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***Ab initio* calculation of the MgO(100) interaction with He and Ne: a HF + MP2 and HF + MP2(B3LYP) comparison**Ruth Martinez-Casado,^{*a} Giuseppe Mallia^a and Nicholas M. Harrison^{ab}

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Second order Rayleigh Schrödinger perturbation theory is applied to calculate the correlation energy contribution to the London dispersion interaction to approximate the interaction of the He and Ne with the MgO(100) surface; single particle orbitals using either Hartree–Fock theory or hybrid-exchange density functional theory are used as the reference state.

The scattering of noble gases atoms by surfaces has been widely studied in the last twenty years.^{1–3} In particular, He-atom scattering is potentially an important tool for the analysis of surface structure and dynamics. The technique is not complicated by surface charging and the associated damage, which affect electron diffraction, microscopy and spectroscopy methods, and is therefore particularly useful in the study of insulating surfaces, such as MgO.^{1,2} In spite of the large amount of experimental data provided by rare gas atom scattering experiments,^{1–4} the use of this technique has an important limitation due to the difficulties involved in the interpretation of the experimental diffraction patterns in the absence of a detailed understanding of the scattering potential. A first principles interaction potential between a noble gas and a surface is difficult to obtain as the widely used approximations based on density functional (DFT) and Hartree–Fock (HF) theory provide a poor treatment of the long range and relatively weak inter-molecular dispersion interactions. Empirical corrections to DFT that approximate dispersion can be used, but prove to be unreliable in many interesting systems. The alternative of using high quality quantum chemical methods, based on clusters, can often be complicated by issues related to convergence with respect to the cluster size and the expense of the calculations. As an alternative, an *ab initio* interaction potential has been computed using periodic local Møller–Plesset perturbation theory at second order (L-MP2), as recently implemented in the CRYSCOR program.⁵ HF + MP2 has been shown to produce a qualitatively correct description of the long range dispersion interaction for He–MgO(100)⁶ but to underestimate the magnitude of the interaction. A quantitatively correct energy surface, which reproduces the observed He binding energy, bound state

energy levels and diffraction pattern, can be obtained by scaling the long range attractive potential by 1.65—a factor correcting for the MP2 underestimate of the correlation energy that is well known from quantum chemical calculations on noble gas dimers⁷ and has recently been found to be effective in correcting the He–MgO(100) MP2 energy surface to improve agreement with diffraction data⁷ and to get a better agreement between CCSD(T) data and MP2 data for cluster models of the He–MgO(100) interaction.⁶ A similar energy surface can be obtained by improving the underlying HF description of the electronic structure using hybrid exchange density functional theory before applying MP2 theory—the so-called HF + MP2(B3LYP) approximation.⁸ These works have demonstrated that the problem of the interpretation of He-atom scattering experiments can be overcome through the application of efficient and reliable first principles theory.

The aim of this paper is to extend the previous work⁸ on He–MgO(100) by presenting a more detailed study of this system and applying the same approach to the Ne–MgO(100) interaction for which there is currently neither an experimental nor reliable theoretical determination of the interaction potential. As a reference and in order to help establish the range of applicability of this approach the HF + MP2 and HF + MP2(B3LYP) binding energy curves for the rare-gas molecules He₂, Ne₂, Ar₂, He–Ne, He–Ar, Ne–Ar are also computed within consistent numerical approximations. In what follows, firstly the computed binding energy (BE) and the equilibrium distance (r_{eq}) for the rare gases molecules are discussed with reference to experimental data and results of high level quantum mechanical calculations. Secondly, the computed BE of He and Ne to the MgO(100) surface systems is analysed and compared with that observed in the case of He.

In Fig. 1 the computed BE[†] for He₂, Ne₂, Ar₂, Ne–Ar, He–Ar and He–Ne is shown. In Table 1, the calculated well depth (D) and r_{eq} for HF + MP2 and HF + MP2(B3LYP) are compared with those computed using CCSD(T),^{†19,20} and values deduced from scattering experiments.^{17,18} CCSD(T) provides a consistent estimate of the BE for all dimers typically underestimating the correlation contribution. HF + MP2(B3LYP) systematically provides stronger binding than HF + MP2 and, for He₂, Ne₂ and He–Ne, is therefore in significantly better agreement with the observed and CCSD(T) well depths and equilibrium distances. The performance of HF + MP2(B3LYP) is however not consistent. In Ar₂ HF + MP2(B3LYP) significantly overbinds

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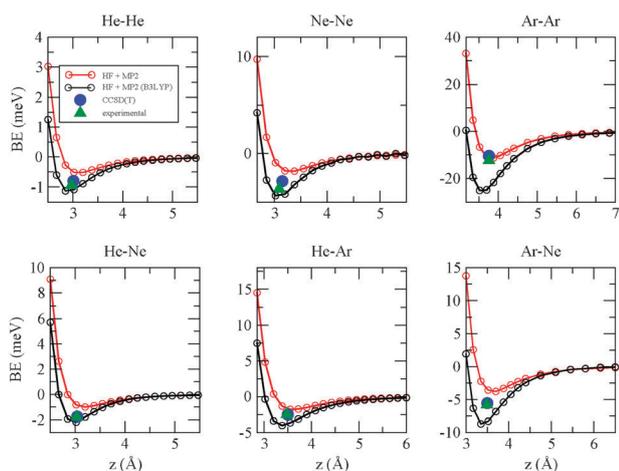


Fig. 1 The HF + MP2 (black) and HF + MP2(B3LYP) (red) counterpoise corrected BE curves for He₂, Ne₂, Ar₂, He–Ne, He–Ar and Ne–Ar. The experimental^{17,18} (green triangles) and CCSD(T)^{19,20} (blue circles) are reported for comparison.

the dimer while HF + MP2 is remarkably accurate (–5%). The HF + MP2 performance in Ar appears to be part of a trend with atomic number towards stronger binding and may therefore be attributed to a fortuitous error cancellation; HF + MP2 significantly overbinds Kr₂ and Xe₂.²¹ For Ne–Ar and He–Ar, HF + MP2 underbinds and HF + MP2(B3LYP) overbinds, as expected from the dimers data.

In a previous work,⁸ the Unsöld expression for the dispersion energy²² was used to analyse the difference between HF + MP2 and HF + MP2(B3LYP). The dispersion energy contribution due to the induced-dipole–induced-dipole interaction (*A* and *B*) at distance *r* is approximated as $E_{\text{disp}} \approx -\frac{3\alpha_A\alpha_B I_A I_B}{4(I_A + I_B)r^6}$, where α and *I* are the polarisabilities and ionisation potentials, respectively. For the atoms considered both α and *I*, calculated with HF and B3LYP, are presented in Table 2. As expected HF underestimates α for He, Ne and Ar, while B3LYP values agree rather well with those measured. A similar trend is observed for *I* (Table 2), with B3LYP results for He, Ne and Ar closer to those observed than the HF results. It appears therefore that the Unsöld expression is not a useful guide to the relative performance of HF + MP2 and HF + MP2(B3LYP), in the case of Ar₂, where both α and *I* are better described by B3LYP than by HF. A recent analysis of the performance of MP2 theory has also documented the tendency to overestimate the correlation energy for heavy atoms.²³

Table 1 Well depth *D* and equilibrium distance *r*_{eq} for the He₂, Ne₂, Ar₂, He–Ne, He–Ar and Ne–Ar interactions. The HF + MP2 and HF + MP2(B3LYP) values are compared with those from CCSD(T)^{19,20} and with those deduced from scattering experiments^{17,18}

	<i>D</i> /meV				<i>r</i> _{eq} /Å			
	HF + MP2	HF + MP2(B3LYP)	CCSD(T)	Exp.	HF + MP2	HF + MP2(B3LYP)	CCSD(T)	Exp.
He ₂	–0.55	–1.15	–0.80	–0.94	3.11	2.92	3.01	2.97
Ne ₂	–1.98	–4.40	–2.87	–3.64	3.26	3.07	3.15	3.09
Ar ₂	–11.68	–25.67	–10.39	–12.34	3.82	3.59	3.82	3.76
He–Ne	–1.05	–2.16	–1.76	–1.78	3.18	2.98	3.04	3.03
He–Ar	–1.85	–4.09	–2.51	–2.49	3.59	3.38	3.51	3.48
Ne–Ar	–3.92	–8.70	–5.57	–5.82	3.63	3.39	3.50	3.49

Table 2 HF, B3LYP and experimental^{24,25} α and *I*

	α /Bohr ³			<i>I</i> /eV		
	HF	B3LYP	Exp.	HF	B3LYP	Exp.
He	1.32	1.50	1.41	23.45	24.85	24.59
Ne	2.33	2.74	2.571	19.66	21.61	21.56
Ar	10.72	11.56	11.23	14.56	15.70	15.76

The (He,Ne)–MgO(100) interaction has been examined by computing the BE at Mg and O surface sites with respect to an isolated He or Ne atom and the bulk cleaved MgO(100) surface. § Adsorptions directly above the surface Mg and O ions are considered. In Fig. 2, the counterpoise corrected^{9,27} BE is displayed for both HF + MP2 and HF + MP2(B3LYP). All curves have an attractive binding interaction between He or Ne and the surface for which *D* and *r*_{eq} are given in Table 3. For both approximations the minimum occurs when a He or Ne atom is adsorbed at the Mg site. The agreement of the HF + MP2(B3LYP) well depth with that observed for He (7.5 meV⁴–12.5 meV¹) is significantly better than HF + MP2. Given the description of Ne₂ it is not unreasonable to expect a similar accuracy using HF + MP2(B3LYP) to compute the Ne–MgO(100) interaction potential. To the authors knowledge there is no experimental determination of *D* and *r*_{eq} available for Ne–MgO(100) and therefore this result is a prediction of the energy surface. Estimates of *D* based on semi-empirical approximations are in the range 17.3–23.4 meV,²⁸ comparable to the HF + MP2(B3LYP) value.

A notable trend is that the predicted *r*_{eq} decreases when moving from He to Ne by ~2% for HF + MP2 and ~9% for

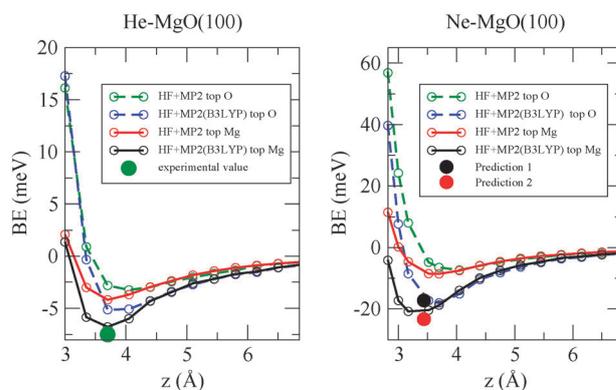


Fig. 2 The HF + MP2 and HF + MP2(B3LYP) counterpoise corrected BE curves for (He,Ne)–MgO(100).

Table 3 Binding energy BE (meV) and r_{eq} (Å) of the interaction between He and Ne with MgO(100)

Mg site	HF + MP2		HF + MP2(B3LYP)	
	BE	r_{eq}	BE	r_{eq}
He–MgO	–4.1	3.75	–6.7	3.65
Ne–MgO	–8.7	3.65	–21.5	3.31
O site	BE	r_{eq}	BE	r_{eq}
He–MgO	–3.6	3.95	–5.5	3.90
Ne–MgO	–7.6	3.90	–18.3	3.61

HF + MP2(B3LYP). This behaviour has been noted previously for semi-empirical predictions of the geometries.²⁸ As the radius of the Ne atom is larger than that of He—as evidenced by the bond lengths of the dimers in Table 1—the trend is, at first sight, counterintuitive. It is apparent that in the (He,Ne)–MgO(100) interaction, the greater polarizability of Ne (see Table 2) is sufficient to overcome the increase in atomic radius in binding the atom closer to the surface. Some support for this notion is provided by the fact that if the attractive component of the He–MgO potential is scaled by the ratio of the Ne and He polarisabilities, as suggested by the Unsöld expression, it reduces the bond length by around 10%.

In conclusion, HF + MP2(B3LYP) has been shown to be a pragmatic and efficient alternative method for the approximation of the correlation energy for noble gas dimers of the first and second rows and for He interacting with an insulating oxide. Based on this a prediction is made for the Ne–MgO(100) interaction potential. The HF + MP2(B3LYP) results obtained for the He₂, Ne₂ and He–Ne are in significantly better agreement with the experimental well depth and equilibrium distance than those computed using HF + MP2. In these systems the periodic HF + MP2(B3LYP) approach is reliable and significantly less computationally expensive than more sophisticated approaches for describing electronic correlation.

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Notes and references

† All calculations (see ref. 9 for details) have been performed using a development version of the CRYSTAL and CRYSCOR software packages.^{10–14} An hierarchy of basis sets have been considered to converge the results presented. He is described by an aug-cc-pVTZ, an aug-cc-pVQZ and the basis set BS4, whose variational accuracy is in between the ones above (see ref. 9); aug-cc-pVTZ and aug-cc-pVQZ

are adopted for Ne, while for Ar an aug-cc-pVTZ and an aug-cc-pVQZ equivalent in number of shells, obtained by taking the aug-cc-pVTZ, adding extra s ($\alpha_s = 0.6957 \text{ bohr}^{-2}$) and p ($\alpha_p = 0.68025 \text{ bohr}^{-2}$) shells by keeping a 2.5 ratio between consecutive exponents, and replacing the d and f shells from the ones given in aug-cc-pVQZ, is used. See previous studies for computational details.^{9,15,16}

‡ CCSD(T) is coupled-cluster theory incorporating single and double excitations explicitly and triple excitations perturbatively.

§ The MgO(100) surface is approximated as a rigid 2D periodic 3 atomic layer thick slab cut from the bulk structure at the experimental lattice constant ($a = 4.211 \text{ Å}$).²⁶ A 2×2 supercell of the primitive surface unit cell is found to be sufficient to reduce the He–He and Ne–Ne lateral interactions to negligible values and therefore the data presented correspond to the adsorption of an isolated atom.

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