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A QUANTUM MODEL FOR INTERATOMIC FORCES APPLIED TO AN INTERNAL SURFACE

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Résumé - Dans les métaux il y a des forces "non pair" importantes dues à la délocalisation quantique des électrons. On propose un modèle pour calculer les potentiels correspondants. On l'applique à l'étude de la relaxation et de la variation de la constante de force d'un atome dans le voisinage d'une surface internal par opposition à surface libre.

Abstract - In metals these are important non-pair forces between atoms due to quantum delocalization of electrons. A model is proposed for calculating such potentials. It is applied to the relaxation and change in spring constant of an atom near an internal surface in contrast to a free surface

Interatomic forces are the most basic yet the most difficult problem in solid state physics. From the rate of chemical reactions¹ to the properties of grain boundaries (see Refs. 2,3 and references therein) to crack propagation¹, these forces govern important and interesting phenomena.

Much work in this area has been done using pair potentials^{2 3 4}. For ionic materials and to some degree other insulators there is a good basis for their use. However in metals they have been widely used despite their known deficiencies (see Ref.5 and references therein). The reason for this has been the problem of determining, or even describing, multicenter potentials.

The physical origin of non-pair forces is the quantum mechanical delocalization of electrons which is present to some extent in insulators and central to the properties of metals. The electrons give rise to the forces between atoms, and so their being spread over many bonds means that the total energy of the solid depends in a complicated way on the geometrical relationships between bonds. For example the structural stability of many metal compounds depends on the orientation of distant bonds⁶.

The way to incorporate non-pair forces is to do a quantum mechanical calculation of the electronic, in particular, the bandstructure^{7,8}, contribution to the total energy. Recently this has been done by several groups^{7,8}. In these and other works on structural stability, relaxation of the atoms was a major computational problem.⁹ However, with recent improvements in methods for solving the Schrodinger equation there should be progress in this area.

The structure and properties of internal surfaces of metals are certainly problems where understanding of interatomic forces will provide insight. In addition to structure, cohesive energy, and elastic properties; barriers to various atomic rearrangements, crack propagation and plastic flow are of importance. In this paper we develop a general model of multicenter forces and apply it to the structure and elastic properties of a very simple internal surface. In this way we illuminate several aspects of grain boundaries.

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I - QUANTUM MECHANICAL MODEL FOR INTERATOMIC FORCES

It is necessary to include the quantum mechanics of electrons in any model of interatomic forces in metals. Such a model must be as simple as possible, so that it may be solved and interpreted, but without becoming unphysical. The essential ingredient for the quantum mechanics is a basis of states which describe the electronic excitations of the system. In terms of this basis the matrix elements of the hamiltonian must then be described as functions of the nuclear coordinate.

A convenient choice of basis is a set of atomic-like orbitals $\{\phi_\alpha\}$. These could literally be the atomic valence orbitals, but their use is greatly simplified if they are modified to take account of neighbouring atoms, generalized Wannier functions¹⁰. We assume that the core states are not affected by the valence electrons and write the ground state of a crystalline solid as

$$\Psi = \Phi_{\text{core}} \wedge \Psi_k$$

where Φ_{core} represents the frozen state of the core electrons, $\wedge$ indicates a produce of wave functions which is antisymmetric in the electron coordinates, $\{\Psi_k\}$ are the occupied Bloch states constructed out of the $\{\phi_\alpha\}$.

If for simplicity we suppose that there is one electron for each orbital ϕ_α , a half filled band, then we may write the energy of the state Ψ as

$$E[\Psi] = (\Phi, \mathcal{H}\Phi) + \int_{k \text{ occupied}} E(k) dk$$

where,

$$\Phi = \Phi_{\text{core}} \wedge \phi_\alpha,$$

$E(k)$ is the energy of the Bloch wave Ψ_k relative to the mean energy of the $\{\phi_\alpha\}$ and $\mathcal{H}$ is the full hamiltonian for the system. The total energy has now been split into two parts, the first is an average energy of the band, and the second is the contribution due to hybridization of the $\{\phi_\alpha\}$ to form the Bloch states. This only assumes that Ψ is the ground state to within correlations between core and valence electrons.

We construct a simple model from this by choosing the way the rigid shell potential,

$$V(L) = (\Phi, \mathcal{H}\Phi)$$

and the valence hamiltonian, $\mathcal{H}_V$, whose band structure is $E(k)$, depend on the nuclear positions. There is some evidence¹¹ that $V(L)$ is well approximated by a sum of repulsive pair potentials which depend on the overlap of charge densities. The simplest form for $\mathcal{H}_V$ is a sum of independent particle tight-binding hamiltonians for pair atoms. Thus,

$$V(L) = \sum_{\alpha\beta} V_{\alpha\beta}(r_{\alpha\beta}),$$

and

$$\mathcal{H}_V = \sum_{\alpha\beta} \{ \epsilon_{\alpha\beta}(r_{\alpha\beta}) |\phi_\alpha\rangle\langle\phi_\alpha| + h_{\alpha\beta}(r_{\alpha\beta}) |\phi_\alpha\rangle\langle\phi_\beta| \}.$$

The eigenstates of the valence hamiltonian are Ψ_k and total energy,

$$E[\Psi] = V(L) + \int_{k \text{ occupied}} (\Psi_k, \mathcal{H}_V \Psi_k) dk.$$

This model for the total energy contains quantum effects explicitly. Although the rigid ion potential and the valence hamiltonian are both the sum of pair energies, the quantum mechanics gives non-pair forces in the total energy.

II - RELAXATION AT AN INTERNAL SURFACE

The simplest model which illustrates the importance of non-pair potentials on the structure, and dynamics of an internal interface is a Holstein¹ model consisting of three atoms in a row. The internal interface is the larger gap between one pair of atoms as shown in the Figure.

Three atom model of an internal interface

Despite the simplicity of the arrangement, we can investigate the relaxation of atom B due to the presence of C, the change in its spring constant, and even the barrier to movement of the interface, the hopping of atom B across the gap to bond C.

Using the ideas of Sec. I we may write a hamiltonian for this model. We assume that the atoms each have one s-electron and further simplify it by using bonding orbitals rather than atomic orbitals as a basis for the electronic states.

$$\mathcal{H} = \frac{1}{2} k (r_1 - D)^2 + \frac{1}{2} k (r_2 - D)^2 + \sum_{\sigma} \left\{ \lambda (r_1 - D) |\phi_{1\sigma}\rangle \langle \phi_{1\sigma}| + \lambda (r_2 - D) |\phi_{2\sigma}\rangle \langle \phi_{2\sigma}| + h (|\phi_{1\sigma}\rangle \langle \phi_{2\sigma}| + |\phi_{2\sigma}\rangle \langle \phi_{1\sigma}|) \right\},$$

for $r_1, r_2 < D$,

where: $|\phi_{1\sigma}\rangle$ and $|\phi_{2\sigma}\rangle$ are kets for the bond orbitals, k is a positive parameter which gives the core repulsion, λ is a positive parameter which gives the dependence of the energy of the bonding orbitals on bond length, h is a negative electronic hopping energy, D is the diameter of the atoms, σ is the spin index, and the zero of energy has been chosen so that there is no constant in $\mathcal{H}$.

This model is solved in Ref. 1 where it is shown that atom B is stable in two positions, next to A, or next to C, if

$$\gamma^2 = -\lambda^2 / 2hk > 1$$

Note that because h is negative and k is positive, γ^2 is always positive. Thus for a given λ and k , the interface is stable for sufficiently small h . We could destroy the interface by compressing the system and thereby increasing h until γ^2 was less than one and atom B had only one stable position. In this example the interface is artificial in that it cannot be stabilized in one dimension by a difference in crystal orientation.

We can now calculate the relaxation of the internal surface compared to that of a free surface. If atom C is removed to give a free surface, then the equilibrium separation of A and B is,

$$r_{1F} = D - 2\lambda/k.$$

In the presence of atom C, the case of the internal surface,

$$r_{1I} = D - [3 + (1 - 4h^2k^2\lambda^{-4})^{1/2}] \lambda / 2k,$$

atom B relates outwards with the formation of a weak bond to C. To lowest order in h , this shift is $h^2k\lambda^3$. We may use the condition that the interface is stable,

$$\gamma^2 > 1,$$

to show that the relaxation is less than one quarter of r_{IF} .

We can also compare the spring constants for small displacements of the atom at the internal surface and the free surface. For the free surface, the spring constant is simply k , but the internal surface has a spring constant, $k_I = k - 4k\gamma^2\lambda^{-4}$.

In this case applying the condition that the surface is stable only implies that k_I is non negative. Thus the internal surface may reduce the spring constant for atom B to zero, thereby making the surface unstable.

In order to compare our results for surfaces with the bulk, we may suppose that the three atoms are now links in a linear chain with one electron per bond. Thus taking h to have its bulk value h_B so that

$$\gamma_B^2 = -\lambda^2/h_B k$$

is less than one for stability of the bulk, and removing one electron from the model, we get a bulk bond length,

$$r_B = D - \lambda/k.$$

The bond length for the atom at the internal surface falls between the bond lengths for the bulk and free surfaces as one would expect. The bulk spring constant, per bond is

$$k_B = k + \lambda^2/h_B.$$

Applying the condition on γ_B^2 for stability, we find that k_B must be positive as one would expect. Thus the spring constant for an atom at an internal surface is also intermediate between the bulk value and that for a free surface.

It is also possible for the surface atom to migrate across the gap. This process could be interpreted as a kind of plasticity, and in Ref.1 the barrier for such migration was shown to be at most $\lambda^2/2k$ which is one eighth the bond energy of the atom at a free surface, and less than one fourth the energy per bond of the bulk. For a typical metal the cohesive energy is a few eV per atom. If it is close packed (12 bonds), then this implies that the barrier for migration from one surface to the other is less than 1/4eV, a reasonable result.

III - NON PAIR FORCES

One important quality of the model solved in the previous Sec. is that it displays the failure of pair potentials to describe forces on atoms. The full potential from Ref.1 is,

$$V(r_1, r_2) = 1/2 k [(r_1 - D)^2 + (r_2 - D)^2] + 3\lambda(r_1 + r_2 - 2D)^2 - [\lambda^2(r_1 - r_2)^2/4 + h^2]^{1/2}.$$

The first two terms can be separated into pair potentials as they are pair terms in the model hamiltonian, but the third term is quantum mechanical and distinctly non-pair. Physically it comes from the delocalization of electronic wavefunctions in a metal. The electrons are spread over more than one bond and so when one bond changes the others are also affected. Even in an insulator, electrons are delocalized over several bonds. In a metal this increases to hundreds of bonds depending on defects and temperature.

Much of the interesting behaviour of the surface atom in the model comes from the non-pair term in the potential $V(r_1, r_2)$. It gives rise to the stability of the surface for small h , the stability of the bulk for large h , and the barrier to migration across the surface. The changes in bond lengths between bulk, internal surface, and free surface also arise from this term. Possibly most important, the changes in spring constants are also a consequence of the quantum mechanics and hence the non-pair forces.

IV - CONCLUSIONS

We have shown that simple arguments about the nature of interatomic bonds lead to a general model for interatomic forces, which is described in terms of pair parameters although the final forces are multicentered. The general model can be applied to a three atom model of an internal surface, in a form due to Holstein.

The atom at an internal surface relaxes outward by up to one quarter of its bond length on a free surface, due to the formation of a weak bond across the gap. This is accompanied by a softening of the elastic constant to a value below that of the free surface but not so soft as the bulk. There is even a reasonable barrier to a kind of plastic flow where an atom migrates from one side of an internal surface to the other.

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