LETTER TO THE EDITOR

On surface ACAR spectra calculated within the mixed-density approximation

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Abstract. Various approaches to the surface problem that enable us to calculate angular correlation of annihilation radiation (ACAR) spectra are discussed. The validity of the mixed-density approximation (MDA) in the neighbourhood of metal surfaces is investigated. For positrons trapped at the Al surface the MDA gives results that strongly disagree with those obtained using the exact ACAR formula. A new formula for use in calculating surface ACAR spectra, allowing avoidance of this deficiency of the MDA, is proposed.

The isotropic shape of experimental spectra of angular correlation of annihilation radiation (ACAR) from clean Al(100) surfaces, measured by Lynn *et al* (1985) using a slow positron beam, gave an impetus for intensive theoretical work aimed at explaining this unexpected feature (Brown *et al* 1987, 1988, Lou 1988, Rubaszek and Lach 1989a, b). The ACAR spectra are defined by

$$N(\boldsymbol{p}) = \sum_{k_{\mathrm{occ}}} \left| \int \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \psi_k^{\mathrm{ep}}(\boldsymbol{r}, \boldsymbol{r}) \, \mathrm{d}^3 r \right|^2 \tag{1}$$

where $\boldsymbol{p}$ is the momentum of the annihilating electron–positron pair, $\psi_k^{\mathrm{ep}}(\boldsymbol{x}_{\mathrm{e}}, \boldsymbol{x}_{\mathrm{p}})$ denotes the pair wavefunction of a (thermalised) positron located at $\boldsymbol{x}_{\mathrm{p}}$ and an electron (in the initial state $\boldsymbol{k}$) at $\boldsymbol{x}_{\mathrm{e}}$. The summation in (1) is over all occupied electronic states $\boldsymbol{k}$.

The one-dimensional distributions of annihilating pairs are given by

$$N(p_x) = \iint N(\boldsymbol{p}) \, \mathrm{d}p_y \, \mathrm{d}p_z \tag{2a}$$

$$N(p_z) = \iint N(\boldsymbol{p}) \, \mathrm{d}p_y \, \mathrm{d}p_x \tag{2b}$$

where p_z is assumed to be perpendicular to the sample.

The wavefunctions ψ_k^{ep} in formula (1) are dependent on the unperturbed electron wavefunctions of the material investigated, $\psi_k^0(\boldsymbol{r})$, the positron wavefunction, $\psi_+(\boldsymbol{r})$, and the strong electron–positron correlations, $f(\boldsymbol{r}, \boldsymbol{k})$, in the following manner:

$$\psi_k^{\mathrm{ep}}(\boldsymbol{r}, \boldsymbol{r}) = f(\boldsymbol{r}, \boldsymbol{k}) \, \psi_k^0(\boldsymbol{r}) \, \psi_+(\boldsymbol{r}). \tag{3}$$

When the electron–positron correlations f are known, the momentum distribution given

by

$$N(p) = \sum_{k_{occ}} \left| \int e^{ip \cdot r} \psi_k^0(r) \psi_+(r) f(r, k) \, d^3r \right|^2 \tag{4}$$

provides useful information about the electronic structure of the material investigated (determined by the functions ψ_k^0). In particular, the slow positron beam, because of its small implantation depth, looks promising as a tool for probing electronic properties of metal surfaces.

The main problem, not solved until now, consists in the proper determination of the correlation function $f(r, k)$ in the neighbourhood of a metal surface. In order to calculate surface ACAR spectra from formula (4), three different approximations have been proposed by authors of theoretical work.

The first of these approximations is the independent-particles model (IPM), completely neglecting electron–positron correlations, i.e. assuming $f(r, k) \equiv 1$. Within the IPM, formula (4) reduces to the well known equation

$$N^{IPM}(p) \sum_{k_{occ}} \left| \int e^{ip \cdot r} \psi_k^0(r) \psi_+(r) \, d^3r \right|^2. \tag{5}$$

Within the jellium model, where

$$\psi_k(r) = \exp[i(k_x x + k_y y)] \, \psi_{k_z}(z) \tag{6a}$$

$$\psi_+(r) = \psi_+(z) \tag{6b}$$

formula (5) simplifies to

$$N^{IPM}(p) = \int_{k_z^2 \leqslant k_F^2 - p_x^2 - p_y^2} dk_z \left| \int e^{ip_z z} \psi_{k_z}(z) \psi_+(z) \, dz \right|^2. \tag{5a}$$

It should be pointed out that using the IPM is rather controversial for the surface problem. In the neighbourhood of a metal surface the electron density rapidly decreases and therefore the effect of electron–positron correlations should be pronounced (Arponen and Pajanne 1979, Lowy 1982, Rubaszek and Stachowiak 1988). On the other hand, the conclusions for the bulk material could not be valid for the metal surface, where the electronic screening charge distribution loses its spherically symmetric shape and, far from the surface, becomes detached (Inglesfield and Stott 1980, Jensen and Walker 1988). Using the electron and positron model (and, resulting from this, the electron and positron wavefunctions ψ_{k_z} and ψ_+), and using formula (5a), some authors obtained almost isotropic ACAR spectra from an Al surface (Lou 1988, Brown *et al* 1988), while in other cases (Brown *et al* 1987, Rozenfeld *et al* 1983, Rubaszek and Lach 1989a, b) the IPM yields anisotropic spectra (this anisotropy varies from 10 to 50%).

Let us discuss the possibilities for full isotropy of IPM surface ACAR spectra calculated according to formula (5a). It is most convenient to use the autocorrelation function $B(r)$ defined as the inverse Fourier transform of $N(p)$, i.e.

$$B^{IPM}(r) = (2\pi)^{-3} \int e^{-ip \cdot r} N^{IPM}(p) \, dp \tag{7}$$

$$= (2\pi)^{-3} \sum_{k_{occ}} \int \psi_k(r_1) \psi_+(r_1) \psi_k^*(r - r_1) \psi_+(r - r_1) \, dr_1.$$

The equality of the one-dimensional distributions $N(p_x)$ and $N(p_z)$ is equivalent to the

equality of the corresponding inverse Fourier transforms—$B^{IPM}(z, 0, 0)$ and $B^{IPM}(0, 0, z)$, respectively. This means that for any z the expression

$$\sum_{k_{occ}} \int dz_1 \; \psi_{k_z}^*(z_1)\psi_+^*(z_1)(\psi_{k_z}(z + z_1)\psi_+(z + z_1) - e^{ik_z z}\psi_{k_z}(z_1)\psi_+(z_1))$$

is exactly equal to zero. This condition is undoubtedly satisfied in the bulk material, where $\psi_{k_z}(z) = e^{ik_z z}$. For the metal surfaces the problem is more complicated and the results are dependent on translational properties of electron and positron wavefunctions perpendicular to the surface. The (exponential) tails of $N(p_z)$ for $p_z > k_F$ could also reproduce small differences between $B(z, 0\,0)$ and $B(0, 0, z)$.

Another approach (Rubaszek and Lach 1989a, b) is based on the local density approximation (LDA), introduced by Daniuk *et al* (1985, 1987). The correlation function $f(r, k)$ in (4) is assumed to be equal to $\sqrt{\varepsilon(k, r_s(r))}$, where the $\varepsilon(p, r_s)$ are the momentum-dependent electron–positron enhancement factors obtained within the self-consistent Kahana approach (Rubaszek and Stachowiak 1988) and $r_s(r)$ corresponds to the local electron density $\rho(r)$. The main advantage of this theory is that it allowed us to obtain a reversal of the direction of the anisotropy of the ACAR spectra for the Al surface (with $N(p_x)$ broader by about 9% than $N(p_z)$), in agreement with the experimental result of Lynn *et al* (1985). The deficiency of the LDA consists in the overestimation of $\varepsilon(p, r_s)$ for the surface problem, causing too strong a narrowing of the ACAR spectra. Self-consistent Kahana theory, giving good agreement with experiment for bulk material, should be modified for metal surfaces. This is, however, very difficult from the conceptual point of view, mainly because of the violation of the periodicity conditions perpendicular to the surface.

The mixed-density approximation (MDA), recently quite frequently applied (Brown *et al* 1987, 1988), is the most controversial way of calculating surface ACAR spectra. The main deficiency of this approach is the disagreement with the exact ACAR formula (4) in the case of metal surfaces, whatever electron–positron correlations are used (the MDA is valid only for bulk material), as will be shown below. Within the MDA the momentum distribution of annihilating pairs is calculated according to the formula

$$N^{MDA}(p) = \int dr \int dr_1 \; \exp[ip \cdot (r - r_1)]\psi_+(r)\psi_+(r_1)\frac{\Gamma[\rho(R)]}{k_F^3(R)}$$

$$\times \int_{k < k_F(R)} \exp[ik \cdot (r - r_1)] \, dk \qquad (8)$$

where $R = (r + r_1)/2$, $k_F(R)$ is the local Fermi momentum, and $\Gamma[\rho(r)]$ is the positron annihilation rate, dependent on the local electron density $\rho(r) = k_F^3(r)/3\pi^2$.

Two disadvantages of the MDA should be discussed. The first is connected with the divergence of the overlap integral in (8) for $R_z \to \infty$ if the annihilation rate Γ corresponding to the bulk material is applied. For $R_z \to \infty$, $\rho(R) \to 0$, $\Gamma(\rho)$ is convergent to $2 \times 10^9\,s^{-1}$, while $k_F(R) \to 0$ and the whole expression diverges. In order to avoid this divergence, Brown *et al* (1987, 1988) imposed an unphysical cut-off in Γ, assuming $\Gamma[\rho(R)] = 0$ for $R_z > z_c$ for some arbitrary z_c. Such a cut-off is difficult to substantiate on physical grounds because the assumption that $\Gamma = 0$ means that the positron is not only bare (as it really occurs far from the surface) but also that there are no electrons at all in its neighbourhood, i.e. that the positron repels electrons instead of attracting them. Moreover, the resulting ACAR spectra appeared to be strongly dependent on the cut-off position z_c (Brown *et al* 1987). If any cut-off is to be used, I suggest using the approximation (more easy to substantiate on physical grounds) $\Gamma^{IPM}[\rho(r)] = \pi r_0^2 c \rho(r) =$
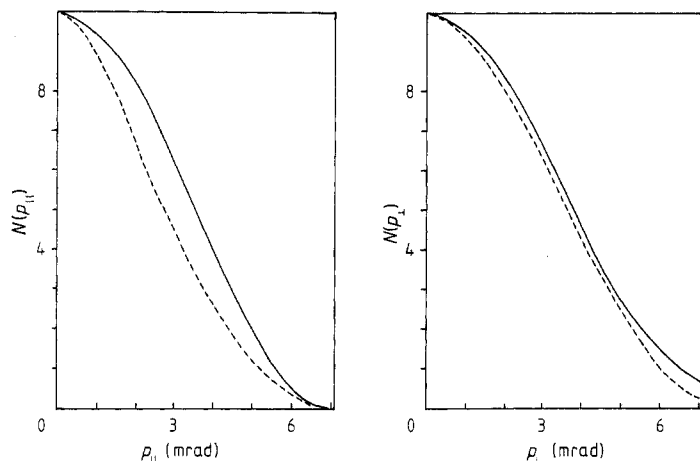
Figure 1. One-dimensional momentum distributions of annihilating pairs from an Al surface obtained within the IPM from definition (5a) (full curves) and according to the MDA formula (8a) (broken curves).

$16\pi\rho(r) \times 10^9 \text{ s}^{-1}$ for $r_z > z_0$, where z_0 is the point of intersection of the image with correlation positron potentials. This modification allows one to avoid the divergence of (8) and is based only on the assumption that the positron is not screened far from the surface (Inglesfield and Stott 1980, Jensen and Walker 1988, Brown *et al* 1988). The problem of the cut-off in the annihilation rate could be easily avoided if instead of using the annihilation rate corresponding to a bulk material, the proper surface values were used (Jensen and Walker 1988).

The second deficiency of the MDA, namely the invalidity for the surface problem (whatever electron–positron correlations Γ are used), is much more serious.

The simplest test for any approach enabling us to calculate $N(p)$ is the IPM. Within the IPM the positron is not screened and $\Gamma^{\text{IPM}}[\rho(R_z)] = 16\pi\rho(R_z) = 16k_F^3(R_z)/9\pi$. Within the jellium model, with the IPM annihilation rate Γ^{IPM}, formula (8) takes the form

$$N_{\text{MDA}}^{\text{IPM}}(p) = \int_{-\infty}^{\infty} \mathrm{d}R_z \int_0^{\infty} \mathrm{d}z_1 \cos(p_z z)\psi_+(R_z + z/2)\psi_+(R_z - z/2)\sin(\kappa z)/z \qquad (8a)$$

where $\kappa^2 = k_F^2(R_z) - p_x^2 - p_y^2$.

In the present work the calculations of $N(p_x)$ and $N(p_z)$ were performed according to formulae (2), (5a) and (8a). The electron and positron wavefunctions, $\psi_{k_z}(z)$ and $\psi_+(z)$, were determined as described in the papers by Rubaszek and Lach (1989a, b). In figure 1 the results obtained according to the definition of momentum distribution given by (5a) are shown as full curves. The broken curves correspond to the MDA formula (8a). In the left-hand panel of figure 1 the momentum distributions parallel to the surface, $N(p_x)$, are presented; in the right-hand panel the $N(p_z)$ are shown. In the case of $N(p_x)$ significant differences are visible, showing a lack of consistency between the MDA and the definition of ACAR spectra. Therefore, it is necessary to exercise a great deal of caution if drawing any conclusions concerning the shape of ACAR spectra from the metal surface when using the MDA (this approximation is reasonable only for bulk material and to some extent for distributions perpendicular to the surface, as is seen from the right-hand panel of figure 1).

Let us explain this feature mathematically. Comparison of formulae (8) and (4) shows that the expression

$$\sum_{k_{\text{occ}}} \psi_k^0(r)\psi_k^{0*}(r_1)f(r, k)f^*(r_1, k)$$

of definition (4) is in the MDA (equation (8)) replaced by

$$\sum_{k < k_F(R)} e^{ik \cdot r} e^{-ik \cdot r_1} \frac{\Gamma[\rho(R)]}{k_F^3(R)}.$$

This means that the MDA not only averages electron–positron correlations over electronic states k (which is very convenient) but also assumes electron wavefunctions in the form of plane waves. The latter assumption, valid in the bulk material, does not hold true in the neighbourhood of the surface. Perpendicularly to the surface the periodicity conditions are violated and electron wavefunctions $\psi_k^0(r)$ are strongly dependent on the z position. This comparison allows us to understand why the MDA is valid in the bulk material and falls down for metal surfaces. The spectra, presented in the right-hand panel of figure 1, $N(p_z)$, confirm these points. Parallel to the surface the wavefunctions $\psi_k^0(r)$ are assumed to be plane waves (cf $(6a)$ and $(6b)$) and therefore differences between corresponding momentum distributions $N(p_z)$ are much smaller than in the case of $N(p_x)$.

Hence, we cannot use the ACAR spectra obtained according to (8) to extract information about the electronic structure of the surface of the material investigated, where the $\psi_k^0(r)$ differ from plane waves. For this reason this method is not recommended for interpretation of experimental ACAR spectra.

The IPM and LDA allow us to avoid both the problem of invalidity for metal surfaces and the divergence of $N(p)$, connected with the MDA (this is removable if a proper local annihilation rate Γ is used in (8)). In the case of the IPM (equation (5)) the situation is clear. The LDA, which is obtained from expression (4) with $f(r, k) = \sqrt{\varepsilon(k, r_s(r))}$, is convergent even if the $\varepsilon(p, r_s(r))$ corresponding to the bulk material are used (for more details see Rubaszek and Lach 1989a, b). If the local surface-momentum-dependent enhancement factors were known, using the LDA would provide the only reliable way of calculating surface ACAR spectra. However, as was mentioned, determining these parameters is very complicated. The electronic cloud screening a positron surface becomes detached from the positron, creating a classical image charge (Inglesfield and Stott 1980, Jensen and Walker 1988). This suggests using $\varepsilon(p, r_s(z)) = 1$ for $z \to \infty$ instead of $\varepsilon(p, r_s(z)) = A(p) r_s^3(z)$, corresponding to the bulk material. The advantage of the MDA in comparison with the LDA consists in averaging electron–positron correlations over electronic states: the MDA requires only the total electron distribution on the positron while the LDA separates particular electronic states. It should be stressed here that determination of the total local annihilation rate $\Gamma(r)$ is much easier than determination of the partial local annihilation rates, $\varepsilon(p, r)$. An attempt to calculate the electron distribution on the positron in the neighbourhood of an Al surface, giving the values of the local annihilation rates, was made by Inglesfield and Stott (1980) and by Jensen and Walker (1988).

In the present work a new formula for calculating surface ACAR spectra is suggested. This new approach is consistent with definition (4) and allows one to average electron–positron correlations over electronic states k, making it convenient for use. If the electronic screening charge distribution on the positron located at r, $\Delta\rho(r)$, is known (Jensen and Walker 1988), we suggest calculating surface ACAR spectra according to the formula

$$N(p) = \sum_{k_{occ}} \int dr \int dr_1 \exp[ip \cdot (r - r_1)] \psi_+(r) \psi_+^*(r_1) \psi_k(r) \psi_k^*(r_1) \left(1 + \frac{\Delta\rho(R)}{\rho(R)}\right). \quad (9)$$

Formula (9) is obtained from (4) by replacing $f(r, k)f(r_1, k)$ by $1 + \Delta\rho(R)/\rho(R)$ and

therefore is consistent with definition (4). The ACAR spectra obtained using (9) provide useful information about the electronic structure of the surface investigated. Replacing $\psi_k(r)$ in (9) by plane waves $e^{ik \cdot r}$ and the total Fermi momentum k_F by the local one $k_F(R)$, we simply switch to MDA formula (8).

In order to make (9) more convenient for numerical calculations, an approximate form could be used:

$$N(p) = \sum_{k_{occ}} \left| \int dr\, e^{ip \cdot r} \psi_+(r) \psi_k(r) \sqrt{1 + \Delta\rho(r)/\rho(r)} \right|^2. \qquad (9a)$$

It should be mentioned here that expression (9a) is always convergent (even if electron–positron correlations corresponding to the bulk material are used), because $|\psi_k(r)|^2/\rho(r)$ is limited by unity for any r, and $\psi_+(r)$ is (squared) integrable while $|e^{ip \cdot r}| = 1$.

The results obtained from the LDA–MDA formula (9a) with the electronic screening charge distribution $\Delta\rho(r)$ (appropriate for the surface problem) calculated in the way proposed by Jensen and Walker (1988) are presented in a subsequent publication (Rubaszek and Lach 1988).

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