

Giant quasi-particle shifts of semiconductor surface states

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 SB75

(<http://iopscience.iop.org/0953-8984/1/SB/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:10

Please note that [terms and conditions apply](#).

Giant quasi-particle shifts of semiconductor surface states

F Bechstedt†, R Del Sole‡ and F Manghi§

† Friedrich-Schiller-Universität, Sektion Physik, Max-Wien-Platz 1, DDR-6900 Jena, German Democratic Republic

‡ Dipartimento di Fisica, II Università degli Studi di Roma 'TorVergata', v. E. Carnevale, I-00173 Roma, Italy

§ Dipartimento di Fisica, Università di Modena, I-41100 Modena, Italy

Received 23 March 1989

Abstract. The differences between the energy positions of surface bands in quasi-particle and local-density approximations are calculated taking into account the different screening properties of a semiconductor and of an electron gas of the same average density. Gap corrections of the order of 1.5 eV are computed for GaP(110) and GaAs(110) surfaces, in good agreement with experiment.

Semiconductor surfaces exhibit a 'band-gap problem' similar to bulk materials [1, 2]. In spite of the success of the local density functional approximation (LDA) of exchange and correlation in explaining surface atomic structures including reconstruction, surface band energies calculated within this approach are shifted with respect to those found by means of photoemission or inverse photoemission [3, 4]. Hitherto the band-gap problem has not been studied for surfaces such as GaAs(100) and GaP(110). The comparison of experimental results [5–11] and LDA calculations [12, 13], however, indicates a large underestimate of surface transition energies by about 100%, or 0.5–1.9 eV. In this paper, we show that such large discrepancies can be explained, within the framework of quasi-particle (QP) theory, in terms of the reduced screening properties of these surfaces.

A correct theoretical description of the energy positions of the electronic states is possible in the framework of the QP formalism [1, 2, 4]. We consider a surface state with band index n , two-dimensional (2D) wavevector \mathbf{k} in the surface Brillouin zone (SBZ) and LDA wavefunction $\varphi_{n\mathbf{k}}(\mathbf{x})$. The correction $\Delta_n(\mathbf{k})$ is determined by the difference $\delta\Sigma$ between the QP self-energy $\Sigma(\mathbf{x}, \mathbf{x}'; E)$ and the local exchange–correlation potential $V_{xc}(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')$ used in the LDA. By extending to surfaces an approximate GW approach which gives reasonable results for bulk states [2] we get

$$\Delta_n(\mathbf{k}) = \pm \sum_{m,b,l} |c_{mb}^n(\mathbf{k})|^2 I_l^{\text{p}}(d_{mb}^{\pm}) \quad (1)$$

with

$$I_l^{\text{p}}(d_{mb}^{\pm}) = \frac{1}{2} \int d^2Q (2\pi)^{-2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_l^{\text{p}}(\mathbf{Q}, z - d_{mb}^{\pm}) \\ \times [W(\mathbf{Q}, z, z'; 0) - W^{\text{h}}(\mathbf{Q}, z, z'; 0)] \rho_l^{\text{p}}(\mathbf{Q}, z' - d_{mb}^{\pm}) \quad (2)$$

$$\rho_l^b(\mathbf{Q}, z) = \int d^2\mathbf{x}_{\parallel} \exp(i\mathbf{Q} \cdot \mathbf{x}_{\parallel}) |\varphi_l^b(\mathbf{x})|^2. \quad (3)$$

Here + holds for empty states and – for filled states, $W(\mathbf{Q}, z, z'; 0)$ denotes the statically screened Coulomb potential of the truncated semiconductor and $W^h(\mathbf{Q}, z, z'; 0)$ that of the homogeneous electron gas, and d_{mb}^{\pm} is the distance from the surface of the atom b (\equiv a for anion c for cation) in the layer m . Atomic orbitals are labelled by l , while the expansion coefficients $c_{mb}^l(\mathbf{k})$ can be taken from band calculations.

The integrals $I_l^b(d_{mb}^{\pm})$ (equation (2)) can be carried out if the screened potential near the semiconductor surface is known. We use for it the classical image potential result, identifying the surface $z = 0$ plane with the plane where the electron density changes more or less abruptly from the bulk value to zero. Hence the integrals in (2) can be approximately evaluated. This results in

$$I_l^b(d_{mb}^{\pm}) = \{U_l^b + [(\epsilon_0 - 1)/(\epsilon_0 + 1)]e^2/(2d_{mb}^{\pm})\}/2\epsilon_0 \quad (4)$$

where U_l^b is the bare Coulomb integral of the localised orbital $\varphi_l^b(\mathbf{x})$ and ϵ_0 is the static dielectric constant. The first term in (4), $U_l^b/2\epsilon_0$, represents the QP shift of an electronic state with the orbital character l and localised at atom b in the bulk case [2, 14]. The additional contribution in (4) indicates that the screening near the surface is lowered for materials where the gap between surface states is larger than that between bulk states, as for (110) surfaces of III–V semiconductors.

Explicit values for the QP shifts of the surface states of (110) relaxed surfaces [3, 15] can be immediately obtained from (4) if the localised orbitals are specified. We use optimised one-parameter s and p Slater orbitals [16]. On the assumption that the surface states of a zincblende (110) surface are essentially localised in the first atomic layer, the corresponding combinations of the integrals $I_l^b(d_{mb}^{\pm})$ represent the QP shifts of empty (positive sign) or occupied (negative sign) surface states according to (1). The values $I_l^b(d_{mb}^{\pm})$ are larger by a factor of 2 than the bulk shifts Δ_{VBM} , owing to the reduced screening near the surface. To check the validity of this prediction of surface-enhanced QP shifts, we study the electronic surface band structure of GaAs(110) and GaP(110) in more detail.

The most important surface bands are the dangling-bond-related ones around the bulk fundamental gap [17]. The highest occupied surface band at Γ is A_5 or A_6 , in both cases related to the anion p states, with $\Delta_{A_5}(\Gamma) = -I_p^a(d_{1a}^{\pm})$; the lowest empty surface state is C_3 at X, mostly related to the cation p states, so that $\Delta_{C_3}(\text{X}) = I_p^c(d_{1c}^{\pm})$; the lowest empty surface state at Γ is also C_3 , related to s and p cation states in the ratio 1:2 [13], so that $\Delta_{C_3}(\Gamma) = (I_s^c(d_{1c}^{\pm}) + 2I_p^c(d_{1c}^{\pm}))/3$. The lowest indirect and direct gaps between surface states are therefore given by the transitions $A_5(\Gamma) \rightarrow C_3(\text{X})$ and $A_5(\Gamma) \rightarrow C_3(\Gamma)$. The QP corrections to the LDA energy values of these surface gaps are defined as $\Delta^{\text{ind}} = \Delta_{C_3}(\text{X}) - \Delta_{A_5}(\Gamma)$ and $\Delta^{\text{dir}} = \Delta_{C_3}(\Gamma) - \Delta_{A_5}(\Gamma)$. The corresponding QP correction to the LDA value of the energy distance of the maximum of occupied surface bands to the top of the bulk valence bands can be written as $\Delta^{\text{val}} = \Delta_{\text{VBM}} - \Delta_{A_5}(\Gamma)$. We obtain, for GaAs, $\Delta^{\text{ind}} = 1.15$ eV, $\Delta^{\text{dir}} = 1.26$ eV and $\Delta^{\text{val}} = 0.34$ and, for GaP, $\Delta^{\text{ind}} = 1.52$ eV, $\Delta^{\text{dir}} = 1.66$ eV and $\Delta^{\text{val}} = 0.44$ eV.

The experimental surface gaps $E_g^{\text{ind}} = E_{C_3}(\text{X}) - E_{A_5}(\Gamma)$ and $E_g^{\text{dir}} = E_{C_3}(\Gamma) - E_{A_5}(\Gamma)$, as well as the energy distance between the maximum of occupied bulk and surface bands, given by $E_g^{\text{val}} = E_{\text{VBM}} - E_{A_5}(\Gamma)$, can be extracted from photoemission and inverse photoemission measurements. We obtain for GaAs, $E_g^{\text{ind}} = 2.3$ eV [6] or 2.8 eV [7], $E_g^{\text{dir}} = 3.0$ eV [6] or 3.5 eV [7] and $E_g^{\text{val}} = 0.6$ eV [5]. The corresponding

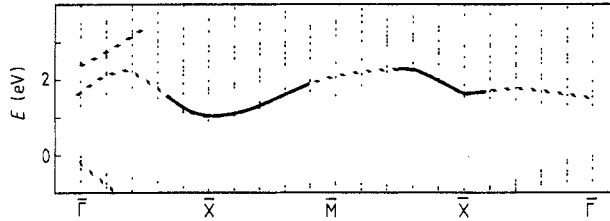


Figure 1. Highest occupied and lowest unoccupied surface states (—) and resonances (---) of GaP(110) resulting from a LDA calculation.

Table 1. Comparison of experimental and calculated corrections to the LDA direct (Δ^{dir}) and indirect (Δ^{ind}) surface gaps. Δ^{val} is the correction to the difference between the tops of occupied bulk and surface bands.

	Experiments	Average value	Theory
GaAs			
Δ^{val} (eV)	0.2 ^a	0.2	0.34
Δ^{ind}	0.5 ^b , 1.0 ^c , 1.4 ^d , 1.9 ^e	1.2	1.15
Δ^{dir}	1.0 ^d , 1.2 ^b , 1.5 ^c , 1.9 ^e	1.35	1.26
GaP			
Δ^{val}	0.4 ^f	0.4	0.44
Δ^{ind}	1.2 ^g , 1.8 ^h	1.5	1.52
Δ^{dir}	1.8 ^h	1.8	1.66

^a Value in [5] minus value in [12] or [13].

^b Value in [6] minus value in [12].

^c Value in [7] minus value in [12].

^d Value in [6] minus value in [13].

^e Value in [7] minus value in [13].

^f Value in [8] minus value in this work.

^g Value in [11] minus value in this work.

^h Value in [10] minus value in this work.

values for GaP are $E_g^{\text{ind}} = 2.4$ eV [11] or 3.0 eV [10], $E_g^{\text{dir}} = 3.4$ eV [10] and $E_g^{\text{val}} = 0.5$ eV [8].

The corresponding theoretical LDA values reported in the literature for GaAs are $E_g^{\text{ind}} = 0.9$ eV [13] or 1.8 eV [12], $E_g^{\text{dir}} = 1.8$ eV [13] or 2.0 eV [12] and $E_g^{\text{val}} = 0.4$ eV [12, 13]. Since analogous LDA results are not available for GaP(110), we have carried out a LDA calculation for a repeated slab of nine (110) layers separated by 14 missing layers. Local pseudopotentials [18] and Ceperley–Alder exchange–correlation have been used. The resulting highest occupied and lowest unoccupied surface bands are shown in figure 1. We obtain $E_g^{\text{ind}} = 1.2$ eV, $E_g^{\text{dir}} = 1.7$ eV and $E_g^{\text{val}} = 0.1$ eV.

The discrepancies between the experimental and LDA data are comparable with the QP shifts derived above. The combination of the two kinds of data yields the ‘experimental’ corrections quoted in the second column of table 1. Our theoretical values for QP shifts agree very well their average values, quoted in the third column of table 1.

In spite of the approximations used to derive equation (4), comparison of the theoretical and ‘experimental’ QP shifts clearly shows that the failure of the LDA to

describe the surface electronic structure, which is more drastic for relaxed (110) surfaces than for the bulk, is correctly described by the present theory. The LDA overestimates the screening involved in the exchange–correlation potential by replacing it with that of a free-electron gas. Near surfaces with surface state gaps larger than the bulk ones, as in the case of (110) surfaces, the difference between semiconductor and free-electron gas screening is enhanced because the effective dielectric constant is of the order of $(\epsilon_0 + 1)/2$, which leads to an approximately doubling of the bulk gap correction.

Acknowledgments

It is a pleasure to acknowledge useful discussions with A Baldereschi, S G Louie and A Zunger. We thank P Perfetti for sending us his unpublished data.

References

- [1] Hybertsen M S and Louie S G 1986 *Phys. Rev. B* **34** 5390
- [2] Bechstedt F and Del Sole R 1988 *Phys. Rev. B* **38** 7710
- [3] Bechstedt F and Enderlein R 1988 *Semiconductor Surfaces and Interfaces* (Berlin: Akademie)
- [4] Hybertsen M S and Louie S G 1988 *Phys. Rev. B* **38** 4033
- [5] Huijser A, van Laar J and van Rooy T L 1978 *Phys. Lett.* **65A** 337
- [6] Straub D, Skibowski M and Himpsel F J 1985 *Phys. Rev. B* **32** 5237
- [7] Reihl B, Riesterer T, Tschudy M and Perfetti P 1988 *Phys. Rev. B* **38** 13456
- [8] Solal F, Jezequel G, Houzay F, Barski A and Pinchaux R 1984 *Solid State Commun.* **52** 37
- [9] Cerrina F, Bommannavar A, Benbow R A and Hurych Z 1985 *Phys. Rev. B* **31** 8314
- [10] Riesterer T, Perfetti P, Tschudy M and Reihl B 1987 *Surf. Sci.* **189–190** 795
- [11] Straub D, Skibowski M and Himpsel F J 1985 *J. Vac. Sci. Technol. A* **3** 1484
- [12] Zunger A 1980 *Phys. Rev. B* **22** 959
- [13] Zhang S B and Cohen M L 1986 *Surf. Sci.* **172** 754
- [14] Harrison W A 1985 *Phys. Rev. B* **31** 2121
- [15] Duke C B 1983 *J. Vac. Sci. Technol. B* **1** 732
- [16] Chen A-B and Sher A 1980 *Phys. Rev. B* **22** 3886
- [17] Chelikowsky J R and Cohen M L 1979 *Phys. Rev. B* **20** 4150
- [18] Frensley W R and Kroemer H 1977 *Phys. Rev. B* **16** 2642