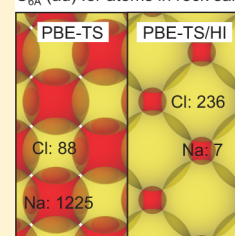


# Improved Density Dependent Correction for the Description of London Dispersion Forces

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## S Supporting Information

**ABSTRACT:** The Tkatchenko–Scheffler method for calculating dispersion correction to standard density-functional theory, which uses fixed neutral atoms as a reference to estimate the effective volumes of atoms-in-molecule and to calibrate their polarizabilities and dispersion coefficients, fails to describe the structure and the energetics of ionic solids. Here, we propose a more appropriate partitioning, based on the iterative Hirshfeld scheme, where the fractionally charged atomic reference state is determined self-consistently. We show that our new method extends the applicability of the original method in particular to study ionic systems and adsorption phenomena on surfaces of ionic solids.

 $C_{6A}$  (au) for atoms in rock salt

## 1. INTRODUCTION

One of the most critical failures of standard exchange-correlation functionals within density functional theory (DFT) is their inability to describe correctly dispersive forces. Recently, efforts to cure this shortcoming have been made at different levels of theory, ranging from simple additive dispersion corrections based on empirical pair potentials<sup>1–3</sup> to sophisticated many-body calculations using the random-phase approximation (RPA).<sup>4–6</sup> While the RPA includes accurate dispersion interactions seamlessly and yields an improved prediction of cohesive properties for a wide variety of molecular and solid-state systems, the price to pay for this performance consists of a computational effort that is for solids about 100 times larger than for standard DFT calculations using semilocal functionals.<sup>6</sup> On the other hand, the semi-empirical dipole–dipole dispersion corrections popularized by Grimme<sup>1–3</sup> demand only a marginally increased computational effort and rely on the hypothesis of a certain transferability of the empirical  $C_6$  coefficients in the pair potentials describing the dispersion corrections. These latter are usually represented in the following form:

$$E_{\text{disp}} = -\frac{1}{2} \sum_{A=1}^N \sum_{B=1}^N \sum_L \frac{C_{6AB}}{R_{AB,L}^6} f_{\text{damp}}(R_{AB,L}^6) \quad (1)$$

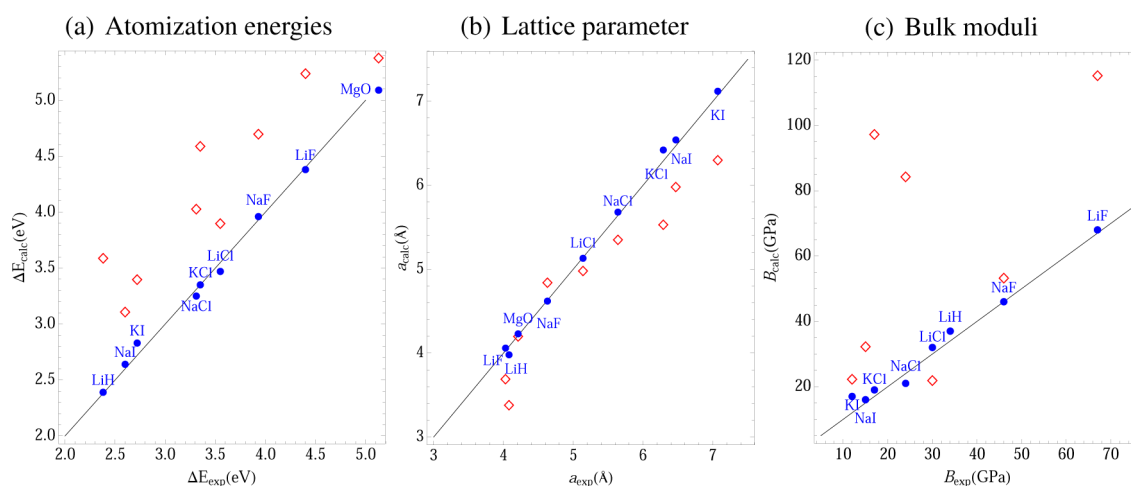
where the summations are over all atoms  $N$  and all translations of the unit cell  $L = (l_1, l_2, l_3)$ , the prime indicates that  $A \neq B$  for  $L = 0$ , and  $f_{\text{damp}}$  is a damping function whose role is to ensure that the  $C_6/R^6$  term contributes to  $E_{\text{disp}}$  only for distances that are longer than typical bonding distances, i.e., outside the region which is supposed to be well described by standard functionals.

Among the methods designed to avoid the strict transferability hypothesis (see e.g. ref 7), the technique proposed by Tkatchenko and Scheffler (TS)<sup>8</sup> calculates the  $C_6$  coefficients for pairs of atoms in a given molecular or solid environment by rescaling the polarizabilities  $\alpha_A^{\text{free}}$  and dispersion coefficients  $C_{6A}^{\text{free}}$  of the free atoms via a proportionality hypothesis linking the polarizabilities and volumes of the free atoms and of the atoms-in-molecule (AIM), as  $\alpha_A^{\text{TS}} = (V_A^{\text{AIM}}/V_A^{\text{free}})\alpha_A^{\text{free}}$ . Relying on the London formula, the AIM dispersion coefficients can be estimated as  $C_{6A}^{\text{TS}} = (V_A^{\text{AIM}}/V_A^{\text{free}})^2 C_{6A}^{\text{free}}$ . The volume ratio

$$\frac{V_A^{\text{AIM}}}{V_A^{\text{free}}} = \frac{\langle r_A^3 \rangle_{\text{AIM}}}{\langle r_A^3 \rangle_{\text{free}}} = \frac{\int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}}{\int r^3 n_A^{\text{free}}(\mathbf{r}) d^3\mathbf{r}} \quad (2)$$

is obtained from the electronic charge density, using the Hirshfeld (or stockholder) partitioning,<sup>9</sup> which attributes an atomic weight of  $w_A(\mathbf{r}) = n_A^{\text{free}}(\mathbf{r})/\sum_B n_B^{\text{free}}(\mathbf{r})$  to each point of space, based on the contribution at this point of each species to the total charge density of the promolecule, i.e., of a hypothetical charge density constructed as a superposition of spherical and neutral atom densities  $n_A^{\text{free}}(\mathbf{r})$ . Indeed, the TS method not only describes quite well molecular systems,<sup>10,11</sup> yielding accurate interaction energies for intermolecular complexes, but leads also to quite accurate cohesive energies, lattice constants, and bulk moduli for molecular solids and layered crystals.<sup>12,13</sup>

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**Figure 1.** Experimental vs calculated properties of several ionic solids. Left plot: atomization energies. Middle plot: lattice parameter. Right plot: bulk moduli. Red diamonds represent the results obtained with the TS method, blue dots the results obtained by the improved TS/HI method.

**Table 1.** The Atoms-in-Molecule Charges  $q_A$ , Volume-Scaling Factors, and the Homo-Atomic Dispersion Coefficients for Atoms in Selected Alkali Halide Crystals (Listed in Parentheses), Computed at the Experimental Geometries Using the Conventional and the Iterative Hirshfeld Partitioning<sup>a</sup>

	standard Hirshfeld			Hirshfeld-I			free atom/ion	
	$q_{\text{AIM}}$	$V_{\text{AIM}}/V_{\text{free}}$	$C_{6A,\text{AIM}}$	$q_{\text{AIM}}$	$V_{\text{AIM}}/V_{\text{free}}$	$C_{6A,\text{AIM}}$	$C_{6A,\text{atom}}$	$C_{6A,\text{ion}}$
Li (LiF)	0.181	0.865	1038.9	1.013	0.009	0.1	1384 <sup>b</sup>	0.078 <sup>c</sup>
F (LiF)	-0.181	0.935	8.3	-1.013	1.817	31.4	9.52 <sup>b</sup>	77.0 <sup>d</sup>
Na (NaCl)	0.202	0.887	1225.3	1.028	0.067	7.0	1444 <sup>b</sup>	1.700 <sup>e</sup>
Cl (NaCl)	-0.202	0.964	87.9	-1.028	1.578	235.5	94.6 <sup>b</sup>	351.0 <sup>d</sup>
K (KI)	0.191	0.884	3048.1	1.021	0.153	91.6	3870 <sup>b</sup>	23.30 <sup>e</sup>
I (KI)	-0.191	0.977	367.4	-1.021	1.449	807.8	385 <sup>b</sup>	1031 <sup>d</sup>

<sup>a</sup>For comparison, the dispersion coefficients for the neutral free atoms and the free cations and anions computed using high-level quantum chemical methods are listed. All quantities are in atomic units. <sup>b</sup>Ref 16. <sup>c</sup>Ref 17. <sup>d</sup>Ref 18. <sup>e</sup>Ref 19.

Recently, it has been suggested that the inclusion of dispersion interactions may improve also the predicted cohesive properties of ionic solids.<sup>14,15</sup> However, it turns out<sup>13</sup> that a straightforward application of the TS method leads to a rather gross overestimation of the influence of dispersion forces resulting in too large atomization energies and bulk moduli and too small lattice parameters of simple ionic solids, as illustrated in Figure 1.

One could argue that for ionic solids one simply does not need any dispersion correction, since they are quite well described already by usual density functional approximations. While it is true, one should bear in mind that there are mixed systems, like molecular adsorbates on the surface of ionic solids, where it is indispensable to include dispersion corrections in a single generic procedure valid for all bonding situations. Therefore, the aim of the present work is to analyze the reasons for the failure of the standard TS method for ionic systems and to propose a novel approach to determine dispersion coefficients applicable to all solids and molecules, irrespective of the oxidation state of their constituents.

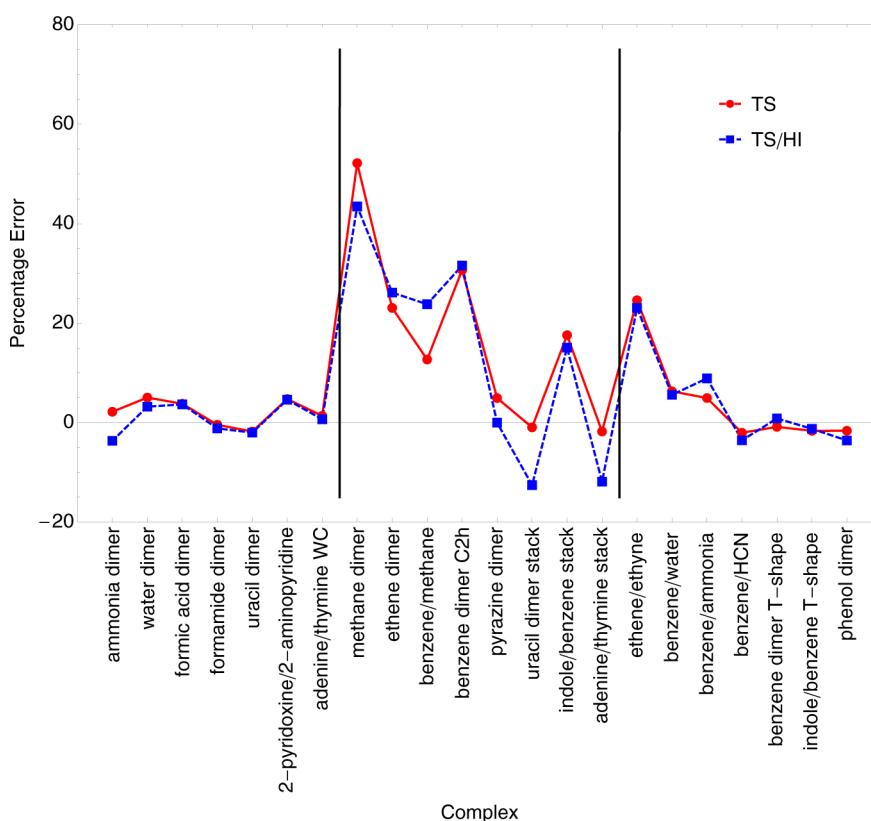
## 2. THE TS METHOD AND THE ROLE OF THE ATOMIC PARTITION

To analyze and understand the failure of the TS method for ionic systems, we have computed the AIM charge  $q_{\text{AIM}}$ , the AIM/free-atom volume ratio ( $V_{\text{AIM}}^{\text{AIM}}/V_{\text{free}}^{\text{free}}$ ), as well as the AIM dispersion coefficient  $C_{6A,\text{AIM}}$  for selected alkali halide crystals using the standard Hirshfeld partitioning (see Table 1), used by

the original TS method. The AIM charges vary around  $\pm 0.2$  electrons. The scaling factors for the volumes are close to unity, and the dispersion coefficients are close to the values calculated for free neutral atoms. These results are rather counterintuitive, since one would rather expect that in strongly ionic crystals the constituent AIMs and their physical properties are close to those of the noninteracting ions, whereas it is obviously not the case here.

As first pointed out by Nalewajski and Parr,<sup>20</sup> the Hirshfeld partitioning scheme can be interpreted as a minimization of the loss of information entropy with respect to the reference system. If neutral atoms are chosen as reference system, the total electronic density is partitioned in such a way that the resulting AIM densities are as similar to neutral atoms as possible. Hence the volume ratio  $V_{\text{AIM}}^{\text{AIM}}/V_{\text{free}}^{\text{free}}$  remains always close to unity and simply can not take significantly different values, as would be expected for ionic systems. As a consequence, the interaction parameters for atomic centers in alkali metal halides computed using the standard TS method are similar to those for neutral atoms, but completely different from those of the noninteracting ions.

As discussed in ref 21, the use of neutral atoms to define the promolecular density  $n_{\text{mol}}^{\text{free}}(\mathbf{r}) = \sum_B n_B^{\text{free}}(\mathbf{r})$  has no strict theoretical basis, and it would seem more natural in some cases to consider promolecular densities consisting of non-interacting cations and anions. Indeed, our exploratory calculations have shown that if noninteracting ions are used as reference in the Hirshfeld partitioning intervening in the TS



**Figure 2.** Relative errors for dimerization energies of intermolecular complexes from the S22 set<sup>27</sup> computed using two different variants of the Tkatchenko–Scheffler method: TS (continuous red line) and TS/HI (dashed blue line).

method, the predicted lattice constants, bulk moduli, and atomization energies are significantly improved for ionic systems. Unfortunately, the applicability of such a method is rather limited because of the unpleasant practical aspect that each reference state requires a different set of reference parameters (static polarizabilities, dispersion coefficients, atomic radii) that have to be computed using high-level *ab initio* methods. As many elements exist in multiple oxidation states, such an approach would require a significantly increased number of parameters. Another problem is that the oxidation state of the atoms constituting the system of interest must be known in advance and must not change significantly during the simulation. This restriction can be very limiting when studying, e.g., chemical reactions or compounds with charge transfer.

A natural solution to this problem consists of using the iterative Hirshfeld partitioning scheme (the Hirshfeld-I algorithm) proposed by Bultinck et al.,<sup>21,22</sup> where the reference state is not predefined, but it is determined iteratively, usually leading to a state with a noninteger electronic population. In the method we propose here, and which we designate hereafter as TS/HI, the weighting functions from the converged Hirshfeld-I method ( $w_A^{\text{HI}}$ ) are then employed in eq 2 to compute the effective volume ratio used in the Tkatchenko–Scheffler method.

In the Hirshfeld-I algorithm,<sup>21</sup> the electronic population of the atomic species  $A$  ( $N_A$ ) is calculated iteratively via

$$N_A^{i+1} = N_A^i + \int [n_A^i(\mathbf{r}) - w_A^i(\mathbf{r}) n(\mathbf{r})] d^3\mathbf{r} \quad (3)$$

where the weighting function for step  $i$  is computed from the previous iteration as  $w_A^i(\mathbf{r}) = n_A^{i-1}(\mathbf{r}) / (\sum_B n_B^{i-1}(\mathbf{r}))$ . The iterative promolecular density can be regarded as the superposition of

spherically symmetric fractionally charged atoms with  $N_A^i$  electrons and electronic densities  $n_A^i(\mathbf{r})$ , obtained by linearly interpolating between two different charge states of the same atom:

$$n_A^i(\mathbf{r}) = n^{\text{lint}(N_A^i)}(\mathbf{r}) [\text{uint}(N_A^i) - N_A^i] + n^{\text{uint}(N_A^i)}(\mathbf{r}) [N_A^i - \text{lint}(N_A^i)] \quad (4)$$

where  $\text{lint}(x)$  expresses the integer part of  $x$  and  $\text{uint}(x) = \text{lint}(x) + 1$ . The procedure defined above is iterated until the difference of the electronic populations in two subsequent steps  $\Delta_A^i = |N_A^i - N_A^{i+1}|$  is less than a predefined threshold for all atoms (in this study,  $\Delta_A^i < 5 \times 10^{-5}e$  was used). The starting charge densities  $n_A^0(\mathbf{r})$  can be chosen arbitrarily; the converged charge state of the atomic species is independent of this choice. A more detailed description can be found in ref 21. The difficult point in the HI algorithm is that the method requires also the charge density distributions for negatively charged free ions, although many of them are unstable. In our implementation, we have used the technique of Watson spheres,<sup>23</sup> where the anions are placed in the center of a sphere with a compensating positive charge (see Supporting Information for details).

In analogy to the standard TS method, only the reference data corresponding to neutral atoms (i.e.,  $\alpha_A^0$ ,  $C_{6,A}^0$ , and  $R_A^0$ ) are required. The AIM charges, scaling factors, and dispersion coefficients calculated for a few ionic solids using the Hirshfeld-I method are compiled in Table 1. The converged AIM charges are now close to  $\pm 1$ . The effective volumes occupied by the anions are much larger than those of the cations, and the dispersion coefficients are close to those of free cations and anions, as expected for ionic systems.

### 3. RESULTS

The calculations presented in this work have been performed by using the periodic DFT code VASP.<sup>24,25</sup> The exchange–correlation energy was determined using the Perdew–Burke–Ernzerhof (PBE) functional.<sup>26</sup> We have programmed in VASP the iterative Hirshfeld partitioning to calculate the corresponding AIM volumes, which optionally replaces the original partitioning scheme in our previous implementation<sup>13</sup> of the TS method. Technical details for all calculations discussed in this paper are presented in the Supporting Information.

**3.1. Ionic Systems.** The improvement due to the use of the iterative Hirshfeld partitioning is spectacular for simple ionic solids, as it has been illustrated in Figure 1: the structural and the energetic properties calculated with the iterative scheme reproduce almost perfectly the experimental values. This improvement can be attributed to the fact that the TS/HI method leads to a partition of the charge density to ionic species; therefore the interaction parameters are reasonably close to the free-ion values and account correctly for the confinement effects that are particularly important for anionic species. Moreover, for systems consisting of atoms with zero or nearly vanishing formal charge (rare-gas solids, apolar crystals, etc.), the TS/HI method predicts results that are practically identical to those with the standard TS method.

**3.2. Molecular Systems.** The above results are promising, since they remedy a notorious failure of the TS method, but we should ensure also that the overall performance is not deteriorated significantly by the use of the iterative Hirshfeld partitioning. One of the simplest tests is the reproduction of the experimental molecular  $C_6$  dispersion coefficients derived from pseudospectral dipole oscillator strength distributions (DOSD).<sup>7</sup> For a set of 1225 unique interaction pairs, formed by 50 molecules or atoms, the mean absolute relative error (MARE) is raised from 5.3% (5.5% reported by Tkatchenko<sup>8</sup>) using the conventional Hirshfeld partitioning to 8.6% in the iterative variant. Details of the calculation of molecular  $C_6$  dispersion coefficients and the numerical results are provided in the Supporting Information.

Similarly, a slight deterioration of the interaction energies has been found for the S22 weak intermolecular interaction database:<sup>27</sup> the MARE increases from 9.3% (TS) to 10.6% (TS/HI), and detailed numerical results for the S22 set are listed in Table S1. As can be seen in Figure 2, the percentage errors of both methods are quite similar for the different complexes. However, we remark that the agreement between TS and TS/HI is excellent for H-bonded and mixed complexes, but a certain deterioration of the interaction energies computed with the TS/HI method can be observed for the vdW complexes, in particular for two stacked structures: the uracil dimer and the adenine/thymine complex. Although several possible factors, like the neglect of anisotropy or of higher order multipole effects, can be evoked to explain this moderately good performance, shared by both the TS and TS/HI methods, we think that the most important factor is the neglect of many-body dispersion effects. Our preliminary results using the many-body correction scheme described in ref 28 seem to confirm this hypothesis. Their detailed discussion is, however, out of the scope of the present work and will be done elsewhere.

**3.3. Molecular Crystals.** Further tests were done on the C21 benchmark set of molecular crystals of Otero-de-la-Roza and Johnson.<sup>29</sup> Our calculations confirmed that the performance of the PBE-TS/HI method is similar to that of the PBE-

TS method: we observed a slight improvement of computed lattice energies (17.32 kJ/mol (PBE-TS) vs 16.71 kJ/mol (PBE-TS/HI)) and a slight deterioration of the lattice parameters (from an error of 0.091 Å to 0.135 Å and from 0.10° to 0.17° for the lattice vector lengths and angles, respectively) for the TS/HI approach with respect to the original TS scheme. Detailed numerical results for the C21 scheme are provided in the Supporting Information (see Tables S2 and S3). We remark that Reilly and Tkatchenko have recently revisited this reference set and added to it two further systems.<sup>30,31</sup> These authors have shown that the lattice energies are dramatically improved when many-body effects are taken into account (MAE = 5.91 kJ/mol), and a further improvement is achieved by replacing the PBE functional with hybrid functional PBE0<sup>32</sup> (MAE = 3.92 kJ/mol). These facts corroborate our hypothesis that many-body effects may improve the behavior of the S22 set too.

**3.4. Molecules Adsorbed on Solids.** In order to illustrate the significantly improved performance of the TS/HI method for adsorption on ionic surfaces, we have studied the H<sub>2</sub>O/MgO(100) and the CO/MgF<sub>2</sub>(110) systems as well as the adsorption of argon and various molecules (O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>) on the Brønsted acid site of the zeolite chabazite. Our results are compared with either experimental data (where available) or with results of high-level wave function-based methods. The interaction energies calculated at the PBE, TS, and TS/HI levels are reported in Table 2 together with the reference data.

**Table 2. Interaction Energies (kJ/mol) of Molecules on Ionic Surfaces and in Zeolite Chabazite (CHA)**

system	PBE	PBE-TS	PBE-TS/ HI	ref.
MgO(100)/H <sub>2</sub> O	−35.6	−54.0	−46.5	−44.4 to −46.4 <sup>a</sup>
MgF <sub>2</sub> (110)/CO	−34.9	−52.4	−43.6	−36.0 <sup>b</sup>
CHA/Ar	−2.9	−21.4	−17.1	−17.1 <sup>c</sup>
CHA/O <sub>2</sub>	−5.3	−25.3	−19.5	−19.8 <sup>c</sup>
CHA/N <sub>2</sub>	−11.7	−33.9	−27.5	−23.7 <sup>c</sup>
CHA/CH <sub>4</sub>	−5.1	−37.7	−27.6	−25.7 <sup>c</sup>

<sup>a</sup>Ref 33. <sup>b</sup>Ref 34. <sup>c</sup>Estimated from experimental values of  $\Delta H_{\text{ads}}$  from refs 35 and 36.

Using cluster model calculations with wave function based methods, Karalti et al.<sup>33</sup> found an adsorption energy of −44.4 kJ/mol, while they obtained −46.4 kJ/mol with a diffusion Monte Carlo (DMC) slab model. Our PBE calculations (−35.6 kJ/mol) strongly underestimate the adsorption energy, while on the contrary the bare TS method gives a too large value of −54.0 kJ/mol. However, when using our newly proposed scheme, we obtain a value of −46.5 kJ/mol, in very good agreement with the data by Karalti et al.<sup>33</sup>

As a reference for the interaction energy between CO and MgF<sub>2</sub>(110), we use the CCSD(T)<sub>incr</sub> and MP2<sub>incr</sub> calculations of Hammerschmidt et al.,<sup>34</sup> which predict a  $\Delta E_{\text{int}}$  of −36.0 and −37.1 kJ/mol, respectively. In this case, PBE predicts an adsorption energy of −34.9 kJ/mol, already in very close agreement with the reference data. As in the previous cases, the TS method strongly overestimates interaction ( $\Delta E_{\text{int}}$  = −52.4 kJ/mol), but the TS/HI method leads to a clear improvement ( $\Delta E_{\text{int}}$  = −43.6 kJ/mol).

The final application we wish to discuss is the adsorption of small probe molecules in the acid zeolite chabazite. Zeolites are microporous aluminosilicates built as a network of SiO<sub>4</sub>



tetrahedra stabilized by ionic-covalent Si–O bonds. The electron deficit created by substituting a Si atom of the framework by an Al atom must be compensated by attaching, e.g., a hydrogen atom to an oxygen atom close to the Al. Formally, the electron is transferred to the framework, creating a OH group with acidic properties. Calculations with the PBE functional without dispersion corrections underestimate the experimental interaction energies for Ar, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> by a factor of 2 to 5. The TS method, again, overestimates the experimental  $\Delta E_{\text{int}}$  by 25–47%, while the TS/HI scheme predicts adsorption energies in very good agreement with experimental data.

As shown in Table 3, the TS and TS/HI methods lead to a qualitatively different description of the dispersion interactions

**Table 3. Homoatomic Dispersion Coefficients  $C_6$  (au) in Selected Adsorbent/Adsorbate Systems Resulting from TS and TS/HI Methods<sup>a</sup>**

system	atom	PBE-TS	PBE-TS/HI
MgO(100)/H <sub>2</sub> O	H'	3.8	1.4
	O'	13.7	32.9
	Mg	415–515	1.4–1.5
	O	14.3–14.7	152–184
MgF <sub>2</sub> (110)/CO	C'	27.7	29.7
	O'	11.0	12.0
	Mg	353–447	2.9–7.2
	F	7.9–9.3	24.1–28.3
CHA/Ar	Ar'	53.1	51.8
	H	3.5	0.5
	O	11.5–13.2	60.3–84.6
	Si	187–195	3.1–3.4
CHA/O <sub>2</sub>	Al	301	1.6
	O'	11.7	11.0
	H	3.4	0.6
	O	12.4–13.2	59.9–84.2
CHA/N <sub>2</sub>	Si	186–195	3.0–3.4
	Al	298	1.6
	N'	16.1	14.7
	H	3.5	0.7
CHA/CH <sub>4</sub>	O	11.6–13.2	59.9–83.6
	Si	187–194	3.0–3.4
	Al	298	1.7
	H'	2.7–3.0	1.4–1.7
	C'	27.5	65.7
	H	3.3	0.4
	O	11.5–13.2	59.9–83.9
	Si	185–192	3.1–3.4
	Al	296	1.7

<sup>a</sup>Prime indicates atoms of the adsorbate molecules.

in all the examples discussed here. In TS calculations, the dominant contributions arise from interactions of the adsorbate with the strongly polarizable neutral Mg and Si(Al) atoms (with large  $C_6$  coefficients), with only very small contributions from O or F atoms. The TS/HI method assigns more realistic charges to the constituents of the solid and predicts stronger dispersion interactions of the adsorbate with the negatively charged and hence more polarizable O or F anions. Interestingly, this does not seem to affect dramatically the geometry of the adsorbate–substrate complex in the studied examples. For MgF<sub>2</sub>/CO and MgO/H<sub>2</sub>O, a rather strong bonding of the adsorbate to the substrate through C–Mg and

O–Mg bonds is predicted already at the PBE level. The dispersion interactions with the anions do not affect the adsorption geometry because the anions are arranged symmetrically around the Mg cation. Similarly, although the TS method predicts a stronger dispersion interaction of the adsorbate with the Si atoms and the TS/HI approach with the O atoms of the framework, the geometry of the adsorption complex remains almost unchanged because of the symmetry of the SiO<sub>4</sub> tetrahedra.

Finally, it is interesting to remark that in the examples studied here, albeit the considerable variations of the  $C_6$  coefficients, the preferred adsorption sites seem to be insensitive to the choice of partitioning scheme. This fact can be illustrated in the case of CO adsorption on the MgF<sub>2</sub>(110) surface. Here the CO⋯Mg dispersion contribution is only 0.9 kJ/mol (out of total vdW energy of 17.9 kJ/mol) when using PBE-TS and 0.7 kJ/mol (out of 7.8 kJ/mol) for the PBE-TS/HI method. It means that, despite the large difference between the  $C_6$  coefficients determined for the adsorption site (Mg) using the TS (472 au) and the TS/HI (7.2 au) methods, the vdW contributions resulting from the interaction between the CO and the adsorption site are very similar. This—at first sight surprising—result can be explained by the fact that in the Tkatchenko–Scheffler method, increasing the value of the dispersion coefficient is automatically accompanied by a stronger damping.

#### 4. SUMMARY AND CONCLUSIONS

In summary, we have examined the performance of the Tkatchenko–Scheffler method for the calculation of the cohesive properties of ionic solids and adsorption energies of molecules on ionic surfaces. We have shown that the original TS method strongly overestimates binding energies, leading to too small lattice constants and too large bulk moduli compared to experimental results. The use of an inadequate charge partitioning scheme (standard Hirshfeld method) has been identified as the origin of this problem. This limitation can be overcome by coupling the TS method with the iterative Hirshfeld partitioning,<sup>21</sup> which permits one to determine realistic effective dispersion coefficients of the atoms in a molecule or a solid by rescaling the values calculated for the free neutral atom according to the effective charge state. We have shown on a set of solid state alkali metal halides that this method overperforms the standard TS method and predicts lattice constants and bulk moduli of comparable quality with the uncorrected PBE functional, while the atomization energies are significantly improved. Moreover, the TS/HI method is particularly valuable for systems of mixed character, such as molecules adsorbed on outer or inner surfaces of predominantly ionic solids, as we demonstrated in the cases of adsorption of small molecules on MgO(100) and MgF<sub>2</sub>(110) surfaces, and in acid chabazite. In all of these cases, the TS/HI method predicted more realistic interaction energies than the standard TS method while keeping a moderate numerical cost.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Details on calculation of reference charge densities used in the iterative Hirshfeld algorithm, molecular  $C_6$  coefficients computed for 1225 pairs of atoms or molecules, numerical results for the S22 and C21 sets, and technical details of simulations presented in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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