

Theory of local-work-function determination by photoemission from rare-gas adsorbates

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Photoemission from rare-gas atoms adsorbed on surfaces offers a unique analytical tool for the determination of the work function appropriate to microscopically small regions of a substrate surface. The chemical activity of small regions, such as steps and corners, and the fact that the local work function determines the relative energies of substrate and adsorbate electronic levels makes the determination of the local work function potentially very important. Here we provide a detailed microscopic picture of the special aspects of rare-gas adsorption that make such measurements possible. The discussion is based on the results of parameter-free self-consistent-field calculations for individual rare-gas atoms on a free-electron metal.

The electrostatic dipole-layer potential is the component of the work function of a solid surface that determines the energy positions of electronic states interior to the solid relative to the vacuum zero of energy outside. The numerical value of the dipole-layer potential varies on a microscopic scale along the surface and can play an important role in positioning substrate levels relative to those of adsorbed atoms and molecules. A means of determining its value in chemically active but spatially restricted regions, such as steps and other imperfections in the solid surface, is very important. Traditional methods of measuring the work function (Kelvin probe, photoemission threshold, e.g.) indicate only the value of the dipole layer potential averaged over a macroscopic portion of the surface, and are therefore of little value in determining the dipole-layer potential in chemically important, but microscopic regions. The photoelectron spectrum of adsorbed rare-gas atoms represents a uniquely important analytical tool in this context, because it reflects the magnitude of the dipole-layer potential in the immediate vicinity of the chemisorption site. The studies of Küppers, Wandelt, Ertl, and co-workers¹⁻⁴ have already shown that such spectra are sensitive to the variation of the dipole-layer potential in regions such as steps. The explanation of this effect offered by these workers is simply that the rare-gas atom sits outside the substrate surface, thereby providing a local vacuum reference. (Comparison of the kinetic energy of electrons photoemitted from a level localized on the rare-gas atom⁵ with that of electrons photoemitted from the Fermi level of the substrate yields the value of the local dipole-layer potential.)

The idea that the rare-gas atom is both bonded to the surface and yet lies completely outside the surface appears, at first sight, to be a paradox. Furthermore, recent work by Lang⁶ indicates that the elec-

tron clouds of the rare-gas atom and of the substrate interpenetrate sufficiently for the bonding and the formation on the atom of a permanent dipole moment to be due primarily to local exchange-correlation forces between the atom's valence electrons and those of the metal. The purpose of the present paper is to eliminate any sense of paradox and to clarify what it means for the rare-gas atom to be sufficiently outside the substrate surface to provide a vacuum reference, and yet to be sufficiently inside the surface to be bound by a few tenths of an electron volt and to develop a substantial dipole moment.

An understanding of these inside/outside aspects of the bonding is provided by Fig. 1, where we show, for a realistic model of adsorbed Xe,⁷ the relative spatial positions of the three important ingredients of our discussion: (i) the valence ($5p$) electron density of the rare-gas atom, (ii) the electrostatic dipole-layer potential (V_{es}), and (iii) the exchange-correlation potential (V_{xc}). The electrostatic and exchange-correlation potentials together constitute the total effective surface potential barrier seen by an electron.⁸ We see in Fig. 1 that the electronic charge associated with even the outermost valence states of the rare-gas atom lies almost completely outside the electrostatic dipole-layer potential of the substrate, while it lies almost entirely within the region where the exchange-correlation potential is appreciable. The point is that electrostatic forces play a much less important role than exchange-correlation forces in the binding of the rare-gas atom to the surface and in the formation on the atom of a permanent dipole moment.⁹ The crucial difference in range between the electrostatic and exchange-correlation potentials in the surface region can be understood simply from the fact that the spatial dependence of the electrostatic potential in this region is similar to that of the sub-

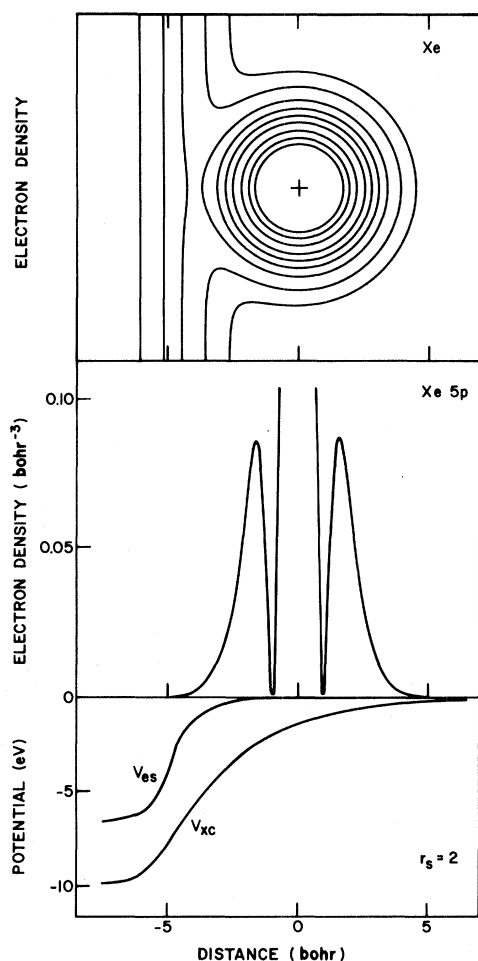


FIG. 1. Results for a single Xe atom adsorbed at its equilibrium position on the surface of a high-density metal, simulated by a jellium model (density appropriate to Al). The top panel shows contours of constant electron density for the combined metal-atom system. The center panel shows the Xe valence- p -electron density, graphed along the surface normal. (This graph includes whatever small polarization of the metal and of the Xe that occur as a consequence of bond formation. Explicitly, the electron density shown is the total in the metal-atom system minus both that of the bare metal and that of all Xe levels other than the valence p . The density within 0.7 bohr of the nucleus is not graphed for pictorial reasons.) The bottom panel shows the two components of the total effective single-particle potential due to the bare metal: (i) the electrostatic dipole-layer potential (V_{es}) and (ii) the exchange-correlation potential (V_{xc}).

strate electron density, whereas the exchange portion of the exchange-correlation potential varies as the cube root of the density, and therefore falls to zero more slowly. (The correlation contribution decreases yet more slowly.)

Two aspects of Fig. 1 warrant further comment.

TABLE I. Core-level binding energies ($4d_{5/2}$) for monolayer adsorption of Xe on two single-crystal substrates. I^F is binding energy relative to the Fermi level. Φ_M is bare-substrate work function and $\Delta\Phi$ is work-function change due to the adsorbed Xe layer. $I^V = I^F + \Phi_M + \Delta\Phi$ is binding energy relative to vacuum. (Since $\Delta\Phi$ is the same in the two cases listed, we need not be concerned in interpreting this table with the fact that while a Xe atom is outside of the dipole layer involved in Φ_M , it is of course in the same spatial region as the dipole layer that gives rise to $\Delta\Phi$. See Ref. 10.)

Substrate	Φ_M (eV)	$\Delta\Phi$ (eV)	$I^F(4d_{5/2})$ (eV)	$I^V(4d_{5/2})$ (eV)
Gd(0001) ^a	3.3	-0.6	62.8	65.5
Pd(100) ^b	5.5	-0.6	60.5	65.4

^aN. D. Lang, A. R. Williams, F. J. Himpsel, B. Reihl, and D. E. Eastman (unpublished).

^bG. Kaindl, T. -C. Chiang, D. E. Eastman, and F. J. Himpsel, Phys. Rev. Lett. **45**, 1808 (1980); and (private communication).

First, the magnitude of the exchange-correlation potential over the region occupied by the valence- p shell suggests that this component of the total effective potential seen by the electrons might lead to a significant chemical, or initial-state, shift of its photoelectron spectrum. This is not the case. The exchange-correlation potential seen by electrons when they are in the interior of the atom is not simply the superposition of the potential associated with the free atom and the potential shown in Fig. 1. The change in the exchange-correlation potential in the atom interior due to the presence of the substrate is negligible fundamentally because the cube root is a weak function of the electron density, when evaluated for large densities. The tail of the metal density distribution therefore changes the exchange-correlation potential from its free-atom values only slightly in the region where the atom electron density is large compared with this tail density, i.e., over most of the atom, implying a negligible effect on the level positions. The final aspect of Fig. 1 to which we call attention is the distinction it indicates between photoemission from core and valence states of the rare-gas atom. The spatial extent of the core orbitals is indicated roughly in Fig. 1 by the sharp minima in the valence electron density. We see in this way that the core orbitals lie even more completely outside the electrostatic dipole-layer potential than do the valence orbitals. Thus photoemission from the core levels should provide a particularly precise method of measuring variations in the dipole-layer potential. Table I provides experimental evidence in support of this claim. The

table shows that the binding energy (I^F) of a Xe 4*d* core electron relative to the Fermi level varies by almost precisely the difference of the work functions of the two substrates considered. That is, the difference between the binding energy of the 4*d* level for adsorption on Gd (62.8 eV) and the binding energy of the same level when the atom is adsorbed on Pd (60.5 eV) is equal to the difference of the work func-

tion of Pd (5.5 eV) and that of Gd (3.3 eV) to within a tenth of an eV. The binding energy of the core level relative to vacuum I^V can be obtained by adding the work function to I^F ; this quantity appears in the final column of Table I, and is seen to have a value that is constant to a tenth of an eV, as it must if the discussion above is correct.¹⁰ (A similar table for the 5*p* levels¹¹ is given in Ref. 3.)

¹J. Küppers, K. Wandelt, and G. Ertl, *Phys. Rev. Lett.* **43**, 928 (1979).

²J. Küppers, H. Michel, F. Nitschké, K. Wandelt, and G. Ertl, *Surf. Sci.* **89**, 361 (1979).

³J. Hulse, J. Küppers, K. Wandelt, and G. Ertl, *Appl. Surf. Sci.* **6**, 453 (1980).

⁴K. Wandelt, J. Hulse, and J. Küppers, *Surf. Sci.* **104**, 212 (1981).

⁵The difference in the observed position of a given level in the spectrum for two different types of adsorption site is composed of an initial-state (chemical) contribution and a final-state (relaxation or screening) contribution. Because the metallic screening of the hole on the rare gas is almost entirely imagelike (as seen in Fig. 4 of Ref. 6), any differences among various sites in the screening contribution to the level position will arise only because of a variation in distance between the rare gas and the local image plane. Since we expect such variations to be negligible, a difference in level position will be almost exclusively an initial-state effect.

⁶N. D. Lang, *Phys. Rev. Lett.* **46**, 842 (1981).

⁷These calculations, in which the substrate is simulated by a jellium model with $r_s = 2$ bohrs, are discussed in Ref. 6. The equilibrium distance is taken to be $d = 5$ bohrs as discussed in this paper (with d the separation between adatom nucleus and positive background edge).

⁸N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 225.

⁹The magnitude of the contribution of these forces is not, however, given by integrating V_{xc} with the atom's valence

density over space. It must be evaluated as discussed, e.g., in Ref. 8.

¹⁰Using this technique to determine the differences of the work functions among different single-crystal surfaces constitutes a check of the ideas presented above, because, unlike the work function appropriate to surface imperfections, that of a uniform surface can be measured by other methods. Now we would ideally like to have data for low coverages, in which the level positions for a given rare-gas atom are unaffected by the other adatoms. Unfortunately, island formation often occurs, in which case the adsorption-induced change in the macroscopic substrate work function may be zero at low coverages, while at the same time there is an appreciable shift in the relative positions of the substrate levels and those on a given adatom due to the nearby adsorbed atoms in the island. In this case, the level positions and the work function will no longer track each other. For monolayer coverage, however, the question of whether or not island formation occurs becomes irrelevant, and the chemical (initial-state) shift between the substrate levels and those of a given adatom due to neighboring adatoms can be taken equal in magnitude to the change in the substrate work function ($\Delta\Phi$) due to the adsorbed atoms. Taking these to be equal assumes the atomic states from which electrons are photoemitted to be effectively outside the polarization responsible for the work-function change. While this is approximately true even for valence states, it is a much more justified assumption for core states.

¹¹See also K. Jacobi, Ya-Po Hsu, and H. H. Rotermund, *Surf. Sci.* (in press).