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An alternative approach for the calculation of correlation energy in periodic systems: a hybrid MP2(B3LYP) study of the He–MgO(100) interaction

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A practical and efficient method for exploiting second order Rayleigh–Schrödinger perturbation theory to approximate the correlation energy contribution to the London dispersion interaction is presented. The correlation energy is estimated as the Møller–Plesset contribution computed using single particle orbitals from hybrid exchange density functional theory as the reference state.

The London dispersion force (LDF) is responsible for many of the physical properties of solids, liquids and gasses; for instance, it largely determines the three dimensional arrangements of biological molecules and polymers. An interesting case where the LDF is of paramount importance is in the interpretation of He-atom scattering data in order to establish the atomic scale structure and dynamic of surfaces. This technique has potential as a high resolution and non-invasive surface probe that is sensitive only to the outermost surface layer. Fully realising this potential requires a quantitative theory of the scattering process that must be based on an accurate and reliable determination of the He-surface interaction. A first principles theory of the inter-action potential requires an accurate description of the LDF and thus of the electronic correlation.

In periodic systems, the effects of electronic exchange and correlation are typically approximated within density functional theory (DFT). The widely used local (local density approximation LDA) and semi-local (generalised gradient approximation, GGA) expressions for the correlation energy depend on the density and its gradients at a point in space. These approximations cannot describe the LDF. The significant improvement to the description of the non-local exchange introduced in hybrid-exchange functionals, which combine Fock exchange and GGA exchange (*e.g.* B3LYP[1] and PBE0, in which the percentage of Fock exchange is 20% and 25%, respectively), does not improve the description of long range LDF which is completely absent in the Hartree–Fock (HF) approximation.

These problems have been addressed by introducing *ad hoc* corrections to the correlation energy. The approach of Wilson-Levi is to introduce a semi-empirical correlation functional[2] and Grimme has introduced an empirical correction term in the total energy.[3] These techniques, which have been parameterised and used successfully in a variety of systems, have recently been shown to be unsuitable for calculating the He-surface interaction.[4]

An efficient and reliable procedure for the calculation of the correlation energy in periodic systems is second order Rayleigh–Schrödinger perturbation theory, often referred to as the Møller–Plesset perturbation theory at second order (MP2), as recently implemented in the CRYSCOR[5,6] program. Taking the HF wavefunction as a reference MP2 theory yields the second order contribution to the correlation energy including contributions from virtual excitations on separated fragments. It thus provides an estimate of the long range interaction that is referred to as the *uncoupled dispersion energy*. The HF + MP2 theory has previously been used to describe the qualitative nature of the He–MgO(100) inter-action.[4] It is important to note that the magnitude of the MP2 correction depends strongly on the reference state. For instance, if the time-dependent HF (TDHF) wavefunction is used as the reference, the MP2 estimate of the correlation energy, referred to as the *coupled dispersion energy*, is 10%–20% larger than the uncoupled dispersion energy in noble gas dimers improving agreement with the observed binding energy.[7]

The physical origin of the underestimate of the LDF computed from the HF orbitals can be understood in terms of the approximate Unsöld expression[8] for the dispersion energy contribution to the interaction between two molecules A and B at a distance r,

$$E_{\text{disp}} \approx -\frac{3\alpha_A \alpha_B I_A I_B}{4(I_A + I_B)} r^{-6} \tag{1}$$

where α and I are the average molecular dipole polarisabilities and ionisation potentials, respectively. The computed polaris-ability is underestimated in the HF approximation due to the significant overestimate of the energy gap between the occupied and unoccupied energy levels;[9] in TD-HF this gap is reduced and thus the polarisability corrected. It is now well established that the density functional theory implemented

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using local and semi-local functionals suffers from a self-interaction error and thus significantly underestimates energy gaps while hybrid exchange theory, such as the B3LYP functional, provides reasonable estimates of single particle energy gaps in a wide variety of materials.[10–12] In the current work this is exploited to define a pragmatic and efficient method for exploiting the second order perturbation theory to compute the correlation energy in periodic systems. The correlation contribution is estimated as the MP2 energy computed using the B3LYP single particle orbitals as the reference state. The total energy is obtained as the sum of the HF energy and the MP2 estimate of the correlation energy; a procedure denoted here as HF + MP2(B3LYP). This choice avoids the potential double counting of the correlation energy contribution at short range if the B3LYP energy were added to the MP2 estimate of the correlation energy; denoted here as B3LYP + MP2(B3LYP). In order to document the reliability of this method the energy of the He dimer and the He–MgO(100) surface are computed using the following energy expressions: HF + MP2; B3LYP + MP2(B3LYP); HF + MP2(B3LYP).

The computed binding energy curve† of the He_2 dimer is presented in Fig. 1. The long range behaviour of the potential in both the HF + MP2 and HF + MP2(B3LYP) reproduces the expected functional form for the He–He interaction, which decays as $\frac{1}{z^6}$, where z is the He–He distance. The strength of the interaction is, however, significantly different. As has previously been reported, HF + MP2 generally underestimates the correlation energy contribution yielding only $\approx 67\%$ of the exact total energy for closed shell molecules.[16,17] This trend is repeated here with the HF + MP2 well depth being $\approx 70\%$ of that computed with HF + MP2(B3LYP). As a consequence the agreement between the well depth given by HF + MP2(B3LYP) and the experimental value (0.91 meV) is excellent. The potential energy curve closely resembles that computed at the CCSD(T) level of theory.[18]

The He–MgO interaction is studied by computing the binding energy of an isolated He atom and the bulk cleaved MgO(100) surface at the Mg surface site. The MgO(100) surface is approximated as a rigid 2D periodic slab 3 atomic layers deep cut from the bulk structure at the experimental
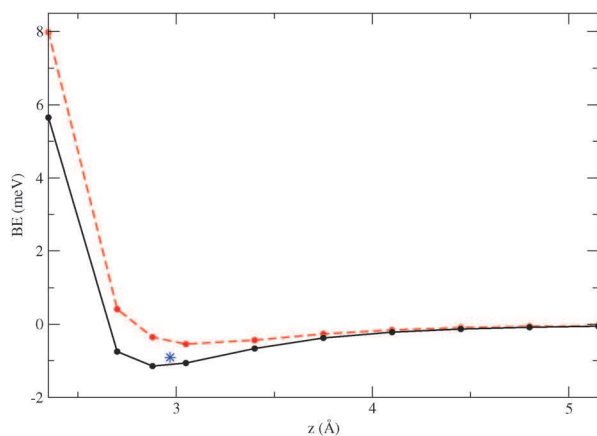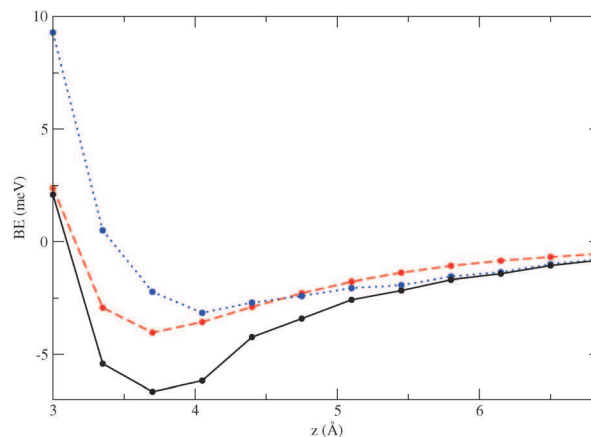

Fig. 2 The counterpoise corrected binding energy BE curve for adsorption above the Mg site of He–MgO(100) with respect to the clean MgO(100) surface and the isolated He atom within the B3LYP + MP2(B3LYP), blue dashed line, HF + MP2, red dashed line and HF + MP2(B3LYP), black solid line.

lattice constant ($a = 4.211$ Å).[19] This system provides a well defined reference geometry for studying the effects of different approximations on electronic exchange and correlation.[4] Adsorption of the He atom directly above the surface of the Mg ion is considered at separations between the He atom and the centroid of the outermost layer in the range: 3 Å : 7 Å. A 2 × 2 supercell of the primitive surface unit cell is found to be sufficient to reduce the He–He lateral interactions to negligible values. In Fig. 2, the computed counterpoise corrected binding energy, BE (defined in Appendix in ref. 4 and 20), is displayed for the following energy expressions: HF + MP2; B3LYP + MP2(B3LYP); HF + MP2(B3LYP). All the curves produce an attractive interaction binding the He atom to the surface in a potential well for which the position and depth of the minimum depend on the reference wavefunction. The value obtained at HF + MP2 is −4.1 meV at an equilibrium distance of 3.75 Å, B3LYP + MP2(B3LYP) provides −3.1 meV at 4.07 Å and HF + MP2(B3LYP) gives −6.7 meV at 3.78 Å. There is no firmly established observation of the well depth with values deduced from He-scattering spectra being in the range 7.5 meV[21]–12.5 meV.[22] The agreement of the HF + MP2(B3LYP) well depth with that observed is significantly better than that obtained using the HF + MP2 energy expression. Further support for the accuracy of the HF + MP2(B3LYP) curve is provided by its consistency with trends known established in previous studies of interactions with He atoms. As noted above the HF + MP2 approach tends to underestimate the bonding interaction yielding 67% of the observed or CCSD(T) computed binding energy for the He dimer. In the current study the HF + MP2 contribution to the He–MgO(100) binding is on average 66% of the HF + MP2(B3LYP) binding energy. This is a strong indication that the HF + MP2(B3LYP) binding energy is within a few percent of that which would be computed in a full CCSD(T) calculation.

The long range behaviour of the potential energy surface is important for the description of the He-scattering process. The expected behaviour for a He atom interacting with a continuum dielectric or with the surface *via* a set of pairwise

Fig. 1 The binding energy curve for the He_2 dimer computed using HF + MP2, red dashed line, and HF + MP2(B3LYP), black solid line. The experimental value is shown by the blue star.[18]

$1/r^6$ interactions is $1/z^3$ where z is the He-surface separation.[23] The expected behaviour when interacting with a single monolayer is $1/z^4$. The computed behaviour at long range for HF + MP2(B3LYP) is $1/z^{3.9}$ and for HF + MP2 is $1/z^4$ as expected for the model used here in which the He atom is interacting with a thin slab consisting of 3 atomic layers of MgO.

In conclusion, a practical and efficient method for the approximation of the correlation energy for a He-atom interacting with an insulating surface has been presented. The method is based on the calculation of the MP2 energy using the B3LYP single particle orbitals as a reference state. The total energy of the system is obtained by adding the Hartree–Fock energy to this MP2 contribution and is denoted as HF + MP2(B3LYP). The results obtained for the He_2 dimer and the He–MgO(001) surface interaction reproduce the expected long range behaviour and the position and value of the observed well depth in the dimer. It seems probable, based on well established trends and the available experimental data, that a similar level of accuracy is achieved for the He–MgO interaction. As the local MP2 formalism is used, the time to completion for these calculations is similar to that for the underlying single particle solution and, thus calculations can be completed without using exceptional computer resources. For this class of systems HF + MP2(B3LYP) provides a reliable and efficient method for obtaining near experimental binding energy curves. This methodology resolves the principal problem in the interpretation of He-atom scattering spectra from insulating surfaces and will facilitate the extraction of surface structures and dynamical data from experimental spectra.

Notes and references

† All calculations (see ref. 4 for details) have been performed using a development version of the CRYSTAL software package.[13] CRYSTAL is based on the expansion of the crystalline orbitals as a linear combination of a local basis set consisting of atom centred Gaussian orbitals. The main approximation is then the choice of the basis set (see basis set BS4 in ref. 4). 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[13,14] and according to the previous paper on the dispersion contribution with the CRYSTAL code.[2,4] For the MP2 calculations, more severe thresholds on the exchange contribution have to be adopted for the calculation of the HF wavefunction:[4,15] 10^{-9}, 10^{-9}, 10^{-9}, 10^{-25} and 10^{-75}.

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