

## Dispersion-corrected Møller–Plesset second-order perturbation theory

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We show that the often unsatisfactory performance of Møller–Plesset second-order perturbation theory (MP2) for the dispersion interaction between closed-shell molecules can be rectified by adding a correction  $\Delta C_n/R^n$ , to its long-range behavior. The dispersion-corrected MP2 (MP2 +  $\Delta$ vdW) results are in excellent agreement with the quantum chemistry “gold standard” [coupled cluster theory with single, double and perturbative triple excitations, CCSD(T)] for a range of systems bounded by hydrogen bonding, electrostatics and dispersion forces. The MP2 +  $\Delta$ vdW method is only mildly dependent on the short-range damping function and consistently outperforms state-of-the-art dispersion-corrected density-functional theory. © 2009 American Institute of Physics. [doi:10.1063/1.3213194]

### I. INTRODUCTION

Electronic-structure theory plays a key role for predicting the structure and function of molecules and materials. The success of an approximate electronic structure method relies upon its ability to yield a consistent description of different interaction energy components. In particular, an accurate description of noncovalent van der Waals (vdW) forces, which play a key role in fields as diverse as supramolecular chemistry, biology, polymer science, condensed matter physics, surface science, and nanotechnology remains a grand challenge for current electronic structure methods.<sup>1,2</sup> At present, only high-level quantum-chemical methods [e.g., coupled cluster with single, double and perturbative triple excitations, CCSD(T)] can attain a consistently accurate description of vdW interactions. Unfortunately, CCSD(T) is limited to rather small systems due to its high computational cost and steep  $O(N^7)$  scaling with system size.

Second-order Møller–Plesset perturbation theory (MP2) is the most economical wave function-based electronic structure method beyond the Hartree–Fock (HF) approximation that provides an approximate description of all relevant vdW interactions—electrostatics, induction, and dispersion. Furthermore, MP2 is free from spurious electron self-interaction, representing a substantial improvement over state-of-the-art density-functional theory (DFT) approximations for molecular geometries, reaction barriers, and hydrogen bonding.<sup>3</sup> Recent theoretical and algorithmic developments<sup>4–6</sup> have extended the regime of applicability of the MP2 methodology, thereby allowing treatment of relevant biomolecular and nanotechnological systems containing hundreds of atoms. However, one of the serious shortcomings of MP2 theory is a noticeable overestimation of the dispersion interaction energy,<sup>7,8</sup> which plays a major role for stability and formation of, e.g., protein secondary structure,

the DNA double helix and nanoassemblies. Current attempts to correct the limitations of MP2 include the spin-component scaled models;<sup>9,10</sup> however, the optimal scaling coefficients change significantly depending on the desired property of interest, as recently demonstrated for noncovalent interactions.<sup>11</sup>

In this work, we show that the main source of error in the MP2 interaction energy for many relevant systems stems from overestimated dispersion coefficients,  $C_n^{\text{MP2}}$ . We then propose a computationally inexpensive MP2-specific dispersion correction scheme, based on a pairwise interatomic  $C_n R^{-n}$  summation, which brings MP2 binding energies into remarkable agreement with CCSD(T) reference data, as illustrated for a range of systems bounded by hydrogen bonding, electrostatics, and dispersion forces. For all of the above systems, we show that the MP2 +  $\Delta$ vdW method is only weakly dependent on the short-range damping function. Moreover, MP2 theory represents a superior starting point for the dispersion correction compared to (semi)-local DFT.

### II. ASYMPTOTIC BEHAVIOR OF THE MP2 DISPERSION ENERGY

The purpose of this section is to briefly show the relationship between  $C_6^{\text{MP2}}$  dispersion coefficients and frequency-dependent polarizabilities obtained at the uncoupled HF (UCHF) level of theory. For further details, we refer the reader to Refs. 12–14. The general ideas of the dispersion correction and the derivation of interatomic  $C_6$  coefficients from first-principles was presented in a previous paper by two of us.<sup>15</sup>

For large distance  $R$  between molecules  $A$  and  $B$ , the MP2 dispersion energy is given by  $E_{AB,\text{disp}}^{\text{MP2}} = -\sum_{n \geq 6} C_n^{\text{MP2}}/R^n$ , in which the leading-order isotropic dispersion coefficient,  $C_6^{\text{MP2}}$ , is obtained via the Casimir–Polder integral (atomic units are used throughout)

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$$C_6^{\text{MP2}} = \frac{3}{\pi} \int_0^\infty \alpha_A^{\text{UCHF}}(i\omega) \alpha_B^{\text{UCHF}}(i\omega) d\omega. \quad (1)$$

In this expression,  $\alpha_A^{\text{UCHF}}$  is the UCHF frequency-dependent dipole polarizability (FDP) of molecule *A*

$$\alpha^{\text{UCHF}}(\omega) = 4 \sum_Q \sum_{i,a} \frac{(\epsilon_a - \epsilon_i) \langle i | \hat{Q} | a \rangle \langle a | \hat{Q} | i \rangle}{(\epsilon_a - \epsilon_i)^2 - \omega^2}, \quad (2)$$

where  $\hat{Q}$  is the dipole operator, *i* and *a* are occupied and virtual HF orbitals, respectively, and  $\epsilon_{i,a}$  are the HF orbital eigenvalues. Similar expressions can be derived for the higher-order dispersion terms ( $C_8^{\text{MP2}}$ , etc.).

All FDP calculations in this work have been performed with a modified version of Q-CHEM.<sup>16</sup> Unless otherwise stated in the text, all FDP calculations use the aug-cc-pVQZ or SPQZ (Ref. 17) basis sets, where the latter is a modified quadruple-zeta basis set designed for convergence of dispersion energy coefficients.

### III. MP2+ $\Delta$ vdW METHOD

In order to illustrate the unsatisfactory performance of MP2 for the dispersion energy, we have calculated  $C_6^{\text{MP2}}$  coefficients for all interaction pairs in a database of 39 closed-shell atoms and molecules (the database of  $C_6^{\text{MP2}}$  and  $C_6^{\text{REF}}$  coefficients is available in Ref. 18). We compared the resulting 780  $C_6^{\text{MP2}}$  coefficients to the reference pseudodipole oscillator strength distribution (DOSD)  $C_6^{\text{REF}}$  values of Meath and co-workers.<sup>19–36</sup> The latter values are accurate within 1%–2% as shown by comparison between different sets of experimental input data.<sup>19,20</sup> We obtain a mean absolute error of 18.1% for  $C_6^{\text{MP2}}$  with the largest deviation of 76% for the interaction between two CS<sub>2</sub> molecules.

To correct for this shortcoming we propose the following expression for the dispersion-corrected potential  $V(R)$ :

$$V(R) = V^{\text{MP2}}(R) + F(R) \sum_{j=0} \frac{\Delta C_{2j+6}}{R^{2j+6}}, \quad (3)$$

where  $\Delta C_{2j+6} = C_{2j+6}^{\text{MP2}} - C_{2j+6}^{\text{REF}}$ . The function  $F(R)$  damps the dispersion multipolar expansion to avoid divergence at short distances. Here we shall concentrate on the leading-order  $C_6$  and  $C_8$  coefficients, since higher-order  $C_n$  coefficients play a role only at relatively small interatomic distances. We show that the correction of the leading  $C_6$  dispersion term is sufficient to obtain excellent agreement with CCSD(T) binding energies for intermolecular interactions. Despite the apparent simplicity of Eq. (3), its accuracy is far from guaranteed since the intermolecular binding results from a subtle interplay of electrostatic, induction, and dispersion energies. Furthermore, it is not obvious that the same damping function  $F(R)$  is applicable to different systems. We will show below that dispersion-corrected MP2 is only mildly dependent on a particular functional form of  $F(R)$ , provided the latter (i) is sufficiently smooth to capture the correlation energy difference between CCSD(T) and MP2 methods, and (ii) goes asymptotically to zero at short distances.

In practice, *interatomic*  $C_{nAB}$  coefficients are required for all atomic pairs *AB* in a molecule to reduce the radius of

divergence of the multipolar expansion in Eq. (3).<sup>1</sup> In this work we choose a simple strategy to obtain interatomic  $C_{6AB}$  coefficients from molecular  $C_6$  coefficients. The cross terms ( $A \neq B$ ) are given by a combination formula

$$C_{6AB} = \frac{2\alpha_A^0 \alpha_B^0 C_{6AA} C_{6BB}}{[(\alpha_B^0)^2 C_{6AA} + (\alpha_A^0)^2 C_{6BB}]}, \quad (4)$$

where  $\alpha_A^0$  and  $\alpha_B^0$  are the static polarizabilities of atoms *A* and *B* in a given molecule. This formula is accurate within 2.7% for a large variety of heteroatomic pairs.<sup>15</sup> The atomic polarizabilities and homoatomic  $C_{6AA}^{\text{MP2}}$  and  $C_{6AA}^{\text{REF}}$  terms are obtained by solving a system of coupled equations for two molecules, composed of two atomic species exclusively (i.e., C and H) in similar hybridization states. This procedure restricts our current benchmarks to small molecules with a maximum of two atomic species (rare-gas atoms and dimers, N<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>). Nevertheless, the intermolecular potential for different combinations of these molecules covers a wide range of interaction types (hydrogen bonding, electrostatics and dispersion) and magnitudes (from 4 to 218 meV). The extension of the MP2+ $\Delta$ vdW scheme to general closed-shell systems including intramolecular interactions will require a way to rigorously partition molecular  $C_6^{\text{MP2}}$  into atomic contributions. We are currently investigating the possibility of using orbital localization procedures in MP2 for such a purpose.

### IV. DAMPING FUNCTION

The main purpose of the damping function  $F(R)$  in Eq. (3) is to eliminate the divergence of the multipolar dispersion energy expansion at short distances between two atoms. At sufficiently large distances (certainly larger than the sum of atomic vdW radii),  $F(R)$  must converge to unity. However, it should also be able to describe accurately the crucial intermediate range, including the interaction potential well. For the dispersion interaction between two hydrogen atoms in the H<sub>2</sub> molecule,  $F(R)$  was derived analytically as a function of *R* (Refs. 37 and 38) and has the form of an incomplete gamma function. Tang and Toennies (TT) have used the incomplete gamma function to construct potential energy models for rare-gas<sup>39</sup> and mercury<sup>40</sup> homonuclear and heteronuclear dimers. The TT damping function has the following form for the  $C_n$  dispersion energy term

$$F(R) = 1 - \exp(-bR) \sum_{k=0}^n \frac{(bR)^k}{k!}, \quad (5)$$

where *b* is a distance scaling parameter inversely proportional to the vdW equilibrium distance. Since all normalized homonuclear and heteronuclear binding curves fall onto the same universal form,<sup>39,40</sup> the law of corresponding states can be applied to derive *b* from the vdW radius by linear interpolation. We exploit the latter fact throughout this work ( $b = -0.334D_{\text{vdW}} + 4.386 \text{ bohr}^{-1}$ , where  $D_{\text{vdW}}$  is the sum of atomic vdW radii). Aziz and co-workers<sup>41,42</sup> proposed a simpler empirical form for the damping function, which, when combined with an exponential repulsion model, yields very accurate binding curves for the rare-gas dimers. The Aziz

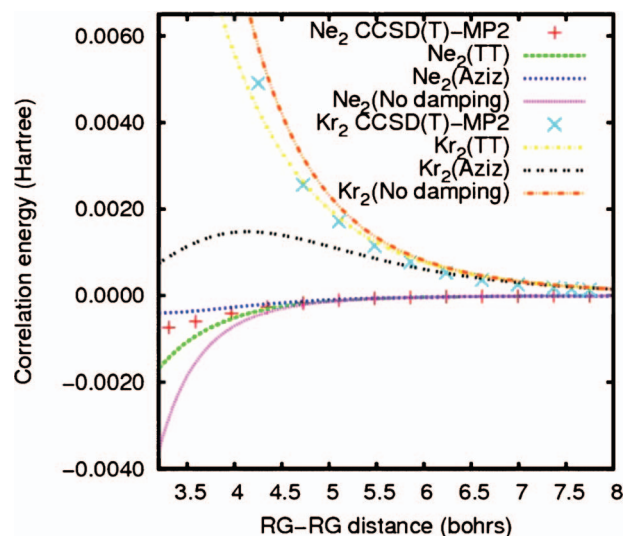


FIG. 1. Comparison of the  $F(R)(\Delta C_6/R^6 + \Delta C_8/R^8)$  term with different damping functions (Aziz, TT, and no damping) with  $\Delta_{MP2}^{CCSD(T)}$  electron correlation energy for  $Ne_2$  and  $Kr_2$ . The employed values are  $\Delta C_6 = -1.09$ ,  $\Delta C_8 = -28.5$ ,  $D_{vdW} = 5.84$ ,  $S = 1.47$ ,  $b = 2.458$  for  $Ne_2$  and  $\Delta C_6 = 42.1$ ,  $\Delta C_8 = -148$ ,  $D_{vdW} = 7.63$ ,  $S = 1.21$ ,  $b = 1.865$  for  $Kr_2$ . All above values are in atomic units.

damping function employs the following form for every order of the dispersion energy multipolar expansion

$$F(R) = \exp[-(SD_{vdW}/R - 1)^2], \quad (6)$$

$$R \leq SD_{vdW} = 1, \quad R \geq SD_{vdW},$$

where  $S$  is a distance scaling parameter. The Aziz damping function converges to unity at  $SD_{vdW}$ . The value of  $S$  decreases for larger rare-gas atoms (1.47 for He, 1.36 for Ne and Ar, and 1.21 for Kr). In this work we assume the corresponding rare-gas value to be transferable for all atoms in the same row of the Periodic Table, so that we use  $S_{He}$  for H and  $S_{Ne}$  for C, N, and O atoms. However, the  $MP2 + \Delta vdW$  binding energies are affected negligibly (less than 2 meV) if we use a fixed value of  $S$  ( $S = 1.4$ ) for all elements. For both the Aziz and TT damping functions, we use our recently presented definition of atomic vdW radii from Hirshfeld partitioning of the electron density in a molecule.<sup>15</sup> The vdW distance  $D_{vdW}$  is given by the sum of corresponding atomic vdW radii,  $D_{vdW}^{AB} = R_{vdW}^A + R_{vdW}^B$ .

Note that Aziz and TT potentials are not fitted to *ab initio* calculations. The only necessary information for these potentials are the asymptotic dispersion energy coefficients and the position (distance and depth) of the potential energy well. Thus, it is encouraging that CCSD(T) calculations at the complete basis set limit essentially reproduce Aziz and TT binding curves for the rare-gas and mercury dimers, except at very short distances.<sup>43,44</sup> The differences between the two damping functions can be appreciated in Fig. 1 and compared to the correlation energy difference between CCSD(T) and MP2 ( $\Delta_{MP2}^{CCSD(T)}$ ) for  $Ne_2$  and  $Kr_2$ . While the Aziz damping function (multiplied by the  $\Delta C_6 R^6 + \Delta C_8 R^8$  term) coincides with the TT one at larger distances, it reaches an inflection point and asymptotically goes to zero at  $\approx 0.7D_{vdW}$ . Similar results are found for the binding curves of  $(N_2)_2$  and

$N_2-C_6H_6$  systems. For dispersion bonded systems, the TT function is clearly more accurate than the Aziz one, reproducing  $\Delta_{MP2}^{CCSD(T)}$  even at quite short distances. However, the correction of higher-order dispersion terms, not taken into account here, must play an increasingly important role at the short range. Furthermore, the correction of the leading-order  $C_6$  term in the dispersion energy makes only a relatively small contribution to the total CCSD(T) binding energy at distances smaller than  $0.7D_{vdW}$  (3% for  $Kr_2$  at  $0.7D_{vdW}$  and decreasing to less than 1% at  $0.3D_{vdW}$ ). Thus, the leading-order dispersion energy correction at distances smaller than  $0.7D_{vdW}$  plays a minor role and will be circumvented here by employing the Aziz damping function. We also compare results with the TT damping function and show that it affects covalent and hydrogen-bonded systems, in which the interatomic distances are shorter than  $0.7D_{vdW}$ .

It is appropriate to compare the above damping functions to the ones used for correcting (semi)-local DFT calculations. In contrast to  $MP2 + \Delta vdW$ , we find that  $DFT + vdW$  requires significantly steeper functions, so that the intermediate and short ranges remain unaffected. Using Aziz or TT damping functions directly for correcting DFT calculations leads to gross overbinding, unless a large value is used for the distance scaling parameter. Furthermore, fitting to CCSD(T) or experimental data leads to significantly different parameterization of the damping function for different DFT functionals.<sup>45-48</sup> In contrast,  $MP2 + \Delta vdW$  method does not require any adjustable parameters in the damping function, since its performance is already remarkable without fitting to CCSD(T) data (see below).

## V. APPLICATIONS

In this section we present the application of the  $MP2 + \Delta vdW$  method to a range of systems, starting with rare-gas dimers—prototypical vdW systems. We follow with binding curves for three different conformations of the benzene dimer—a classic benchmark system for noncovalent interactions. Finally, we show  $MP2 + \Delta vdW$  results for a database of hydrogen bonding, electrostatics and dispersion bounded systems.

### A. Rare-gas dimers

In a rare-gas (RG) dimer the bonding is largely determined by the interplay between Pauli repulsion and London dispersion attraction. We use the RG dimer dispersion coefficients from the recent work of Mitroy and Zhang<sup>49</sup> ( $\Delta C_6 = -1.09$  for  $Ne_2$  and 42.1 for  $Kr_2$ , atomic units used throughout) in Eq. (3). These coefficients are obtained from a combination of experimental data and theoretical many-body calculations and are in excellent agreement with DOSD data of Kumar and Meath.<sup>20</sup> Figure 2 shows MP2 and CCSD(T) binding curves for the Ne and Kr dimers calculated at the basis set superposition error-corrected aug-cc-pVQZ level (with the corresponding effective core potential for Kr). It can be seen that the underestimation (overestimation) in the  $C_6$  coefficients is directly mirrored in the performance of the MP2 method for the Ne (Kr) dimer. Indeed, the binding energy at the respective equilibrium distance is underestimated

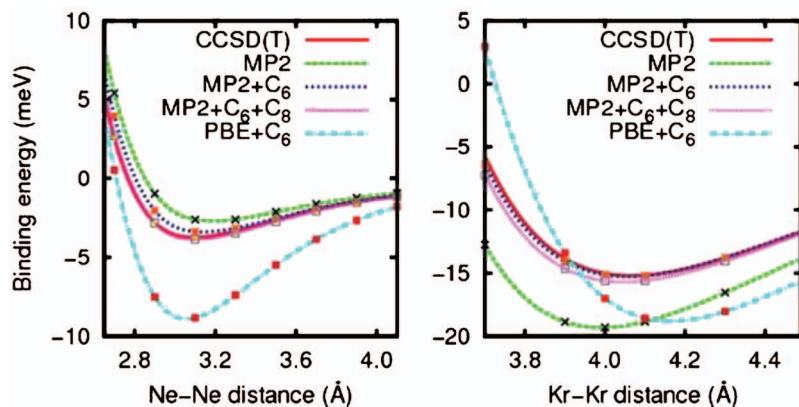


FIG. 2. Comparison of MP2 and MP2+ $\Delta$ vdW with CCSD(T) binding energy curves for Ne and Kr dimers. Dispersion-corrected DFT-PBE curves (Ref. 15) are also shown for comparison. The parameters for the Aziz damping function are  $S=1.36$  and  $R_{\text{eq}}=3.09$  Å for Ne (Ref. 42) and  $S=1.21$  and  $R_{\text{eq}}=4.04$  Å for Kr (Ref. 41).

(overestimated) by  $\approx 27\%$  for Ne (Kr) dimer. Correcting the MP2 binding energy curves for the leading  $C_6$  coefficient using Eq. (3) brings them into a significantly better agreement with CCSD(T). Not only is the long-range behavior now correct but also most of the underbinding (overbinding) for Ne (Kr) is eliminated by the correction. For Ne, correcting the higher-order  $C_8$  term ( $\Delta C_8=-28.5$ ), brings the MP2 curve into even better agreement with CCSD(T). For Kr, the curve becomes slightly more attractive than the CCSD(T) reference ( $\Delta C_8=-148$ ). The difference in the binding energy at the equilibrium distance between dispersion-corrected MP2 and CCSD(T) is just 0.1 meV for Ne (2.7% error) and 0.5 meV (3.3% error) for Kr.

We have also tested the TT damping function<sup>39</sup> for the rare-gas binding curves and found them to be modified by less than 3% near the equilibrium distance compared with the Aziz damping function. The PBE+ $C_6$  method performs significantly worse compared to MP2+ $\Delta$ vdW for RG dimers (see Fig. 2).

## B. Benzene dimer

Benzene dimer has become a classic benchmark system for noncovalent interactions. Different conformations on its complex potential energy surface are stabilized by a subtle interplay between electrostatics, induction and dispersion forces.<sup>50,51</sup> High-level correlated calculations, e.g., CCSD(T), along with large basis sets are needed to unequivocally distinguish between the stability of different conformations of the benzene dimer.<sup>52</sup> The MP2 method yields unsatisfactory results with a binding energy of 217 meV [118 meV for CCSD(T)] for the parallel-displaced configuration.<sup>7</sup> The spin-component scaled MP2 models im-

prove the agreement with CCSD(T),<sup>53</sup> however the reasons behind such an improvement are not well understood at present.

Using MP2 we get a value of 2356 hartree bohr<sup>6</sup> for the isotropic  $C_6$  coefficient for the benzene-benzene interaction, an overestimation of 37% compared to the accurate value of 1723 from the DOSD method of Kumar and Meath.<sup>36</sup> We use the  $C_6$  coefficients for benzene and ethylene molecules to solve a system of two quadratic equations and obtain the interatomic  $C_{6\text{CC}}$ ,  $C_{6\text{HH}}$ , and  $C_{6\text{CH}}$  coefficients. Using DOSD reference values yields  $C_{6\text{CC}}=27.2$  and  $C_{6\text{HH}}=3.26$ , while MP2 yields  $C_{6\text{CC}}=52.8$  and  $C_{6\text{HH}}=1.69$ . A large underestimation of the  $C_6$  coefficient for hydrogen and an overestimation for carbon is indeed found for all hydrocarbon molecules (alkanes, alkenes, and alkynes) and is not a feature of our choice in the benzene and ethylene molecules.

The benzene dimer has been the focus of intense theoretical and computational investigation.<sup>50-54</sup> In this work, we took the MP2 and CCSD(T) binding curves for the parallel displaced, sandwich, and T-shaped configurations of the benzene dimer from the work of Sinnokrot and Sherrill.<sup>55</sup> The reference CCSD(T) data along with MP2 and dispersion-corrected MP2 binding curves are shown in Fig. 3. For the parallel-displaced configuration we get a positive correction of 80 meV for the binding energy at a distance of 3.55 Å between the monomers, while for the T-shaped one we get a correction of 24 meV at 5.0 Å. This yields corrected MP2 binding energies of -109 and -123 meV, respectively. This should be compared to CCSD(T) estimates of -118 meV for the parallel displaced and -119 meV for the T-shaped structure.<sup>52</sup> Using the TT damping function instead of the Aziz one changes the binding energies by less than 5 meV

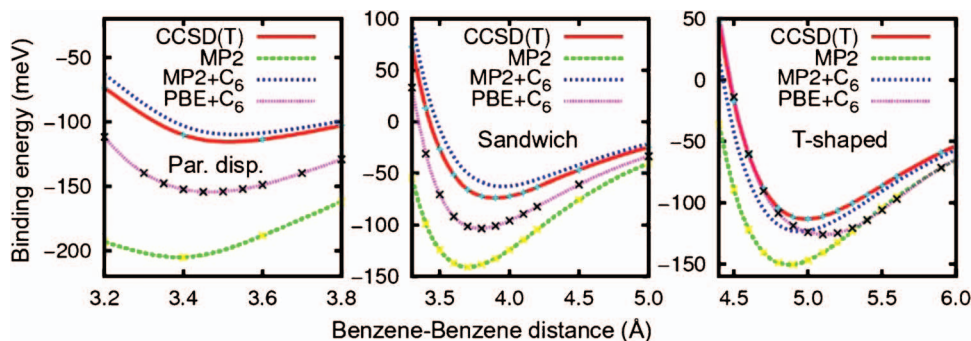


FIG. 3. Comparison of CCSD(T), MP2, and MP2+ $\Delta$ vdW binding energy curves for parallel-displaced, sandwich, and T-shaped conformers of benzene dimer. The MP2 and CCSD(T) binding curves are from the work of Sinnokrot and Sherrill (Ref. 55).

TABLE I. Comparison of MP2, MP2+ $\Delta$ vdW using Aziz and TT damping functions and PBE+vdW methods with CCSD(T) reference intermolecular binding energies (in meV). Different intermolecular orientations are marked with “T” for T-shaped, “P” for parallel and “PD” for parallel-displaced configuration.

	MP2	Aziz	TT	PBE+vdW	CCSD(T)
Hydrogen-bonded					
(NH <sub>3</sub> ) <sub>2</sub>	-139	-142	-146	-141	-137 <sup>a</sup>
(H <sub>2</sub> O) <sub>2</sub>	-218	-222	-226	-228	-218 <sup>a</sup>
Electrostatics and dispersion					
H <sub>2</sub> O-C <sub>6</sub> H <sub>6</sub>	-157	-139	-137	-153	-142 <sup>a</sup>
NH <sub>3</sub> -C <sub>6</sub> H <sub>6</sub>	-118	-99	-99	-107	-102 <sup>a</sup>
N <sub>2</sub> -C <sub>6</sub> H <sub>6</sub> -T	-52	-22	-28	-42	-26 <sup>b</sup>
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> -T	-157	-129	-134	-115	-119 <sup>a</sup>
(N <sub>2</sub> ) <sub>2</sub> -T	-15	-12	-11	-11	-12 <sup>b</sup>
Dispersion					
Ne <sub>2</sub>	-3	-4	-4	-8	-4 <sup>b</sup>
Kr <sub>2</sub>	-19	-16	-16	-17	-15 <sup>b</sup>
Ar-C <sub>6</sub> H <sub>6</sub>	-69	-49	-47	-54	-50 <sup>b</sup>
N <sub>2</sub> -C <sub>6</sub> H <sub>6</sub> -P	-97	-60	-61	-83	-60 <sup>b</sup>
(N <sub>2</sub> ) <sub>2</sub> -P	-13	-8	-7	-18	-9 <sup>b</sup>
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> -PD	-215	-116	-102	-144	-118 <sup>a</sup>
(CH <sub>4</sub> ) <sub>2</sub>	-22	-24	-25	-34	-23 <sup>a</sup>
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	-70	-73	-74	-82	-65 <sup>a</sup>
CH <sub>4</sub> -C <sub>6</sub> H <sub>6</sub>	-81	-62	-64	-71	-65 <sup>a</sup>
MAE	18	3	5	10	...
MARE (%)	31.0	4.8	7.5	28.6	...

<sup>a</sup>Jurecka *et al.* (Ref. 7).

<sup>b</sup>Our CCSD(T) calculations.

near the equilibrium distance for all conformations, once again confirming the low sensitivity of the MP2+ $\Delta$ vdW method to the damping function.

To assess whether higher-order dispersion coefficients could alter the above results, we have calculated the MP2  $C_8$  coefficient for benzene ( $C_8^{\text{MP2}}=230,511$  hartree bohr<sup>8</sup>), an overestimation of 16% compared to the accurate value of 198 508 from time-dependent many-body perturbation theory calculations.<sup>50</sup> Since the summation of atomic  $C_8$  coefficients contributes only 25% of the dispersion energy for the T-shaped and parallel-displaced benzene conformations,<sup>56</sup> the correction of the  $C_8$  term amounts to 4% of the binding energy. We conclude that a major part of the overestimation in the MP2 method for the benzene dimer stems from the rather large MP2  $C_6$  coefficient. Similar to RG dimers, the PBE+ $C_6$  method is not nearly as accurate as dispersion-corrected MP2 for the benzene dimer (see Fig. 3).

### C. Database of hydrogen-bonded, electrostatic, and dispersion systems

In order to further assess the accuracy and transferability of the MP2+ $\Delta$ vdW scheme, we assembled a database of hydrogen bonded, electrostatics and dispersion bounded systems shown in Table I. Most of the CCSD(T) binding energies are taken from the work of Hobza *et al.*<sup>7</sup> and supplemented by our own calculations for several interesting systems, such as Ar-benzene and N<sub>2</sub>-benzene. All our CCSD(T) binding energies are generated following the procedure of Jurecka *et al.*<sup>7</sup> First, a complete basis set limit MP2

binding energy is obtained with the FHI-AIMS code<sup>57</sup> and then a  $\Delta_{\text{MP2}}^{\text{CCSD(T)}}$  correction is added, calculated with the aug-cc-pVTZ basis set using the tensor contraction engine module<sup>58</sup> in the NWChem 5.1 code.<sup>59</sup> In all cases, the energies are reported for the minimum of the binding energy curve generated with the above procedure.

As can be seen from Table I, MP2 has a large mean absolute relative error (MARE) of 31% from the CCSD(T) reference data and a mean absolute error (MAE) of 18 meV. For the MP2+ $\Delta$ vdW method with the Aziz damping function the MARE is reduced to 4.8% and the MAE is only 3 meV. Similar results hold for the TT damping function, however, it shows a slight overestimation of the hydrogen-bonded systems due to its influence even for quite short interatomic distances. One of the largest differences between Aziz and TT damping functions (14 meV) in Table I is for the parallel-displaced benzene dimer. This, however, is due to the fact that the CCSD(T) calculation in Ref. 7 was carried out at the MP2 geometry, which underestimates the equilibrium distance. At CCSD(T) equilibrium distance, the difference between Aziz and TT damping functions decreases to 5 meV.

It is encouraging that the Aziz damping function does not significantly worsen the already good agreement of MP2 with CCSD(T) for hydrogen-bonded systems. The effect of the  $\Delta C_6$  dispersion correction for both NH<sub>3</sub> and H<sub>2</sub>O dimers is less than 4 meV. This finding is in marked contrast to the SCS-MP2 methods,<sup>9,10</sup> which improve results for dispersion

bonded systems but significantly worsen the description of hydrogen bonding.<sup>11,60</sup>

The MP2+ $\Delta$ vdW method is also significantly more accurate than state-of-the-art dispersion-corrected DFT approaches. Using the PBE xc functional along with our recently presented DFT+vdW method,<sup>15</sup> we obtain a MARE of 28.6% and MAE of 10 meV on the database in Table I.

## VI. DISCUSSION

Several schemes have been recently presented to correct the dispersion energy in supermolecular MP2 calculations.<sup>8,61</sup> Cybulski and Lytle<sup>8</sup> proposed to use scaled time-dependent HF  $C_6$  coefficients to improve on UCHF values and thus correct the long-range dispersion in MP2 calculations. Hesselmann<sup>61</sup> proposed to improve MP2 with the dispersion energy treated at the time-dependent DFT level. Thus, these approaches are similar in scope to the MP2+ $\Delta$ vdW method. The main difference in our method consists in obtaining the reference  $C_6$  coefficients from accurate DOSD data or TS-vdW method,<sup>15</sup> the fact that we require *interatomic* rather than *intermolecular* coefficients, and the use of a damping function. A clear advantage of the MP2+ $\Delta$ vdW procedure is that it is applicable even to large molecules since the interatomic  $C_6$  coefficients allow to extend the validity of the dispersion energy multipolar expansion to shorter distances. We showed that MP2+ $\Delta$ vdW is indeed valid at quite short distances by presenting a comparison with CCSD(T) binding energies for hydrogen-bonded systems. Hesselmann noticed that hydrogen-bonded systems were problematic to handle in the MP2+TDDFT approach since MP2 was already sufficiently accurate before the dispersion energy correction.<sup>61</sup> In our method, the short-range damping function is able to rectify this problem, yielding accurate results for a wide range of noncovalent interactions. Nevertheless, it is fair to say that additional work is required to obtain the damping function from first-principles, since it is highly dependent on the electronic structure method used for the shorter range. This is also clearly illustrated by different dispersion correction methods for DFT.<sup>15,45,46,62,63</sup> However, it is encouraging that the MP2+ $\Delta$ vdW method shows a weak sensitivity to different damping function parametrizations. Future work will include extending the MP2+ $\Delta$ vdW method to general intermolecular and intramolecular interactions by projecting the molecular MP2  $C_6$  coefficients on atoms and benchmarking the method for larger systems, where the difference between MP2 and CCSD(T) binding energies may become even more pronounced than shown in Table I.<sup>64</sup>

## VII. SUMMARY

We have developed a dispersion correction method for MP2 calculations, which yields results close to CCSD(T) for a wide range of intermolecular interactions. We found relatively weak sensitivity of the results to the damping function parameters and functional form, in contrast to DFT+vdW methods. Extending this scheme to intramolecular interactions requires partitioning the molecular  $C_n^{\text{MP2}}$  coefficients into atomic contributions, a work currently in progress. The

MP2+ $\Delta$ vdW method represents an improvement over dispersion correction schemes for approximate DFT functionals<sup>45,46</sup> since MP2 is free from spurious electron self-interaction.

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