# Exchange-correlation potentials at semiconductor interfaces

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(Received 26 April 1993)

We investigate the exact Kohn-Sham exchange-correlation potential at semiconductor interfaces, including Schottky barriers, heterojunctions, and semiconductor surfaces. By considering the electron density at the interface, we deduce the way in which the exact exchange-correlation potential differs from its bulk counterpart. The potential has a slow spatial variation related to the discontinuity, $\Delta$, that occurs on addition of an electron to the bulk semiconductor. This variation, which corresponds to an ultra-non-local "vertex correction" in the Kohn-Sham formulation of the dielectric response of the semiconductor, results in correction terms for Schottky barrier heights and band offsets calculated using Kohn-Sham orbital energies. The effect is exhibited numerically for a model semiconductor.

## I. INTRODUCTION

In the Kohn-Sham formulation of density-functional theory (DFT),[1] the exact ground-state electron density $n_0(\mathbf{r})$ and total energy $E_0$ of a system of interacting electrons moving in an external potential $V_{\text{ext}}(\mathbf{r})$ are reproduced by a fictitious system of *noninteracting* electrons (the so-called Kohn-Sham electrons) moving in an effective potential

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) , \tag{1}$$

where the additional parts of the effective potential are the Hartree potential

$$V_H(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

and the exchange-correlation potential

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \tag{3}$$

defined in terms of two universal functionals of the electron density: the Hartree energy

$$E_H = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{4}$$

and the exchange-correlation energy $E_{\text{xc}}[n]$, defined by

$$E[n] = \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d^3r + T_s[n] + E_H[n] + E_{\text{xc}}[n] , \tag{5}$$

where $E[n]$ is the functional (whose existence was proved by Hohenberg and Kohn[2]) which has a minimum value [with respect to particle-conserving variations in $n(\mathbf{r})$] of $E_0$ when $n$ is equal to $n_0$; and $T_s[n]$ is the kinetic energy of noninteracting electrons with density $n$. Neither the exchange-correlation energy functional $E_{\text{xc}}[n]$ nor its functional derivative $V_{\text{xc}}(\mathbf{r})$ are known exactly for any but the simplest systems, and in practical calculations the local-density approximation (LDA) is normally used:

$$E_{\text{xc}} = \int n(\mathbf{r})\varepsilon_{\text{xc}}(n(\mathbf{r}))d^3r, \quad V_{\text{xc}}(\mathbf{r}) = \mu_{\text{xc}}(n(\mathbf{r})) , \tag{6}$$

where $\varepsilon_{\text{xc}}(n)$ is the exchange-correlation energy per electron in a homogeneous electron gas of density $n$ (which is known very accurately from numerical calculations[3]), and $\mu_{\text{xc}}(n) = d(n\varepsilon_{\text{xc}}(n))/dn$.

Although in the LDA $E_{\text{xc}}[n]$ is explicitly a smooth functional of $n$ [since $\varepsilon_{\text{xc}}(n)$ is], there is strong evidence that the exact functional is far from analytic. In an infinite semiconductor, it has been shown[4,5] that $V_{\text{xc}}(\mathbf{r})$ jumps by an amount $\Delta$, of the order of the band gap $E_g$, between the ($N$)-electron system (valence band exactly filled) and the ($N+1$)-electron system (one electron in the conduction band), where $\Delta$ is equal to the difference between the exact band gap of the semiconductor, $E_g$, and the band gap of the Kohn-Sham electrons, $E_g^{\text{DFT}}$:

$$E_g = E_g^{\text{DFT}} + \Delta, \quad \Delta = V_{\text{xc}}^{(N+1)}(\mathbf{r}) - V_{\text{xc}}^{(N)}(\mathbf{r}) . \tag{7}$$

$\Delta$ has been evaluated for several semiconductors[6] and found to be a substantial fraction of the gap. Moreover, the calculated values of $\Delta$ are close to the differences between the Kohn-Sham band gaps calculated using the LDA, and the experimental bad gaps, suggesting that the LDA is rather close to the exact exchange-correlation potential in these bulk semiconductors. In addition, the exchange-correlation potential itself is found to be remarkably close to the LDA exchange-correlation potential.

In a previous paper[7] we discussed the variation of the exact exchange-correlation potential in a Schottky barrier, and deduced that in the depletion layer $V_{\text{xc}}(\mathbf{r})$ shows a slow *spatial* variation which is related to $\Delta$, the discontinuous change in $V_{\text{xc}}$ with particle number in bulk semiconductors. In this paper we describe the origin of this spatial behavior, extend our results to other semiconductor systems with depletion layers, and present the results of a model calculation which exhibits this effect.

## II. GENERAL PRINCIPLES DISCUSSED FOR A METAL-SEMICONDUCTOR INTERFACE

For definiteness we shall explain the effect in detail for the example of a metal-semiconductor interface, before going on in later sections to extend the results to other systems. In the usual picture of the formation of a Schottky barrier in the absence of defects (Fig. 1), the Fermi energy of the metal is "pinned" relative to the valence and conduction bands of the semiconductor because of the formation of *metal-induced gap states* (MIGS) decaying exponentially into the semiconductor, with energies in the band gap, and the self-consistency requirement that the electrostatic potential produced by the filling of those MIGS below the chemical potential, $\mu$, be consistent with the local variation of the band edges.[8] In a doped semiconductor (or, indeed, any semiconductor in which the bands are pinned in a particular way by some other mechanism far from the interface) a slowly varying electrostatic (Hartree) potential is set up which bends the semiconductor bands so that, in the bulklike semiconductor region far from the interface, the chemical potential lies just below the valence-band maximum in a *p*-type semiconductor, or just above the conduction-band minimum in an *n*-type semiconductor.

The subject of this paper is the slowly varying electrostatic potential and its counterpart in DFT. Certainly the electrostatic potential itself is equal to the Hartree potential in DFT (since the Hartree potential is a simple
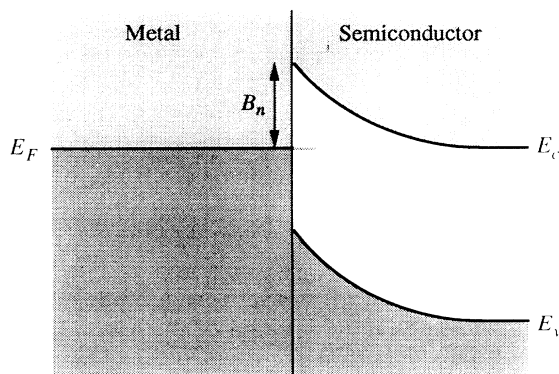


FIG. 1. The principles of Schottky barrier formation, in the usual one-electron picture, illustrated for an *n*-type semiconductor. The metal Fermi energy is "pinned" by the constraint that the filling of the exponentially decaying metal-induced gap states in the first few layers of the semiconductor (shown in light grey) be electrostatistically consistent with the band alignment. The *n*-type barrier height $B_n$ is the difference between the Fermi energy and the valence-band edge adjacent to the interface. The band banding inside the semiconductor, which occurs over many hundreds of Å, is electrostatic in origin and usually described within the depletion approximation. This picture remains valid within a many-body theory, since the self-energy operator, which describes exchange and correlation, does not contribute to any band bending on the scale of this diagram, and serves only to set the correct band gap in the first place. However, as discussed in this paper, in DFT the exchange-correlation potential also shows a slow spatial variation which alters the band bending.

analytical functional of the electron density, which is given correctly by the DFT calculation). But the DFT effective potential has a further component, the exchange-correlation potential $V_{xc}(\mathbf{r})$, which (unlike its counterpart in many-body theory, the self-energy operator) has been shown to be a rather nonanalytical functional of the electron density when the particle number is varied.[4,9,6] Our central point is that in systems with slowly varying external potentials such as depletion layers, $V_{xc}(\mathbf{r})$ must also exhibit a similar slow spatial variation [making it an ultra-non-local functional of the density: the density is the same from unit cell to unit cell (apart from exponentially small differences), but $V_{xc}(\mathbf{r})$ is not]. This spatial variation in $V_{xc}$ is necessary to ensure that the fictitious noninteracting electrons of DFT reproduce the true ground-state electron density of the interacting system.

We demonstrate that this spatial variation in $V_{xc}(\mathbf{r})$ is nonzero in Secs. III and IV below. But for the moment we shall assume that the slow spatial variation in $V_{xc}(\mathbf{r})$ exists, and examine its consequences. The major effect is that the local band edges in the DFT calculation, which of course bend according to the slow spatial variation of the DFT effective potential, have a different spatial dependence from the true (quasiparticle bands). This is illustrated in Fig. 2. At the interface the DFT bands are pinned by MIGS in an analogous way to the quasiparticle bands, but in general there is no requirement that either the DFT conduction-band minimum or DFT valence-band maximum be aligned with the corresponding quasiparticle band extremum. On the other hand, far to the right, the DFT and quasiparticle valence-band maxima in a *p*-type semiconductor (or conduction-band minima in *n* type) must be aligned (since the highest occupied DFT eigenvalue equals the ionization potential[9]). Therefore the slow variation in $V_{xc}(\mathbf{r})$ is exactly sufficient to bend the DFT bands *relative to the quasiparticle bands*, so that these requirements can both be satisfied; we call the total amount of such bending $\Gamma_p$ in the *p*-type case and $\Gamma_n$ in the *n*-type case. Since the electron density, and hence the exchange-correlation potential,[10] in the immediate vicinity of the interface is independent of any doping of the semiconductor, the disposition of the DFT bands relative to the quasiparticle bands at the interface is the same in Figs. 2(a) and 2(b), so that we obtain the relationship

$$\Gamma_p + \Gamma_n = \Delta , \tag{8}$$

where $\Delta$ is the discontinuity described above.

We define the DFT *p*- and *n*-type Schottky barrier heights as $B_p^{\mathrm{DFT}} = \mu - E_v^{\mathrm{DFT}}$ and $B_n^{\mathrm{DFT}} = E_c^{\mathrm{DFT}} - \mu$, where $\mu$ is the chemical potential and $E_v^{\mathrm{DFT}}$ and $E_c^{\mathrm{DFT}}$ the DFT band edges immediately to the right of the interface. This corresponds to the definitions of the quasiparticle Schottky barrier heights $B_p = \mu - E_v$ and $B_n = E_c - \mu$. From Fig. 2 it is evident that $\Gamma_p$ and $\Gamma_n$ are the corrections to the exact Kohn-Sham barrier heights:

$$B_p^{\mathrm{DFT}} = B_p - \Gamma_p, \quad B_n^{\mathrm{DFT}} = B_n - \Gamma_n . \tag{9}$$

### III. THE SLOW VARIATION IN $V_{xc}$

We shall now demonstrate that the variations in $V_{xc}(\mathbf{r})$ within the depletion layers in both $p$- and $n$-type cases are nonzero. The argument hinges on the slight change of the electron density within each unit cell of the semiconductor when a slowly varying potential is applied (essentially a polarization charge). Since the DFT electron density is exact, the Kohn-Sham electrons must also reproduce this polarization charge. But the Kohn-Sham electrons feel a different potential from the "potential" appearing in many-body theory (the Kohn-Sham effective potential is a local, energy-independent potential, whereas the self-energy operator is nonlocal and energy dependent). Moreover the Kohn-Sham electrons have a band gap $E_{g,\mathrm{DFT}}$, which differs from the quasiparticle band gap by the discontinuity $\Delta$. Therefore, as we now show, the slowly varying potential felt by the Kohn-Sham electrons, $V_{\mathrm{eff}}$, must show a different spatial variation from that appearing in the electrostatic potential ( $V_H$ ).

A simple first-order perturbation theory argument gives an estimate for this effect. We consider a bulk semiconductor (with gap $E_g$ and DFT gap deviation $\Delta$) to which a slowly varying additional potential is applied
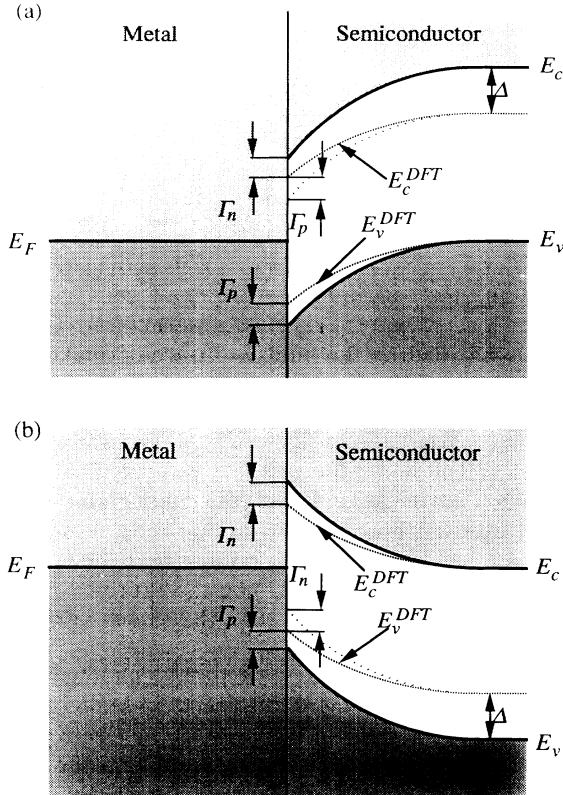
(a)

Metal                    Semiconductor

FIG. 2. Quasiparticle and DFT bands at a Schottky barrier: (a) $p$-type semiconductor; (b) $n$-type semiconductor. The DFT bands are bent relative to the quasiparticle bands by a slow spatial variation of $V_{xc}(\mathbf{r})$ by a net amount of $\Gamma_p$ or $\Gamma_n$, respectively. Correspondingly, the $n$- and $p$-type Schottky barrier heights are in error by amounts $\Gamma_p$ and $\Gamma_n$, respectively, where $\Gamma_p + \Gamma_n = \Delta$. The disposition of the DFT bands relative to the quasiparticle bands at the interface is the same in (a) and (b).

(whose origin might be the electrostatics of a depletion layer, but this is not relevant to the argument). Let the resulting (self-consistent) net variation of the external potential plus the Hartree potential (i.e., the electrostatically screened potential) across a given small region (several unit cells) be $\Delta V$. This will cause both valence- and conduction-band wave functions to be mixed into a given valence-band wave function. But the admixture of the other valence-band wave functions is merely a unitary transformation among the valence-band wave functions which does not affect the electron density. What *does* affect the electron density is the admixture of conduction-band wave functions, and this is dominated by the lowest conduction band $\Psi_{c,\mathrm{bulk}}$: locally,

$$\Psi_v \approx \Psi_{v,\mathrm{bulk}} + \text{other valence bands}$$

$$- \frac{\langle \Psi_{c,\mathrm{bulk}} | \Delta V | \Psi_{v,\mathrm{bulk}} \rangle}{E_g} \Psi_{c,\mathrm{bulk}} \tag{10}$$

in many-body theory (where we have made the quasiparticle approximation), and also

$$\Psi_v^{\mathrm{DFT}} \approx \Psi_{v,\mathrm{bulk}}^{\mathrm{DFT}} + \text{other valence bands}$$

$$- \frac{\langle \Psi_{c,\mathrm{bulk}}^{\mathrm{DFT}} | (\Delta V + \Delta V_{xc}) | \Psi_{v,\mathrm{bulk}}^{\mathrm{DFT}} \rangle}{E_g^{\mathrm{DFT}}} \Psi_{c,\mathrm{bulk}}^{\mathrm{DFT}} \tag{11}$$

in DFT. We make the approximation that the DFT wave functions are equal to the quasiparticle wave functions (which is known to be approximately true[11,6]). The electrostatic potential variation $\Delta V$ varies slowly on the scale of a unit cell, and in DFT $\Delta V_{xc}$ must also be slowly varying so as not to disturb the electron density. This allows us to write

$$\frac{\langle \Psi_{c,\mathrm{bulk}}^{\mathrm{DFT}} | (\Delta V + \Delta V_{xc}) | \Psi_{v,\mathrm{bulk}}^{\mathrm{DFT}} \rangle}{\langle \Psi_{c,\mathrm{bulk}} | \Delta V | \Psi_{v,\mathrm{bulk}} \rangle} \approx \frac{\Delta V + \Delta V_{xc}}{\Delta V}, \tag{12}$$

where $\Delta V$ and $\Delta V_{xc}$ are the net variations over a given length (several unit cells). The condition that DFT reproduce the correct electron density then reduces to the condition that the coefficient of the conduction-band wave function in Eqs. (10) and (11) be equal. Using (7), we then obtain

$$\frac{\Delta V_{xc}}{\Delta V} \approx - \frac{\Delta}{E_g}, \tag{13}$$

which is about $-0.5$ in silicon, for example.[6] If this relation applies throughout the $p$-type depletion layer, then $\Gamma_p$, the total slow variation in $V_{xc}$, will be $-\Delta/E_g$ times the total variation in the electrostatic potential. But the latter is simply the Schottky barrier height, $B_p$. Therefore we have the results

$$\Gamma_p \approx \frac{\Delta}{E_g} B_p,$$

and similarly, $\tag{14}$

$$\Gamma_n \approx \frac{\Delta}{E_g} B_n,$$

which correctly add up to $\Delta$ (since $B_p + B_n = E_g$).

We note that although this effect is straightforward when presented in terms of the elementary ideas used above, when couched in the language of many-body theory it is part of the so-called vertex correction to the random-phase approximation (RPA) dielectric function: the effect of exchange and correlation on the density response function of the system to a change in the applied potential. As noted previously in connection with the validity of arguments based on the ability of DFT to give the correct static density response function,[12] any nonanalytic dependence of $V_{xc}$ on the density is reflected, and emphasized, in the exchange-correlation kernel $K_{xc}$ which enters the expression for the vertex correction to the static response function when expressed in terms of quantities calculable using DFT. Here we are observing the same thing, but in connection with a spatial variation in $V_{xc}$ which is related to its nonanalytic dependence on the number of electrons in a bulk semiconductor.

We note further that since the present nonanalytic behavior of $V_{xc}$ and $K_{xc}$ is completely missing from the local-density approximation, it is not possible for the LDA to produce an accurate account of the long-wavelength, static dielectric screening of a bulk semiconductor, whether or not the LDA exchange-correlation kernel is taken into account. This also explains the improvement in the static dielectric constants of semiconductors obtained[13] when the LDA band gap is artificially opened to the experimental value by applying a "scissors operator" (i.e., rigidly shifting the conduction bands upwards to cause the minimum band gap to agree with experiment) before calculating the dielectric response. However, such a procedure is not likely to represent the *full* effect of going from the LDA static dielectric response to the true DFT static dielectric response (the latter being exactly correct): in particular, there seems to be no reason to expect that details of the short-range screening should be improved.

From consideration of the disposition of the DFT band edges relative to the Fermi energy, it is possible to provide rigorous bounds on the errors $\Gamma_p$ and $\Gamma_n$, since if the DFT conduction band fell below the Fermi level (or the DFT valence band rose above it), the number of electrons in a macroscopic region would be incorrect. The $p$- and $n$-type cases thus provide four limiting cases, from which the bounds

$$\Delta - B_n \leq \Gamma_p \leq B_p, \quad \Delta - B_p \leq \Gamma_n \leq B_n \qquad (15)$$

are immediately obtained. [These are correctly obeyed by the approximate expressions (14)].

## IV. MODEL CALCULATIONS

Godby, Schlüter, and Sham[6] showed that the self-energy operator of four semiconductors as calculated from first principles using the GW approximation could be approximated by the functional form

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) \approx \frac{f(\mathbf{r}) + f(\mathbf{r}')}{2} g(|\mathbf{r} - \mathbf{r}'|) h(\omega) . \qquad (16)$$

Moreover, the nonlocality ($g$) was the major factor responsible for the increase in the band gap on going from

the LDA (or exact DFT) exchange-correlation potential to the self-energy operator. [The other essential difference, the energy-dependence ($h$), gave a small decrease in the band gap.[6]] Here we use this model self-energy operator (ignoring the energy dependence) to investigate the behavior of the exact exchange-correlation potential in a semiconductor's depletion layer.

We consider a model one-dimensional semiconductor, which will be treated numerically in a supercell consisting of 20 basic unit cells (to allow for the possibility of a slowly varying potential which will have the periodicity of the large supercell). We first consider the many-body-theory description of the interacting system, in which the single-particle Green's function obeys the equation

$$\left[ i\frac{\partial}{\partial t} - [ -\tfrac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})] \right] G(\mathbf{r}t\mathbf{r}'t')$$

$$- \int d^3r'' dt'' \Sigma(\mathbf{r}t\mathbf{r}''t'') G(\mathbf{r}''t''\mathbf{r}'t')$$

$$= \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \qquad (17)$$

where the external potential plus the Hartree potential is taken to be

$$V_{ext}(x) + V_H(x) = V_0 \cos\frac{2\pi x}{a} + \lambda \cos\frac{2\pi x}{20a} \qquad (18)$$

[where $a$ is the lattice parameter, $V_0$ is the amplitude of the potential, and $\lambda$ is the amplitude of an (optional) slowly varying potential (with a period of 20 unit cells)], and the self-energy operator is taken to be the nonlocal potential

$$\Sigma(x, x', \omega) = \frac{f(x) + f(x')}{2} g(|x - x'|) , \qquad (19)$$

where $f(x) = -F_0[1 - \cos(2\pi x/a)]$ is a negative function with the periodicity of one unit cell, and $g(y) = \pi^{-1/2} w^{-1} \exp - (y/w)^2$ is a normalized Gaussian of width $w$ (which in the limit $w \to 0$ would make $\Sigma$ a local potential). The electron density of this model semiconductor is then simply calculated by direct diagonalization using a basis set of plane waves, and sampling the supercell's Brillouin zone at the $\Gamma$ point. The electron density in a particular unit cell (the cell where the slowly varying external potential is varying most rapidly, i.e., 60–64 a.u.) is shown in Fig. 3 for zero and nonzero values of $\lambda$ (see below), displaying the expected polarization of the electron density when the slowly varying potential is turned on.

Note that the self-energy operator $\Sigma$, although nonlocal, does not have any nonlocality on the scale of the supercell, and is the same in two cells whose electron density is the same, as is physically reasonable in the absence of long-range Coulomb effects. In contrast, we shall see that the exchange-correlation potential, which is not a quantity with direct physical significance, *does* have an ultra-non-local functional dependence on the electron density, and is *not* the same in two cells whose electron density is the same.

We then construct an *exact* density-functional theory for this model system. Using standard iterative nonlinear optimization techniques,[14] we determine the *local* poten-

tial[15] $V_{eff}(x)$ which, when filled with noninteracting electrons, reproduces the known electron density. The exact exchange-correlation potential is then $V_{xc} = V_{eff} - (V_{ext} + V_H)$. Performing this procedure for $\lambda = 0$ allows us to calculate the "bulk" exchange-correlation potential, and comparing the energy gap calculated using this potential with that calculated using the nonlocal potential gives the value of the discontinuity $\Delta$. Then we repeat the calculation with $\lambda \neq 0$, allowing us to calculate whether $V_{xc}$ acquires any slow variation in the presence of a slowly varying external and Hartree potential.

With $V_0 = 0$, $F_0 = 4.1$ eV, $a = 4$ a.u., and $w = 2$ a.u. (noncritical values, chosen to be reasonably representative of a real semiconductor such as silicon), the following are true.

(a) With $\lambda = 0$, we obtain $E_g = 2.20$ eV, and $E_{g,DFT} = 1.89$ eV, giving a DFT inherent band-gap error (the discontinuity in the exchange-correlation potential on addition of an electron) of $\Delta = 0.31$ eV.

(b) With $\lambda = 0.95$ eV, across the unit cell shown in Fig. 3 we obtain a net variation of $\Delta V = \Delta V_{ext} + \Delta V_H = 0.29$ eV, while $\Delta V_{xc} = -0.04$ eV.

The total Kohn-Sham potential $V_{ext}(x) + V_H(x) + V_{xc}(x)$ obtained for the values of the parameters in case (b) is shown in Fig. 4, together with its slowly varying component [the last term in Eq. (18) plus the slowly varying part of $V_{xc}(x)$]. The Fourier components of the exchange-correlation potential are shown in Fig. 5, for cases (a) and (b) above.

The nonlinear optimization is very stable, and reproduces the "target" electron density to one part in $10^5$ at each point in space ($10^2$ times smaller than the amplitude of the change in electron density on turning on $\lambda$ to a typical value). The corresponding Fourier components of the calculated potential, and the resulting band gaps, are accurate to approximately $10^{-4}$ eV. Therefore the two decimal places given above are fully significant.

The results given confirm the existence of the effect discussed earlier. They also justify the simple perturbation-theory argument given in Sec. III, which would predict



FIG. 4. The model one-dimensional semiconductor. The calculated Kohn-Sham potential $V_{ext}(x) + V_H(x) + V_{xc}(x)$ is shown as a function of position. The slowly varying component with period 80 a.u. is additionally displayed separately.
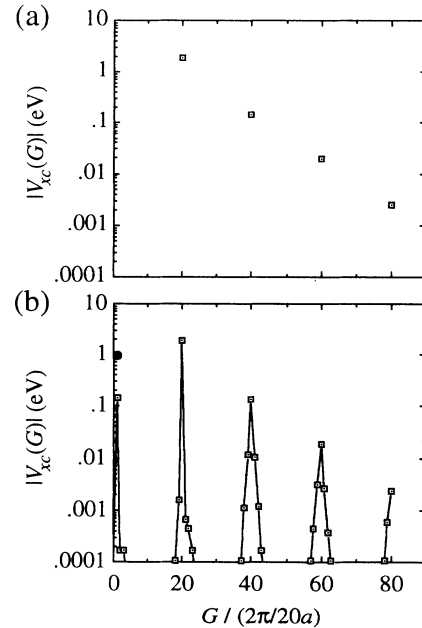


FIG. 5. The Fourier components (i.e., the coefficients of $\cos Gx$) of the exchange-correlation potential $V_{xc}(x)$ in the model semiconductor without and with a slowly varying applied potential: (a) $\lambda = 0$, (b) $\lambda = 0.95$ eV. In case (a), the Fourier components of the potential are zero except at the reciprocal-lattice vectors of the underlying unit cell (multiples of $2\pi/a$), whereas in case (b) these peaks have acquired "satellites" corresponding to the slow variation in $V_{xc}$ discussed in this paper (in particular, the large new Fourier component at $G = 2\pi/20a$, the same wave vector as that of the applied slowly varying potential). In graph (b), the lines join adjacent points to guide the eye, and, for comparison, the slowly varying part of $V_{ext} + V_H$ (i.e., $\lambda$) is denoted by a solid circle. The $G = 0$ component of $V_{xc}$, which is arbitrary in the present procedure, is set to zero in both (a) and (b).
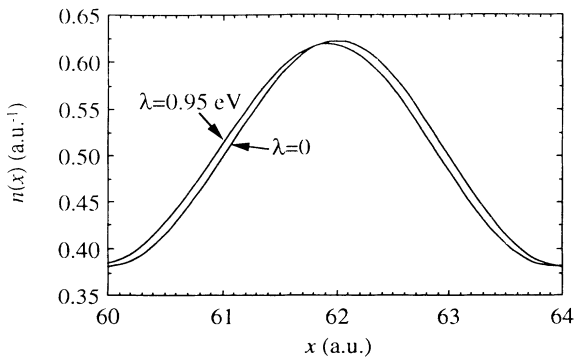


FIG. 3. The electron density in a particular semiconductor cell (the cell from 60 to 64 a.u.) with and without an imposed slowly varying potential (with overall amplitude $\lambda = 0.95$ eV). The polarization of the electron density is responsible for the induced slow variation in the exchange-correlation potential.
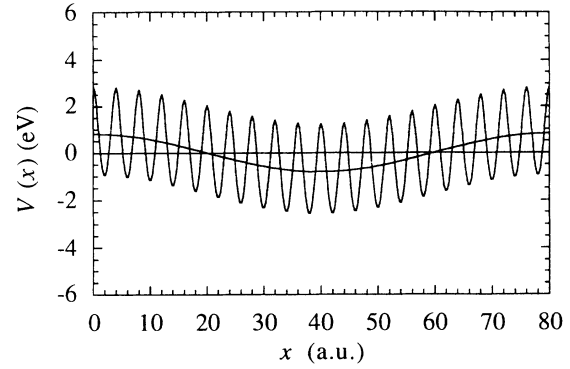
$$\frac{\Delta V_{\text{xc}}}{\Delta V} \approx -\frac{\Delta}{E_g} = -0.143 , \tag{20}$$

in good agreement with the value of $-0.148$ obtained from our numerical calculations (see above). An alternative measure of the same effect is obtained by taking the ratio of the $G = 2\pi/a$ Fourier component of $V_{\text{xc}}$ ($-0.141$ eV) to that of $V_{\text{ext}} + V_H$ (0.95 eV), which is also $-0.148$.

## V. HETEROJUNCTIONS AND SURFACES

Identical considerations apply to other systems with depletion layers. In Fig. 6 we show the corresponding disposition of the quasiparticle and DFT band edges in a semiconductor heterojunction. This time there are four possibilities if the semiconductors are doped: p-p, n-n, p-n, and n-p; we show p-p for purposes of illustration. In such systems there is a depletion layer on each side of the interface, so that $V_{\text{xc}}$ will have a slow spatial variation on each side, giving rise to a correction to the Kohn-Sham valence-band offset which is the difference between the variations:

$$E_{vA} - E_{vB} = (E_{vA}^{\text{DFT}} - E_{vB}^{\text{DFT}}) + (\Gamma_{vA} - \Gamma_{vB}) \tag{21}$$

and, correspondingly, for the conduction-band offset,

$$E_{cB} - E_{cA} = (E_{cB}^{\text{DFT}} - E_{cA}^{\text{DFT}}) - (\Gamma_{cB} - \Gamma_{cA}) , \tag{22}$$

where we call the total amount of bending in semiconductor $A$ $\Gamma_{vA}$ for the case where semiconductor $A$ is $p$ type, and so on.[16] It is clear that the DFT valence-band offset is in error by $\Gamma_v = \Gamma_{vA} - \Gamma_{vB}$. Similarly in the $n$-$n$ case it is clear that the conduction-band offset is in error by $\Gamma_c = \Gamma_{cA} - \Gamma_{cB}$. Furthermore, since (as in the case of the
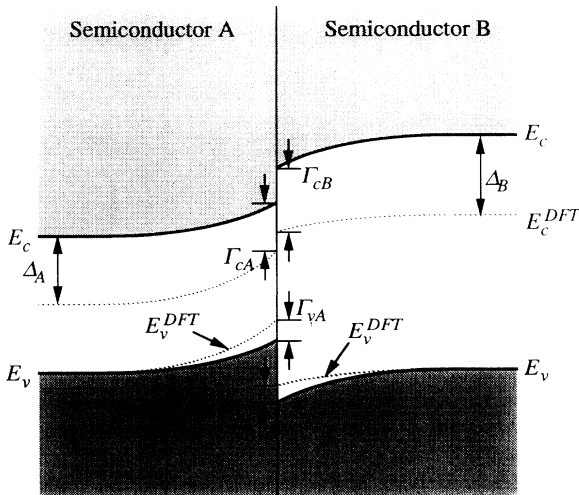


FIG. 6. Quasiparticle and DFT bands near a $p$-type–$p$-type semiconductor heterojunction. The DFT bands are bent relative to the quasiparticle bands by a slow spatial variation of $V_{\text{xc}}(\mathbf{r})$ by a net amount $\Gamma_{cA}$ or $\Gamma_{vA}$, respectively, in semiconductor $A$, and $\Gamma_{cB}$ or $\Gamma_{vB}$, respectively, in semiconductor $B$. Correspondingly, the conduction- and valence-band offsets are in error by amounts $\Gamma_c = \Gamma_{cA} - \Gamma_{cB}$ and $\Gamma_v = \Gamma_{vA} - \Gamma_{vB}$, respectively, where $\Gamma_c + \Gamma_v = \Delta_A - \Delta_B$.

Schottky barrier) the alignment of the DFT bands relative to the quasiparticle bands must be independent of the interface,[17] we obtain

$$\Gamma_v + \Gamma_c = \Delta_A - \Delta_B . \tag{23}$$

To estimate the corrections, we may construct a similar perturbation theory argument to that given above. This yields the estimates

$$\Gamma_{vA} \approx \frac{\Delta_A}{E_{gA}} X_{vA} , \quad \Gamma_{cA} \approx \frac{\Delta_A}{E_{gA}} X_{cA} , \tag{24}$$

etc., where $X_{vA}$ is the total amount of quasiparticle band bending in $A$, where $A$ is $p$ type, and so on.

We note that the corrections $\Gamma_v$ and $\Gamma_c$ are expected to be small, in contrast to the case of a Schottky barrier. This is because $\Delta$, $E_g$ (especially $\Delta/E_g$), $X_v$ and $X_c$ are generally of similar size in each of the two components of a typical heterojunction (for example, see Ref. 6 for the values of $\Delta$). Therefore $\Gamma_{vA} \approx \Gamma_{vB}$, so that $\Gamma_v \approx 0$; and similarly $\Gamma_c \approx 0$. This is consistent with the known success of LDA calculations[18] in predicting the values of valence-band offsets.

One may also apply the arguments to the case of a semiconductor surface in which occupation of a surface state (or states) causes the semiconductor bands to bend. This is very similar to the case of a Schottky barrier, except that the role of the metal is played by the vacuum, and the role of the Fermi energy by the vacuum level. In the case of a $p$-type semiconductor, the valence band is aligned with the vacuum level far to the right, and the total amount of surface band bending is in error in the DFT calculation by an amount $\Gamma_p$. Similarly in the $n$-type case the band bending is in error by $\Gamma_n$, where $\Gamma_p + \Gamma_n = \Delta$.

## VI. IMPLICATIONS
## FOR PRACTICAL CALCULATIONS

The local-density approximation for the exchange-correlation potential causes $V_{\text{xc}}$ at a given point to have a (continuous) functional dependence only on the electron density at that point. Therefore, two systems in which the electron densities have identical (or very nearly identical) forms in particular regions of space will have identical (or very nearly identical) exchange-correlation potentials in those regions. In particular, the LDA will not be capable of exhibiting the "healing" of the exchange-correlation potential toward a particular bulk value within a region in which the electrostatic potential varies (as discussed in Sec. III for exact DFT), just as the LDA exchange-correlation potential does not exhibit the discontinuity $\Delta$ on addition of an electron to the bulk semiconductor. However, there is evidence that $V_{\text{xc}}^{\text{LDA}}$ is rather close to the exact exchange-correlation potential in many systems, even bulk semiconductors,[6] apart from a possible overall constant (which would accommodate the missing discontinuity $\Delta$, for example). It is therefore appropriate to consider how much of the behavior of the exact $V_{\text{xc}}$ deduced in this paper also applies to $V_{\text{xc}}^{\text{LDA}}$, especially since most practical DFT calculations use the LDA.

Let us first consider a LDA calculation of a Schottky barrier. If we take it that the electron density in the interface region is reproduced accurately by the LDA (for a discussion of which see below), the electrostatic contribution to the barrier will be correct. It is only then necessary to determine how the quasiparticle band edges (and, in the metal, the Fermi energy) are aligned relative to their LDA counterparts. This may be done by calculating the quasiparticle and LDA band edges in a bulk semiconductor, and the quasiparticle and LDA Fermi energies in a bulk metal, and the quasiparticle barrier height is then

$$
\begin{aligned}
B_p &= E_F - E_v \\
&= B_p^{\text{LDA}} + (E_F - E_F^{\text{LDA}}) - (E_v - E_v^{\text{LDA}}) \\
&= B_p^{\text{LDA}} + (E_F - E_F^{\text{LDA}})_{\text{bulk metal}} \\
&\quad - (E_v - E_v^{\text{LDA}})_{\text{bulk semiconductor}}
\end{aligned}
\tag{25}
$$

since $E_F$ and $E_v$ may be evaluated in the bulklike metal and semiconductor regions several unit cells from the interface, where the self-energy operator and LDA exchange-correlation potential have attained their bulklike form. Therefore the correction to the LDA barrier height is a difference between two terms, one a property of the semiconductor only and the other a property of the metal only, and independent, for example, of the orientation of the interface. This provides a convenient method for calculating the quasiparticle Schottky barrier height in practice, which circumvents the difficulties of the behavior of the exact exchange-correlation potential: correct the LDA barrier height by calculating the quasi-

particle corrections to the metal's Fermi energy and the semiconductor's valence-band edge in two separate self-energy calculations for the bulk materials. The only sources of error in this procedure are possible errors in the bulk quasiparticle calculation and the electrostatic contribution to the LDA band offset. This was done, for example, in Ref. 19, in which the quasiparticle correction (calculated in the GW approximation) to the Fermi energy of Al was $-0.14$ eV, and the correction to the valence-band maximum of GaAs was $-0.36$ eV, giving a self-energy correction to the LDA $p$-type Schottky barrier heights of various Al/GaAs interfaces of $+0.22$ eV.

In a (hypothetical) exact DFT calculation, however, the exchange-correlation potential in the semiconductor near the interface will, in general, differ from the value in the bulk calculation by a constant, as discussed in Sec. III. If, for definiteness, we take it that the bulk calculation is performed for the $N$-electron intrinsic semiconductor, so that the DFT and quasiparticle valence-band maxima are aligned, near the interface:

$$
V_{\text{xc}}(\mathbf{r}) = (V_{\text{xc}}(\mathbf{r}))_{\text{bulk semiconductor}} + \Gamma_p
\tag{26}
$$

and, correspondingly,

$$
E_v^{\text{DFT}} = (E_v^{\text{DFT}})_{\text{bulk semiconductor}} + \Gamma_p \, .
\tag{27}
$$

On the other hand, by the "highest occupied eigenvalue" theorem[9] for the bulk metal and semiconductor,

$$
(E_F - E_F^{\text{DFT}})_{\text{bulk metal}}
= (E_v - E_v^{\text{DFT}})_{\text{bulk semiconductor}} = 0 \, ,
\tag{28}
$$

so that the expression equivalent to (24) is

$$
\begin{aligned}
B_p &= E_F - E_v \\
&= B_p^{\text{DFT}} + (E_F - E_F^{\text{DFT}}) - (E_v - E_v^{\text{DFT}}) \\
&= B_p^{\text{DFT}} + (E_F - E_F^{\text{DFT}})_{\text{bulk metal}} - \{(E_v - E_v^{\text{DFT}})_{\text{bulk semiconductor}} + [(E_v^{\text{DFT}})_{\text{bulk semiconductor}} - E_v^{\text{DFT}}]\} \\
&= B_p^{\text{DFT}} + \Gamma_p \, ,
\end{aligned}
\tag{29}
$$

as expected. In other words, the information required to correct the DFT $p$-type barrier height would be present in the DFT calculation itself: the correction is simply the difference between $V_{\text{xc}}$ in the neighborhood of the interface and $V_{\text{xc}}$ in the bulk ($p$-type) semiconductor. Since, as discussed above, $\Gamma_p$ is a property of the particular interface, not just of the semiconductor, this means that (in contrast to the LDA) the correction to the exact DFT barrier height is interface dependent, but at least it is not necessary to perform separate quasiparticle calculations.

It is possible to make use of the knowledge of the success of the LDA to deduce something about the $\Gamma$ corrections. The most favorable possibility is that $V_{\text{xc}}^{\text{LDA}}$ throughout the interface region of a Schottky barrier is exactly equal to the exact $V_{\text{xc}}$ plus a constant $c$. In this case the density will be reproduced exactly, and the only practical failing of the LDA would be its inability to reproduce the "healing" of the exchange-correlation potential at large distances (which, in the case of an explicit

LDA calculation for a Schottky barrier involving a doped semiconductor, for example, would result in an incorrectly sized depletion layer). However, in general the error in $V_{\text{xc}}^{\text{LDA}}$ will be more severe than a simple constant. It would usually be at least as bad as two different constants, $c_{\text{metal}}$ and $c_{\text{semiconductor}}$ in the metal and semiconductor regions, with a smooth variation across the thin interface region (about 5 Å) in which the electron density differs from its bulk behavior. If we consider $(V_{\text{xc}}^{\text{LDA}} - V_{\text{xc}})$ as a perturbing potential applied to the exact Kohn-Sham calculation, this perturbing potential now has a (mainly slow, according to the above assumption, except in the interface region) spatial variation, which will result in the electron density of the Schottky barrier being incorrect. But in practice the perturbing potential will be substantially screened out by the Hartree potential, owing to the large effective dielectric constant of the barrier.[20] Therefore the density (and band alignment) may be expected to be similar to exact DFT. We

then have $B_p^{\mathrm{DFT}} \approx B_p^{\mathrm{DFT}}$, and a comparison of Eq. (25) with Eq. (29) yields

$$\Gamma_p \approx (E_F - E_F^{\mathrm{LDA}})_{\text{bulk metal}} - (E_v - E_v^{\mathrm{LDA}})_{\text{bulk semiconductor}}$$

(30)

showing that $\Gamma_p$, the barrier height correction for exact DFT, may be written *approximately* as the difference between the bulk metal correction and a bulk semiconductor correction. In the case of the Al/GaAs study mentioned above this may be confirmed: the self-energy correction to the $p$-type barrier height, $+0.22$ eV, is indeed of the order of the estimate of $\Gamma_p$ given in Sec. III, to an accuracy of about 0.1 eV resulting from the variation in barrier height with interface structure.

Similar considerations apply to band offsets in semiconductors. The quasiparticle band offsets may be obtained from a LDA calculation by correcting the LDA band offset with the quasiparticle corrections for the band edges obtained from two bulk self-energy calculations, the correction being independent of the interface arrangement. Here it is again assumed that the electron density given by the LDA calculation is sufficiently accurate. For example, Hybertsen[21] found excellent agreement with experimental results for valence-band offsets between $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$, $\mathrm{In}_x\mathrm{Al}_{1-x}\mathrm{As}$ and InP, the self-energy corrections to the three different types of interfaces ranging from 0.04 to 0.12 eV. [As discussed in Sec. V, the self-energy corrections to the LDA band offsets — which are expected to be similar to the $\Gamma$ corrections in exact DFT (see above) — are smaller in the case of band

offsets then in the case of Schottky barrier heights.] Again, however, it must be pointed out that in exact DFT the $\Gamma$ corrections are not *exactly* independent of the interface arrangement.

## VII. CONCLUSIONS

We have demonstrated that Schottky barrier heights, band offsets, and surface band bending in exact DFT have inherent errors, which result from a slow variation in the exchange-correlation potential which necessarily accompanies electrostatic band bending. This spatial variation, in turn, has an ultra-non-local functional dependence on the electron density, and is directly related to $\Delta$, the discontinuity in the exchange-correlation potential with respect to particle number in the bulk semiconductor. It also reflects an ultra-non-local "vertex correction" in the DFT formulation of the long-wavelength dielectric response of the semiconductor.

## ACKNOWLEDGMENTS

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[15] We use "local" here to mean that $V(\mathbf{r})$ operates on a wave function $\varphi(\mathbf{r})$ according to $V(\mathbf{r}) \, \varphi(\mathbf{r})$, not $\int V(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')d\mathbf{r}'$. This should not be confused with the question of how local the functional dependence of $V_{\mathrm{eff}}(\mathbf{r})$ is on the electron density $n(\mathbf{r})$ (in fact $V_{\mathrm{eff}}$ can be a very *nonlocal* functional of the electron density).

[16] A comment on the "transitivity" of these corrections is appropriate. The various $\Gamma$ quantities in all the systems considered in this paper are not universal for the material in which they occur, but are specific to the particular interface considered (including its orientation). Therefore the value of the corrections for, say, GaAs cannot be transferred from one interface to another. However, as discussed in Sec. VI, the corrections are likely to be *approximately* transitive.

[17] The case of a heterojunction is more subtle than a Schottky barrier, since there is no Fermi energy to pin the DFT bands. At first sight it seems that the DFT bands might move rigidly relative to the quasiparticle bands between, say, a $p$-$n$ junction and a $p$-$p$ junction. However, this is not correct: since the mechanism by which the slow variation in $V_{\mathrm{xc}}$ is generated (Sec. III) within one semiconductor is not affected by the long-distance pinning in the other semiconductor, it may be seen by consideration of the progression $p$-$p \rightarrow p$-$n \rightarrow n$-

$n \rightarrow n\text{-}p$ that the disposition of the DFT bands relative to the quasiparticle bands is independent of the long-distance pinning of the chemical potential in the two semiconductors.

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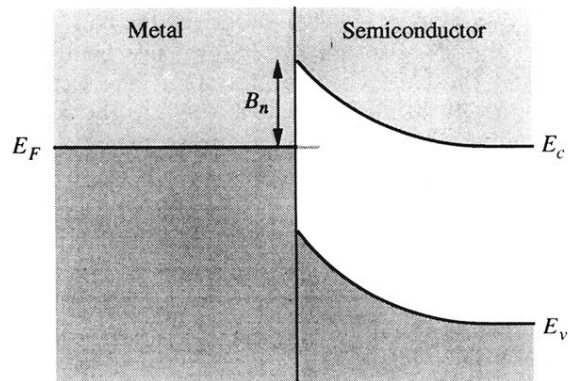[21]M. S. Hybertsen, Appl. Phys. Lett. **58**, 1759 (1991).

FIG. 1. The principles of Schottky barrier formation, in the usual one-electron picture, illustrated for an $n$-type semiconductor. The metal Fermi energy is "pinned" by the constraint that the filling of the exponentially decaying metal-induced gap states in the first few layers of the semiconductor (shown in light grey) be electrostatistically consistent with the band alignment. The $n$-type barrier height $B_n$ is the difference between the Fermi energy and the valence-band edge adjacent to the interface. The **band banding inside the semiconductor, which occurs over many hundreds of Å**, is electrostatic in origin and usually described within the depletion approximation. **This picture remains valid within a many-body theory, since the self-energy** operator, which describes exchange and correlation, does not contribute to any band bending on the scale of this diagram, and serves only to set the correct band gap in the first place. However, as discussed in this paper, in DFT the exchange-correlation potential also shows a slow spatial variation which alters the band bending.
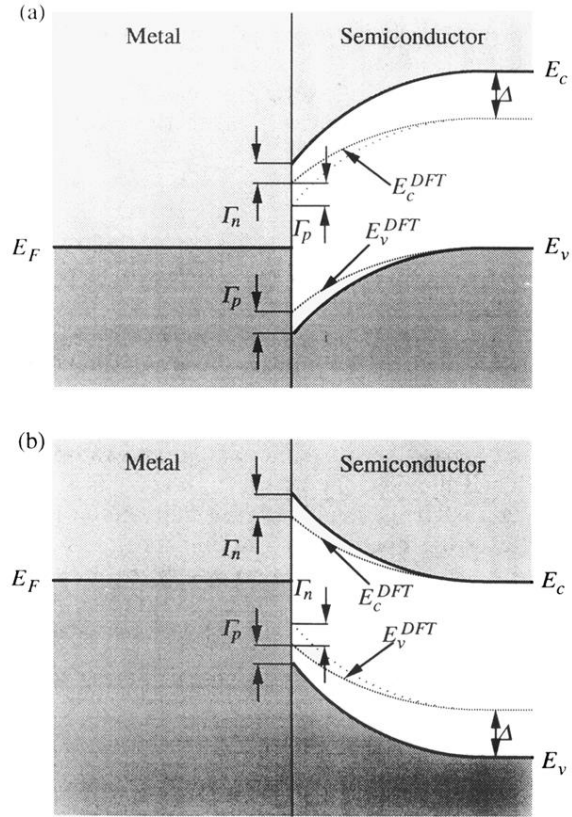
FIG. 2. Quasiparticle and DFT bands at a Schottky barrier:
(a) $p$-type semiconductor; (b) $n$-type semiconductor. The DFT
bands are bent relative to the quasiparticle bands by a slow spa-
tial variation of $V_{xc}(\mathbf{r})$ by a net amount of $\Gamma_p$ or $\Gamma_n$, respective-
ly. Correspondingly, the $n$- and $p$-type Schottky barrier heights
are in error by amounts $\Gamma_p$ and $\Gamma_n$, respectively, where
$\Gamma_p + \Gamma_n = \Delta$. The disposition of the DFT bands relative to the
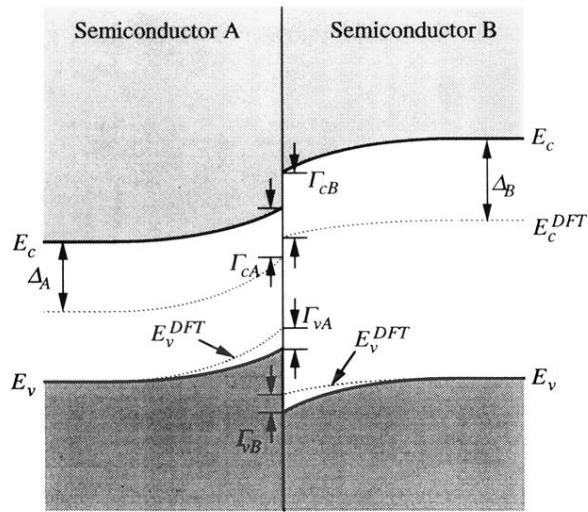quasiparticle bands at the interface is the same in (a) and (b).

FIG. 6. Quasiparticle and DFT bands near a $p$-type–$p$-type semiconductor heterojunction. The DFT bands are bent relative to the quasiparticle bands by a slow spatial variation of $V_{xc}(\mathbf{r})$ by a net amount $\Gamma_{cA}$ or $\Gamma_{vA}$, respectively, in semiconductor $A$, and $\Gamma_{cB}$ or $\Gamma_{vB}$, respectively, in semiconductor $B$. Correspondingly, the conduction- and valence-band offsets are in error by amounts $\Gamma_c = \Gamma_{cA} - \Gamma_{cB}$ and $\Gamma_v = \Gamma_{vA} - \Gamma_{vB}$, respectively, where $\Gamma_c + \Gamma_v = \Delta_A - \Delta_B$.