



The accuracy of molecular dipole moments in standard electronic structure calculations

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Abstract

A systematic investigation has been carried out of the accuracy of calculated molecular equilibrium dipole moments of 11 polar closed-shell molecules, using the HF, MP2, CCSD and CCSD(T) models and correlation-consistent basis sets. Augmented basis sets are important for improving the basis-set convergence, but the quality of the results depends more on the correlation treatment than on the cardinal number of the basis set. Augmented triple-zeta basis sets are sufficient for most calculations. The mean absolute error of the HF calculations is 0.16 D, which is reduced at the MP2 and CCSD levels to 0.048 and 0.025 D, respectively. The CCSD(T) errors are small – typically < 0.01 D. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In ab initio electronic structure theory, an approximate solution is obtained to the electronic Schrödinger equation by introducing approximations in the one- and N -electron spaces. The approximations in the one-electron space are introduced through the choice of the atomic orbital basis, while the choice of the N -electron wavefunction model determines the approximations in the N -electron space. In elec-

tronic structure calculations, the one- and N -electron spaces may be explored in a systematic, hierarchical fashion where the errors are controlled and the solution is improved upon until in principle the desired accuracy is obtained.

In this Letter, we present a systematic investigation of the accuracy that can be obtained in standard ab initio electronic structure calculations of molecular equilibrium dipole moments. In the calculations, we consider the hierarchy of wavefunction models Hartree–Fock (HF), second-order Møller–Plesset perturbation theory (MP2), coupled-cluster singles-and-doubles (CCSD) [1] and CCSD with perturbative triples [CCSD(T)] [2] and the standard hierarchies of correlation consistent basis sets of Dunning et al. [3–5]. For statistical significance, we have carried out calculations on 11 small polar molecules. In

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similar previous studies, we have investigated the accuracy that can be obtained for equilibrium structures [6], atomization energies and reaction enthalpies [7]. In this Letter, the polar molecules of the previous investigations are considered but ozone is excluded as it has significant multiconfiguration character. The molecules are closed-shell single-configuration dominated systems and contain a variety of chemical bonds between hydrogen and first-row atoms, as well as single, double and triple bonds between first-row atoms.

In the previous investigations, accurate experimental equilibrium data were used to establish the accuracy of the calculated properties. Since accurate experimental equilibrium dipole moments are available only for a few of the considered molecules, we have in this investigation used a different reference measure: We first show that our best calculated equilibrium dipole moments have an accuracy similar to that of the experimental numbers (where available). Consequently, our best calculated equilibrium numbers are used as reference data, with respect to which the performance of the remaining models and basis sets is measured.

2. Reference dipole moments

Experimental dipole moments for the molecules in their vibrational ground states, μ_0 , are available for all systems except HNO, CH₂ and HOF. However, experimental equilibrium dipole moments μ_e are available only for CO, NH₃, HF and H₂O. Comparing μ_0 and μ_e for these four molecules, the deviations are found to range from 0.01 to 0.09 D. Compared with the accuracy of our best calculations, these deviations are clearly too large to warrant that μ_e is approximated by μ_0 . Preferably, we should therefore calculate μ_0 by vibrational averaging. However, such an averaging is expensive and has not been attempted here. For comparison with the calculated μ_e , we have therefore used our best calculated equilibrium dipole moments obtained using the CCSD(T) wavefunction and the aug-pVQZ basis (see Section 3 for details) as reference numbers. These numbers are also given in Table 1.

To justify the use of the best calculated dipole moments as reference numbers, we note that for

Table 1

Experimental vibrational ground state (μ_0) and equilibrium (μ_e) dipole moments (in D) together with the calculated equilibrium dipole moments at the CCSD(T) level in the aug-cc-pVQZ basis

	Experimental		Calculated μ_e
	μ_0	μ_e	
CO	0.1097(1) [8]	0.123(2) [8]	0.118
NH ₃	1.471932(7) [9]	1.561(5) [10]	1.521
HNO	–	–	1.694
CH ₂	–	–	1.695
H ₂ O ₂	2.2 [11]	–	1.750
HF	1.826178(3) [12]	1.803(2) [12]	1.800
H ₂ O	1.8546(6) [13]	1.8473(10) [13]	1.853
HOF	–	–	1.888
CH ₂ O	2.3321(5) [14]	–	2.392
HCN	2.985188(3) [15]	–	3.017
HNC	3.05(1) [16]	–	3.110

three of the four molecules for which experimental equilibrium dipole moments are available (CO, HF and H₂O), the calculated dipole moments are within 0.01 D of the experimental values. For HF, an estimate of the full configuration interaction basis set limit is 1.8037(7)D [17] in accordance with the experimental value. For the fourth molecule, NH₃, the best calculated dipole moment differs by 0.04 D from the experimental one. However, in Ref. [18], it was argued that the experimental μ_e for NH₃ is too large by several hundredths of a debye, which is also consistent with our results. Based on the results for CO, HF and H₂O, it is therefore reasonable to assume that the calculated μ_e in Table 1 are accurate to a few hundredths of a debye and may therefore be used as reference values to establish the accuracy of the more approximate calculations.

3. Calculated dipole moments

The equilibrium dipole moments have been calculated at the HF, MP2, CCSD and CCSD(T) levels (all electrons correlated) in the aug-cc-pVxZ basis sets with $x = D, T, Q$. Augmented basis sets have been used to ensure a flexible description of the outer-valence region. The dipole moments are computed for the correlated wavefunction models as energy derivatives with orbital relaxation included. The dipole moments have been calculated at geome-

Table 2

Equilibrium dipole moments μ_e (in D) calculated at geometries that are optimized using the same wavefunction as for the dipole moments. For CO, the sign is relative to the indicated polarity of the molecule

	HF	MP2	CCSD	CCSD(T)		
	aug-cc-pVQZ	aug-cc-pVQZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
C^-O^+	-0.137	0.265	0.084	0.083	0.120	0.118
NH_3	1.544	1.517	1.530	1.541	1.513	1.521
HNO	1.877	1.708	1.718	1.674	1.683	1.694
CH_2	1.904	1.829	1.733	1.637	1.689	1.695
H_2O_2	1.863	1.764	1.782	1.747	1.742	1.750
HF	1.884	1.811	1.813	1.799	1.797	1.800
H_2O	1.936	1.864	1.870	1.859	1.845	1.853
HOF	2.024	1.875	1.901	1.914	1.883	1.888
CH_2O	2.703	2.395	2.440	2.397	2.385	2.392
HCN	3.262	3.029	3.059	3.005	3.003	3.017
HNC	2.956	3.271	3.104	3.072	3.107	3.110

tries that have been optimized using the same wavefunction and basis set as for the dipole moments. The calculations have been carried out with the ACESII program [19,20].

The obtained dipole moments are listed in Table 2 for some selected basis sets; for CCSD(T), we have listed the dipole moments for the aug-cc-pV x Z, $x = D, T, Q$ basis sets. From the convergence of these numbers, it appears that the aug-cc-pVQZ results are

typically within a few millidebye of the basis-set limit. Considering the convergence as function of the N -electron treatment, we observe at the aug-cc-pVQZ level a much larger change in the dipole moments going from HF to CCSD (in average 0.138 D) than going from CCSD to CCSD(T) (in average 0.025 D). Thus, the convergence in the N -electron treatment seems to be rapid and the correlation effects beyond CCSD(T) are expected to be less than a few hun-

Table 3

Deviations of equilibrium dipole moments relative to the values calculated at the CCSD(T)/aug-cc-pV x Z level

		cc-pV x Z			cc-pCV x Z			aug-cc-pV x Z		
		D	T	Q	D	T	Q	D	T	Q
$\bar{\Delta}$	HF	0.117	0.108	0.100	0.119	0.107	0.100	0.108	0.092	0.089
	MP2	0.046	0.054	0.057	0.048	0.053	0.056	0.047	0.040	0.045
	CCSD	0.004	0.024	0.029	0.006	0.023	0.029	0.007	0.011	0.018
	CCSD(T)	-0.014	0.006	0.012	-0.012	0.006	0.012	-0.010	-0.006	0.000
Δ_{std}	HF	0.179	0.163	0.167	0.177	0.165	0.167	0.188	0.173	0.168
	MP2	0.176	0.099	0.073	0.177	0.095	0.072	0.053	0.069	0.067
	CCSD	0.133	0.047	0.030	0.133	0.048	0.029	0.034	0.020	0.024
	CCSD(T)	0.149	0.060	0.028	0.149	0.059	0.028	0.026	0.004	0.000
$\bar{\Delta}_{abs}$	HF	0.199	0.180	0.174	0.199	0.181	0.174	0.191	0.169	0.163
	MP2	0.145	0.089	0.068	0.146	0.086	0.067	0.047	0.045	0.048
	CCSD	0.095	0.043	0.036	0.096	0.044	0.035	0.029	0.018	0.025
	CCSD(T)	0.105	0.043	0.025	0.104	0.042	0.024	0.020	0.007	0.000
Δ_{max}	HF	0.272	0.262	0.290	0.272	0.261	0.289	0.357	0.324	0.311
	MP2	0.314	0.185	0.164	0.315	0.177	0.160	0.149	0.159	0.161
	CCSD	0.254	0.081	0.066	0.251	0.094	0.064	0.061	0.038	0.047
	CCSD(T)	0.306	0.123	0.049	0.305	0.120	0.048	0.058	0.014	0.000

dredths of a debye and usually significantly smaller. This is in accordance with a previous study of dipole moments for BH and HF where the difference between full configuration interaction (FCI) dipole moments and CCSD(T) dipole moments were found to be 0.004 D for BH in a d-aug-cc-pVQZ basis set and 0.002 D for HF in an aug-cc-pVDZ basis set [21]. Altogether, it appears to be justified to use the CCSD(T)/aug-cc-pVQZ results as reference numbers.

To examine basis-set saturation, we have in addition to the aug-cc-pV x Z basis sets carried out calculations using the cc-pV x Z and cc-pCV x Z, $x = D, T, Q$ basis sets. In Table 3, the statistical errors, $\bar{\Delta}$ (the mean error), Δ_{std} (the standard deviation in the error), $\bar{\Delta}_{\text{abs}}$ (the mean absolute error) and Δ_{max} (the maximum absolute error) are given for the various levels of theory. All errors have been calculated relative to the CCSD(T) reference numbers.

The effect of the core-correlating orbitals is seen by comparing the (all-electron) cc-pV x Z and cc-pCV x Z results in Table 3. The statistical errors in the two basis sets are very similar. A closer inspection of the data reveals that, at the quadruple-zeta level, the largest observed effect of using core-correlating orbitals is 0.006 D for H₂O₂ at the MP2 and CCSD(T) levels but most effects are smaller than 0.002 D. At the double- and triple-zeta levels, the effect of using core-correlating orbitals is larger but never exceeds 0.007 and 0.018 D, respectively. The reason for the small impact of the core-correlation orbitals is probably that the correlation of the core-electrons has very minor influence on the dipole moments. This is supported by a previous study of the dipole moments for BH and HF [17] where the difference between all-electron CCSD(T)/aug-cc-pCV6Z and valence-only CCSD(T)/aug-cc-pV6Z calculations was found to be 0.003 D for BH and 0.002 D for HF. Valence-only calculations have not been attempted in this work but will be studied for the same set of molecules in forthcoming work.

Comparing the cc-pV x Z and aug-cc-pV x Z dipole moments, we find that the effect of augmentation is significant but decreases with increasing cardinal number. For CCSD(T), the mean absolute changes due to augmentation are 0.101, 0.045 and 0.025 D at the double-, triple- and quadruple-zeta levels, respectively. Generally, the dipole moments converge fast

with increasing cardinal number, in particular for the augmented basis sets. This is illustrated in Fig. 1, where the mean absolute error and the maximum absolute error are displayed for the CCSD(T) wavefunction and the cc-pV x Z and aug-cc-pV x Z; $x = D, T, Q$ basis sets. Augmentation with a second set of diffuse functions does not affect the calculated dipole moments significantly [22].

For the calculated dipole moments in the aug-cc-pV x Z basis sets we have in Fig. 2 plotted the mean absolute errors and the maximum absolute errors, and in Fig. 3 the normal distribution function of errors, which is defined from the mean error and the standard deviation in the error as

$$\rho(P) = \frac{1}{\Delta_{\text{std}}\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{P - \bar{\Delta}}{\Delta_{\text{std}}}\right)^2\right].$$

The plots indicate that the calculated dipole moments depend in a systematic manner on the correlation treatment. From Fig. 2, it is clear that dipole

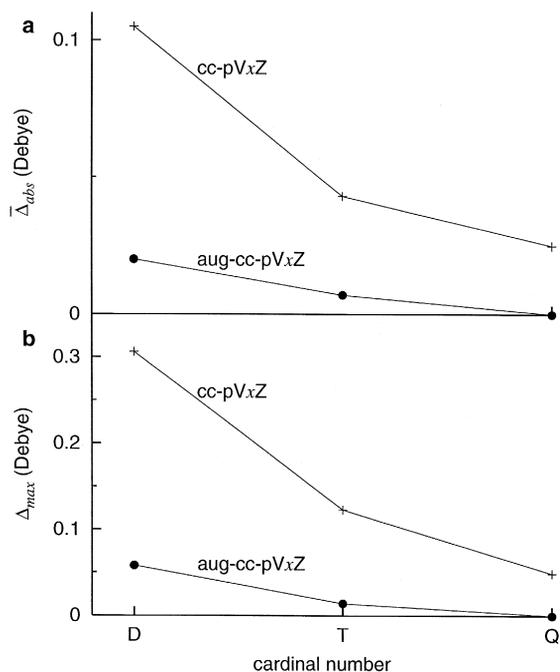


Fig. 1. Mean absolute errors ($\bar{\Delta}_{\text{abs}}$) and maximum absolute errors (Δ_{max}) in CCSD(T) calculations of the dipole moment using the cc-pV x Z and aug-cc-pV x Z basis sets for $x = D, T, Q$ (see text).

moments are more sensitive to the choice of the N -electron model than to the choice of cardinal number for the basis set. Even in the smallest basis, the CCSD(T) model is more accurate than the CCSD and MP2 basis set limit results. In general, the dipole moments are reduced as we improve the correlation treatment. Indeed, with the exceptions of CO and HNC, the dipole moment is always reduced as we go from Hartree–Fock to CCSD and then on to CCSD(T) – see Table 2. The MP2 dipole moments are less systematic but are usually slightly smaller than the CCSD numbers. The normal distribution functions in Fig. 3 reveals that the dipole moments are systematically improved with the correlation treatment going from MP2 to CCSD and further to CCSD(T). For a given basis set level the normal distribution function becomes more narrow when moving up in the correlation hierarchy and the peaks approach zero. The only exception occurs for the aug-cc-pVDZ basis set going from CCSD to CCSD(T) where the peak moves from 0.007 to

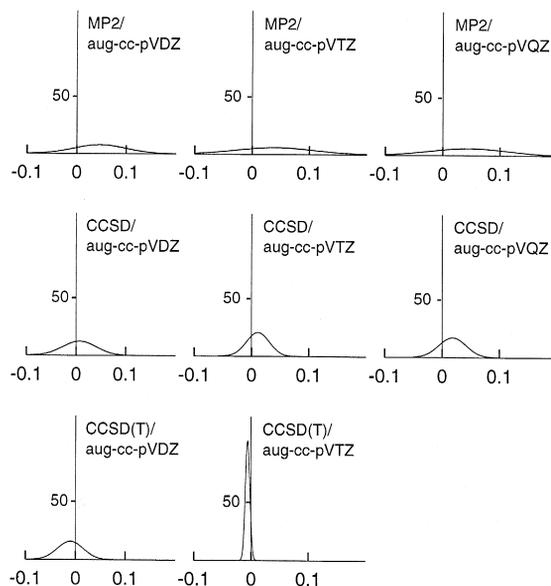


Fig. 3. Normal distribution of errors in the calculation of dipole moments (D).

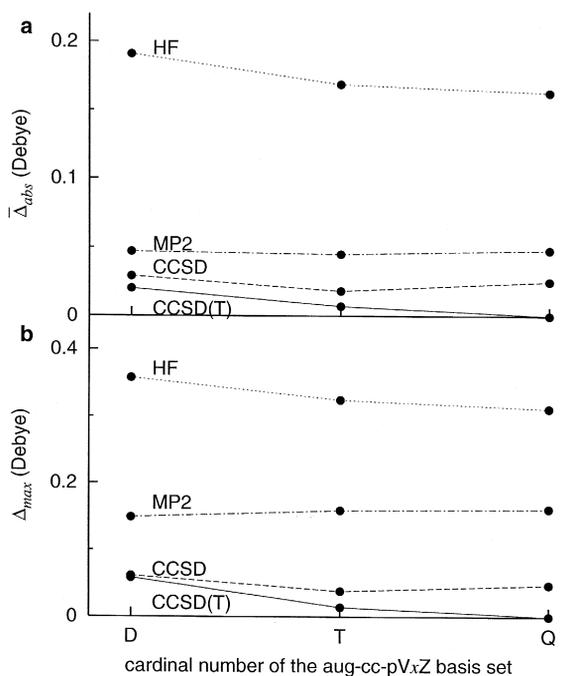


Fig. 2. Mean absolute errors ($\bar{\Delta}_{\text{abs}}$) and maximum absolute errors (Δ_{max}) in HF, MP2, CCSD and CCSD(T) calculations of the dipole moment using the aug-cc-pVxZ basis sets for $x = D, T, Q$ (see text).

–0.010 D. At the aug-cc-pVQZ level, the mean absolute errors are 0.16 D for the Hartree–Fock model, 0.05 D for the MP2 model and 0.03 D for the CCSD model. These numbers may be taken as indicative of the typical intrinsic errors in these models. The corresponding maximum absolute errors are 0.31, 0.16 and 0.05 D for the Hartree–Fock, MP2 and CCSD models, respectively.

4. Summary

When Dunning’s correlation consistent basis sets are used for the calculation of dipole moments, the accuracy of the calculated dipole moments depends more on the correlation treatment than on the cardinal number. However, for a flexible description of the outer valence regions, augmented basis sets are recommended and the aug-cc-pVTZ basis is sufficient for most applications. Whereas the Hartree–Fock model is typically in error by 0.1–0.2 D, the introduction of correlation at the MP2 and CCSD levels reduces the errors to ~ 0.05 and ~ 0.03 D, respectively. The CCSD(T) errors are small – typically < 0.01 D.

The excellent performance of the CCSD(T) relies on the fact that the chosen molecules are all dominated by a single configuration. When several configurations are important, the performance of the CCSD(T) model degrades. Thus, for ozone, which is a typical two-configuration system, we observe a rather different trend in the calculated numbers. In the aug-cc-pVQZ basis, which gives results close to basis set limit, the change in the dipole moment from CCSD to CCSD(T) is large (0.08 D) compared with the changes for the molecules in Table 2. This suggests that the contributions from full relaxation of the triples at the CCSDT level and from connected quadruples at the CCSDTQ level may be substantial in agreement with a previous study of the structure and frequencies of ozone [23]. A comparison for ozone of the dipole moments calculated at the Hartree-Fock, CCSD and CCSD(T) levels (0.837, 0.642 and 0.559 D, respectively) indicates that the true dipole moment of O₃ is several hundredths of a debye smaller than 0.559 D. For molecules dominated by a single configuration, correlation effects beyond CCSD(T) appear to be small.

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