

# Semiempirical van der Waals correction to the density functional description of solids and molecular structures

F. Ortmann and F. Bechstedt

*Institut für Festkörperteorie und -optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany*

W. G. Schmidt

*Theoretische Physik, Universität Paderborn, Warburger Straße 100, 33098 Paderborn, Germany*

(Received 8 February 2006; published 2 May 2006)

The influence of a simple semiempirical van der Waals (vdW) correction on the description of dispersive, covalent, and ionic bonds within density functional theory is studied. The correction is based on the asymptotic London form of dispersive forces and a damping function for each pair of atoms. It thus depends solely on the properties of the two atoms irrespective of their environment and is numerically very efficient. The correction is tested in comparison with results obtained using the generalized gradient approximation or the local density approximation for exchange and correlation. The results are also compared with reference values from experiment or quantum chemistry methods. In order to probe the universality and transferability of the semiempirical vdW correction, a range of solids and molecular systems with covalent, heteropolar, and vdW bonds are studied.

DOI: [10.1103/PhysRevB.73.205101](https://doi.org/10.1103/PhysRevB.73.205101)

PACS number(s): 61.50.Lt, 71.15.Mb, 71.15.Nc

## I. INTRODUCTION

The dispersive interaction between atoms and molecules is important for many molecular and solid structures. The bonding and energetics of such systems is often studied using density functional theory (DFT).<sup>1,2</sup> Thereby the exchange-correlation (XC) functional is usually modeled using the local density approximation (LDA) (Ref. 2) or the generalized gradient approximation (GGA) in various flavors, e.g., Refs. 3–5. In many instances, e.g., for hydrogen-bonded systems,<sup>6</sup> GGA allows for a systematic improvement over the LDA in describing chemical bonds. Whereas LDA or GGA give excellent results for many dense matter systems, these approaches are often far less accurate in describing layered and liquid crystals, polymers, proteins, and biomolecular surfaces. Crystalline graphite is one prominent example in that respect. Moreover, the interaction of atoms, molecules, or surfaces at large separations is often not correctly described within LDA or GGA.

This failure is attributed to the van der Waals (vdW) or dispersive interaction between the electrons. Its nonlocality necessarily renders all trials to include vdW effects in the XC functional numerically extremely expensive. The adiabatic connection-fluctuation theorem for the correlation energy of an inhomogeneous electron gas<sup>7</sup> leads to a seamless vdW density functional.<sup>8,9</sup> However, the numerical expense restricts its application to the interaction between atoms in molecules or to the interaction between jellium slabs. This holds also for the recently proposed general density functional for asymptotic vdW forces.<sup>10,11</sup> The spirit of the latter approach<sup>12</sup> is close to that of London,<sup>13,14</sup> describing the interaction of atoms separated by large distances.

The increasing interest in soft condensed matter requires appropriate computational tools that allow for an efficient yet accurate treatment of dispersive interactions. Although electron correlation is a quantum-mechanical phenomenon, the

vdW interaction can be understood as interaction between instantaneous fluctuating dipoles. The resulting asymptotic behavior proportional to  $R^{-6}$  with  $R$  as the distance between two neutral fragments suggests the replacement of the vdW contribution to the energy functional by an empirical correction. This has been studied by several groups, see, e.g., Refs. 15–21. They add an attraction  $\propto -f(R)C_6R^{-6}$  to the interaction of two atoms separated at a distance  $R$ . The corrections differ with respect to the damping function  $f(R)$  and the coefficient  $C_6$  of the pair interaction. The approaches have been applied to the hydrogen bonding and stacking interaction of nucleic acid pairs, rare-gas diatomic molecules, graphite, and larger molecules or molecular dimers or trimers. Furthermore, the approach has been applied to investigate molecular adsorption on graphite.<sup>22</sup> Despite these large number of applications, a comprehensive investigation of the reliability of such an empirical correction—using a fixed set of parameters and a fixed damping procedure—for a variety of typical bonding scenarios is still missing. Therefore it is difficult to assess the merits of such an approach for routine calculations. This issue is addressed in the present work. We use the pair interaction energy in the damped form and keep the functional dependence of  $f(R)$  as well as the occurring scaling parameters and the  $C_6$  coefficients fixed, in order to investigate the universality and transferability of such an empirical scheme.

The limits of the approach are immediately obvious. (i) Terms higher in power than  $R^{-6}$  due to interacting pairs with additional partners are neglected. These modifications are not included here because they dominate for intermediate distances where the damping is applied. (ii) Metals have been shown to obey a different power law, due to the free electron motion. However, following Dobson<sup>23</sup> we can assume that for finite metallic systems (e.g., with impurities) and finite temperature the  $R^{-6}$  dependence is recovered. (iii) The approach may also be inadequate in the limit of ionized frag-

ments where the atomic polarizabilities change significantly. However, these systems are not our primary targets, because they are dominantly bonded through classical electrostatics. (iv) Even for covalently bonded atoms, changes in the polarizability of up to 30% can be expected for different bonding configurations, see, e.g., Ref. 24. While this effect can easily be taken into account using the semiempirical method described here, it requires an *a priori* knowledge about the bonding configuration.

Below, first the DFT implementation and the empirical vdW correction are described, before results for various systems with covalent, ionic and vdW bonds are presented and discussed. The quantities considered are binding energies, bond lengths, vibrational frequencies (or corresponding force constants/elastic constants), and bulk moduli (for solids only).

## II. COMPUTATIONAL METHODS

### A. Implementation of the density functional theory

The total-energy and electronic-structure calculations have been performed within the DFT (Refs. 1 and 2) using the Vienna *ab initio* Simulation Package (VASP).<sup>25,26</sup> Apart from the vdW interaction discussed below, exchange and correlation effects are treated within two approximations: For the XC functional either the (i) LDA using the Perdew-Zunger parametrization<sup>27</sup> of quantum Monte Carlo results for the homogeneous electron gas<sup>28</sup> or (ii) the GGA according to Perdew and Wang<sup>4</sup> (PW91) is applied.

The interaction of the valence electrons with the nuclei is modeled either by means of non-norm-conserving Vanderbilt pseudopotentials<sup>29,30</sup> or using the projector-augmented wave method.<sup>31</sup> The wave functions are expanded in plane waves. For molecular systems a cutoff energy  $E_{\text{cut}}=35$  Ry was found to be sufficient,<sup>32</sup> for graphite convergence was achieved with  $E_{\text{cut}}=26.3$  Ry. Nonlinear core corrections<sup>33</sup> are taken into account for Cl, Na, Si, Ne, Ar, and S.

The atomic geometries of the studied solids, molecules and dimers are optimized by minimizing the energy functionals within the respective approximations. The convergence criterion for the Hellmann-Feynman forces is set to 10 meV/Å. Zero-point energies and zero-point vibrations are neglected in the calculation of cohesive energies and bond lengths, respectively. Their influence is small in most crystalline solids. For BN, e.g., the zero-point energy amounts to approximately 2% of the cohesive energy.<sup>34</sup> For crystalline solids we apply the Birch equation of state<sup>35</sup> to fit total energy curves. The fit yields the equilibrium energy, the isothermal bulk modulus  $B_0$  and the equilibrium volume. Thereby the energy alignment is done using the spin interpolation formula<sup>36</sup> for the spin-polarized ground state of each atom. The relaxed equilibrium geometries serve as starting points for the calculation of characteristic vibrational modes using the frozen-phonon approximation.<sup>37</sup>

In order to model molecules in the gas phase, we use a periodic arrangement of supercells. These must be large enough to avoid interactions between the molecule and its images. As convergence criterion we require that the Kohn-Sham eigenvalues of the occupied molecular states show a

band dispersion below 0.1 eV and are converged within 0.1 eV. In the case of molecules and dimers we use  $20 \times 20 \times 20 \text{ \AA}^3$  supercells in order to guarantee a distance of about 10 Å between the outermost atoms of the molecule and its images.

We perform the Brillouin zone (BZ) integration using Monkhorst-Pack points.<sup>38</sup> Sets of  $16 \times 16 \times 7$  and  $8 \times 8 \times 8$  points are used for graphitic systems and fcc crystals, respectively. In the case of large supercells containing molecules, the dispersion of the electron bands is vanishing. Therefore we sample the BZ just with the  $\Gamma$  point.

### B. Semiempirical description of van der Waals interaction

In order to account for the long-range electron correlation, the interaction of each pair  $i, j$  of atoms at  $\mathbf{R}_i$  and  $\mathbf{R}_j$  with  $R=|\mathbf{R}_i-\mathbf{R}_j|$  is corrected by the additional attractive energy

$$\varepsilon_{ij}^{\text{vdW}} = -f_{ij}(R) \frac{C_6^{ij}}{R^6}, \quad (1)$$

where  $f_{ij}(R)$  is the damping function which equals one for large values of  $R$  and zero for small values of  $R$ . The asymptotic form of (1) for  $R \rightarrow \infty$  is chosen in agreement with the original description of the dispersion energy by London.<sup>13,14,39</sup> He derived a virial coefficient of

$$C_6^{ij} = \frac{3}{2} \alpha_i \alpha_j \frac{I_i I_j}{I_i + I_j}, \quad (2)$$

where  $I_i$  is the ionization potential and  $\alpha_i$  the polarizability of the atom at  $\mathbf{R}_i$ . London interpreted  $I_i$  to be a characteristic energy (or frequency) of the atom  $i$ . Its replacement by the ionization potential should be sufficient since the main frequency gives rise to the leading contribution to the molecular forces.<sup>39</sup> The experience with the use of Eq. (2) in molecular-mechanics force fields shows a tendency for an overestimation of the vdW interaction.<sup>24</sup> We will come back to this point later in the paper.

The vdW interaction in formulas (1) and (2) applies to pairs of atoms irrespective of their environment. In order for the approach to be universal, we apply formula (2) to both homogeneous and heterogenous pairs of atoms. According to Halgren,<sup>24</sup> good results for the vdW interaction of different species require combination rules to calculate the coefficients  $C_6^{ij}$ . One of these approximations is the Slater-Kirkwood formula,<sup>40</sup> which should give a better description for different atoms than the original London version.<sup>24,41</sup> Nevertheless, to avoid additional assumptions, we use the original description of the dispersion forces according to Eq. (2).

The polarizabilities<sup>41,42</sup> and ionization potentials<sup>32</sup> may in principle be calculated from first principles. The polarizability can be constructed from the eigenfunctions and eigenvalues of the Kohn-Sham equation which is solved for the free atoms in an all-electron scheme. The ionization potentials can be derived within the delta-self-consistent field method.<sup>43</sup> For simplicity, however, we use the experimental values.<sup>44</sup>

For small atomic distances the vdW interaction does not play a role. Several damping functions  $f_{ij}(R)$  have been sug-

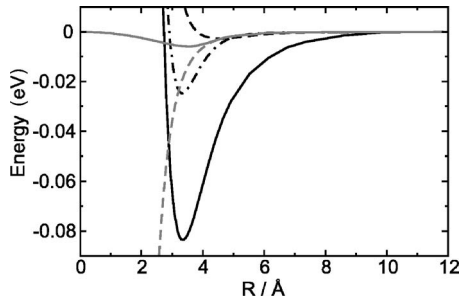


FIG. 1. Van der Waals interaction energy (1) of a pair of carbon atoms (solid grey line) versus atom distance. For comparison, the shape of the pure London form (dashed grey line) is also shown. Black lines represent total energy curves of one carbon atom in bulk graphite as a function of interlayer distance within LDA (dashed-dotted), GGA (dashed), and GGA+vdW (solid). The vdW energy (difference between GGA and GGA+vdW) results as the sum over all pair interactions as described in the text.

gested to cancel the  $R^{-6}$  singularity.<sup>15,17,18,45,46</sup> A Fermi function was included in our test studies and gave reasonable results. The data presented here, however, have been computed using an exponential decay function

$$f_{ij}(R) = 1 - \exp[-\lambda x_{ij}^n], \quad (3)$$

$$x_{ij} = R/(r_{\text{cov}}^i + r_{\text{cov}}^j), \quad (4)$$

for which all derivatives exist. In Eq. (4) the atomic distance  $R$  is normalized to a characteristic covalent bond length that is represented as the sum of the covalent radii  $r_{\text{cov}}^i$  and  $r_{\text{cov}}^j$  of the two interacting atoms. We use the values from Ref. 47. This normalization completes the scheme in a coherent manner and allows for the application of the damping function (3) to any pair of atoms. The smallest exponent  $n$  in Eq. (3) for which the singularity and, more accurately, the vdW interaction disappears at  $R=0$  is  $n=7$ . We choose  $n=8$  for which expression (3) goes quadratically to zero for small distances. The damping constant  $\lambda=7.5 \times 10^{-4}$  is chosen to reproduce the  $c$ -lattice constant of graphite and then used throughout this study.

The vdW interaction (1) with the damping function (3) is presented in Fig. 1 for a pair of carbon atoms. For  $R \rightarrow \infty$  it shows the asymptotic behavior of the London formula. Its shape for small separations  $R$  is governed by the damping function. The interplay of both for intermediate distances leads to an attractive potential in the vdW regime that takes its minimum at an atomic distance  $R_{\text{min}} \approx 2.3(r_{\text{cov}}^i + r_{\text{cov}}^j)$ . Its effect at covalent distances is weak. This means that the vdW pair interaction of the form (1) mainly acts at large distances and tends to decrease the bond lengths. However, the effect of attraction is relatively small. For a pair of carbon atoms it only amounts to 3 meV at about  $R \approx R_{\text{min}}$  (see Fig. 1). Despite the smooth damping function the approach cannot be proved to be seamless in the intermediate regime for arbitrary systems. Until now, however, we have not yet seen deviations from well behavior on the relevant energy scale.

TABLE I. Cubic lattice constant  $a_0$  (Å), bulk modulus  $B_0$  (GPa), and cohesive energy  $E_{\text{coh}}$  (eV/atom) of diamond (first line), silicon (second line), and NaCl (third line) crystals in three approximations for exchange and correlation. The relative difference of the experimental data with respect to the values from GGA ( $\Delta_{\text{GGA}}$ ) and GGA+vdW ( $\Delta_{\text{vdW}}$ ), respectively, is expressed in the last columns in percent.

	LDA	GGA	GGA+vdW	Expt.	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$a_0$	3.528	3.568	3.549	3.567 <sup>a</sup>	$\sim 0$	+0.5
	5.393	5.459	5.450	5.431 <sup>a</sup>	-0.5	-0.3
	5.455	5.674	5.612	5.595 <sup>b</sup>	-1.4	-0.3
$B_0$	464	431	442	442 <sup>a</sup>	+2.6	$\sim 0$
	95.1	87.9	88.9	98.8 <sup>a</sup>	+12	+11
	32.0	22.9	27.0	24.9 <sup>c</sup>	+8.7	-7.8
$E_{\text{coh}}$	8.79	7.55	7.80	7.35 <sup>d,e</sup>	-2.6	-5.8
	5.28	4.57	4.64	4.62 <sup>d</sup>	+1.1	-0.4
	6.99	6.30	6.70	6.61 <sup>d</sup>	+4.9	-1.3

<sup>a</sup>Reference 49.

<sup>b</sup>Reference 50.

<sup>c</sup>Reference 51.

<sup>d</sup>Reference 44.

<sup>e</sup>Reference 52.

For the use in the total energy functional of the DFT, the pair interaction energies are summed up over all possible combinations of two atoms in the considered system. The resulting vdW energy  $E^{\text{vdW}} = \frac{1}{2} \sum_{i,j} \epsilon_{ij}^{\text{vdW}}$  is added to the total energy functional of the DFT. This influences the calculated equilibrium positions and thus, indirectly, the electronic structure. It is not expected that remarkable changes for the polarizabilities are induced by the vdW forces. This assumption is corroborated by the work of von Lilienfeld *et al.* who concluded that electronic quantities remained unchanged in spite of an additional electron core potential to account for dispersion interaction.<sup>48</sup>

In the following, we present results obtained by using the PW91 energy functional corrected by  $E^{\text{vdW}}$ . This can be interpreted as the use of a DFT in which the XC functional in LDA is corrected by generalized gradient corrections at intermediate distances (of the order of the bond lengths) and by the vdW interaction at larger distances (of the order of several bond lengths). We mention, that other authors also probed successfully a vdW correction of LDA results.<sup>18</sup> However, for soft matter systems with typically high electron-density gradients, the GGA is expected to be the more accurate starting point for electronic structure calculations than the LDA.

### III. RESULTS AND DISCUSSION

#### A. Solids

##### 1. Covalent and ionic bonding in crystals

After having adjusted our damping model with the graphite lattice constant, we investigate its influence on the covalently bonded bulk silicon and diamond. Here only little

TABLE II. Structural, elastic, and energetic parameters of graphite (first line) and h-BN (second line) from DFT calculations within the three approximations in comparison to experimental data and other semi-empirical methods (units as in Table I,  $E_{\text{ex}}$  in meV,  $c_0$  in Å, and  $C_{33}$  in GPa). Energies in units per atom (C) and units per pair (BN). The difference of the latter with respect to the values from GGA ( $\Delta_{\text{GGA}}$ ) and GGA+vdW ( $\Delta_{\text{vdW}}$ ), respectively, is expressed in the last columns in %.

	LDA	GGA	GGA + vdW	Expt.	other methods	$\Delta_{\text{GGA}}$	$\Delta_{\text{GGA+vdW}}$
$a_0$	2.441	2.462	2.455	2.459 <sup>a</sup>	2.465 <sup>j</sup>	-0.1	+0.2
	2.481	2.504	2.496	2.504 <sup>b</sup>		~0	+0.3
$c_0$	6.66	~9.1	6.69	6.672 <sup>a</sup>	6.76 <sup>j</sup>	-27	-0.3
	6.49	~9.0	6.55	6.652 <sup>b</sup>		-26	+1.6
$C_{33}$	29.8	~1.3	41.7	41 <sup>c</sup>			-1.7
	29.4	~1	43.2	32.4 <sup>d</sup>			-25
$E_{\text{ex}}$	24.8	~3	83.5	35–52 <sup>e-g</sup>	38.5 <sup>j</sup> , 54–57 <sup>k</sup>		
	55	~5	191				
$E_{\text{coh}}$	8.78	7.72	7.86	7.37 <sup>h</sup>	9.01 <sup>j</sup>	-4.5	-6.2
	15.70	13.78	14.09	13.3 <sup>h,i</sup>		-3.5	-5.6

<sup>a</sup>Reference 55.

<sup>b</sup>Reference 54.

<sup>c</sup>Reference 58.

<sup>d</sup>Reference 59.

<sup>e</sup>Reference 60.

<sup>f</sup>Reference 56.

<sup>g</sup>Reference 57.

<sup>h</sup>Reference 44.

<sup>i</sup>Reference 49.

<sup>j</sup>Reference 20.

<sup>k</sup>Reference 18.

changes are expected to result from the inclusion of the vdW term. Results for structural properties and total energies of both crystals are listed in Table I for the three different approximations LDA, GGA, and GGA+vdW. They are compared with experimental findings.<sup>44,49–52</sup> Indeed, the effect of the vdW interaction on covalently bonded crystals is small but measurable. It reduces the relatively strong correction of the LDA overbinding by generalized gradient corrections. Therefore all the data influenced by the vdW interaction (but based on the GGA functional) are in between the values calculated within the “pure” density functional theory but different LDA and GGA XC functionals. The vdW interaction reduces the bond lengths and gives rise to larger bulk moduli and cohesive energies. In comparison to measured values, the GGA and GGA+vdW treatments lead to better agreement with experiment than the LDA. However, there is no clear trend in the performance of GGA+vdW with respect to GGA. Obviously, however, the vdW correction does not worsen the agreement with experiment.

Results for the ionic crystal NaCl, also displayed in Table I, show the same behavior as observed for covalent crystals. However, the dispersion corrections to GGA are more emphasized for NaCl than for diamond or silicon. We mentioned earlier that interactions between ionized fragments are not necessarily improved. For NaCl, however, this is not obvious, showing the robustness of the approach. Since both GGA and GGA+vdW outcomes for structural, energetic, and elastic properties agree well with experiment, we conclude that using the additional van der Waals term does not worsen

the results obtained for covalent and ionic bonds in bulk materials. This is important, e.g., for studies of surface-molecule interactions and can be understood comparing covalent (or even electrostatic) and dispersive energies: Commonly the latter is orders of magnitude smaller.

## 2. Graphitic structures

We now turn to electronic systems which deviate more strongly from homogeneous electron gases. The reliability of standard DFT approximations is questionable for large scaled density gradients ( $\propto |\nabla n|/n^{4/3}$  or  $\propto |\nabla n|/n^{7/6}$ )<sup>53</sup> such as in the cases of graphite and graphitic BN. The geometry of the hexagonal polytype of boron nitride (*h*-BN) is shown in Ref. 54. The *a*- and *c*-lattice constant of hexagonal crystals determine the structure. From the point of view of interlayer bonding, the most interesting vibrational quantity is the longitudinal-optical (LO) vibration accompanied by atomic displacements in the *c*-axis direction. We calculate the corresponding elastic coefficients  $C_{33}$ . The energetics of the crystal is characterized by two quantities, the cohesive energy  $E_{\text{coh}}$  and the exfoliation energy  $E_{\text{ex}}$ . In particular the latter is very sensitive to the interlayer bonding. The results in the three approximations LDA, GGA, and GGA+vdW are compared in Table II. Additionally we list experimental data<sup>44,49,54–60</sup> following Hasegawa and Nishidate<sup>18</sup> for the re-interpretation of the results for the graphite interplanar cohesive energy.<sup>56</sup>

We first discuss carbon-based graphite. The LDA shows the characteristic overbinding, apart from two quantities re-



TABLE III. Structural and elastic properties of neon (first line) and argon (second line) crystals. Units and deviations  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA+vdW	CCSD(T)	Expt.	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$a_0$	3.865	4.585	4.562	4.3 <sup>a</sup>	4.464 <sup>b</sup>	-2.6	-2.1
	4.943	6.068	6.002	5.3 <sup>a</sup>	5.311 <sup>c</sup>	-12	-12
$B_0$	8.6	1.8	2.1	1.9 <sup>a</sup>	1.12 <sup>b</sup>	-38	-47
	7.2	0.83	0.91	3.8 <sup>a</sup>	2.66 <sup>c</sup>		

<sup>a</sup>Reference 64.<sup>b</sup>Reference 66.<sup>c</sup>Reference 65.

lated to its layered structure, namely,  $E_{\text{ex}}$  and  $C_{33}$ . They demonstrate that the interlayer binding energy is underestimated despite a  $c$ -lattice constant slightly smaller than the experimental value. In Fig. 1 the corresponding total energy curves are compared revealing the sensitivity of the graphite structures to details of the XC functional. The GGA approach does not result in a stable graphite crystal for reasonable lattice constants. According to the calculation, the crystal decays into isolated graphene sheets. This result is well-known from other GGA calculations.<sup>18,61–63</sup>

The inclusion of the vdW interaction stabilizes the graphite crystal. The lattice constants resemble the measurement. The elastic constant  $C_{33}$  agrees well with findings of Gauster<sup>58</sup> in the low temperature regime. For the corresponding LO phonon at the  $\Gamma$  point, we find a frequency of 4.1 THz. The binding energy  $E_{\text{ex}}$  shows some overestimation of the interlayer bonding. Slight differences between our values for  $E_{\text{ex}}$  and the experiment are expected due to the neglect of the zero-point energy. More important, however, is probably the use of the ionization potentials<sup>24</sup> in the London formula (2) for the vdW molecular coefficients (see also Ref. 18). In any case, Table II shows that the semiempirical correction  $E^{\text{vdW}}$  to the density functional in GGA yields reliable results for the atomic distances and force constants of graphitic structures.

This also holds for boron nitride where the  $c$ -lattice constant calculated in GGA+vdW is in very good agreement with experimental data (see Table II). GGA and even LDA perform significantly worse for this quantity, with deviations of +3.3 and  $-0.17$  Å, respectively. Additionally, the improvement of elastic properties in GGA+vdW is obvious, but in comparison to experiment the results are not as good as for graphite. Unfortunately there are no experimental data available on the interlayer cohesive energy for hexagonal boron nitride. From Lennard-Jones interaction potentials one has derived values similar to graphite, namely, 83 meV per BN pair.<sup>59</sup>

### 3. Rare-gas solids

The electron density between the graphene layers is very low, similar to rare-gas systems. As seen for graphite and hexagonal boron nitride, properties such as lattice parameters not associated with covalent bonds, e.g., the  $c$ -lattice constant, often agree better with experiment for LDA than for

GGA. By contrast, LDA gives rather bad results for the lattice constant of the Ne crystal when compared to GGA, GGA+vdW, and experimental<sup>64–66</sup> values (see Table III). This shows that the LDA fortuitously describes the graphite structure correctly.

For crystalline argon we find a strong underestimation of the lattice constant in LDA. The deviation from experiment is even worse, however, in GGA and GGA+vdW. Quantum chemistry methods<sup>64</sup> come close to the experimental data for argon,<sup>65</sup> depending on the specifics of the computation and basis sets. For both rare-gas solids the vdW approach corrects the GGA results towards the experimental values, but the corrections are not sufficient.

The LDA bulk moduli are far from the experimental findings, which correlates to the underestimation of the lattice constant. The neon bulk modulus is determined to be unacceptable high in this approximation and moderately overestimated in GGA and GGA+vdW, respectively. The experimental values, derived from elastic constants, are 1.1 and 2.7 GPa for neon and argon, respectively. This trend is not obtained using either LDA, GGA, or GGA+vdW. Similar behavior is found for rare-gas dimers discussed below.

## B. Molecules

Van der Waals forces should play no major role for the chemical bonds of diatomic molecules with strong covalent bonds. We study  $\text{N}_2$  and CO as typical examples, see Table IV. The interatomic distance of the interacting nitrogens (re-

TABLE IV. Equilibrium bond length  $d$  (Å), force constant of bond  $f$  (N/cm), and binding energy  $E$  (eV/atom) calculated for the diatomic molecules  $\text{N}_2$  (first line) and CO (second line). Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA + vdW	Expt. <sup>a</sup>	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$	1.107	1.112	1.112	1.0977	-1.3	-1.3
	1.138	1.145	1.145	1.1283	-1.5	-1.5
$f$	22.66	22.08	22.07	22.95	+3.9	+4.0
	18.52	17.82	17.82	19.02	+6.7	+6.7
$E$	10.65	9.68	9.68	9.76	+0.8	+0.8
	12.34	11.10	11.10	11.11	+0.1	+0.1

<sup>a</sup>Reference 44.

TABLE V. Bond length  $d$  (Å) of the CO bond and vibrational frequencies  $\nu$  (cm<sup>-1</sup>) of the CO<sub>2</sub> molecule. Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA+vdW	Expt. <sup>a</sup>	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$	1.165	1.173	1.173	1.1600	-1.1	-1.1
$\nu$ (S. str.)	1322	1323	1330	1333	+0.8	+0.2
$\nu$ (A. str.)	2373	2321	2347	2349	+1.2	+0.1
$\nu$ (Bend)	648	617	605	667	+8.1	+10

<sup>a</sup>Reference 44.

spectively, carbon and oxygen) is smaller than a typical covalent bond length because of the triple bond. Here vdW forces result in nonperceptible modifications of the bonding strength and distance. The correction (1) can therefore be transferred to such systems without loss of accuracy.

Intuitively, the van der Waals term is expected to be more important for larger molecules. The O-O distance in the linear CO<sub>2</sub> is in the regime of non-negligible dispersion forces. The heteropolar bonding between the oxygens and the carbon atom, however, is well described within LDA or GGA. Bonding distances differ less than 1% from experimental values (see Table V). Even dynamical properties like vibrational frequencies are obtained with high accuracy. When applied to this system, the GGA+vdW approximation results in rather small corrections to GGA. The bending mode is most affected with a frequency shift of 2%.

More sensitive test systems are angular molecules. On the one hand, additional forces between more distant atoms may not exclusively act along molecular bonds. On the other hand, regions of charge depletion may occur between fragments of larger molecules. To figure out the influence of vdW interaction, we study H<sub>2</sub>O, H<sub>2</sub>S, and NH<sub>3</sub>, see Table VI.

Although the hydrogens attract each other due to the vdW term, the effect is small in H<sub>2</sub>O. Attractive forces result in a slight decrease of the bonding angle, whereas the OH bond length is hardly affected. The effect is somewhat larger for H<sub>2</sub>S, where the bonds to the hydrogens are weaker than in H<sub>2</sub>O. The lower stiffness results in a larger decrease of the bonding angle. Nevertheless, the structures of both molecules are obtained in high accuracy both in GGA and GGA+vdW. This also holds for NH<sub>3</sub>, see Table VI. There is

TABLE VI. Bond length  $d$  (Å) of HX bond and bonding angle  $\angle\text{HXH}$  (°) of the H<sub>2</sub>O molecule (first line,  $X=O$ ), H<sub>2</sub>S (second line,  $X=S$ ), and NH<sub>3</sub> (third line,  $X=N$ ). Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA+vdW	Expt. <sup>a</sup>	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$	0.975	0.973	0.973	0.9575	-1.6	-1.6
	1.349	1.346	1.343	1.3356	-0.8	-0.6
	1.022	1.020	1.018	1.012	-0.8	-0.6
$\angle\text{HXH}$	105.6	104.9	104.4	104.51	-0.4	+0.1
	91.3	91.6	90.2	92.1	+0.5	+2.1
	108.4	107.6	106.2	106.7	-0.8	+0.5

<sup>a</sup>Reference 44.

TABLE VII. Equilibrium bond lengths  $d$  (Å) for CC and CH bonds of the benzene molecule. Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA+vdW	Expt. <sup>a</sup>	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$ (CC)	1.383	1.394	1.394	1.399	+0.4	+0.4
$d$ (CH)	1.093	1.089	1.088	1.101	+1.1	+1.2

<sup>a</sup>Reference 44.

no clear trend whether the vdW term improves the accuracy or not. In any event, the induced changes are of minor magnitude.

We investigate benzene as model for larger molecules. The resulting bond lengths are listed in Table VII for the three approaches. Again, only small corrections to the GGA geometry are observed within the GGA+vdW approach.

The problem of describing dispersive forces across regions of sparse electron density, resulting from the locality of the XC functional, has little effect on chemical bonds of small molecules. Since we do not find a substantial improvement of the calculations in LDA or GGA for the above mentioned molecules, we conclude that the correction due to the vdW term is rather small for all studied molecules, but it is comparable to the magnitude of the deviations due to the variation of the XC functional in the DFT implementations.

## C. Dimers

### 1. Rare-gas atoms

Dispersion interaction is particularly important for systems containing more than one molecule. Typically many degrees of freedom have to be considered. Therefore we restrict our investigation to dimers which are the most common and easiest test systems. Rare-gas dimers are often considered in connection with the discussion of the DFT problem (see, e.g., van Mourik<sup>67</sup> and references therein). In addition they can be treated using accurate quantum chemistry methods, and potential energy curves have been constructed from experimental data.

The equilibrium distances in LDA are too small by 14% for Ne<sub>2</sub> and 10% for Ar<sub>2</sub> (see Table VIII) compared to experiment. This confirms the overbinding typical for the local approximation of the XC functional. GGA improves the LDA results for the bond length of both dimers coming close to experimental findings. However, no further modification is found switching on the vdW term. For both dimers the values for GGA and GGA+vdW differ less than 0.01 Å. This is explained by the strong overestimation of the binding energies in GGA, especially for the Ne dimer, which reduces the impact of the vdW energies.

The binding energies themselves are overestimated irrespective of the approximation used. For the Ar dimer the values in GGA and GGA+vdW agree with the experimental results within 1.5 and 3 meV, respectively, but for Ne all approximations fail completely to give reasonable results. As stated by van Mourik,<sup>67</sup> the overestimation cannot be attributed to the basis set superposition error (BSSE). This is con-

TABLE VIII. Structural and elastic properties of neon (first line) and argon (second line) dimer. The binding energy  $E$  (meV/atom) and the bond length  $d$  (Å) are compared to experiment and quantum chemistry methods. Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I.

	LDA	GGA	GGA+vdW	CCSD(T)	Expt.	Ref. 17	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$	2.65	3.01	3.01	3.10 <sup>a</sup>	3.094 <sup>b</sup>	2.9	+2.8	+2.8
	3.40	3.97	3.97	3.8 <sup>c</sup>	3.761 <sup>d</sup>	3.7	-5.3	-5.3
$E$	20.3	15.1	16.0	3.58 <sup>a</sup>	3.65 <sup>b</sup>	19		
	31.0	13.8	15.3	12.26 <sup>c</sup>	12.3 <sup>d</sup>	26	-11	-20

<sup>a</sup>Reference 68.

<sup>b</sup>Reference 69.

<sup>c</sup>Reference 70.

<sup>d</sup>Reference 71.

firmed by the present calculations which are BSSE-free. Rather, the overbinding is related to the exchange energy as shown by Wu *et al.*<sup>16</sup> The pure exchange part already yields a minimum in the interaction energy curve, at least for Ar<sub>2</sub> and Kr<sub>2</sub>. As with the rare gas crystals, simulations for Ar<sub>2</sub> and Ne<sub>2</sub> in GGA-PW91 are not worsened with the vdW term. An improvement within the dispersion approach cannot be expected, since an accurate description of the exchange part is required first.

For the rare-gas dimers the B3LYP functional in conjunction with additional dispersion interaction may improve the results<sup>17</sup> because the functional yields a repulsive potential energy curve unlike PW91.

## 2. N<sub>2</sub> dimers

After having calculated the N<sub>2</sub> molecule, we now study the pair interaction of such species which is three orders of magnitude smaller than the bonding within the molecule. Due to their chemical inactivity, N<sub>2</sub> molecules are ideal test systems for dispersive intermolecular interactions. All N<sub>2</sub> dimer conformations are parametrized as described in Fig. 2. The most prominent structures are T-shaped, defined by ( $\theta_1 = 90^\circ, \theta_2 = 0^\circ, \varphi = 0^\circ$ ), parallel  $H(90, 90, 0)$ , and Z50(50, 50, 0). These specific orientations are a subset of all possible arrangements included in the N<sub>2</sub>-N<sub>2</sub> potential energy surface (PES) determined from scattering experiments and second virial coefficient data.<sup>72</sup> Experimental and calculated values are listed in Table IX together with those obtained within an advanced quantum-chemical computation.<sup>73</sup>

First of all, the calculations result in overestimated binding energies  $E$  for LDA in contrast to the findings for the

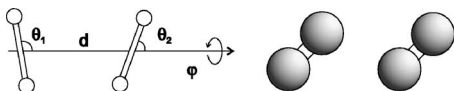


FIG. 2. Relative orientation of two N<sub>2</sub> molecules (left part) where  $d$  is the distance between the molecular centers of mass on the displayed axis. The orientation of the  $i$ th molecule with respect to that axis is given as  $\theta_i$ ,  $\varphi$  is the difference angle in the plane perpendicular to that axis. Z $\theta$  conformation of the dimer (as described in the text for  $\theta = 50^\circ$ ) resulting from structural relaxation (right part).

interplanar bonding in layered crystals within this approximation but in accordance to the rare-gas dimer results. This overestimation is accompanied with an underestimation of the dimer lengths. Furthermore, the results in Table IX show irrespective of the specific conformation a rather good agreement between GGA and experiment. The results of our GGA calculations agree within few % with those of Couronne *et al.*<sup>74</sup> corrected for BSSE. They concluded that the use of PW91 gives frequencies for the intermolecular vibrations in excellent agreement with IR measurements.<sup>75</sup> These characteristics are again unlike the respective outcomes for layered crystals, where one hardly finds bonding.

In each conformation, the vdW contribution to  $E$  at the equilibrium distances is comparable to the experimental binding energies, but unlike graphite, the N<sub>2</sub> dimer is already bonded in GGA. This yields overestimated energies for the GGA+vdW approach, but the values mostly remain lower than those of the LDA calculations. Irrespective of the approximation of the XC functional, we find an energetic ordering of the dimer geometries in accordance with the other theoretical findings. The dimer lengths are most accurately obtained in GGA+vdW for each conformation.

Additional relaxations are carried out to confirm the structural minimum at one of the Z positions (Z45/Z50). Thereby residual forces are smaller than 5 meV/Å. Results for the N<sub>2</sub>

TABLE IX. Equilibrium distances  $d$  (Å) and binding energies  $E$  (meV) of the  $H$  (first line),  $T$  (second line), and Z50 conformation (third line) of the N<sub>2</sub> dimer. Quantities  $\Delta_{\text{GGA}}$  and  $\Delta_{\text{vdW}}$  as in Table I. Reference 72 gives values for a slightly different structure (Z45 instead of Z50) and estimates uncertainties to be 0.8 meV and 0.07 Å.

	LDA	GGA	GGA+vdW	MP2 <sup>a</sup>	Expt. <sup>b</sup>	$\Delta_{\text{GGA}}$	$\Delta_{\text{vdW}}$
$d$	3.38	3.94	3.81	3.7	3.81	-3.3	~0
	3.79	4.29	4.21	4.2	4.03	-6.1	-4.3
	3.60	4.16	4.06	4.02	4.30	+3.4	+5.9
$E$	18.9	11.0	22.4	9.2	11.8	+7.3	-47
	24.9	15.4	24.1	12.0	13.3	-14	-45
	31.9	16.1	25.4	13.7	9.1		

<sup>a</sup>Reference 73.

<sup>b</sup>Reference 72.

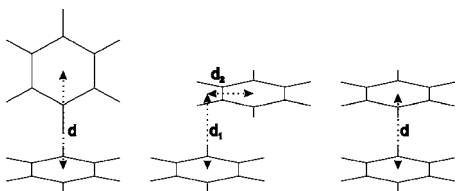


FIG. 3. Benzene dimer structures for  $T$ -shaped ( $T$ ), parallel-displaced (PD), and sandwich ( $S$ ) conformation.

dimer systems obtained within GGA, GGA+vdW, and LDA confirm that the minimum lies in-between  $45^\circ$  and  $50^\circ$ .

### 3. Benzene dimer

Benzene dimers have been studied by numerous groups, see, e.g., in Refs. 76–79, and references therein. The most often examined dimer structures are the sandwich ( $S$ ),  $T$ -shaped ( $T$ ), and parallel-displaced (PD) conformations<sup>80</sup> whose structural parameters are given in terms of the distances  $d$  or  $d_1$  and  $d_2$  (see Fig. 3).  $d$  connects the centers of mass. For the PD structure the quantity  $d_1$  gives the distance between the molecular planes, and  $d_2$  is defined as the lateral shift of the molecules. If  $d_2$  equals zero the  $S$  structure is obtained with  $d=d_1$ . In Table X structural parameters and binding energies for local minima on the PES of the benzene dimer are compared with earlier theoretical calculations.<sup>78,79,77</sup>

Table X indicates that the potential energy well depths are overestimated in GGA+vdW. However, the quality of the structural properties is clearly enhanced by the vdW approach. As already concluded by Meijer and Sprik,<sup>82</sup> a dispersion correction to XC functionals containing gradient corrections can cure the lack of bonding. Especially purely repulsive energy curves are avoided resulting in reasonable equilibrium distances, whereas the energies come out with lower accuracy. Moreover, the correction does not change the physics of orbital interaction as we have shown earlier for the case of adenine adsorption on graphite.<sup>22</sup>

Whether PD or  $T$ -shaped structures are energetically favored is answered differently in LDA and GGA+vdW. LDA favors the PD geometry energetically by 23% with respect to the  $T$  structure, which is most stable in GGA+vdW with an energy difference of about 6%. This preference in GGA+vdW clearly comes from the  $T$ -shaped bonding in GGA (see Table X), which is traced back to an attractive electrostatic interaction according to Tsuzuki.<sup>76</sup> For the parallel conformations no reasonable bonding is obtained in GGA, neither for the laterally displaced nor for the sandwich structure. The unreasonable equilibrium distance of 4.9 Å for the  $S$  structure within the GGA approach as listed in Table X results from a line search in that direction. This procedure is comparable to the determination of the equilibrium separation of adenine on graphite<sup>22</sup> and may be discussed analogous to graphene sheets. As with the sheets preferring  $AB$  stacking over  $AA$ , the molecule drifts away perpendicular to this direction which is characteristic for a saddle point. These findings are in accordance with Walsh,<sup>78</sup> who stated that GGA functionals are unsuitable for the description of benzene dimers and reported that except for unreasonable distances

TABLE X.  $S$ ,  $T$ , and PD conformations of the benzene dimer in the first, second, and third line, respectively, from several computational methods. Minimum conformations are given in terms of the distances  $d$  or  $d_1$  and  $d_2$  (Å) with the corresponding energies  $E$  (meV). Quantities  $\Delta d$ ,  $\Delta d_{1/2}$ , and  $\Delta E$  are related to the MP2 +  $\Delta$ CCSD(T) (Ref. 77) results. Assuming a  $T$ -shaped structure, an experimental study (Ref. 81) gives a dimer separation of  $d = 4.96$  Å.

method	$d$		$E$	$\Delta d$		$\Delta E$
	$d_1$	$d_2$		$\Delta d_1$	$\Delta d_2$	
LDA <sup>a</sup>	3.78		45	+3.2		+76
	4.77		95	+4.8		+25
	3.32	1.73	117	+8.4	-7.5	+3.4
GGA <sup>a</sup>	4.9		6	-20		
	5.39		47	-7.2		
GGA+vdW <sup>a</sup>	3.74		199	+4.3		
	4.82		277	+3.7		
	3.36	1.71	260	+7.1	-6.4	
HF+WL <sup>b</sup>	3.7		35			
	4.7		139			
	3.3	1.8	122			
LC-DFT+ALL <sup>c</sup>	3.9		92			
	5.0		143			
	3.6	1.7	137			
MP2+ $\Delta$ CCSD(T) <sup>d</sup>	3.9		79			
	5.0		119			
	3.6	1.6	121			
DFT-PBE+vdW <sup>e</sup>	4.04		44			
	5.06		95			
	3.57		79			
DFT-BLYP+vdW <sup>e</sup>	3.90		45			
	5.06		88			
	3.52		87			

<sup>a</sup>This work.

<sup>b</sup>Reference 78.

<sup>c</sup>Reference 79.

<sup>d</sup>Reference 77.

<sup>e</sup>Reference 19.

the dimers fail to bond. We confirm this statement for the PW91 functional and for the parallel conformations. For the  $T$  geometry, however, weak bonding is obtained.

In the literature there is no consensus about the minimum position on the PES. Walsh<sup>78</sup> used an approximation which tends to give relative small monomer distances. It prefers the  $T$  geometry over the PD structure. A recent DFT-based description in the LC-DFT+ALL approach from Sato *et al.*,<sup>79</sup> however, predicts that the PD structure is more stable than the  $T$  structure. Sinnokrot and Sherrill<sup>77</sup> performed MP2 +  $\Delta$ CCSD(T) simulations again yielding a slight preference for the PD conformation for the estimated basis set limit.



#### IV. CONCLUSIONS

In conclusion, we implemented a semiempirical method based on few simple assumptions that corrects DFT-GGA for dispersion forces. The asymptotic form of the quantum-mechanical interaction of two atoms is recovered using the London formula. The dispersion forces for small distances are damped. The resulting GGA+vdW (semiempirically vdW-corrected GGA) functional is applied to crystalline, molecular, and dimerized systems comparing the results to GGA and LDA data as well as other theoretical schemes and experimental findings.

In general, in the case of covalent or heteropolar crystals and molecules the semiempirical vdW correction gives rise to minor changes of the GGA results. Small changes in bonding angles of the *HXH* type ( $X=N,O,S$ ) are noticed. Bulk properties remain nearly unchanged. As may be expected, the semiempirical correction is much more important for systems, which are bonded by the long-range vdW interaction. The geometrical data and the effective elastic constants of the corresponding vibrations are calculated in reasonable agreement with measured values. In the extreme case of carbon-derived graphite the interlayer bonding between the graphene sheets vanishes in the framework of the GGA. The vdW corrections restore the correct distance of these layers. The accompanying energy gains, however, are overestimated. This is probably due to the use of the London formula for the asymptotic behavior.

The correct description of rare-gas crystals which evade an adequate simulation remains an open question. GGA gives no consistent picture of long range interactions for

rare-gas atoms. Bond lengths and dimer binding energies are already overestimated within GGA. Therefore no improvement can result from the inclusion of an additional attractive vdW term.

However, apart from the rare-gas systems, the quality of the calculated parameters found for all systems clearly demonstrates that the semiempirical correction is universally applicable to atomic aggregates of relevant systems independent of their characteristic bondings. This is mainly due to two facts: The vdW energy has the correct magnitude acting at long distances, and the damping function is well adapted for various fragment sizes. It does not outperform LDA and GGA in all cases, but the present implementation of the vdW interaction is a valuable supplement to the common approximations for the XC functional. Given the complexity and numerical expense of an *ab initio* description of dispersive interactions, schemes such as the one presented here present a very helpful and (presently probably the only available) tool to address vdW interactions in large and complex systems.

#### ACKNOWLEDGMENTS

This work was supported by the European Community in the framework of the Network of Excellence NANOQUANTA (Contract No. NMP4-CT-2004-500198). Grants of computer time from the Höchstleistungsrechenzentrum Stuttgart, the Leibniz-Rechenzentrum München, and the Paderborn Center for Parallel Computing are gratefully acknowledged.

- 
- <sup>1</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).  
<sup>2</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).  
<sup>3</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, R8800 (1986).  
<sup>4</sup>J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991), p. 11.  
<sup>5</sup>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).  
<sup>6</sup>D. R. Hamann, *Phys. Rev. B* **55**, R10157 (1997).  
<sup>7</sup>K. Rapcewicz and N. W. Ashcroft, *Phys. Rev. B* **44**, 4032 (1991).  
<sup>8</sup>J. F. Dobson and J. Wang, *Phys. Rev. Lett.* **82**, 2123 (1999).  
<sup>9</sup>M. Lein, J. F. Dobson, and E. K. U. Gross, *J. Comput. Chem.* **20**, 12 (1999).  
<sup>10</sup>E. Hult, H. Rydberg, B. I. Lundqvist, and D. C. Langreth, *Phys. Rev. B* **59**, 4708 (1999).  
<sup>11</sup>E. Hult, P. Hyldgaard, J. Rossmeisl, and B. I. Lundqvist, *Phys. Rev. B* **64**, 195414 (2001).  
<sup>12</sup>Y. Andersson, E. Hult, H. Rydberg, P. Apell, B. I. Lundqvist, and D. C. Langreth, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum Press, New York, 1998), p. 243.  
<sup>13</sup>R. Eisenschitz and F. London, *Z. Phys.* **60**, 491 (1930).  
<sup>14</sup>F. London, *Z. Phys.* **63**, 245 (1930).  
<sup>15</sup>M. Elstner, P. Hobza, T. Fraunheim, S. Suhai, and E. Kaxiras, *J. Chem. Phys.* **114**, 5149 (2001).  
<sup>16</sup>X. Wu, M. C. Vargas, S. Nayak, V. Lotrich, and G. Scoles, *J. Chem. Phys.* **115**, 8748 (2001).  
<sup>17</sup>Q. Wu and W. Yang, *J. Chem. Phys.* **116**, 515 (2002).  
<sup>18</sup>M. Hasegawa and K. Nishidate, *Phys. Rev. B* **70**, 205431(R) (2004).  
<sup>19</sup>S. Grimme, *J. Comput. Chem.* **25**, 1463 (2004).  
<sup>20</sup>L. Zhechkov, T. Heine, S. Patchkovskii, G. Seifert, and H. A. Duarte, *J. Chem. Theory Comput.* **1**, 841 (2005).  
<sup>21</sup>M. A. Neumann and M.-A. Perrin, *J. Phys. Chem. B* **109**, 15531 (2005).  
<sup>22</sup>F. Ortman, W. G. Schmidt, and F. Bechstedt, *Phys. Rev. Lett.* **95**, 186101 (2005).  
<sup>23</sup>J. F. Dobson, J. Wang, B. P. Dinte, K. McLennan, and H. M. Le, *Int. J. Quantum Chem.* **101**, 579 (2005).  
<sup>24</sup>T. A. Halgren, *J. Am. Chem. Soc.* **114**, 7827 (1992).  
<sup>25</sup>G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).  
<sup>26</sup>G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).  
<sup>27</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).  
<sup>28</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).  
<sup>29</sup>D. Vanderbilt, *Phys. Rev. B* **41**, R7892 (1990).  
<sup>30</sup>J. Furthmüller, P. Käckell, F. Bechstedt, and G. Kresse, *Phys. Rev. B* **61**, 4576 (2000).  
<sup>31</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1998).  
<sup>32</sup>M. Preuss, W. G. Schmidt, K. Seino, J. Furthmüller, and F. Bechstedt, *J. Comput. Chem.* **25**, 112 (2004).

- <sup>33</sup>S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- <sup>34</sup>G. Kern, G. Kresse, and J. Hafner, *Phys. Rev. B* **59**, 8551 (1999).
- <sup>35</sup>F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- <sup>36</sup>S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- <sup>37</sup>W. G. Schmidt, F. Bechstedt, and G. P. Srivastava, *Phys. Rev. B* **52**, 2001 (1995).
- <sup>38</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- <sup>39</sup>F. London, *Z. Phys. Chem. Abt. B* **12**, 222 (1930).
- <sup>40</sup>J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).
- <sup>41</sup>Y. K. Kang and M. S. Jhon, *Theor. Chim. Acta* **61**, 41 (1982).
- <sup>42</sup>K. J. Miller, *J. Am. Chem. Soc.* **112**, 8533 (1990).
- <sup>43</sup>R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
- <sup>44</sup>*CRC Handbook of Chemistry and Physics 79<sup>th</sup> Edition*, edited by D. R. Lide (CRC Press, Boca Raton, 1998).
- <sup>45</sup>R. Ahrlichs, R. Penco, and G. Scoles, *Chem. Phys.* **19**, 119 (1977).
- <sup>46</sup>W. T. M. Mooij, F. B. van Duijneveldt, J. G. C. M. van Duijneveldt-van de Rijdt, and B. P. van Eijck, *J. Phys. Chem. A* **103**, 9872 (1999).
- <sup>47</sup>*CRC Handbook of Chemistry and Physics 80<sup>th</sup> Edition*, edited by D. R. Lide (CRC Press, Boca Raton, 1999).
- <sup>48</sup>O. A. von Lilienfeld, I. Tavernelli, U. Rothlisberger, and D. Sebastiani, *Phys. Rev. Lett.* **93**, 153004 (2004).
- <sup>49</sup>*Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series Group III*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1982), Vol. 17a.
- <sup>50</sup>*Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series Group III*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1973), Vol. 7.
- <sup>51</sup>*Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series Group III*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1979), Vol. 11.
- <sup>52</sup>A. C. Victor, *J. Chem. Phys.* **36**, 1903 (1962).
- <sup>53</sup>D. C. Langreth and M. J. Mehl, *Phys. Rev. B* **28**, 1809 (1983).
- <sup>54</sup>R. S. Peace, *Acta Crystallogr.* **5**, 356 (1952).
- <sup>55</sup>Y. Baskin and L. Meyer, *Phys. Rev.* **100**, 544 (1955).
- <sup>56</sup>L. A. Girifalco and R. A. Lad, *J. Chem. Phys.* **25**, 693 (1956).
- <sup>57</sup>R. Zacharia, H. Ulbricht, and T. Hertel, *Phys. Rev. B* **69**, 155406 (2004).
- <sup>58</sup>W. B. Gauster and I. J. Fritz, *J. Appl. Phys.* **45**, 3309 (1974).
- <sup>59</sup>J. F. Green, T. K. Bolland, and J. W. Bolland, *J. Chem. Phys.* **64**, 656 (1976).
- <sup>60</sup>L. X. Benedict, N. G. Chopra, M. L. Cohen, A. Zettl, S. G. Louie, and V. H. Crespi, *Chem. Phys. Lett.* **286**, 490 (1998).
- <sup>61</sup>G. Kern and J. Hafner, *Phys. Rev. B* **58**, 13167 (1998).
- <sup>62</sup>K. R. Kganyago and P. E. Ngoepe, *Mol. Simul.* **22**, 39 (1999).
- <sup>63</sup>H. Rydberg, N. Jacobson, P. Hyldgaard, S. I. Simak, B. I. Lundqvist, and D. C. Langreth, *Surf. Sci.* **532**, 606 (2003).
- <sup>64</sup>K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **60**, 7905 (1999).
- <sup>65</sup>O. G. Peterson, D. N. Batchelder, and R. O. Simmons, *Phys. Rev.* **150**, 703 (1966).
- <sup>66</sup>D. N. Batchelder, D. L. Losee, and R. O. Simmons, *Phys. Rev.* **162**, 767 (1967).
- <sup>67</sup>T. van Mourik and R. J. Gdanitz, *J. Chem. Phys.* **116**, 9620 (2002).
- <sup>68</sup>R. J. Gdanitz, *Chem. Phys. Lett.* **348**, 67 (2001).
- <sup>69</sup>A. Wüest and F. Merkt, *J. Chem. Phys.* **118**, 8807 (2003).
- <sup>70</sup>P. Slavíček, R. Kalus, P. Paška, I. Odvárková, P. Hobza, and A. Malíjevsý, *J. Chem. Phys.* **119**, 2102 (2003).
- <sup>71</sup>P. R. Herman, P. E. LaRocque, and B. P. Stoicheff, *J. Chem. Phys.* **89**, 4535 (1988).
- <sup>72</sup>V. Aquilanti, M. Bartolomei, D. Cappelletti, E. Carmona-Novillo, and F. Pirani, *J. Chem. Phys.* **117**, 615 (2002).
- <sup>73</sup>M. H. K. Jafari, A. Maghari, and S. Shahbazian, *Chem. Phys.* **314**, 249 (2005).
- <sup>74</sup>O. Couronne and Y. Ellinger, *Chem. Phys. Lett.* **306**, 71 (1999).
- <sup>75</sup>C. A. Long, G. Henderson, and G. E. Ewing, *Chem. Phys.* **2**, 485 (1973).
- <sup>76</sup>S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Am. Chem. Soc.* **124**, 104 (2002).
- <sup>77</sup>M. O. Sinnokrot and C. D. Sherrill, *J. Phys. Chem.* **108**, 10200 (2004).
- <sup>78</sup>T. R. Walsh, *Phys. Chem. Chem. Phys.* **7**, 443 (2005).
- <sup>79</sup>T. Sato, T. Tsuneda, and K. Hirao, *J. Chem. Phys.* **123**, 104307 (2005).
- <sup>80</sup>P. Hobza, H. L. Selzle, and E. W. Schlag, *J. Chem. Phys.* **100**, 18790 (1996).
- <sup>81</sup>E. Arunan and H. S. Gutowsky, *J. Chem. Phys.* **98**, 4294 (1993).
- <sup>82</sup>E. J. Meijer and M. Sprik, *J. Chem. Phys.* **105**, 8684 (1996).