NUKLEONIKA 2013;58(1):211–214

ORIGINAL PAPER

Momentum distributions in positron annihilation with tightly bound electrons in Al

Edward Boroński

Abstract. An approach based on Carbotte, Salvadori and Chiba two-body schemes for calculation of electron-positron (e-p) momentum densities $\rho(p)$ for core electrons in solids is developed. The approach allows to avoid such common approximations as the local density approximation (LDA) etc. in determination of $\rho(p)$ of deeper atomic shells and reduces the contribution to $\rho(p)$ for higher momenta. Thus, the final calculations of the Doppler spectra of annihilation radiation yield lower values for greater momenta than those obtained within the LDA scheme. The exemplary calculations for Al are presented.

Key words: positron annihilation • electronic structure

Introduction

Studies of the Doppler broadening of the electron--positron (e-p) annihilation radiation become more and more advanced and common method of investigating bulk and defected materials. Since the application of two-detector coincidence technique allowed to get quite accurate data for great momenta in e-p momentum distribution of annihilating pair $\rho(p)$ (up to $p_L = 60 \times 10^{-3} m_0 c$) [16], it is now possible to investigate core electron states in the sampled material. In particular, this tool is very important in identification of many kinds of defects.

For a proper interpretation of the experimental results, it is useful, however, to support the studies with calculation of the corresponding spectra. The older and recent calculations, though close to the experimental data, exhibit some deviations both in low and in high momentum regime. Therefore, there is a necessity to reconsider the ways of taking into account the positron interaction with bound electrons of atoms in solids. The common approximations in use in positron physics and in calculations of Doppler spectra based on density functional theory, are local density approximation (LDA) [5, 10, 11], (see also e.g. [1]), generalized gradient approximation (GGA) [2, 3] and weighted density approximation (WDA) [19]. The GGA and WDA give better results than the LDA, however, GGA is parameter dependent and WDA is, in practice, very difficult in common applications.

In the low momentum regime, thus in case of annihilation of the positron with valence electrons one should lend from some experiences reached in studies of the electronic structure of metals and Fermi surface by positrons, presented in a series of papers of e.g.

E. Boroński
Opole University,
Institute of Physics,
48 Oleska Str., 45-052 Opole, Poland,
Tel.: +48 77 452 7250, Fax: +48 77 452 7290,
E-mail: e.boronski@uni.opole.pl

Received: 14 June 2012
Accepted: 12 October 2012

Kontrym-Sznajd and Sormann [14, 21, 22] and others [15]. One should take into account the Bloch character of the electron wave function (Bloch modified ladder theory). This kind of approach seems to be too complicated for present purposes, i.e. for localized electron states, as well as such are the methods devoted to positron annihilation in gases (see e.g. [12]) and a simpler treatment of the e-p interaction close to the atom would be desirable.

In this paper one is interested in calculations of the momentum densities of core electrons interacting with a positron by developing the method presented by Chiba *et al*. in Ref. [9], based on earlier papers of Carbotte and Salvadori [8, 20].

Theory and results

The momentum distribution of the e-p pair can be written in terms of two-body wave function as

$$\rho(\mathbf{p}) = \pi r_0^2 c \sum_j \left| \int d\mathbf{r}\; e^{-i\mathbf{pr}} \Psi_j(\mathbf{r},\mathbf{r}) \right|^2 \tag{1}$$

where r_0 and c are the classical electron radius and the velocity of light, respectively, and the summation is over the occupied electron states.

The Doppler spectra, corresponding to the annihilation of the positron with an electron in a core state c, can be obtained by

$$N_c(p_z) = 2\pi \int_{|p_z|}^{\infty} p\rho_c(p)dp \tag{2}$$

where $\rho_c(p)$ is the contribution to $\rho(\mathbf{p})$ from the core state c.

According to the approach presented in Refs. [8, 20] the wave function ψ_c of the positron-core electron pair can be approximately given by

$$\begin{aligned} \Psi_c(\mathbf{x}_e, \mathbf{x}_p) &= \psi_c(\mathbf{x}_e)\phi_{+0}(\mathbf{x}_p) \\ &+ \frac{2}{\Omega}\sum_{\mathbf{k},\mathbf{k}'} \frac{\psi_{\mathbf{k}}(\mathbf{x}_e)\phi_{+\mathbf{k}'}(\mathbf{x}_p)}{k^2 + k'^2 + 2\Delta_c} V(k') \\ &\times \int d\mathbf{x}\, \psi_c(\mathbf{x})\psi^*_{\mathbf{k}}(\mathbf{x}) e^{-i\mathbf{k}'\mathbf{x}} \end{aligned} \tag{3}$$

where ψ_c and ϕ_{+0} are the wave functions of the core electron and the positron, respectively, in its lowest state within the independent particle model (IPM). Δ_c is the difference between the core electron energy level and the Fermi energy (the bottom of conductivity band in a non-metal). The indexes k and k' are reserved for unoccupied states of the electron and the positron. $V(k)$ is the Fourier transform of the e-p interaction potential and, in general, should describe some screening of the positron by surrounding electrons. There are, however, arguments of Bonderup *et al*. [5] who showed that for the case of positron surrounded by the electrons of high density one can successfully use the bare Coulomb potential if the perturbation series for the above wave function is limited to the first order. Thus, we use here the Born approximation for the wave function and the Coulomb potential instead of the screened one (for general purposes, the following expressions still contain the screening length parameter α, which is put to zero in our computations).

In order to perform simple calculation of formula (3), avoiding tedious and impractical summations over higher states, Chiba *et al*. [9] proposed the following approximations for the positron and electron wave functions corresponding to unoccupied states (in fact Eq. (4) had been given already by Carbotte and Salvadori [8])

$$\psi_{\mathbf{k}}(\mathbf{x}) \approx \phi_{+0}(\mathbf{x}) e^{-i\mathbf{kx}} \tag{4}$$

$$\phi_{+\mathbf{k}'}(\mathbf{x}) \approx \phi_{+0}(\mathbf{x}) e^{-i\mathbf{k}'\mathbf{x}} \tag{5}$$

whereas the second approximation is rather obvious, the first one, concerning the electron can be justified by the fact that the electron wave function corresponding to higher states resembles more the plane wave and, moreover, near the core is damped due to an orthogonality to the core states of the atom. Thus, in practice, the electron feels the repulsive potential (see e.g. the discussion in Ref. [18]) and the situation resembles that of positron near the nucleus. An example is given in Figs. 1 and 2 and in Ref. [20]. However, Eq. (4) is simpler than the OPW formula of Ref. [20]. The above formulas allowed Chiba *et al*. to simplify Eq. (3) by the application of Dirac delta function, according to the following approximation

$$\int d\mathbf{x}\, \phi_{+0}(\mathbf{x})^2 e^{i(\mathbf{k}+\mathbf{k}'-\mathbf{p})\mathbf{x}} \approx \delta(\mathbf{k}+\mathbf{k}'-\mathbf{p}) \tag{6}$$

The approximations [8, 20] similar to Eq. (6) lead, as shown in Ref. [5], to a considerable overestimation of the enhancement of the electron density at the positron. Therefore Bonderup *et al*. [5] proposed instead to apply the LDA approximation to the enhancement for the positron-core interaction. Then, the schemes based on the LDA approximation given in a series of papers of Daniuk *et al*. [10, 11] as well as GGA schemes by Barbiellini *et al*. [1–3] and others (see e.g. Refs. [7, 13, 17]) have been utilized in many theoretical investigations of core electrons in solids.

The approximation (6) can be, however, simply corrected if one expands the square of the positron wave function into a Fourier series with respect to reciprocal lattice vectors of the investigated crystal

$$\phi^2_{+0}(\mathbf{x}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G}\mathbf{x}} \tag{7}$$

and

$$\begin{aligned} &\int d\mathbf{x}\, \psi_{\mathbf{k}}(\mathbf{x})\phi_{+\mathbf{k}'}(\mathbf{x}) e^{-i\mathbf{p}\mathbf{x}} \\ &\approx \int d\mathbf{x}\, \phi_{+0}(\mathbf{x})^2 e^{i(\mathbf{k}+\mathbf{k}'-\mathbf{p})\mathbf{x}} \\ &= \sum_{\mathbf{G}} a_{\mathbf{G}} \int e^{i(\mathbf{k}+\mathbf{k}'+\mathbf{G}-\mathbf{p})\mathbf{x}} \\ &= \Omega \sum_{\mathbf{G}} a_{\mathbf{G}} \delta(\mathbf{k}+\mathbf{k}'+\mathbf{G}-\mathbf{p}) \end{aligned} \tag{8}$$

The Fourier coefficients $a_{\mathbf{G}}$ are such that the next terms of the expansion are subtracted from the first leading term and hence a suppression of the positron function near the core can be taken into account.

Then, the formula for the e-p momentum density for a given core electron state c reads

(9) $$\rho_c(\mathbf{p}) = \left|J_0(\mathbf{p}) + \eta(\mathbf{p})\right|^2$$

where the contribution to $\rho_c(\mathbf{p})$, related to non-interacting particles is

(10) $$J_0(\mathbf{p}) = \int d\mathbf{x}\, \psi_c(\mathbf{x})\phi_{+0}(\mathbf{x})e^{-i\mathbf{p}\mathbf{x}}$$

and the correction $\eta(\mathbf{p})$ with respect to the e-p interaction, can be expressed as

(11) $$\eta(\mathbf{p}) = 8\pi \sum_{\mathbf{k},\mathbf{G}} \frac{a_{\mathbf{G}}}{(k^2 + (\mathbf{k}-\mathbf{p}+\mathbf{G})^2 + 2\Delta_c)(k^2+\alpha^2)} \times J_0(\mathbf{p}-\mathbf{G})$$

In our exemplary calculations for Al we used computer codes developed by Alatalo *et al*. [1], appropriately modified for our purposes. Thus, the electron wave functions calculated in the atomic part of the code have been used for determining the electron density within the atomic superposition method. On this ground, the potential for the positron including the e-p correlation has been found and the corresponding Schrödinger equation for the positron wave function was solved. In the original scheme, all partial momentum densities corresponding to different scheme are calculated within the LDA or GGA approximation in which contact values of e-p correlation function are used according to Boroński-Nieminen [6] or Barbiellini [2, 3] formulas.

In our method we use this prescription, at least for now, only for the valence states. For core states, the approach presented above is applied. The values Δ_c are found by employing the WIEN2k code [4] which supports the calculation with the value of the corresponding Fermi energy. These values are 55.2435, 3.9085, 2.5205 a.u. for the 1*s*, 2*s*, and 2*p* states, respectively.

The influence of the correction due to e-p interaction on $J_0(p)$ is shown in Figs. 1 and 2. The factor enhancing $J_0(\mathbf{p} - \mathbf{G})$ in Eq. (11) only for $\mathbf{G} = 0$ can be presented as a monotonously decreasing function, as shown in Fig. 1 of Ref. [9]. The next terms, corresponding to the vectors $\mathbf{G} \neq 0$, contribute almost equally to the leading one, however, their signs are negative and

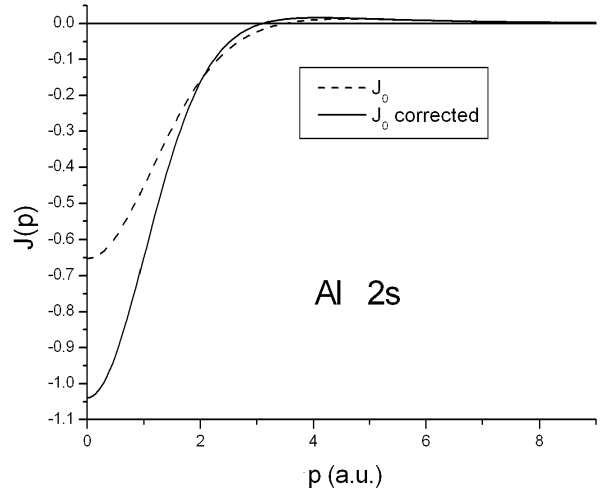

Fig. 1. The effect of positron-electron interaction for 2*s* electron state in Al. The dashed curve corresponds to the function J_0 calculated in the IPM approximation, whereas the solid curve relates to calculations performed within the presented approach.

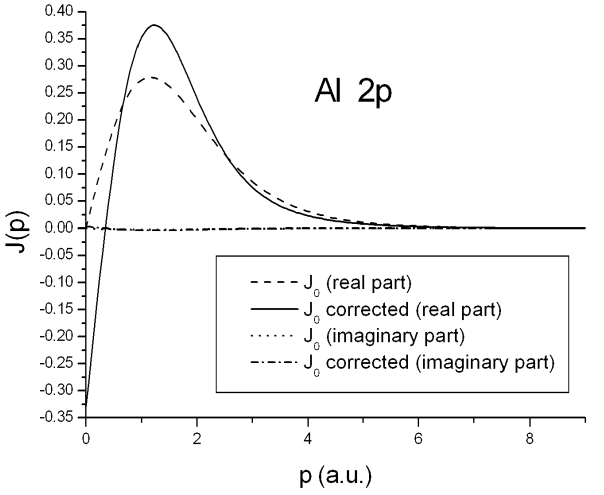

Fig. 2. The same quantities as in Fig. 1, but for the 2*p* core state.

in some regions of p the net values of $J(p)$ can be even less than $J_0(p)$. It is worth reminding that in the scheme of Alatalo *et al*. [1] the squares of the partial momentum densities $|J_0(p)|^2$ are simply multiplied by the constant enhancement based on the LDA calculation for a given atomic shell and normalized to the total annihilation rate. Though practical, contrary to our method the approach [1] presents an artificial way of treating the complicated effect of change of the electron states due to the positron.

In Figure 3 we showed the calculated Doppler spectra for 1*s*, 2*s* and 2*p* electron states in Al. The results of our calculations are compared to the corresponding LDA curves. As seen, all the spectra are slightly lower than the LDA values and the values of the enhancement of different shells is decreasing with momentum. This feature is transferred to the total one-dimensional momentum densities (Fig. 4) which are also lower for high values of momenta than LDA curve. Whereas the latter distribution, if properly normalized, is slightly too high if comparing to the experimental points (see e.g. [1, 13, 17]) our curve runs slightly below the data.

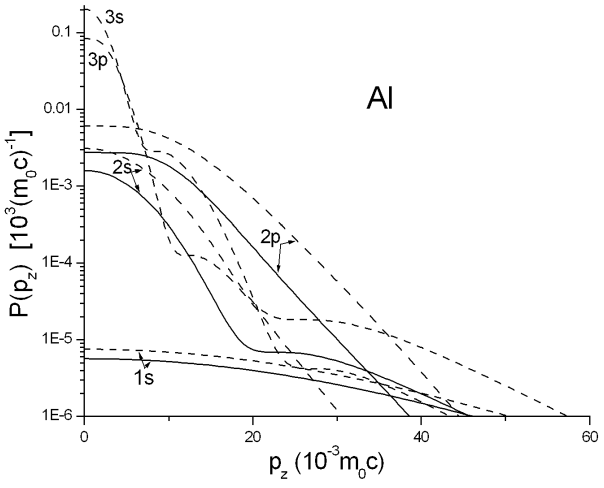

Fig. 3. Partial one-dimensional momentum densities for 1*s*, 2*s*, 2*p*, 3*s* and 3*p* electron states in Al. Solid curves represent the distributions found according to the presented method and dashed curves correspond to calculations performed within the LDA approximation.

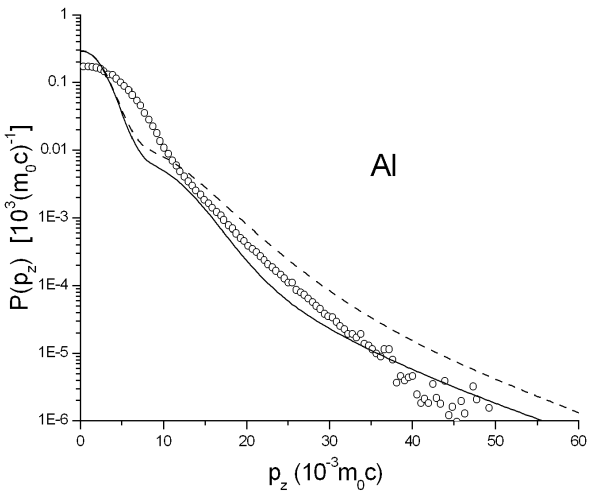

Fig. 4. Total distributions corresponding to the Doppler spectra in positron annihilation. The solid and dashed curves relate to our and the LDA approximations, respectively. The experimental points are taken from Fig. 2 of Ref. [1].

Conclusions

We have presented an approach to calculations of Doppler spectra that bases on some older ideas, however, correcting their weaknesses criticized by Bonderup *et al.* [5]. Owing to the new representation of matrix elements (Eq. (8)) we have avoided the unphysical overestimation of the contribution of these elements to $J_0(p)$ and the general behaviour of the enhancement, i.e. diminishing of their values with momentum agrees with the commonly known rules of quantum mechanics that the scattering amplitude of two colliding particles is decreasing with their relative velocities. Even if our values for partial enhancement are too low, one should remember, however, that in our preliminary tests we used atomic electron wave functions whereas , as already shown by Mijnarends *et al.* [17], using solid state 2*s* and 2*p* wave functions for core electrons is necessary. Independently, the problem of screening of the positron-core electron interaction and using of the Born approximation for this case still requires reconsidering.

In our present calculations we still used LDA approximation for valence electrons according to Alatalo's [1] prescription. To be consistent, one should take into account that the enhancement for these states should be dependent on momentum as well, as is usually necessary to take this into account in studies of the Fermi surface. All theoretical curves based on the LDA or GGA exhibit marked differences in relation to experimental data in the range between 7 and 20 $\times$ 10^{-3} m_0c, just in the region near the Fermi surface. This is also a deficiency of our curve, corresponding to the total momentum density and the explanation is as given above. The studies on this subject and calculations for other elements are going on.

References

1. Alatalo M, Barbiellini B, Hakala M *et al.* (1996) Theoretical and experimental study of positron annihilation with core electrons in solids. Phys Rev B 54:2397–2409
2. Barbiellini B, Hakala M, Puska MJ, Nieminen RM, Manuel AA (1997) Correlation effects for electron-positron momentum density in solids. Phys Rev B 56:7136–7142
3. Barbiellini B, Puska MJ, Torsti T, Nieminen RM (1995) Gradient correction for positron states in solids. Phys Rev B 51:7341–7344
4. Blaha P, Schwarz K, Madsen GKH, Kvasnicka D, Luitz J (2001) WIEN2k, An augmented plane wave local orbitals program for calculating crystal properties. Karlheinz Schwarz Techn Universität Wien, Austria
5. Bonderup E, Andersen JU, Lowy DN (1979) Enhancement of positron annihilation with core electrons. Phys Rev B 20:883–899
6. Boroński E, Nieminen RM (1986) Electron-positron density functional theory. Phys Rev B 34:3820–3831
7. Campillo Robles JM, Ogando E, Plazaola F (2007) Positron lifetime calculation for the elements of the periodic table. J Phys: Condens Matter 19:176222 (19 pp)
8. Carbotte JP, Salvadori A (1967) Positron annihilation in real metals. II. Calculation of core enhancement factors. Phys Rev 162:290–300
9. Chiba T, Dürr GB, Brandt W (1977) Enhancement effect on positron annihilation with tightly bound electrons. Phys Status Solidi B 81:609–614
10. Daniuk S, Kontrym-Sznajd G, Majsnerowski J, Šob M, Stachowiak H (1989) Electron-positron interaction in metals: momentum dependence of HMC and ionic core enhancement effects. J Phys: Condens Matter 1:6321–6326
11. Daniuk S, Šob M, Rubaszek A (1991) Theoretical calculations of positron annihilation with rare-gas core electrons in simple and transition metals. Phys Rev B 43:2580–2593
12. Dzuba VA, Flambaum VV, Gribakin GF, King WA (1996) Many-body calculations of positron scattering and annihilation from noble-gas atoms. J Phys B: At Mol Opt Phys 29:3151–3175
13. Ghosh VJ, Alatalo M, Asoka-Kumar P *et al.* (2000) Calculation of the Doppler broadening of the electron-positron annihilation radiation in defect-free bulk materials. Phys Rev B 61:10092–10099
14. Kontrym-Sznajd G, Sormann H, Boroński E (2012) General properties of electron-positron momentum densities. Phys Rev B 85:245104 (9 pp)
15. Laverock J, Haynes TD, Alam MA, Dugdale SB (2010) Experimental determination of the state-dependent enhancement of the electron-positron momentum density in solids. Phys Rev B 82:125127 (13 pp)
16. Lynn KG, MacDonald JR, Boie RA *et al.* (1977) Positron--annihilation momentum profiles in aluminum: core contribution and the independent-particle model. Phys Rev Lett 38:241–244
17. Mijnarends PE, Kruseman AC, van Veen A, Shut H, Bansil A (1998) Two-detector Doppler broadening study of enhancement in Al. J Phys: Condens Matter 10:10383–10390
18. Phillips JC, Kleinman L (1959) New method for calculating wave functions in crystals and molecules. Phys Rev 116:287–294
19. Rubaszek A, Szotek Z, Temmerman WM (1998) Nonlocal electron-positron correlations in solids within the weighted density approximation. Phys Rev B 58:11285–11302
20. Salvadori A, Carbotte JP (1969) Theory of positron annihilation in inert-gas solids. Phys Rev 188:550–556
21. Sormann H (1996) Influence of lattice effects on the electron-positron interaction in metals. Phys Rev B 54:4558–4580
22. Sormann H, Kontrym-Sznajd G (2006) Many-body effects on the electron-positron momentum density in simple and transition metals: comparison with positron annihilation spectroscopy data. Phys Rev B 73:075111 (11 pp)