Electronic properties of a simple metal-metal interface

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The properties of metal-metal interfaces are of interest in many metallurgical applications. These include grain boundaries, crack growth, friction, and bimetallic adhesion. The present work is a study of the electronic properties of a simple bimetallic junction. The methods employed to investigate the interface are the Green's-function technique and the phase-shift method. We calculate the Green's function of a simple junction within the tight-binding approximation. The conditions for the occurrence of bound states are deduced from the poles of the Green's function. Using the phase-shift method we derive an expression for the change in density of states due to the creation of the interface. From this expression we derive the corresponding single-particle contribution to the interface energy and the interface specific heat.

I. INTRODUCTION

The properties of metal-metal interfaces are of interest in many metallurgical applications. These include, for example, grain boundaries, crack growth, friction, and bimetallic adhesion. The general metal-metal interface is a much more complicated problem than the corresponding metal-vacuum interface. Recently there has been, however, some success in applying certain methods developed for surface phenomena to the investigation of bimetallic interfaces.

The electronic properties of one-dimensional bimetallic junctions were discussed by several authors using various types of models. Aerts[1] studied the electronic structure of a one-dimensional Kronig-Penney model, in the limit of a δ-like potential. In this work, he established the possibility of the existence of bound interface states. A tight-binding approach, which was used successfully for several surface problems, was also applied to the one-dimensional interface. Davison and Cheng[2] investigated the electronic properties of such a system using the molecular-orbital method. The model they use associates a single s-type orbial with each atom. A similar model was studied by Allan and Lannoo,[3] using an approximate, Gaussian density of states, having the correct second moment. Green's-function formalism was used by Foo and Wong[4] to study the interface states of a one-dimension sp-hybrid junction.

As far as we know, the study of three-dimensional bimetallic interfaces was carried out by the density-functional formalism only. This formalism, developed by Hobenberg, Kohn, and Sham,[5,6] was applied recently to bimetallic interfaces by Bennett and Duke,[7,8] Ferrante and Smith,[9,10] Rouhani and Schuttler,[11] and Mehrotra, Pant, and Das.[12]

Whereas the density-functional formalism is applicable mainly to simple metals, the tight-binding approximation is more suitable for the description of transition metals. Since the purpose of the present work is to investigate the electronic structure of a bimetallic junction, formed by two transition metals, we shall use the tight-binding approach. The model we consider is a highly simplified one. The two metals, on each side of the junction, are described by s-type tight-binding Hamiltonians. The interface we consider is formed by bringing together two semi-infinite, simple-cubic crystals, and creating bonds between the atoms on the two sides of the interface. We assume that the two semi-infinite crystals have the same two-dimensional translation symmetry parallel to the interface. The electronic properties of this model are investigated by using the Green's-function method, described in detail by Kalkstein and Soven.[13]

The details of the tight-binding model are outlined in Sec. II. Within this model we allow for a change in the self-consistent potential of the electrons near the interface. The diagonal matrix elements of the Green's function are calculated in Sec. III by considering the formation of the interface as a perturbation on the two semi-infinite crystals. This is accomplished by the use of Dyson's equation. Using the expression for the Green's function, we discuss the electronic structure of the interface in Sec. IV. We show that there are three types of wave functions associated with the interface. The first one extends throughout the entire system, the second type extends on one side of the junction only, and the third, associated with bound states, is localized near the interface. The behavior of the bound states as a function of the coupling constant between the two metals is also discussed. The "phase-shift" method is applied in Sec. V to determine the change in the total density of states due to the creation of the interface. Applying this result, we obtain an expression for the single-particle energy contribution to the interface energy and the corresponding contribution to the electronic specific heat. An application of the model to the interface formed between two transition metals of the same series is presented in Sec. VI, where we calculate numerically the local densities of states, the change in density of states, and the interface energy.

II. MODEL

Consider the formation of a metal-metal interface by bringing together two semi-infinite metallic crystals. As soon as a contact is formed, electrons will flow from the metal having the higher Fermi energy to the one having the lower energy. This flow of electrons stops when the potential-energy difference between the two sides of the junction, which is created by the dipole layer produced at the interface, is equal in magnitude and opposite in sign to the difference between the two Fermi levels. Thus, the Fermi levels of the two metals are aligned, due to the interface dipole layer, when the bimetallic junction is formed. If $-\Delta v$ and $+\Delta v$ are the electrostatic potential created by the dipole layer on the right- and the left-hand sides far away from the interface, then we have

$$e\Delta v=\tfrac{1}{2}(E_F^a-E_F^b)\,, \tag{2.1}$$

where $-e$ is the charge of the electron, and E_F^a and E_F^b are the original Fermi levels of metals a and b, located to the right and to the left of the junction, respectively. The common Fermi level, after the junction is formed, is given by

$$E_F=E_F^a-e\Delta v=E_F^b+e\Delta v=\tfrac{1}{2}(E_F^a+E_F^b)\,. \tag{2.2}$$

In order to describe the electronic properties of the two bulk metals, the two metal-vacuum interfaces, and the metal-metal interface, we apply the tight-binding approximation for the various Hamiltonians. For simplicity we associate one s-type orbital with each lattice site. It is also assumed that each orbital has a g-fold degeneracy in order to account partially for the 10-fold degeneracy of the d orbitals in transition metals. Therefore, the Hamiltonians of the two bulk metals H_a and H_b are given, respectively, by

$$H_a=\sum_{i,j}{}' t_{ij}^a a_i^\dagger a_j\,,\quad H_b=\sum_{i,j}{}' t_{ij}^b b_i^\dagger b_j\,, \tag{2.3}$$

where $a_i^\dagger, a_j$ and $b_i^\dagger, b_j$ are the creation and destruction operators of the Wannier-type orbitals, associated with metals a and b, localized near sites i and j. The prime on the summation signs denotes a summation over nearest neighbors only. The matrix elements t_{ij}^a and t_{ij}^b are given by

$$t_{ij}^a=\langle i|H_a|j\rangle=\begin{cases}E_{oa} \text{ if } i=j\\ E_{1a} \text{ or } E_{1a}^*,\\ \text{if } i \text{ and } j \text{ are nearest neighbors}\\ 0 \text{ otherwise},\end{cases} \tag{2.4a}$$

$$t_{ij}^b=\langle i|H_b|j\rangle=\begin{cases}E_{ob} \text{ if } i=j\\ E_{1b} \text{ or } E_{1b}^*,\\ \text{if } i \text{ and } j \text{ are nearest neighbors}\\ 0 \text{ otherwise}.\end{cases} \tag{2.4b}$$

To cleave the crystal along a given low-order crystallographic plane, we have to break the bonds between two adjacent planes, parallel to the corresponding direction. We neglect any geometrical reconstruction of the crystal due to the formation of the surface and assume that the transfer integrals t_{ij}^a and t_{ij}^b with $i\neq j$ have the same value as in the bulk systems, provided that both sites i and j are occupied. In addition, we assume that the effect of the surface on the redistribution of the electronic charge near the surface can be described as a change in the self-consistent potential of the electrons near the first surface layer only. Therefore, the diagonal matrix elements of the Hamiltonian for sites located on the surface plane will be different from the corresponding bulk value. Thus, for the metal-vacuum systems we have

$$\langle i|H_a'|i\rangle=E_{oa}+\overline{U}_a\delta_{i,0}\,, \tag{2.5a}$$

$$\langle i|H_b'|i\rangle=E_{ob}+\overline{U}_b\delta_{i,-1}\,, \tag{2.5b}$$

where $\overline{U}_a$ and $\overline{U}_b$ denote the change in the self-consistent potential of the electrons near the surface. In the above expressions, we assumed that $i=0$ and $i=-1$ denote surface sites of metal a and b, respectively.

In order to form the metal-metal interface we start from two noninteracting semi-infinite metal-vacuum interfaces (the free surfaces), having the same translational symmetry parallel to the surface, and introduce a coupling between the two surface layers. The Hamiltonian of the noninteracting system is given by

$$H^0=\sum_{i,j}{}' t_{ij}c_i^\dagger c_j\,, \tag{2.6a}$$

where

$$t_{ij}=\begin{cases}\langle i|H_a'|j\rangle\\ \text{if both } i \text{ and } j \text{ are } a \text{ sites}\\ \langle i|H_b'|j\rangle\\ \text{if both } i \text{ and } j \text{ are } b \text{ sites}\\ 0 \text{ otherwise}\end{cases}$$

and

$$c_i, c_i^\dagger = \begin{cases} a_i, a_i^\dagger \text{ if } i \text{ is an } a \text{ site} \\ b_i, b_i^\dagger \text{ if } i \text{ is a } b \text{ site.} \end{cases} \quad (2.6c)$$

The interaction between the two surface layers is characterized by a transfer matrix element.

$$\langle \vec{R}_{-1} | H | \vec{R}_0 \rangle = \langle \vec{R}_0 | H | \vec{R}_{-1} \rangle^* , \quad (2.7)$$

where $\vec{R}_{-1}$ and $\vec{R}_0$ denote two nearest-neighbor sites located on the two sides of the interface. We also note that the dipole layer created at the interface will change the self-consistent potentials on the two sides of the junction. If we assume that charge redistribution is confined to the near vicinity of the interface we can write

$$\langle \vec{R}_i | H | \vec{R}_i \rangle = E_{0a} - e\,\Delta V + U_a \delta_{i,0} , \quad (2.8a)$$

if i is an a site and

$$\langle \vec{R}_j | H | \vec{R}_j \rangle = E_{0b} + e\Delta V + U_b \delta_{j,-1} , \quad (2.8b)$$

if j is a b site, where $i=0$ and $j=-1$ denote interface sites of metals a and b, respectively. In the above expressions U_a and U_b denote the change in the self-consistent potential of electrons near the interface relative to the bulk.

III. BIMETALLIC INTERFACE GREEN'S FUNCTION

As we already noted before, we assume that the two crystals forming the interface have the same translational symmetry parallel to the interface plane. As a result, the wave vector parallel to the interface, $\vec{k}_\parallel$, is a good quantum number. In the following we assume that the interface is in the zy plane, and that metals a and b are to the right and to the left of the interface, respectively. The integers $m, n, \ldots$ will be used to label the various planes parallel to the interface. Metal a is assumed to occupy the planes $m \geq 0$, whereas $m \leq -1$ planes are occupied by b atoms. Following Kalkstein and Soven,[13] we denote by $\vec{\tau}_n$ the translation vector parallel to the interface which brings the atoms in the nth plane to coincide with the transverse positions of the atoms on the plane $n=0$. The general coordinate of an atomic site on the nth plane is thus given by

$$\vec{R}_n = \vec{R}_{n\perp} + \vec{R}_\parallel + \vec{\tau}_n , \quad (3.1)$$

where $\vec{R}_{n\perp}$ is the distance between the planes 0 and n, and $\vec{R}_\parallel$ is a general translation vector parallel to the interface. Using the localized Wannier orbitals $|\vec{R}_{n\perp} + \vec{R}_\parallel + \vec{\tau}_n\rangle$, we define the mixed Bloch-Wannier representation by the following two-dimensional Bloch sum[14]

$$|\vec{k}_\parallel, n\rangle = (N_\parallel)^{-1/2} \sum_{\vec{R}_\parallel} |\vec{R}_{n\perp} + \vec{R}_\parallel + \vec{\tau}_n\rangle e^{i\vec{k}_\parallel \cdot (\vec{R}_\parallel + \vec{\tau}_n)} , \quad (3.2)$$

where $N_\parallel$ is the number of atoms in the plane parallel to the interface. These functions are localized near the nth plane.

In order to derive the various densities of states of the bimetallic interface we shall use the Green's-function technique. Let H and H^0 be the Hamiltonians of the interfaced crystal and of the free metal-vacuum interfaces, respectively. The metal-metal interface Green's operator G is defined by the following equation

$$(E - i\delta - H)G = 1 , \quad (3.3)$$

where E is the energy and δ is a positive infinitesimal. The surface Green's operator G^0 is related to the Hamiltonian H^0 by a similar equation. The Green's operator of the interface is related to the surface Green's operator via Dyson's equation

$$G = G^0 + G^0 V G , \quad (3.4)$$

where V is the perturbation necessary to create the metal-metal interface from the free surfaces of metals a and b, i.e.,

$$V = H - H^0 . \quad (3.5)$$

We note that because of the translational symmetry parallel to the interface, G, G^0, and V will all be diagonal in the wave-vector index $\vec{k}_\parallel$, in the Bloch-Wannier representation (3.2). Omitting the corresponding δ function, $\delta(\vec{k}_\parallel - \vec{k}_\parallel')$, we use the notations $G(m,n;\vec{k}_\parallel)$, $G^0(m,n;\vec{k}_\parallel)$, and $V(m,n;\vec{k}_\parallel)$ for the matrix elements of G, G^0, and V in the Bloch-Wannier representation. To simplify the notation further, we shall generally omit the explicit $\vec{k}_\parallel$ dependence in these expressions.

The various densities of states are simply related to the imaginary part of the diagonal matrix elements $G(m,m;\vec{k}_\parallel)$ by

$$\rho(E) = \frac{1}{\pi N} \mathrm{Im}\,\mathrm{Tr}G = \frac{1}{\pi N} \mathrm{Im} \sum_{m,\vec{k}_\parallel} G(m,m;\vec{k}_\parallel) , \quad (3.6)$$

$$\rho_n(E) = \frac{1}{\pi N_\parallel} \mathrm{Im} \sum_{\vec{k}_\parallel} G(n,n;\vec{k}_\parallel) , \quad (3.7)$$

$$\rho_n(E,\vec{k}_\parallel) = \frac{1}{\pi} \mathrm{Im} G(n,n;\vec{k}_\parallel) , \quad (3.8)$$

where $\rho(E)$, $\rho_n(E)$, and $\rho_n(E,\vec{k}_\parallel)$ are the total density of states, the local density of states, and the local density of states with a given $\vec{k}_\parallel$.

We turn now to the evaluation of the interface Green's function from Dyson's equation (3.4). This operator equation is reduced to the following algebraic equation in the Bloch-Wannier representation:

$$G(m,n) = G^0(m,n) + \sum_{l,r} G^0(m,l) V(l,r) G(r,n) . \quad (3.9)$$

From the discussion of the model given in Sec. II, it is obvious that the perturbation potential V has off-diagonal matrix elements, which couple the interface planes $n=0$ and $n=-1$. In addition, on each side of the interface V has two types of diagonal matrix elements. The first one, due to the interface dipole layer, is given by $\pm e\Delta v$. This is just the perturbation necessary to align the Fermi levels on the two sides of the junction, Eq. (2.1). The second type of diagonal matrix elements is due to the change in the self-consistent potential of the electrons near the interface. This is given by $U_a - \overline{U}_a$ and $U_b - \overline{U}_b$ where U_a, $\overline{U}_a$ and $U_b, \overline{U}_b$ are the self-consistent potentials, relative to the bulk, of interface and surface electrons of metals a and b, respectively.

As we shall see later on, it is possible to determine the surface Green's functions for an arbitrary value of the surface self-consistent potentials $\overline{U}_a$ and $\overline{U}_b$. It is, therefore, simpler to start from a fictitious, intermediate surface problem where the surface self-consistent potentials $\overline{U}_a$ and $\overline{U}_b$ have already the correct interface values U_a and U_b, respectively. Using this system as our starting point, the perturbation potential necessary to create the metal-metal interface is simpler than in the original problem. It consists of diagonal terms $\pm e\Delta v$, which align the Fermi levels of the two metals and of an off-diagonal term, which couples the two semi-infinite crystals. Thus, the only nonvanishing matrix elements of the perturbation are given by

$$V(m,m) = \begin{cases} -e\Delta v \text{ for } m \geq 0 \\ +e\Delta v \text{ for } m \leq -1 \end{cases} \tag{3.10}$$

and

$$V(-1,0) = V(0,-1)^* = \beta(\vec{k}_\parallel)e^{i\phi(\vec{k}_\parallel)}, \tag{3.11}$$

where β and ϕ are derived from the relation

$$V(-1,0) = \sum_{\vec{R}_0}{}' \langle \vec{R}_{-1}|V|\vec{R}_0\rangle e^{i\vec{k}_\parallel\cdot(\vec{R}_{0\parallel}+\vec{\tau})}. \tag{3.12}$$

In this expression, $\vec{\tau}$ is a translation vector parallel to the interface which brings the transverse atomic sites of the two interface planes to coincide. In Eq. (3.11), the phase ϕ was chosen in such a way that $\beta > 0$.

We start now from the intermediate surface problem discussed above, whose Green's function we denote by G^0, and apply the perturbation in two steps. First, we align the Fermi levels of the two metals by applying constant electrostatic potentials $+\Delta v$ on metal a and $-\Delta V$ on metal b. The only effect of applying these constant potentials on the surface Green's functions is a shift in the corresponding energies. Explicitly, we have

$$\tilde{G}_a^0(E) = G_a^0(E + e\Delta v), \tag{3.13a}$$

$$\tilde{G}_b^0(E) = G_b^0(E - e\Delta v), \tag{3.13b}$$

where $\tilde{G}$ denotes the value of the Green's functions in the intermediate problem, after the application of the potentials $\pm\Delta v$. To simplify the notation, we drop the tilde from these Green's functions, remembering that the energies have to be shifted according to (3.13).

At this stage, we turn to the second part of the perturbation, i.e., the off-diagonal coupling between the two metals. Due to the localized nature of this perturbation, the Dyson's equation (3.9) is greatly simplified, and we obtain

$$G(m,n) = G^0(m,n) + G^0(m,-1)V(-1,0)G(0,n) + G^0(m,0)V(0,-1)G(-1,n). \tag{3.14}$$

Using the fact that the surface Green's function $G^0(m,n)$ vanishes if m and n refer to planes on opposite sides of the interface, we can easily solve equation (3.14) for the perturbed Green's function. In this way we get

$$G(m,n) = G^0(m,n) + G^0(m,0)[V(0,-1)G^0(-1,n) + |V(0,-1)|^2G^0(-1,-1)G^0(0,n)] \times [1 - |V(0,-1)|^2G^0(0,0)G^0(-1,-1)]^{-1}, \tag{3.15a}$$

for $m \geq 0$ and

$$G(m,n) = G^0(m,n) + G^0(m,-1)[V(-1,0)G^0(0,n) + |V(0,-1)|^2G^0(0,0)G^0(-1,n)] \times [1 - |V(0,-1)|^2G^0(0,0)G^0(-1,-1)]^{-1}, \tag{3.15}$$

for $m \leqslant -1$. In particular, the diagonal matrix elements of the interface Green's function are given by

$$G(m,m)=G^0(m,m)+\beta^2 G^0(-1,-1)G^0(m,0)G^0(0,m)\times[1-\beta^2 G^0(0,0)G^0(-1,-1)]^{-1}, \quad (3.16a)$$

for $m \geqslant 0$ and by

$$G(m,m)=G^0(m,m)+\beta^2 G^0(0,0)G^0(m,-1)G^0(-1,m)\times[1-\beta^2 G^0(0,0)G^0(-1,-1)]^{-1}, \quad (3.16b)$$

for $m \leqslant -1$. In the above expressions, β is related to the off-diagonal coupling between the two metals through Eq. (3.11), i.e.,

$$\beta=|V(0,-1)|\ .$$

The diagonal matrix elements of the surface Green's function were calculated by Kalkstein and Soven.[13] Using the same method, one can also derive the general matrix elements of this Green's function. It can be shown that these matrix elements are given by

$$G^0(m,n)=i\mu_a^{-1}e^{-i(m-n)\theta_a}\left[\left(\frac{\omega_a+i\mu_a}{2T_a}\right)^{|m-n|}+\left(\frac{\omega_a+i\mu_a}{2T_a}\right)^{m+n}\frac{i\mu_a+(\omega_a-2\overline{U}_a)}{i\mu_a-(\omega_a-2\overline{U}_a)}\right] \quad (3.17a)$$

for $m,n \geqslant 0$, by

$$G^0(m,n)=i\mu_b^{-1}e^{-i(m-n)\theta_b}\left[\left(\frac{\omega_b+i\mu_b}{2T_b}\right)^{|m-n|}+\left(\frac{\omega_b+i\mu_b}{2T_b}\right)^{|m|+|n|-2}\times\frac{i\mu_b+(\omega_b-2\overline{U}_b)}{i\mu_b-(\omega_b-2\overline{U}_b)}\right]\ , \quad (3.17b)$$

for $m,n \leqslant -1$ and by

$$G^0(m,n)=0 \quad (3.17c)$$

otherwise. In these expressions, μ and ω are defined by

$$\mu=\begin{cases}(4T^2-\omega^2)^{1/2} & \text{for } \omega^2\leqslant 4T^2\\ i\,\text{sgn}(\omega)(\omega^2-4T^2)^{1/2} & \text{for } \omega^2>4T^2\end{cases} \quad (3.17d)$$

and

$$\omega=E-W(\vec{k}_\parallel)\ ,$$

where W, T, and θ are related to the matrix elements of the bulk Hamiltonians of the two metals, in the Bloch-Wannier representation, as follows:

$$W_{a(b)}(\vec{k}_\parallel)=\langle n\vec{k}_\parallel|H_{a(b)}|n\vec{k}_\parallel\rangle\ ,$$

$$T_{a(b)}(\vec{k}_\parallel)e^{i\theta_{a(b)}(\vec{k}_\parallel)}=\langle n\vec{k}_\parallel|H_{a(b)}|n+1,\vec{k}_\parallel\rangle\ .$$

In order to apply the expressions (3.17) to the solution of the interface problem, we replace first $\overline{U}_a$ and $\overline{U}_b$ by the corresponding interface values U_a and U_b, respectively. In addition, we have to shift the energies according to Eq. (3.13) in order to align the Fermi levels of the two metals. This can be achieved by redefining the ω's in the following way:

$$\omega_a=E-W_a(\vec{k}_\parallel)+e\Delta v\ , \quad (3.18a)$$

$$\omega_b=E-W_b(\vec{k}_\parallel)-e\Delta v\ . \quad (3.18b)$$

Substituting the explicit expression (3.17) for the surface Green's function into Eq. (3.16), we obtain that the diagonal matrix elements of the interface Green's function are given by

$$G(m,m)=\frac{i}{\mu_a}+\frac{1}{\mu_a+i(\omega_a-2U_a)}\left(\frac{\omega_a+i\mu_a}{2T_a}\right)^{2m}\left(\frac{i\mu_a+(\omega_a-2U_a)}{\mu_a}-\frac{8\beta^2 i}{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}\right), \quad (3.19a)$$

for $m \geqslant 0$, and by

$$G(m,m)=\frac{i}{\mu_b}+\frac{1}{\mu_b+i(\omega_b-2U_b)}\left(\frac{\omega_b+i\mu_b}{2T_b}\right)^{2|m|-2}\left(\frac{i\mu_b+(\omega_b-2U_b)}{\mu_b}-\frac{8\beta^2 i}{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}\right), \quad (3.19b)$$

for $m \leq -1$. We recall that ω_a and ω_b in these equations are defined by the energy-shifted expressions (3.18a) and (3.18b), respectively.

It is straightforward to confirm that in the limit where the two metals a and b are the same, expression (3.19) for the interface Green's function reduces to the corresponding bulk expression.

IV. ELECTRONIC STRUCTURE OF THE INTERFACE

In this section, we apply the Green's function derived in Sec. III in order to investigate the electronic structure of the interface. From the explicit expression (3.19), it follows that the diagonal matrix elements of the interface Green's function have a nonvanishing, continuous imaginary part for energies which are either inside the band of metal a or inside the band of metal b [shifted, of course, according to (3.13)]. Therefore, as follows from Eq. (3.8), the bandwidth of the crystal with the interface is the union of the shifted bands of the two separate crystals. However, the wave functions of the combined crystal can be classified into three distinct classes according to their different localization properties. To facilitate our further discussion we define the $\vec{k}_\parallel$ subbands of the two metals as the band structure obtained by the intersection of $E_a(\vec{k})$ and $E_b(\vec{k})$ with the plane $\vec{k}_\parallel = \text{constant}$, where $E_a(\vec{k})$ and $E_b(\vec{k})$ are the single-particle energy spectra of the two bulk crystals.

The first type of states has wave functions which extend throughout the entire crystal. As can be seen from Eq. (3.19), this kind of behavior is associated with states whose energy lies in the $\vec{k}_\parallel$ subband of the two metals, i.e., their energy and wave vector satisfy the relations

$$|E - W_a(\vec{k}_\parallel) + e\Delta v| < 2T_a(\vec{k}_\parallel), \quad |E - W_b(\vec{k}_\parallel) - e\Delta v| < 2T_b(\vec{k}_\parallel). \tag{4.1}$$

The second type of states has wave functions which extend to infinity on only one side of the interface, and which decay exponentially with the distance from the interface on the other side. Using expression (3.19) for the Green's function, it is not hard to see that this behavior occurs when the energy lies in the $\vec{k}_\parallel$ subband of one metal but outside the corresponding subband of the other. Thus, for energies and wave vectors that satisfy

$$|E - W_a(\vec{k}_\parallel) + e\Delta v| < 2T_a(\vec{k}_\parallel), \quad |E - W_b(\vec{k}_\parallel) - e\Delta v| > 2T_b(\vec{k}_\parallel), \tag{4.2}$$

the corresponding wave functions are Bloch-like inside metal a, but decay exponentially from the interface inside metal b. In a similar way, the wave functions of states whose energies and wave vectors satisfy

$$|E - W_a(\vec{k}_\parallel) + e\Delta v| > 2T_a(\vec{k}_\parallel), \quad |E - W_b(\vec{k}_\parallel) - e\Delta v| < 2T_a(\vec{k}_\parallel), \tag{4.3}$$

extend to infinity on the b side of the interface, but decay exponentially on the a side. The decay coefficient of the wave function is determined by the energy measured relative to the corresponding $\vec{k}_\parallel$ subband center. If we express this energy in units of the subband half-width, and write

$$\omega(\vec{k}_\parallel) = \alpha 2T(\vec{k}_\parallel), \quad |\alpha| > 1 \tag{4.4}$$

where $\omega(\vec{k}_\parallel)$ and $T(\vec{k}_\parallel)$ refer to the corresponding values on the side of the interface where the wave function decays exponentially, we obtain from Eq. (3.19) that on the decaying side, the wave function on plane m is proportional to $e^{-\lambda m}$. The decay coefficient $\lambda > 0$ is given by

$$\lambda = -\ln[\alpha - \text{sgn}(\alpha)(\alpha^2 - 1)^{1/2}]. \tag{4.5}$$

Thus, the further the energy is from the center of the subband, the stronger is the exponential decay of the corresponding wave function.

We note that the behavior of the wave functions extending throughout the entire system and those extending only on one side of the interface is as expected. If we try to propagate a wave through the interfaced crystal this wave can propagate from one side to the other only if its frequency is in the common subbands. If, however, the frequency is in the subband of one of the crystals but outside the subband of the other, this wave cannot penetrate into the second crystal, and its amplitude will decay exponentially.

The third type of wave function is associated with the existence of bound interface states. For a given $\vec{k}_\parallel$ the energy of the possible bound states is determined by the poles of the Green's function, which lie outside the $\vec{k}_\parallel$ subbands of the two metals forming the junction. Using the explicit expression (3.19) for the interface Green's function, we see that the bound-state energies are given by the roots of the equation

$$4\beta^2 - [\text{sgn}(\omega_a)\bar{\mu}_a + \omega_a - 2U_a][\text{sgn}(\omega_b)\bar{\mu}_b + \omega_b - 2U_b] = 0 \tag{4.6}$$

outside the $\vec{k}_\parallel$ subbands. In this equation $\bar{\mu}$ is defined by

$$\bar{\mu} = (\omega^2 - 4T^2)^{1/2}.$$

As will be shown later, Eq. (4.6) can have either 0, 1, or 2 solutions, depending on the nature of the coupling between the two metals and the value of $\vec{k}_\parallel$. Let $E_i(\vec{k}_\parallel)$ denote these solutions for a given $\vec{k}_\parallel$. As $\vec{k}_\parallel$ varies over the two-dimensional Brillouin zone, the energies $E_i(\vec{k}_\parallel)$ span a continuum of either 0, 1, or 2 interface bands. It follows from

Eq. (3.19) that the wave function of a bound interface state is localized near the interface, and decays exponentially with distance on both sides of the interface. Thus, the bound electron is free to propagate parallel to the interface, but is confined to a finite stripe of width $\lambda_a+\lambda_b$ [defined by Eq. (4.9) below] in the direction perpendicular to the interface. The above-mentioned free motion of the electron, parallel to the interface, actually causes the interface states to form continuous bands, rather than a truly isolated bound state. The decay coefficients of the bound-state wave function will be different, in general, on the two sides of the interface. If we express the bound-state energy, relative to the center of the two $\vec{k}_\parallel$ subbands, in terms of the corresponding subbands half-widths, we can write

$$\omega_a^0=\alpha_a 2T_a, \quad |\alpha_a|>1; \quad \omega_b^0=\alpha_b 2T_b, \quad |\alpha_b|>1, \tag{4.7}$$

where

$$\omega_a^0=E^0-W_a+e\Delta v; \quad \omega_b^0=E^0-W_b-e\Delta v, \tag{4.8}$$

and E^0 is the energy of the bound state. It is easy to see from Eq. (3.19) that the exponential-decay coefficients on side a and side b, λ_a, and λ_b, respectively, are given by

$$\lambda_a=-\ln[\alpha_a-\mathrm{sgn}(\alpha_a)(\alpha_a^2-1)^{1/2}], \tag{4.9a}$$

$$\lambda_n=-\ln[\alpha_b-\mathrm{sgn}(\alpha_b)(\alpha_b^2-1)^{1/2}]. \tag{4.9b}$$

Thus, the greater the distance of the bound-state energy from the center of the $\vec{k}_\parallel$ subbands, the more localized is the corresponding wave function.

We note that a general property of the bound interface states, derived from Eq. (4.6), is that whenever two interface states exist simultaneously an increase in the coupling constant β will increase the energy of the interface state having the higher energy and will decrease the energy of the lower-energy bound state. Another remark that should be added here is that for very strong coupling between the two metals there will always be two interface states, a bonding state below the subbands and an antibonding one above the subbands. The asymptotic energies of these bound states are given by

$$E_1=U_a+W_a-e\Delta v+\beta, \quad E_2=U_b+W_b+e\Delta v-\beta,$$

if

$$|U_a+W_a-e\Delta v|>|U_b+W_b+e\Delta v|,$$

and by

$$E_1=U_b+W_b+e\Delta v+\beta,$$
$$E_2=U_a+W_a-e\Delta v-\beta,$$

if

$$|U_b+W_b+e\Delta v|>|U_a+W_a-e\Delta v|.$$

The analytical solution of Eq. (4.6) for the bound-state energies is not possible in general. However, by a suitable graphical analysis, one can determine the conditions for the occurrence of bound states, their number, and their position with respect to the bands, as a function of the strength of the coupling constant. It turns out to be very convenient to analyze the interface bound states in terms of the properties of the bound surface states of the intermediate surface problem considered in Sec. III (i.e., the surface problem having a surface self-consistent potential equal to the respective value of the interface problem). It is well known that the bound surface states are given by the roots of the equation[13]

$$\mathrm{sgn}(\omega)\bar{\mu}+\omega-2U=0.$$

The corresponding surface bound-state energies are given by

$$E_a^0=W_a(\vec{k}_\parallel)-e\Delta v+U_a+[T_a^2(\vec{k}_\parallel)/U_a], \tag{4.10a}$$

$$E_b^0=W_b(\vec{k}_\parallel)+e\Delta v+U_b+[T_b^2(\vec{k}_\parallel)/U_b], \tag{4.10b}$$

provided $|U_a|>T_a$ and $|U_b|>T_b$. For $U<T$ there are no surface states.

In the following analysis, we shall use the indices 1 and 2 to denote the metal having the higher subband top edge and the lower subband bottom edge, respectively. For a fixed $\vec{k}_\parallel$, the behavior of the interface bound states can be described as follows:

(a) When in the intermediate surface problem there are no bound states (i.e., $|U_a|<T_a$ and $|U_b|<T_b$) there will be no bound interface states for small values of the coupling constant β. As the coupling constant is increased, a bound state will appear as soon as the critical value β_1 is reached, where

$$\beta_1=\{\min[-\tfrac{1}{2}(T_2+U_2)f_1(E_{2,\min}),\ \tfrac{1}{2}(T_1-U_1)f_2(E_{1,\max})]\}^{1/2} \tag{4.11}$$

and

$$f_i(E)\equiv\mathrm{sgn}(\omega_i)\bar{\mu}_i+\omega_i-2U_i. \tag{4.12}$$

$E_{1,\max}$ and $E_{2,\min}$ are the top-edge and the bottom-edge energies of the higher and the lower of the two $\vec{k}_\parallel$ subbands, respectively. If $-(T_2+U_2)f_1(E_{2,\min})<(T_1-U_1)f_2(E_{1,\max})$, the bound state will appear below the subbands. If, however, $-(T_2+U_2)f_1(E_{2,\max})>(T_1-U_1)f_2(E_{1,\max})$, the bound state will appear above the subbands. The bound state described above exists as long as $\beta>\beta_1$. When the coupling constant is further increased and the value β_2 is reached, a second bound state appears. The second critical coupling is given by

$$\beta_2 = \{ \max[-\tfrac{1}{2}(T_2 + U_2) f_1(E_{2,\min}), \tfrac{1}{2}(T_1 - U_1) f_2(E_{1,\max})] \}^{1/2} ; \quad (4.13)$$

for $\beta > \beta_2$ there are always two bound states, one below and the other above the subbands.

(b) Suppose that in the intermediate surface problem one of the following four situations holds: (i) There is one bound state avove the subbands and the two subbands overlap. (ii) There is one bound state above the subbands, which is associated with the metal having the higher subband, and there is a gap between the two subbands. (iii) There are two surface states, one above the subbands and the other in the subband of the second metal, and there is an overlap between the subbands. (iv) There are two bound states, a gap exists between the subbands, and the bound state of the lower subband lies above the subbands, whereas, the one associated with the upper subband falls in the lower subband. Then the behavior of the interface bound states is as follows: For a small coupling constant, there will be one bound state above the subbands. This state develops in a continuous way from the corresponding surface state. If E_i^0 is the energy of the surface state, which lies above the subbands, then for small β the energy of the corresponding interface state is given approximately by

$$E \simeq E_i^0 - 4\beta^2 / f_j(E_i^0)(1 - U_i/T_i) , \quad (4.14)$$

where $f_j(E)$ is the function defined by (4.12). As long as β is in the range $0 \leqslant \beta \leqslant \beta_3$, where β_3 is defined by

$$\beta_3 = [-\tfrac{1}{2}(T_2 + U_2) f_1(E_{2,\min})]^{1/2} , \quad (4.15)$$

there is one bound state above the subbands. For $\beta \geqslant \beta_3$, there are two bound interface states, one above and other below the subbands.

(c) Suppose that in the intermediate surface problem one of the following four situations exists: (i) There is an overlap between the subbands, and a bound state exists below the subbands. (ii) There is a gap between the subbands, and there is one surface state below the subbands which is associated with the lower subband. (iii) There is an overlap between the subbands and there are two surface states, one below the subbands and the other inside the subband of the second metal. (iv) There is a gap between the subbands and there are two surface states, the one associated with the higher subband lying below the subbands, and the other falling inside the higher subband. Then the behavior of the interface bound states is as follows: for small β there will be one bound state below the subbands, with an energy given approximately by (4.14). When the coupling constant is increased, a critical value β_4 is reached, where a second bound state appears above the subbands, β_4 is defined by

$$\beta_4 = [\tfrac{1}{2}(T_1 - U_1) f_2(E_{1,\max})]^{1/2} . \quad (4.16)$$

For $\beta \geqslant \beta_4$ there are, thus, two bound states, one below and the other above the subbands.

(d) Suppose that in the intermediate surface problem one of the following situation holds: (i) There is a gap between the subbands and there exists one surface state above the subbands, which is associated with the lower subband. (ii) There is a gap between the subbands and there exist two surface states. The one associated with the higher subband is located above the subbands and the other lies inside the higher subband. Then the behavior of the interface states is as follows: for a small coupling constant there is one interface state above the subbands. When β reaches the critical value β_5, where

$$\beta_5 = [-\tfrac{1}{2}(T_1 + U_1) f_2(E_{1,\min})]^{1/2} \quad (4.17)$$

($E_{1,\min}$ being the bottom-edge energy of the higher subband), a second bound state appears inside the gap. This bound state exists as long as the coupling constant is in the range $\beta_5 \leqslant \beta \leqslant \beta_6$, where β_6 is given by

$$\beta_6 = [\tfrac{1}{2}(T_2 - U_2) f_1(E_{2,\max})]^{1/2} . \quad (4.18)$$

$E_{2,\max}$ is the energy at the top of the lower subband. For $\beta > \beta_6$, the bound state disappears from the gap. When β reaches the value β_3, given by Eq. (4.15), a new interface state appears below the subbands. For $\beta > \beta_3$ there are two interface states, one below and the other above the subbands.

(e) Suppose that in the intermediate surface problem one of the following situations holds: (i) There is a gap between the subbands, and there exists one surface state associated with the higher subband which lies below the subbands. (ii) There is a gap between the subbands and there are two surface states. The one associated with the lower subband lies below the subbands and the other one lies in the lower subband. Then the behavior of the interface states is as follows: for small values of the coupling constant there is one interface state below the subbands, whose energy is given approximately by (4.14). When β is increased, and reaches the value β_6 given by (4.18), a new interface state appears in the gap. This bound state exists in the gap for $\beta_6 \leqslant \beta \leqslant \beta_5$, where β_5 is given by (4.17). For $\beta > \beta_5$, the bound state disappears from the gap and a new bound interface state appears above the subbands for $\beta \geqslant \beta_4$, where β_4 is given by (4.16). For $\beta \geqslant \beta_4$, there are two bound states, one below and the other above the subbands.

(f) Suppose that one of the following situations holds in the intermediate surface problem: (i) There is a gap between the subbands and there is a single surface state which lies in the gap. (ii) There is a gap between the subbands and there are two surface states, one in the gap and the other lies inside the subband of the other metal. Then the behavior of the interface bound state is as follows: for small values of the coupling constant there is a single interface state which lies in the gap. When β is increased and reaches the value β_7, where

$$\beta_7 = \{\max[-\tfrac{1}{2}(T_1+U_1)f_2(E_{1,\min}),\ \tfrac{1}{2}(T_2-U_2)f_1(E_{2,\max})]\}^{1/2}, \qquad (4.19)$$

this bound state disappears. For $\beta \geq \beta_3$, there appears a new interface state below the subbands where β_3 is given by (4.15). If $\beta \geq \beta_4$ there is also a bound state above the subbands, where β_4 is determined by (4.16).

(g) Suppose that in the intermediate surface problem there are two surface states below the subbands, and a gap exists between these subbands. Then for small values of β there will be two interface states below the subbands [with energies given approximately by (4.14)]. When β reaches the value given by (4.15), the interface state having the higher energy disappears. A new bound interface state appears in the gap when β reaches the value of β_6, where β_6 is given by (4.18). This bound state exists as long as $\beta_6 \leq \beta \leq \beta_5$, where β_5 is determined by (4.17). For $\beta > \beta_5$, the interface state disappears from the gap and a new bound state appears above the subbands when $\beta \geq \beta_4$, where β_4 is given by (4.16).

(h) Suppose that the situation in the intermediate surface problem is the same as described in (g) except that there is an overlap between the subbands. There will be two interface states below the subbands for $0 \leq \beta \leq \beta_3$, where β_3 is given by (4.15). A new interface state appears above the subbands for $\beta \geq \beta_4$, where β_4 is given by (4.16).

(i) Suppose that in the intermediate surface problem there are two surface states above the subbands, and a gap exists. Then for small values of β there are two interface states above the subbands. When β reaches the value β_4 given by (4.16), the interface state having the lower energy disappears. A new bound state appears inside the gap when β reaches the value β_5 given by (4.17). This bound interface state exists as long as $\beta_5 \leq \beta \leq \beta_6$, where β_6 is given by (4.18). If β is further increased, the bound state disappears from the gap and a new interface state appears below the subbands when $\beta \geq \beta_3$ where β_3 is given by (4.15).

(j) Suppose that in the intermediate surface problem there are two surface states inside the gap, then for small values of the coupling constant there will be two interface states inside the gap. Their energies are given approximately by (4.14). When β reaches the value β_8 where

$$\beta_8 = \{\min[\tfrac{1}{2}(T_2-U_2^s)f_1(E_{2,\max}),\ -\tfrac{1}{2}(T_1-U_1)f_2(E_{1,\min})]\}^{1/2}, \qquad (4.20)$$

one of these bound states disappears. When β is further increased and reaches the value β_9 given by

$$\beta_9 = \{\max[\tfrac{1}{2}(T_2-U_2)f_1(E_{2,\max}),\ -\tfrac{1}{2}(T_1+U_1)f_2(E_{1,\min})]\}^{1/2}. \qquad (4.21)$$

The other bound states also disappears from the gap. For $\beta \geq \beta_3$, where β_3 is given by (4.15), an interface state appears below the subbands, whereas for $\beta \geq \beta_4$, where β_4 is given by (4.16), there is a bound state above the subbands.

(k) Suppose that in the intermediate surface problem there are two surface states, one below and the other above the subbands. Then for any value of the coupling constant β there will be two interface states, one below and the other above the subbands.

(l) Suppose that in the intermediate surface problem there are two surface states, one in the gap and the other below (above) the subbands, then for small values of β there will also be two interface states, one in the gap and the other below (above) the subbands. The bound state in the gap disappears for $\beta > \beta_7$, where β_7 is given by (4.10). For $\beta \geq \beta_4$ ($\beta \geq \beta_3$) a new bound state appears above (below) the subbands, where β_4 (β_3) is given by (4.16) and (4.15). This analysis covers the various possible bound interface states.

In Sec. VI we shall return to the problem of the interface states while discussing a numerical example.

V. INTERFACE ENERGY

If many-body effects are neglected, the total energy of the crystal with the interface is just the sum of the occupied single-particle energy levels. This, in turn, can be expressed as a corresponding integral over the system's density of states. The total density of states of the interfaced crystal can be obtained from the Green's function derived in Sec. III, by summing the imaginary part over the various planes parallel to the interface. However, in order to determine the energy needed to break the metal-metal interface into two metal-vacuum interfaces we need to know the change in the total density of states due to this cleavage process. This can be evaluated directly, without calculating the density of states of the two systems, by using the phase-shift method described by De Witt,[15] Callaway,[16] and Toulouse.[17] This method can be summarized as follows: let $H=H^0+V$ be the perturbed Hamiltonian. The change in density of states due to the perturbation V can be written

$$\Delta\rho(E)=\frac{1}{\pi}\,\mathrm{Im}\,\frac{\partial}{\partial E}\,\mathrm{Tr}[\ln(1-G^0V)]$$
$$=\frac{1}{\pi}\mathrm{Im}\,\frac{\partial}{\partial E}\,\ln[\det(1-G^0V)]. \qquad (5.1)$$

The application of Eq. (5.1) is especially useful for a localized perturbation, when $\det(1-G^0V)$ can be expressed as a finite-order determinant.

Let us turn now to the specific problem of the interface. In this case we start from the two semi-infinite surface systems (the a and the b surfaces), and apply the perturbation necessary to create the interface. This perturbation was described in detail in Sec. V. We introduce the perturbation in two steps. In the first one, we apply a constant electrostatic potential Δv on metal a and $-\Delta v$ on metal b. As we have seen before, the application of these potentials causes a shift in the densities of states of the two surface systems, which aligns the Fermi levels of the two metals. Since each metal is electrically neutral, there will be no net change in their energies due to the application of this perturbation. Our second and final step is to apply the remaining perturbation V needed to form the interface. As we have seen in Secs. II and III, the only nonvanishing matrix elements of this perturbation are given by

$$V(0,0)=U_a-\overline{U}_a, \qquad (5.2a)$$

$$V(-1,-1)=U_b-\overline{U}_b, \qquad (5.2b)$$

and

$$V(-1,0)=V(0,-1)^*=\beta e^{i\phi}, \qquad (5.2c)$$

where, as before, U_a, U_b, and $\overline{U}_a, \overline{U}_b$ are the self-consistent potentials near the interface and near the surface, respectively. Thus, in the present case we have

$$\det(1-G^0V)=\begin{vmatrix}1-G^0(-1,-1)V(-1,-1) & -G^0(-1,-1)V(-1,0)\\ -G^0(0,0)V(0-1) & 1-G^0(0,0)V(0,0)\end{vmatrix}, \qquad (5.3)$$

where $G^0(0,0)$ and $G^0(-,-1)$ are the corresponding surface Green's functions of metals a and b, respectively, with the energies shifted according to (3.17). We note that the surface self-consistent potentials in $G^0(0,0)$ and $G^0(-1,-1)$ are $\overline{U}_a$ and $\overline{U}_b$, respectively, and not U_a and U_b, as was the case in Sec. IV. Since G^0 and V are diagonal in the wave vector $\vec{k}_{\parallel}$, the determinant (5.3) factorizes into similar terms with different $\vec{k}_{\parallel}$ values. Expanding (5.3) in terms of the indices m and n shows that each such factor is given by

$$\det_{\vec{k}_{\parallel}}(1-G^0V)=[1-V(-1,-1)G^0(-1,-1)]$$
$$\times[1-V(0,0)G^0(0,0)]$$
$$-\beta^2G^0(0,0)G^0(-1,-1). \qquad (5.4)$$

In this expression, we used the notation $\det_{\vec{k}_{\parallel}}$ for the partial determinant, with a specific $\vec{k}_{\parallel}$.

Substituting the explicit expressions for the surface Green's functions $G^0(0,0)$ and $G^0(-1,-1)$, from the general expression (3.17), into Eq. (5.4) gives

$$\det_{\vec{k}_{\parallel}}(1-G^0V)$$
$$=\frac{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}. \qquad (5.5)$$

The bound-state energies of the crystal with the interface are given by the roots of the equation[16,17]

$$\det(1-G^0V)=0 \qquad (5.6)$$

outside the shifted bands of the two metals. Using the explicit expression (5.5), we see that this is exactly the same condition derived earlier from the poles of the interface Green's function, Eq. (4.6).

In analogy with ordinary scattering theory, one defines the partial phase shifts by[16,17]

$$\eta(E,\vec{k}_{\parallel})=\mathrm{Im}\ln[\det\vec{k}_{\parallel}(1-G^0V)]=\arg\left(\frac{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}\right). \qquad (5.7)$$

In the second step, we applied the explicit expression (5.5) and used the identity $\mathrm{Im}\ln f=\arg f$, where arg denotes the argument of the complex function.

If we take the determinant of (5.5) with respect to $\vec{k}_\parallel$, and use the relation (5.1), we see that the change in the density of states per surface atom, relative to the shifted bands, due to the formation of the interface, is given by

$$\Delta\rho(E)=\frac{g}{\pi}\frac{A_\parallel}{(2\pi)^2}\frac{\partial}{\partial E}\int d\vec{k}_\parallel\,\eta(E,\vec{k}_\parallel)=\frac{g}{\pi}\frac{A_\parallel}{(2\pi)^2}\frac{\partial}{\partial E}\int d\vec{k}_\parallel \arg\left[\frac{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}\right]. \tag{5.8}$$

In this expression we introduced explicitly the g-fold degeneracy of the bands under consideration. We also note that $A_\parallel$ is the area of the unit cell parallel to the interface and that the $\vec{k}_\parallel$ integration goes over the two-dimensional Brillouin zone defined by the crystals structure parallel to the interface.

Equation (5.8) can be used to derive a relatively simple expression for the change in the integrated density of states. This is given by

$$\Delta N(E)=\int_{-\infty}^{E}\Delta\rho(E)\,dE=\frac{g}{\pi}\frac{A_\parallel}{(2\pi)^2}\int d\vec{k}_\parallel \arg\left[\frac{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}\right]. \tag{5.9}$$

The single-particle contribution to the interface energy σ_{ab} at $T=0$ (i.e., the energy per interface atom necessary to break the interface into two semi-infinite crystals, at $T=0$) is given by

$$\sigma_{ab}=-\int_{-\infty}^{E'_F}\Delta\rho(E)E\,dE\,, \tag{5.10}$$

where the Fermi energy E'_F differs from the value given by Eq. (2.2) by a term which is $O(1/N_\perp)$, where $N_\perp$ is the number of atomic layers parallel to the interface. This E'_F guarantees the charge neutrality of the interfaced crystal. Expanding (5.10) to first order in E'_F-E_F, we can express the interface energy as follows:

$$\begin{aligned}\sigma_{ab}&=-\int_{-\infty}^{E_F}\Delta\rho(E)(E-E_F)\,dE=\int_{-\infty}^{E_F}\Delta N(E)\,dE\\&=\frac{g}{\pi}\frac{A_\parallel}{(2\pi)^2}\int_{-\infty}^{E_F}dE\int d\vec{k}_\parallel \arg\left[\frac{4\beta^2+[\mu_a+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}\right].\end{aligned} \tag{5.11}$$

Also, E_F is the common Fermi energy of the two metals, i.e., $E_F=\frac{1}{2}(E_F^a+E_F^b)$, and ω_a and ω_b include the corresponding shifts in the energies, according to Eq. (3.22).

In a similar way, one can determine the single-particle contribution to the change in the electronic specific heat. This change is given by

$$\Delta C_V=\int_{\infty}^{\infty}E\Delta\rho(E)\frac{\partial f}{\partial T}\,dE\,,$$

where $F(E)$ is the Fermi-Dirac distribution function. For temperatures much lower than the Fermi temperature, the change in the electronic specific heat is linear in the temperature and proportional to the change in the density of states at the Fermi level (assuming no Van Hove singularity occurring at the Fermi energy). Explicitly, we have

$$\Delta C_v=\tfrac{1}{3}\pi^2K_B^2\Delta\rho(E_f)T\equiv\gamma T\,,$$

where K_B is the Boltzmann constant. For the interface system the constant γ is given by

$$\gamma=\frac{gK_B^2}{12\pi}A_\parallel\int d\vec{k}_\parallel\frac{\partial}{\partial E}\arg\left[\frac{4\beta^2+[\mu_2+i(\omega_a-2U_a)][\mu_b+i(\omega_b-2U_b)]}{[\mu_a+i(\omega_a-2\overline{U}_a)][\mu_b+i(\omega_b-2\overline{U}_b)]}\right], \tag{5.12}$$

where the integrand has to be evaluated at the common Fermi level.

VI. NUMERICAL RESULTS AND DISCUSSION

As an application of the formalism developed in Secs. III–V we consider in the following the interface formed parallel to the (100) plane of two crystals described by the same tight-binding parameters, but having different Fermi energies. The coupling between the two metals is taken to be the same as the bulk coupling, we also neglect the interface perturbation U_a and U_b (i.e., we set $T_a = T_b = \beta$, and $U_a = U_b = 0$). We note that in general, one would expect the interface perturbations to be different from zero. However, a calculation of the surface energy,[19] where a similar difficulty exists, shows that the difference between the surface energies calculated by either neglecting the surface perturbation, or by determining it self-consistently is very small. A similar situation can be expected in the present model. We stress that the abovementioned simplifications are done in this section mainly to reduce the number of independent parameters in the problem. The general case, discussed earlier, can be analyzed in a completely analogous way. The specific case, considered here, can serve as a crude model, describing the electronic properties of a (100) interface formed between two transition metals belonging to the same series, and will be referred to as such in the following.

From the preceding discussion, presented in Sec. IV, it is obvious that there are no interface bound states in the model under consideration. The electronic wave functions are delocalized, and extend on either one side or on both sides of the interface, according to the corresponding electron energy. For the (100) interface we have

$$W(\vec{k}_{\parallel}) = 2E_1[\cos(ak_y) + \cos(ak_z)], \tag{6.1a}$$

$$T = E_1 . \tag{6.1b}$$

Using these relations and Eq. (3.19) for the diagonal matrix elements of the Green's function, and expression (3.7), we can calculate the local densities of states on the various planes of the interfaced crystal. Figure 1 shows the results of such a numerical calculation of the local density of states $\rho_n(E)$ for the first three atomic layers adjacent to the interface ($n=0$, 1, and 2, respectively). The difference in the Fermi energies of the two metals was chosen to be $\Delta E_F = 2E_1$. Figure 2 shows the corresponding density of states for the case of $\Delta E_F = 8E_1$. For comparison, the shifted bulk density of states is also shown in these figures. All the density of states presented here are normalized to unity (i.e., we set $g=1$). We note that Figs. 1 and 2 refer to the side of the interface on which the metal having the higher Fermi energy is located. The local densities of states on the

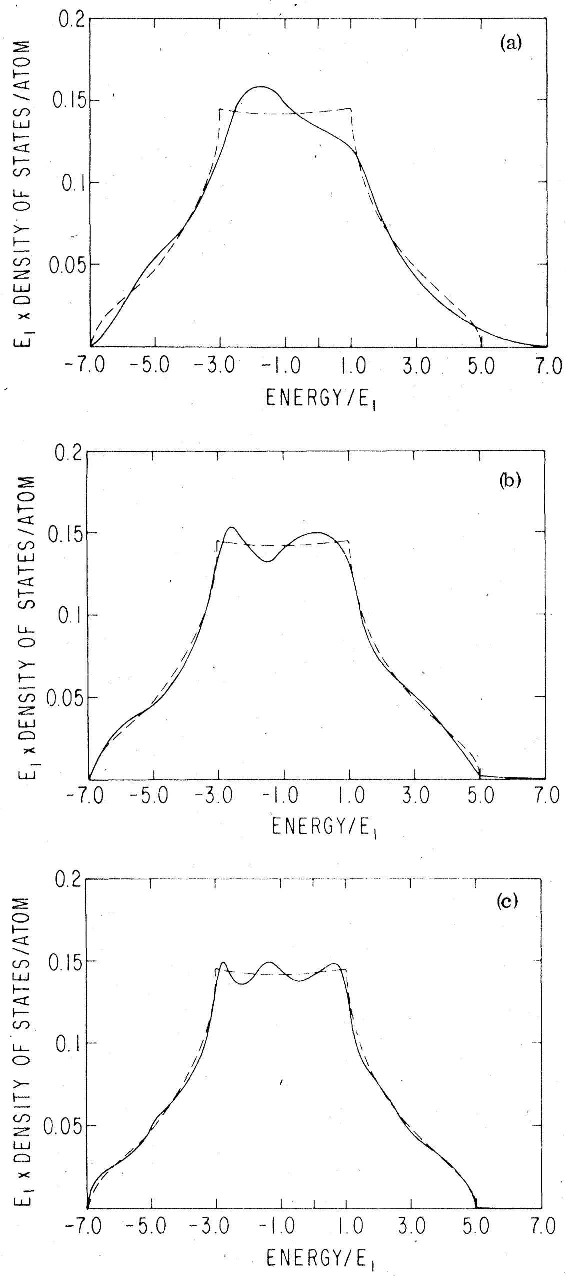

FIG. 1. Local density of states of a (100) interfaced crystal. The difference in the Fermi energies of the two metals is $2E_1$. (a) First atomic layer, $n=0$. (b) Second atomic layer, $n=1$. (c) Third atomic layer, $n=2$. Shifted bulk density of states is shown as a dashed curve.

other side of the interface can be obtained from the curves in Figs. 1 and 2 by taking their mirror images, with respect to the $E=0$ line. As can be seen from the above-mentioned figures, the local densities of states have a "tail" extending outside the shifted bulk band. This tail is contributed en-

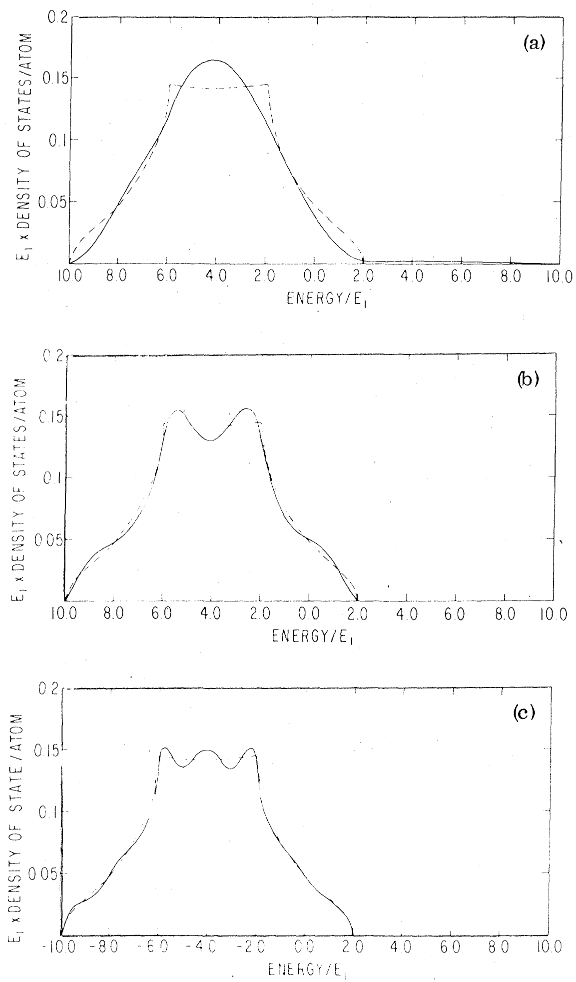

FIG. 2. Local density of states of a (100) interfaced crystal. The difference in the Fermi energies of the two metals is $8E_1$. (a) First atomic layer, $n=0$. (b) Second atomic layer, $n=1$. (c) Third atomic layer, $n=2$. Shifted bulk density of states is shown as a dashed curve.

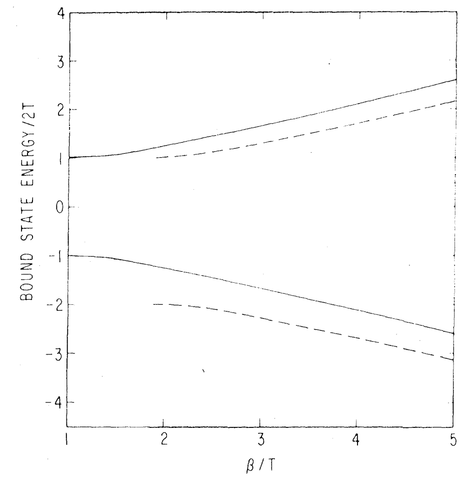

FIG. 3. Interface bound-states energies as a function of the coupling constant. The full and the dashed curves correspond to $\Delta E_F=0$, and $\Delta E_F=2T$, respectively.

tirely by electrons tunneling from the other side of the interface. From Figs. 1 and 2, it is obvious that the penetration distance of these electrons is essentially limited to only a few atomic layers. In general, the most pronounced effect on the local density of state occurs near the interface itself (i.e., $n=0$). As one proceeds away from the interface, the density of states approaches asymptotically the bulk density of states. For $n=2$ (the third layer near the interface) the density of states of the interfaced crystal is already very close to the corresponding shifted bulk density of states.

When, in the model under consideration, the coupling constant between the two metals is allowed to vary, it is possible to form bound interface states. Following the discussion of Sec. IV, it is not difficult to show that for the present model the two critical values β_1 and β_2 coincide. Therefore, in this case there will be either no bound states at all or there will be two of them, one above and the other below the subbands. It can be easily shown that the critical coupling constant β_c, to which both β_1 and β_2 reduce, is related to the difference in the Fermi energies of the two metals as follows

$$\beta_c = [T + \tfrac{1}{2}\Delta E_F + (\tfrac{1}{4}\Delta E_F^2 + T\Delta E_F)^{1/2}]^{1/2}. \qquad (6.2)$$

Thus, the bigger the difference in the Fermi energies the larger is the coupling necessary to create a bound state. This is quite expected since the greater is the difference in the Fermi energies the larger is the minimum distance of the bound states from the center of the subbands. The minimum possible critical coupling is obtained for $\Delta E_F=0$, and is given by $\beta_c = T$. Therefore, in the present model, every coupling constant which exceeds the bulk coupling will produce a bound state. Figure 3 shows the dependence of the bound-state energies on the coupling constant for the case of $\Delta E_F = 0$ and $\Delta E_F = 2T$. As can be seen from these curves, an increase in the coupling constant increases the energy of the upper bound state and decreases that of the lower. This behavior agrees with our general discussion given in Sec. IV.

We now turn to the calculation of the change in the total density of states and the interface energy of two transition metals belonging to the same series. Using Eq. (5.8) it is not difficult to see that the change in the density of states, in the model under consideration, is an even function of the energy relative to the center of the band. Using Eq. (5.9) we calculated numerically the change in

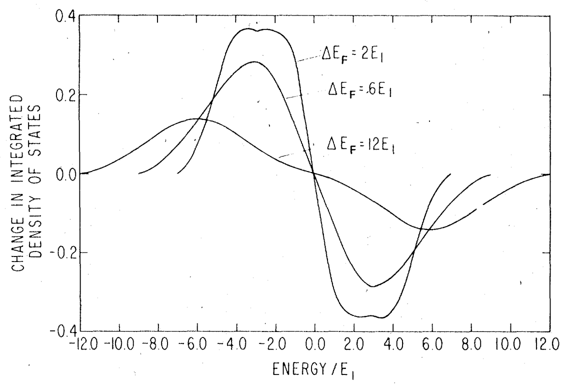

FIG. 4. Change in the integrated density of states due to the creation of the interface.

the integrated density of states $\Delta N(E)$ due to the creation of the interface. Figure 4 shows the change in the integrated density of states, which is an odd function of the energy, for the cases of $\Delta E_F = 2E_1$, $\Delta E_F = 6E_1$, and $\Delta E_F = 12E_1$, respectively. In this figure we used the value $g = 10$ to account for the 10-fold degeneracy of the d orbitals in transition metals. To obtain the corresponding

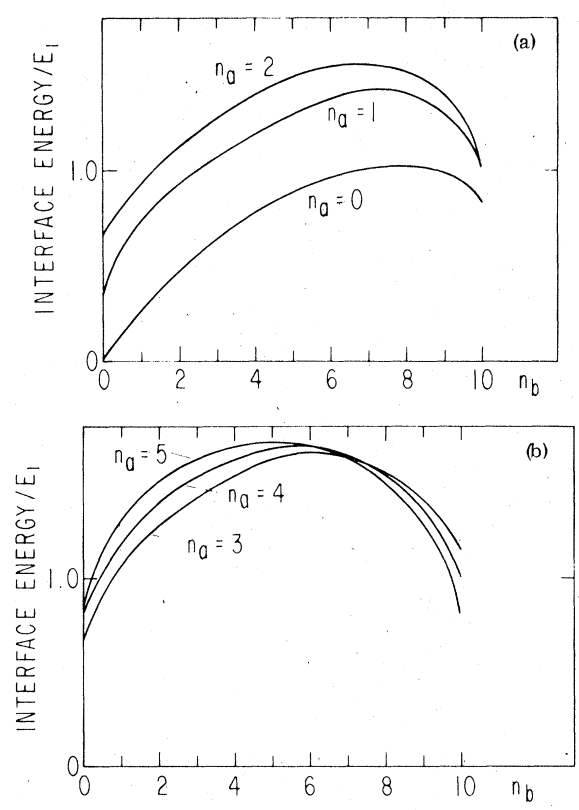

FIG. 5. Interface energy of transition metals having n_a and n_b d electrons. (a) $n_a = 0, 1, 2$. (b) $n_a = 3, 4, 5$.

interface energy we have, according to Eq. (5.11), to integrate $\Delta N(E)$ with respect to the energy, up to the common Fermi energy. The results of such a numerical calculation are shown in Fig. 5, where the interface energy for a given transition metal with $n_a d$ electrons is plotted vs n_b, the number of d electrons of the other metal forming the interface. The curves in Fig. 5 correspond to the cases where $n_a = 0, 1, \ldots, 5$. The corresponding graphs for $n_a > 5$ (i.e., $n_a = 6, \ldots, 10$) can be obtained by taking the mirror images of the curves of $10 - n_a$ electrons, with respect to the $n_b = 5$ line. This is due to the fact that in the present model, the following symmetry holds:

$$\sigma(n_a, n_b) = \sigma(10 - n_a, 10 - n_b),$$

where $n_a \leq 5$ and $n_b \leq 5$. The surface energy of transition metals can be read off the curves of Fig. 5 by looking at the points where $n_a = n_b$. Our results for the surface energies are the same as those derived earlier by Cyrot-Lackmann[18] and by Allan.[19] This is as expected, since in the limit of two identical transition metals our interface model, discussed in this section reduces to the free surface model investigated by these authors.

As can be seen from Fig. 5, the electronic contribution to the interface energy between two transition metals, of the same series, is always less than the corresponding contribution to the surface energy of a half-filled band metal (belonging to the same series). We also note that for a given transition metal, with $n_a d$ electrons, there exists another transition metal, with n_b^0 electrons, whose combined interface has the maximum interface energy. As n_a is varied, the position of this maximum drops down from $n_b^0 \approx 8$ for an empty band ($n_a = 0$) to $n_b^0 \approx 2$ for a full band ($n_a = 10$).

The interface model developed in the present work is a highly simplified and crude one. Nevertheless, we believe that certain features of a real interface, such as interface states and electron tunneling across the interface, are illustrated by our model. Thus, although a realistic physical description of a bimetallic interface might be much more complicated, we feel that many of the qualitative properties of such an interface will be similar to those described in this article.

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