Adsorption of Ar on graphite using London dispersion forces corrected Kohn-Sham density functional theory

Alexandre Tkatchenko[1,2,*] and O. Anatole von Lilienfeld[2,3,†]
[1]*Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, México D.F., Mexico*
[2]*Institute for Pure and Applied Mathematics, 460 Portola Plaza, University of California Los Angeles, Los Angeles, California 90095-7121, USA*
[3]*Department of Chemistry, New York University, New York, New York 10003, USA*
(Received 24 December 2005; revised manuscript received 3 February 2006; published 25 April 2006)

Using Kohn-Sham (KS) density functional theory, the adsorption of Ar on graphite has been computed with various conventional exchange-correlation functionals. While the local density approximation yields a reasonable estimate of equilibrium distance and energy, three generalized gradient approximated functionals fail. Extending the KS Hamiltonian by an empirical nonlocal and atom-centered potential enables quantitative predictions. The adsorption on the on-top, hollow, and bridge sites has been investigated, and it is found that the London dispersion corrected calculations prefer the hollow site which is in agreement with other studies. Furthermore, the adsorption effect of several submonolayer coverages and of the graphitic bulk has been studied.

DOI: 10.1103/PhysRevB.73.153406 PACS number(s): 68.35.Md, 71.15.Ap, 31.15.Ew, 31.30.−i

I. INTRODUCTION

An accurate understanding of adsorption processes is crucial for the purposes of many rational compound design (such as materials or catalysts design) efforts.[1,2] The adsorption of rare-gas atoms on metallic surfaces is prototypical for physisorption because of the closed-shell nature of the adatoms. While adsorption of rare gases on metallic surfaces has been serving as a benchmark system for studies of surface phenomena for a long time,[3] (*ab initio*) calculations are still rare and provide only qualitative agreement with experiments.[4] Interestingly, graphitic surfaces constitute an exception among metallic surfaces in that a high-coordination adsorption site is usually preferred. The adsorption of rare gases is thought to be due to an equilibrium between attractive long-ranged London dispersion forces—resulting from the correlated fluctuation of nonoverlapping electron densities[5]—and Pauli repulsion.[6] While within Kohn-Sham (KS) density functional theory (DFT),[7,8] the latter is well described by most of the standard approximations to the exchange-correlation (*xc*) potential, the former constitute an important difficulty.[9] Unfortunately, it is not generally possible to accurately describe these interactions within DFT using the local density approximation (LDA), the generalized gradient approximation (GGA), or even the—on average more accurate—hybrid exchange-correlation functionals.[9–14] In this study, results are presented for the adsorption of Ar on graphite using London dispersion corrected KS-DFT calculations according to Refs. 15–18, and without discussing in detail the many alternative corrections and improved *xc* functionals available in the literature by now.[19–32] First, the performance of a few London dispersion uncorrected *xc* functionals for the Ar-graphite system is assessed. Second, the preference regarding the on-top, hollow, and bridge adsorption sites has been determined. Third, the effect of several coverages and layers of graphite sheets has been investigated.

II. COMPUTATIONAL DETAILS

The here employed London dispersion correction was recently introduced as a semiempirical dispersion calibrated atom-centered potential (DCACP), $\hat{v}_I^{\mathrm{disp}}$, which is added to the KS Hamiltonian.[15] Specifically, we see it as a nonlocal extension of a given, local for LDA or GGA, *xc*-potential,

$$\hat{v}_{xc}^{\mathrm{extended}} = \hat{v}_{xc}(\mathbf{r}) + \sum_I \hat{v}_I^{\mathrm{disp}}(\mathbf{r},\mathbf{r}',\{\sigma_i\}_J), \tag{1}$$

where index I, J, and i enumerate all atoms, all atom types, and all empirical parameters σ, respectively. For the sake of convenience and computational efficiency, the functional form of the correction corresponds to the nonlocal angular-momentum dependent term of the analytic pseudopotentials introduced by Goedecker *et al.*[33] As generally suggested in Ref. 16, the atom-type J dependent parameters $\{\sigma_i\}$ are obtained from preliminary calibrations yielding an improved electronic structure fulfilling additional requirements, e.g., exerting a London dispersion force on the nuclei. For this study, the BLYP+DCACP parameters for carbon and argon—as introduced, calibrated, and assessed for their transferability in Refs. 15, 17, and 34—are employed. For their calibration, Møller-Plesset second-order perturbation theory (MP2) results for the benzene dimer and for the argon dimer had been used as a reference. Generalization of this correction, to *xc*-functionals other than BLYP, other references, other functional forms of the correction, and other atoms, is the subject of current research activities.[35] The DFT calculations have been carried out using the plane-wave basis set electronic structure program CPMD 3.92,[36] the *xc*-functionals BLYP,[37–39] BP,[37,40] PBE,[41] LDA [using the Perdew and Zunger fit (Ref. 42) to the data of Ceperley and Alder],[43] Goedecker's pseudopotentials from Refs. 33, 44, and 45, and a plane-wave basis set energy cutoff of 100 Ry. Periodic boundary conditions have been imposed upon a triclinic box of $9.824^2 \times 15$ Å^3 for one, $9.824^2 \times 18$ Å^3 for two, and $8.824^2 \times 21$ Å^3 for three graphite sheets. These box sizes

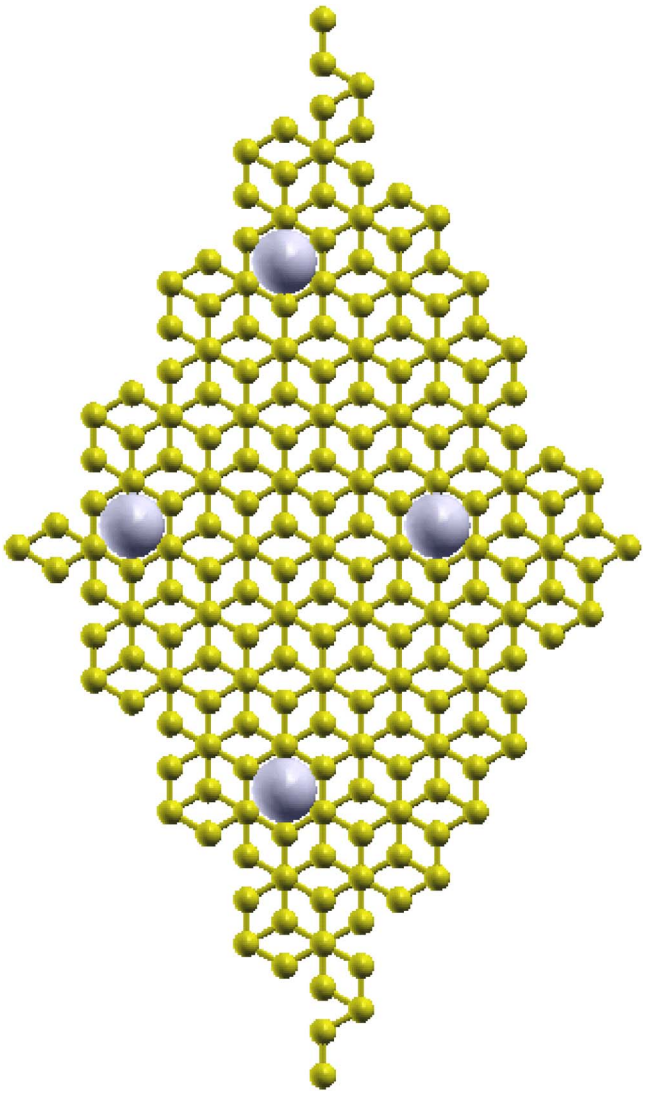

FIG. 1. (Color online) Sketch of four triclinic unit cells of 1/32 coverage of Ar on the hollow site on graphite. The interatomic Ar–Ar distance corresponds to four graphite lattice constants (9.824 Å).

correspond to 32 carbon atoms per graphitic layer. For this study, contributions of the *k*-point sampling have been neglected and only the Gamma-point has been considered, which, as has also been pointed out recently,[46] is a reasonable approximation for boxes of this size. The graphite geometry, as employed in Ref. 15, has been used and kept fixed. Relative adsorption energies have been computed for identical box sizes and cutoffs being defined as total potential energy differences between the adsorbed system and the sum over the isolated systems, normalized with respect to the number of Ar atoms. Five coverages have been studied, consisting of submonolayer hollow-site depositions of one, two, and four Ar atoms per unit cell. The interatomic distance for 1 Ar atom per unit cell (1/32 coverage) is four graphite lattice constants (glc) amounting to 9.824 Å, which corresponds to the (4×4)-structure. Four unit cells of this structure are sketched in Fig. 1. For two atoms per unit cell (1/16 coverage), three calculations have been performed, namely at

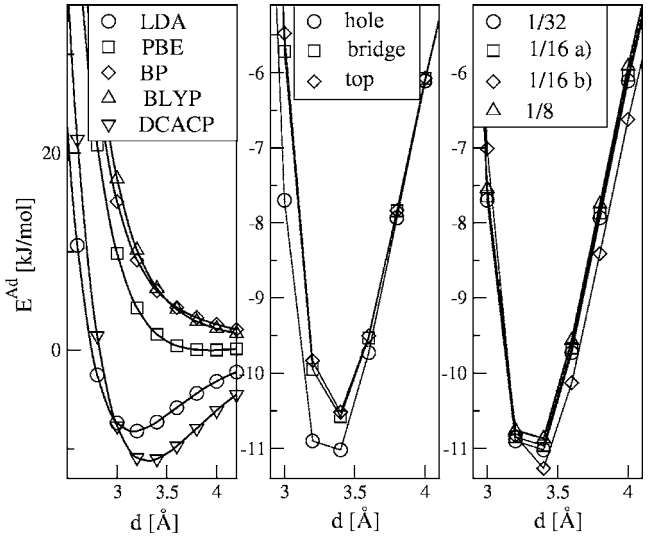

FIG. 2. KS DFT results for argon–graphite adsorption, E^{Ad} as a function of distance *d*. Left hand panel: 1/32 coverage adsorption curves for hollow sites from several exchange-correlation functionals, DCACP corresponds to DCACP+BLYP. Middle panel: 1/32 coverage adsorption energies for the hole, bridge, and on-top sites using the DCACP+BLYP functional. Right hand panel: adsorption energies of 1/32, 1/16, and 1/8 coverage using the DCACP +BLYP functional. 1/16 a) corresponds to the interatomic distance of two graphite lattice constants (4.912 Å), and 1/16 b) to $\sqrt{3}$ graphite lattice constants (4.254 Å).

interatomic distances in the submonolayer of one glc (2.456 Å), of $\sqrt{3}$ glc (4.254 Å), and of 2 glc (4.912 Å). For four atoms per unit cell (1/8 coverage), the interatomic distances are 2 glc (4.912 Å) corresponding to a (2×2) structure.

III. RESULTS AND DISCUSSION

A. Functionals

Computed adsorption curves for the 1/32 coverage using the LDA, PBE, BP, BLYP, and BLYP+DCACP functionals are displayed in the left-hand side panel of Fig. 2. All employed GGAs predict an increasing repulsion when going from PBE to BP to BLYP—the same trend as for $\pi-\pi$ stacking polyaromatic hydrocarbons.[18] LDA predicts an interpolated adsorption energy of 8.3 kJ/mol at a distance of 3.17 Å being in perfect agreement with another recent LDA study.[47] The BLYP+DCACP yields a slightly increased and more distant result for the interpolated equilibrium, namely 11.2 kJ/mol and 3.33 Å, respectively. We have not found direct experimental data for heats of adsorption of argon–graphite system. However, the here reported London dispersion corrected adsorption energy is in good agreement with anisotropic empirical potentials, which are consistent with a large amount of thermodynamic data, namely 9.2 kJ/mol.[48] Furthermore, the equilibrium distance is in excellent agreement with MP2 calculations for the argon–benzene distance[49] which can be seen as a model–system for the argon-graphite interaction. Having in mind that on the one

TABLE I. Adsorption energy (Ad) of argon on graphite, and its kinetic (kin), electrostatic (ele), i.e., Hartree and Coulomb-repulsion, and exchange-correlation (xc) contributions at 3.2 (for LDA) and 3.4 (for all other functionals) Å distance. All values are in kJ/mol.

	Ad	kin	ele	*xc*
LDA	−8.2	−5.8	14.7	−17.1
PBE	0.6	16.8	−6.1	−10.1
BP	6.0	18.3	−7.6	−4.7
BLYP	6.2	34.6	−17.5	−10.9
BLYP+DCACP	−10.9	19.0	−23.8	−6.1

hand LDA is known to overestimate the Ar-dimer interaction[11,50,51] and that on the other hand LDA underestimates the π-stacking interaction between graphitic structures,[18] it seems plausible that in the case of an argon–graphite interaction, LDA yields a fortuitous cancellation of errors which brings the adsorption into somewhat good agreement with the London dispersion corrected GGA results. In order to investigate this point in more detail, the energetic contributions to the adsorption are listed in Table I. While the contributions of all the GGA functionals exhibit the same sign, an opposite trend is observed for the kinetic and the electrostatic components of the LDA energy of interaction. Apparently, the slope of the LDA density varies less in the complex than in the case of the isolated Ar and graphite, leading to an overall attractive kinetic contribution. It is interesting to note the changes in the BLYP contributions upon inclusion of the London dispersion correction. Since the dispersion correction is an integral operator, it modifies the electron density and thereby all the contributions. While the kinetic repulsion and the exchange-correlation attraction decrease toward values corresponding to the BP-functional, the electrostatic attraction increases by roughly one-third turning into the largest attractive component of all employed functionals. Hence, the slightly decreased binding due to the exchange correlation is more than counterbalanced by the change in the kinetic repulsion, and in the electrostatic attraction resulting in the overall attraction. As already shown for Ar–benzene in Ref. 15, the correction delocalizes the BLYP electron density in the long-range distance ($\approx$1.5 Å away from the atoms), probably causing thereby the increased electrostatic (additional overlap) and decreased kinetic (smoother wave functions) contributions.

B. Adsorption energy corrugation

For lateral shifts of the argon submonolayer with the 1/32 coverage, likewise a qualitative and quantitative agreement with the corrugation of the anisotropic model of Ref. 48 is found, namely that the hollow site is preferred over the bridge which is preferred over the on-top adsorption site. This result also agrees with experimental findings for Xe on graphite[52] and with the LDA calculations in Ref. 47. The obtained curves are depicted in the middle panel of Fig. 2 and, when going from the hollow site to bridge, show a loss of adsorption energy of roughly half a kJ/mol and an increase in distance of $\approx$0.1 Å. It is understood, however, that for this order of magnitude, the accuracy of plane-wave-based pseudopotential density functional implementations is at its limits. Interestingly, rare-gas atoms usually prefer to adsorb on-top on metals, as recently pointed out by Da Silva *et al.*[4] using LDA calculations. It therefore seems reasonable that the here-observed effect is largely due to the interplay between the chemically inert rare-gas atom and the exceptional structure of graphite when compared to other metallic surface structures. Specifically, the graphite hole has such a large radius that it can favorably accommodate the rare-gas atom allowing for simultaneous nondirectional attractive interaction with all six nearest-neighbor carbon atoms at an average carbon–argon distance of $\approx$3.4 Å (which is the typical range of binding distances due to London dispersion forces). This adsorption configuration must be compared to the on-top situation with one nearest-neighbor and three second-nearest-neighbor carbons. Already when assuming a simple atom pair-wise Lennard-Jones adsorption potential, adding up the interactions will result into less adsorption energy for the latter arrangement of interatomic distances than for the hollow site. We note, however, that this simplified rationale is only legitimate because no bond formation is possible in the case of a rare-gas adsorbate.

C. Coverage and bulk

The effect of varying the coverage in the submonolayer becomes only measurable for the 1/16 coverage at 1 and $\sqrt{3}$ glc distances. For 1 glc (2.456 Å), the effect is grossly repulsive. In the right-hand panel of Fig. 2, adsorption curves for all other coverages are reported. In the case of the $\sqrt{3}$ glc distance (4.254 Å) additional adsorption is obtained, as at this distance the interaction between adjacent Ar atoms becomes attractive. These effects can be further rationalized by taking into account that the short distance falls into the strongly repulsive and the long distance into the attractive long range region of an isolated argon–argon dimer interaction curve, as reported for instance in Ref. 15. However, these effects are very small and likewise at the limit of the standard DFT accuracy. The influence of the graphite bulk in comparison to a single graphite sheet was also measured for the 1/32 coverage on the hollow site. The intergraphitic distances have been set to 3.35 Å in correspondence with Ref. 15, and the planes have been shifted in order to yield an AB-packing (see Fig. 1). Within the BLYP+DCACP calculations, no quantitative variation of the adsorption curve has been found when going from one to two up to three layers. We believe that this finding is largely due to the large interlayer distance of graphite (which is untypical for "true" metals). Furthermore, this finding is backed up by the fact that empirical pair-wise potentials work quite well for London dispersion dominated interactions,[18,28,29,32,53] i.e., that the contribution due to cooperative many-body effects of the graphite bulk can safely be discarded for these coverages. However, it should be noted that the employed London dispersion correction was calibrated only at the equilibrium distance and was not explicitly designed to correctly reproduce the dissociative behavior.[15,17]

IV. CONCLUSIONS

The data collected here suggest the corrugation of Ar on graphite to be roughly 0.5 kJ/mol, the most favorable site being the maximally coordinated hollow one, and the adsorption energy ≈11 kJ/mol. Several coverages have been investigated for submonolayer depositions and only when the Ar–Ar distance is small enough to fall into the repulsive or attractive Ar-dimer interaction potential, can an effect on the adsorption be measured. Furthermore, our model predicts the contribution of the graphitic bulk to the adsorption to be negligible. Finally, the GGA DFT KS-potentials BP, PBE, or BLYP fail to correctly predict the adsorption of Ar on graphite. Further indications have been found that the very reasonable results of LDA are fortuitous. The BLYP+DCACP results are in very good agreement with the available literature, coming along without any computational overhead or necessity of *a priori* assignments of fragments. It appears that for the study of adsorption processes the inclusion of London dispersion forces is important, as also recently pointed out by Ortmann *et al.*[32] Our findings are especially relevant for systems, such as hydrogen bonded aromatic complexes—e.g., deoxyribonucleic acid-base pairs—adsorbed on graphitic surfaces. In such cases, LDA is expected to fail to account correctly for the hydrogen bonding, while the pure GGAs will have difficulties in describing the adsorption.

ACKNOWLEDGMENTS

M. Galván and A. P. Seitsonen are acknowledged for helpful comments. Both authors thank the organizers of the culminating Lake Arrowhead meeting within the workshop *Bridging Time and Length Scales in Materials Science and Bio-Physics* which was held at the Institute for Pure and Applied Mathematics at the University of California Los Angeles and which inspired this study. All calculations were performed at the *Laboratorio de Supercomputo y Visualizacion en Paralelo (LSVP)* at UAM-Iztapalapa. A.T. thanks CONACYT for financial support and O.A.vL. is grateful for support from the SNF, Grant No. PBEL2-110243.

*Electronic address: sanix@ixil.izt.uam.mx
†Electronic address: ovt203@nyu.edu

[1] O. A. von Lilienfeld *et al.*, Phys. Rev. Lett. **95**, 153002 (2005).
[2] M. Wang *et al.*, J. Am. Chem. Soc. **128**, 3228 (2006).
[3] L. W. Bruch *et al.*, *Physical Adsorption: Forces and Phenomena* (Oxford University Press, New York, 1997).
[4] J. L. F. Da Silva *et al.*, Phys. Rev. Lett. **90**, 066104 (2003).
[5] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Dover, New York, 1998).
[6] R. D. Diehl *et al.*, J. Phys.: Condens. Matter **16**, 2839 (2004).
[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[9] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, New York, 2002).
[10] S. Kristyán and P. Pulay, Chem. Phys. Lett. **229**, 175 (1994).
[11] J. M. Pérez-Jordá and A. D. Becke, Chem. Phys. Lett. **233**, 134 (1995).
[12] E. J. Meijer and M. Sprik, J. Chem. Phys. **105**, 8684 (1996).
[13] T. van Mourik and R. J. Gdanitz, J. Chem. Phys. **116**, 9620 (2002).
[14] X. Wu *et al.*, J. Chem. Phys. **115**, 8748 (2001).
[15] O. A. von Lilienfeld *et al.*, Phys. Rev. Lett. **93**, 153004 (2004).
[16] O. A. von Lilienfeld *et al.*, J. Chem. Phys. **122**, 014113 (2005).
[17] O. A. von Lilienfeld *et al.*, Phys. Rev. B **71**, 195119 (2005).
[18] O. A. von Lilienfeld and D. Andrienko, J. Chem. Phys. **124**, 054307 (2006).
[19] T. A. Wesolowski *et al.*, J. Chem. Phys. **116**, 6411 (2002).
[20] T. A. Wesolowski and F. Tran, J. Chem. Phys. **118**, 2072 (2003).
[21] Y. Andersson *et al.*, Phys. Rev. Lett. **76**, 102 (1996).
[22] E. Hult *et al.*, Phys. Rev. Lett. **77**, 2029 (1996).
[23] H. Rydberg *et al.*, Phys. Rev. B **62**, 6997 (2000).
[24] H. Rydberg *et al.*, Phys. Rev. Lett. **91**, 126402 (2003).
[25] M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004).
[26] A. J. Misquitta *et al.*, Phys. Rev. Lett. **91**, 033201 (2003).
[27] W. Kohn *et al.*, Phys. Rev. Lett. **80**, 4153 (1998).
[28] R. LeSar, J. Phys. Chem. **88**, 4272 (1984).
[29] S. Grimme, J. Comput. Chem. **25**, 1463 (2004).
[30] S. J. A. van Gisbergen *et al.*, J. Chem. Phys. **103**, 9347 (1995).
[31] E. R. Johnson and A. D. Becke, J. Chem. Phys. **123**, 24101 (2005).
[32] F. Ortmann *et al.*, Phys. Rev. Lett. **95**, 186101 (2005).
[33] S. Goedecker *et al.*, Phys. Rev. B **54**, 1703 (1996).
[34] E. Tapavicza, *et al.* (unpublished).
[35] M. Coutinho *et al.* (unpublished).
[36] J. Hutter *et al.*, *Computer code CPMD, version 3.92*, Copyright IBM Corp. 1990–2001, Copyright MPI-FKF Stuttgart 1997–2004, ⟨http://www.cpmd.org⟩.
[37] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[38] R. Colle and D. Salvetti, Theor. Chim. Acta **37**, 329 (1975).
[39] C. Lee *et al.*, Phys. Rev. B **37**, 785 (1988).
[40] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[41] J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
[42] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[43] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[44] C. Hartwigsen *et al.*, Phys. Rev. B **58**, 3641 (1998).
[45] M. Krack, Theor. Chim. Acta **114**, 145 (2005).
[46] M. H. Matus *et al.*, J. Chem. Phys. **120**, 10359 (2004).
[47] Y. L. Bai *et al.*, Chin. Phys. Lett. **20**, 2019 (2003).
[48] G. Vidali and M. W. Cole, Phys. Rev. B **29**, 6736 (1984).
[49] W. Klopper *et al.*, J. Chem. Phys. **101**, 9747 (1994).
[50] M. Hasegawa and K. Nishidate, Phys. Rev. B **70**, 205431 (2004).
[51] F. Tournus *et al.*, J. Chem. Phys. **122**, 094315 (2005).
[52] K. Pussi *et al.*, Surf. Sci. **548**, 157 (2004).
[53] W. A. Steele, Surf. Sci. **36**, 317 (1973).