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Transferability and accuracy by combining dispersionless density functional and incremental post-Hartree-Fock theories: Noble gases adsorption on coronene/graphene/graphite surfaces

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The accuracy and transferability of the electronic structure approach combining dispersionless density functional theory (DFT) [K. Pernal *et al.*, Phys. Rev. Lett. **103**, 263201 (2009)] with the method of increments [H. Stoll, J. Chem. Phys. **97**, 8449 (1992)], are validated for the interaction between the noble-gas Ne, Ar, Kr, and Xe atoms and coronene/graphene/graphite surfaces. This approach uses the method of increments for surface cluster models to extract *intermonomer* dispersion-like (2- and 3-body) correlation terms at coupled cluster singles and doubles and perturbative triples level, while periodic dispersionless density functionals calculations are performed to estimate the sum of Hartree-Fock and *intramonomer* correlation contributions. Dispersion energy contributions are also obtained using DFT-based symmetry-adapted perturbation theory [SAPT(DFT)]. An analysis of the structure of the X/surface (X = Ne, Ar, Kr, and Xe) interaction energies shows the excellent transferability properties of the leading *intermonomer* correlation contributions across the sequence of noble-gas atoms, which are also discussed using the Drude oscillator model. We further compare these results with van der Waals-(vdW)-corrected DFT-based approaches. As a test of accuracy, the energies of the low-lying nuclear bound states supported by the laterally averaged X/graphite potentials (X = ³He, ⁴He, Ne, Ar, Kr, and Xe) are calculated and compared with the best estimations from experimental measurements and an atom-bond potential model using the *ab initio*-assisted fine-tuning of semiempirical parameters. The bound-state energies determined differ by less than 6–7 meV (6%) from the atom-bond potential model. The crucial importance of including incremental 3-body dispersion-type terms is clearly demonstrated, showing that the SAPT(DFT) approach effectively account for these terms. With the deviations from the best experimental-based estimations smaller than 2.3 meV (1.9%), the accuracy of the combined DFT and post-HF incremental scheme is established for all the noble-gas atoms. With relative deviations smaller than 4% and 11%, good agreement is also achieved by applying the vdW-corrected DFT treatments PBE-D3 and vdW-DF2 for noble-gas atoms heavier than neon. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935511>]

I. INTRODUCTION

The adsorption of noble gases atoms on solid surfaces is relevant as a prototypical van der Waals (vdW) dispersion-dominated interaction problem in surface science. In the context of nano-technologies, recently developed experimental tools such as the helium droplet-mediated deposition technique^{1–5} or that using the fast flow of rarefied gases in micro-porous media have provided a renewed impetus for addressing the noble gases adsorption issue. Recently, noble gases have been used as benchmark systems to assess the accuracy of coarse-grained electronic structure models for the dispersion interaction such as the quantum extension⁶ of the classical Drude oscillator model.^{7,8} The theory and modelling of the dispersion interaction between atoms and

solid surfaces, using Drude oscillators⁹ has been extensively developed by, for example, Bruch, Cole and Zaremba.¹⁰ The refinement of these models is an important goal and the *ab initio* benchmarking of the dispersion adsorbate/surface interaction is ideally suited for this purpose, specially if the *ab initio* treatment allows for a natural separation of this contribution.

In the last few years, the development of vdW-corrected methods based on Density Functional Theory (DFT) has received strong attention and very efficient implementations exist within numerous periodic electronic structure codes. As a result, a rich tool-box of different vdW-corrected density functionals is now available to determine noble-gas atom/surface interactions (for a recent review see, e.g., Ref. 11). Concurrently, an intense effort has been dedicated to advanced methods and high-profile algorithms making possible accurate fully *ab initio* descriptions of these extended systems (see, e.g., Ref. 12 and following articles).

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As an alternative to DFT-based or fully *ab initio* approaches, a combined post-Hartree-Fock/DFT scheme has been recently proposed and successfully applied to calculate He/surface global interaction potentials^{13–15} as well as the interaction forces between the silver dimer and graphene.¹⁶ By construction, the dispersion-type interaction is obtained separately at *ab initio* level, allowing for the benchmarking of electronic structure models for the dispersion. The scheme can be viewed as a complementary extended version of the dispersionless density functional (dIDF) + D_{as} approach proposed by Pernal *et al.*,¹⁷ with D_{as} being a general-purpose effective pairwise functional for the dispersion.^{17–19} The idea underlying the scheme (denoted then as the periodic dIDF + incremental D_{as}^* approach¹³) is the partition of the global interaction energy into Hartree-Fock (HF) and *intermonomer* (dispersion-like) as well as *intramonomer* correlation contributions, as univocally defined within the method of increments proposed by Stoll.²⁰ Applying the periodic dispersionless dIDF approach, the sum of HF and *intramonomer* correlation contributions is approximated by that obtained through dIDF calculations on periodic surface models (see, e.g., Ref. 15 for benchmark tests of this approximation). Next, 2- and 3-body *intermonomer* correlation contributions are calculated at coupled cluster singles and doubles and perturbative triples [CCSD(T)] level via the application of the method of increments on surface cluster models, allowing the D_{as} function parametrization (the so-named incremental D_{as}^* parametrization). The D_{as} function is then employed to extrapolate the adsorbate/cluster dispersion contribution to the extended adsorbate/surface system (see, e.g., Ref. 16 for a recent overview of the scheme).

According to previous studies,^{13–16} the efficiency and accuracy of the periodic dIDF + incremental D_{as}^* approach rely on: (1) the short-range nature of the *intramonomer* correlation contribution; (2) the transferability of the long-range *intermonomer* correlation terms upon increasing the size of the surface cluster model. On the other hand, the long-range nature of the induction contribution is accounted for by performing the dIDF or HF calculations on periodic models of the surface. Importantly, it has been shown (see, e.g., Ref. 13) that the incremental D_{as}^* scheme provides results that are very close to those obtained via the D_{as} parametrization in which the dispersion is calculated at DFT-based symmetry-adapted perturbation level of theory on surface cluster models of increasing size (i.e., using the SAPT(DFT)^{21,22} approach). In this way, better interaction energies than those using the original general-purpose D_{as} parametrization are obtained.¹³ Very recently, this dIDF + D_{as} scheme has been applied to get the pair interaction potentials which are necessary to simulate the flow of rare gases on gold surfaces.²³

This work is mainly aimed to analyze if the good performance of the periodic dIDF + incremental D_{as}^*/D_{as} approaches for helium can be generalized to the rest of the noble-gas atoms. For this purpose, we have considered the Ne, Ar, Kr, and Xe atoms (collectively denoted as X atoms), and the graphene and graphite surfaces. As an accuracy test, the nuclear bound-state energies of the laterally averaged X/graphite potentials have been calculated and compared to the experimental measurements and those obtained via

the semiempirical atom-bond potential model by Bartolomei *et al.*²⁴ Applying the dIDF + incremental D_{as}^*/D_{as} schemes, the average absolute deviation from scattering measurements on ⁴He/graphite²⁵ was below 1 meV¹³ and so we investigate here whether the same level of accuracy can be achieved for heavier noble-gas atoms. Besides the accuracy, the present study is intended to prove transferability properties across the noble-gas sequence, with the emphasis on the leading *intermonomer* 2- and 3-body correlation contributions to the interaction. For the same purpose, the Drude oscillator model has been also applied.^{9,10} The third objective is to compare the performance of the periodic dIDF + incremental D_{as}^*/D_{as} approaches with that of dispersion-inclusive DFT-based treatments.

The structure of this paper is as follows: Section II presents the structural models, the applied theoretical approaches, and the computational details of both the electronic structure and the nuclear bound-state calculations. The interaction of the noble-gas atoms with coronene and graphene surfaces is analyzed in Sections III and IV, respectively, while Section V is focused on the low-lying nuclear bound-states for the noble gases adsorbed on the graphite substrate. Finally, Section VI closes with the concluding remarks and future prospects.

II. STRUCTURAL MODELS, THEORETICAL APPROACHES, AND COMPUTATIONAL DETAILS

A. Structural models

The structural models used in this work are illustrated in Figure 1. A coronene-like fragment was chosen as the surface cluster model with the C—C bond lengths set to

FIG. 1. Figure illustrating a graphene sheet and the coronene-like fragment chosen to perform the CCSD(T) and SAPT(DFT) calculations. The $\sigma + \pi$ groups oriented radially and tangentially with respect to the central benzene-like ring are colored in yellow and red, respectively. Z is defined as the distance between the noble-gas atom and the carbon-ring plane. Different positions of the noble-gas atom are also indicated: at the “hollow” site above the ring center (H), on top of one carbon atom (T), and at a “bridge” site above the middle of a C—C bond (B).

the experimental value (1.42 Å). The dangling bonds were saturated with hydrogen atoms, with the C—H distance chosen to be 1.09 Å. For cluster calculations, the noble-gas atoms were located on top of the central carbon hexagon (the “hollow” adsorption position). The periodic calculations were carried out using 3×3 and 5×5 graphene supercell models and considering the three adsorption sites shown in Figure 1. The graphite substrate was modeled as an assembly of graphene layers (as many as needed to reach convergence, see below).

B. Theoretical approaches

The periodic dIDF + incremental D_{as}^* approach is briefly overviewed here and the interested reader is referred to Ref. 16 for additional details. The total interaction energy E_{int}^{tot} is first partitioned into Hartree-Fock E_{int}^{HF} along with *intermonomer* and *intramonomer* correlation contributions (E_{int}^{inter} and E_{int}^{intra}),

$$E_{int}^{total} = E_{int}^{HF} + E_{int}^{inter} + E_{int}^{intra}. \quad (1)$$

For vdW-dominated interactions, the *intermonomer* correlation term can be well identified with the dispersion. To evaluate it by applying the method of increments, the localized orbital groups (LOGs) centered at the noble-gas atom (X) and the surface cluster ($i, j, \dots$), which are close enough to interact, are first determined and then independently correlated. This yields one-body correlation-energy increments $\epsilon_X, \epsilon_i, \epsilon_j$. Next, E_{int}^{inter} is expressed as a cumulant expansion in terms of contributions (increments) as

$$E_{int}^{inter} = \sum_i \eta_{Xi} + \sum_{i < j} \eta_{Xij} + \dots,$$

where the 2-body η_{Xi} increments are defined as the non-additive portion of the correlation energy ϵ obtained when the electrons occupying the LOGs X and i are simultaneously correlated, via excitations into the available virtual orbitals, and freezing the rest of LOGs, $\eta_{Xi} = \epsilon_{Xi} - \epsilon_X - \epsilon_i$. The third-order incremental terms η_{Xij} are evaluated by removing the one- and two-body increments involving the LOGs X, i , and j from the correlation energy obtained upon the simultaneous correlation of the electrons within these groups,

$$\eta_{Xij} = \epsilon_{Xij} - \epsilon_X - \epsilon_i - \epsilon_j - \eta_{Xi} - \eta_{Xj} - \eta_{ij}.$$

Higher order increments are defined analogously.²⁰ The increment values decrease rapidly with the order of the increment and the distance between the centers of the involved LOGs so that 4- and higher-order contributions can be typically ignored (see, e.g., Ref. 14). All the increments have been computed at CCSD(T) level of theory, considering the “hollow” adsorption site (see Figure 1).

Applying the dIDF approach of Szalewicz and co-workers,¹⁷ the term E_{int}^{intra} of Eq. (1) is simply approximated as the difference between the HF contribution and the interaction energy evaluated with the dIDF functional (E_{int}^{dIDF}), $E_{int}^{intra} \approx -E_{int}^{HF} + E_{int}^{dIDF}$. The dIDF functional¹⁷ is a hybrid meta-GGA functional containing 61.44% of HF-type exchange and differing from the Minnesota M05-2X functional²⁶ in the number and values of parameters. These parameters

were optimized with the purpose of reproducing dispersion-free interaction energies of small weakly bound dimers.¹⁷ The accuracy of the dIDF functional to estimate the E_{int}^{intra} term has been previously validated for helium adsorption (see, e.g., Ref. 15).

For the X/graphene complex, a supercell model was used and the periodic dIDF approach was applied.¹³ Next, within the incremental D_{as}^* approach, the D_{as} function¹⁹ was parametrized to estimate the *intermonomer* correlation contribution E_{int}^{inter} in the extended system. The total interaction energy E_{int}^{tot} was then expressed as

$$E_{int}^{tot} = E_{int}^{dIDF} - \sum_C \sum_{n=6,8} \frac{\sqrt{C_n^X C_n^C}}{R_{XC}^n} f_n(\sqrt{\beta_X \beta_C} R_{XC}),$$

where the sum in the second term runs over as many graphene C atoms as necessary to get convergence and f_n are the damping functions of Tang and Toennies.²⁷ In this work, the C_n^X and β_X parameters were fitted while the C_n^C and β_C values were kept frozen to those reported for the general-purpose D_{as} parametrization in Ref. 19. Along with the method of increments, the SAPT(DFT) method has been applied to decompose the X/coronene interaction energy using the Perdew-Burke-Ernzerhof (PBE) density functional.²⁸ Next, the evaluated SAPT(DFT) dispersion energies were fitted for the D_{as} function parametrization using the same procedure as described above. Our SAPT(DFT) calculations considered the three different positions shown in Figure 1.

For comparison purposes, vdW-corrected DFT-based treatments were also applied using periodic models of the graphene surface. We have employed the PBE density functional together with the D3 dispersion corrections of Grimme *et al.*²⁹ Within the framework of the non-local vdW density functionals developed by Langreth and co-workers, we have chosen the original vdW-DF approach³⁰ as well as the second-generation vdW-DF2 treatment.³¹

C. Computational details

1. Electronic structure calculations

a. Surface cluster calculations. All surface cluster calculations were carried out employing correlation consistent basis sets with the MOLPRO package³² including the dIDF implementation.¹⁴ When applying the method of increments, LOGs were defined using the Foster-Boys localization procedure.³³ The full basis set of the X/coronene system was used in all cases so that the increments were counterpoise-corrected.³⁴ To evaluate these increments at CCSD(T) level, pseudo-canonical orbitals within the active space of the LOGs constituting a given increment were employed. The (augmented) polarized correlation-consistent triple- ζ basis of Woon and Dunning, Jr.³⁵ [(aug)-cc-pVTZ] was adopted for the coronene atoms defining the LOGs of (2-body) 3-body increments, and the polarized correlation-consistent double- ζ basis (cc-pVDZ) otherwise. The aug-cc-pVTZ basis set was also employed for Ne and Ar atoms while the aug-cc-pVTZ-PP basis set³⁶ together with the corresponding relativistic pseudopotentials was used for Kr and Xe atoms. Comparison of the 2-body increments using the aug-cc-pVTZ and cc-pVTZ

basis sets for the carbon atoms showed a convergence to within 5% (see the supplementary material³⁷).

The SAPT(DFT) calculations were performed using the computational setup reported in Ref. 24 but adopting the aug-cc-pV5Z basis set for Ne and Ar atoms, and the aug-cc-pVTZ and aug-cc-pVTZ-PP basis³⁶ for krypton and xenon, respectively. The aug-cc-pVTZ set was used for carbon atoms but with the most diffuse function of each angular momentum function multiplied by a factor of 2.3 to avoid linear dependence problems.^{24,38} The aug-cc-pVTZ (Ne and Ar) and the aug-cc-pVTZ-PP (Kr and Xe) basis sets were employed in cluster dIDF and HF calculations. A spatial Z grid of 12–20 values in the interval [2–7] Å was considered for the three adsorption positions shown in Figure 1. SAPT(HF) calculations were also performed to estimate the δ (HF) contribution^{39,40} (see below).

b. Periodic calculations. The CRYSTAL14 code^{41,42} was used for all the periodic calculations applying the periodic dIDF implementation.¹³ These calculations were done following the computational setups reported in Refs. 13 and 16 with a few differences: the aug-cc-pVTZ basis was used for Ne and Ar atoms while the aug-cc-pVTZ-PP set³⁶ was employed for Kr and Xe atoms. To avoid the interaction between periodic replicas of the rare-gas atoms, a 3×3 graphene supercell model was used for adatoms lighter than xenon. At the potential minimum region, the dIDF interaction energies differed by less than 3 meV (about 3%) from those obtained with a 5×5 supercell. To achieve the same level of accuracy, the 5×5 model was used for the Xe/graphene complex, along with an all-electron basis including contracted valence triple- ζ plus polarization functions for carbon atoms.⁴³ The PBE-D3, vdW-DF, and vdW-DF2 calculations have been performed using the Vienna *Ab initio* Simulation Package,^{44,45} based on the projector augmented-wave method.^{46,45} Plane wave basis sets with a kinetic energy cutoff of 600 eV and PAW-PBE pseudopotentials were employed. The total energy calculations used a Γ -centered $9 \times 9 \times 1$ k -point mesh and the linear tetrahedron method to smear out the single particle wave-functions. Structural relaxation effects of the carbon atom positions were not included. All the periodic calculations considered the three adsorption sites shown in Figure 1 and an unevenly spaced Z grid of 15 values ranging from 2.4 to 12 Å.

2. D_{as} parameterizations

Three different parameterizations of the D_{as} function have been considered. When fitting the CCSD(T) *intermonomer* correlation contributions, the increments calculated at four different distances Z from the noble-gas atom to the “hollow” position of the carbon-ring plane were considered (see Fig. 1). The reference parametrization [referred to as incremental D_{as}^* (2-body + 3-body) or simply incremental D_{as}^*] excludes the contributions of the capping C—H bonds to the dispersion and includes 3-body incremental terms. The incremental D_{as}^* (2-body) parametrization includes the C—H contributions but excludes the 3-body terms. The relative root-mean-square (rms) errors from the fittings ranged from about 1.5% for neon to 3% for xenon.

As for the carbon atoms, the parametrization including the dispersion interaction with the terminal C—H bonds of coronene employed C_n^H and β_H coefficients from Ref. 19. Our graphene and graphite cluster models exclude the capping C—H bonds and, then, the adatom/C—H dispersion interaction. This interaction should have a negligible influence on the values of the optimized rare-gas atom parameters. In fact, the difference between the extrapolated dispersion energies with and without considering C—H bonds in the parametrization using reference clusters (e.g., coronene) is considered as a diagnostic of convergence with respect to the size of these clusters and an uncertainty limit estimation.

The third parametrization (denoted as D_{as}) uses the SAPT(DFT) dispersion energies calculated at 12–20 different separations from the noble-gas atom to the “bridge” position of the carbon-ring plane (see Figure 1). The relative rms errors ranged from about 0.3% for neon to 1% for xenon. It was also tested that the D_{as} parametrization on the “bridge” position provided estimations for the dispersion interaction at the “hollow” and “on top” positions with relative rms errors in the range of 0.5–2.5% (i.e., with respect to the calculated SAPT(DFT) dispersion energies).

3. Nuclear bound states calculations

We have determined the energies of the nuclear bound states supported by the laterally averaged X/graphite potentials. First, the interaction energies were calculated for the noble-gas atom above the “hollow,” “bridge,” and “on top” adsorption sites of the graphene surface shown in Figure 1. Next, the average potential was obtained from these curves using geometrical (i.e., positions density counting) weighting. The graphite substrate was modeled as an assembly of graphene sheets, assuming the same dispersionless interaction as for graphene and adding the dispersion contributions from internal graphite layers. The calculation of the nuclear bound states was accomplished using the Truhlar-Numerov procedure,⁴⁷ as described in Ref. 14.

When using vdW-corrected DFT-based approaches, the dispersionless interaction energy is not separated so that a different procedure was followed. Specifically, the average potential energy curves obtained for the X/graphene system were first fitted to the functional form

$$V(Z) = Ae^{-\alpha Z} Z^\gamma - \sum_{n=4}^{n_{max}} \frac{C_n}{Z^n}, \quad (2)$$

where the value of γ was set to zero for noble gases lighter than xenon and the n_{max} parameter was chosen so that the rms error of the fitting stayed below 2 meV. Next, the X/graphite interaction potential was modeled as

$$V(Z) = Ae^{-\alpha Z} Z^\gamma - \sum_{n=4}^{n_{max}} \sum_{m_l} \frac{C_n}{(Z + m_l d_0)^n}, \quad (3)$$

where m_l is an index numbering the graphene sheets of the graphite model, with d_0 as the separation between consecutive layers. Using the dIDF + incremental D_{as} approach, it was possible to test that this procedure is equivalent to that adding the dispersion contributions directly on X/graphite

models, at different adatom positions, and then averaging the resulting interaction energies. The estimated well depth for the laterally-averaged potential amounted to -166 meV. This value is consistent with the vdW-DF2 binding energy of 0.17 eV recently reported by Chen *et al.*⁴⁸ for the Xe/graphite interaction (hollow site).

III. ANALYSIS OF THE INTERACTION ON CORONENE: METHOD OF INCREMENTS AND SYMMETRY-ADAPTED PERTURBATION THEORY

A. Analysis of the X/coronene interaction ($X = \text{Ne, Ar, Kr, and Xe}$) via the method of increments

We begin by analyzing the X/coronene interaction ($X = \text{Ne, Ar, Kr, and Xe}$) via the application of the method of increments. As shown in Figure 1, the six LOGs characterizing the system are formed from: (1) the LOG centered on the X atom; (2) the six σ C—C bond orbitals located at the inner ring; (3) the twelve σ orbitals of the outer rings; (4) the six $\sigma + \pi$ C=C bond orbitals, oriented radially from the midpoint, connecting inner ring to outer rings; (5) the six $\sigma + \pi$ C=C bond orbitals of outer rings, oriented tangentially from the midpoint; (6) and the twelve capping C—H σ orbitals.⁴⁹

The values of the most relevant *intermonomer* increments at different distances Z of the noble-gas atom from the coronene plane are provided in Table I (see the supplementary material for the complete list of calculated increments³⁷). The HF and the estimated *intramonomer* correlation terms with the dIDF approach are collected in the same table. For the particular Ne/coronene case, Figure 2 illustrates how much the individual 2-body increments contribute into the total *intermonomer* correlation.

The 2-body *intermonomer* correlation contributions arise from the attractive interaction between the fluctuating dipoles located at the noble-gas atom and the different surface LOGs. As can be seen in Table I and Figure 2, they are clearly dominated by the 2-body $\eta_{X/C=C}$ increments that involve the more delocalized $\sigma + \pi$ bonds closest to the noble-gas atom (the radial C=C LOGs, see Fig. 1). Notice also in the inset of Figure 2 that its weight decays slowly as the Ne-coronene distance increases. Figure 2 also illustrates that the dispersion interaction between the noble-gas atoms and the C—C σ orbitals is not only less attractive than that with the more delocalized π orbitals but also shorter ranged. As occurs with the $\eta_{X/C=C}$ contributions (see inset of Figure 2) the relative weights of the farthestmost σ orbitals increase with the X-coronene distance while the opposite behaviour is found for the σ orbitals located in the central carbon ring. Although the 2-body $\eta_{X/C-H}$ increments represent a fraction below 3% of the total 2-body dispersion contribution at the potential well region (see Figure 2), their absolute values become significant as the noble-gas atomic size increases, raising from about -1.7 meV for neon to -13.6 meV for xenon.³⁷ It reflects that the spread of the LOG located at the xenon adatom is large enough to interact with the terminal σ C—H bond of coronene.

As found in previous studies of the He/surface interaction,^{14,13,15} the leading 3-body increments are repulsive

TABLE I. Decomposition of the X/coronene interaction energy ($X = \text{Ne, Ar, Kr, Xe}$) at different distances between the coronene plane and the X atom. The most relevant increments are given in meV. The increments η already include the appropriate weight factors (see also the supplementary material³⁷). The estimations of the *intramonomer* correlation contribution were obtained within the dIDF approach (see text). Values in parentheses and brackets have been obtained by rescaling the total *intermonomer* correlation by the factor $(C_3^{\text{Ne}}/C_3^{\text{X}})$, with C_3^{X} as model dispersion coefficients for the X/graphite interaction^{10,6} (see text).

	Energy (meV)			
	2.4 Å	3.3 Å	4.5 Å	6.0 Å
Neon on the “hollow” coronene site				
<i>Intermonomer</i> contributions				
$\eta(\text{Ne/C—C inner})$	−51.95	−9.06	−1.42	−0.27
$\eta(\text{Ne/C = C radial})$	−125.5	−30.71	−5.68	−1.11
$\sum\eta$ (two-body)	−212.3	−52.14	−10.95	−2.50
$\sum\eta$ (three-body)	20.19	4.87	0.94	0.20
$E_{\text{int}}^{\text{inter}}$ (total <i>intermonomer</i>)	−192.1	−47.26	−10.01	−2.29
$E_{\text{int}}^{\text{HF}}$	284.0	14.19	0.10	−0.05
$E_{\text{int}}^{\text{intra}}$ (total <i>intramonomer</i> estimations)	73.58	4.63	−0.72	−0.03
$E_{\text{int}}^{\text{tot}}$ (total)	165.5	−28.44	−10.63	−2.37
Argon on the “hollow” coronene site				
<i>Intermonomer</i> contributions				
$\eta(\text{Ar/C—C inner})$	−176.0	−33.61	−5.15	−0.89
$\eta(\text{Ar/C = C radial})$	−401.39	−113.7	−22.28	−4.35
$\sum\eta$ (two-body)	−698.6	−193.5	−41.78	−9.38
$\sum\eta$ (three-body)	68.14	18.32	3.59	0.39
$E_{\text{int}}^{\text{inter}}$ (total <i>intermonomer</i>)	−630.5	−175.2	−38.19	−8.98
	(−192.1)	(−53.0)	(−11.56)	(−2.72)
	[−191.9]	[−53.30]	[−11.62]	[−2.73]
$E_{\text{int}}^{\text{HF}}$	1185	73.61	0.74	−0.22
$E_{\text{int}}^{\text{intra}}$ (total <i>intramonomer</i> estimations)	205.9	19.22	0.96	−0.13
$E_{\text{int}}^{\text{tot}}$ (total)	759.5	−82.37	−36.49	−9.32
Krypton on the “hollow” coronene site				
<i>Intermonomer</i> contributions				
$\eta(\text{Kr/C—C inner})$	−244.1	−49.67	−7.59	−1.28
$\eta(\text{Kr/C = C radial})$	−545.7	−164.9	−33.22	−6.42
$\sum\eta$ (two-body)	−965.1	−282.0	−61.90	−13.72
$\sum\eta$ (three-body)	111.8	36.84	8.71	1.88
$E_{\text{int}}^{\text{inter}}$ (total <i>intermonomer</i>)	−853.3	−245.2	−53.19	−11.83
	(−185.2)	(−53.21)	(−11.54)	(−2.57)
	[−185.3]	[−53.25]	[−11.55]	[−2.57]
$E_{\text{int}}^{\text{HF}}$	1819	126.7	1.65	−0.14
$E_{\text{int}}^{\text{intra}}$ (total <i>intramonomer</i> estimations)	315.3	34.86	1.35	−0.15
$E_{\text{int}}^{\text{tot}}$ (total)	1281	−83.64	−50.19	−12.12
Xenon on the “hollow” coronene site				
<i>Intermonomer</i> contributions				
$\eta(\text{Xe/C—C inner})$	−352.8	−77.58	−12.02	−1.95
$\eta(\text{Xe/C = C radial})$	−780.4	−251.9	−52.64	−9.97
$\sum\eta$ (two-body)	−1406	−433.9	−97.35	−21.16
$\sum\eta$ (three-body)	157.5	55.54	13.63	3.04
$E_{\text{int}}^{\text{inter}}$ (total <i>intermonomer</i>)	−1248	−378.3	−83.73	−18.12
	(−181.3)	(−54.96)	(−12.16)	(−2.63)
	[−188.5]	[−57.13]	[−12.64]	[−2.74]
$E_{\text{int}}^{\text{HF}}$	2975	249.6	4.35	−0.11
$E_{\text{int}}^{\text{intra}}$ (total <i>intramonomer</i> estimations)	465.3	71.43	1.34	−0.11
$E_{\text{int}}^{\text{tot}}$ (total)	2192	−57.27	−78.04	−18.34

FIG. 2. Magnitude of the individual 2-body increments as a function of the distance Z of the Ne atom from the coronene plane. Inset: Weights of the 2-body increments in the total 2-body *intermonomer* correlation contribution.

throughout. These 3-body increments stem from the screening between the fluctuating dipoles located at three different LOGs. For example, the sum of the attractive pair interactions between the dipoles located at the adatom and one of the radial $\sigma + \pi$ bonds becomes screened by about 6–7% when a second radial nearest-neighbor $\sigma + \pi$ bond is also considered.³⁷ These 3-body increments contribute to about 10% of the total *intermonomer* correlation contribution at the potential well for Ne through Ar. This weight increases up to 15% for heavier noble-gas atoms (see Table I) as expected from the larger spatial extension of the corresponding atomic localized orbitals.

To make evident the transferability properties of the different dispersion-type components along the sequence of noble-gas atoms, the left panel of Figure 3 plots the weights of the individual attractive 2-body increments in the total 2-body *intermonomer* correlation contributions at the potential well region. The right panel of the same figure shows how much the repulsive HF, 3-body *intermonomer* correlation, and *intramonomer* correlation contributes to the repulsive component of the total interaction energy. The most important

features to notice are the almost identical weights of the individual 2-body increments (left panel of Figure 3) and the tiny variations of the 3-body increments (inset of right panel) going down the noble-gas series. The inset of Figure 3 also shows that the repulsive 3-body contribution is clearly dominated by the increments involving either one or two π localized orbitals closest to the noble-gas atom. We stress that 3-body increments comprising the outermost localized π and σ orbitals become important for the two heaviest noble-gas atoms (see the supplementary material³⁷), with percentages in the total dispersion-type energy ranging from 2% (21 meV), at the repulsive potential wall, to 4% (~15 meV) at the vdW minima for the Xe/coronene interaction, respectively.

Let us now analyze the HF and estimated *intramonomer* correlation contributions. Both energy components are repulsive at short- and medium-ranges and very slightly attractive (below -0.5 meV, see Table I) at long range. This is of course expected for ultimate dispersion-dominated vdW systems. As extensively discussed in previous studies (see, e.g., Refs. 15 and 16), the *intramonomer* correlation contribution is repulsive due to the correlation space truncation for each monomer.^{20,50,14} In the free surface, the electrons occupying the carbon rings LOGs are correlated through their excitations to all virtual orbitals. Part of the available virtual orbital space becomes blocked by the noble-gas atom occupied LOG.

As can be seen in Figure 3 (right panel), the estimated *intramonomer* correlation contributes to about 20% of the repulsive component of the total interaction. Actually, this term is estimated with the dIDF functional and not calculated at CCSD(T) level. The adequacy of this functional to predict the *intramonomer* correlation contribution has been validated for the He/TiO₂(110) interaction.^{14,15} It is anticipated that the accuracy of the X/graphite energy levels (see Section V) indicates the adequacy of the dIDF functional for the considered interactions. Interestingly, the *intramonomer* correlation term weights similarly to the 3-body *intermonomer* correlation component. Similarly to the 3-body term (see above), the *intramonomer* correlation contribution partially

FIG. 3. Left panel: weights of the individual 2-body increments in the total 2-body *intermonomer* correlation contribution to the X/coronene interaction. Right panel: Weights of the Hartree-Fock [E^{HF}], 3-body *intermonomer* correlation contribution [E^{inter} (3-body)], and estimated *intramonomer* correlation term [E^{intra} (dIDF)] in the repulsive portion of the X/coronene interaction (X = Ne, Ar, Kr, and Xe). Inset panel: weight of three leading 3-body increments to the 3-body *intermonomer* correlation contribution involving the same incremental terms (see also Table I). The distance from the noble-gas atom to the coronene plane has been fixed to 3.3 Å.

arises from screening effects between fluctuating dipoles. For the *intramonomer* term, the screening would be exerted in the dipole-dipole interaction between surface bonds by the adatom. To get additional insights, a further analysis of incremental correlation effects is in progress by adapting the quantum Drude oscillator model.⁶

On the whole, the almost identical weighting of the attractive dispersion-type contributions along the noble-gas series (see left panel of Figure 3), and the small variations of the repulsive energy components (right panel) point out a central result of this work: the interaction between the rare-gas atoms and the surface is mostly determined by the atomic responses to the surface while surface properties such as bond polarizabilities are either unaffected by the presence of the rare gases or modified by the same scale factor.

1. Further insights on the transferability of the dispersion from the Drude oscillator model

We have proved the almost equivalent weights of the individual *intermonomer* increments for all noble-gas atoms (see Figure 3). The transferability of the total *intermonomer* contributions is explored by considering a single noble-gas atom as the reference and by scaling the *intermonomer* correlation contributions of the other atoms by a factor that allows us to estimate the reference noble-gas atom contribution. One possibility is to scale by the factor $C_3^{\text{Ne}}/C_3^{\text{X}}$, with C_3^{X} as model dispersion coefficients for the long-range X/graphite dispersion interaction,¹⁰

$$C_3^{\text{X}} = \hbar \frac{g_0 \alpha_0^{\text{X}} \omega_a^{\text{X}} \omega_s}{8(\omega_a^{\text{X}} + \omega_s)}, \quad (4)$$

where α_0^{X} and ω_a^{X} stand for the static dipole polarizability and the characteristic excitation frequency of the noble-gas atom X, and g_0 and ω_s are the substrate-dependent *counterparts* of the atomic polarizability and the excitation frequency, modelling thus the dielectric response of the graphite surface. Using the parameters taken from Ref. 10 and the CCSD(T) α_0^{X} values⁵¹ of about 2.7, 11.2, 16.8, and 27.1 a.u. for X = Ne, Ar, Kr, and Xe, the rescaled *intermonomer* correlation contributions presented in Table I (in parentheses) have been obtained. To test the influence of the dispersion model parameters entering Eq. (4), the atomic dipole polarizabilities and excitation frequencies very recently reported by Martyna and co-workers⁶ have been also used. As can be seen by comparing the values presented in parentheses and square brackets (see Table I), the new set of parameters provide very similar results for Ar and Kr, differing somewhat for the xenon case. Notice also that rescaled values depart from those actually calculated for the Ne/coronene interaction by less than 10 meV and that the major deviations are peaked at the vdW minima.

B. Analysis of the interaction via symmetry-adapted perturbation theory

The global X/coronene interaction (X = He, Ne, Ar, and Kr) has been analyzed by applying the SAPT(DFT) treatment in Ref. 24. Therefore, we will focus here on the weighting of the individual SAPT energy contribution as a function

FIG. 4. SAPT(DFT) decomposition of the X/coronene interaction energy (X = Ne, Ar, Kr, and Xe) as a function of the X-coronene distance. The X atom is located at the “hollow” adsorption site (see Figure 1). The equilibrium minimum positions are indicated with vertical dashed lines.

TABLE II. Decomposition of the X/coronene interaction energy (X = Ne, Ar, Kr, and Xe) using SAPT. The noble-gas atom is located above the “hollow” site (see Figure 1), with the distance from the coronene plane fixed to 3.44 Å.

Energy (meV)	Ne	Ar	Kr	Xe
$E_{\text{elec}}/\text{SAPT(DFT)}$	-5.27	-29.1	-57.7	-129
$E_{\text{elec}}/\text{SAPT(HF)}$	-4.37	-27.9	-56.4	-121
$E_{\text{exch-rep}}/\text{SAPT(DFT)}$	16.7	85.2	157	304
$E_{\text{exch-rep}}/\text{SAPT(HF)}$	13.6	79.4	149	288
$E_{\text{ind}}/\text{SAPT(DFT)}$	-0.41	-4.83	-9.74	-8.29
$E_{\text{ind}}/\text{SAPT(HF)}$	-0.61	-5.26	-10.4	-3.31
$E_{\text{disp}}/\text{SAPT(DFT)}$	-37.9	-133	-191	-296
$E_{\text{total}}/\text{SAPT(DFT)}$	-26.9	-81.7	-102	-129
$E_{\text{total}}/\text{HF}$	8.53	46.3	82.7	164

of both the noble-gas atomic number and the intermonomer X-coronene distance. The SAPT(DFT) method^{21,22} decomposes the interaction energy as a sum of first- and second-order interaction terms, namely, first-order electrostatic E_{elst} and exchange E_{exch} , second-order induction E_{ind} and dispersion E_{disp} terms, along with their respective exchange corrections ($E_{\text{exch-ind}}$ and $E_{\text{exch-disp}}$). The $\delta(\text{HF})$ estimate^{39,40} of the higher-order induction plus exchange-induction contributions has been also included in SAPT(DFT) interaction energies. The total dispersion energy was obtained as the sum of dispersion and exchange-dispersion contributions. Similarly, the total induction energy was evaluated by adding the induction, exchange-induction, and $\delta(\text{HF})$ terms.

Placing the noble-gas atom at the “hollow” adsorption site, Fig. 4 presents the DFT-based SAPT partition of the interaction energies as a function of the distance from the carbon-ring plane. Choosing as the distance the average of the minimum energy positions, Table II presents the values of the individual energy components along with the SAPT(HF) decomposition excluding the dispersion term. Kysilka *et al.*⁵² have reported a value of -84 meV for the well-depth of the Ar/coronene potential, using the CCSD(T) method and estimating the complete basis set limit. This value agrees to within 0.5 meV (1%) with that shown in Fig. 4 and also with the dIDF + incremental D_{as}^* interaction energy at 3.3 Å (-83.6 meV, see Table I).

The vdW interaction essentially results from the balance of the exchange-repulsion and the attractive dispersion interaction (notice the small magnitude of the induction contribution). The electrostatic component is also attractive and reaches large values for the heavier noble gases (krypton and xenon). However, notice that the HF-based SAPT decomposition provides rather similar magnitudes for the electrostatic portion and that the interaction is repulsive at the dispersion-free HF level. Besides the lack of dispersion, the comparison of SAPT(HF) and SAPT(DFT) values reveals that the inclusion of *intramonomer* correlation with the latter intensifies the exchange-repulsion. As discussed above, *intramonomer* correlation effects in vdW-dominated systems are typically repulsive due to the correlation space truncation effect. From Table II, it can be also seen that the magnitude of the different energy contributions increases strongly from neon to argon and changes much less otherwise. This simply

reflects that the atomic polarizability increases by a factor of ~ 4 when going from neon to argon, and ~ 1.5 otherwise.

Figure 4 shows the individual energy contributions as a function of the X-coronene separation. The total energy is completely determined by dispersion at the medium-range potential region (~ 4.6 Å) and at larger distances. In the potential well region, the magnitude of the dispersion term is about 50% of the total interaction energy, reflecting its quenching by the exchange-repulsion. On the contrary, the induction component contributes very little at the relevant potential region. Notice also that for all X-coronene distances, the heavier the noble-gas atom, the larger the weight of the attractive electrostatic term. The SAPT electrostatic term is defined as the Coulomb interaction between the electrons and nuclei of the two monomers (i.e., the rare-gas atom and coronene). The larger values of this term for the heavier rare-gas atoms simply reflect the stronger charge overlap between the monomer densities as the adatom size increases and the X-coronene distance decreases. Naturally, the exchange-repulsion becomes also intensified. This enhanced exchange-repulsion is not counterbalanced by the larger polarizability as the atomic volume increases, resulting in the shifting of the minimum energy positions (see Fig. 4).

IV. EXTENSION TO GRAPHENE AND COMPARISON WITH VDW-CORRECTED DENSITY FUNCTIONALS

A. From the coronene cluster model to the extended graphene system

For complexes with noble-gas atoms on the graphene “hollow” site, the separation of the interaction energies into HF, *intermonomer*, and *intramonomer* correlation contributions is presented in Table III along with DFT-based interaction energies. The laterally averaged potentials obtained by means of both the dIDF + incremental D_{as}^* treatment and DFT-based approaches are shown in Figure 5. The tabulated *intermonomer* correlation contributions have been extrapolated from those determined on coronene at the CCSD(T) level. By construction of the dIDF + incremental D_{as}^* treatment, the dispersion interaction increases when moving from coronene to graphene.

Comparing Tables I and III for X/coronene and X/graphene, respectively, it can be noticed that the Hartree-Fock contribution varies very little for the two lightest noble gases, while it decreases by 12% for Kr and increases by up to 20% for Xe. As compared to coronene, the *intramonomer* correlation contribution becomes relatively less repulsive on graphene at short X-graphene distances and more attractive at the long-range potential region for all the noble-gas atoms. For example, at the repulsive potential wall, it is about 12% less repulsive for the Ar/graphene complex than for the Ar/coronene system. As extensively discussed in previous studies (see, e.g., Ref. 14), this can be explained as the result of the compression of the substrate densities on the extended system as compared to the finite cluster model. The long-range nature of the attractive induction interaction might be responsible for the intensification of this contribution at long X-graphene distances. This is specially

TABLE III. Decomposition of the interaction energies calculated for X/graphene (X = Ne, Ar, Kr, and Xe; H = hollow site) via the dIDF + incremental D_{as}^* method. Interaction energies calculated with DFT-based approaches are also shown.

	Energy (meV)			
	2.4 Å	3.3 Å	4.5 Å	6.0 Å
dIDF + incremental D_{as}^* : Ne(H)/graphene				
E_{int}^{HF}	290	15.7	-0.25	-0.02
$E_{int}^{inter}/CCSD(T)$	-190	-50.5	-12.1	-3.22
$E_{int}^{intra}/dIDF$	72.5	4.7	-1.40	-0.02
E_{int}^{tot}	172	-30.1	-13.7	-3.26
E_{int}^{PBE}	183	-7.73	-2.77	-0.15
E_{int}^{PBE-D3}	76.6	-44.6	-14.3	-3.53
$E_{int}^{vdW-DF2}$	111	-51.6	-12.2	-2.28
E_{int}^{vdW-DF}	127	-75.8	-27.6	-5.12
dIDF + incremental D_{as}^* : Ar(H)/graphene				
E_{int}^{HF}	1197	74.9	1.27	-0.05
$E_{int}^{inter}/CCSD(T)$	-638	-184	-44.4	-11.5
$E_{int}^{intra}/dIDF$	181	19.2	0.29	-0.35
E_{int}^{tot}	736	-89.5	-42.9	-11.9
E_{int}^{PBE}	813	16.7	-7.55	-0.44
E_{int}^{PBE-D3}	669	-91.4	-38.7	-9.58
$E_{int}^{vdW-DF2}$	735	-109	-44.2	-6.96
E_{int}^{vdW-DF}	749	-125	-76.2	-16.9
dIDF + incremental D_{as}^* : Kr(H)/graphene				
E_{int}^{HF}	1666	110	1.41	-0.12
$E_{int}^{inter}/CCSD(T)$	-861	-255	-60.6	-14.8
$E_{int}^{intra}/dIDF$	297	36.0	-0.26	-0.34
E_{int}^{tot}	1082	-121.1	-64.0	-16.8
E_{int}^{PBE}	1295	44.7	-9.71	-0.96
E_{int}^{PBE-D3}	1145	-102	-67.5	-17.1
$E_{int}^{vdW-DF2}$	1272	-116	-65.8	-11.0
E_{int}^{vdW-DF}	1252	-123	-103	-25.2
dIDF + incremental D_{as}^* : Xe(H)/graphene				
E_{int}^{HF}	3071	287	7.97	0.22
$E_{int}^{inter}/CCSD(T)$	-1259	-393	-94.7	-22.3
$E_{int}^{intra}/dIDF$	441	22.5	-14.0	-2.24
E_{int}^{tot}	2253	-83.5	-100	-24.3
E_{int}^{PBE}	2245	114	-12.0	-1.77
E_{int}^{PBE-D3}	2074	-83.8	-99.7	-26.5
$E_{int}^{vdW-DF2}$	2354	-85.8	-103	-18.8
E_{int}^{vdW-DF}	2250	-84.8	-143	-39.7

evident by comparing the *intramonomer* correlation energy at the distance of 4.5 Å for Xe/coronene (1.34 meV) and Xe/graphene (-14 meV). On the whole, our results illustrate that the dispersionless X/graphene interaction energy depends on the surface/delocalization properties and thus it needs to be evaluated using a periodic model.

B. Comparison with vdW-corrected density functionals

Let us now compare the total interaction energies obtained via the dIDF + incremental D_{as}^* approach with those evaluated by means of vdW-corrected DFT-based treatments. From Table III and Figure 5, notice that all the vdW-corrected

density functionals provide very different interaction energies at short Ne-graphene distances and at the minimum potential region. At medium- and long-ranges, however, the PBE-D3 and vdW-DF2 treatments yield quite similar interaction energies to those obtained with the dIDF + incremental D_{as}^* approach. Actually (see Figure 5), the agreement is especially good for the PBE-D3 long-range tails, and this is valid for all noble gases. In contrast, the vdW-DF interaction energies are considerably overestimated throughout. The vdW-DF and vdW-DF2 approaches^{30,31} include a non-local correlation functional to account for the long-range *intermonomer* correlation contributions. As previously discussed,¹⁶ the gradient correction factor of the non-local vdW-DF2 functional follows atomic scaling laws instead of that of the electron gas with a slower varying density, as in the vdW-DF precursor. This explains why the attractive vdW-DF long range tail decay too slowly.

The good performance of the PBE-D3 and vdW-DF2 treatments in the medium- and long-range region makes clear that the dispersion is reasonably well accounted for by means of the semiempirical D3 treatment or the vdW-DF2 non-local density functional for all noble-gas atoms. Hence, the less repulsive potential wall and the too attractive potential well for the Ne/graphene interaction reflect the deficiency of the considered semilocal density functionals to describe short-range correlation effects. This is even more evident for the case of the He/graphene complex (see Sec. V). In contrast to the rest of noble-gas atoms (see Table III), the bare PBE functional provides a significant value of the potential well for the Ne/graphene interaction. As previously discussed using a localized molecular orbital decomposition analysis,¹⁴ the underestimation of the exchange-repulsion by the PBE functional for very light atomic species is likely responsible for this behaviour.

As the noble-gas atom size increases (see Table III), all the vdW-corrected interaction energies become progressively closer to the bare PBE counterparts and those provided by the dIDF + incremental D_{as}^* treatment at the repulsive potential wall. In fact, since the semilocal functional PBE already incorporates the short-range *intermonomer* correlation contribution, the vdW correction must be relatively small in this region. The dIDF was specifically designed to exclude *intermonomer* correlation effects so that the vdW correction (i.e., the incremental D_{as}^* term) contributes at all X-graphene distances. For noble-gas atoms heavier than neon, the laterally averaged potentials obtained with the PBE-D3 and vdW-DF2 approaches and the dIDF + incremental D_{as}^* treatment are rather close to each other (see Figure 5 and Sec. V).

Overall, our results show that the adequacy of vdW-inclusive DFT-based treatments depends strongly on the adatom size and how the accuracy of vdW-corrections in predicting long-range tails can be quenched by shortcomings of the underlying density functional in describing short-range correlation effects. It is worth stressing that the so-named DFT/CC method by Bludský and co-workers⁵³ explicitly corrects the deficiencies of standard density functionals at the CCSD(T) level, on reference cluster models of the surface. The value reported for the well-depth of the Ar/graphene potential energy surface using this method (-93 meV) differs

FIG. 5. Laterally average potentials for the X/graphene interaction ($X = \text{Ne, Ar, Kr, and Xe}$) using different approaches. They have been obtained from the interaction energies averaged over the “hollow,” “bridge,” and “on top” sites (see Fig. 1), using geometrical weighting factors.

by about 1 meV from the dIDF + incremental D_{as}^* counterpart. This good agreement points out the efficiency of schemes combining DFT and post-HF perspectives.

V. LOW-LYING NUCLEAR BOUND STATES OF NOBLE GAS ATOMS ON GRAPHITE SURFACES

As a stringent test of the accuracy of the dIDF + incremental D_{as}^*/D_{as} treatments, the nuclear bound states supported by the laterally averaged atom/graphite potentials have been calculated. The graphite surface has been chosen because of the availability of experimental data (see also the supplementary material³⁷). Since several adsorption positions are considered to obtain the average potentials and the bound-state energies are very sensitive to the potential shapes, the similarities between the different approaches are better analyzed by comparing these vibrational energies. Precise estimations of the nuclear bound-state energies have been reported by Bartolomei *et al.*²⁴ by fine-tuning atom-bond potential model parameters with SAPT(DFT) and coupled MP2⁵⁴ benchmark interaction energies. Figure 6 plots these theoretical reference vibrational energies along with those obtained in the present work and the experimen-

based values from Ref. 55 (see also the supplementary material³⁷ for a complete list of the calculated bound-state energies). The deviation with respect to the best estimations⁵⁵ is presented in Figure 7. Absolute deviations (in meV) are shown in the inset of the same figure by considering the dIDF + incremental D_{as}^* (2-body + 3-body) approach.

Figure 6 shows smooth profiles for the low-lying bound-state energies as a function of the vibrational quantum number. Notice the transition from X-graphite complexes characterized by wide-amplitude nuclear motions, with strong anharmonic effects ($X = {}^3\text{He, Ne}$), to harmonic X-graphite oscillators where the vibrational energies can be almost perfectly fitted to straight lines ($X = \text{Kr, Xe}$).

Focusing first on the vibrational energies obtained with the dIDF + incremental D_{as}^* (2-body + 3-body) approach, the absolute (relative) deviations from the best estimations are less than 0.5 meV (1.5%) with the exception of krypton.³⁷ The lowest bound-state supported by the Kr/graphite potential is overestimated by 2.3 meV (1.9%). This value lies within the experimental error of 5 meV, and we have tested that it becomes even closer to experiment if a larger 5×5 supercell is used (see the supplementary material³⁷). By comparing

FIG. 6. Vibrational energies of the low-lying nuclear bound states (in meV) supported by laterally averaged X/graphite potentials (X = ^4He , ^3He , Ne, Ar, Kr, and Xe). The theoretical reference values correspond to the semiempirical atom-bond potential model of Ref. 24, using an *ab initio*-assisted tuning of parameters (see text). The theoretical estimations with the dIDF + incremental D_{as}^* (2-body + 3-body) approach have been plotted along with error bars corresponding to the differences obtained with and without including the capping C—H bond contributions in the D_{as}^* parametrization. The experimental values are those reported in Ref. 25 for ^4He , Ref. 56 for ^3He , and the best estimates from Ref. 55 otherwise (see also the supplementary material³⁷). Additional values of the lowest bound-state energy collected in Ref. 55 are also plotted with red crosses. For Kr and Xe atoms, bound-state energies obtained by rescaling the Ar/surface dispersion interaction via the Drude oscillator model are also shown (see text).

the results obtained with D_{as}^* (2-body) and D_{as}^* (2-body + 3-body) parameterizations, it can be noticed that 3-body terms become very important for the heavier atoms so that the values obtained with the D_{as}^* (2-body) treatment largely undershoot both the best estimations and those obtained with the rest of theoretical approaches. It has been also found that the additional 3-body terms involving outer σ and π bonds³⁷

contribute significantly to the Kr/surface and Xe/surface dispersion interaction; without these terms the vibrational energies are overestimated by about 10%. Also, while for helium, neon, and argon, the role of the capping C—H σ bonds in the D_{as}^* parametrization is insignificant, for krypton and xenon they amount to about 4 and 8 meV.³⁷ These energy differences are shown in Figure 6 with error bars because

FIG. 7. Percentage deviation of the calculated low-lying bound-state energies from the experimental values reported in Ref. 25 for the six bound states of ^4He /graphite, and the best estimates for the lowest bound state of X /graphite ($\text{X} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) from Ref. 55 otherwise (see also Figure 6). Inset: Absolute deviation (in meV) using our best theoretical estimations with the periodic dIDF + incremental D_{as}^* (2-body + 3-body) approach.

they can be considered as estimations of the uncertainty limits. As mentioned above, they measure how much the adatom response becomes modified by the interaction with the terminal C—H bonds of the coronene cluster model; ideally, this interaction should be negligible. Still, the effective exclusion of this interaction for the dispersion parametrization is possible with the method of increments. This strategy clearly predicts more accurate dispersion energies for the extended system. It is also important to notice that the energy differences between the specific D_{as}^* parameterizations are almost constant for all bound states. In fact, the profiles shown in Figure 6 as a function of the vibrational quantum number are parallel to each other. Thus, these parameterizations differ mainly in the well-depths but not in the global potential shapes.

Comparing now the vibrational energies calculated with the dIDF + D_{as} and the dIDF + incremental D_{as}^* (2-body + 3-body) approaches, we notice that the values are very close to each other. In contrast, the dIDF + incremental D_{as}^* (2-body) vibrational energies are clearly shifted down. This comparison proves that the SAPT(DFT) method effectively accounts for the 3-body incremental terms in the second-order dispersion contributions. Averaging over the deviations from the experimental data for all the noble-gas atoms,³⁷ we obtain a value below 1 meV for the dIDF + incremental D_{as}^* (2-body + 3-body) and the dIDF + D_{as} treatments. With average (relative) deviations of 0.1 meV (1.5%) and 0.6 meV (9%), respectively,³⁷ the major difference is found for the He/graphite interaction (see Fig. 6). It should be stressed that the inclusion of 3-body incremental terms beyond the leading $\text{X/C}=\text{C/C}=\text{C}$ contributions reported in Ref. 13 brings a significant improvement of the relative errors.

As an additional test of the transferability of the dispersion using the Drude oscillator approximation, the total *intermonomer* correlation contributions obtained for the Ne/coronene interaction (see Table I) were rescaled by the factors $C_3^{\text{Kr}}/C_3^{\text{Ne}}$ and $C_3^{\text{Xe}}/C_3^{\text{Ne}}$ (see Eq. (4)). Next, the resulting dispersion-type energies at each Z distance from the noble-gas atom to the coronene plane were used in model

D_{as} parameterizations for the dispersion Kr/graphite and Xe/graphite interactions. The bound-state energies supported by the resulting average dIDF + model D_{as} potentials are shown with cyan squares in the two lowest panels of Figure 6. The transferability is clearly reflected in the fact that vibrational energies depart by less than 10% from those calculated using the true *intermonomer* correlation contributions for krypton and xenon.

A. Comparison with the pairwise atom-bond potential model

The differences between the vibrational energies calculated with the dIDF + incremental D_{as}^* (2-body + 3-body) approach and those estimated with the atom-bond potential model²⁴ are below $\sim 6\text{--}7$ meV (see also the supplementary material³⁷). This good agreement indicates the adequacy of the model which exploits the sum of $\text{X/C}—\text{C}$ σ pairwise interaction contributions and therefore it is similar to the use of localized C—C σ and C=C π orbital groups as the elementary surface building blocks with the method of increments. For each interaction contribution the improved Lennard-Jones (ILJ) functional form⁵⁷ is adopted, which corrects the inadequacies of the standard LJ expression at both short and long-ranges. The model implicitly assumes that the X/surface interaction is determined by the atomic responses to the surface. Notice that our results and, in particular, the close percentage of the different surface increments across the noble-gas sequence (see Fig. 3) supports this assumption. However, as can be seen in Figure 6, the bound-state energies calculated within the atom-bond approach appear to overestimate the best estimations⁵⁵ and this is more evident for the heavier rare gases. This overestimation is not attributed to the exclusion of 3-body $\text{X/C}—\text{C/C}—\text{C}$ terms in the atom-bond potential model because the vibrational energies calculated with the dIDF + incremental D_{as}^* (2-body) treatment are always shifted at lower (more negative) energies (see Fig. 6).

B. Comparison with vdW-corrected DFT-based approaches

Considering the vibrational energies calculated with vdW-corrected DFT-based approaches (see Figure 6 and the supplementary material³⁷), notice the systematic improvement of the predicted values upon increasing the noble-gas atomic number. For helium and neon, the vibrational energies deviate by up to 46% from the best estimations.⁵⁵ In contrast, for the heaviest noble-gas atoms, the percentage deviations are within 11% and 4% when the vdW-DF2 and PBE-D3 approaches are used, respectively. Starting with the Ar/graphite complex,³⁷ the vibrational energies obtained with the PBE-D3 treatment differ by less than 1.6 meV from those calculated with the dIDF + incremental D_{as}^* treatment. As shown in Figure 5 for the Ar/graphene and Kr/graphene complexes, the average potentials obtained with the dIDF + incremental D_{as}^* and PBE-D3 treatments are very close to each other. For the Xe/graphene system, the vdW-DF2 potential becomes closer to that calculated using the dIDF + incremental D_{as}^* method. A very good agreement between vdW-DF2 and dIDF + incremental D_{as}^* treatments was also found for the

Ag₂/graphene complex.¹⁶ This is translated in the very similar nuclear bound states supported by the average potentials (see Fig. 6 and the supplementary material³⁷). On the whole (see Fig. 7), the PBE-D3 treatment is the vdW-corrected DF approach providing the vibrational energies closest to the best estimations for noble gases heavier than neon (differing by at most 3.5 meV). The repulsive 3-body corrections of the DFT-D3 treatment hold the key for this accuracy. As a matter of fact, the vibrational energies become overestimated by 10 meV when the DFT-D2⁵⁸ precursor, excluding 3-body contributions, is applied.

VI. SUMMARY AND CONCLUDING REMARKS

Summarizing, this work has been mainly aimed to analyze if the good performance of the dIDF + incremental D_{as}^* method demonstrated for the He/surface interaction problem^{13–15} is also valid for other noble gases. For this purpose, carbon-based coronene, graphene, and graphite surfaces have been chosen. When the incremental expansion of the dispersion contribution includes 2- and the leading repulsive 3-body increments, involving the noble-gas atom and up to two surface localized orbital groups, an excellent accuracy has been found for all the noble-gas atoms. Thus, similarly to the He/surface system,¹³ the average deviation of the lowest bound-state energies from the best estimations⁵⁵ is less than 1 meV. The dramatic influence of 3-body terms is clearly revealed by the gross overestimation of bound-state energies when only the attractive 2-body contributions are considered. The inclusion of these 3-body contributions is highly relevant to achieve accuracy in the values of the van der Waals well-depths while the overall shapes of the potentials are much less influenced.

As a second conclusion, almost indistinguishable profiles for the nuclear bound-state energies are obtained for the X/surface ($X = {}^3, {}^4\text{He}$, Ne, Ar, Kr, and Xe) complexes when the dispersion energies are calculated via the SAPT(DFT) treatment. A similar accuracy to that evaluated with the dIDF + incremental D_{as}^* treatment is found with the lowest bound-state energies differing by less than 2 meV from the experimental-based estimations.⁵⁵ Hence, our results indicate that the second-order SAPT(DFT) dispersion energies effectively account for the 3-body terms in the incremental expansion of the *intermonomer* correlation energy evaluated at the CCSD(T) level. Also, the SAPT(DFT) decomposition demonstrates that the role of exchange-repulsion and electrostatic terms arising from charge overlap effects becomes more important for the heavier noble-gas atoms.

An excellent agreement (to within 6–7 meV) is also found between the nuclear-bound state energies of X/graphite complexes ($X = {}^3, {}^4\text{He}$, Ne, Ar, and Kr) calculated with the dIDF + incremental D_{as}^* treatment and estimated by means of the atom-bond pairwise potential model.²⁴ VdW-corrected DFT-based treatments have been also applied to get X/graphene ($X = \text{He}$, Ne, Ar, Kr, and Xe) potential energy surfaces. Nuclear bound-state energies evaluated with the PBE-D3 and vdW-DF2 approaches for noble-gas atoms heavier than neon are in good agreement with our theoretical estimations. In contrast, none of the considered treatments

provides a satisfactory description of complexes involving He and Ne atoms. However, the medium- and long-range PBE-D3 and vdW-DF2 dispersion tails are similar to the benchmark counterparts for all the noble-gas atoms. As in previous studies, the failure for helium and neon is attributed to shortcomings in the semilocal exchange-correlation functional and, particularly, to the underestimated exchange-repulsion. These deficiencies are explicitly corrected at the CCSD(T) level on reference clusters when the CC/DFT method is applied. It should be stressed that the Ar/graphene CC/DFT binding energy agrees very well with our results (to within 1 meV). Both treatments have been found to provide H₂/graphene bound-state energies differing by less than 6 meV.^{59,60}

Using the method of increments, an analysis of the transferability properties of the dispersion interaction indicates that localized surface orbitals contribute with nearly the same weight for all the noble-gas atoms. A further analysis shows that the dispersion energies scale with the dynamic polarizabilities of the noble-gas atoms, when approximated with the Drude oscillator model.¹⁰ The transfer of the dispersion energies from argon to krypton and xenon using the Drude oscillator model provides dIDF + model D_{as}^* nuclear-bound states energies for the Kr/graphite and Xe/graphite interactions differing by less than 10% from the dIDF + incremental D_{as}^* counterparts.

In conclusion, this work clearly highlights the accuracy and transferability of the dIDF + incremental D_{as}^*/D_{as} approaches for the interaction of noble gases with carbon-based surfaces, with a performance surpassing that of state-of-the-art vdW-corrected DFT-based treatments. The recently demonstrated accuracy of the treatment to predict the spectroscopy energy levels of molecular hydrogen physisorbed on graphite⁶⁰ (to within 1.4 meV) motivates its extension to molecular spectroscopy of vdW-dominated adsorbate/surface complexes, including open-shell adsorbates as well as metallic and transition metal-oxide surfaces. The physical insights provided by the Drude oscillator model encourage further work on the coarse-grained electronic structure methods modelling the adsorbate/surface dispersion interaction. The analysis of structural relaxation effects in molecular crystals is another direction for future research.

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