Binding energies of surface polarons outside polar crystals calculated using a multi-branch

vibrational model model

LETTER TO THE EDITOR

Binding energies of surface polarons outside polar crystals calculated using a multi-branch vibrational mode model

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Abstract. Binding energies of surface polarons outside polar crystal surfaces are calculated quantum mechanically by considering the interactions of outside electrons with both electronic and ionic polarizations of the crystals. Results show that quantum mechanical modifications of image potentials due to electronic polarization reduce polaron binding energies by 40–50% compared with those calculated with image potentials due to electronic polarization approximated by their electrostatic limits. Substitution of infinitely high frequencies for the finite vibrational frequencies of electronic polarizations changes the calculated polaron binding energies by less than 5% for the materials considered.

Surface polaron states outside polar crystal surfaces have been extensively studied (Sak 1972, Evans and Mills 1973, Ueba 1980, de Bodas and Hipolito 1983, Trninic-Radja *et al* 1989, Lee and Antoniewicz 1989) ever since the pioneering work of Sak (1972) and Evans and Mills (1973). In most of these works (Sak 1972, Ueba 1980, Trninic-Radja *et al* 1989, Lee and Antoniewicz 1989), however, image potentials acting upon electrons due to electronic polarizations, which localize electrons to surfaces and determine dominantly surface polaron binding energies, are approximated by their classical electrostatic limits with the seemingly reasonable argument that the vibrational frequencies of electronic polarizations are much higher than those of ionic polarizations caused by the relative separations of positive and negative ions when crystals vibrate in optical modes. Recently, a number of authors (Nieminen and Hodges 1978, Manson and Ritchie 1981, Echenique 1985, Zheng *et al* 1989) have reported on quantum mechanical calculations of image potentials, with the conclusion that quantum mechanical corrections to electrostatic image potentials are not negligible, especially when electrons are in the near vicinity of crystal surfaces. Evans and Mills (1973) pointed out that quantum mechanical non-local image potentials will reduce surface polaron binding energies by a factor of $16/25$ compared with those calculated with electrostatic image potentials, though in their calculation they have neglected electronic polarizations by assuming the high-frequency dielectric constant $\varepsilon_\infty = 1$. In this letter, we report a

calculation of surface polaron binding energies outside polar crystal surfaces with image potentials due to both electronic and ionic polarizations treated quantum mechanically.

The electronic polarization of the crystal considered is approximated by point dipoles vibrating harmonically at a single frequency. It is straightforward to refine the model by considering point dipoles vibrating at several different frequencies if necessary. An electron outside the polar crystal surface interacts with both the electronic and ionic polarization fields. The calculation method is mathematically equivalent to that for a polaron near a polyatomic crystal surface with many optical vibrational branches (Matsuura 1977, Lepine 1981, Sols and Ritchie 1987). The polaron Hamiltonian reads

$$H_{\text{pol}} = -\frac{\hbar^2}{2m_{\text{e}}} \nabla^2 + \sum_q \sum_{j=1}^{2} \hbar \omega_{sj} a_{qj}^{+} a_{qj} + \sum_q \sum_{j=1}^{2} [V_{qj}(z) \, e^{i q \cdot \rho} a_{qj} + \text{HC}] \tag{1}$$

where m_{e} is the electron mass outside the surface ($z > 0$). q and ρ are the in-plane component of the wavevector of the surface vibrational modes and the positional vector of the electron, respectively. a_{qj}^{+} creates a surface vibrational mode in branch j with wave vector q. $V_{qj}(z)$ is the interaction constant for the interaction between the electron and surface vibrational modes given by

$$V_{qj}(z) = -i \left(\frac{4\pi e^2 \hbar}{q A_0 (d\varepsilon/d\omega)|_{\omega = \omega_{sj}}} \right)^{1/2} \exp(-qz) \tag{2}$$

with A_0 ($A_0 \to \infty$) the surface area of the crystal. The dielectric function $\varepsilon(\omega)$ of the crystal is given by

$$\varepsilon(\omega) = \frac{\omega_{L1}^2 - \omega^2}{\omega_{T1}^2 - \omega^2} \frac{\omega_{L2}^2 - \omega^2}{\omega_{T2}^2 - \omega^2} \tag{3}$$

with ω_{L1} and ω_{T1} (ω_{L2} and ω_{T2}) the longitudinal and transverse vibration frequencies respectively related to the electronic (ionic) polarization field. The eigenfrequencies of the surface modes ω_{sj} ($j = 1, 2$) are determined by

$$\varepsilon(\omega_{sj}) = -1 \tag{4}$$

with ω_{s1} and ω_{s2} ($\omega_{s1} \gg \omega_{s2}$) originating from the electronic and ionic polarizations, respectively. The derivation of H_{pol} (1) and relationships between ω_{Lj}, ω_{Tj} and microscopic quantities of the crystal will be given later in a more detailed paper. In order to retain the familiar surface polaron theory, where one considers only the vibrational modes of the ionic polarization and approximates the electronic polarization by an electrostatic image potential and when one lets ω_{L1} and ω_{T1} go to infinity, we define the high-frequency dielectric constant of the crystal by

$$\varepsilon_\infty = \omega_{L1}^2 / \omega_{T1}^2. \tag{5}$$

If we set $\omega = 0$ in equation (3) we have

$$\varepsilon_s / \varepsilon_\infty = \omega_{L1}^2 / \omega_{T1}^2 \tag{6}$$

where $\varepsilon_s = \varepsilon(0)$ is the static dielectric constant of the crystal.

For simplicity, we assume that the bottom of the conduction band of the crystal lies far above the vacuum level, so the crystal surface represents an infinitely high potential barrier. The *ansatz* of the polaron ground state is taken as

$$\psi = \varphi(z) U_1 U_2 |0\rangle \tag{7}$$

where $|0\rangle$ is the vacuum state of the surface polarization fields, U_1 and U_2 are the Lee–

Low–Pines unitary transformations often used in surface polaron theory (de Bodas and Hipolito 1983), and $\varphi(z)$ is the trial wavefunction of the electron distribution perpendicular to the surface. The polaron ground state energy with the polaron in-plane wavevector $k_\parallel = 0$ is given variationally by

$$E_g = \langle\varphi| - (\hbar^2/2m_e) \nabla^2|\varphi\rangle - \sum_{qj} \frac{|\langle\varphi|V_{qj}(z)|\varphi\rangle|^2}{\hbar\omega_{sj} + \hbar^2 q^2/2m_e}. \qquad (8)$$

If we suppose the electron is localized near $z = z_0$ and take $\varphi(z) = \delta(z - z_0)$ as a consequence, then the potential energy term in equation (8) becomes

$$V_{eff}(z_0) = - \sum_j \alpha_{sj}\hbar\omega_{sj} \int_0^\infty \mathrm{d}q\, \frac{\exp(-2u_{sj}z_0 q)}{1 + q^2} \to -\frac{\varepsilon_s - 1}{\varepsilon_s + 1}\frac{e^2}{4z_0} \qquad (9)$$

where $\alpha_{sj} = 4m_e e^2[\hbar^2 u_{sj}\omega_{sj}(\mathrm{d}\varepsilon/\mathrm{d}\omega)|_{\omega=\omega_{sj}}]^{-1}$ is the polar coupling constant of the surface mode ω_{sj}. $V_{eff}(z_0)$ approaches the electrostatic image potential (the last limit in (9)) when the electron is far away from the surface, i.e. $z_0 \gg u_{sj}^{-1} = (\hbar/2m_e \omega_{sj})^{1/2}$. When the electron is in the near vicinity of the surface ($z_0 \to 0$), $V_{eff}(z_0)$ is finite, while the electrostatic image potential tends to infinity. The effective potential associated with the vibrational mode of branch $j = 1$ in equation (9) is the image potential due to the electronic polarization. To show this we set ω_{L1} and $\omega_{T1} \to \infty$ in equation (9), but keep $\omega_{L1}^2/\omega_{T1}^2 = \varepsilon_\infty$, and we have

$$V_{eff,1}(z_0) = - \alpha_{sj}\hbar\omega_{sj} \int_0^\infty \mathrm{d}q\, \frac{\exp(-2u_{sj}z_0 q)}{1 + q^2}\bigg|_{j=1} \to -\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 1}\frac{e^2}{4z_0}. \qquad (10)$$

When the electron has a spatial distribution perpendicular to the surface, the potential energy term in equation (8) cannot, in principle, be approximated by a local one-electron image potential. The polaron energy and effective potential of (8) must be calculated self-consistently. We calculate the polaron ground state energy E_g (equation (8)) variationally using the function

$$\varphi(z) = 2\beta^{3/2}z\, \mathrm{e}^{-\beta z} \qquad (11)$$

with β the variational parameter. In order to make comparisons we also calculate the polaron ground state energy by approximating the potential energy associated with the vibrational mode of branch $j = 1$ in (8) by a local potential $V_{eff,1}(z)$ (equation (10)). That is, we calculate

$$\tilde{E}_g = \langle\varphi| - (\hbar^2/2m_e) \nabla^2 + V_{eff,1}(z)|\varphi\rangle - \sum_q \frac{|\langle\varphi|V_{qj}(z)|\varphi\rangle|^2}{\hbar\omega_{sj} + \hbar^2 q^2/2m_e}\bigg|_{j=2}. \qquad (12)$$

If we set ω_{L1} and $\omega_{T1} \to \infty$ but keep $\omega_{L1}^2/\omega_{T1}^2 = \varepsilon_\infty$, $\tilde{E}_g$ goes to the polaron ground state energy calculated in the literature (Sak 1972, Ueba 1980, Trninic-Radja *et al* 1989, Lee and Antoniewicz 1989) with the assumption that the image potential due to the electronic polarization is approximated by its electrostatic limit. In figure 1 E_g and $\tilde{E}_g$ are plotted as functions of ω_{L1}/ω_{L2} with other parameters taken as those of a ZnO surface (see table 1).

Two points are noteworthy from the numerical results in figure 1: (i) the polaron binding energy calculated with non-local image potentials ($E_b = -E_g$) is much less than that calculated with an approximated local image potential due to the electronic polarization ($\tilde{E}_b = -\tilde{E}_g$), even in the limit $\omega_{L1} \to \infty$; (ii) if we assume that ω_{T1} is of
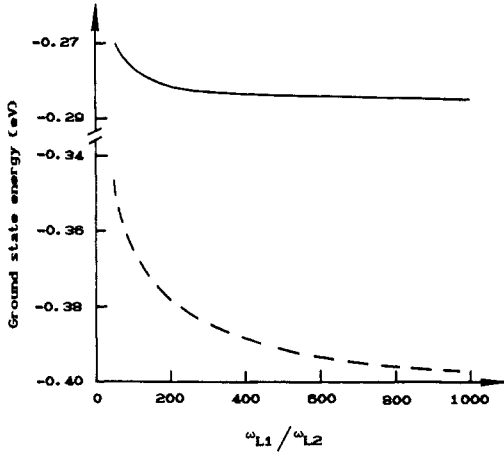
Figure 1. Surface polaron binding energies outside a polar crystal surface calculated with the non-local image potentials (full curve) and with the image potential due to the electronic polarization approximated by its electrostatic limit (broken curve). The results are given as functions of ω_{L1}/ω_{L2} with other parameters taken as those of a ZnO crystal (see table 1).

Table 1. Surface polaron binding energies for several polar crystal surfaces calculated with non-local image potentials $E_b^{(0)}$ and with image potentials due to electronic polarizations approximated by their electrostatic limits $\bar{E}_b^{(0)}$, and their ratios $\lambda = E_b^{(0)}/\bar{E}_b^{(0)}$, in the limit $\omega_{L1} \to \infty$. The experimental parameters used in the calculation are taken from Beni and Rice (1978).

Polar crystal	ε_s	ε_∞	$\hbar\omega_{L2}$ (meV)	$E_b^{(0)}$ (eV)	$\bar{E}_b^{(0)}$ (eV)	λ
ZnO	8.59	4.0	72.0	0.2860	0.4080	0.701
CdS	8.58	5.86	36.8	0.3096	0.4675	0.662
CdTe	10.31	6.90	21.2	0.3335	0.5072	0.657
GaAs	12.35	10.48	36.8	0.3827	0.5927	0.646
InSb	17.90	15.70	23.9	0.4278	0.6655	0.643

about the same order of magnitude as the crystal band gap, then for the ZnO surface we have $\omega_{L1}/\omega_{L2} \approx 100$.

From figure 1 we see that substitution of an infinitely high frequency for the finite vibrational frequency of the electronic polarization changes the polaron binding energy by less than 5% (see the full curve in figure 1), while the polaron binding energy is overestimated by 40% for the calculation which approximates the non-local image potential due to electronic polarization by its electrostatic limit (compare the broken and full curves in figure 1). In table 1, polaron binding energies calculated with non-local image potentials $E_b^{(0)}$ and with image potentials due to electronic polarizations approximated by their electrostatic limits $\bar{E}_b^{(0)}$ in the limit $\omega_{L1} \to \infty$ are listed for a number of polar crystal surfaces.

Detailed calculations show that if one approximates finite vibrational frequencies of electronic polarizations by infinitely high frequencies, the effects of non-local image potentials on polaron binding energies can be described by introducing a multiplication factor α into the electrostatic image potentials due to electronic polarizations. For the trial wavefunction $\varphi(z)$ we used (equation (11)) α equal to $\frac{4}{5}$ and independent of material parameters.

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