, CT, 2009.

(25) Valiev, M.; Bylaska, E.; Govind, N.; Kowalski, K.; Straatsma, T.; Dam, H. V.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T.; et al. NWChem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. *Comput. Phys. Commun.* **2010**, *181*, 1477−1489.

(26) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(27) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta−Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(28) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0Model. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(29) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(30) Zhao, Y.; Truhlar, D. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(31) Grimme, S. Semiempirical Hybrid Density Functional with Perturbative Second-Order Correlation. *J. Chem. Phys.* **2006**, *124*, 034108.

(32) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(33) Woon, D. E.; Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum Through Argon. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(34) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level-Correlated Calculations of Molecular Electric Properties. *Theor. Chem. Acc.* **1992**, *81*, 339−354.

(35) Sekino, H.; Maeda, Y.; Kamiya, M.; Hirao, K. Polarizability and Second Hyperpolarizability Evaluation of Long Molecules by the Density Functional Theory with Long-Range Correction. *J. Chem. Phys.* **2007**, *126*, 014107.

(36) Kaminski, G. A.; Stern, H. A.; Berne, B. J.; Friesner, R. A. Development of an Accurate and Robust Polarizable Molecular Mechanics Force Field from ab Initio Quantum Chemistry. *J. Phys. Chem. A* **2004**, *108*, 621−627.

(37) Champagne, B.; Perpète, E. A.; van Gisbergen, S. J. A.; Baerends, E.-J.; Snijders, J. G.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. Assessment of Conventional Density Functional Schemes for Computing the Polarizabilities and Hyperpolarizabilities of Conjugated Oligomers: an Ab Initio Investigation of Polyacetylene Chains. *J. Chem. Phys.* **1998**, *109*, 10489−10498.

(38) Champagne, B.; Perpète, E. A.; Jacquemin, D.; van Gisbergen, S. J. A.; Baerends, E.-J.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. Assessment of Conventional Density Functional Schemes for Computing the Dipole Moment and (Hyper)polarizabilities of Push−Pull π-Conjugated Systems. *J. Phys. Chem. A* **2000**, *104*, 4755−4763.

(39) Polo, V.; Kraka, E.; Cremer, D. Electron Correlation and the Self-Interaction Error of Density Functional Theory. *Mol. Phys.* **2002**, *100*, 1771−1790.

(40) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **2008**, *321*, 792−794.

(41) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Development of Exchange-Correlation Functionals with Minimal Many-Electron Self-Interaction Error. *J. Chem. Phys.* **2007**, *126*, 191109.

(42) Johnson, E. R.; Salamone, M.; Bietti, M.; DiLabio, G. A. Modeling Noncovalent Radical-Molecule Interactions Using Conventional Density-Functional Theory: Beware Erroneous Charge Transfer. *J. Phys. Chem. A* **2013**, *117*, 947−952.

(43) Smith, J. M.; Jami Alahmadi, Y.; Rowley, C. N. Range-Separated DFT Functionals are Necessary to Model Thio-Michael Additions. *J. Chem. Theory Comput.* **2013**, *9*, 4860−4865.

(44) Lamoureux, G.; MacKerell, A. D.; Roux, B. A Simple Polarizable Model of Water Based on Classical Drude Oscillators. *J. Chem. Phys.* **2003**, *119*, 5185−5197.

(45) Lamoureux, G.; Harder, E.; Vorobyov, I. V.; Roux, B.; A, D. M., Jr. A Polarizable Model of Water for Molecular Dynamics Simulations of Biomolecules. *Chem. Phys. Lett.* **2006**, *418*, 245−249.

(46) Riahi, S.; Rowley, C. N. A Drude Polarizable Model for Liquid Hydrogen Sulfide. *J. Phys. Chem. B* **2013**, *117*, 5222−5229.

(47) Kaminski, G. A.; Stern, H. A.; Berne, B. J.; Friesner, R. A.; Cao, Y. X.; Murphy, R. B.; Zhou, R.; Halgren, T. A. Development of a Polarizable Force Field for Proteins via Ab Initio Quantum Chemistry: First Generation Model and Gas Phase Tests. *J. Comput. Chem.* **2002**, *23*, 1515−1531.

(48) Mobley, D. L.; Dumont, E.; Chodera, J. D.; Dill, K. A. Comparison of Charge Models for Fixed-Charge Force Fields: Small-Molecule Hydration Free Energies in Explicit Solvent. *J. Phys. Chem. B* **2007**, *111*, 2242−2254.

(49) Murphy, W. F. The Rayleigh Depolarization Ratio and Rotational Raman Spectrum of Water Vapor and the Polarizability Components for the Water Molecule. *J. Chem. Phys.* **1977**, *67*, 5877−5882.

(50) Spackman, M. A. Accurate Prediction of Static Dipole Polarizabilities with Moderately Sized Basis Sets. *J. Phys. Chem.* **1989**, *93*, 7594−7603.

(51) Marchese, F. T.; Jaffé, H. The Calculation of Ground and Excited State Molecular Polarizabilities: A Simple Perturbation Treatment. *Theor. Chem. Acc.* **1977**, *45*, 241−247.

(52) Hills, G. W.; Jones, W. J. Raman Spectra of Asymmetric Top Molecules. Part 1. - The Pure Rotational Spectrum of Ethylene. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 812−826.

(53) Alms, G. R.; Burnham, A.; Flygare, W. H. Measurement of the Dispersion in Polarizability Anisotropies. *J. Chem. Phys.* **1975**, *63*, 3321−3326.

(54) Coonan, M. H.; Craven, I. E.; Hesling, M. R.; Ritchie, G. L. D.; Spackman, M. A. Anisotropic Molecular Polarizabilities, Dipole Moments, and Quadrupole Moments of $(CH_2)_2X$, $(CH_3)_2X$, and C_4H_4X (X = O, S, Se). Comparison of Experimental Results and Ab Initio Calculations. *J. Phys. Chem.* **1992**, *96*, 7301−7307.

(55) Le Fevre, C. G.; Le Fevre, R. J. W.; Rao, B. P.; Smith, M. R. 233. Molecular Polarisability. Ellipsoids of Polarisability for Certain Fundamental Heterocycles. *J. Chem. Soc.* **1959**, 1188−1192.

(56) Stuart, H. A. *Molekülstruktur*, 3rd ed.; Springer Verlag: Berlin, 1967.