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LETTER TO THE EDITOR

Neglecting local-field effects in the band-offset problem

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Abstract. We investigate the electronic screening at semiconductor heterojunctions, and through calculations over selected systems we show that local-field effects are capable of affecting the band offset by some tenths of an eV. Our results indicate the limits of accuracy attainable with models that emphasize the line up of some reference level and implicitly use only macroscopic screening.

In spite of the significant effort that has been devoted to the understanding of the physical mechanisms which govern potential discontinuities at semiconductor interfaces, several important issues are still open. Although the importance of fermionic response at the interface is generally recognized, arguments currently used are mostly based on macroscopic linear screening. A popular class of models (RLMs) is based on the pinning of a suitable reference level [1–4]: they use only bulk properties of the constituent materials—this results in orientation independence and transitivity of potential line ups—and the concept of macroscopic dielectric screening. One of these RLMs uses the latter just to put all semiconductors on a common absolute energy scale [2] (metallic screening), while the others use the value of the dielectric constant explicitly [3, 4] or a suitable screening factor [1] for predicting the band-edge discontinuities. The validity of the macroscopic and linear screening assumptions has never been investigated until now. The aim of this communication is to study up to what point microscopic screening can be neglected in the band-offset problem.

There is no general agreement—and even some confusion [5] in the literature—about the very starting point: what are the 'screening medium', the 'bare' perturbation and the 'screened' perturbation? In order to relate to the traditional theory of screening, we proceed as follows: we assume that the screening medium is some reference system having no interface; we then change the chemical nature of some atoms in order to build the actual interface; the electrons of the reference system respond to this perturbation, and this is precisely the screening process we wish to investigate.

In all-electron schemes the problem can be attacked in this way only if the chemical transformation involves isocoric atoms; otherwise linear response is out of the question since it is unable to account for core relaxation. General transformations can be handled

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assuming a pseudopotential viewpoint and studying the response of the valence electrons only. We notice that such a logical step is implicit in most RLMs, and in particular is crucial to the arguments of Tersoff [2].

We consider as a specific example the heterovalent GaAs/Ge (110) lattice-matched interface. Choice of the non-polar (110) orientation is made in order to avoid charged interfaces [6–8], which introduce unnecessary complications in this work. In this case, the reference crystal is CA, where C is the *virtual* (i.e. average) cation $(Ga)_{1/2}(Ge)_{1/2}$, and A is the virtual anion $(As)_{1/2}(Ge)_{1/2}$. The unperturbed periodic crystal is chosen arbitrarily in principle, our choice being that which minimizes the strength of the perturbation. The actual interface is built by chemical substitutions in this reference system: each virtual cation C is transformed into Ga (or Ge), and each virtual anion A is replaced by As (or Ge). Recent calculations [6–8] have shown that first-principles linear-response theory (LRT) gives a very good description of the electronic charge density for this case, as well as for other lattice-matched heterojunctions.

The striking success of LRT in the band-offset problem is owed basically to the fact that the valence charge density responsible for the effect is a tiny fraction of the total charge. The accuracy is further enhanced by the choice of the reference crystal: in fact the quadratic terms (responsible for the strongest non-linear effect) are in this way minimized [8].

The LRT calculations performed to date for the band-offset problem [8] do not separate the electronic response into macroscopic and microscopic terms, and hence do not allow one to check the ideas upon which RLMs are based. Nevertheless—once the linear screening problem is stated in the form given above—such separation can be performed. The response of a periodic medium to any bare perturbation $V_{\rm bare}$ generates a screened perturbation V given in reciprocal space by

$$\tilde{V}(\boldsymbol{q}+\boldsymbol{G}) = \sum_{\boldsymbol{G}'} \varepsilon^{-1}(\boldsymbol{q}+\boldsymbol{G};\boldsymbol{q}+\boldsymbol{G}')\tilde{V}_{\rm bare}(\boldsymbol{q}+\boldsymbol{G}') \tag{1}$$

where ε^{-1} is the inverse dielectric matrix. The *Umklapp* effects due to off-diagonal elements of ε^{-1} go under the name of local-field effects and reflect the microscopic inhomogeneity of a real solid [9]. When applying LRT to an interface problem, the screened potential has a $1/q$ singularity at low q (and $\boldsymbol{G}=0$), and the coefficient of $1/q$ is proportional to the electrostatic potential line up in which we are interested. Use of macroscopic screening amounts to approximating ε^{-1} in equation (1) with a diagonal response, i.e.:

$$\tilde{V}(\boldsymbol{q}) \simeq \tilde{V}_{\rm bare}(\boldsymbol{q})/\varepsilon_\infty \tag{2}$$

where ε_∞ is the electronic dielectric constant of the reference system. Such an approximation has apparently been assumed without discussion [10] in all of the RLMs. In the long-wavelength limit $\boldsymbol{q}\rightarrow 0$, the exact expression, equation (1), is re-cast in the form

$$\tilde{V}(\boldsymbol{q}) \overset{q\rightarrow 0}{=} \tilde{V}_{\rm bare}(\boldsymbol{q})/\varepsilon_\infty + \tilde{\Delta}_{\rm LF}(\boldsymbol{q}) \tag{3}$$

where the local field contribution is given by

$$\tilde{\Delta}_{\rm LF}(\boldsymbol{q}) = \sum_{\boldsymbol{G}'\neq 0} \varepsilon^{-1}(\boldsymbol{q};\boldsymbol{q}+\boldsymbol{G}')\tilde{V}_{\rm bare}(\boldsymbol{q}+\boldsymbol{G}'). \tag{4}$$

Both terms on the right-hand side of equation (3) contribute to the leading $1/q$ term and hence to the band offset. This fact demonstrates how the microscopic oscillating part of the bare perturbation gives a macroscopic contribution to the screened potential line

up. It is clear that the relative magnitude between macroscopic and local-field effects will depend on both the response of the reference crystal and the strength of the perturbing potential. We also notice that equation (3) can be interpreted both in a pseudopotential sense and in an all-electron sense; the latter case however only applies to isocoric bare perturbations V_{bare}.

To study macroscopic as well as local-field effects at the GaAs/Ge (110) interface, we performed self-consistent calculations for a periodically repeated 3 + 3 supercell with 12 atoms per unit cell and cubic lattice constant $a_0 = 10.50$ au. We used the density functional formalism [11] in the local approximation [12], a kinetic energy cut off of 14 Ryd and the Ceperley–Alder exchange-correlation energy [13]; k-space integrations have been performed with the special point technique. The LRT results have been obtained using the 'direct' method; by difference of two independent calculations. This procedure gives linear and non-linear terms together: technically the linear term is extracted by considering a suitably reduced bare perturbation, and then rescaling the screened result to unit strength. More details are given in [6–8]; the results presented here have been obtained along the same lines.

The physical quantities in which we are interested (i.e. charge densities and potentials) are periodic in the xy-planes parallel to the interface. In order to subtract off bulk effects and to enhance the interface features, we use the concept of *macroscopic* average [14, 8], which is basic to both classical and quantum electrodynamics [15]. The macroscopic quantity $\bar{\bar{f}}(z)$ is obtained from its microscopic counterpart $f(\boldsymbol{r})$ through a convolution integral:

$$\bar{\bar{f}}(z) = (1/p) \int_{z-p/2}^{z+p/2} \bar{f}(a)\, \mathrm{d}s \tag{5}$$

where p is the linear period and $\bar{f}(z)$ is the planar average of $f(\boldsymbol{r})$ in the xy-plane. For an isolated interface the discontinuity of the physical quantity $\bar{\bar{f}}(z)$ is given by $\Delta\bar{\bar{f}} = \bar{\bar{f}}(z \to -\infty) - \bar{\bar{f}}(z \to \infty)$. In our supercell calculation, we obtain the discontinuity as the difference between $\bar{\bar{f}}$ values evaluated at points where bulk-like properties are reproduced in each slab of material, which requires the use of a sufficiently thick supercell in the z direction.

We now present the results obtained for GaAs/Ge (110) using two different types of ion-core pseudopotentials: the Berkeley local potentials [16] and the non-local norm-conserving pseudopotentials [17]. We start from the local potentials for which the bare macroscopic discontinuity is uniquely defined. The planar and macroscopic averages of the bare perturbation V_{bare} are shown in figure 1(a) for the Berkeley local potentials [16]; the bare discontinuity is given by

$$\Delta\bar{\bar{V}}_{\text{bare}} = \Delta\alpha = \alpha_{\text{Ga}} + \alpha_{\text{As}} - 2\alpha_{\text{Ge}} \tag{6}$$

where α_j is defined as

$$\alpha_j = \frac{1}{\Omega} \int \left(V^{(j)}(r) + \frac{Z_j e^2}{r} \right) \mathrm{d}\boldsymbol{r} \tag{7}$$

in terms of the pseudopotenttial $V^{(j)}$ of atom j, its core charge $Z_j|e|$ and the cell volume Ω.

In the self-consistent solution, electrons polarize in response to the bare perturbation; the result is shown in figure 1(b). In the neighbourhood of the interface the electron distribution manifestly differs from in the bulk, its macroscopic average showing

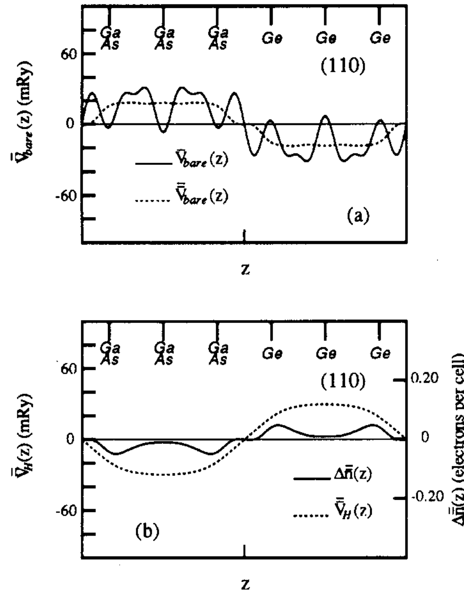

Figure 1. (*a*) Planar and macroscopic averages of the bare ionic perturbation for the GaAs/Ge (110) interface, and (*b*) macroscopic average of the electron density and Hartree potential. The results have been obtained with the local pseudopotentials of [16].

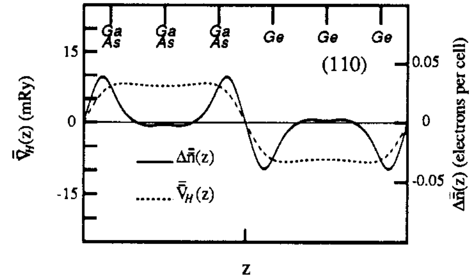

Figure 2. Macroscopic average of the electron density and Hartree potential for the GaAs/Ge (110) interface. The norm-conserving pseudopotentials of [17] are used here.

a dipole which is the origin of the potential shift. We are interested in the drop in the total self-consistent potential $\Delta\overline{\overline{V}}_{\mathrm{T}}$, which is the sum of three terms: the bare ($\Delta\overline{\overline{V}}_{\mathrm{bare}}$, equation (6)), Hartree ($\Delta\overline{\overline{V}}_{\mathrm{H}}$), and exchange-correlation ($\Delta\overline{\overline{V}}_{\mathrm{xc}}$) discontinuities. Our results are: $\Delta\overline{\overline{V}}_{\mathrm{bare}} = 0.49$ eV (figure 1(*a*)); $\Delta\overline{\overline{V}}_{\mathrm{H}} = -0.78$ eV (figure 1(*b*)) and $\Delta\overline{\overline{V}}_{\mathrm{xc}} \simeq -0.001$ eV. Therefore the total self-consistent potential line up is $\Delta\overline{\overline{V}}_{\mathrm{T}} = -0.29$ eV. Assuming the validity of the macroscopic-screening model, the electrons would readjust so as to produce a potential drop at the interface which is just the bare one divided by the dielectric constant ε_∞ of the reference crystal, i.e. $\Delta\overline{\overline{V}}_{\mathrm{T,model}} = \Delta\overline{\overline{V}}_{\mathrm{bare}}/\varepsilon_\infty$. Considering that in our case [6–8] $\varepsilon_\infty \sim 2(\varepsilon^{-1}_{\infty,\mathrm{GaAs}} + \varepsilon^{-1}_{\infty,\mathrm{Ge}})^{-1} \sim 12.5$, the model total line up is $\Delta\overline{\overline{V}}_{\mathrm{T,model}} = 0.04$ eV and, following equation (3) which can be recast as

$$\Delta_{\mathrm{LF}} = \Delta\overline{\overline{V}}_{\mathrm{T}} - \Delta\overline{\overline{V}}_{\mathrm{T,model}} \tag{8}$$

we obtained a local-field contribution $\Delta_{\mathrm{LF}}(\mathrm{GaAs/Ge}) = -0.33$ eV. We conclude that local-field effects cannot be neglected in this test case.

In the ideal situation, corresponding to $\Delta\overline{\overline{V}}_{\mathrm{T}} = 0$ (metallic-screening assumption), we would have found the reference level with respect to which we could measure energies and *ergo* we would have solved the band-offset problem. This is indeed the point of view of Tersoff [2]. Because of overscreening, it is evident that the metallic-screening assumption gives a better description than the macroscopic-screening one. Nevertheless our results indicate that local-field effects have to be taken into account, and that the

simple model described above and based on either macroscopic or metallic screening is not generally valid.

We discuss now the results obtained for GaAs/Ge (110) using modern norm-conserving pseudopotentials [17]. The resulting value for the electrostatic potential discontinuity is [7] $\Delta\bar{\bar{V}}_H = 0.22$ eV, and practically coincides with the discontinuity of the total electronic potential, since the exchange-correlation term is negligible as in the previous case. The radial part of norm-conserving pseudopotentials is angular-momentum dependent [17], which is a complication in our analysis of the screening mechanisms since $\Delta\bar{\bar{V}}_{bare}$ is not defined. However, the GaAs/Ge system discussed here is a particularly simple case, its constituents being isocoric atoms. In fact, since the non-local contribution to the ionic pseudopotential originates from core orthogonalization, we expect the *difference* between the Ga, As and Ge pseudopotentials—and hence the bare perturbation V_{bare}—to be essentially local: this has been checked by calculating the quantity $\Delta\alpha$ separately for the different l-components of V_{bare}: we get (in eV) $\Delta\alpha_0 = -0.151$, $\Delta\alpha_1 = -0.143$, $\Delta\alpha_2 = -0.152$, and $\Delta\alpha_{l>2} = -0.167$. Therefore the bare discontinuity, although not exactly defined, can be assumed to be $\Delta\bar{\bar{V}}_{bare} = -0.155 \pm 0.012$ eV, where the error bar is intrinsic to the non-locality. Using this value within diagonal screening, one gets

$$\Delta\bar{\bar{V}}_{H,model} = ((1/\varepsilon_\infty) - 1)\Delta\bar{\bar{V}}_{bare} = 0.14 \pm 0.01 \text{ eV}$$

which amounts to a local-field contribution

$$\Delta_{LF} = \Delta\bar{\bar{V}}_H - \Delta\bar{\bar{V}}_{H,model} = 0.08 \mp 0.01 \text{ eV}.$$

Though in this calculation the absolute magnitude of the local-field contribution to the line up is smaller than in the previous one (i.e. for the local pseudopotentials), its value represents a sizeable fraction of the whole effect.

To provide additional evidence of the relevance of local-field effects we present results for the AlP/Si (110) interface obtained with norm-conserving pseudopotentials [17] and a cubic lattice constant $a_0 = 10.26$ au. The calculated electrostatic discontinuity amounts to $\Delta\bar{\bar{V}}_H = 0.12$ eV. We observe that, in this case too, the atomic constituents are isocoric and the perturbation is essentially local. Proceeding as described above we obtain a bare discontinuity $\Delta\bar{\bar{V}}_{bare} = -0.07 \pm 0.03$ eV and assuming $\varepsilon_\infty \sim 10$, the local-field contribution is $\Delta_{LF} = 0.06 \mp 0.03$ eV. We notice that the local field contribution to the potential line up is relatively more important in this case than in GaAs/Ge. This is not surprising since local-field effects are more important in less metallic systems.

All results presented above have been obtained using first-principles LRT. In order to check the validity of the LRT results, we also performed standard supercell SCF calculations; the results of the latter are in excellent agreement with LRT predictions, the accuracy being better than 0.01 eV for all the systems studied. The same accuracy was found in [6–8].

We have so far discussed the relevance of local-field effects in the context of the popular models based on alignment of reference levels [1–4]. Models have been proposed where the concept of charge distribution is the basic one [18, 14, 19]. The present work has little to say with respect to them, simply because they are *not* related to a traditional screening problem: in these models either there is no screening at all [18, 14], or the 'screening medium' has a built-in interface [19].

In conclusion, we have investigated, in selected examples, the validity of the macroscopic screening ansatz, which is crucial to all RLMS. We have shown that, although

macroscopic screening gives a qualitative picture of charge readjustment at the interface, the microscopic-field contributions cannot always be acritically neglected [10]—in fact they can possibly be of the same order of magnitude as the band offset itself.

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