

Computational aspects of electron–phonon coupling at surfaces

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Received 8 November 2007, in final form 27 December 2007

Published 13 May 2008

Online at stacks.iop.org/JPhysCM/20/224017

Abstract

We study the validity of two frequently used approximations in calculations of electron–phonon coupling at surfaces. The rigid-ion approximation is a standard approximation used for the bulk metals. On the basis of density functional theory calculations, we find that for Be this approximation is as valid for surface atoms as for bulk atoms. In addition, the slab method for calculations of a phonon induced surface state lifetime is examined. The convergence of the electron–phonon matrix element with respect to the thickness of the slab is studied for several systems. When the number of slab layers is increased, the net effect of decreasing overlap and increasing number of final states depends strongly on the decay length of the surface state wavefunction and the band structure.

1. Introduction

Recent progress in experimental surface science techniques, such as photoemission spectroscopy and low-temperature scanning tunneling microscopy, reveals the importance of the electron–phonon (e–p) coupling in many ultra-fast processes at surfaces such as the decay of excited surface states or quantum-well states [1–3]. In chemical reactions the e–p coupling also plays an important role in dissipative processes such as vibrational damping. To get further understanding of the e–p coupling from experimental studies, theoretical investigations are indispensable.

The estimation of the lifetime broadening due to the e–p coupling from experimentally determined λ values has often been based on a simple phonon Debye or Einstein model. These phonon models seem to be too crude as the detailed microscopic ingredients of the e–p coupling is not contained in the analysis [4–10]. Recently more elaborate studies including the electronic band structures and/or phonon structures have been reported [11–16].

Very recently several papers have been published where the electron–phonon coupling is accounted for by applying *first principles* calculations based on the density functional perturbation theory (DFPT) [17–19]. In these types of more realistic calculations, including the phonon and electronic structure, the slab method is used to mimic the semi-infinite systems. For several decades reliable electronic structure

calculations of metal surfaces have been performed with the slab method. However, for the electron–phonon coupling calculations, the requirements applying this method has not been analyzed in any details. In this paper, we investigate, within a simple model, some convergence aspects of the slab method in calculations of the e–p matrix element.

Another approximation often used in the calculations of the e–p coupling is the rigid-ion approximation (RIA) [20]. Due to efficient screening by the conduction electrons the atomic deformation potential is assumed to localize around the atom, valence charge follows the ion motion rigidly. This leads to RIA. RIA has been used to study the e–p coupling in bulk metals [20] and recently, for the calculation of the e–p coupling at surfaces [12–15]. However, as far as we know, nobody addressed the validity of this approximation for the surface atoms. In this paper we analyze these aspects applying *first principles* method based on density functional theory (DFT).

In the next two sections we discuss the validity of the rigid-ion approximation and the convergence of the e–p coupling with respect to the number of atomic layers in a slab calculation.

2. Rigid-ion approximation

As mentioned above, RIA was discussed several decades ago for bulk systems but only more recently for surfaces. RIA deals

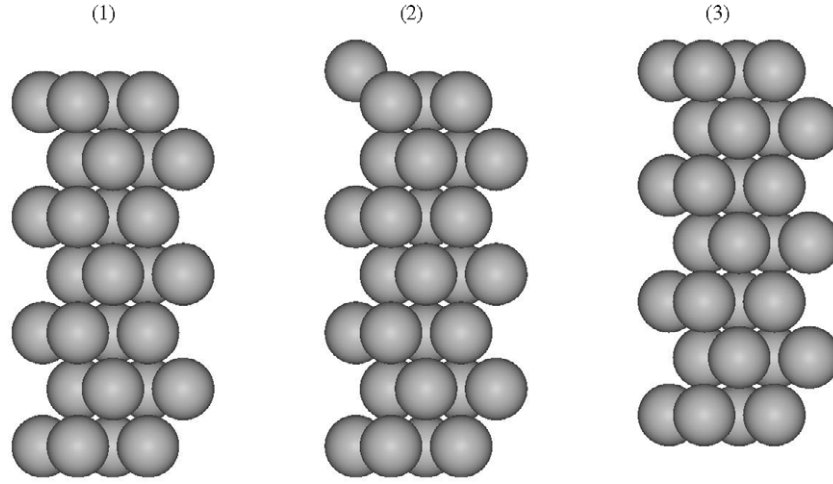


Figure 1. Super cell geometries of Be(0001) for the three (1)–(3) configurations used in the test of the RIA. The details are given in the text.

with a simplification of the deformation potential caused by the vibrating lattice of a solid. Roughly, the strength of the e–p coupling is determined by the basic e–p matrix element which reads

$$M_{\text{ep}}^{nm} \sim \left\langle n \left| \frac{\partial U_{\text{ie}}}{\partial R} \right| m \right\rangle \quad (1)$$

where the change of the ion–electron potential U_{ie} —the deformation potential—, induced by phonon emission or absorption, drives the scattering of an electron from state m to state n . R is here some collective notation for the nuclei coordinates. U_{ie} is the potential experienced by the conduction electrons in a solid due to the presence of the ions (the screened atomic nuclei). When an ion moves, surrounded by other ions in a phonon mode, the electron density will in principle be locally deformed. However, in RIA, it is assumed that the valence electron density follows the ion motion and is independent of the neighboring ion positions. As a result U_{ie} is assumed to follow rigidly the motion of the ions. For small displacement vectors \vec{u}_j of an ion labeled j , the potential change according to RIA goes as

$$\begin{aligned} U_{\text{ie}}(\vec{R}_j^0 + \vec{u}_j; \vec{r}) - U_{\text{ie}}(\vec{R}_j^0; \vec{r}) &\approx U_{\text{ie}}(\vec{R}_j^0 + \vec{u}_j - \vec{r}) \\ &- U_{\text{ie}}(\vec{R}_j^0 - \vec{r}) \approx \vec{u}_j \cdot \vec{\nabla}_{\vec{R}_j} U_{\text{ie}}(\vec{R}_j^0 - \vec{r}) \\ &= \vec{u}_j \cdot \vec{\nabla}_{\vec{r}} U_{\text{ie}}(\vec{R}_j^0 - \vec{r}) \end{aligned} \quad (2)$$

where \vec{R}_j^0 is the equilibrium position of the ion j and \vec{r} is electron coordinate. The benefit from RIA is that in a calculation we do not have to move the atoms from the equilibrium positions as the derivative with respect to the nuclear coordinate is transformed to the electron coordinate. In the calculation of the e–p matrix elements (equation (1)) we can further utilize partial integration over electron coordinates.

To check the validity of RIA, in particular for surface atoms, we have performed *first principles* calculations based on the density functional theory (DFT). We study the Be(0001)-(2 × 2) surface in a 7-layers-thick slab. The (2 × 2) surface cell is used instead of the (1 × 1) to avoid that the nearest neighbor atoms are moved when a particular atom is displaced. The DFT calculations were performed with the PWscf code [21]

with the local density approximations (LDA) for the exchange correlation potential.

The calculations were done for three different slabs. First, (1), the self-consistent potential of Be slab with optimized structure was calculated. Then, (2), one of the first layer atoms was moved into the vacuum by 0.1 Å (a typical vibrational amplitude of an atom in a solid) and the self-consistent potential was calculated. Thirdly, (3), the whole slab was moved rigidly perpendicular to the surface (into the vacuum) from the configuration (1) by 0.1 Å, which is the simple translation of (1), and the self-consistent potential was calculated. The atomic positions in the calculations (1)–(3) are shown in figure 1. To compare the difference of the screening by the conduction electrons for surface atoms and bulk atoms, we performed the same procedure of (2) described above for the bulk atom. In this case one atom in the third layer was chosen as a bulk atom. To check the effect of the surface layer on bulk atoms, the same calculation for the middle layer in 13-layers-thick slab was performed. The result is almost identical to that of 7-layers-thick slab.

The results of the potential difference between (1) and (2) as a function of the distance from the atom moved perpendicular to the surface are shown in figures 2(a) and (b). The potential difference has decayed sufficiently within 2 a.u. from the equilibrium position ($z = 0$). This result clearly shows that the deformation potential is quite localized around the displaced Be atom within the atomic radius of Be (2.1 a.u.) due to the screening by the conduction electrons. The result is quite similar to that of the bulk atom, which indicates the difference of the screening by the conduction electron between surface and bulk is small. We note however, as expected, that the screening is slightly less efficient in the positive direction when the surface atom is displaced.

The validity of RIA is judged by the difference between (2) and (3). In the case of (2) the atom is really moved whereas in the case of (3), all atoms are displaced rigidly. In RIA, the screened electron–ion potential U_{ie} , which is determined by the valence electron density, follows the ion motion and so the potential difference between (2) and (3) is small compared with

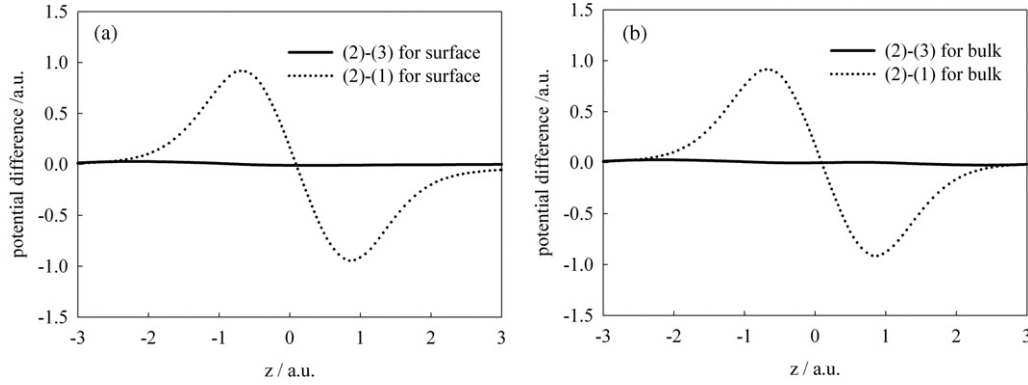


Figure 2. Results of the RIA test. Left: surface atom displacement; right: bulk atom displacement. Details in the text.

the difference between (1) and (2). The results are also shown in figures 2(a) and (b). These results indicate that the difference is quite small, comparing the surface and bulk atoms. This analysis shows the validity of RIA for Be(0001), not only for the bulk atoms but also for the atoms in the surface layer.

3. Slab calculation of electron–phonon coupling

In this section we investigate some aspects of the convergence of the e–p coupling at surfaces in a slab calculation. We focus on the e–p matrix element related to the phonon induced decay of a surface state hole. The convergence with respect to the number of atomic layers is studied for the surface states of Cu(111), Al(001) and Be(0001). The model potential and wavefunction used in this section are as follows. The surface state wavefunctions are approximated with the crude wavefunction

$$|0\rangle = \begin{cases} \frac{1}{\sqrt{l\Omega}} & (0 \leq z \leq l) \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

where l characterizes the extension of the surface state in the direction normal to the surface plane and Ω is the sample surface area. The energy of the surface state we denote E_0 .

We have in mind a metal surface with a surface state band partly occupied in the $\bar{\Gamma}$ -point and located in a projected band gap. These general features are present for e.g. the (111) surface of the noble metals. In the paper [22] the authors pointed out that the decay constant (inverse of l), describing the decay of the surface state wavefunction into the bulk, is approximately proportional to the energy difference between the surface state in the $\bar{\Gamma}$ -point E_0 and the lower band edge of the bulk band gap E_{\max} . We utilize this idea to determine l in our calculations. Both the minimum of the surface state and the lower edge of the bulk band gap is obtained from a previous publication [23]. The results are shown in table 1.

As we are only interested in finding out the important parameters to explain trends of the convergence, we choose simple bulk band wavefunctions given by the simple one-dimensional ‘particle-in-box’ potential in the z direction and

free electron like in the direction parallel to the surface.

$$|n\vec{k}_{\parallel}\rangle = \sqrt{\frac{2}{L\Omega}} e^{i\vec{k}_{\parallel}\cdot\vec{x}} \sin\left(\frac{n\pi}{L}z\right). \quad (4)$$

The energy eigenvalues are then

$$E_{n\vec{k}_{\parallel}} = E_n + \frac{\hbar^2 |\vec{k}_{\parallel}|^2}{2m^*} \quad (5)$$

where $1 \leq n \leq n_{\max}$ and n_{\max} labels the bulk band corresponding to the lower edge of the projected band gap ($E_n = E_{\max}$). The bulk bands are assumed to exist up to the lower edge of the band gap.

In order to focus on trends for different systems we simplify rather drastically the expression for the hole lifetime broadening. We neglect differences in phonon structures of the systems and consider a single Einstein mode polarized perpendicular to the surface and with frequency ω . The mode is assumed to be confined within a fixed depth of at least l . The RIA is applied with a deformation potential D independent of the system.

We consider a normal photoemission experiment in which the removed surface state electron in the $\bar{\Gamma}$ -point is analyzed. The e–p induced lifetime broadening, Γ_{ep} , corresponds to the lifetime of the hole left behind. We have then

$$\Gamma_{\text{ep}} = \frac{\hbar}{2M\omega N_{\parallel}} \sum_{n,\vec{k}_{\parallel}} |\langle n\vec{k}_{\parallel} | D | 0 \rangle|^2 \delta(E_0 - E_{n\vec{k}_{\parallel}}) \quad (6)$$

where N_{\parallel} is the number of atoms in each layer. In equation (6) we have applied the quasi-static approximation, neglecting the phonon energy in the energy conservation of e–p scattering process. The atomic screened one-electron potential is taken to have the form

$$V(r) = -V_0 \exp(-\alpha r) \quad (7)$$

where α is the inverse screening length which has to be chosen large enough that V decays within half the distance between nearby layers. In the calculations we have used $\alpha = 10/d$, where d is the interlayer distance. Within the RIA the atomic deformation potential averaged over x and y within the Wigner–Seitz radius R_{ws} is then

$$D_{\alpha} = \langle V'(z) \rangle_{xy} \approx V_0 \frac{z}{R_{\text{ws}}^2} \exp(-\alpha |z|). \quad (8)$$

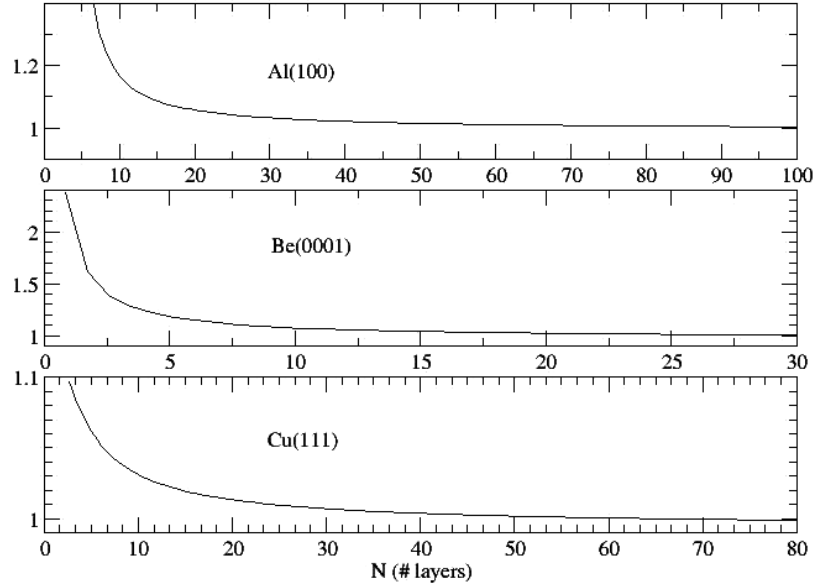


Figure 3. Illustration of convergence of the normalized Γ_{ep} as a function of the number of the slab layers. The normalization is done with respect to the asymptotic value ($L \rightarrow \infty$).

Table 1. Parameters used in the convergence test of the slab approximation. Definitions of parameters are shown in the text.

	Al(001)	Be(0001)	Cu(111)
$E_0 - E_{\max}$ (eV)	0.23	2.0	0.5
l (a.u.)	24.6	2.84	11.8
W (eV)	9.0	10	6.0
d (a.u.)	3.8	3.1	4.8

Thus we can write the deformation potential, to be inserted in equation (6),

$$D(z) = \sum_{j=0}^{N_l-1} \frac{1}{\sqrt{N_l}} D_\alpha(z - jd) \quad (9)$$

where N_l is the number of layers within l . The delta function on equation (6) will pick up a particular $|\vec{k}_\parallel|$ for each band n , we label these k_n .

$$k_n = \frac{\sqrt{2m^*(E_0 - E_n)}}{\hbar}. \quad (10)$$

We then have the L dependence of the lifetime broadening

$$\Gamma_{ep}(L) = \frac{1}{2\pi} \frac{n_l}{\hbar\omega} \frac{m^*}{M} \frac{1}{lL} \sum_{n=1}^{n_{\max}} I_z^2(n) I_\parallel^2(n) \sim \frac{1}{lL} \sum_{n=1}^{n_{\max}} I_z^2(n) \quad (11)$$

where n_l is the density of atoms in each layer, $L = n_{\max}\pi\sqrt{2W}$, where W is the band width in the $\bar{\Gamma}$ -point, and $I_\parallel^2(n) \approx \pi R_{ws}^2$ and

$$I_z(n) = \int_0^l D(z) \sin(n\pi z/L) dz. \quad (12)$$

The parameter W and d are given in table 1.

If we increase the number of layers in the slab the number of contributing bulk bands increases whereas the overlap for each band with the surface state becomes smaller. The results for Γ_{ep} , normalized with its asymptotic value ($L \rightarrow \infty$), are shown for surface states of three clean metal surfaces in figure 3. From these results, it is obvious that convergence in terms of the number of slab layers, N , are different for different surfaces. In general, for all surfaces, the line width decreases with increasing number of slab layers. This means that the reduced overlap between bulk states and surface state kills the effect of the increasing number of contributing states. To reach an error less than 10% of the asymptotic value of Γ_{ep} we need $N > 3$ for Cu(111) surface state, for Be(0001) $N > 8$, and for Al(001) $N > 13$. We note here that the short extension of the surface state into the bulk l for Be(0001) does not mean that the needed number of layers to reach convergence of Γ_{ep} is the smallest for this surface. The reason why the smallest number of layers is found for Cu(111) is due to its relatively small band width of 6 eV (see table). Although the l is a factor 4 times larger for Cu(111) than for Be(0001) the convergence of Γ_{ep} is reach within 3 layers. A small band width means a small slab thickness L for small n_{\max} as $L = n_{\max}\pi\sqrt{2W}$ and thus large overlaps between the surface state wavefunctions and the bulk wavefunctions. The reason why the convergence is slightly slower for Al(001) in comparison with Be(0001) is due to the large spread of the surface state (l) for Al(001).

Although the model here is very simple we think it illustrates that we should be careful about the convergence of e-p with respect to the slab thickness. The extension of the surface state into the bulk, l , guides us for the choice of slab thickness in the case of a static electronic structure calculation. However, for a dynamical calculation such as the surface e-p coupling, the bulk band width, W seems to be an important parameter.

4. Summary and conclusions

In this paper we have investigated the validity of commonly used approximations in the calculations of the e–p coupling at surfaces.

Applying a simple model, we explore the influence of basic properties of the electronic structure on the convergence, with respect to the slab thickness, of phonon induced surface state hole lifetimes broadening, Γ_{ep} . We find that even if the extension of a surface state is small, within a few atomic layers, as in the case of Be(0001), the convergence of Γ_{ep} is relatively slow. Our model study indicates that the bulk band width W is a crucial parameter. The needed number of slab layers to mimic the semi-infinite system, will increase with increasing bulk band width.

We also studied, applying the *first principles* methods, the validity of the rigid-ion approximation, RIA, for surface atoms. For Be(0001), we find that RIA is valid for both bulk and surface atoms. This indicates that we can expect RIA to be valid in general for clean metal surface as the screening properties in the surface and bulk of Be(0001) is expected to be rather different, metallic and semi-metallic, respectively.

Acknowledgments

This work was supported by the global COE program for Chemistry Innovation. The authors thank the Computer Center of the Institute for Molecular Science for the use of computers.

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