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Periodic quantum mechanical simulation of the He–MgO(100) interaction potential

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He-atom scattering is a well established and valuable tool for investigating surface structure. The correct interpretation of the experimental data requires an accurate description of the He-surface interaction potential. A quantum-mechanical treatment of the interaction potential is presented using the current dominant methodologies for computing ground state energies (Hartree–Fock, local and hybrid-exchange density functional theory) and also a novel post-Hartree–Fock *ab initio* technique for periodic systems (a local implementation of Møller–Plesset perturbation theory at second order). The predicted adsorption well depth and long range behavior of the interaction are compared with that deduced from experimental data in order to assess the accuracy of the interaction potential. © *2011 American Institute of Physics*. [doi:10.1063/1.3517868]

I. INTRODUCTION

A detailed understanding of surface structure is important in surface science, heterogeneous catalysis, much of nanoscience, and the technologies based on them. Unlike other techniques for measuring surface structure [such as, low energy electron diffraction (LEED), scanning tunneling microscopy (STM) or field ion microscopy (FIM)], He-atom scattering causes no damage to the surface, is very surface sensitive probing only the outermost layer, and does not suffer from the effects of surface charging. The use of He-scattering has, however, an important limitation related to the difficulty in the interpretation of the scattering spectra due to the lack of a detailed understanding of the scattering interaction potential.[1] The first step in the quantitative analysis and correct interpretation of He-atom experiments consists of determining the He-surface interaction potential. Empirical modelling of the He-surface interaction is inadequate, as simple potentials, if fitted extensively to the observed spectra, are nonunique and thus may miss the essential physics of the surface interaction or, if based on empirical force fields, provide an inaccurate and nontransferable description.[2] To date, a first-principles description of the He-surface interaction has not been possible, because the current methodology dealing with extended systems is based on density functional theory (DFT), Hartree–Fock (HF) and hybrid DFT/HF approaches. Neither HF or the semilocal (LDA, GGA) approximations to DFT describe dispersion interactions reliably, for different reasons: HF is affected by a systematic error related to its neglect of electronic correlation, while the LDA and GGA cannot correctly describe dispersive interactions between distant parts of the system. These approaches are therefore unsuitable for calculating the interaction between weakly bonded systems. In order to take into account the dispersive contributions to the He-surface interaction at geometries far from equilibrium, a more sophisticated description is required that includes an accurate treatment of electronic correlation. Periodic Local Møller–Plesset second order (MP2) perturbation theory calculations, as recently implemented in CRYSCOR[3–5] may provide a reliable and accurate solution to this problem. In particular, MP2 describes in a qualitatively correct way the dispersive interaction at long range. The implementation of fast integral evaluation techniques such as density fitting[4,6–10] mean that the computational cost of a MP2 calculation is now not significantly higher than that of an HF or DFT calculation. Two other methods have been recently proposed to approximate the dispersive contribution. The first is documented in a recent study by Civalleri *et al.*,[11] which demonstrates the application of the semiempirical Wilson–Levi (WL) correlational functional that has been constructed to describe interaction energies for weakly bonded molecular systems near equilibrium geometry. The second method is the addition of a London-type empirical correction adopted by Grimme[12] and has also been applied to gas–surface interactions.[13]

The aim of this work is to evaluate the effects of approximating electronic exchange and correlation on the He–MgO interaction potential in order to select an appropriate approach for the interpretation of He-scattering data. For this purpose, the following methods have been employed: periodic Hartree–Fock, local MP2 and DFT, the latter using the PBE functional with the WL correlation part (PBEWL), hybrid-exchange (B3LYP and PBE0) functionals with and without Grimme dispersion correction, as implemented in the CRYSTAL09[14] and CRYSCOR09[3] *ab initio* programs.

It has been observed that PBEWL and the Grimme method provide a reasonable description of the energy surface near the equilibrium geometries but the accuracy of these

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approaches away from equilibrium geometries has not been previously discussed. He-atom scattering probes the energy surface at a variety of energies between 26 and 60 meV. Therefore, an *ab initio* method that provides a reliable and unbiased description of the energy surface significantly away from equilibrium is required.

The paper is organized as follows: Sec. II contains computational details. In Sec. III the results for the He–MgO(100) interaction potential are presented and discussed in terms of the binding energy and long range behavior. The main conclusions of this study are summarized in Sec. IV. The influence of the choice of basis set is documented in the Appendices A and B, and the effects of the coverage in Appendix C. Auxiliary calculations employing a small $Mg_3Na_2O_4$ cluster plus He are reported and discussed in Appendix D.

II. COMPUTATIONAL DETAILS

All calculations have been performed using the CRYSTAL09[14] and CRYSCOR09[3] software packages, both based on the expansion of the crystalline orbitals as a linear combination of a local basis set (BS) consisting of atom centred Gaussian orbitals. The main approximation common to all used methods is then the choice of the BS. In order to approach the BS limit, a hierarchy of all-electron basis sets has been selected for O, Mg, and He; they are labeled as BS1, BS2, BS3, and BS4 (see Table I). These BSs are documented in detail in Appendix A. If not otherwise indicated, BS4 is adopted for the calculations.

The exchange and correlation potentials and energy functional are integrated numerically on an atom centered grid of points. The integration over radial and angular coordinates is performed using Gauss–Legendre and Lebedev schemes, respectively. A pruned grid consisting of 99 radial points and 5 subintervals with (146, 302, 590, 1454, 590) angular points has been used for all calculations [the XXLGRID option implemented in CRYSTAL09[14]]. This grid converges the integrated charge density to an accuracy of about $\times 10^{-6}$ electrons per unit cell of MgO bulk.

The Coulomb and exchange series are summed directly and truncated using overlap criteria with thresholds of 10^{-9}, 10^{-9}, 10^{-9}, 10^{-9}, and 10^{-17} as described previously,[14,15] the effects of this choice have been documented in a previous paper on the calculation of the dispersion contribution with the CRYSTAL code.[11] For the MP2 calculations, more severe thresholds on the exchange contribution have to be adopted for the calculation of the HF wave function, 10^{-9}, 10^{-9}, 10^{-9}, 10^{-25}, and 10^{-75}.[16,17]

TABLE I. All-electron basis set hierarchy for O, Mg, and He. See Appendix A for details.

BS	Mg	O	He
BS1	8-511 d(1)	8-411 d(1)	411 p(11) d(1)
BS2	10-7111 d(1)	10-6111 d(1)	4111 p(111) d(11)
BS3	10-7111 d(11)	10-6111 d(111)	4111 p(111) d(111)
BS4	10-7111 d(11) f(1)	10-6111 d(111) f(11)	4111 p(111) d(111) f(11)

Reciprocal space sampling was performed on a Pack–Monkhorst net with a shrinking factor, IS = 8, which defines 75 symmetry unique *k*-points in the bulk structure and 15 in the 2D periodic system (slab). The self-consistent field procedure was converged up to a tolerance in the total energy of $\Delta E = 1 \cdot 10^{-7} E_h$ per unit cell.

In the Local MP2 part of the calculations[3,18] the localized virtual orbitals [projected atomic orbitals (PAOs)] were generated with IS = 16.[19] Since the Wannier functions (WFs) of the slab are centered on oxygen atoms, the excitation domains comprised the PAOs of the corresponding O and the nearest-neighbor Mg atoms. For the adsorbate WFs the domains consisted of PAOs belonging to the corresponding He atom. The excitation pair-list included the inter-slab and inter-adsorbate pairs with the inter-orbital separation up to 6 Å and slab–adsorbate pairs (responsible for describing the dispersion interaction) up to 12 Å. The two-electron integrals for the pairs up to 6 Å were calculated using the local density fitting technique[4] and beyond that region via the multipole approximation.

III. RESULTS

In this section, the description of the He–MgO interaction is analyzed by computing the binding energy of an isolated He atom and the clean surface. The MgO(100) surface is approximated as a rigid 2D periodic 3-layer sheet cut from the bulk structure at the experimental lattice constant ($a = 4.211$ Å).[20] This provides a well defined reference geometry for studying the effects of different approximations to electronic exchange and correlation. Adsorption of the He atom at two sites is considered, directly above either an O or Mg ion. In each case a set of configurations is considered, where the distance between the He atom and the centroid of the outermost layer is varied in the range 2.5–7.0 Å. If not indicated otherwise, the He atoms are adsorbed in a 2×2 supercell of the primitive surface unit cell.

In Fig. 1, the counterpoise corrected binding energy, BE^C (defined in Appendix B), computed in the HF and HF+MP2 approximations is plotted as a function of He-surface distance for both sites. Physically the interaction is expected to be dominated by the combination of a short-range exchange repulsion and a long range van der Waals attraction. The latter interaction, being purely an electron correlation effect, is completely absent in the HF description, which produces no binding to the surface and the adsorption curve is dominated by the short range repulsive interaction. The HF+MP2 approximation recovers the long range dispersion and produces attractive interaction, binding the He atom to the surface in a potential well of depth 4.15 meV above the Mg ion and 3.83 meV above the O ion. The well depth can be compared to that estimated from He scattering data, which has been reported to be 7.5 meV[21] or 12.5 meV.[1]

The binding energy curves for various other approximations are presented in Fig. 2 for the Mg adsorption site. The

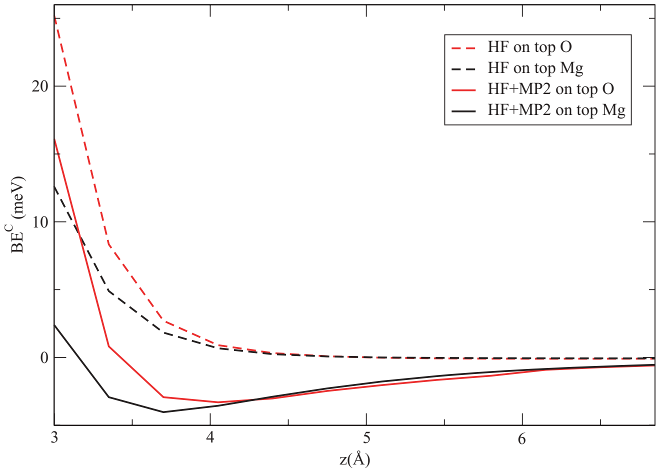

FIG. 1. The corrected binding energy BE^C of the system He–MgO(100) with respect to the bare MgO(100) surface and the isolated He atom within the HF (dashed lines) and MP2 level of theory (solid lines). Red lines show BE^C when the He atom is on top of the O and black lines when it is on top of the Mg. (If not indicated, BS4 is adopted for the calculations.)

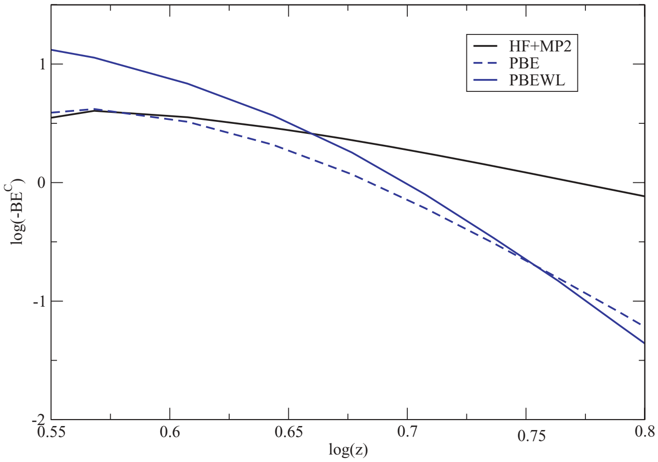

FIG. 3. Logarithm ($\log_{10}$) of corrected binding energy BE^C of the system He–MgO(100) with respect to the bare MgO(100) surface and the isolated He atom for adsorption of He on the Mg site for HF+MP2 (black line), PBE (dashed blue line) and PBEWL (continuous blue line).

following observations can be made:

- the HF and B3LYP approximations have a very similar behavior and provide no binding;
- the PBEWL approximation overestimates the binding between He and MgO at short distances and does not provide a long range attractive interaction;
- PBE and PBE0 provide a short range attraction which binds the He to the surface but do not provide a long range one.

As expected, the dominant methodologies for dealing with extended systems, based on HF, local and semilocal approximations to DFT, and hybrid exchange DFT approaches, cannot describe the He–MgO interaction reliable as they do not describe correctly long range dispersion forces. In addition to being essential to the surface binding the long range form of the potential is vital to the description of the He-scattering process. In Fig. 3 the long-range part of the curves of Fig. 2 is reported on a logarithmic scale, thus showing that DFT methods at 6 Å and beyond provide a binding, which is two orders of magnitude smaller than the MP2 one. The expected behavior for a dielectric surface or a simple sum over pairwise interactions is $1/z^3$ at long range. However, such a slow decay is not observed even with MP2, which, in fact, gives $1/z^4$ for HF+MP2. MP2 performs qualitatively correct at long range, and, as experience shows often provides quantitatively accurate results, if benchmarked against more accurate approaches.[22]

The empirical Grimme correction (reported in Fig. 4) provides a binding interaction which can be used in conjunction with any of the DFT functionals considered here (denoted, e.g., as B3LYP-D, where "-D" indicates the use of

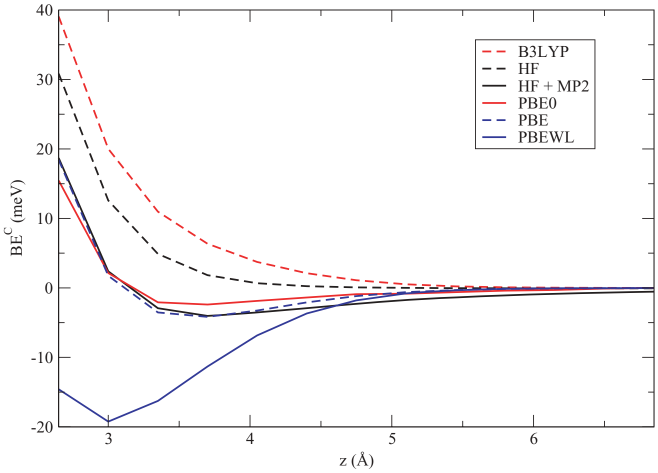

FIG. 2. Corrected binding energy BE^C of the system He−MgO(100) with respect to the bare MgO(100) surface and the isolated He atom for adsorption of He on the Mg site, when different functionals are used. Black lines represent the HF (dashed) and HF + MP2 (solid) level of theory, red lines show the B3LYP (dashed) and PBE0 (solid) and blue lines the PBE (dashed) and PBEWL (solid).

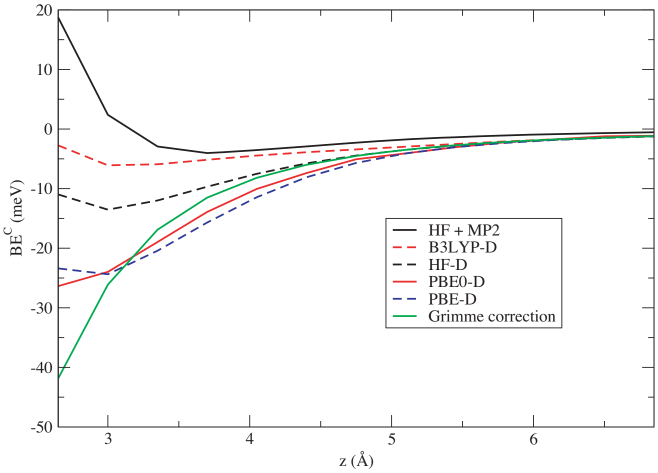

FIG. 4. The corrected binding energy BE^C of the system He–MgO(100) with respect to the bare MgO(100) surface and the isolated He atom for different functionals using the Grimme correction. Black lines represent the HF-D (dashed) and HF+MP2 (solid), red lines B3LYP-D (dashed) and PBE0-D (solid), and the blue solid line PBE-D. The pure Grimme dispersion curve is also plotted in green for a comparison.

TABLE II. BE^C at $d^{min}_{He–MgO}$ bound above Mg for the different functionals that present binding.

H	$d^{min}_{He–MgO}$(Å)	BE^C(meV)
PBE	3.59	−3.8
PBE0	3.60	−2.2
HF+MP2	3.75	−4.1
PBEWL	2.93	−20.2
B3LYP-D	3.00	−6.2
PBE0-D	2.84	−26.5
PBE-D	2.84	−24.7
HF-D	2.98	−12.9

Grimme correction). Previous reports have suggested that, when correctly calibrated, this empirical dispersion correction reproduces the long-range interaction, which is comparable to the MP2 one of the MP2 correlation energy.[23] However, taking into account the smallness of the interaction in the current case, one cannot expect accurate results from this relatively rough approach without extensive basis-set- and functional-specific recalibration.

A summary of the data regarding BE^C is given for all of the tretaments of electronic exchange and correlation considered here in Table II, along with the predicted He–Mg equilibrium distance. It is apparent that both the well depth and the position of the minimum ($d^{min}_{He–MgO}$) depend strongly on the particular choice of the functional considered, varying in a range of 2.2–26.5 meV and 2.8–3.7 Å, respectively. The B3LYP-D result agrees of all the methods the best with the experimentally measured well depth. At the same time, PBE-D, presents overbinding. The relative success of the B3LYP-D approach is apparently fortuitous and mainly due to the the absence of the binding at the B3LYP level, while all other DFT functionals studied here produce an artificial binding term, which is then added to the D-correction (double counting of electron correlation). For $d^{min}_{He–MgO}$, there are two regimes. In the former (2.8–3.0 Å), the Grimme corrected functionals and PBEWL, bind He too close to the surface. In the latter, HF+MP2, PBE, and PBE0 produce a distance of 3.5–3.8 Å, which seems to be more reasonable (see Appendix D for the discussion). It has to be noticed that no experimental data on He-surface distance are available in the literature.

When analyzing the whole shape of the He–MgO interaction potential, all methodologies based on uncorrected DFT, HF and/or hybrid DFT/HF approximations fail to provide a qualitatively correct description at long distance which is vital for understanding the scattering process.

The HF+MP2 level of theory provides a qualitatively correct description both for the long and short range binding interaction. At the same time, the well depth obtained using this method is noticeably smaller than the experimental estimates. There are two likely explanations for this discrepancy, either the slow basis set convergence of the correlation energy and a deficiency of the local MP2 method itself. Both issues are discussed on the example of the small cluster in Appendix D. The basis sets used in the current work are rather large but yet do not provide the basis set limit values. A further expansion of the basis set or further extrapolation are currently inhibited in the periodic LCAO approach due to numerical instabilities accociated with pseudolinear dependency. As for the MP2 approximation, it is the lowest in the hierarchy of the quantum-chemical correlated methods. In particular, it treats dispersion at the uncoupled Hartree–Fock level,[22] which can lead to errors in the interaction energies. The feature of the MP2 method to overbind systems with high polarizability and to be rather accurate for those with moderate one, is well known. Underestimation of the interaction energy for weakly polarizable systems (like, e.g., MgO and helium) by MP2 is less commonly mentioned, but has also been observed in the molecular[24] and periodic[23,25] contexts, including studies of adsorption on the MgO surface.[26] This effect is also supported by our cluster calculations in Appendix D. As the overall binding energy itself is very small, the MP2 result obtained here can be regarded as a satisfactory first step towards a fully converged *ab initio* description.

IV. CONCLUSIONS

The interaction of the He with a MgO (100) surface have been calculated for the adsorption of the He atom at two sites, directly above either an O or Mg ion. Periodic HF+MP2 theory and also a variety of other *ab initio* and semiempirical techniques have been adopted. HF and B3LYP provide no binding; PBEWL overestimates the binding between He and MgO at short distance and underestimates it at long distances. PBE and PBE0 provide short range binding but are qualitatively incorrect at long range.

The Grimme correction produces a qualitatively correct binding, but the predicted well depth is very sensitive to the choice of exchange correlation functional, and the adsorbate is consistently bound too close to the surface.

The HF+MP2 binding is qualitatively correct, giving a minimum for adsorption of the He atom at Mg site and reasonable value of the He–Mg distance (3.7 Å), but the well depth (4 meV) is significantly smaller than that observed (7–12 meV). This is by no means surprising, since MP2 is able to qualitatively describe the correct physics of the physisorption process, and can be considered as a first step to the fully correlated answer.

Currently, the MP2 method is the best treatment available in the periodic framework. More accurate methods such as coupled cluster theory including single, double, and perturbative triple excitations [the CCSD(T) method], might provide a more quantitative description of the well depth but at present are only practical in combination with a finite cluster approximation to the periodic surfaces within an incremental scheme[27–29] or hierarchical method.[30] At the same time, the qualitatively correct shape of the periodic MP2 He–MgO potential surface reported here opens the way for further studies of the adsorption phenomenon and He-atom scattering process.

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APPENDIX A: BASIS SETS

In this appendix, the hierarchy of all-electron basis sets, used and labeled as BS1, BS2, BS3, and BS4, is described in detail. With regards to MgO, the following types of BS (with polarization functions) have been used:

BS1: a triple valence BS consisting of an 8-511d(1) contraction for Mg and an 8-411d(1) for O (in both cases, one *s*, three *sp* and one *d* shells); the most diffuse *sp* exponents are $\alpha_{sp}^{\mathrm{Mg}} = 0.28$ and $\alpha_{sp}^{\mathrm{O}} = 0.191$, while the *d* exponent is the same for both ions, $\alpha_{d}^{\mathrm{Mg}} = \alpha_{d}^{\mathrm{O}} = 0.5$ (exponent unit in a_0^{-2});[31]

BS2: a quadruple valence BS defined by a 10-7111d(1) contraction for Mg and a 10-6111d(1) for O (one *s*, four *sp* and one *d* shells);[32] the most diffuse *sp* and *d* exponents, which have been optimized in bulk MgO for the B3LYP functional, are: $\alpha_{sp}^{\mathrm{Mg}} = 0.28$ and $\alpha_{sp}^{\mathrm{O}} = 0.115$, while $\alpha_{d}^{\mathrm{Mg}} = 0.64$ and $\alpha_{d}^{\mathrm{O}} = 0.5$.

The effects of *d* and *f* symmetry polarization functions have been evaluated in two steps, while keeping the sp shells of BS2 constant. These are:

BS3: an extra *d* shell added to Mg atom ($\alpha_{d}^{\mathrm{Mg}} = 1.6$) and two *d* shells on the O atom ($\alpha_{d}^{\mathrm{O}} = 1.25$ and $\alpha_{d}^{\mathrm{O}} = 0.2$), resulting in a 10-7111d(2) for Mg and 10-6111d(3) for O;

BS4: *f* functions are included, $\alpha_{f}^{\mathrm{Mg}} = 1.6$ for Mg and $\alpha_{f}^{\mathrm{O}} = 1.428$ and $\alpha_{f}^{\mathrm{O}} = 0.5$ for O; corresponding to 10-7111d(2)f(1) for Mg and 10-6111d(3)f(2) for O.

These added exponents for each shell type have been chosen by keeping a ratio of 2.5, in order to avoid linear dependency problem. The basis sets used for He are as follows:

BS1: a 411p(11)d(1) contraction, the cc-pVTZ basis set[33,34]

BS2: a quadruple valence BS, 4111*p*(111)*d*(11), aug-cc-pVTZ,[33,34] where an extra function has been added to each shell;

BS3: analogously to the Mg and O BS, the *d* shell of BS2 has been enhanced by replacing the two *d* shells with three *d* shells of exponents $\alpha_{d_1}^{\mathrm{He}} = 4.299$, $\alpha_{d_2}^{\mathrm{He}} = 1.223$, and $\alpha_{d_3}^{\mathrm{He}} = 0.351$, taken from aug-cc-pVQZ;[33,34] this BS in thus 4111p(111)d(111);

BS4: additional *f* shells are introduced, with the exponents $\alpha_{f_1}^{\mathrm{He}} = 2.68$ and $\alpha_{f_2}^{\mathrm{He}} = 0.6906$, also taken from aug-cc-pVQZ;[33,34] the BS is 4111*p*(111)*d*(111)*f*(11).

APPENDIX B: BINDING ENERGY

In this appendix, the formulas necessary to calculate the binding energy of He–MgO (100) (1×1) with respect to:

- the clean surface and the monolayer with a 1 × 1 periodicity;
- the clean surface and the isolated atom

are provided and the effects of the basis set adopted described thoroughly.

1. Binding energy with respect to the clean surface and the monolayer with a 1 × 1 periodicity

The binding energy BE^{P} is calculated with respect to the bare MgO(100) surface and a free periodic monolayer of He atoms, with a 1 × 1 periodicity, as described in detail in,[35]

$$\mathrm{BE}^{\mathrm{P}} = E_{\mathrm{sys}} - (E_{\mathrm{slab}} + E_{\mathrm{mon}}), \tag{B1}$$

where E_{sys}, E_{slab}, and E_{mon} are, respectively, the energy of the interacting system, the bare surface and the free monolayer. The binding energy corrected for for the basis set superposition error (BSSE), $\mathrm{BE}^{\mathrm{PC}}$, is estimated using the counterpoise technique,

$$\mathrm{BE}^{\mathrm{PC}} = E_{\mathrm{sys}} - \left(E_{\mathrm{slab}}^{G} + E_{\mathrm{mon}}^{G}\right), \tag{B2}$$

where E_{slab}^{G} and E_{mon}^{G} are the energy of the slab in the presence of the ghost functions of He and vice versa.

The binding energy is reported in Table III along with the separate contributions to the BSSE,

$$\mathrm{BSSE}_{\mathrm{slab}} = E_{\mathrm{slab}}^{G} - E_{\mathrm{slab}}, \tag{B3}$$

$$\mathrm{BSSE}_{\mathrm{mon}} = E_{\mathrm{mon}}^{G} - E_{\mathrm{mon}}, \tag{B4}$$

therefore,

$$\mathrm{BE}^{\mathrm{PC}} = \mathrm{BE}^{\mathrm{P}} - \mathrm{BSSE}_{\mathrm{slab}} - \mathrm{BSSE}_{\mathrm{mon}}. \tag{B5}$$

In order to estimate the deficiencies due to the finiteness of the basis set, the adsorption above the Mg site has been computed using a hierarchy of BS (BS1–BS4 as defined in Sec. II and in Appendix A), at a fixed geometry. The He–Mg distance was fixed to the minimum energy obtained with BS4, $d_{\mathrm{He-Mg}}^{\mathrm{BS4}}$.

At the HF level the BSSE is relatively small (especially for He), but not completely negligible. It becomes substantially more pronounced at the MP2 level,[16] where it is comparable to the interaction energy itself. This trend also occurs when the He atom is adsorbed perpendicularly on the top of O, as evident by comparing the BS4 case for O and Mg in Table III, where the distance He–O has been set equal to $d_{\mathrm{He-Mg}}^{\mathrm{BS4}}$. Therefore, for the evaluation of the small binding energies, the counterpoise correction becomes vital.

Analyzing the convergence of the results with basis set size, it can be seen that the $\mathrm{BSSE}_{\mathrm{slab}}$ and $\mathrm{BSSE}_{\mathrm{mon}}$ decrease when increasing the basis set from BS1 to BS4, as expected. However, even with BS4 it remains significant, and the interaction energy does not seem to completely converge. The

TABLE III. Binding energy BE^P and BSSE corrected binding energy BE^{PC} of the system He–MgO(100) with respect to the bare MgO(100) surface and the free monolayer of He atoms for a 1 × 1 coverage within the HF and MP2 level of theory. All the values are given in meV.

		HF				HF+MP2			
Adsorption site	BS	BE^P	BE^{PC}	$BSSE_{slab}$	$BSSE_{mon}$	BE^P	BE^{PC}	$BSSE_{slab}$	$BSSE_{mon}$
Mg	BS1	−1.8	0.9	−2.6	−0.1	−5.8	−2.0	−3.7	−0.1
	BS2	−0.9	1.6	−2.4	−0.1	−9.0	−3.2	−5.7	−0.2
	BS3	0.0	1.7	−1.5	−0.1	−9.0	−3.5	−5.5	−0.2
	BS4	0.0	1.7	−1.5	−0.1	−8.9	**−4.2**	−4.8	−0.2
O	BS4	1.5	2.8	−1.3	−0.1	−6.7	**−2.8**	−3.7	−0.2

slow basis set convergence is a common feature of correlation methods, especially when applied to weakly bound systems (see also Appendix D for discussion). At the same time, a further expansion of the the basis set beyond BS4 is a rather difficult task in our case. Due to the linear dependency problem, richer basis sets ruin the convergence of the HF procedure. Besides, no significant improvement (<4%) for the binding energy occurs when the BS4 basis has been enhanced by adding extra *d* and *f* functions (the GUESDUAL keyword has been exploited[14, 18]). Basis set extrapolation techniques, powerful in the molecular correlation methods, are inapplicable here due to the convergence problems of the periodic HF method with the well-balanced molecular basis sets. Under these circumstances, we consider the basis set BS4, which is in fact relatively rich, as an optimal compromise, and have used it in the reported calculations, if not indicated otherwise.

2. Binding energy with respect to the clean surface and the isolated atom

It has to be highlighted that the binding energy of the system He–MgO with respect to the monolayer of He and the bare MgO(100) surface, evaluated above, is a necessary prerequisite for the calculation of the BE with respect to the surface and the isolated He atom. With this aim, it is required to take into account the interaction between He atoms in the monolayer. Therefore, the BE is defined by the formula

$$\mathrm{BE} = E_{\mathrm{sys}} - (E_{\mathrm{slab}} + E_{\mathrm{atom}}), \tag{B6}$$

where E_{atom} is the energy of the isolated He atom. As explained elsewhere,[35] the BSSE corrected binding energy, BE^C, is evaluated by using

$$\mathrm{BE}^{\mathrm{C}} = \mathrm{BE}^{\mathrm{PC}} + \mathrm{BE}^{\mathrm{LC}}, \tag{B7}$$

in which BE^{LC} is the true lateral energy due to the interaction between the He atoms in the monolayer and, in turn, is calculated,

$$\mathrm{BE}^{\mathrm{LC}} = E_{\mathrm{mon}} - E^{G}_{\mathrm{atom}}, \tag{B8}$$

with E^G_{atom} equal to the energy of the He atom in the presence of the ghost functions of the neighboring He atoms in the monolayer. In Table IV, where BE and BE^C have been reported for HF and HF+MP2, it is interesting to observe that the HF method demonstrates a repulsive He–He interaction, which reduces the overall binding. However, the inclusion of the correlation reverts this effect, providing a stabilizing contribution of the He–He interaction. At the same time, this He–He stabilization can be to a large extent counterbalanced by the intra-adsorbate zero-point vibrations.[36]

APPENDIX C: THE EFFECTS OF THE COVERAGE

In Fig. 5, BE^C of the system He–MgO(100) with respect to the clean surface and the isolated atom are reported for HF and HF+MP2; two periodicities, 1 × 1 and 2 × 2, have been considered, corresponding to the He–He distance of 2.978 and 5.955 Å, respectively.

Nearly within the whole range, the denser 1 × 1 coverage accounts for a virtually parallel upward (in case of HF) or downward (in case of MP2) shift of the potential curve relative to the 2 × 2 coverage, indicating the absence of significant three-body effects. We note, however, that the pure correlation three-body effects (like the Axilrod–Teller three-body dispersion) cannot be reproduced within the MP2 approximation.[37] In case of the DFT calculations, presented in Fig. 6, the nonadditive 3 body effects are more pronounced at least at short range. In the case of the 1 × 1 periodicity, BE^C corresponds to the lateral binding energy BE^{LC} in the 1 × 1 monolayer since at infinite distance there is no interaction between He and MgO. The 2 × 2 BE^{LC} is null and the HF and HF+MP2 curves go to zero at infinite distance. As a consequence, the 2 × 2 periodicity can be used to assess the study the He adsorption on MgO in the limit of low coverage (with respect to an isolated atom), as given in Sec. III.

TABLE IV. The binding energy BE and the corrected one BE^C of the system He–MgO(100)- 1 × 1 with respect to the bare MgO(100) surface and the isolated He atom within the HF and MP2 level of theory. All the values are given in meV.

		HF		HF+MP2	
Adsorption site	BS	BE	BE^C	BE	BE^C
Mg	BS1	−0.7	2.3	–	−1.5
	BS2	0.4	3.1	–	−4.1
	BS3	1.3	3.3	–	−4.6
	BS4	1.3	3.3	–	**−5.3**
O	BS4	2.7	4.4	–	**−3.9**

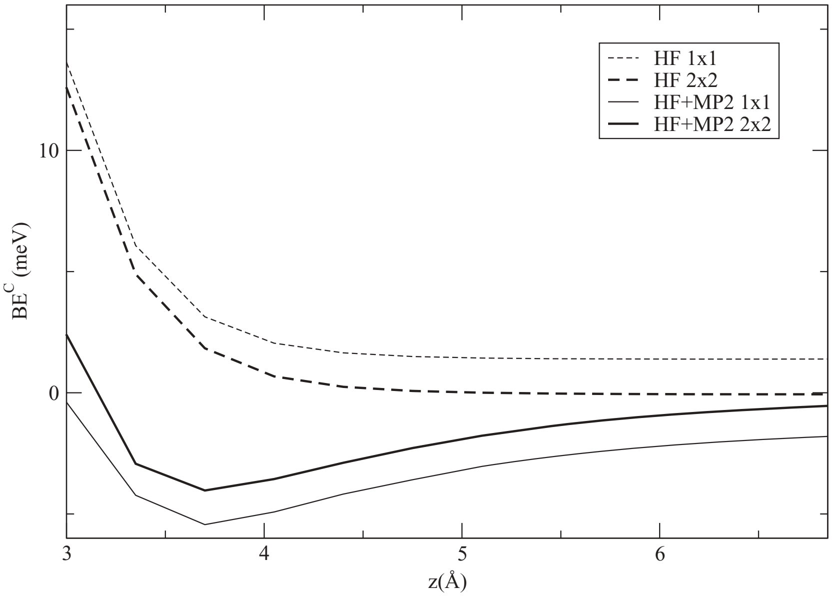

FIG. 5. The corrected binding energy BE^C of the system He–MgO(100) with respect to the bare MgO(100) surface and the isolated He atom at the HF (dashed line) and HF+MP2 level (solid line); two periodicities have been considered: 1 × 1 (thin lines) and 2 × 2 (thick lines).

APPENDIX D: TEST CLUSTER CALCULATION

In order to estimate the quality of our MP2 calculations in the absence of an unambiguous experimental reference, we have performed auxiliary calculations on a small prototypical cluster using the MP2 and CCSD(T) methods, the latter being used as the reference. A rather small cluster $Na_2Mg_3O_4He$ was chosen in order to employ reasonably large basis sets. The geometry of the cluster has been taken as a cutout from the upper layer of the slab with the Mg atom in the center and two opposite Mg atoms substituted with Na atoms in order to preserve the neutrality of the cluster. The He atoms have been positioned on top of the center Mg and the Mg–He distance has been varied. The standard aug-cc-pVDZ and aug-cc-pVTZ basis sets have been employed with a subsequent inverse cubic basis set extrapolation of the correlation energy. The MOLPRO code[38] has been utilized for the calculations. All the results have been counterpoise-corrected.

Table V compiles the binding energies of He with the cluster and the equilibrium He–Mg distance, calculated using the mentioned methods and basis sets. Although these results cannot be directly transferred to our periodic problem due to the finiteness and smallness of the studied cluster, some important general trend can be discussed. First, the problem of the slow basis set convergence is evident here, especially referring to the binding energies. Indeed the augmented triple zeta result does not yet provide the converged values. Secondly, the MP2 method substantially underestimates the binding with respect to the CCSD(T) reference. The combination of both deficiencies leads to only nearly half of the extrapolated CCSD(T) binding energy recovered in the augmented-triple-zeta MP2 calculation. This observation very well correlates with the well depths obtained in our periodic Local MP2 calculations when compared to the experimental data. Finally, the 3.9 Å equilibrium He–Mg distance in this system advocates for the 3.5–3.7 Å region for the physisorption of He on the real MgO surface, obtained with the periodic MP2 method, rather than 3.0 Å delivered by the DFT-D.

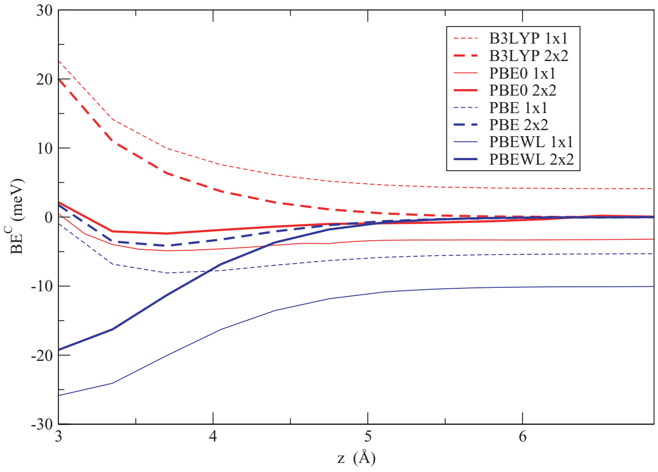

FIG. 6. The corrected binding energy BE^C of the system He–MgO(100) with respect to the bare MgO(100) surface and the He atom for different functionals; red lines represent B3LYP (dashed) and PBE0 (solid) and the blue ones PBE (dashed) and PBEWL (solid). Two periodicities have been considered: 1 × 1 (thin lines) and 2 × 2 (thick lines).

TABLE V. BE^C and location of the minimum for the He–$Na_2Mg_3O_4$-cluster potential curve.

	MP2		CCSD(T)	
Basis set	BE^C(meV)	d^{min}_{He-Mg}(Å)	BE^C(meV)	d^{min}_{He-Mg}(Å)
aug-cc-pVDZ	−1.49	4.35	−2.57	4.10
aug-cc-pVTZ	−1.94	4.25	−3.31	3.95
Extrapolated	−2.09	4.20	−3.65	3.90

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