Exchangelike Effects for Closed-Shell Adsorbates: Interface Dipole and Work Function

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Based on detailed theoretical analyses, we present, for the first time, direct evidence that the significant interface dipole commonly observed for atoms and molecules physisorbed on metal surfaces originates from exchangelike effects. In the case of Xe, previously proposed contributions from chemical interactions do not play a significant role.

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The use of molecules as active components in electronic devices is currently attracting a significant amount of attention. For the fabrication of molecular electronic devices, it would be desirable to be able to predict the electronic structure of the molecule/metal interface. In particular, the band-level alignment is of crucial importance for the performance of such devices [1,2]. Experimental data have been collected for a large number of systems [1–3], but even the properties of the most simple system, a saturated hydrocarbon adsorbed on a noble metal surface, are not well understood theoretically. More precisely, for these systems the formation of an interface dipole is observed, which shifts the molecular levels by a large amount relative to the Fermi energy and substantially lowers the work function ϕ of the metal. For alkanes on Au, where one would expect all chemical effects to be absent, the lowering amounts to 0.7 eV [3], for other molecules values above 1 eV have been seen [1]. The direction of this work-function change is the same as observed for donors, e.g., alkali atoms, on a metal surface. Of course, saturated hydrocarbons do not act as donors of electric charge and the origin of the changes in ϕ must stem from effects other than charge transfer from the molecule to the metal [4–7]. These unexpected interface dipoles call for theoretical investigations, which, however, for molecular systems are rather difficult and have not yet, to our knowledge, been carried out with the required level of accuracy.

Very similar work-function changes [2], however, have been seen for a much simpler case, noble gas atoms deposited on metal surfaces [8]. Some authors have explained the formation of an interface dipole for this simple system on the basis of physical interactions only and related the work-function change to perturbations of the electronic structure at the metal surface caused by Pauli repulsion. This repulsion occurs when noble gas atoms are being pulled towards the surface by van der Waals (vdW) interactions and their electronic wave functions overlap with those of the metal. It has been argued that the distortion of the metal electron wave functions required to reduce this overlap will raise the kinetic energy of the electrons [9] and push some of the (metallic) charge between molecule and surface back into the metal [3].

Although these heuristic explanations are rather intuitive, previous theoretical work so far has failed to corroborate these ideas. Early theoretical studies on Xe adsorbed on Al [4] yielded a rather good agreement between experimental and theoretical work-function changes and suggested the presence of a substantial amount of chemical interactions. Similar results were reported for Xe on Pt(111) [4,10]. When considering this rather surprising presence of chemical interactions for a noble gas atom like Xe, it is important to realize that all previous theoretical studies known to us have been obtained in the framework of density functional theory (DFT) or with model Hamiltonians [4,6,9–11]. DFT methods, applied in cases where vdW interactions are important, give results that depend strongly on the density functional used [12,13]. When DFT is used to study such systems, care must be exercised in the choice and the validation of the density functional that is used. Here we report an *ab initio* electronic structure study using a wave function (WF) based approach. The properties of Hartree-Fock self-consistent field (SCF), WFs are analyzed to separate the various contributions to the interaction; vdW dispersion forces are accounted for by including electronic correlation effects using second order perturbation theory (MP2). Our results demonstrate that the formation of the interface dipole for both, noble gas atoms and simple hydrocarbons, does not arise from chemical effects, as suggested in earlier work [4,10], or from electrostatic interactions, as proposed in some of the intuitive models put forward previously. Rather, the dominant origin of this dipole is a quantum effect related to the antisymmetrization of the electronic wave functions.

The present calculations used a 10 atom Cu cluster to model the unrelaxed Cu(111) surface. Because of the large distance of the Xe and cyclohexane adsorbates above the Cu surface, chemical interactions involving the Cu $3d$ orbitals are not expected to be important. Thus, most calculations were carried out using a pseudopotential, or effective core potential (ECP), where only the Cu $4s$ electron was treated explicitly [14]. The use of this ECP was validated by the very similar results that we obtained from all-electron calculations for $Cu_{10}Xe$. For Xe, we

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normally used a relativistic ECP due to Stevens *et al.* [15] to describe the 1*s* to 4*d* core electrons, and only the eight outermost electrons, $5s^2 5p^6$ are explicitly included in the WF. The Xe basis set [15] was augmented with diffuse *s* and *p* functions primarily to properly represent the static dipole polarizability, α_D, of Xe [16,17]. With this basis set, the SCF WF for an Xe atom gives $\alpha_D = 3.89$ Å^3, within 96% of the experimental $\alpha_D = 4.04$ Å^3 [18]. For C_6H_{12}, large all-electron basis sets, described in Ref. [19], were used. Adsorbate-substrate distances and, in the case of C_6H_{12}, the internal adsorbate structure were optimized on the MP2 level (thus including corrections for electron correlation) with a commercial program package [20]. In the optimizations the structure of the Cu_{10} cluster was kept fixed and the symmetry of the whole system was restricted to C_{3v}. Estimates of the basis set superposition errors showed that any errors due to the incompleteness of the basis sets are negligible.

We find a Xe-surface distance for Xe at an on-top site of Cu(111) to be $z(\mathrm{Xe}) = 4.23$ Å, somewhat larger than the experimental value of $z(\mathrm{Xe}) = 3.60$ Å [21]. Our error for z(Xe) is due, in large part, to the fact that the polarizability of the Cu_{10} cluster is smaller than that of the extended Cu surface, and, thus, the vdW attraction is too small. This reduced vdW bond strength also explains why our calculated binding energy of 95.1 meV is smaller than the experimental value of 190 meV [22]. Of course, for weak bonds it is difficult to calculate precise values of the bond distance. On the other hand, for the Xe frustrated translation normal to Cu(111), we find an energy of 2.2 meV in good agreement with the experimental value of 2.6 meV [23]; this indicates that our calculations have reproduced the shape of the potential curve.

SCF WF for $Cu_{10}Xe$ with $z(\mathrm{Xe}) = 4.20$ Å gives an induced dipole moment of $\mu = 0.18$ D per Xe atom. Since μ has not been measured in the limit of low coverage of Xe/Cu(111), only indirect comparison with experiment can be made. From the 0.5 eV work-function change for a saturated monolayer of Xe/Cu(111) [24], we use Topping's formula to estimate that a single Xe atom induces a change in μ of $\Delta\mu = 0.22$ D. From comparison to the situation for Xe/Pd, where Wandelt and Hulse [6] have determined the $\Delta\mu$ associated with a single Xe atom, we estimate that a more correct value for a single Xe atom on Cu(111) will be significantly larger than the value given above, i.e., ~0.3–0.4 D. This is somewhat larger than our calculated value for $z(\mathrm{Xe}) = 4.20$ Å. However, we know that our calculations underestimate the Xe-Cu(111) attraction and thus yield too large bonding distances. When we use the experimental z(Xe), we obtain a Xe induced $\Delta\mu = 0.58$ D, which is in better agreement with the estimated value from the data of Wandelt and Hulse [6].

Our calculations thus reproduce the experimental interface dipole for Xe adsorbed on Cu(111) with the validity of the present theoretical approach. We now analyze the theoretical results in more detail to reveal the underlying physical mechanisms responsible for $\Delta\mu$; this analysis is performed at the SCF level.

Our analysis is carried out by going stepwise from a noninteracting situation where the Xe atom is placed at a given distance above the Cu cluster with all orbitals frozen to the fully interacting situation where all orbitals are allowed to vary without constraints. In the first step, we consider frozen orbital (FO) WF's. The WF for the open shell system Cu_{10}, $\Psi(Cu_{10})$, which has $^3A_2$ symmetry, is either one or two Slater determinants depending on whether $M_S = \pm 1$ or $M_S = 0$. We choose to use $M_S = 1$ so that $\Psi(Cu_{10})$ is a single determinant. The WF for Xe(^1S), Ψ(Xe), is also single determinant. The FO WF for $Cu_{10}Xe$ is simply the antisymmetrized product of the Slater determinants for Cu_{10} and Xe, $\Psi(\mathrm{FO}) = A\{\Psi(Cu_{10}) \times \Psi(\mathrm{Xe})\}$ [25,26], using the SCF orbitals for the isolated systems. In succeeding steps of the constrained space orbital variation (CSOV) method [26,27], we include variational freedom for the Xe and Cu_{10} orbitals, and hence we allow, in a controlled way, chemical changes to take place. In step 2, denoted Vary Cu, the Xe orbitals are kept frozen but Cu_{10} can respond to the presence of Xe. In step 3, Vary Xe, the Xe orbitals are allowed to vary. The final CSOV step, denoted full SCF, is the unconstrained, simultaneous variation of both the Cu_{10} and the Xe orbitals and includes all possible chemical effects. In Table I, the results of the CSOV analysis for the interaction energy, E_{int}, and for μ are given for several values of z(Xe). The E_{int} is the difference between the energy for $\Psi(Cu_{10}Xe)$ and the sum of the energies for $\Psi(Cu_{10})$ and Ψ(Xe).

Inspection of Table I shows that the dominant contribution to the interface dipole is due to the FO step. This demonstrates that the origin of the interface dipole for Xe

TABLE I. Decomposition of the changes in E_{int} and μ for wave functions where different constraints are imposed on the orbital variation for $Cu_{10}Xe$; see text. The entries for δE_{int} and for $\delta\mu$ are the changes in the values of the respective quantity with respect to the preceding step.

z(Cu − Xe) − Å	WF	δE_{int} (eV)	$\delta\mu$ (Debye)
4.20	FO	$(-0.094)^a$	$(+0.214)^b$
	Vary Cu	+0.037	−0.041
	Vary Xe	+0.004	+0.014
	Full SCF	+0.000	−0.005
3.80	FO	$(-0.206)^a$	$(+0.357)^b$
	Vary Cu	+0.078	−0.077
	Vary Xe	+0.013	+0.118
	Full SCF	+0.000	+0.014
3.60	FO	$(-0.300)^a$	$(+0.453)^b$
	Vary Cu	+0.115	−0.107
	Vary Xe	+0.025	+0.204
	Full SCF	+0.000	+0.027

[a] Value of E_{int} for the FO WF; the negative sign indicates repulsion. The exchange repulsion increases exponentially as z(Cu-Xe) becomes smaller.

[b] Difference of μ for Ψ(FO) and μ for $\Psi(Cu_{10})$.

on Cu surfaces is an exchange effect, i.e., a pure physical phenomenon, which dominates all chemical and polarization effects included in steps 2 and 3. This is the most important new effect presented in this Letter. In the following we will explore the origin of the interface dipole moment by considering the z component of μ for $Cu_{10}Xe$. Using the Born-Oppenheimer approximation, μ_z is, in atomic units,

$$\mu_z = \sum_N Z_N Q_N - \langle\psi| \sum_i z_i |\psi\rangle / \langle\psi|\psi\rangle, \tag{1}$$

where N and i sum over nuclei and electrons and where the Nth nucleus has position Z_N and charge Q_N. If Ψ is written as [28] $\Psi = (n!)^{-1/2} \det\{\varphi_1, \varphi_2, \ldots, \varphi_N\}$, where n is the number of electrons, then

$$\mu_z = \sum_N Z_N Q_N - \sum_{k,l} \frac{\langle\varphi_k|z|\varphi_l\rangle \times D(kl)}{D}, \tag{2}$$

where $D(kl)$ is the kl cofactor of the determinant D of the overlap integrals $S_{ij} = \langle\varphi_i|\varphi_j\rangle$, and the sums k and l run over all occupied spin orbitals. If and only if $S_{ij} = \delta_{ij}$, then Eq. (2) reduces to the usual formula

$$\mu_z = \sum_N Z_N Q_N - \sum_k \langle\varphi_k|z|\varphi_k\rangle. \tag{3}$$

Since in the FO WF, the Cu and Xe orbitals are not mutually orthogonal, the complex Eq. (2) has to be used instead of the simple Eq. (3). In order to see the importance of the off-diagonal matrix elements, $z_{kl} = \langle\varphi_k|z|\varphi_l\rangle$ and S_{kl}, we consider the much simpler case of a Li atom interacting with an H atom placed along the z axis at $Z(\mathrm{Li})$ and $Z(\mathrm{H})$, respectively. Further, we consider only the Li $2s$ and the H $1s$ electrons coupled to a triplet state; in effect, the Li $1s^2$ electrons are included in the Li nucleus giving an effective $Q(\mathrm{Li}) = 1$. The unnormalized $\Psi(\mathrm{FO})$ for this model is

$$\Psi(\mathrm{FO}) = (1/\sqrt{2}) \times [\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)] \times \alpha(1)\alpha(2). \tag{4}$$

Here α is the $m_s = +1/2$ spin function and φ_a and φ_b denote the $\mathrm{H}(1s)$ and $\mathrm{Li}(2s)$ atomic orbitals, respectively. For this WF, Eq. (2) reduces to

$$\mu_z(\mathrm{FO}) = S_{ab}\{2z_{ab} - S_{ab} \times [Z(\mathrm{Li}) + Z(\mathrm{H})]\}/(1 - S_{ab}^2) \approx 2z_{ab} \times S_{ab}, \tag{5}$$

and the last term is obtained assuming that S_{ab} is small and that $Z(\mathrm{H}) = \Delta z/2 = -Z(\mathrm{Li})$.

Thus, even on the frozen orbital level the dimer exhibits a μ that is proportional to the overlap between the two orbitals. Since the Li $2s$ is larger than the H $1s$ orbital, the overlap region of the two wave functions is shifted towards the H atom, resulting in a positive value of z_{ab} and, accordingly, a dipole moment that is directed from the H towards the Li atom. From this simple system one can derive the general prediction that the sign of $\Delta\mu$ for the exchangelike correction given by the FO WF is such that charge appears to "flow" from the unit with the more contracted orbitals toward the unit with more diffuse orbitals. This apparent flow of charge (see also Fig. 1) is not included in the usual description of chemical interactions at surfaces as involving intraunit polarizations and interunit charge transfers, donations, and backdonations. The apparent flow occurs exclusively because the full n-electron WF must have the correct symmetry property for a Fermion system of being antisymmetric with respect to permutation of the electrons.

An inspection of Fig. 1 reveals that in addition to charge pushed back into the metal there is also a significant amount of charge pushed sidewise. We speculate that these observations may explain the anomaly observed for the Xe-Xe interaction reported in previous work for Xe adlayers on the three low-indexed surfaces of Cu [23,29,30].

Having analyzed the most important changes that occur in the FO step, we now consider the polarization of the Cu surface. In this Vary Cu step, the occupied orbitals of Xe are kept fixed but the Cu_{10} orbitals are allowed to vary using the full space of virtual orbitals of Cu_{10} and Xe. The most important result shown in Table I is that the change in μ for the Vary Cu step is rather small. In the Vary Xe step, the Xe orbitals are allowed to vary and polarize due to the presence of the Cu surface. The changes at this step are also rather small; see Table I.

In previous work, it has been proposed that the $\mathrm{Xe}(6s)$ orbital may be populated as a result of the electronic Xe-metal interaction [7,11]. This effect would involve a

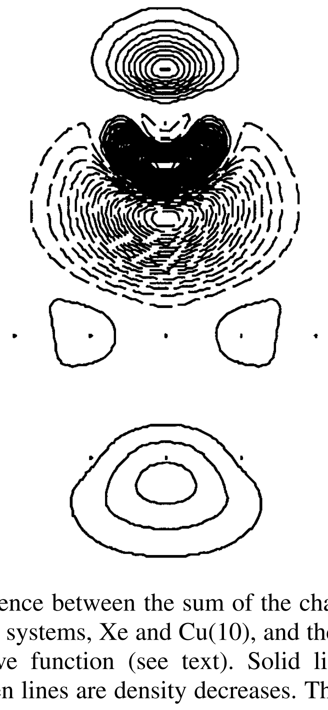

FIG. 1. Difference between the sum of the charge densities of the two isolated systems, Xe and Cu(10), and the total charge of the $\Psi(\mathrm{FO})$ wave function (see text). Solid lines are density increases, broken lines are density decreases. The plotting plane passes through the Xe atom and the central Cu atom; dots denote the projected positions of the atoms.

motion of Cu charge towards Xe, i.e., a negative change in μ. Further, this change of μ would involve motion of charge of a_1, σ, symmetry. For the Vary Cu step, we separated the changes in μ, $\delta\mu$, into contributions from the a_1 and the e, π, orbitals. For $z(\mathrm{Xe}) = 3.60$ Å, $\delta\mu(a_1) = +0.51$ D, while $\delta\mu(e) = -0.61$ D. The direction of the motion of the Cu σ charge is downward, away from Xe, to reduce the Cu-Xe steric repulsion while the motion of the Cu π charge not involved in bonding to the Xe(6s), is upward and acts to reduce the change in the surface dipole. Thus, for Xe/Cu(111), we can safely rule out the presence of any charge backdonation from Cu to the Xe 6s.

Although these results clearly reveal that the major contribution to the change in the work function for Xe adsorbed on Cu(111) does not originate from electrostatic repulsion, polarization, or chemical contributions, as frequently proposed in earlier work [2,7], but from an exchangelike mechanism.

We now turn our attention to the adsorption of a typical saturated hydrocarbon, cyclohexane, on the same Cu cluster. In this case our MP2 results yield a binding energy of 330 meV, which is in reasonable agreement with the experimental value of 520 meV [31]. The theoretical value for the energy of the frustrated translation mode of cyclohexane normal to the surface amounts to 30 cm^{-1}, in reasonable agreement with the experimental value of 50 cm^{-1} for cyclohexane adsorbed on Cu(100) [32]. A CSOV analysis of the bonding of cyclohexane on the same Cu(10) cluster yields a scenario rather similar to that given for Xe. In this case Ψ (full SCF) has a dipole moment of 0.7 D per cyclohexane molecule. As in the case of Xe, the most important contribution (0.6 D) again comes from the exchange repulsion described by the first step, FO. Applying the Topping formula to the experimental value for the work-function change of 0.3 eV seen for a longer saturated hydrocarbon on Cu(100) [3] yields a dipole moment of 0.29 D when assuming a density of 2.7×10^{14} cm^{-2} for a C_6H_{12} monolayer. Because of depolarization effects for the full monolayer (see discussion above), we expect the dipole moment of a single cyclohexane molecule to be significantly larger, i.e., 0.5–0.6 D, in fair agreement with the present theoretical result. Note that in contrast to Xe for adsorbed saturated hydrocarbons a weak chemical interaction involving a small backdonation of charge to the molecule [19,31] has been proposed recently, which will slightly affect the interface dipole.

Since the MP2 results for our cluster models of the physisorption of Xe and C_6H_{12} on Cu(111) reproduce the main features of experiment, we are confident that our model includes the essential physics of the interaction. The decomposition of the contributions of various mechanisms, made using SCF wave functions, demonstrates that exchange (or Pauli) repulsion, a purely quantum mechanical phenomenon, can quantitatively explain the experimentally observed, unexpectedly large interface dipoles. The rather significant changes in work function caused by these interface dipoles even in the case of physisorbed, closed-shell particles need to be considered when tailoring metal/molecule interfaces in order to optimize electron injection into molecular materials.

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