A novel correction scheme for DFT: A combined vdW-DF/CCSD(T) approach

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A system-specific but very accurate density functional theory (DFT) correction scheme is proposed for precise calculations of adsorbent–adsorbate interactions by combining the non-empirical van der Waals density functional (vdW-DF) method and the empirical DFT/CC correction scheme to reach accuracy of the coupled clusters method with single, double and perturbative triple excitations (CCSD(T)). The new approach is applied to small molecules (CH_4, CO_2, H_2, H_2O, N_2) interacting with silica surfaces and purely siliceous microporous solids. The vdW-DF/CC results for a perfectly reconstructed α-quartz surface are consistent with other dispersion-corrected DFT methods. Corrected for ZPVE, the vdW-DF/CC enthalpies of adsorption in pure-silica zeolite LTA ($\Delta H_{ads}(0\,K)$) of 3.6 and 5.2 kcal/mol for methane and carbon dioxide, respectively, are in excellent agreement with experimental values of 3.6 and 5.0 kcal/mol. The very high accuracy of the new scheme and its relatively easy use and numerical stability as compared to the earlier DFT/CC scheme offer a straightforward solution for obtaining reliable predictions of adsorption energies. [http://dx.doi.org/10.1063/1.4813826]

I. INTRODUCTION

Dispersion interactions play a major role in many chemical and biological processes and their technological applications. A much studied example of such a dispersion-dominated process is the physisorption of industrial gases (e.g., methane, carbon dioxide) on both exterior and interior surfaces of various porous materials. A major tool in computational chemistry for studying physisorption in extended systems is density functional theory (DFT). However, traditional local and semi-local DFT functionals (LDA, GGAs, hybrids) either do not cover long-range correlation interactions at all or simulate them unreliably with non-physical binding by exchange energy.[1] In the last two decades, significant efforts have been made to include dispersion reliably into DFT (see Refs. 2–5 for a review). The most recent dispersion-corrected DFT (DC-DFT) methods achieve an impressive accuracy of several tenths of kcal/mol in the non-covalent databases of Jurečka *et al.*[6] However sufficient for general use, this may still not be accurate enough for modeling certain processes where a subchemical accuracy (∼0.1 kcal/mol) is needed. It has been recently shown that such an accuracy is necessary for a quantitative comparison of computational results with some experiments, e.g., measurements of adsorption isotherms.[7] Due to the limitations imposed by the quality of the (semi-)local parts of the DC-DFT methods, the subchemical accuracy is still a domain of system-specific correction schemes.

Recently, the DFT/CC dispersion correction method has been proposed for precise calculations of weakly bound molecular systems.[8] The correction scheme has been successfully applied to molecular crystals[9] and to the physical adsorption of molecules on graphene,[10] zeolites,[11] and metal-organic frameworks (MOFs).[12] The major advantage of DFT/CC is that being system-specific, it yields accurate adsorption enthalpies even for systems where proper treatment of long-range correlation contributions is only a part of the problem. A typical example is the interaction of adsorbed molecules with coordinatively unsaturated sites of the CuBTC MOF. In this particular case, the excellent performance of DFT/CC as compared to general DC-DFT methods obviously stems more from deficiencies of the underlying GGA exchange-correlation functionals than from the applied dispersion corrections. Many other problems have been reported, such as the DFT description of charge transfer or polarization in extended conjugated systems.[13] Correcting such deficiencies in the framework of general DC-DFT methods can be very difficult.

Although a comparison with experimental data on various systems has clearly demonstrated the accuracy and reliability of DFT/CC, its implementation for adsorbent–adsorbate interactions can be very tedious for complex molecular systems, thus hindering a wider applicability of the method. In this paper, we present a novel correction scheme for DFT where the laborious parametrization of DFT/CC corrections is simplified by physical constraints obtained directly from the nonlocal vdW-DF functional.

The paper is organized as follows. Section II presents the specific implementation of vdW-DF used in our correction scheme (Sec. II A), reviews the DFT/CC scheme (Sec. II B), introduces the novel vdW-DF/CC scheme (Sec. II C), and defines the details of the numerical computations (Sec. II D). Section III presents a prototypical application of our scheme on silica-based materials. This comprises parametrization on the 1T and 2T models (Sec. III A) and calculations on the perfectly reconstructed α-quartz surface (Sec. III B), and on the purely siliceous zeolite LTA (Sec. III C). Finally, Sec. IV draws conclusions on the presented results.

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II. METHODS

A. vdW-DF

The van der Waals density functional (vdW-DF), a general first-generation non-empirical method for dispersion within the DFT framework,[14] is used as a starting point for our correction scheme. In vdW-DF, dispersion energy is equaled to nonlocal correlation energy,

$$E^{\mathrm{nlc}} = \int\int \rho(\mathbf{r}_1)\phi[\rho](\mathbf{r}_1, \mathbf{r}_2)\rho(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{1}$$

where ρ is electron density and ϕ is a nonlocal kernel, which depends on the values of ρ and $\nabla\rho$ at points $\mathbf{r}_1$, $\mathbf{r}_2$. vdW-DF has been shown to provide binding energies in good agreement with benchmark methods or experiment.[15]

We use a custom code for the evaluation of the integral in Eq. (1). It is based on Becke's multi-center integration scheme, which uses radial integration grids centered on atoms.[16] This naturally translates the double integral into a sum,

$$E^{\mathrm{nlc}} = \sum_{i,j}\sum_{m,n} \rho(\mathbf{r}_{im})\phi[\rho](\mathbf{r}_{im}, \mathbf{r}_{jn})\rho(\mathbf{r}_{jn})\omega_{im}\omega_{jn} = \sum_{i,j} E_{ij}^{\mathrm{nlc}},$$

where i, j denote atoms, m, n label individual points of the atom-centered grids, and ω is the weight of the points. In this way, the nonlocal energy is expressed as a sum of atom-pair contributions.

In the case of the interaction between two fragments A, B, the total nonlocal energy can be divided into the interaction part and the self-energy part,

$$\sum_{i,j} = 2\sum_{\substack{i\in A\\ j\in B}} + \left(\sum_{i,j\in A} + \sum_{i,j\in B}\right).$$

Likewise, the contribution of the nonlocal energy to the interaction energy is two-fold,

$$2\sum_{\substack{i\in A\\ j\in B}} E_{ij}^{\mathrm{nlc}}[\rho] + \left(\sum_{i,j\in A}\left(E_{ij}^{\mathrm{nlc}}[\rho] - E_{ij}^{\mathrm{nlc}}[\rho_A]\right) + \sum_{i,j\in B}\left(E_{ij}^{\mathrm{nlc}}[\rho] - E_{ij}^{\mathrm{nlc}}[\rho_B]\right)\right),$$

where ρ_A, ρ_B are the electron densities of the individual isolated fragments.

Our tests have shown that the expression in parentheses, i.e., the difference in the nonlocal self-energies of the fragments between the interacting and isolated cases, is negligible (a few percent at most). This justifies the representation of the dispersion energy by atom-pair curves between the fragments.

B. DFT/CC

The empirical part of our method, which brings in the required accuracy, draws on the ideas of DFT/CC, an empirical scheme for correcting DFT.[8] Here, the difference ΔE between the accurate CCSD(T) and DFT interaction energies is approximated by a set of correction curves ε_{XY},

$$\Delta E = \sum_{i\in A}\sum_{j\in B} \varepsilon_{T(i)T(j)}(R_{ij}), \tag{2}$$

where the summation is over the pairs of atoms i, j, $T(k)$ is the type (H, C,...) of atom k, and R_{ij} is the interatomic distance. To parametrize ε_{XY}, one has to devise a series of models where each model serves for parametrizing a new correction curve while all the others have to be known from previous models. For example, for parametrizing $\varepsilon_{\mathrm{HH}}$, $\varepsilon_{\mathrm{CH}}$, $\varepsilon_{\mathrm{CC}}$, one uses $H_2\cdots H_2$, $Bz\cdots H_2$, $Bz\cdots Bz$, respectively.[8]

The individual curves are obtained by RKHS interpolation,[17,18] which enables finding function f such that

$$y_k = \sum_l f(x_l), \tag{3}$$

where y_k and x_l are given. In DFT/CC, k and l correspond to different interfragment distances and atom pairs, respectively, and y_k, f, and x_l correspond to ΔE, ε_{XY}, and R_{ij}, respectively. The resulting function f is defined on a grid produced by the RKHS procedure. Function f can be constrained to satisfy some required asymptote for $x \to \infty$ by selecting a proper RKHS kernel. In DFT/CC, it is required that $\varepsilon_{XY} \sim R_{ij}^{-6} + R_{ij}^{-8}$ for $R_{ij} \to \infty$. If more than one atom-type pair is present, RKHS is utilized successively, each time using ΔE reduced by already parametrized ε_{XY}.

The DFT/CC approach can provide superb accuracy, but the multi-step parametrization has some deficiencies. It can be tedious in cases with many atom types, and it can also be numerically unstable, e.g., when there are regularly alternating atoms of different types, such as Si and O in silica-based materials.

C. vdW-DF/CC

Our new correction scheme, dubbed vdW-DF/CC, overcomes the drawbacks of DFT/CC while preserving its accuracy and high specificity. It uses only one correction curve ε, whereas the weight functions w_{ij}, obtained from vdW-DF, are used to differentiate between atom types. The correction energy is approximated as

$$\Delta E = \sum_{i\in A}\sum_{j\in B} w_{T(i)T(j)}(R_{ij})\varepsilon(R_{ij}) \tag{4}$$

Having no more than one correction curve, this scheme needs only a single cluster model to be parametrized for any given adsorbent–adsorbate system. The parametrization of vdW-DF/CC is done in two steps.

First, interfragment $E_{ij}^{\mathrm{nlc}}(R_{ij})$ are calculated for a grid of cluster interfragment distances. To turn from E_{ij}^{nlc} for individual atom pairs (ij) to ϵ_{XY} for atom-type pairs (XY), RKHS is used for each XY such that

$$\sum_{i\in X}\sum_{j\in Y} E_{ij}^{\mathrm{nlc}}(R_{ij}) = \sum_{i\in X}\sum_{j\in Y} \epsilon_{XY}(R_{ij}),$$

where the whole left side, ε_{XY} and R_{ij} correspond to y_k, f and x_k from Eq. (3), respectively. The dimensionless weights w_{XY}

are given as

$$w_{XY} = \frac{\epsilon_{XY}}{\epsilon_{X'Y'}},$$

where any ϵ_{XY} is chosen as the reference curve $\epsilon_{X'Y'}$.

Second, a slightly modified RKHS interpolation is used to obtain the correction curve ε. This "weighted" RKHS gives function f such that (compare to Eq. (3))

$$y_k = \sum_l u_l f(x_l), \tag{5}$$

where y_k, u_l and x_l are given. In vdW-DF/CC, y_k, u_l, f and x_k correspond to ΔE, w_{XY}, ε, and R_{ij}, respectively. As ε is a single function, RKHS needs to be used only once. Having w_{XY} and ε, one can then proceed to the evaluation of the correction energy defined in Eq. (4).

The interpretation of our method as a modified DFT/CC method is not the only possible. After rewriting Eq. (4) as

$$\Delta E = \sum_{i\in A}\sum_{j\in B} \frac{\varepsilon(R_{ij})}{\epsilon_{X'Y'}(R_{ij})} \epsilon_{T(i)T(j)}(R_{ij}),$$

vdW-DF/CC can be seen as a scaling of vdW-DF by $\varepsilon/\epsilon_{X'Y'}$. However, we prefer the modified-DFT/CC interpretation, because vdW-DF/CC attempts to correct empirically for everything that is missing in DFT as compared to CCSD(T), whereas vdW-DF adds only dispersion in a non-empirical manner. In this sense, our method is much closer to DFT/CC than to vdW-DF.

D. Computational details

The numerical work uses the vdW-DF2 flavor (PW86 exchange and LDA correlation functional, parameter Z_{ab} = 1.887), because it provides more accurate and consistent interaction energies than the original vdW-DF.[19] For vdW-DF/CC, we use the same underlying semi-local XC functional as vdW-DF2. On cluster models, the nonlocal energy is evaluated only non-self-consistently, but it has been shown that the effect of self-consistency is negligible.[20]

The CCSD(T) energies used for the parametrization of vdW-DF/CC were calculated using MOLPRO.[21] A standard procedure for obtaining the complete basis set (CBS) limit was used,[22]

$$\text{CCSD(T)/CBS} = \text{CCSD(T)/AV}n\text{Z} + \text{MP2/CBS} - \text{MP2/AV}n\text{Z}$$

where AVnZ denotes Dunning's correlation-consistent basis sets augmented with diffuse functions.[23] We used either $n = 2$ or $n = 3$. MP2/CBS was obtained by an extrapolation of

$$\text{MP2/AV}m\text{Z} = \text{MP2/CBS} + A \times m^{-3}$$

from $m = 3$ and $m = 4$ to $m \to \infty$. The MP2 energies were calculated also in MOLPRO, using density fitting.

The DFT energies were calculated in GAUSSIAN 09 using the AVQZ basis set and density fitting.[24] The electron densities used for the evaluation of the vdW-DF nonlocal energy were obtained by MOLPRO. As the nonlocal energy is quite insensitive to the exact shape of the electron density, there is no inconsistency in using different codes for the (semi-)local and nonlocal parts of the total energy. D2[25] and D3[26] dispersion corrections of Grimme were calculated in MOLPRO.

Periodic systems were modeled in VASP.[27] The PREC keyword was set to ACCURATE. The geometry optimizations were performed using vdW-DF2, the ENCUT value of 400 eV and soft pseudopotentials (ENMAX values of 400, 250, 400, 400, and 245 eV for C, H, N, O, and Si, respectively). The forces were converged to 10^{-4} eV/Å. The interaction energies were obtained using the ENCUT value of 800 eV and hard pseudopotentials (ENMAX values of 700, 700, 756, 700, and 380 eV for C, H, N, O, and Si, respectively). Γ-centered grids were used for k-point sampling.

III. APPLICATIONS

To illustrate the performance of vdW-DF/CC, we have parametrized it for silica-based materials and applied it to the problem of the adsorption of small molecules (CH_4, CO_2, H_2, H_2O, N_2) on the quartz surface and in the purely siliceous zeolite LTA. We used the simple quartz surface for comparison with other computational methods, and zeolite LTA for comparison with experiment.

A. Parametrization for silica on 1T and 2T models

To parametrize vdW-DF/CC for use on large systems, one has to choose a suitable small model. For materials derived from silica, the nT family of models has proven useful. An nT model contains n Si atoms, linked by an appropriate number of O atoms and the cluster is terminated with silanol groups. Here, we consider the 1T model $Si(OH)_4$ and the 2T model $OSi_2(OH)_6$. Figure 1 defines the relative orientations

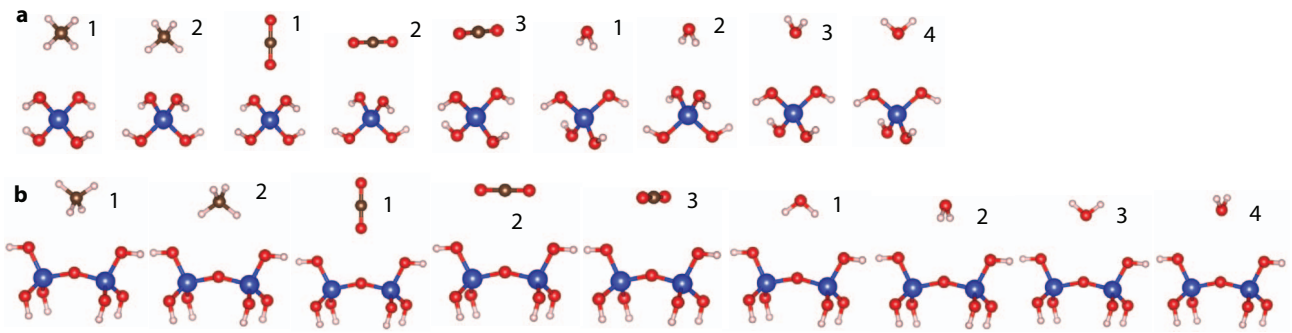

FIG. 1. The geometries of the 1T (a) and 2T (b) adsorption complexes. The numbers denote the geometry index used throughout this paper. The geometries of the models with H_2 and N_2 are defined equivalently to CO_2.

TABLE I. The differences in binding energies (kcal/mol) and the distances (Å) between CCSD(T)/CBS with CC using AVDZ and AVTZ.

Molecule	Geometry	D	E_{int}	ΔD	ΔE_{int}
CH_4	1	4.46	− 0.893	− 0.010	− 0.02
CO_2	2	3.74	− 3.43	− 0.007	− 0.05
H_2	1	4.03	− 0.685	− 0.013	− 0.018
H_2O	2	3.74	− 5.29	− 0.006	− 0.08
N_2	2	4.11	− 1.155	− 0.007	− 0.016

considered here of the adsorbent molecules and silica models. All orientations have the C_{2v} symmetry to facilitate CCSD(T) calculations.

The use of CCSD(T)/CBS as the reference method poses the question of its own accuracy. Marshall *et al.* have recently reported MAE from the reference data of about 0.1 kcal/mol for the S22 database for the CCSD(T)/CBS values obtained with the AVDZ basis set. Here, we have investigated the effect of basis set convergence on the CCSD(T)/AVnZ energies for the most stable orientations of the 1T complexes. Table I presents the differences for AVDZ and AVTZ basis sets ($n = 2$ and $n = 3$). The differences in equilibrium distances are less than 0.015 Å and the relative errors in energies do not exceed 3%. These errors are within the intended accuracy of our method.

The orientation of each molecule most strongly binding to the 1T model according to CCSD(T) was used for parametrization. Figures 2 and 3 show the obtained curves ϵ_{XY} and ε, respectively. All the correction curves ε have a similar shape, but they are displaced along the x axis. On the contrary, a hypothetical correction curve $\varepsilon = \epsilon_{X'Y'}$ which would reproduce the vdW-DF2 energies exactly has a different shape. This suggests that there is a systemic error and that it might be possible to devise a universal correction curve for all molecules which would still provide better energies than vdW-DF2.

Figure 4 and Table II present the calculated interaction energies of the molecules with the 2T model, which serve as a verification of the transferability. The root-mean-square error in the binding energies of our method is 0.08 kcal/mol

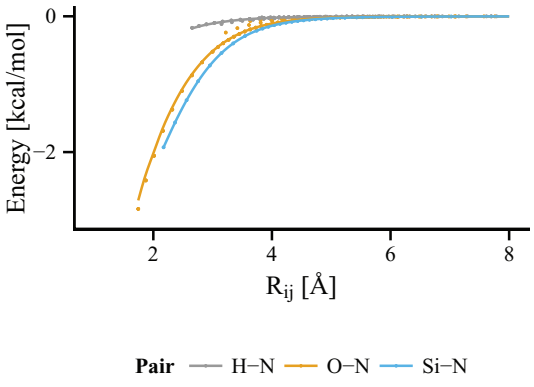

FIG. 2. Example vdW-DF curves ϵ_{XY} obtained for N_2 from an interaction with the 1T model. Note that while the individual atom-pair vdW-DF curves E_{ij}^{nlc} (dotted) differ and cannot be represented by a single curve, the total vdW-DF energy is represented exactly by the atom-type vdW-DF curves ϵ_{XY} (solid) obtained by the RKHS interpolation.

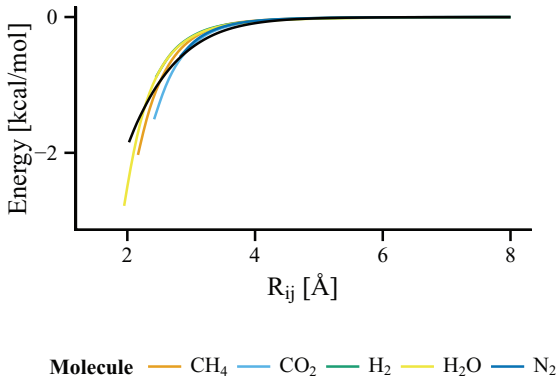

FIG. 3. The vdW-DF/CC correction curves ε for different molecules parametrized on the 1T model. The black curve is a hypothetical correction curve that would reproduce vdW-DF2 interaction energies if used.

(all molecules and orientations) while it is 0.45 kcal/mol for vdW-DF2. The mean absolute percentage error is 7% for our method and 57% for vdW-DF2. This shows that our method

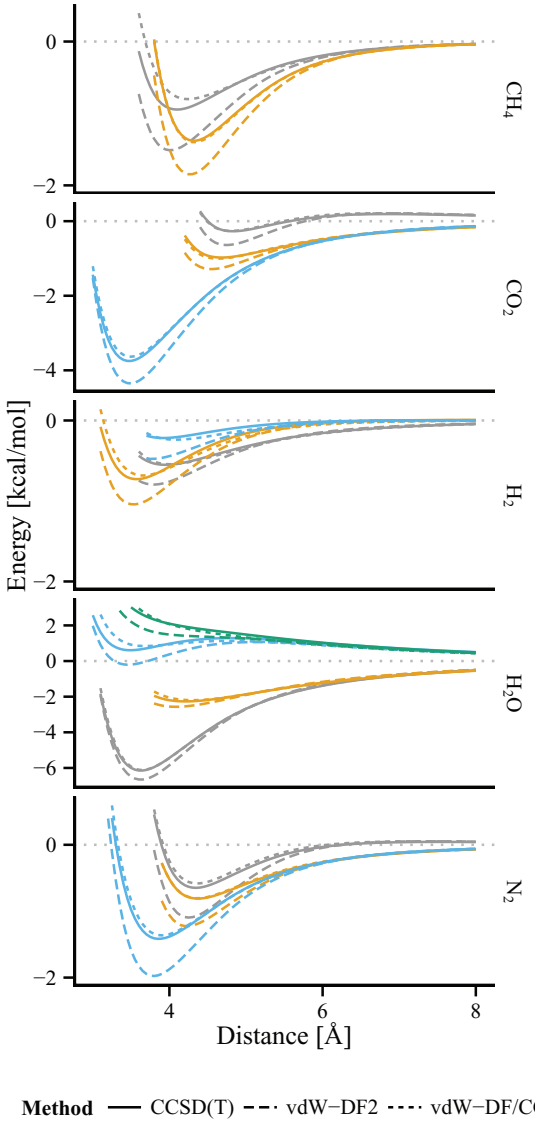

FIG. 4. The interaction curves of different molecules with the 2T model. The different colors correspond to the different orientations of the molecule with respect to 2T. The vdW-DF/CC is our method parametrized on the 1T model.

TABLE II. Binding energies (kcal/mol) of the 2T model systems by different methods.

Molecule	Geometry[a]	vdW-DF2	vdW-DF/CC	CCSD(T)	ΔvdW-DF2[b]	ΔCCSD(T)[c]	PBE-D2	PBE-D3
CH_4	1	− 1.5	− 0.8	− 0.9	0.7	− 0.15	− 1.2	− 1.4
	2	− 1.8	− 1.4	− 1.4	0.4	0.02	− 1.7	− 1.8
CO_2	1	− 0.6	− 0.3	− 0.3	0.4	− 0.01	− 0.3	− 0.4
	2	− 1.3	− 1.0	− 1.0	0.3	0.03	− 1.1	− 1.3
	3	− 4.4	− 3.6	− 3.8	0.7	− 0.12	− 3.6	− 3.4
H_2	1	− 0.8	− 0.5	− 0.6	0.3	− 0.01	− 0.7	− 0.9
	2	− 1.0	− 0.7	− 0.7	0.4	− 0.05	− 1.0	− 1.1
	3	− 0.5	− 0.2	− 0.2	0.2	0.02	− 0.4	− 0.6
H_2O	1	− 6.7	− 6.1	− 6.1	0.5	− 0.03	− 6.7	− 6.4
	2	− 2.6	− 2.2	− 2.3	0.4	− 0.07	− 2.5	− 2.8
	3				non-bonding			
	4				non-bonding			
N_2	1	− 1.1	− 0.6	− 0.6	0.5	− 0.07	− 0.7	− 0.9
	2	− 1.2	− 0.8	− 0.8	0.4	− 0.01	− 1.0	− 1.2
	3	− 2.0	− 1.4	− 1.4	0.6	− 0.05	− 1.5	− 1.7

[a]The geometry index defined in Figure 1.
[b]The difference vdW-DF/CC − vdW-DF2.
[c]The difference CCSD(T) − vdW-DF/CC.

provides roughly an order of magnitude better binding energies for the systems for which it has been parametrized than vdW-DF2. For comparison, PBE-D2 and PBE-D3 interaction energies were also calculated. Both versions perform quite similarly, the differences between them being 0.2 kcal/mol at most. Generally, the D*x* energies are within the margins marked out by vdW-DF2 and vdW-DF/CC (∼CCSD(T)).

B. Quartz surface

Table III presents the calculated binding energies of the molecules with a perfectly reconstructed α-quartz surface (in Figure 5).[28] The geometries of the complexes were preoptimized using vdW-DF2. This is justified by the fact that while vdW-DF2 generally overbinds on 1T and 2T models, it provides fairly accurate bonding distances. The geometries of the isolated quartz slab and adsorbate molecules were not relaxed when calculating the interaction energies. Two different sites on the silica surface are considered: site A above a 6-ring and site B above a Si atom. The difference ΔvdW-DF2 between our method and vdW-DF2 ranges from +0.5 to +1.2 kcal/mol (vdW-DF2 overbinds). This difference can be more than 50% in the case of weakly bound molecules (H_2, N_2, CH_4). Two other DC-DFT methods implemented in VASP were also used, namely PBE-D2 of Grimme[25] and optPBE of Klimeš *et al.*[29] Like in the case of the 2T model, the PBE-D2 interaction energies range from those of vdW-DF2 to those of our method, being close to their average in most cases. CH_4 is a notable case where PBE-D2 is much closer to vdW-DF2 and thus is likely to overbind significantly. The optPBE energies are strongly overbinded, even when compared to vdW-DF2. This might stem from the fact that optPBE is based on the original version of vdW-DF, which overbinds even more than vdW-DF2.

The mean relative difference between vdW-DF2 and vdW-DF/CC is 60% in the case of the 2T complexes while

TABLE III. The calculated binding energies (kcal/mol) of the molecules with the quartz surface. Two different sites, A and B, are considered.

Molecule	Site	vdW-DF2	vdW-DF/CC	ΔvdW-DF2[a]	PBE-D2	optPBE
CH_4	A	− 2.9	− 1.9	1.1	− 2.7	− 4.3
	B	− 3.1	− 1.8	1.3	− 2.8	− 4.5
CO_2	A	− 5.1	− 3.9	1.2	− 4.1	− 6.7
	B	− 4.0	− 3.0	1.0	− 3.3	− 5.6
H_2	A	− 1.7	− 1.1	0.6	− 1.4	− 2.3
	B	− 1.3	− 0.8	0.5	− 1.1	− 2.0
H_2O	A	− 4.8	− 4.3	0.5	− 4.6	− 5.6
	B	− 3.5	− 2.7	0.7	− 3.2	− 4.4
N_2	A	− 3.1	− 1.9	1.2	− 2.3	− 4.4
	B	− 2.4	− 1.4	1.0	− 1.9	− 3.7

[a]vdW-DF/CC − vdW-DF2

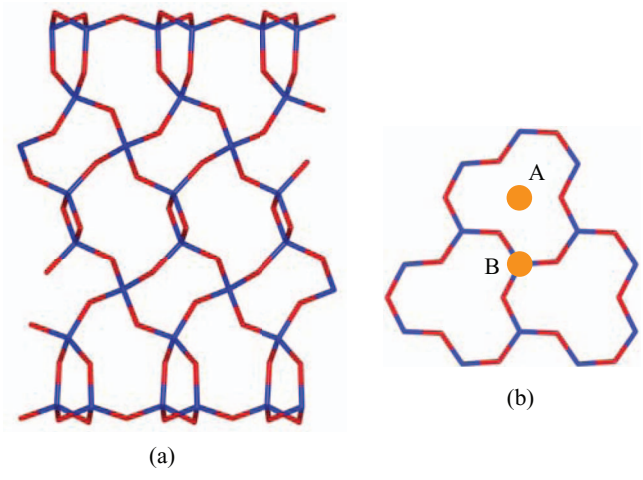

FIG. 5. The side (a) and top (b) views of the perfectly reconstructed α-quartz quartz surface slab for which the binding energies of the molecules were calculated. Sites A and B are marked by orange circles.

it is 50% in case of the quartz surface. In addition, a more detailed comparison reveals that the correspondence is present also in individual cases. This consistency can serve as an indirect evidence that the transferability of the parametrization from the cluster models to the extended surfaces is well-behaved. When this is combined with the excellent performance of vdW-DF/CC with respect to CCSD(T)/CBS on the 2T model, we can conclude that our method provides a comparable accuracy also for periodic systems.

C. Zeolite LTA

Isosteric heats of gas adsorption in purely siliceous microporous materials have been reported for general zeolite framework topologies. For comparison with experiment, we have calculated the binding energies of CH_4 and CO_2 with pure-silica zeolite LTA. These systems have been studied both experimentally and computationally.[30,31] The adsorption sites of the molecules in the purely siliceous LTA were taken from Ref. 31 and relaxed using vdW-DF2. The geometries of the isolated LTA and molecules were relaxed using vdW-DF2 when calculating the interaction energies to account for the deformation energy of adsorption. The vdW-DF/CC binding energies were evaluated to be 4.1 and 5.7 kcal/mol for CH_4 and CO_2, respectively. These values are very close to those of the original DFT/CC method. Corrected for zero-point vibrations (~ -0.5 kcal/mol),[31] they can also be very well compared to the experimental values of 3.6 and 5.0 kcal/mol for zero-coverage isosteric heats of adsorption.[30]

IV. SUMMARY

A novel correction scheme, vdW-DF/CC, has been implemented and tested for precise calculations of adsorbate–adsorbent interactions. The proposed scheme combines the reliable but not-so-accurate vdW-DF2 method and the system-specific DFT/CC correction scheme. The performance of vdW-DF/CC has been tested for a set of small molecules (CH_4, CO_2, H_2O, H_2, N_2) interacting with the perfectly reconstructed α-quartz surface and its cluster representation (the 2T model). The vdW-DF/CC results for the 2T model agree ($\sim$0.1 kcal/mol) with the binding energies calculated at the reference level of theory, CCSD(T)/CBS, whereas other DC-DFT methods tend to overbind for all investigated systems. Moreover, vdW-DF/CC results are fully consistent with the vdW-DF2 and PBE-D2 methods for quartz, indicating a very good performance of the method for real silica surfaces as well. This conclusion is further supported by the excellent agreement of vdW-DF/CC, DFT/CC, and the experimental adsorption heats for methane and carbon dioxide in the pure-silica zeolite LTA. In summary, the vdW-DF/CC correction scheme preserves the accuracy of DFT/CC and greatly simplifies its parametrization, thus extending its applicability to complex adsorbent–adsorbate systems.

ACKNOWLEDGMENTS

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