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MAPW Calculation of the Anisotropic Positron Annihilation in Copper*

H. Bross and H. Stöhr
Sektion Physik, Universität, D-8000 München, Fed. Rep. Germany

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Abstract. The wave function ψ_+ of a positron in Cu is calculated using the MAPW (modified augmented plane wave) method. This method, taking into account the correct symmetry of ψ_+ inside the atomic polyhedron and yielding the appropriate behaviour near the nucleus, leads to rapidly converging results. The Hartree potential seen by the positron is constructed from the electronic wave functions determined by the MAPW method. It is found that the lowest eigenstate of the positron is a Γ_1 state. In a provisional calculation, the matrix elements describing the two-quantum angular distribution of positron annihilation radiation are computed using recent MAPW electron wave functions. Good agreement with the measured anisotropic positron annihilation is found.

Index Headings: Positron wave function – Anisotropic positron annihilation

In the last decade different measurements of the angular distribution of radiation due to annihilation of positrons in single crystals of Cu have been reported [1–7]. They allow to investigate electronic properties of metals, particularly the momentum distribution of conduction electrons. The accuracy of the experimental methods has progressed to the extent that highly structured results of the anisotropic angular distributions are available. The theoretical description of this anisotropy requires a proper account of the crystal symmetry. That means, crystal wave functions for positrons and electrons have to be inserted and the matrix elements have to be evaluated integrating over the atomic polyhedron. The investigation of Berko and Plaskett [1] is incomplete in this respect. Their wave functions of positrons and electrons were determined by the Wigner-Seitz method in which the $\boldsymbol{k}$-dependence of the electron wave functions is neglected. In the spirit of the Wigner-Seitz method, the atomic polyhedron is replaced by a sphere; to allow for the fact that the wave functions do not vanish at the Wigner-Seitz radius, a correction term is added. Both approximations seem to be serious since the main contribution to the matrix elements, describing the two-quantum angular distribution, comes from the outer part of the atomic polyhedron where the actual positron wave function exhibits a substantial anisotropy which cannot be produced by the Wigner-Seitz method. In order to avoid the disadvantages of the Wigner-Seitz method, not correctly describing the distribution at small angles, Gould *et al.* [6] make use of a procedure originally applied by Stroud and Ehrenreich [8] to the case of Al and Si. They represent the positron wave function by a plane wave expansion in terms of reciprocal lattice vectors $\boldsymbol{K}_l$. This procedure yields a crystal wave function which incorporates the proper symmetry. In addition, it allows to take into account the shape of the atomic polyhedron correctly. However, they find that the amplitude of the positron wave function at the origin tends to decrease as the number of plane waves is increased. We believe that this overestimate of $\psi_+(0)$ enhances the annihilation with the low lying electron states and produces a momentum distribution extending to considerably larger momenta than those observed

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experimentally. The weak convergence of the positron wave functions near the origin can be explained in the following way: In any case, near the nucleus, the positron feels a spherically symmetric potential. From its Schrödinger equation follows that the ground state wave function having Γ_1 symmetry may be approximated by

$$\psi_+ = A_0(1 + Zr/2) + O(r^2), \tag{1}$$

where Z is the positive charge of the nucleus. The absolute value of r is expressed in atomic units. Note that ψ_+ consists of even and odd powers of $|\boldsymbol{r}|$. On the other hand, an expansion in terms of powers of $|\boldsymbol{r}|$, in the vicinity of the nucleus, of a sum over plane waves with vectors $\boldsymbol{K}_l$ of the cubic reciprocal lattice, yields even powers only. Therefore, in principle only the infinite sum of plane waves will produce the correct behaviour of ψ_+ near the origin. From (1) we deduce that the coefficients of the plane wave expansion decrease as

$$\left[\frac{\partial \psi_+}{\partial r}\bigg|_{r\to 0}\right] |\boldsymbol{K}_l|^{-4}$$

for large values of $\boldsymbol{K}_l$.

This proportionality to $(\partial\psi_+/\partial r)_{r\to 0}$, i.e. to Z, explains the result found by Gould *et al.* [6] that the convergence of the plane wave expansion of the positron wave function in Cu turns out to be slower than in Al or Si. A natural way to circumvent these drawbacks is to use different representations for the positron wave function: near the nucleus one may use a representation for ψ_+ similar to the Wigner-Seitz method while in the remaining part of the atomic polyhedron a plane wave expansion may be more appropriate. Wave functions constructed in this way may be generated by the APW (augmented plane wave) method proposed by Slater [9].

In this paper we shall apply a modified version of this method (MAPW) which yields wave functions and their first derivatives which are continuous everywhere in the crystal [10]. Similar to the plane wave expansion this procedure allows to take into account an anisotropic potential and, in addition, to calculate possible positron states having symmetries different from Γ_1. We found that these other states have energies more than 2 Rydbergs higher than the Γ_1 ground state. Furthermore, the matrix elements describing the two-quantum angular distribution are computed with realistic $\boldsymbol{k}$-dependent electron wave functions produced by MAPW calculations.

1. Calculation of the Positron Wave Function

1.1. Formalism

In order to calculate the wave function of the positron in Cu we solve its time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\Delta\psi + V(\boldsymbol{r})\,\psi = E\psi\,. \tag{2}$$

For $V(\boldsymbol{r})$ we use, according to the so-called Sommerfeld approximation, the Hartree potential seen by an electron, with opposite sign.

This approach is not justified in calculations of the positron lifetime in matter, but explains quite satisfactorily the angular correlation in many metals [11, 12].

The main problem in the use of $V(\boldsymbol{r})$ is that we must well take into account all its anisotropies. However, detailed calculations published elsewhere [13, 14] show that for Cu, inside the sphere touching the atomic polyhedron (APW-sphere), the anisotropic components of the potential do not exceed 1% of the spherical mean value. (The arbitrary constant was adjusted so that the mean value of the potential in region outside the spheres vanishes, leading to an average of 1.354 Ry in the whole atomic polyhedron.) Outside this sphere, we use the plane wave expansion which properly accounts for the symmetry of the potential. As in the original APW method the Schrödinger equation (2) is solved by the corresponding variational principle.

In contrast to other versions of the APW method [15] we do not use exact solutions inside the APW-sphere, even if the potential is spherical. Similar to Stroud and Ehrenreich [2], outside the APW-sphere, we choose a linear combination of plane waves as a trial function for the Rayleigh-Ritz procedure

$$\psi^{\gamma}_{+\alpha}(\boldsymbol{r}) = \sum_{j\alpha'} V^{\gamma}_{\alpha'}(j)\, S^{\gamma}_{\alpha\alpha'}(\boldsymbol{r}, \boldsymbol{K}_j) \tag{3}$$

which has definite symmetry properties. In accordance with Lee-Whiting [16] we assume that the positron is thermalized. Hence the momentum of the positron is negligible compared to a characteristic length of the reciprocal lattice. Bloch's theorem then implies, that the corresponding wave function transforms as any representation of the cubic point group. The symmetrized plane waves used in expansion (3) account for the point symmetry and are defined by [17]

$$S^{\gamma}_{\alpha\alpha'}(\boldsymbol{r}, \boldsymbol{K}_j) = \frac{1}{G^{\gamma}_{\alpha\alpha'}} \sum_R D^{\gamma}_{\alpha\alpha'}(R)\, e^{i R \boldsymbol{K}_j \boldsymbol{r}}\,, \tag{4}$$

where R denotes an operation of the full cubic group, and $D^{\gamma}(R)$ is the matrix belonging to R in the representation γ. We use Slater's [18] choice of the D's and the notation for the irreducible representations due to Bouckaert *et al.* [19]. We define the shell of the vector $\boldsymbol{K}_j$ as the set of vectors obtainable from $\boldsymbol{K}_j$ by applying on it all the operations of the cubic group. Different shells are ordered according to the magnitude of their vectors. The quantity j then denominates the shells where $\boldsymbol{K}_j$ is a fixed representative of the shell. The G's are normalization constants. The subscripts α, α' denote the different rows and columns of a representation.

Inside the APW-sphere, products of radial functions and of linear combinations of spherical harmonics are used. These linear combinations $Z^{\gamma}_{\alpha\iota}(\hat{\boldsymbol{r}}, l)$ are defined in a way analogous to (4). The Z's are then basis functions for the row α of the representation γ. The subscript ι distinguishes the different linear combinations which are possible for fixed γ, α, and l. The radial dependence of the partial waves with $l \leqq L$ is described by the functions $R_{nl}(r, E_{nl})$ which are solutions of the differential equation

$$R''_{nl} + \frac{2}{r} R'_{nl} + \left[E_{nl} - \frac{l(l+1)}{r^2} - V_{sph}(r)\right] R_{nl} = 0\,, \quad (5)$$

where V_{sph} denotes the spherical mean value of the potential $V(\boldsymbol{r})$. We considered solutions of (5) in the intervall $0 \leqq r \leqq r_0$ with $r_0 > r_i$, where r_i is the radius of the APW-sphere. Details of the determination of the $R_{nl}(r, E_{nl})$ may be found elsewhere [10]. The radial dependence of the partial waves with $l > L$ is represented by spherical Bessel functions denoted by j_l. Making use of the identity

$$S^{\gamma}_{\alpha\alpha'}(\boldsymbol{r}, \boldsymbol{K}_j) = \sum_{\substack{l=0 \\ \iota}}^{\infty} i^l Z^{\gamma *}_{\alpha'\iota}(\hat{\boldsymbol{K}}_j, l)\, Z^{\gamma}_{\alpha\iota}(\hat{\boldsymbol{r}}, l)\, j_l(|\boldsymbol{K}_j|\, r) \quad (6)$$

the wave function inside the APW-sphere is described by

$$\begin{aligned}\psi^{\gamma}_{+\alpha}(\boldsymbol{r}) = &\sum_{\substack{l=0 \\ n,\iota}}^{L} i^l A^{\gamma}_{nl\iota} Z^{\gamma}_{\alpha\iota}(\hat{\boldsymbol{r}}, l)\, R_{nl}(r) \\ &+ \sum_{\substack{l=L+1 \\ \iota}}^{\infty} i^l Z^{\gamma}_{\alpha\iota}(\hat{\boldsymbol{r}}, l) \sum_{j,\alpha'} V^{\gamma}_{\alpha'}(j) Z^{\gamma *}_{\alpha'\iota}(\hat{\boldsymbol{K}}_j, l) j_l(|\boldsymbol{K}_j| r) \quad (7a)\end{aligned}$$

$$\begin{aligned}= &\sum_{j,\alpha'} V^{\gamma}_{\alpha'}(j)\, S^{\gamma}_{\alpha\alpha'}(\boldsymbol{r}, \boldsymbol{K}_j) \\ &+ \sum_{\substack{l=0 \\ \iota}}^{L} i^l Z^{\gamma}_{\alpha\iota}(\hat{\boldsymbol{r}}, l) \left[\sum_n A^{\gamma}_{nl\iota} R_{nl}(r) \right. \\ &\left. - \sum_{j,\alpha'} V^{\gamma}_{\alpha'}(j) Z^{\gamma *}_{\alpha'\iota}(\hat{\boldsymbol{K}}_j, l) j_l(|\boldsymbol{K}_j| r)\right], \quad (7b)\end{aligned}$$

where $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{K}}$ describe unit vectors.

In (7a) the second sum implies the continuity of the partial waves and their derivatives for $l > L$. In order to fulfil these conditions for $l \leqq L$ we demand for all pairs l, ι

$$\sum_n A^{\gamma}_{nl\iota} R_{nl}(r_i) = \sum_{j\alpha'} V^{\gamma}_{\alpha'}(j)\, Z^{\gamma *}_{\alpha'\iota}(\hat{\boldsymbol{K}}_j, l)\, j_l(|\boldsymbol{K}_j|\, r_i) \quad (8a)$$

$$\sum_n A^{\gamma}_{nl\iota} \left.\frac{dR_{nl}}{dr}\right|_{r_i} = \sum_{j\alpha'} V^{\gamma}_{\alpha'}(j) Z^{\gamma *}_{\alpha'\iota}(\hat{\boldsymbol{K}}_j, l) \left.\frac{dj_l(|\boldsymbol{K}_j| r)}{dr}\right|_{r=r_i}. \quad (8b)$$

Furthermore, the presence of the second sum in (7a) makes it possible to work with a rather small value of L, e.g. $L = 2$ in the case of the Cu positron wave functions. We proceed in the usual manner and make stationary the expectation value of the energy under the constraints of normalization and continuity of the wave function and its derivative. For a definite representation γ this leads to an algebraic eigenvalue problem. Its solution gives the energy eigenvalues as well as the expansion coefficients $V^{\gamma}_{\alpha}(j)$ and $A^{\gamma}_{nl\iota}$. Details of the formalism and the numerical procedure are described elsewhere [10].

Here we want to make some remarks on the Hartree potential used. Starting from the semi-empirical potential of Chodorow [20] the electron wave function in Cu is calculated at 15 points in the 48th part of the Brillouin zone using the MAPW method. Poisson's equation and the Ewald method lead from this charge density to the Hartree potential for electrons. The Fourier coefficients as well as the r-dependent potential inside the APW-sphere are given in [14]. The arbitrary constant in the potential was determined by demanding that the average of the potential outside the APW-sphere be zero.

1.2. Results

In order to find out which of the positron eigenstates is the lowest one, the eigenvalue problem was solved for several representations at Γ. We used $L = 2$ and up to seven partners R_{nl} for fixed l. For the expansion in the outer region of the atomic polyhedron up to seven cubic shells were used (equivalent to 65 plane waves).

In Table 1 the eigenvalues up to 7.5 Ry are listed. The representations not contained in the table have energy values higher than this value. From Table 1 it is infered that the lowest eigenstate belongs to the representation Γ_1 in agreement with other calculations [1, 6, 8].

The wave function of this state is shown in Fig. 1 for the directions [100], [110], and [111], within the Wigner-Seitz cell. The overall shape of the positron

Table 1. Positron eigenvalues in Ry. The mean value of the positron potential in the atomic polyhedron is 1.354 Ry

Γ_1	0.495	3.128	5.676
Γ_2'	2.764		
Γ_{25}'	2.934	7.380	
Γ_{15}	3.055	4.275	
Γ_{12}	3.902	7.319	
Γ_{25}	7.308		

ground-state wave function agrees with the results derived by Berko and Plaskett [1] as well as by Gould *et al.* [6]. In the latter case a comparison of the anisotropy of the wave function is possible and again gives a close resemblence. An obvious difference is seen in the behaviour of ψ_+ along the [100]-direction. Whereas the curves for all directions in [6] coincide up to more than half the radius of the inscribed sphere, i.e. to about 1.4 a.u., our curve in the [100]-direction turns away from the curves in the other two directions at about 0.7 a.u. At the bottom right corner of Fig. 1 the wave function near the nucleus is plotted enlarged. It is seen that at $r=0$ the amplitude of the wave function is very small but definitely not zero, in accordance with (1).

Because the ansatz in (7a) seems appropriate we expect that the wave function shown near the nucleus is more realistic than that obtained by the plane wave expansion [6, 7], even if 145 reciprocal lattice vectors were used in the latter case.

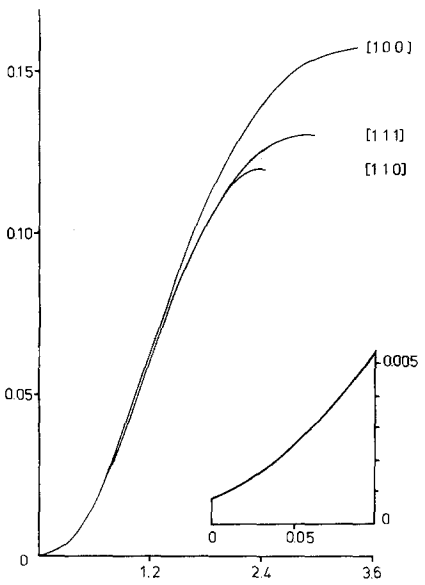

Fig. 1. Normalized positron wave function in Cu along three different crystal directions. In the bottom right corner the wave function near the nucleus is plotted in an enlarged scale

2. Preliminary Results of the Calculations of the Two-Quantum Angular Distribution

In a preliminary calculation Blumen [13] has calculated the matrix elements characterizing the positron-electron annihilation interaction. The wave functions of the conduction and valence electrons ψ_{nk} were taken from the MAPW calculations whereas the positron wave function was computed by means of a plane wave method [8] using the MAPW potential described in Section 1. As the ψ_{nk}'s are known along directions of high symmetry in the reciprocal space only, the angular dependence of the probability that the center-of-mass momentum of the annihilation pair is $\boldsymbol{p}$,

$$\varrho(\boldsymbol{p}) = \sum_n \int_{\mathrm{BZ}} d^3k \left| \int \psi_{nk}^* \, e^{i\boldsymbol{p}\boldsymbol{r}} \psi_+ \, d^3r \right|^2 , \tag{9}$$

was fitted by a cubic harmonic expansion following [3]. Using this expansion the two-quantum angular correlation function $N_{\hat{n}}(p_z)$ as measured by the long-slit geometry, may be produced straightforwardly as a function of the sample orientation $\hat{n}$.

For a first survey many-body effects have roughly been taken into account by an enhancement factor which is assumed to be momentum-independent. To compare quantitatively the results with the observed anisotropies [2, 4], in Fig. 2 we plotted the difference in the angular distribution along the Λ- and Σ-directions, $N_{[111]} - N_{[110]}$. The agreement of the theoretical and experimental results is surprisingly good. Similar behaviour is found for the difference

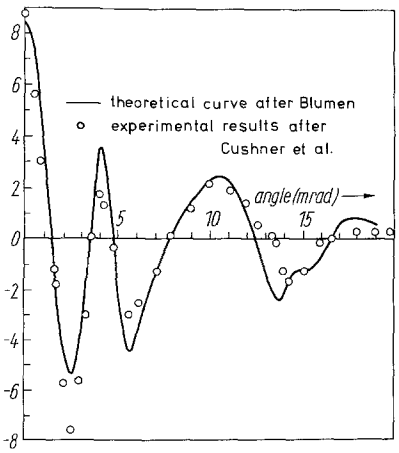

Fig. 2. Difference of the angular correlations of positron annihilation in Cu between directions [110] and [111] of $\boldsymbol{p}$-space. The circles represent the experimental values, the solid line gives the theoretical result. The ordinate values are in arbitrary units

$N_{[100]} - N_{[111]}$. The deviations present may be due to many-body correlations leading to a momentum-dependent enhancement factor which is caused, among other things, by the different effective masses of the valence and conduction electrons of Cu [21–24].

This suggestion is supported by the fact that the averaged angular distribution calculated from $N_{[100]}$, $N_{[110]}$, and $N_{[111]}$ cannot be fitted to the experimental curve of Mijnarends [3] over the whole range by a suitable choice of a multiplicative factor.

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