

Bimetallic interface: A periodic planar jellium approach

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The problem of the bimetallic interface is studied within the periodic planar jellium (PPJ) approximation. According to the PPJ approach, the positive charge of the crystal is considered uniformly distributed on the lattice planes parallel to the interface. As a result, the PPJ method, while it retains the simplicity of the one-dimensional character of the jellium approximation, additionally incorporates explicitly within a self-consistent calculational scheme effects due to crystal anisotropies and zeroth-order band-structure effects. These characteristics make the proposed method suitable for various applications to bimetallic systems that cannot be studied either within the jellium approximation or by an *ab initio* calculation. The general applicability of the method as well as the major differences between the results of the proposed PPJ method and the results of the ordinary jellium model are demonstrated by the presentation of results obtained by applying the PPJ method to the bimetallic system Na(001)/K(001).

Although the problem of the metal surface has been extensively and systematically studied within various approximations, the problem of the bimetallic interface has not been given analogous interest. The lack of the periodicity along the direction perpendicular to the interface, and the breaking off, of the two-dimensional periodicity along planes parallel to the interface, have limited the studies of the bimetallic interface to those described mostly within the jellium model.

Within the jellium approximation, Bennett and Duke¹ have developed a formalism that has been recently used and extended by Ferrante and Smith² who obtained a self-consistent solution for bimetallic systems. Self-consistent solutions of bimetallic systems beyond the jellium-model approximation have not, to the best of our knowledge, yet been presented. However, the embedding approach of Inglesfield³ and the real-space multiple-scattering approach of Zhang and Gonis⁴ indicate promising ways for attacking the problem of the bimetallic interface.

In the present paper, we will present a model description of the bimetallic system which goes beyond the jellium approximation and incorporates explicitly the interface anisotropy as well as zeroth-order band-structure effects.

In particular our model approximation is based on the "periodic planar jellium" (PPJ) model that was first introduced⁵ in order to study the metal-vacuum interface in a way that can explicitly include the surface anisotropy within a self-consistent calculational scheme. According to the PPJ model, the positive charge of the ions of a semi-infinite metal is distributed uniformly along the lattice planes which are parallel to the metal surface. Assuming that the semi-infinite metal has a Bravais lattice and exhibits a specified $\langle hkl \rangle$ orientation, the positive charge density on the (hkl) planes (which are parallel to the surface) can be completely determined by knowing the type of the metal and its crystal orientation $\langle hkl \rangle$. For this model description, periodicity is retained in the bulk crystal along the (hkl) axis, which is perpendicular

to the surface, which is assigned to the z axis of the system. Thus although this model is one dimensional, surface anisotropy and band-structure effects [associated with the bulk crystal periodicity along the (hkl) axis] are explicitly included in the proposed description.

Within the PPJ approximation the solution of the Schrödinger equation goes along the following self-consistent calculational scheme: First Poisson's equation is solved^{5,6} for the periodic planar positive charge distribution and an assumed electron density $\rho(z)$ that satisfies an overall charge neutrality. The Ashcroft local pseudopotential⁷ is used to describe the ion-electron interaction and its core radius parameter for the ions of the metal are among the inputs of the problem. The Coulomb (pseudo)potential, $V_{Cb}(z)$, obtained from the solution of Poisson's equation, is added to the exchange and correlation potential $V_{xc}(z)$ obtained within the local electron density approximation (LDA) and Wigner's formula for the exchange and correlation energy per electron. The so-obtained single electron potential, $V_{eff}(z)$,

$$V_{eff}(z) = V_{Cb}(z) + V_{xc}(z), \quad (1)$$

is inserted into the Schrödinger equation (atomic units are used)

$$-\frac{1}{2} \frac{d^2 \xi_E}{dz^2} + V_{eff}(z) \xi_E(z) = E \xi_E \quad (2)$$

which is solved self-consistently by a wave-function-matching technique (described elsewhere⁵) from which the wave function $\xi_E(z)$ and the corresponding eigenvalues E are determined.

The PPJ approach to the semi-infinite metals described above is now applied in the case of a bimetallic system which is specified by giving the types of its left and right metal constituents, their separation as well as their orientation $\langle hkl \rangle$ and $\langle h'k'l' \rangle$, with respect to their interface. Assuming that both the metal constituents of the bimetallic system possess a Bravais lattice, the bimetallic

system exhibits the picture shown in Fig. 1 when approximated with the PPJ approximation. The orientations $\langle hkl \rangle$ and $\langle h'k'l' \rangle$ specify the periodicity in the left and right bulk parts of the system as well as the density of the positive charge on the (hkl) and $(h'k'l')$ lattice planes of the left and right metal, respectively. The interface region is assumed to be extended a few lattice constants from the interface plane towards each metal constituent. The interface region may exhibit interface relaxation effects, interface defects, etc. However such considerations will not be discussed in the present work for which it will be assumed that the bulk periodicities are extended up to the interface plane.

From Fig. 1 it becomes clear that the bimetallic system exhibits three physically different regions: the left bulk, the interface, and the right bulk. In each of these regions Schrödinger's equation, Eq. (2), is solved separately after having solved Poisson's equation and having calculated $V_{\text{eff}}(z)$ for the whole system.

The solution of Poisson's equation is a major step in the present methodology and according to our solution it is based on the knowledge of the electron density profiles $\rho_L(z)$ and $\rho_R(z)$ of the semi-infinite metals each of which is, respectively, the left and the right metal constituent of the bimetallic system. The electron densities $\rho_L(z)$ and $\rho_R(z)$ need not be the self-consistent solutions of the corresponding semi-infinite metals. However, they have to be chosen in such a way so that they can neutralize the positive charges of the left and right metal constituents, respectively. On the other hand, if, as in the present case, $\rho_L(z)$ and $\rho_R(z)$ are taken to be the self-consistently obtained densities of the corresponding semi-infinite metals that constitute the bimetallic system, one can make use of the assumption that to the left of $z=z_L$ and to the right of $z=z_R$ the electron density $\rho(z)$ of the bimetal is identical to $\rho_L(z)$ and $\rho_R(z)$, respectively. This observation allows us to restrict our self-consistent solution only within the interface region with the result that the self-consistent solution of the bimetallic system is greatly facilitated.

Having obtained the single-electron potential $V_{\text{eff}}^{(S)}(z)$,

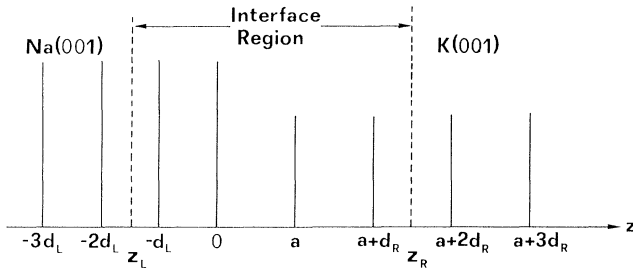


FIG. 1. The positive charge distribution of the bimetal Na(001)/K(001) as approximated within the periodic planar jellium model. On the (001) lattice planes of Na and K, the positive charge density is $2\pi/\alpha_{\text{Na}}$ and $2\pi/\alpha_{\text{K}}$, respectively, where α_i , $i = \text{Na, K}$ are the areas of the unit cells of the (001) planes of Na and K. The interplane distance is d_L and d_R for Na and K, respectively, and the distance a between the first Na plane and the first K plane is taken equal to $a = 0.5(d_L + d_R)$.

in the interface region we make sure that this matches the $V_{\text{eff}}^{(L)}(z)$ and $V_{\text{eff}}^{(R)}(z)$ in the left and right bulk regions, respectively. The matching between $V_{\text{eff}}^{(S)}(z)$ and $V_{\text{eff}}^{(L)}(z)$ at the interface boundary at $z=z_L$ can be obtained directly by considering the interface region as an extension of the left bulk region. However the matching between $V_{\text{eff}}^{(S)}(z)$ and $V_{\text{eff}}^{(R)}(z)$ at the interface boundary at $z=z_R$ is initially obtained by shifting $V_{\text{eff}}^{(R)}(z)$ by a constant value so that the Fermi energies in the two bulk regions are equated. Such correcting potential shifts appear to be necessary in every iteration towards self-consistency although their value gets smaller and smaller as self-consistency is achieved.

After having constructed $V_{\text{eff}}(z)$ for the whole system we solve Schrödinger's equation (2) in three different regions. The solutions in the bulk are expressed by the propagation matrix $P_E^{(i)}(z)$, $i = L, R$ and the eigenvectors $\mathbf{Q}_E^{(i)}$ of the propagation matrices $P_E(d_i)$ calculated at $z=d_i$, $i = L, R$, the corresponding periods along the z axis within each bulk region,^{8,5} i.e.,

$$\xi_E^{(j)}(z) = A_E^{(j)} P_E^{(j)}(z) \mathbf{Q}_E^{(j)} \begin{bmatrix} i \sin \varphi_E^{(j)} \\ \cos \varphi_E^{(j)} \end{bmatrix}, \quad j = L, R, \quad (3)$$

where $A^{(i)}$, $\varphi^{(i)}$, $i = L, R$ are constants of integration. The vector $\xi_E^{(i)}(z)$, $i = L, R$, is a two-component vector whose first component refers to the eigenfunction $\xi_E^{(i)}(z)$ and its second component refers to the derivative $\partial \xi_E^{(i)}(z) / \partial z$. The propagation matrices $P_E^{(j)}(z)$, $j = L, R$, are (2×2) matrices obtained under the boundary condition $P_E^{(j)}(0) = 1$, $j = L, R$. The solution in the interface region takes the form

$$\xi_E^{(S)}(z) = P^{(S)}(z) \mathbf{a}, \quad (4)$$

where \mathbf{a} is the two-component vector whose components are the two constants of integration. Continuum normalization applied to $\xi_E^{(i)}$, $i = L, R$, consistent with the average electron densities in the bulk, allows us to determine the ratio $A_E^{(L)} / A_E^{(R)}$. Then, the matching of the wave functions at the interface boundaries at z_L and z_R allows us to determine the other four constants of integration. In particular the matching procedure reduces to the following matrix equation for the constants $\varphi_E^{(L)}$ and $\varphi_E^{(R)}$:

$$\mathbf{M} \begin{bmatrix} \sin \varphi_E^{(L)} \\ \cos \varphi_E^{(L)} \end{bmatrix} = \begin{bmatrix} \sin \varphi_E^{(R)} \\ \cos \varphi_E^{(R)} \end{bmatrix}. \quad (5)$$

The matrix \mathbf{M} is given in terms of the known ratio $A_E^{(L)} / A_E^{(R)}$, the matrices $P_E^{(L)}(z_L)$, $P_E^{(R)}(z_R)$, $P_E^{(S)}(z_L)$, $P_E^{(S)}(z_R)$, and the vectors $\mathbf{Q}_E^{(L)}$ and $\mathbf{Q}_E^{(R)}$. Equation (5) is then reduced to an algebraic quadratic equation in either $\sin^2 \varphi_E^{(L)}$ or $\sin^2 \varphi_E^{(R)}$ from which both $\varphi_E^{(L)}$ and $\varphi_E^{(R)}$ are obtained.

The determination of the wave functions leads to a new electron density function $\rho(z)$ obtained from the equation

$$\rho(z) = \frac{2}{\pi^2} \int_0^{E_F} dE (E_F - E) \frac{|\xi_E(z)|^2}{\sqrt{2E}}, \quad (6)$$

where E_F is the Fermi energy of the system.

The next step is to use the calculated new electron den-

sity and obtain a new single electron potential $V_{\text{eff}}(z)$ according to the process described above. The new $V_{\text{eff}}(z)$ replaces the old one in the Schrödinger equation (2) and the described calculational process is repeated until self-consistency is achieved. Our criteria for self-consistency refer to the changes in the average values of the bulk electron densities, the potential misfit constant between the interface and the right bulk regions, and the charge neutrality of the interface region. When these criteria satisfy our numerical tolerances for these quantities, the self-consistent process is terminated.

We have applied the presented method to the bimetallic system Na(001)/K(001), in other words, to the bimetal that has as left metal constituent the Na metal with its (001) lattice plane parallel to the interface and as right metal constituent the K metal with its (001) lattice plane parallel to the interface. In Fig. 2 the self-consistently obtained single electron potential $V_{\text{eff}}(z)$ is shown. In Fig. 3 we present the self-consistently obtained electron density $\rho(z)$ (solid curve) which is compared with the electron density, $\rho_0(z)$, resulting from the superposition of the self-consistently obtained densities of the Na(001) and the K(001) semi-infinite metals (dashed curve). The distance between the first Na-(001) lattice plane from the first K-(001) lattice plane is taken equal to $\alpha = 0.5(d_L + d_R)$.

In our calculations it has been found that the initial iterations towards self-consistency are very unstable. In every iteration we had to check upon the charge neutrality of the interface region and restore it if necessary by adding and/or subtracting a charge distribution described by three diffuse Gaussians arbitrarily located in the interface region. Also we found it necessary to use the mixing of the input ρ_{in} and output ρ_{out} electron densities at every iteration, i.e.,

$$\rho_{\text{in}}^{(i)}(z) = \alpha \rho_{\text{in}}^{(i-1)} + (1 - \alpha) \rho_{\text{out}}^{(i-1)}, \quad (7)$$

where i refers to the iteration number and α to the mixing constant; the latter had to be taken as large as 0.95. Our numerical tolerances were as follows: The misfit potential constants were kept smaller than 1 mRy and the charge neutrality in the interface region close to 1%.

Our results shown in Figs. 2 and 3 indicate that contrary to the jellium model results,² the bimetal electron density $\rho(z)$ exhibits significant differences as compared with $\rho_0(z)$ which is obtained by superimposing the self-consistently obtained electron densities of the semi-infinite metals that constitute the bimetal. Besides the new shoulder that $\rho(z)$ exhibits in the interface region between the Na-(001) and the K-(001) lattice planes two other major differences between $\rho(z)$ and $\rho_0(z)$ are apparent in Fig. 3. First, it is clear that the Friedel oscillations tend to reduce in size on both sides of the interface. Second, it is observed that the electron charge associated with the Friedel oscillations in the semi-infinite metals Na(001) and K(001) is concentrated in the interface region and preferably to the K side in the case of the bimetal. This significant result, shown in more detail in Fig. 4, is opposite to the expected result following from the statement that in a bimetal interface charge transfer will

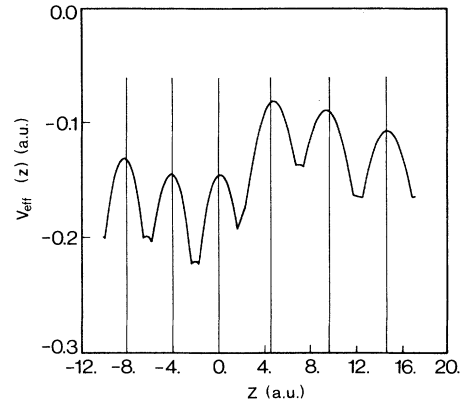


FIG. 2. Self-consistently obtained single electron potential $V_{\text{eff}}(z)$ for the system Na(001)/K(001) approximated within the periodic planar jellium model as shown in Fig. 1. The vertical lines indicate the position of the lattice planes as in Fig. 1. Its wavy form and the elevated shoulder in the interface point out its significant differences from the results of the jellium approach.

take place from the metal of lower work function (K) towards the metal of the higher work function (Na). This statement is not true in general as the electrostatic surface dipole moments which contribute to the work function of each metal should not be considered in the dynamics of the interface problem. Instead, as Bennett and Duke¹ observe, the quantities that govern charge transfer in a bimetallic interface are the bulk "separation energies," i.e., the quantity $S^{(i)} = \langle V_{\text{eff}}^{(i)}(z) \rangle + \frac{1}{2}(k_F^{(i)})^2$, $i = L, R$, of each metal. As our quantitative analysis indicates, for the bimetal Na(001)/K(001), $S^{(\text{K})} - S^{(\text{Na})} < 0$ and correctly our calculation indicates a charge transfer from Na to

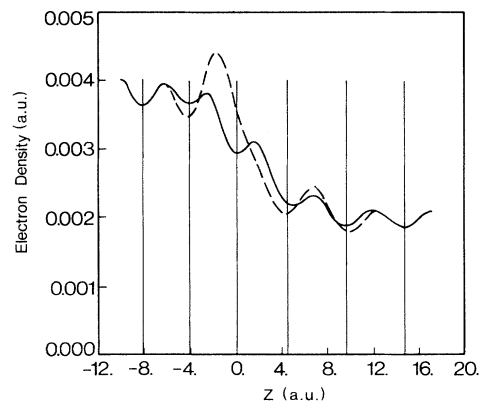


FIG. 3. Self-consistently obtained electron charge density $\rho(z)$ for the system Na(001)/K(001) approximated within the periodic planar jellium model as shown in Fig. 1 (solid curve). The dashed curve indicates the density $\rho_0(z)$ obtained by superimposing the self-consistently obtained electron densities of the Na(001) and the K(001) semi-infinite metals. The vertical lines indicate the position of the lattice planes as in Fig. 1.

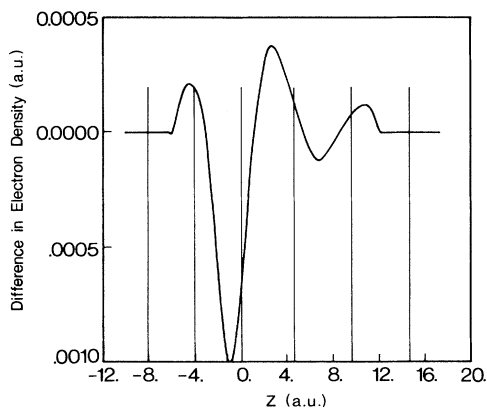


FIG. 4. The difference $\Delta\rho(z)=\rho(z)-\rho_0(z)$ of the electron densities shown in Fig. 3. It exhibits oscillations that tend to reduce in amplitude towards the bulk regions. The values of $\Delta\rho(z)$ at the boundaries of the bulk regions indicate the adequacy of the assumed spatial extent of the interface region.

the K side.

Figure 4 indicates also the adequacy of the assumed spatial extent of our interface region. It is observed that our choice can be considered adequate enough for the assumed separation α of the Na-K crystals because the amplitude of the Friedel oscillations becomes satisfactorily small at the interface boundaries. This appears to be less than 20% of the main difference density peak and less than 5% of the bulk value of the electron density. As much of the transferred charge is concentrated in the Na and K interlayer spaces that are adjacent to the interface region, an increased spatial extent of the interface region is not expected to alter appreciably the present results. On the other hand, if the distance α is allowed to increase, the interface boundary planes that we have chosen

will take the place of the boundary of the surface region of the Na and K semi-infinite crystals, respectively, for which this choice was found to be very satisfactory.

In addition to the possibility of varying the distance α , the present model allows one to study interlayer relaxations and their effect on the charge transfer through the interface (for given separation α). The charge transfer across the interface depends critically on the Coulombic contribution to the bulk "separation energy" which in turn depends on the parameter α and the interlayer relaxations. The latter quantities specify an interface configuration (geometry) whose optimum configuration should be obtained from an energy minimization. In the absence of interlayer relaxation, for example, we expect in terms of the bulk "separation energies," an increase in α to be followed by a gradual reversion of the charge transfer.

It is worth noting that for the system Na(001)/K(001) the conduction bands of both the Na and the K metals are within the first Brillouin zone and no band gaps appear along the $\langle 001 \rangle$ direction for energies within the occupied portion of the conduction band (up to the Fermi level). For some other combinations, like Al(001)/Na(001), this situation is not satisfied and the present approach can be used to study zeroth-order band-structure effects on the electronic structure of the bimetallic interface. It should be also pointed out that within the present method one can study the energies of (interface) crystal defects by considering interfaces between crystals of the same metal, M , but of different orientations, i.e., $M(hkl)/M(h'k'l')$.

In conclusion, we have presented a method to study bimetallic interfaces which is based on the PPJ model description. This approach is the natural zeroth-order approximation of a complete three-dimensional solution⁵ of the semi-infinite metals based on the propagation matrix method^{5,8} and as that it incorporates anisotropy and band-structure effects in a more natural and explicit way.

¹A. J. Bennett and C. B. Duke, Phys. Rev. **160**, 541 (1967); **162**, 578 (1967).

²J. Ferrante and J. R. Smith, Phys. Rev. B **31**, 3427 (1985).

³J. E. Inglesfield, J. Phys. C **14**, 3795 (1981).

⁴X.-G. Zhang and A. Gonis, Phys. Rev. Lett. **62**, 1161 (1989).

⁵A. N. Andriotis Surf. Sci. **116**, 501 (1982); Phys. Rev. B **32**, 5062 (1985).

⁶A. N. Andriotis and C. A. Nicolaides, Surf. Sci. **116**, 513 (1982).

⁷N. W. Ashcroft, Phys. Lett. **23**, 48 (1966).

⁸D. W. Jepsen and P. M. Marcus, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).