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Effective-medium theory of chemical binding: Application to chemisorption

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An approximate theory of the total energy change connected with the embedding of an atom in an inhomogeneous host is developed. The primary effect of the inhomogeneous environment is included by replacing it with a homogeneous electron gas of a density equal to that of the host at the atom site. The lowest-order corrections to this simple picture are derived. The scheme, which is computationally very simple, is tested against first-principles calculations for several chemisorption systems. It is found that including a simple first-order correction gives excellent agreement for H and O adsorbates. For less electronegative atoms like Si and Li, it seems that a second-order term involving the polarizability of the atom in a homogeneous electron gas must be included.

I. INTRODUCTION

The total energy change connected with, e.g., introducing an impurity in a solid, chemisorbing an atom on a solid surface, or forming a molecule has only been calculated accurately in rather few, simple cases.[1-5] Even with the simplifications offered by the local-density approximation[6] relative to the Hartree-Fock approach, for example, the direct calculation of total energies is very complicated, especially in situations where the symmetry is low. A simple way of determining the energy of a combined system from the properties of the constituents has therefore been an important goal for the theoretical description of such systems.

In the present paper, we present such a scheme for the calculation of the energy change ΔE accompanying the embedding of an atom or a group of atoms in an inhomogeneous host. The basic idea is to approximate ΔE by $\Delta E^{\text{hom}}(\rho_0(\vec{r}))$, the energy of the atom embedded in a homogeneous electron gas of a density equal to that of the host at the atom position, $\rho_0(\vec{r})$. The effect of the true inhomogeneous environment on the atom is thus simulated by that of an effective homogeneous medium. In the simplest formulation, the effect of the host therefore only enters through its electron density distribution, $\rho_0(\vec{r})$, and the atom properties are included through $\Delta E^{\text{hom}}(\rho_0)$ which, owing to the spherical symmetry, is much easier to calculate than ΔE. Furthermore, $\Delta E^{\text{hom}}(\rho_0)$ can be calculated once and for all for each atom. The scheme can be viewed as a local-density approximation for a whole atom. The formal justification for the method will be described in Sec. II, and the leading correction terms will be found.

We will concentrate in the present paper on chemisorption systems. Apart from being interesting in themselves, they represent a convenient test case where a few first-principles calculations[3,4] exist for comparison. These tests are described in Sec. III. The implications of the theory for the understanding of the chemisorptive bond are discussed. Finally, in Sec. IV, the possibilities of using the method in more complicated situations are considered, as well as the limitations of the method.

II. THE EFFECTIVE-MEDIUM APPROXIMATION

In connection with a study of the properties of hydrogen impurities in simple metals, Nørskov[7] found that the electronic structure and total energy of hydrogen impurities depends primarily on the local environment. The energy change associated with the embedding of a hydrogen atom in a homogeneous electron gas $\Delta E^{\text{hom}}(\rho_0)$, considered as a function of electron gas density ρ_0, is shown in Fig. 1.[7] Given $\Delta E^{\text{hom}}(\rho_0)$, one can, for instance, determine very accurately the energy of hydrogen in a vacancy simply by reading off the energy in Fig. 1 corresponding to the electron density in the middle of an undisturbed vacancy.[7] This approach was used to obtain the energy of hydrogen in a vacancy as a function of the distance from the vacancy center.[2] The same type of approach has been successfully used to obtain the binding energy of H_2 outside a metal surface based on far simpler calculations for H_2 embedded in homogeneous electron gases of different densities.[8] Stott and Zaremba[9] have developed the idea as a way of obtaining binding energies of atoms in any inhomogeneous electron system and have, for instance, applied it to diatomic hydride molecules. They also derive the leading corrections to the simple picture outlined above.[9] In the following, we will give a short derivation of these corrections in a way somewhat different from that of Stott and Zaremba.[9]

We are looking for the binding energy ΔE of

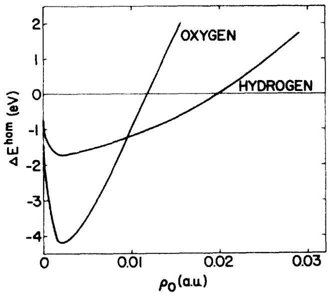

FIG. 1. Energy ΔE^{hom} of hydrogen and oxygen embedded in infinite jellium as a function of jellium density ρ_0. The energy zero is the energy of the free atom. Calculations (non-spin-polarized) were done for densities down to 0.001 a.u., after which each curve was joined to a point at zero density corresponding to the negative of the measured electron affinity of the free atom.

an atom (or cluster of atoms) embedded in an inhomogeneous electron system of density $\rho_0(\vec{r})$ (e.g., the bare surface electron density). Since we want to express ΔE in terms of the binding energy of the atom in a homogeneous system, consider as a starting point an atom embedded in a homogeneous electron gas with a uniform positive background to ensure charge neutrality (infinite jellium). The electron gas (or background) density will be denoted $\bar{\rho}_0$, in order to indicate that we will in fact choose it as some average of the inhomogeneous electron density $\rho_0(\vec{r})$ over the atom. The energy of the atom-plus-jellium minus the energies of the bare jellium and the free atom is $\Delta E^{\mathrm{hom}}(\bar{\rho}_0)$. The electron density of the atom-plus-jellium system is denoted $\rho(\vec{r})$, so that the atom-induced density in jellium is $\Delta\rho(\vec{r}) = \rho(\vec{r}) - \bar{\rho}_0$. We now introduce an external perturbation $\delta v(\vec{r})$ which changes the homogeneous electron density $\bar{\rho}_0$ to that of the inhomogeneous system: $\rho_0(\vec{r}) = \bar{\rho}_0 + \delta\rho_0(\vec{r})$. In the case of, e.g., a surface calculation, $\delta v(\vec{r})$ will be the difference between the potential due to the positive background of infinite jellium and the potential due to the ion cores of the bounded substrate. We also introduce the change in atom-induced density $\delta\Delta\rho(\vec{r}) = \delta\rho(\vec{r}) - \delta\rho_0(\vec{r})$. Atom-induced changes are thus denoted by Δ, while the perturbation-induced changes are denoted by δ. To second order in δv, the change in $\Delta E^{\mathrm{hom}}(\bar{\rho}_0)$ will be[10]

$$\delta\Delta E = \int [\Delta\rho(\vec{r}) - Z\delta(\vec{r})]\delta v(\vec{r})d\vec{r} + \frac{1}{2}\int \delta\Delta\rho(\vec{r})\delta v(\vec{r})d\vec{r}\,. \tag{1}$$

The atom is taken to have charge Z and to be situated at $\vec{r} = 0$. In most cases of interest, $\delta v(\vec{r})$ itself is a large perturbation, but all that is needed for the second-order expression to hold is that the perturbation does not vary too strongly over the size of the atom [as defined by $\Delta\rho(\vec{r})$ or $\delta\Delta\rho(\vec{r})$].

If we choose the average density $\bar{\rho}_0$ such that[11]

$$\int \Delta\phi(\vec{r})\delta\rho_0(\vec{r})d\vec{r} = \int \Delta\phi(\vec{r})[\rho_0(\vec{r}) - \bar{\rho}_0]d\vec{r} = 0\,,$$

where $\Delta\phi(\vec{r}) = \int [\Delta\rho(\vec{r}\,') - Z\delta(\vec{r}\,')]|\vec{r} - \vec{r}\,'|^{-1}d\vec{r}\,'$ is the atom-induced electrostatic potential in the homogeneous jellium, we can express the first-order term in Eq. (1) in terms of the change in total electrostatic potential $\delta\phi_0(\vec{r}) = \delta v(\vec{r}) + \int \delta\rho_0(\vec{r}\,')|\vec{r} - \vec{r}\,'|^{-1}d\vec{r}\,'$ instead of $\delta v(\vec{r})$ alone:

$$\delta\Delta E^{(1)} = \int [\Delta\rho(\vec{r}) - Z\delta(\vec{r})]\delta\phi_0(\vec{r})d\vec{r}\,. \tag{2}$$

The second-order term can be written

$$\delta\Delta E^{(2)} = \frac{1}{2}\int \delta\Delta\rho(\vec{r})\delta\phi_0(\vec{r})d\vec{r} - \frac{1}{2}\int \delta\Delta\phi(\vec{r})\delta\rho_0(\vec{r})d\vec{r}\,. \tag{3}$$

Defining the response functions R and R' by

$$\begin{aligned} \delta\Delta\rho(\vec{r}) &= \int R(\vec{r}, \vec{r}\,')\delta\rho_0(\vec{r}\,')d\vec{r}\,', \\ \delta\Delta\phi(\vec{r}) &= \int R'(\vec{r}, \vec{r}\,')\delta\phi_0(\vec{r}\,')d\vec{r}\,', \end{aligned} \tag{4}$$

we can write Eq. (3) as

$$\delta\Delta E^{(2)} = \frac{1}{2}\int\int [R(\vec{r}, \vec{r}\,') - R'(\vec{r}\,', \vec{r})]\delta\phi_0(\vec{r})\delta\rho_0(\vec{r}\,')d\vec{r}\,d\vec{r}\,'\,. \tag{5}$$

R and R' can be expressed in terms of the static polarizabilities P and P_0 and dielectric functions ϵ and ϵ_0 of the homogeneous electron gas with and without the atom through the formal equations[12]

$$\begin{aligned} R &= (P\epsilon^{-1} - P_0\epsilon_0^{-1})(P_0\epsilon_0^{-1})^{-1}, \\ R' &= (\epsilon^{-1} - \epsilon_0^{-1})\epsilon_0, \\ R - R' &= (P - P_0)\epsilon^{-1}(P_0\epsilon_0^{-1})^{-1}. \end{aligned} \tag{6}$$

R, R', and $R - R'$ are obviously connected with the relative strength of the response of the atom embedded in a homogeneous system. This will depend on the detailed atom-induced electronic structure. Since the usual second-order expression for a response function such as P involves a sum of the inverse excitation energies of the system,[12] the existence of a resonance in the atom-induced density of states close to the Fermi level will make the second-order term large. If, on the other hand, there are no atom-induced states near the Fermi level, we expect this term to be small.

From the above, we extract the following set of rules for obtaining approximately the energy ΔE of an atom in an inhomogeneous electron system whose electron density in the absence of the atom is $\rho_0(\vec{r})$:

(1) Choose an average density $\bar{\rho}_0$ such that

$$\int \Delta\phi(\vec{r})\delta\rho_0(\vec{r})d\vec{r} \equiv \int \Delta\phi(\vec{r})[\rho_0(\vec{r})-\bar{\rho}_0]d\vec{r}=0\,, \qquad (7)$$

where $\Delta\phi(\vec{r})$ is the atom-induced electrostatic potential in the homogeneous electron gas of the density $\bar{\rho}_0$.[13]

(2) Then the zeroth-order contribution to $\Delta E[\rho_0]$ is

$$\Delta E^{(0)} = \Delta E^{\mathrm{hom}}(\bar{\rho}_0)\,. \qquad (8)$$

(3) The first-order correction to this is

$$\Delta E^{(1)} = \int [\Delta\rho(\vec{r}) - Z\delta(\vec{r})]\phi_0(\vec{r})d\vec{r}\,, \qquad (9)$$

where $\phi_0(\vec{r})$ is the substrate electrostatic potential and $\Delta\rho(\vec{r})$ is the atom-induced density in the homogeneous electron gas of density $\bar{\rho}_0$. (Note that $\delta\phi_0=\phi_0$ because the electrostatic potential for a homogeneous electron gas is a constant which is taken to be zero.)

(4) The second-order correction is given by

$$\Delta E^{(2)} = \frac{1}{2}\int\int [R(\vec{r},\vec{r}\,') - R'(\vec{r}\,',\vec{r})]\phi_0(\vec{r})\delta\rho_0(\vec{r}\,')d\vec{r}\,d\vec{r}\,'\,, \qquad (10)$$

where again $\delta\rho_0(\vec{r})$ is the deviation of the substrate density $\rho_0(\vec{r})$ from $\bar{\rho}_0$.

It is thus seen that $\Delta E[\rho_0]$ can be obtained to second order in the deviations of $\rho_0(\vec{r})$ from its averaged value from only a knowledge of the substrate density $\rho_0(\vec{r})$ and electrostatic potential $\phi_0(\vec{r})$, and the energy $\Delta E^{\mathrm{hom}}(\bar{\rho}_0)$, induced density $\Delta\rho(\vec{r})$, and response functions R and R' of the atom in a homogeneous electron gas. From Eq. (7) we see that the atom samples the surroundings over a volume determined by $\Delta\phi(\vec{r})$, which is very localized.

III. APPLICATION TO CHEMISORPTION SYSTEMS

The scheme suggested in Sec. II is only formally justified in cases where the substrate electron density and electrostatic potential do not vary too strongly over a typical atomic volume. The question is whether the density variations at a metal surface are too rapid for the approximation to work for chemisorption energies. To test this, we apply the scheme to a number of cases of light-atom chemisorption on jellium surfaces. To make a jellium surface, one half-space of the uniform positive background, which plays the role of the metal ions of a real metal, is cut away.[10] This model for the substrate is chosen simply because first-principles calculations exist for these chemisorption systems.[3,4] In making these comparisons we will be working within the local-density approximation of Kohn and Sham.[6]

In Fig. 2, the first-principles results of Hjelmberg[4] for the chemisorption energy $\Delta E(d)$ of hydrogen as a function of distance d outside the positive background edge is compared[14] to the zeroth-order approximation $\Delta E^{\mathrm{hom}}(\bar{\rho}_0(d))$ for two different substrate densities. It is seen that the zeroth-order approximation reproduces the true equilibrium binding energies within a few tenths of an eV. Figure 2 also illustrates the fact that the distance at which the substrate electron density $\rho_0(d)$ is around 0.002 a.u., where $\Delta E^{\mathrm{hom}}(\rho_0)$ has its minimum (see Fig. 1), is clearly correlated with the equilibrium distance d_{eq}. This means that on a high-density substrate, d_{eq} is larger than on a lower-density substrate. For very low substrate densities (bulk density 0.0039 a.u., corresponding to Na) virtually no minimum

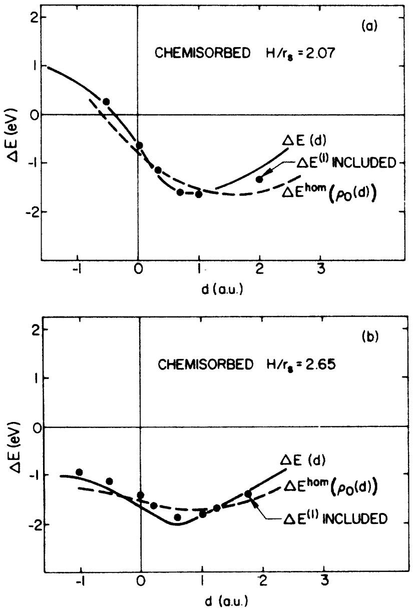

FIG. 2. Chemisorption energy of hydrogen on jellium surfaces as a function of distance d outside the jellium background edge. Full curves are first-principles results (Ref. 4), dashed curves give the zeroth-order approximation, and dots give the first-order approximation. (a) High-density substrate ($r_s=2.07$ corresponding to Al), (b) intermediate-density substrate ($r_s=2.65$ corresponding to Mg). The density parameter r_s is defined in terms of the bulk substrate density $\rho_0(-\infty)$ through $1/\rho_0(-\infty)=\frac{4}{3}\pi r_s^3$.

in $\Delta E(d)$ is seen in the first-principles results,[4] as one would expect from Fig. 1.

The zeroth-order result is seen generally to be too low at large d [small $\rho_0(d)$]. This is because $\Delta E^{\mathrm{hom}}(\rho_0(d))$ goes to a limit other than $\Delta E(d)$ as d becomes large. Because the atomic affinity A_{H} of hydrogen is smaller than metallic work functions, hydrogen goes towards the limit of a neutral atom when it is moved away from a surface. $\Delta E(d)$, which in Fig. 2 is shown relative to the energy of a free atom, therefore goes to zero. $\Delta E^{\mathrm{hom}}(\rho_0)$, on the other hand, goes to $-A_{\mathrm{H}}$ when ρ_0 goes to zero, as indicated in Fig. 1. This is because as ρ_0 of the infinite jellium goes to zero, the chemical potential also goes to zero, making the filling of the hydrogen affinity level energetically favorable.[7] The $d\rightarrow\infty$ limit of $\Delta E^{\mathrm{hom}}(\rho_0(d))$ is therefore $-A_{\mathrm{H}}$. The problem noted here only arises at rather large d, well away from d_{eq}.

In Fig. 1, $\Delta E^{\mathrm{hom}}(\rho_0)$ is also shown for oxygen.[15] The general shape of the curve is quite like that for hydrogen. These curves are conveniently discussed in terms of their slope $d\Delta E^{\mathrm{hom}}(\rho_0)/d\rho_0$. As shown by Stott and Zaremba,[9] it is easily seen from Eq. (1) that if we consider a perturbation representing an overall change of the jellium density, then to first order

$$\delta\Delta E = -\int \Delta\phi(\vec{r})\delta\rho_0(\vec{r})d\vec{r},$$

giving

$$\frac{d\Delta E^{\mathrm{hom}}}{d\rho_0} = -\int \Delta\phi(\vec{r})d\vec{r}. \qquad (11)$$

For a free negative ion, the integral (11) diverges. This means that for atoms like H and O where the $\rho_0 = 0$ limit is a negative ion, the initial slope of the ΔE^{hom} curve will be $-\infty$. As the negative ion is screened out more efficiently at higher ρ_0, the slope increases, passes zero around the lowest metallic densities ($\rho_0 \simeq 0.002$ a.u.), and reaches an almost constant positive value. This accounts for the existence of the minimum in $\Delta E^{\mathrm{hom}}(\rho_0)$ for these atoms. For an atom such as He, where no negative ion exists, there is no minimum[7] in $\Delta E^{\mathrm{hom}}(\rho_0)$.

The zeroth-order approximation $\Delta E^{\mathrm{hom}}(\bar{\rho}_0(d))$ for the binding energy of oxygen outside a high- and a low-density jellium surface is compared with the first-principles results of Lang and Williams[3] in Fig. 3. Again agreement is seen so far as the general characteristics of the curves are concerned. For the high-density substrate, a minimum exists at about 1 a.u. outside the surface, while oxygen tends to penetrate the low-density surface, because the bulk density of the latter substrate is close to the position of the minimum in the $\Delta E^{\mathrm{hom}}(\bar{\rho}_0)$ curve of Fig. 1. The absolute errors are greater, though, than in the hydrogen case. Also the fine structure of the low-density curve is not described.

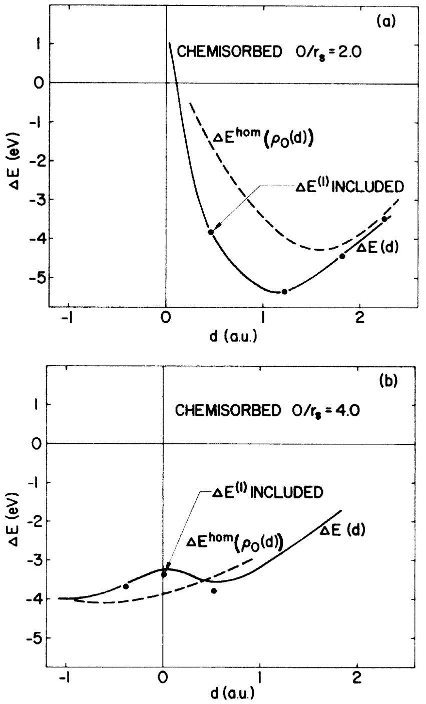

FIG. 3. Chemisorption energy of oxygen on jellium surfaces as a function of distance d outside the jellium background edge. Full curves are first-principles results (Ref. 3), dashed curves give the zeroth-order approximation, and dots give the first-order approximation. (a) High-density substrate ($r_s = 2$ corresponding approximately to Al), (b) low-density substrate ($r_s = 4$ corresponding approximately to Na).

Including the first-order correction (9) significantly improves the agreement. In Fig. 3 the dots indicate the values of $\Delta E^{\mathrm{hom}}(\bar{\rho}_0(d)) + \Delta E^{(1)}(d)$. It is seen that now only a small discrepancy persists at the lowest substrate densities [Fig. 3(b)]. This is probably again connected with the fact that $\Delta E^{\mathrm{hom}}(\rho_0)$ goes to the ionic instead of the atomic limit when ρ_0 goes to zero. The effect of $\Delta E^{(1)}$ is mainly to lower the energy just outside the surface and increase it just inside. This can be understood in the following way. Since the density distribution $[\Delta\rho(\vec{r}) - Z\delta(\vec{r}-\vec{d})]$ is spherically symmetric, $\Delta E^{(1)}$ can be written approximately as[3]

$$\begin{aligned}\Delta E^{(1)}(d) &= \int [\Delta\rho(\vec{r}) - Z\delta(\vec{r}-\vec{d})]\phi_0(\vec{r})d\vec{r} \\ &\sim \phi_0(d+a) + \phi_0(d-a) - 2\phi_0(d) \\ &\simeq a^2 \left.\frac{d^2\phi_0(z)}{dz^2}\right|_{z=d},\end{aligned} \qquad (12)$$

where a is the characteristic size of the adatom. Therefore $\Delta E^{(1)}$ is negative just outside the surface where the curvature of ϕ_0 is negative, changes sign around the inflection point at $d=0$, and becomes positive at smaller d.

The success of the first-order approximation suggests that the second-order contribution is small for oxygen. This seems to be a very reasonable assumption in view of the fact that the oxygen is completely ionic in homogeneous electron gases of the densities $\bar{\rho}_0(d)$ considered here. This means that the oxygen $2p$ resonance is well below the Fermi level, and thus the response functions of Eqs. (4) and (6) will be small. One further indication that this is true comes from the finding that using the $\Delta\rho(\vec{r})$ of the first-principles surface calculation instead of the infinite jellium $\Delta\rho(\vec{r})$ in the calculation of $\Delta E^{(1)}$ only changes the values insignificantly.

For hydrogen we also expect the second-order term to be small since the hydrogen-induced state is well below the Fermi level,[7] as it is for oxygen. This is again reflected in the good agreement shown in Fig. 2 between the first-order approximation[16] $\Delta E^{\text{hom}}(\bar{\rho}_0(d))+\Delta E^{(1)}(d)$ and the first-principles result.

The success of the simple first-order theory for oxygen and hydrogen chemisorption has also some bearing on the understanding of the chemisorption bond for these adsorbates. It means that the bond should not be discussed in terms of covalency or related concepts which concentrate on the buildup of charge in the region between the adsorbate and the substrate. Because most of the binding stems from ΔE^{hom}, the discussion of ΔE^{hom} vs ρ_0 above suggests that the binding should rather be attributed to the tendency of these atoms to form negative ions.

The validity of the first-order approximation has also been tested for silicon and lithium adsorbates.[15] In these cases the agreement was not as good as for oxygen and hydrogen. This must mean that the second- (and perhaps higher-) order terms are important for these atoms. This can be understood from the electronic structure of the atoms in jellium. At a typical jellium density, both the hydrogen- and oxygen-induced resonances are well below the Fermi level, as mentioned above. The silicon resonance is situated further up and the lithium $2s$ resonance is right at the Fermi level. According to the discussion in Sec. II, this means that the response functions and therefore the second-order terms should be larger for silicon and lithium than for the other two atoms. The ordering of the atom-induced resonances is obviously connected to the tendency of the atoms involved to form a closed-shell configuration. It should be mentioned that at low jellium densities, the hydrogen and oxygen states also come close to the Fermi level. These densities, however, correspond to distances from the surface outside the range we are considering here.

IV. CONCLUSIONS

We have developed a theory for the interaction of an atom or cluster of atoms with an inhomogeneous electron system according to which the true inhomogeneous host can be replaced by an effective homogeneous environment for which calculations are much simpler. For host densities that do not vary too strongly over the spatial extent of the atom, the interaction energy is shown to be obtainable from the density and electrostatic potential of the host and properties of the atom embedded in a homogeneous electron gas (energy, atom-induced density, and polarizability).

The scheme has been tested for light atoms outside jellium, where first-principles calculations exist for comparison. For the electronegative adsorbates hydrogen and oxygen, a simple first-order approximation not involving the polarizability gives results in excellent agreement with the first-principles calculations. For adsorbates such as silicon and lithium, it appeared that the second-order term, which takes the nonspherical deformation of the adsorbate into account, must be included. Since the generalized polarizability of an atom embedded in a homogeneous electron gas has not been calculated at present, this term is much harder to handle. The immediate usefulness of the scheme is thus limited to adsorbates like hydrogen and oxygen that are not particularly polarizable.

The density variation at a jellium surface is typical of at least simple-metal surfaces. The method can therefore be expected to work as well for such surfaces as it does in Figs. 2 and 3. Whether the d electrons at transition-metal surfaces introduce density variations that are too large for the simple theory to work remains to be seen. The simplicity of the scheme does, however, make it appealing even if the quantitative agreement is not as good as in the cases tested in this paper. Again the inclusion of the second-order term would improve the agreement.

Finally, we point out that, although the application above to the case of chemisorption has been based on the local-density approximation,[6] the scheme is completely independent of the approximations used in the actual calculation of the energies involved.

ACKNOWLEDGMENTS

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[13] This means that Eq. (7) should be solved iteratively (self-consistently) for $\bar{\rho}_0$. In practice, $\bar{\rho}_0$ does not depend strongly on $\Delta\phi$, and the $\Delta\phi(\vec{r})$ corresponding to the value of $\bar{\rho}_0(\vec{r})$ at the position of the atomic nucleus can be used in most cases. The exception to this is the instance in which $\int \Delta\phi(\vec{r})\,d\vec{r}$ is close to zero; it is then necessary to solve Eq. (7) self-consistently.

[14] In both Figs. 2 and 3, $\rho_0(d)$ has been used instead of the averaged $\bar{\rho}_0(d)$ in calculating $\Delta E^{\mathrm{hom}}(\bar{\rho}_0(d))$. Tests have shown that at least for H and O outside a jellium surface, this makes no difference. In other cases where the curvature of $\rho_0(\vec{r})$ is larger, this may not be the case. $\Delta E^{\mathrm{hom}}(\rho_0)$ has been taken from Ref. 7.

[15] The calculations for oxygen, lithium, and silicon in jellium are done using the chemisorption calculation method described in Ref. 3, with the atom put far inside the surface.

[16] The correction $\Delta E^{(1)}$ is here calculated using the $\Delta\rho$ of the full surface calculation since these numbers were readily available (H. Hjelmberg, private communication). In view of the experience with the oxygen corrections, this should not make any difference.