

# Basis-set correction for coupled-cluster estimation of dipole moments

Cite as: J. Chem. Phys. 156, 174101 (2022); doi: 10.1063/5.0087794

Submitted: 9 February 2022 • Accepted: 11 April 2022 •

Published Online: 2 May 2022



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## ABSTRACT

The present work proposes an approach to obtain a basis-set correction based on density-functional theory (DFT) for the computation of molecular properties in wave-function theory (WFT). This approach allows one to accelerate the basis-set convergence of any energy derivative of a non-variational WFT method, generalizing previous works on the DFT-based basis-set correction where either only ground-state energies could be computed with non-variational wave functions [Loos *et al.*, J. Phys. Chem. Lett. **10**, 2931 (2019)] or properties could be computed as expectation values over variational wave functions [Giner *et al.*, J. Chem. Phys. **155**, 044109 (2021)]. This work focuses on the basis-set correction of dipole moments in coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)], which is numerically tested on a set of 14 molecules with dipole moments covering two orders of magnitude. As the basis-set correction relies only on Hartree–Fock densities, its computational cost is marginal with respect to the one of the CCSD(T) calculations. Statistical analysis of the numerical results shows a clear improvement of the basis convergence of the dipole moment with respect to the usual CCSD(T) calculations.

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## I. INTRODUCTION

Quantum chemistry aims to provide theoretical methods to predict molecular properties starting from the many-body quantum mechanical problem. To solve this problem, a wide range of methods were developed in the last few decades mainly based on wave-function theory (WFT) and density-functional theory (DFT). The purpose of both approaches is to accurately treat correlation effects or, in other terms, the quantum effects that go beyond a mean-field description, such as Hartree–Fock (HF). In the context of WFT, there exists a wide range of methods of increasing computational cost—ranging from Møller–Plesset perturbation theory<sup>1</sup> to coupled-cluster methods<sup>2</sup>—which, in principle, systematically converge to the full configuration interaction (FCI) limit, which is the exact solution within a given basis set. Nevertheless, the accuracy of the results of a WFT method—even at the FCI level—strongly depends on the quality of the basis set, mainly because of the slow convergence of the wave function near the electron–electron

coalescence point.<sup>3,4</sup> The combination of the slow basis-set convergence and the strong increase of the computational cost with both the size of the basis set and the number of electrons makes it very difficult to obtain well converged WFT calculations on large systems.

There are mainly two approaches to tackle the basis-set convergence problem of WFT: basis-set extrapolation techniques<sup>5,6</sup> and explicitly correlated F12 methods.<sup>7–12</sup> The basis-set extrapolation techniques rely on a known asymptotic behavior of the correlation energy with the size of the basis set but requires WFT calculations with basis sets of increasing sizes, which makes their application limited to small or medium system size. The F12 methods accelerate the basis-set convergence of the results, thanks to the inclusion of a correlation factor explicitly depending on electron–electron distances and restoring Kato’s electron–electron cusp condition.<sup>4</sup> Although F12 methods improve indeed the results (typically, energy differences obtained with a F12 method using a triple-zeta basis set are as accurate as the ones obtained with the corresponding

uncorrected WFT method using a quintuple-zeta basis set<sup>13</sup>), the F12 methods necessarily induce computational overheads due to the large auxiliary basis sets required to resolve three- and four-electron integrals.<sup>14</sup>

An alternative path has been recently introduced by some of the present authors in Ref. 15 where a rigorous framework was proposed to correct for the basis-set incompleteness of WFT using DFT. A central idea of this work is the fact that the Coulomb electron–electron interaction projected in an incomplete basis set is non-divergent and quite similar to the long-range interaction used in range-separated DFT (RSDFT). A basis-set correction density functional can then be built from RSDFT short-range correlation functionals using a local range-separation parameter, which automatically adapts to the basis set used. This results in a relatively cheap way of correcting the basis-set incompleteness of WFT, which has the desirable property of leading to an unaltered complete-basis-set (CBS) limit. Two versions of this theory were proposed: (i) a non-self-consistent version where the basis-set correction functional is evaluated with any accurate approximation of the FCI density and then simply added to an approximation of the FCI energy in a given basis set;<sup>15</sup> and (ii) a recently introduced self-consistent variant where the energy is minimized in the presence of the basis-set correction functional and, therefore, allows for the wave function to be changed by the DFT correction.<sup>16</sup> The efficiency of the non-self-consistent approach for computing the total energies and chemically relevant energy differences of relatively large magnitudes (such as ionization potentials,<sup>15,17</sup> molecular atomization energies,<sup>18–21</sup> or excitation energies<sup>22</sup>) has been well established in previous works on a quite wide range of atomic and molecular systems, including light to transition-metal elements, and it was numerically shown that the self-consistent framework does not give any significant improvement of total energies.<sup>16</sup>

The main advantage of the self-consistent formulation is nevertheless to allow for the computation of first-order properties as expectation values over the minimized wave function, thanks to the variational property of the theory. In Ref. 16, the present authors have focused on the dipole moments that are known to exhibit a slow convergence with respect to the size of the basis set.<sup>23–25</sup> It was shown that the dipole moments computed at the near FCI level with the self-consistent basis-set correction method are close to the CBS limit in triple-zeta basis sets, which contrasts with the slow basis-set convergence of the usual WFT approaches. The drawback of the self-consistent framework is nonetheless to require a self-consistent variational WFT calculation, which, therefore, excludes its application to non-variational approaches, such as coupled-cluster with singles, doubles, and perturbative triple excitations [CCSD(T)].

In the present work, we propose to overcome this limitation and target the computation of first-order molecular properties as energy derivatives of the non-self-consistent basis-set correction approach. We apply this strategy to the computation of dipole moments at the CCSD(T) level and propose a cheap computational strategy for the basis-set correction, which uses only densities at the HF level, similarly to what have been done in the context of atomization energies in Ref. 18.

This paper is organized as follows: In Sec. II, we introduce the theory of the basis-set correction extended to the computation of dipole moments. In Sec. III, we provide computational details of our

study on a set of 14 molecules with dipole moments covering two orders of magnitude. The numerical results are discussed in Sec. IV and compared for some molecules with the fully self-consistent formalism of Ref. 16. Detailed results, as well as the molecular geometries used, are available in the [supplementary material](#).

## II. THEORY

### A. Dipole moment from the self-consistent basis-set correction

In this section, we generalize the framework of the basis-set correction to the presence of a static external electric field. Consider the Hamiltonian of a  $N$ -electron system under an external electric field  $\epsilon = \epsilon\mathbf{u}$  of strength  $\epsilon$  along a direction  $\mathbf{u}$ ,

$$\hat{H}(\epsilon) = \hat{H}_0 - \epsilon\hat{\mathbf{d}}, \quad (1)$$

where  $\hat{H}_0$  is the Hamiltonian of the system without the electric field,

$$\hat{H}_0 = \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}, \quad (2)$$

with  $\hat{T}$  being the kinetic-energy operator,  $\hat{V}_{ne}$  being the electron–nuclei interaction operator, and  $\hat{W}_{ee}$  the electron–electron interaction operator, and  $\hat{\mathbf{d}} = \hat{\mathbf{d}} \cdot \mathbf{u}$ , where  $\hat{\mathbf{d}}$  is the total (electron + nuclear) dipole-moment operator,

$$\hat{\mathbf{d}} = -\sum_{i=1}^N \mathbf{r}_i + \sum_{A=1}^{N_{\text{nuclei}}} Z_A \mathbf{R}_A, \quad (3)$$

where  $\mathbf{r}_i$  are the electron coordinates and  $Z_A$  and  $\mathbf{R}_A$  are the nuclei charges and coordinates.

In the basis-set correction formalism,<sup>15,16,19</sup> the ground-state energy  $E_0(\epsilon)$  of the Hamiltonian in Eq. (1) is approximated by

$$E_0^B(\epsilon) = \min_{\Psi^B} \{ \langle \Psi^B | \hat{H}(\epsilon) | \Psi^B \rangle + \tilde{E}^B[n_{\Psi^B}] \}, \quad (4)$$

where the minimization is performed over the set of  $N$ -electron wave functions  $\Psi^B$  expanded on the  $N$ -electron Hilbert space generated by the one-electron basis set  $\mathcal{B}$  and  $\tilde{E}^B[n_{\Psi^B}]$  is the basis-set correction functional evaluated at the density  $n_{\Psi^B}$  of  $\Psi^B$ . The energy functional  $\tilde{E}^B[n]$  (introduced in Ref. 15) compensates for the restriction on the wave functions  $\Psi^B$  due to the incompleteness of the basis set  $\mathcal{B}$ . The restriction coming from the basis set  $\mathcal{B}$  in Eq. (4) then applies only to densities  $n_{\Psi^B}$ . Roughly speaking, since the density converges much faster than the wave function with respect to the basis set,  $E_0^B(\epsilon)$  is a much better approximation to the exact energy  $E_0(\epsilon)$  than the corresponding FCI ground-state energy  $E_{\text{FCI}}^B(\epsilon)$  calculated with the same basis set  $\mathcal{B}$ . Moreover, in the CBS limit,  $\tilde{E}^B[n]$  vanishes and, thus,  $E_0^B(\epsilon)$  correctly converges to the exact energy  $E_0(\epsilon)$ .

From the basis-set corrected energy  $E_0^B(\epsilon)$  in Eq. (4), one can define the corresponding basis-set corrected dipole moment  $d^B$  as the first-order derivative with respect to the electric field,

$$d^B = - \frac{dE_0^B(\epsilon)}{d\epsilon} \Big|_{\epsilon=0}. \quad (5)$$

It is important to stress here that  $d^B$  is different from the FCI dipole moment  $d_{\text{FCI}}^B$  with the same basis set  $\mathcal{B}$ , as the former is taken as the derivative of  $E_0^B(\epsilon)$ , which contains the basis-set correction functional  $\bar{E}^B[n]$ . Similar to the case of the energy, we expect  $d^B$  to have a faster basis-set convergence than  $d_{\text{FCI}}^B$ .

Since  $E_0^B(\epsilon)$  is stationary with respect to  $\Psi^B$ , the Hellmann–Feynman theorem applies and gives  $d^B$  as a simple expectation value,

$$d^B = \langle \Psi_0^B(\epsilon=0) | \hat{d} | \Psi_0^B(\epsilon=0) \rangle, \quad (6)$$

where  $\Psi_0^B(\epsilon=0)$  is the minimizing wave function of the self-consistent equation in Eq. (4) at  $\epsilon=0$ . This was the approach used in Ref. 16.

Note that the Hellmann–Feynman theorem applies because the basis set  $\mathcal{B}$  is independent from the perturbing electric field. By contrast, if we wanted to calculate the gradient of the energy with respect to nuclear coordinates, we would have to take into account the dependence of the atomic basis set  $\mathcal{B}$  on the nuclei coordinates. In that case, the Hellmann–Feynman theorem would not apply, and we would have to consider additional Pulay terms coming from the dependence of both the wave function  $\Psi_0^B$  and the basis-set correction energy  $\bar{E}^B$  on the nuclei coordinates.

## B. Dipole moment from the non-self-consistent basis-set correction

As initially proposed in Ref. 15 for the case without the electric field, one can avoid the minimization in Eq. (4) and approximate the energy  $E_0^B(\epsilon)$  by approximating the minimizing wave function  $\Psi_0^B(\epsilon)$  in Eq. (4) by the FCI wave function  $\Psi_{\text{FCI}}^B(\epsilon)$  in a given basis set  $\mathcal{B}$ . This leads to the following estimation of the ground-state energy:

$$E_0^B(\epsilon) \approx E_{\text{FCI}}^B(\epsilon) + \bar{E}^B[n_{\text{FCI}}^B(\epsilon)], \quad (7)$$

where  $n_{\text{FCI}}^B(\epsilon)$  is the ground-state FCI density obtained in the presence of the electric field of strength  $\epsilon$ . The corresponding non-self-consistent basis-set corrected dipole moment is thus

$$d^B \approx d_{\text{FCI}}^B + \bar{d}^B, \quad (8)$$

where

$$\bar{d}^B = - \frac{d\bar{E}^B[n_{\text{FCI}}^B(\epsilon)]}{d\epsilon} \Big|_{\epsilon=0} \quad (9)$$

is the non-self-consistent basis-set correction to the dipole moment.

As obtaining both the dipole moment and the density at FCI level is often computationally prohibitive, we follow Ref. 18 and approximate the FCI energy by the CCSD(T) energy and the FCI density by the HF density (in the presence of the electric field),

$$E_0^B(\epsilon) \approx E_{\text{CCSD(T)}}^B(\epsilon) + \bar{E}^B[n_{\text{HF}}^B(\epsilon)]. \quad (10)$$

Within these approximations, the basis-set corrected dipole moment in Eq. (8) becomes

$$d^B \approx d_{\text{CCSD(T)}}^B + \bar{d}^B, \quad (11)$$

where  $d_{\text{CCSD(T)}}^B$  is the dipole moment at the CCSD(T) level, and the basis-set correction  $\bar{d}^B$  is

$$\bar{d}^B = - \frac{d\bar{E}^B[n_{\text{HF}}^B(\epsilon)]}{d\epsilon} \Big|_{\epsilon=0}. \quad (12)$$

We approximate the basis-set correction functional  $\bar{E}^B[n]$  with the so-called (spin-dependent) PBEUEG energy functional introduced in Ref. 18 where the local range-separation parameter  $\mu^B(r)$  is obtained using the HF wave function in the basis set  $\mathcal{B}$  as proposed in Refs. 15 and 18. The results obtained with Eq. (11) with the PBEUEG approximation for  $\bar{E}^B[n]$  evaluated at the HF density will be referred to as CCSD(T) + PBEUEG.

In practice, we calculate the CCSD(T) dipole moment and the basis-set correction to the dipole moment using a finite-difference approximation for the energy derivatives with respect to the electric field,

$$d_{\text{CCSD(T)}}^B \simeq - \frac{E_{\text{CCSD(T)}}^B(\epsilon) - E_{\text{CCSD(T)}}^B(-\epsilon)}{2\epsilon} \quad (13)$$

and

$$\bar{d}^B \simeq - \frac{\bar{E}^B[n_{\text{HF}}^B(\epsilon)] - \bar{E}^B[n_{\text{HF}}^B(-\epsilon)]}{2\epsilon}, \quad (14)$$

using a finite field strength of  $\epsilon = 10^{-4}$  a.u., as suggested in Ref. 23.

## III. COMPUTATIONAL DETAILS

The computation of the basis-set correction to the dipole moment  $\bar{d}^B$  was performed using the Quantum Package program,<sup>26</sup> and the CCSD(T) dipole moment was obtained with the Gaussian program.<sup>27</sup> We used the augmented Dunning basis sets (Refs. 28 and 29) aug-cc-pVXZ (abbreviated as AVXZ in Figs. 1–3 and Tables I–III), where  $X$  is the cardinal number of the basis set  $X \in \{D, T, Q, 5\}$ . As no core-valence functions are used, the frozen-core approximation is used throughout this paper, where the 1s orbital is kept frozen for the elements from Li to F.

The tests are done on a set of  $n = 14$  molecules among which there are six open-shell molecules, for which we use restricted open-shell CCSD(T) [ROCCSD(T)] energies and restricted open-shell HF (ROHF) densities, and eight closed-shell molecules. Experimental geometries used for the computations are taken from Ref. 25 for the entire set, except in the case of BH and FH for which the geometries are taken from Ref. 23. We also report the results obtained in Ref. 16 for the BH, FH, CH<sub>2</sub>, and H<sub>2</sub>O molecules using the self-consistent formalism [Eq. (6)] at the near-FCI level in order to compare with the present non-self-consistent formalism.

**TABLE I.** HF, CCSD(T), and CCSD(T) + PBEUEG dipole moments in atomic units. For the open-shell systems, we use the spin-restricted open-shell (RO) version of these methods.

	AVDZ	AVTZ	AVQZ	AV5Z	CBS
CO					
HF	-0.101 99	-0.104 99	-0.104 33	-0.104 21	
CCSD(T)	0.055 50	0.050 00	0.046 00	0.045 50	0.044 85
CCSD(T) + PBEUEG	0.043 98	0.044 14	0.042 73	0.043 60	
BeH					
ROHF	0.110 17	0.110 76	0.111 99	0.112 18	
ROCCSD(T)	0.095 50	0.091 00	0.090 50	0.090 50	0.090 30
ROCCSD(T) + PBEUEG	0.084 16	0.087 46	0.089 41	0.089 80	
BF					
HF	0.344 36	0.333 90	0.333 14	0.333 28	
CCSD(T)	0.341 00	0.327 00	0.323 00	0.322 00	0.320 81
CCSD(T) + PBEUEG	0.332 87	0.323 51	0.320 82	0.320 68	
BH					
HF	0.687 96	0.686 49	0.684 94	0.684 96	
CCSD(T)	0.529 50	0.545 00	0.547 50	0.548 50	0.549 53
CCSD(T) + PBEUEG	0.541 62	0.550 02	0.549 86	0.549 80	
CH					
ROHF	0.623 48	0.620 00	0.618 71	0.618 58	
ROCCSD(T)	0.541 50	0.549 50	0.551 50	0.552 50	0.553 68
ROCCSD(T) + PBEUEG	0.554 27	0.554 81	0.554 05	0.553 96	
NH					
ROHF	0.638 50	0.635 05	0.633 81	0.633 84	
ROCCSD(T)	0.593 50	0.599 50	0.602 00	0.603 50	0.605 04
ROCCSD(T) + PBEUEG	0.607 92	0.605 19	0.604 64	0.605 06	
CH <sub>2</sub> (singlet)					
HF	0.748 77	0.744 77	0.743 55	0.743 53	
CCSD(T)	0.656 00	0.660 00	0.662 00	0.663 50	0.665 10
CCSD(T) + PBEUEG	0.666 66	0.664 55	0.664 20	0.664 78	
FH					
HF	0.759 76	0.757 51	0.756 34	0.756 17	
CCSD(T)	0.703 50	0.704 50	0.707 00	0.707 50	0.708 20
CCSD(T) + PBEUEG	0.713 71	0.709 03	0.709 46	0.709 00	
H <sub>2</sub> O					
HF	0.786 71	0.780 39	0.779 56	0.779 56	
CCSD(T)	0.727 00	0.724 00	0.726 50	0.728 00	0.729 57
CCSD(T) + PBEUEG	0.738 91	0.729 30	0.729 12	0.729 20	
BN					
ROHF	1.134 51	1.138 62	1.138 31	1.138 40	
ROCCSD(T)	0.762 50	0.775 50	0.784 00	0.786 50	0.789 02
ROCCSD(T) + PBEUEG	0.775 17	0.781 45	0.787 56	0.788 46	

TABLE I. (Continued.)

	AVDZ	AVTZ	AVQZ	AV5Z	CBS
BO					
ROHF	1.178 03	1.185 33	1.185 27	1.185 39	
ROCCSD(T)	0.883 00	0.895 50	0.902 50	0.904 50	0.906 47
ROCCSD(T) + PBEUEG	0.894 17	0.901 53	0.906 22	0.906 98	
LiH					
HF	2.370 55	2.362 35	2.361 53	2.361 29	
CCSD(T)	2.325 00	2.310 00	2.308 00	2.308 00	2.308 25
CCSD(T) + PBEUEG	2.325 01	2.309 65	2.307 95	2.308 02	
LiF					
HF	2.561 11	2.541 03	2.539 49	2.539 05	
CCSD(T)	2.504 00	2.483 00	2.482 50	2.482 50	2.482 97
CCSD(T) + PBEUEG	2.509 42	2.485 42	2.483 67	2.483 21	
LiN					
ROHF	2.903 09	2.903 79	2.903 72	2.903 17	
ROCCSD(T)	2.742 00	2.773 00	2.782 50	2.784 50	2.787 18
ROCCSD(T) + PBEUEG	2.752 15	2.777 14	2.784 64	2.785 83	

The accuracy of the dipole moments obtained with a given basis set and a given level of approximation is evaluated with respect to the CBS limit of the CCSD(T) dipole moments,  $d_{\text{CCSD(T)}}^{\text{CBS}}$ , which are evaluated as in Ref. 23. In particular, the CBS results are computed as follows:

$$d_{\text{CCSD(T)}}^{\text{CBS}} = d_{\text{HF}}^{\text{CBS}} + d_c^{\text{CBS}}, \quad (15)$$

where  $d_c^{\text{CBS}}$  is the CBS limit of the correlation contribution to the CCSD(T) dipole moment that is computed using the following two-point  $X^{-3}$  extrapolation formula:

TABLE II. Mean error (ME), mean absolute error (MAE), mean absolute relative error (MARE), maximal absolute error (MAX), and root-mean-square deviation (RMSD) (in atomic units) for the CCSD(T) and CCSD(T) + PBEUEG dipole moments of 14 molecules. See Fig. 3 for the corresponding plots of the normal distributions of errors.

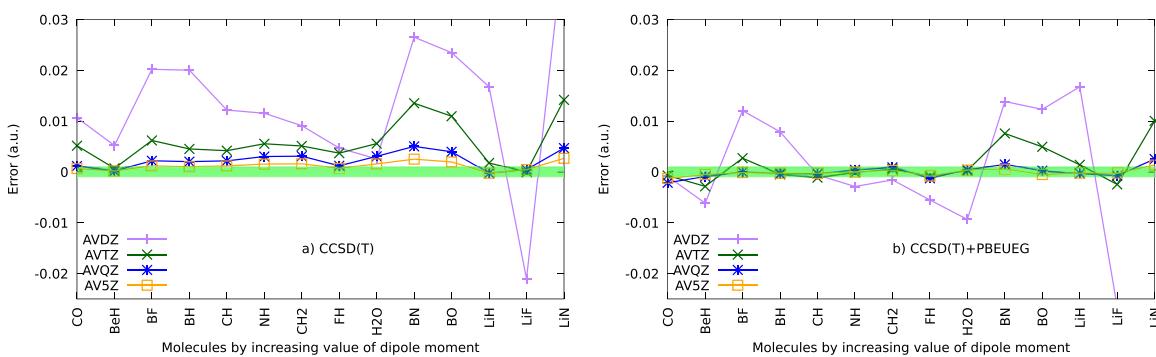
	AVDZ	AVTZ	AVQZ	AV5Z
ME				
CCSD(T)	0.013 36	0.005 79	0.002 29	0.001 22
CCSD(T) + PBEUEG	0.003 19	0.001 35	0.000 004	-0.000 12
MAE				
CCSD(T)	0.016 37	0.005 79	0.002 33	0.001 25
CCSD(T) + PBEUEG	0.010 80	0.002 58	0.000 86	0.000 49
MARE (in %)				
CCSD(T)	3.9	1.5	0.5	0.3
CCSD(T) + PBEUEG	1.6	0.6	0.4	0.3
MAX				
CCSD(T)	0.045 18 (LiN)	0.014 18 (LiN)	0.005 02 (BN)	0.002 68 (LiN)
CCSD(T) + PBEUEG	0.035 04 (LiN)	0.010 04 (LiN)	0.002 54 (LiN)	0.001 36 (LiN)
RMSD				
CCSD(T)	0.014 84	0.004 32	0.001 63	0.000 84
CCSD(T) + PBEUEG	0.014 64	0.003 76	0.001 16	0.000 63

**TABLE III.** Dipole moments obtained with near-FCI (CIPSI) and CCSD(T) calculations and with the self-consistent basis-set correction method (SC CIPSI + PBEUEG) of Ref. 16 and different non-self-consistent basis-set correction methods [CIPSI + PBEUEG@CIPSI, CCSD(T) + PBEUEG@CIPSI, and CCSD(T) + PBEUEG]. Estimated CBS values using Eq. (16) with  $X = 5$  are reported when computations could be done with the aug-cc-pV5Z basis set.

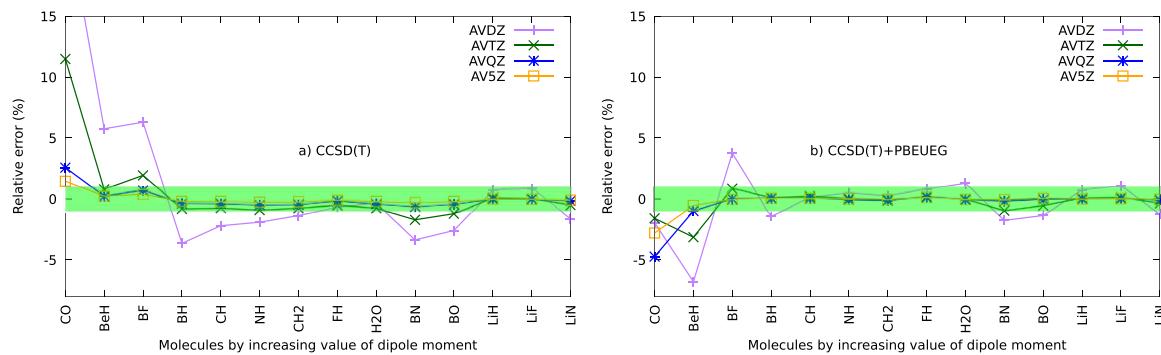
	AVDZ	AVTZ	AVQZ	AV5Z	CBS
BH					
CIPSI <sup>a</sup>	0.527 82	0.543 34	0.545 63	0.546 91	0.548 23
SC CIPSI + PBEUEG <sup>a</sup>	0.537 91	0.548 15	0.547 90	0.548 15	
CIPSI + PBEUEG@CIPSI	0.541 39	0.548 52	0.547 95	0.548 25	
CCSD(T)	0.529 50	0.545 00	0.547 50	0.548 50	0.549 53
CCSD(T) + PBEUEG@CIPSI	0.543 07	0.550 23	0.549 88	0.549 96	
CCSD(T) + PBEUEG	0.541 62	0.550 02	0.549 86	0.549 80	
$\text{CH}_2$ (singlet)					
CIPSI <sup>a</sup>	0.651 20	0.654 46	0.656 43	0.657 80	0.659 26
SC CIPSI + PBEUEG <sup>a</sup>	0.662 49	0.659 58	0.658 90	...	
CIPSI + PBEUEG@CIPSI	0.663 82	0.660 29	0.659 52	...	
CCSD(T)	0.656 00	0.660 00	0.662 00	0.663 50	0.665 10
CCSD(T) + PBEUEG@CIPSI	0.668 74	0.665 56	0.664 48	...	
CCSD(T) + PBEUEG	0.666 66	0.664 55	0.664 20	0.664 78	
FH					
CIPSI <sup>a</sup>	0.702 49	0.704 06	0.706 62	...	...
SC CIPSI + PBEUEG <sup>a</sup>	0.713 26	0.708 73	...	...	
CIPSI + PBEUEG@CIPSI	0.713 29	0.711 88	...	...	
CCSD(T)	0.703 50	0.704 50	0.707 00	0.707 50	0.708 20
CCSD(T) + PBEUEG@CIPSI	0.714 25	0.712 09	...	...	
CCSD(T) + PBEUEG	0.713 71	0.709 03	0.709 46	0.709 00	
$\text{H}_2\text{O}$					
CIPSI <sup>a</sup>	0.726 10	0.722 94	...	...	...
SC CIPSI + PBEUEG <sup>a</sup>	0.738 09	0.728 18	...	...	
CIPSI + PBEUEG@CIPSI	0.736 56	0.727 62	...	...	
CCSD(T)	0.727 00	0.724 00	0.726 50	0.728 00	0.729 57
CCSD(T) + PBEUEG@CIPSI	0.737 34	0.728 19	0.728 72	...	
CCSD(T) + PBEUEG	0.738 91	0.729 30	0.729 12	0.729 20	

<sup>a</sup>From Ref. 16.

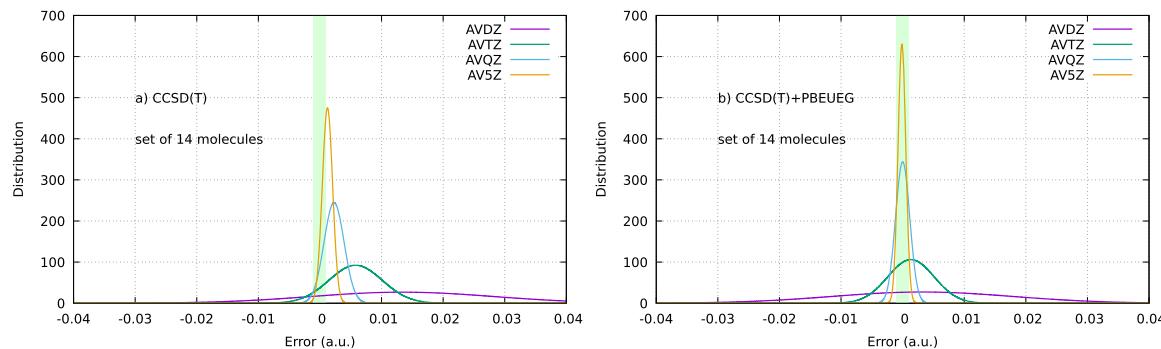
<sup>b</sup>Results not available due to the computational requirement.



**FIG. 1.** (a) CCSD(T) and (b) CCSD(T) + PBEUEG errors on the dipole moments of 14 molecules compared to CCSD(T)/CBS reference values. The green area indicates an error of  $\pm 0.001$  a.u.



**FIG. 2.** (a) CCSD(T) and (b) CCSD(T) + PBEUEG relative errors on the dipole moments of 14 molecules compared to CCSD(T)/CBS reference values. The green area indicates an error of  $\pm 1\%$ .



**FIG. 3.** (a) CCSD(T) and (b) CCSD(T) + PBEUEG normal distribution of errors on the dipole moments of 14 molecules compared to CCSD(T)/CBS reference values. The green area indicates an error of  $\pm 0.001$  a.u.

$$d_c^{\text{CBS}} = \frac{d_c^X X^3 - d_c^{(X-1)} (X-1)^3}{X^3 - (X-1)^3}, \quad (16)$$

with

$$d_c^X = d_{\text{CCSD(T)}}^X - d_{\text{HF}}^X, \quad (17)$$

where  $d_c^X$  and  $d_{\text{HF}}^X$  are the correlation and HF contributions, respectively, to the CCSD(T) dipole moment using the aug-cc-pVXZ basis set. In the present calculations, we evaluate Eq. (16) at  $X = 5$ , and we estimate the CBS limit of HF dipole moment  $d_{\text{HF}}^{\text{CBS}}$  in Eq. (15) simply by using the HF dipole moment in the aug-cc-pV5Z basis set. For all the systems studied here, the HF dipole moments are converged with an accuracy better than 0.001 a.u. (as measured by the difference between the aug-cc-pVQZ and aug-cc-pV5Z dipole moments).

At a given level of calculation in a basis set  $\mathcal{B}$ , we report the error on the dipole moment with respect to the CBS reference  $\Delta^{\mathcal{B}} = d^{\mathcal{B}} - d_{\text{CCSD(T)}}^{\text{CBS}}$  and the relative error  $\Delta_{\text{rel}}^{\mathcal{B}} = \Delta^{\mathcal{B}} / d_{\text{CCSD(T)}}^{\text{CBS}}$ . To statistically analyze the results, we also calculate the normal distribution function of the errors for a given basis set  $\mathcal{B}$ ,

$$\rho(\Delta^{\mathcal{B}}) = \frac{1}{\Delta_{\text{std}}^{\mathcal{B}} \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left( \frac{\Delta^{\mathcal{B}} - \bar{\Delta}^{\mathcal{B}}}{\Delta_{\text{std}}^{\mathcal{B}}} \right)^2\right], \quad (18)$$

where  $\bar{\Delta}^{\mathcal{B}} = (\sum_{i=1}^n \Delta_i^{\mathcal{B}}) / n$  is the mean error (ME) and  $\Delta_{\text{std}}^{\mathcal{B}} = \sqrt{\sum_{i=1}^n (\Delta_i^{\mathcal{B}} - \bar{\Delta}^{\mathcal{B}})^2 / (n-1)}$  is the root-mean-square deviation (RMSD).

#### IV. RESULTS AND DISCUSSION

In Table I, we report the dipole moments at various levels of approximations [HF, CCSD(T), and CCSD(T) + PBEUEG] with different basis sets, as well as the CCSD(T)/CBS reference values, for the set of 14 molecules. Note the wide range of magnitudes of the dipole moments (from 0.044 85 a.u. for CO to 2.787 18 a.u. for LiN). The mean error (ME), mean absolute error (MAE), mean absolute relative error (MARE), maximal absolute error (MAX), and root-mean-square deviation (RMSD) obtained with CCSD(T) and CCSD(T) + PBEUEG are reported in Table II. The graphical representations of these data are provided in Figs. 1 and 2 for the errors and relative errors and in Fig. 3 for the normal distributions of errors.

Analyzing first the results at the CCSD(T) level in Table II, one can note that, as expected, the ME and MAE systematically decrease with the size of the basis set. Moreover, as noted in previous studies,<sup>18</sup> not only the average values of the errors but also the RMSD tends to decrease with the basis-set size. Nevertheless, the improvement of the results is rather slow as a MAE below 0.001 a.u. is not reached even with the aug-cc-pV5Z basis set, illustrating the slow convergence of properties with respect to the basis set at the CCSD(T) level. Regarding the relative errors in Fig. 2, not surprisingly, the largest errors with respect to the CBS reference come from the molecules with smallest dipole moments (i.e. CO and BeH). More quantitatively, an aug-cc-pVQZ basis set is needed to obtain a MARE smaller than 1%.

Going from CCSD(T) to CCSD(T) + PBEUEG, one observes a systematic decrease in the MAE, ME, MARE, and RMSD. Focusing on the MAE, an error below 0.001 a.u. is reached with the aug-cc-pVQZ basis set, whereas such an accuracy is not even reached at the CCSD(T) level with the aug-cc-pV5Z basis set. Qualitatively, for the aug-cc-pVTZ basis set and larger basis sets, the MAEs obtained with CCSD(T) + PBEUEG with a basis set of cardinal number  $X$  are comparable to the MAEs obtained with CCSD(T) with a basis set of cardinal number  $X + 1$ . Regarding the MARE, an error below 1% is reached with CCSD(T) + PBEUEG already with the aug-cc-pVTZ basis set. One nevertheless observes that the effects of the basis-set correction on the RMSD are very weak. From the plots of Fig. 1, one notes that even if the basis-set correction systematically improves the results for the aug-cc-pVTZ basis set, its effect is less impressive when there is both a large error and a large dipole moment (i.e. for BN, BO, and LiN).

In order to further demonstrate the validity of the different approximations leading to the CCSD(T) + PBEUEG method, we conclude this study by a comparison with the self-consistent basis-set correction formalism of Ref. 16, as well as different flavors of non-self-consistent approximations. In Ref. 16, the self-consistent method referred to as SC CIPSI + PBEUEG was introduced, which can be considered as the nearly exact theory within our framework, thanks to the use of near-FCI (CIPSI; see Ref. 26 and references therein) wave functions. In all the calculations reported below, the absolute value of the second-order perturbative contribution to the energy in the CIPSI calculations is below  $10^{-4}$  a.u., which implies that the CIPSI energy and density can indeed be considered as near-FCI quantities. We also consider two different levels of non-self-consistent approximations: (i) CIPSI + PBEUEG@CIPSI where the CIPSI energy is corrected with the PBEUEG functional evaluated at the CIPSI density, and (ii) CCSD(T) + PBEUEG@CIPSI where the CIPSI energy is approximated by the CCSD(T) energy but the PBEUEG functional is still evaluated at the CIPSI density. Therefore, we have a hierarchy of approximations for the basis-set correction method using the PBEUEG functional: SC CIPSI + PBEUEG as the exact self-consistent theory, then CIPSI + PBEUEG@CIPSI as the exact non-self-consistent theory, then CCSD(T) + PBEUEG@CIPSI where only the WFT energy part is approximated with respect to CIPSI + PBEUEG@CIPSI, and finally CCSD(T) + PBEUEG where both the WFT energy and the density are approximated with respect to CIPSI + PBEUEG@CIPSI.

We report in Table III the results obtained with these different levels of theory for the dipole moments of the BH, CH<sub>2</sub>, FH, and H<sub>2</sub>O molecules. The results obtained with the self-consistent

method SC CIPSI + PBEUEG are in close agreement with that obtained with the different non-self-consistent approximations, the largest discrepancy being less than 0.006 a.u. for BH in the aug-cc-pVDZ basis set with CCSD(T) + PBEUEG@CIPSI. Comparing the two methods at the extremities of our hierarchy of approximations, one can note that the absolute deviation between CCSD(T) + PBEUEG and SC CIPSI + PBEUEG in a given basis set is never larger than 0.001 a.u. for FH and H<sub>2</sub>O, and the discrepancy slightly increases up to 0.006 and 0.003 a.u. in the case of CH<sub>2</sub> and BH, respectively. Nevertheless, as originally reported in Ref. 16 and apparent from Table III, discrepancies of the same order of magnitude also appear between the uncorrected CIPSI and CCSD(T) results in the case of the CH<sub>2</sub> and BH molecules. This suggests that the main source of differences between the CCSD(T) + PBEUEG and SC CIPSI + PBEUEG methods actually comes from the parent WFT theory. Focusing now specifically on the effect of the density in the non-self-consistent basis-set correction, one can note that the use of either a HF or CIPSI density does not significantly change the results, as the largest deviation between CCSD(T) + PBEUEG@CIPSI and CCSD(T) + PBEUEG are about 0.002 a.u. in the case of CH<sub>2</sub> in the aug-cc-pVDZ basis set. These results illustrate the validity of the different approximations leading to the CCSD(T) + PBEUEG approach and are encouraging, considering that the latter has a much lower computational cost with respect to the self-consistent basis-set formalism. Indeed, CCSD(T) + PBEUEG relies only on a standard CCSD(T) calculation and HF calculations for the basis-set correction, which is of negligible computational cost with respect to CCSD(T).

## V. CONCLUSION

In the present study, we have proposed an extension of the recently introduced non-self-consistent basis-set correction of CCSD(T) ground-state energies<sup>18</sup> to the computation of properties as energy derivatives, focusing here on the dipole moment. The theory relies on the originally proposed DFT-based basis-set correction approach,<sup>15</sup> which accelerates the basis-set convergence to the unaltered CBS limit. Numerical tests on a set of 14 molecules (including both closed and open-shell) with dipole moments spanning two orders of magnitude have been carried in order to obtain a representative study of the performance of the present approach.

Although this study aims at correcting the basis-set convergence of the CCSD(T) dipole moments, it can be formally generalized to any wave-function method and any energy derivative with respect to a static perturbation. In its present form, the basis-set correction relies only on HF calculations, which makes the basis-set correction essentially computationally free compared to the correlated wave-function calculation. This approach is an alternative to the recently proposed self-consistent basis-set correction,<sup>16</sup> which allows for the computation of first-order properties through expectation values over an energy-minimized wave function. In contrast with the self-consistent formalism, the present approach does not require a variational wave function, which considerably extends the domain of application of the basis-set correction.

Regarding now the numerical results, we have shown that the present approach significantly accelerates the basis-set convergence

of CCSD(T) dipole moments. Typically, the error obtained in a basis set of cardinal  $X$  with the basis-set correction is comparable to the error of the uncorrected CCSD(T) calculation with cardinal number  $X + 1$ . We also compared the present non-self-consistent basis-set correction with the self-consistent formalism of Ref. 16 and showed that the two theories agree within a few milli-atomic units, illustrating the soundness of the approximations leading to the non-self-consistent approach.

Considering the generality, the global performance, and the small computational cost of the present approach, it could be an alternative to explicitly correlated approaches for calculation of molecular properties. In the near future, we will extend the method to higher-order static properties, such as static polarizabilities, and also to more general dynamic properties, leading, in particular, to the possibility of accelerating the basis-set convergence of excitation energies.

## SUPPLEMENTARY MATERIAL

The [supplementary material](#) contains (i) all the geometries of the molecules studied here, (ii) a graphical representation of the convergence of the dipole moment at CCSD(T) and CCSD(T) + PBEUEG levels for each system studied, and (iii) the absolute and relative errors with respect to the estimated CBS and the CCSD(T) and CCSD(T) + PBEUEG levels.

## ACKNOWLEDGMENTS

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Program (Grant Agreement No. 810367) (EMC2).

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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