# The energetics of oxide surfaces by quantum Monte Carlo

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Density functional theory is widely used in surface science, but gives poor accuracy for surface energetics in many cases. We propose a practical strategy for using quantum Monte Carlo techniques to correct DFT predictions, and we demonstrate the operation of this strategy for the formation energy of the MgO (001) surface and the adsorption energy of the $H_2O$ molecule on this surface. We note the possibility of applying the strategy to other surface problems that may be affected by large DFT errors.

For many years, electronic-structure techniques have played a major role in surface and interface science. The most widely used of these techniques is density functional theory (DFT) [1], which has been employed to study many problems, including metal-oxide adhesion, catalysis and corrosion. Yet there is evidence that commonly used DFT approximations are often seriously in error for basic quantities like surface formation energies and molecular adsorption energies. It has been noted [2] that quantum Monte Carlo (QMC) techniques may be able to overcome these problems, because of their higher accuracy. We propose here a general strategy for using QMC to assess and correct DFT predictions for surface formation and molecular adsorption energies, based on the idea that the important DFT errors are localised near the surface, so that the comparison of QMC with DFT for small systems may often suffice to give the information needed. We will show the practical operation of this strategy for the formation energy of the MgO (001) surface and the adsorption energy of water on this surface, comparing where possible with experimental data.

Insight into DFT errors for surface energetics comes from work on the jellium surface [3,4]. Jellium is the homogeneous interacting electron gas neutralised by a uniform background; its density $n$ is characterised by the mean inter-electron distance $r_s$, defined by $(4\pi r_s^3/3)n = 1$, with $r_s$ in atomic units. The planar jellium surface is formed by having the neutralising background occupy only the half-space $x < 0$, so that the electron number density $n(x)$ in the ground state goes to its bulk value $n$ for $x \to -\infty$ and to 0 for $x \to \infty$. Accurate results for the formation energy of the jellium surface have been obtained [4] by extrapolating QMC calculations on neutral jellium spheres of different radius $R$. The extrapolation was performed by studying the large-$R$ behaviour of the difference between the QMC total energy and the total energy calculated with DFT approximations, the main such approximations being: the local density approximation (LDA) [1]; the generalised gradient approximation (GGA) in the Perdew-Burke-Ernzerhof form (PBE) [5];

and the meta-GGA [6]. This jellium surface work showed that: (i) for $2 \leq r_s \leq 5$, typical of simple metals such as Al and Na, the meta-GGA gives a very accurate surface energy $\sigma$, followed closely by LDA, with GGA being too low by a significant amount; (ii) as $r_s$ falls below 2, the GGA errors rapidly worsen. In the region $r_s \sim 1.5$, characteristic of transition metals and many oxides, the GGA $\sigma$ is too low by $\sim 0.3$ J m$^{-2}$, a serious error, because the surface energies of these materials are themselves in the region of 1 J m$^{-2}$.

Indirect confirmation for large GGA errors in surface energies comes from a study [7] of the work of adhesion $W_{adh}$ of Pd (111) to $\alpha$-$Al_2O_3$ (0001), for which accurate measurements are available. (Here, $W_{adh}$ is the reversible work per unit area needed to separate the system containing the oxide-metal interface into its metal and oxide consituents.) The GGA value $W_{adh} = 1.6$ J m$^{-2}$ is far below the LDA and experimental values of 2.4 and 2.8 J m$^{-2}$. The authors argue [7] that the GGA error comes mainly from errors in the free surface energies, and semiquantitatively relate these errors to GGA errors for the jellium surface. They suggest the general use of QMC jellium surface energies to correct DFT predictions for the surface energies of real materials [7].

The strategy we propose also uses QMC to correct DFT, but we apply QMC directly to the system of interest. In principle, QMC could be applied by brute force to the large slab systems commonly used to model surfaces in DFT calculations. However, since QMC is far more costly than DFT, this is not generally feasible at present. It is also unnecessary, and not the best way of gaining insight. Since DFT errors for surface energetics are expected to be localised in the surface region [8], an accurate assessment of these errors should be given by QMC calculations only on the atoms in the surface region. This implies that thin slabs, containing only a few atomic layers, should suffice to assess the *difference* between the surface energy given by QMC and by DFT approximations, so that this difference will converge more rapidly with increasing slab thickness than the separate

surface energies. This strategy resembles that used to extract the energy of the jellium surface from calculations on jellium spheres [4]. We propose to use the same scheme for molecular adsorption energies. The molecule is placed on the surface of a thin slab, and we study the difference between the QMC and DFT adsorption energies, seeking convergence of this difference with increasing slab thickness.

We have studied the practical feasibility of this strategy for the formation energy $\sigma$ of the MgO (001) surface. Our DFT calculations used the standard pseudopotential/plane-wave techniques [1], and were performed using the VASP code [9]. The surface was modelled using periodically repeated slab geometry, the calculation conditions being characterised by basis-set completeness (plane-wave cut-off energy $E_{\rm cut}$), Brillouin-zone sampling of the electronic states, the width $L$ of the vacuum layer separating successive slabs, and the number of layers $N_{\rm layer}$ in each slab. The surface formation energy is $\sigma = (E_{\rm slab} - E_{\rm bulk})/A$, with $E_{\rm slab}$ the energy of the slab system, per repeating cell, $E_{\rm bulk}$ the energy of the same number of atoms of the bulk material, and $A$ the total surface area (both faces) of the slab, per repeating cell. This definition applies for all $N_{\rm layer} \geq 1$. The bulk energy $E_{\rm bulk}$ is $N_{\rm layer}$ times the bulk energy per layer $e_{\rm bulk}$, and it is convenient to obtain $e_{\rm bulk}$ from the difference of $E_{\rm slab}$ values for successive values of $N_{\rm layer}$ in the limit of large $N_{\rm layer}$. For given $N_{\rm layer}$, we always insist on convergence of the calculated $\sigma$ with respect to $E_{\rm cut}$, BZ sampling and $L$ to within 0.01 J m$^{-2}$ (this tolerance is satisfied for $L > 6$ Å). As expected from earlier work, $\sigma$ for MgO (001) converges rapidly with respect to $N_{\rm layer}$, the residual errors being below 0.01 J m$^{-2}$ for $N_{\rm layer} \geq 2$. For a given DFT approximation, the calculated $\sigma$ depends a little on MgO lattice parameter $a_0$. For the experimental value $a_0 = 4.21$ Å, we obtain $\sigma = 1.24$ and 0.87 J m$^{-2}$ with LDA and GGA(PBE) respectively. The difference of 0.37 J m$^{-2}$ between the two is very similar to the difference of $\sim 0.4$ J m$^{-2}$ between the LDA and GGA surface energies of $\alpha$-Al$_2$O$_3$ (0001) [7].

The calculation of $\sigma$ by QMC is not standard, and we are not aware of previous calculations of $\sigma$ for any oxide surface using QMC, though our recent QMC calculations on perfect and defective MgO crystals [10] indicated the feasibility of the present calculations. We refer the reader to reviews for details of QMC (e.g. [11]). We recall that for high-precision results it is essential to use diffusion Monte Carlo (DMC), in which the many-electron wavefunction is evolved in imaginary time, starting from an optimised trial wavefunction generated in prior variational Monte Carlo calculations. The only error inherent in DMC is "fixed-node" error, due to the fact the nodes of the many-electron wavefunction are constrained to be those of the trial wavefunction. For many systems, including jellium, the evidence is that fixed-node error is extremely small. For wide-gap sys-

tems such as MgO, the errors should be no greater. Our calculations were performed with the CASINO code [12], using the same Hartree-Fock pseudopotentials as in our previous work [10]. The trial wavefunctions were of the usual Slater-Jastrow type, with single-electron orbitals obtained with the plane-wave code PWSCF [13], generally using the large plane-wave cut-off of 4082 eV. These orbitals were represented in CASINO using the recently reported "blip-function" real-space basis set [14]. The DMC calculations all used a time-step of 0.005 a.u., and mean number of walkers equal to 10,240. The calculations were done with free boundary conditions (i.e. no periodicity) normal to the surface.

Our DMC calculations were performed on a series of MgO slabs with the number of layers $N_{\rm layer}$ running from 1 to 5. For each $N_{\rm layer}$, convergence must be demonstrated with respect to basis-set completeness and size of repeating surface unit cell. Basis-set errors with the blip basis set are readily made negligible, as shown earlier [14]. In DMC calculations, the wavefunctions are real, so that Brillouin-zone sampling is generally impossible, and calculations are usually performed at the $\Gamma$-point; this is why convergence with respect to size of surface unit cell must be checked. Our main DMC calculations used the $2 \times 2$ surface unit cell, for which the repeating cells contain from 16 ($N_{\rm layer} = 1$) to 80 ($N_{\rm layer} = 5$) ions; we show below that larger surface cells would give almost identical results.

The raw output from these calculations is DMC total energies $E_{\rm slab}^{\rm DMC}$ for the five $N_{\rm layer}$ values. Following our strategy, we now study the difference $\Delta E_{\rm slab} \equiv E_{\rm slab}^{\rm DMC} - E_{\rm slab}^{\rm DFT}$, with the DFT slab energy calculated with exactly the same slab and the same ($\Gamma$-point) BZ sampling as in the DMC calculations. Since the jellium results indicate that LDA surface energies are likely to be closer to DMC than those from GGA, we use LDA values for $E_{\rm slab}^{\rm DFT}$. When plotted against $N_{\rm layer}$, $\Delta E_{\rm slab}$ will tend asymptotically ($N_{\rm layer} \to \infty$) to a straight line, whose slope is equal to the difference between the DMC and LDA bulk energies $\Delta e_{\rm bulk}$ per layer, and whose $N_{\rm layer} = 0$ intercept divided by $A$ gives the difference of DMC and DFT surface energies $\Delta \sigma \equiv \sigma^{\rm DMC} - \sigma^{\rm DFT}$. Since $\Delta e_{\rm bulk}$ is large, and since $\Delta E_{\rm slab}$ contains the statistical errors of DMC, it is helpful to start this analysis by performing a least-squares straight-line fit $a + bN_{\rm layer}$ to the values of $\Delta E_{\rm slab}$, and then to use the resulting $b$ value to form the quantity $\tilde{\Delta} E_{\rm slab} \equiv \Delta E_{\rm slab} - bN_{\rm layer}$. The $N_{\rm layer} \to \infty$ straight-line asymptote of $\tilde{\Delta} E_{\rm slab}$ has the same $N_{\rm layer} = 0$ intercept as that of $\Delta E_{\rm slab}$. For $N_{\rm layer} = 1, 2, \ldots 5$, we find the five values $\tilde{\Delta} E_{\rm slab} = -0.019(2), -0.009(6), -0.007(9), -0.011(13)$ and $-0.014(15)$ J m$^{-2}$. This immediately shows that the DMC and LDA values of $\sigma$ are almost exactly the same. Within our rather small statistical errors of at worst 0.015 J m$^{-2}$, the difference between the DMC and LDA surface energies has the very

small value of $-0.01$ J m$^{-2}$. To check the errors due to use of the $2\times2$ surface cell (i.e. errors of BZ sampling), we have performed LDA calculations on slabs having large surface cells with a series of $N_{\mathrm{layer}}$ values, using $\Gamma$-point sampling. The $\sigma$ values thus obtained differ from the LDA $\sigma$ value extracted by similar $\Gamma$-point calculations with the $2\times2$ surface cell by only 0.01 J m$^{-2}$. The LDA value of $\sigma$ for the lattice parameter we are using, converged with respect to BZ sampling and slab thickness, is 1.20 J m$^{-2}$, and we conclude from our $\tilde{\Delta}E_{\mathrm{slab}}$ values that the fully converged DMC value is $1.19\pm0.01$ J m$^{-2}$. MgO is one of the few oxides for which reasonably reliable experimental values of the surface energy are available [15]. Exploiting the fact that MgO cleaves readily along the (001) plane, the experiments measure the work of cleavage, thus ensuring that the results for $\sigma$ cannot be influenced by surface contamination. Our $\sigma_{\mathrm{DMC}}$ value of 1.19 J m$^{-2}$ is consistent with the measured values [15], which fall in the range $1.04-1.20$ J m$^{-2}$.

In applying QMC to correct DFT predictions for the adsorption energy $E_{\mathrm{ads}}$ of H$_2$O on MgO (001), we assume, in accord with experimental and theoretical indications [16,17], that the molecule lies almost flat on the surface, with the water O atom almost above a surface Mg ion, the water O–H bonds pointing towards surface O ions (Fig. 1). The adsorption energy is defined to be $E_{\mathrm{ads}} = E_{\mathrm{H_2O}} + E_{\mathrm{bare\ slab}} - E_{\mathrm{slab+H_2O}}$, where the terms on the right are the energy of the isolated H$_2$O molecule, the energy of the bare MgO (001) slab, and the energy of the slab with the H$_2$O molecule adsorbed on the surface, all three systems being fully relaxed to equilibrium. In our DFT calculations, we require that $E_{\mathrm{ads}}$ be converged to within 10 meV with respect to plane-wave cut-off $E_{\mathrm{cut}}$, BZ sampling, and vacuum width $L$. Furthermore, since we want $E_{\mathrm{ads}}$ for an isolated molecule, we examine the dependence of $E_{\mathrm{ads}}$ on the size of the surface unit cell. We find that with the $2\times2$ cell, $E_{\mathrm{ads}}$ is already converged to better than 10 meV (this was tested by doing calculations up to $5\times5$ surface unit cells). With these tolerances always applied, we then study the dependence of $E_{\mathrm{ads}}$ on the number of layers in the slab $N_{\mathrm{layer}}$. As $N_{\mathrm{layer}}$ increases, $E_{\mathrm{ads}}$ ceases to change by more than 2 meV for $N_{\mathrm{layer}} \geq 2$. Our calculated values of $E_{\mathrm{ads}}$ with LDA and GGA(PBE) are 0.92 and 0.43 eV respectively.

In the DMC calculations, we obtained $E_{\mathrm{H_2O}}$ using periodically repeated cubes of different lengths $d$, with a single molecule in each cube, using the molecular geometry taken from PBE (O–H bond length $= 0.978$ Å, bond-angle $= 104.4°$). There is a weak dipole-dipole correction, going as $d^{-3}$, but we extrapolate to infinite $d$ to obtain $E_{\mathrm{H_2O}}$ with a technical error uncertainty of only a few meV. The slab energy $E_{\mathrm{bare\ slab}}$ is taken from our DMC calculations on $\sigma$ (see above). For H$_2$O on the slab, strict application of our strategy would require us to use the relaxed configuration obtained from DMC calculations. We are not yet able to do this, since the calculation of

ionic forces with DMC is problematic for the moment (though see Ref. [21]). Instead, we use a relaxed configuration from the DFT approximation which appears to reproduce DMC most closely. Our DFT calculations show that the relaxed height of the molecule above the surface differs by $\sim 0.15$ Å between LDA and PBE. We calculated the DMC energy fo H$_2$O on the 1-layer slab, with a series of geometries on a linear path between the relaxed LDA and PBE geometries, and we find that the PBE geometry is very close to giving the lowest DMC energy. All our DMC results therefore refer to relaxed PBE geometries.

Since DFT calculations of $E_{\mathrm{ads}}$ are converged with respect to surface cell size for $2\times2$ cells, our DMC calculations are all done with this surface cell. With $N_{\mathrm{layer}} = 1$, we find $E_{\mathrm{DMC}}^{\mathrm{ads}} = 0.63(3)$ eV, $E_{\mathrm{PBE}}^{\mathrm{ads}} = 0.48$ eV, so that $\Delta E^{\mathrm{ads}} \equiv E_{\mathrm{DMC}}^{\mathrm{ads}} - E_{\mathrm{PBE}}^{\mathrm{ads}} = 0.15$ eV. For $N_{\mathrm{layer}} = 2$, the results are $E_{\mathrm{DMC}}^{\mathrm{ads}} = 0.57(4)$ eV, $E_{\mathrm{PBE}}^{\mathrm{ads}} = 0.42$ eV, so that $\Delta E^{\mathrm{ads}} = 0.15$ eV, identical to the $N_{\mathrm{layer}} = 1$ value within statistical errors. Using the $N_{\mathrm{layer}} \to \infty$ PBE value of 0.43 eV, we thus estimate the $N_{\mathrm{layer}} \to \infty$ DMC value as 0.58(3) eV.

For $E_{\mathrm{ads}}$, a comparison with experiment can only be indicative at present. Measurements of LEED isotherms and isobars for H$_2$O adsorption on MgO (001) as a function of coverage, extrapolated to zero coverage gives $E_{\mathrm{ads}} = 0.52 \pm 0.10$ eV [18]. Temperature programmed desorption experiments show a peak at $T = 235 - 260$ K due to desorption of water at initial monolayer coverage [16,19]. The standard Redhead analysis, using the commonly assumed frequency prefactor of $10^{13}$ sec$^{-1}$, yields an effective $E_{\mathrm{ads}}$ of $0.63 - 0.67$ eV. However, this must include a significant contribution from attractive water-water interactions, so that $E_{\mathrm{ads}}$ for isolated H$_2$O should be somewhat lower, and thus perhaps consistent with the LEED value of $0.52 \pm 0.10$ eV. To compare our DMC value with this, a correction for vibrational energies is needed. We have performed GGA(PBE) calculations on the adsorbed molecule, which indicate that adsorption lowers the symmetric and asymmetric stretch modes of H$_2$O by 12 and 9 THz respectively, and raises the bond-bending mode by 2 THz. The associated zero-point energies raise the adsorption energy by 39 meV. Translational and rotational energies of the H$_2$O molecule in free space, and vibrations and librations of the adsorbed molecule relative to the surface [20] raise and lower the adsorption energy by 64 meV and 167 meV respectively. Altogether, vibrational effects lower the adsorption energy by 64 meV, so that our corrected DMC adsorption energy is 0.51 eV. Our calculated value thus appears to be consistent with the experimental evidence, but clearly a more elaborate analysis would be needed to make this comparison robust. Our comparisons make it fairly clear that LDA gives a serious overestimate of the adsorption energy, while GGA (PBE) is considerably more accurate.

Our proposed strategy is therefore feasible and useful

for MgO surface energetics. Many other important problems could be addressed in the same way, including the $\alpha$-$Al_2O_3$ (0001) surface energy mentioned earlier [7]; the computational effort needed for this case would similar to MgO. For this and other applications of the strategy, we believe that current progress in the calculation of ionic forces and structural relaxation with DMC [21] will be very helpful.

The ability to validate QMC against experiment for molecular adsorption energies is limited by the lack of adequate techniques for putting modelling and data into close contact. Progress in the *ab initio* prediction of TPD spectra [22] is encouraging in this respect. Finally, we note the importance of quantum chemistry methods. For wide-gap materials, techniques such as MP2 and CCSD(T) should deliver an accuracy similar to that of DMC. Major improvements in the scaling of these techniques with number of atoms and size of basis sets [23] and to perform them in periodic boundary conditions [24] should make it possible to use them within our proposed strategy.

In summary, we have described a practical general strategy for using QMC calculations to assess and correct the errors of DFT approximations for the energetics of surfaces. Our calculations on the surface formation energy of MgO (001) and the adsorption energy of $H_2O$ on this surface confirm the feasibility and usefulness of the strategy. The results support earlier inferences from the energetics of the jellium surface that the GGA surface formation energy for this type of material is substantially too low, and that LDA is more accurate. However, for the molecular adsorption energy, the reverse is true, with LDA errors being much greater than those of GGA.

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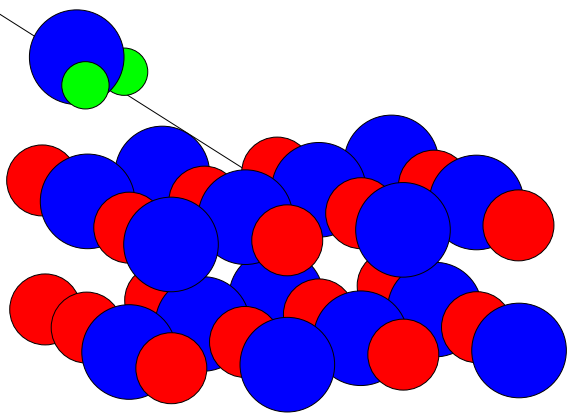[24] C. Pisani, G. Capecchi, S. Cassassa, and L. Maschio, Molec. Phys. **103**, 2527 (2005).

FIG. 1. Adsorption geometry of the $H_2O$ molecule on MgO(001) from DFT with PBE exchange-correlation functional.