An LCAO method for the construction of positron wavefunctions in crystalline solids.

Application to lithium

An LCAO method for the construction of positron wavefunctions in crystalline solids. Application to lithium

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Abstract. A new method for calculating delocalized positron wavefunctions in crystalline solids is presented. The wavefunction is expressed by a superposition of localized spherical orbitals (LSO) centred at atomic sites. The orbitals are constructed using an effective numerical-basis-set LCAO expansion: the basis functions are the solutions of an atomic-like differential equation and have, therefore, the correct cusp near the nuclei. The resulting wavefunction is continuous and has derivatives of first order except at the Coulomb singular points of the potential where it is exact by construction. It is shown that the LSO *ansatz* gives accurate results for the positron wavefunction, especially in solids with high (e.g. cubic) symmetry of the crystal lattice, and, if necessary, how it can be augmented effectively. The simple representation of the wavefunction makes it suitable for a direct use in the calculation of expectation values, as e.g. annihilation rates. As an example, our method is applied to a positron in BCC lithium: the results obtained for the wavefunction and the ground-state energy are compared with those of an expansion in terms of symmetrized plane waves.

1. Introduction

Measurements of positron annihilation radiation are a valuable method to obtain information about the momentum distribution of electrons in solids. For interpretations of experimental results or for calculations of annihilation rates by theoretical means, the knowledge of the electronic structure and also of the spatial distribution of the positron is necessary. This paper deals with the determination of the positron wavefunction. For this purpose, many traditional band-structure models have been used in the literature: the Wigner–Seitz approximation of a spherical cell (Berko and Plaskett 1958), the expansion in terms of symmetrized plane waves (Stroud and Ehrenreich 1968), the pseudopotential theory (Stott and Kubica 1975) and the augmented-plane-wave (APW) approach (Gupta and Siegel 1977, 1980), Green-function techniques in the KKR method (Korringa 1947, Kohn and Rostoker 1954) for perfect-crystal band theory and in the multiple scattering approach to deal with random alloys (for review articles see: Ehrenreich and Schwartz 1976, Mijnarends 1987), the linear-muffin-tin-orbital method (LMTO) within the atomic spheres approximation (ASA) (Singh and Jarlborg 1985, Puska *et al* 1986, Boev *et al* 1987), the linear combination of gaussian orbitals (LCGO) (Sundararajan *et al* 1988), numerical methods using finite-element techniques (Puska and Nieminen 1983) and others (for review articles see: Mijnarends 1979, Puska 1987).

For the determination of accurate expectation values as—for example—high-momentum components (HMC) of annihilation rates, three aspects are of importance: Firstly, the (local) potential for the positron should be as general as possible (without restrictions in contrast to muffin-tin or ASA, etc). Secondly, the positron wavefunction should be accurate both in the core region and in the interstitial region and thirdly, the mathematical representation of the wavefunction should be simple enough for a direct use in the calculation of expectation values—without further approximations necessary.

These conditions are fulfilled by the method described in this work: the delocalized positron wavefunction is represented by the superposition of localized spherical (s-type) orbitals (LSO) centred at atomic sites. The orbitals are constructed using a (theoretically complete) numerical-basis-set LCAO (linear combination of atomic orbitals) expansion (subsection 2.1). The basis functions are calculated in a manner very similar to the method Zunger and Freeman (1976, 1977) used in electron band-structure calculations: they are the solutions of a one-particle central-field Schrödinger equation with a potential near the centre which is almost identical with the potential around the atoms in the crystal. Therefore the functions have the correct cusp and are very effective in the expansion. In subsection 2.2 is shown how the LSO method gives highly accurate results for the positron wavefunction both in the vicinity of the nucleus (by construction) and in the interstitial region (compared with the plane-wave expansion). In section 3 the method is applied to a positron in lithium: the wavefunction and the expectation values for the ground-state energy are calculated and compared with the results of a plane-wave expansion. The determination of annihilation rates, using the LSO method, is discussed: accurate results may be obtained by direct numerical computation of the matrix elements.

2. Method of calculation

2.1. Construction of the positron wavefunction

Using the two-component density-functional theory (Chakraborty and Siegel 1983, Boroński and Nieminen 1986), the Kohn–Sham method (Kohn and Sham 1965) and the local density approximation (LDA) for the electron–positron correlation energy, the Schrödinger equation for a delocalized positron in a metal can be written, in atomic units, as

$$H^+ \, \psi^+(r) = E^+ \, \psi^+(r) \tag{1}$$

with

$$H^+ = -\frac{1}{2}\nabla^2 + \sum_{R_i} \frac{Z}{|r - R_i|} - \int \frac{n^-(r')}{|r - r'|} \, d^3 r' + \epsilon_{c,n^+ \to 0}^{+-}(n^-(r)).$$

Z is the atomic number and R_i are the vectors of the crystal lattice. n^+ and n^- are the positron and electron densities, respectively, and $\epsilon_{c,n^+ \to 0}^{+-}$ is the electron–positron correlation-potential for *one* positron in a homogeneous electron gas. The result of Arponen and Pajanne (1979) as interpolated by Boroński and Nieminen (1986) was used for the calculations in section 3. For the sake of clarity, a metal is chosen which contains one atom per unit cell, but this is not a restriction on the method described;

it can be generalised easily to more complex solids. In contrast to other methods (for example, the muffin-tin approach or ASA), no approximation of the (local) potential is necessary.

On account of its thermalization (Lee-Whiting 1955), the positron is assumed to be in the ground-state at $k = \Gamma$ with energy $E^+(\Gamma_1)$. For this special case it follows from the Schrödinger equation that the function ψ^+ is real (apart from a phase factor) and that it has the periodicity and the point symmetry of the crystal lattice. Therefore it can be written as

$$\psi^+(r) = \sum_{R_i} \chi(r - R_i) \tag{2}$$

and a suitable function $\chi(r)$ has to be determined.

In order to satisfy the principles of quantum mechanics, χ has to fulfil the following conditions:

(i) ψ^+ may be normalized to the Wigner–Seitz cell. Therefore χ is square integrable and in particular

$$\chi(r) \to 0 \qquad \text{if } |r| \to \infty$$

is valid: χ is a localized function.

(ii) ψ^+ is a continuous function and has derivatives of first order except at the Coulomb singular points of the potential. In the vicinity of the nuclei, the potential has spherical symmetry; separating the Schrödinger equation in spherical coordinates one easily finds (Kato 1957)

$$\left. \frac{\psi^{+\prime}(\xi)}{\psi^+(\xi)} \right|_{\xi=|r-R_i|\to 0} = Z$$

which requires

$$\left. \frac{\chi'(r)}{\chi(r)} \right|_{r\to 0} = Z. \tag{3}$$

(iii) Since the positron is in the ground state Γ_1, ψ^+ possesses the same point symmetry as the crystal lattice. For further investigations it is useful to expand $\chi(r)$ in spherical harmonics $Y_{lm}(r)$

$$\chi(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm}(r) \, Y_{lm}(r) \tag{4}$$

where c_{lm} are the expansion coefficients. Applying the point symmetry operations of the lattice to the wavefunction, the symmetry conditions may easily be derived: if there exists a centre of inversion, only even l participate in the expansion. Further symmetries lead to additional conditions: for example, in cubic crystals, orbitals with $l = 2$ give no contribution to the expansion (for cubic harmonics see, e.g., Mueller and Priestley 1966). In the case that there is no contribution of $l = 1$ (lattice with a centre of inversion), the cusps of the positron wavefunction at the atomic sites are

exclusively described by the orbital with $l = 0$: due to $c_{lm}(r) \sim r^l \, c_{lm}(0)$, orbitals with $l \geq 2$ have no effect on the relation (3).

Neglecting orbitals with $l \geq 2$ for crystals with a centre of inversion and with $l \geq 4$ in cubic lattices, the function $\chi(r)$ may be simplified to $\chi(r)$ and ψ^+ in equation (2) reduces to

$$\psi^+(r) = \sum_{R_i} \chi(|r - R_i|). \tag{5}$$

$\chi(r)$ is a localized (see condition (i)) spherical orbital (LSO). If χ is determined by the variational method due to the minimal property of the positron ground-state energy, it is not identical with $c_{00}(r)$ of equation (4): it also contains some (averaged) parts of higher orbitals, and the overlap of the $\chi(r)$, centred at different atomic sites, leads to the anisotropies in the interstitial region. This is also illuminated by a different theoretical point of view given in subsection 2.2.

For the determination of $\chi(r)$, an optimized LCAO version is used. Therefore it is expanded in terms of appropriate (s-type) functions φ_n

$$\chi^N(r) = \sum_{n=1}^{N} c_n \, \varphi_n(r). \tag{6}$$

Theoretically, each function set that is complete in $(0, \infty)$ may be used, but many of them are not favourable, because they do not have the correct cusp near the nuclei (condition (ii)): in materials where the cusp of the positron wavefunction is weak (this is common for heavy atoms), s Gaussian orbitals (see Wang and Callaway 1978) may be used (see, e.g. for copper, Sundararajan *et al* 1988) whereas in the other case (light materials, see e.g. lithium in section 3), Slater-type orbitals are more appropriate.

In the present work, the φ_n have been calculated numerically in a way similar to the method Zunger and Freeman (1976, 1977) developed for the electron basis-set in LCAO band-structure calculations: they are chosen as the solutions of a central-field one-particle atomic-like Schrödinger equation. Due to (5), only the angular-momentum $l = 0$ is needed. Therefore, the radial part φ satisfies the differential equation

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} [r\varphi(r)] + 2 \left[E - \frac{Z}{r} + v(r) - A(r) \right] \varphi(r) = 0. \tag{7}$$

$v(r)$ is the spherical part of the effective positron potential in H^+ of equation (1). $A(r)$ is a potential term used for *two* reasons: Firstly it is necessary to get localized states and secondly it can be chosen to tailor the functions for their use in the variational calculation. The *ansatz*

$$A(r) = \left(\frac{r}{r_0} \right)^\gamma \qquad \gamma > 0$$

is appropriate and guarantees a *complete* set of localized states φ_n.

The potential $A(r)$ is also used in electron LCAO band-structure calculations to cut off the long-range tail of atomic states (Eschrig and Bergert 1978). It has the advantage that the orbitals used in the expansion are of higher efficiency and that the enormous number of multi-centre integrals is reduced. According to this work, the value $\gamma = 4$ is chosen for the present calculations.

The choice of r_0 is performed in order to get an optimized basis-set $\{\varphi_n\}$ which is well suited for the construction of $\chi(r)$—that means that a minimum number N of functions is sufficient to achieve good convergency in the expansion (6) (see also figure 1). For this reason, the differential equation (7) is solved for the ground-state wavefunction $\varphi_1(r; r_0)$ with r_0 as a parameter, and the expectation value for the positron energy in the crystal is then calculated by

$$\langle \psi^{+1}(r_0) | H^+ | \psi^{+1}(r_0) \rangle = E_1^+(r_0)$$

with

$$\psi^{+1}(r; r_0) = c_1 \sum_{R_i} \varphi_1(|r - R_i|; r_0).$$

H^+ is the Hamiltonian of the crystal for the positron of equation (1) and c_1 is a constant used to normalize ψ^{+1}. The value of r_0 with the lowest energy E_1^+ is chosen for the further calculations: it produces a potential which yields eigenfunctions converging rapidly towards $\chi(r)$ in the expansion (6) and, therefore, minimizes the numerical effort.
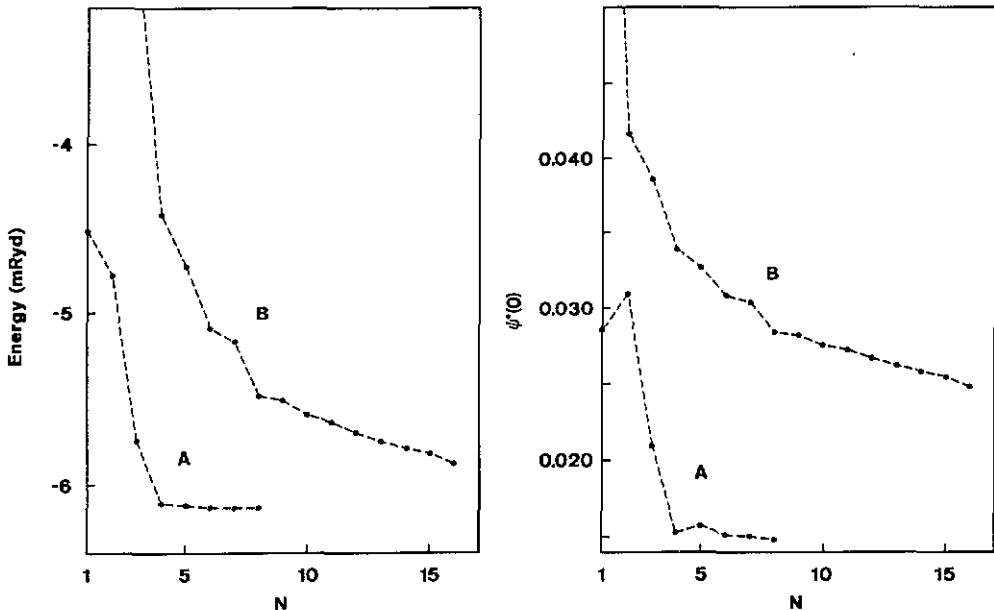

Figure 1. The convergence of (a) the ground-state energy (the energy zero is arbitrary) and of (b) the value of the positron wavefunction at atomic site versus the number N of functions used in the numerical basis-set LCAO expansion within the LSO approach (curves A), and in the expansion in terms of symmetrized plane waves (curves B).

That a minimum value for the energy exists can be seen from the extreme values for r_0: if it is chosen very small the positron wavefunction ψ^{+1} is located very close to the nuclei and the potential energy is very high. If r_0 is increased, the energy is lowered as long as the positron goes from the atomic to the interstitial region. Here

the minimum value is found. If r_0 is further enlarged, the wavefunction becomes very flat and the positron is closer to the nuclei again (due to the overlap of the φ_1 located on different atomic sites) resulting in a higher energy. By the way it can be seen that the r_0 which belongs to the lowest energy E_1^+, would tend to infinity only if the exact positron wavefunction were constant, and this is excluded by the presence of the nuclei.

When r_0 is determined, the eigenfunctions of equation (7) with $n > 1$ are calculated and used in the expansion (6). The coefficients c_n are found by the minimum principle for the positron ground-state energy in the crystal. Writing the positron wavefunction (5) as

$$\psi^{+N}(r) = \sum_{n=1}^{N} c_n \, \psi_n^+(r)$$

with

$$\psi_n^+(r) = \sum_{R_i} \varphi_n(|r - R_i|)$$

variation leads to the $N \times N$ *generalized eigenvalue problem*

$$\sum_j H_{ij} \, c_j = \varepsilon \sum_j S_{ij} \, c_j$$

$$H_{ij} = \langle \psi_i^+ \, | \, H^+ \, | \, \psi_j^+ \rangle \qquad S_{ij} = \langle \psi_i^+ \, | \, \psi_j^+ \rangle .$$

The matrix elements H_{ij} are calculated numerically by a three-dimensional integration over the irreducible wedge of the Wigner–Seitz cell—thus no approximation of the potential is necessary. Since the functions $\varphi_n(r)$ are solutions of equation (7) with a potential which is around the atom equivalent to the potential in H^+, the number N of functions needed is small (four to five). This is demonstrated in the case of lithium in figure 1.

2.2. On the representability of the positron wavefunction by the localized-spherical-orbital (LSO) ansatz

The positron wavefunction ψ^+ can be represented without any approximation by a symmetrized plane wave ψ_{PW}^+:

$$\psi^+(r) \equiv \psi_{PW}^+(r) = \sum_{S_i} a_{S_i} \, f_{S_i}(r) \qquad f_{S_i}(r) = \sum_{G \in S_i} \exp(iG \cdot r) \quad (8)$$

S_i stands for the ith star of vectors of the reciprocal lattice G: all coefficients a belonging to lattice vectors of the same star are equal.

It is of interest to find out which positron waves can be described by the LSO *ansatz* (5)

$$\psi_{LSO}^+(r) = \sum_{R_i} \chi(|r - R_i|) .$$

Since only s-type orbitals are used in this *ansatz*, it is obvious that it is not as powerful as (8). To find the connexion between (5) and (8) we determine the Fourier components c_G of ψ^+_{LSO}. Using the Fourier transform $\chi(p)$ of $\chi(r)$

$$\chi(p) = \int \chi(r)\,\exp(-i\,p\cdot r)\,\mathrm{d}^3 r$$

we obtain

$$\frac{1}{V_{cell}}\int_{cell}\psi^+_{LSO}(r)\,\exp(-i\,G\cdot r)\,\mathrm{d}^3 r = \frac{1}{V_{cell}}\chi(|G|) = c_{|G|}$$

and therefore

$$c_G = c_{|G|}. \qquad (9)$$

The Fourier coefficients of ψ^+_{LSO} depend only on the absolute value of the reciprocal lattice vector G. This variety is smaller than in the case of the symmetrized plane wave (8) because there exist different stars with the same absolute values. In other words, the relation (9) is a necessary condition for the construction of a function using the expansion (5).

This gives—for example in cubic lattices—an explanation for the high accuracy of ψ^+_{LSO}, both in the core and in the interstitial region: In a FCC lattice the first stars with the same absolute values are S_{10} and S_{11} (see figure 2), in a BCC lattice this is the case for S_{11} and S_{12}. In (8), the corresponding coefficients contribute to the positron wavefunction almost only in the vicinity of the nuclei where the curvature is strong: but in this region ψ^+_{LSO} is exact by construction (see point (iii) of subsection 2.1). Therefore it can be concluded that for the exact positron wavefunction relation (9) is fulfilled to a very high degree and by far sufficient for numerical calculations. This result is demonstrated for lithium in figure 2.

If the positron wavefunction is not represented sufficiently accurate by the LSO *ansatz* (5) (this may happen in materials with low symmetry of the crystal lattice (see point (iii)) or with a basis), it can be augmented by two additional function sets:

(1) orbitals χ_l with higher angular-momentum l can be included, and/or

(2) a fast convergent symmetrized plane wave expansion can be added: the orbitals χ describe the strong curvature of the positron wavefunction near the nuclei and the plane waves improve the wavefunction in the interstitial region.

3. Application to lithium: results and discussion

The electronic structure of BCC lithium was calculated by the method of Zunger and Freeman (1976, 1977). We want to emphasize that the same computer programs as written for the electrons can be applied without any modification to the positron wavefunction by the use of the present method.

In figure 1(a), the convergence of the positron ground-state energy in dependence of the number N of functions used is shown. It can be seen that four numerical LCAO functions give a lower energy than 16 symmetrized plane waves (this are 321 plane waves). The results for five and six LCAO functions show that enough functions have been included to obtain good convergency.
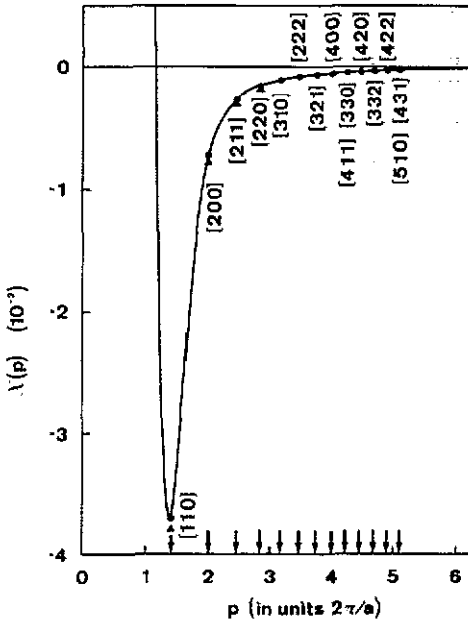
Figure 2. The Fourier transform $\chi(p)$ of $\chi(r)$ (———) compared with the coefficients of the expansions in terms of five (▲)and 16 (●) symmetrized plane waves. The values for the coefficient [000] are 0.99151, 0.99100 and 0.99141, respectively. a is the lattice constant.

A similar situation is found for the value of the positron wavefunction at the atomic site $\psi^+(R_i)$ (see figure 1(b)). It shows the behaviour of the wavefunction around the nuclei. The (finite) plane-wave expansion leads to a too high value and including more coefficients, the convergency is very slow. Comparing figures 1(a) and 1(b), it can be found that there exists a correlation between this function value and the ground-state energy: a decrease of the function value results in a similar amount of decrease of the energy value. This shows that the energy is very sensitive to the behaviour of the wavefunction around the nuclei (due to the singular point of the Coulomb potential).

The effort of the calculation of the numerical expansion functions $\varphi(r)$ is rewarded by a fast convergency to the function $\chi(r)$ of (5). $\chi(r)$ is shown in figure 3(a) and the resulting positron wavefunction in figure 3(b). It is not only exact around the nuclei by construction (cusp condition (3)) but also very accurate in the interstitial region: by graphical resolution no difference to the plane-wave result, using 16 symmetrized plane waves, is found.

An important application of the knowledge of the positron and electron wavefunctions is their use in the calculation of annihilation rates. In the independent particle approximation (IPA) (Lee 1958, for a review article see e.g. Mijnarends 1979), the probability per unit time of annihilation under emission of a photon pair carrying away a total momentum p is proportional to the 'two-photon momentum density' (TPMD) $\rho(p)$, which is given by

$$\rho(p) = \sum_{k,n}^{occ} \left| \sum_{R_i} \exp[\mathrm{i}(k-p) \cdot R_i] \int_{\text{cell}} \exp(-\mathrm{i}\, p \cdot r)\, \psi^-_{k,n}(r)\, \psi^+(r)\, \mathrm{d}^3 r \right|^2. \tag{10}$$

The temperature is assumed to be zero. ψ^- and ψ^+ are the electron and positron Bloch wavefunctions, respectively, k is the wave vector and n the band index. The
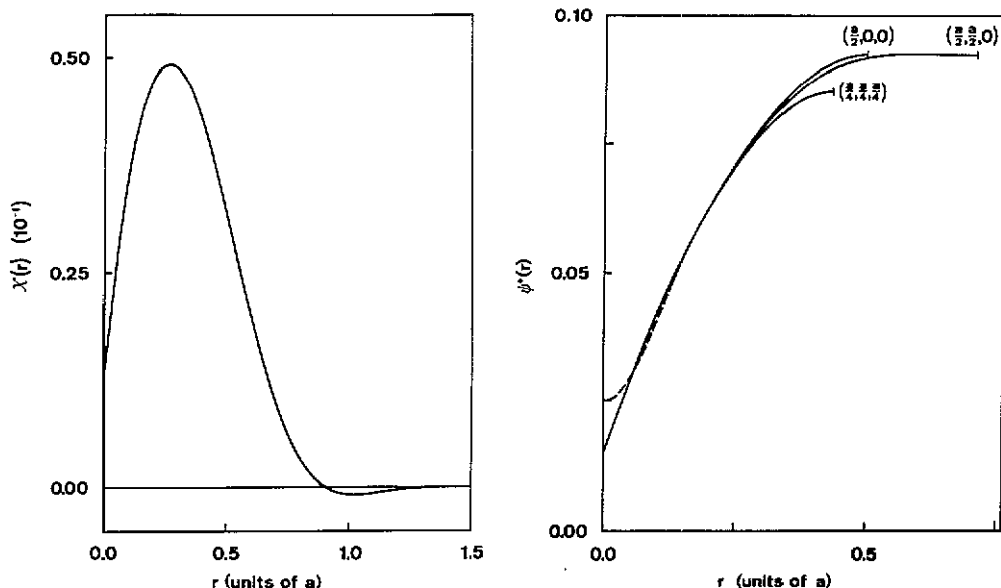
Figure 3. (a) The function $\chi(r)$ within the LSO-method and (b) the positron wavefunction in (BCC) lithium along symmetry directions: the result of the LSO-method (——) compared with an expansion using 16 symmetrized plane waves (321 plane waves) (– – –) (The positron wavefunction is normalized to one in the unit cell, a is the lattice constant.).

positron is in the ground-state and the summation extends over all occupied electron states. For large p ('Umklapp' processes: p is outside the first Brillouin zone) the exponential factor varies rapidly over the cell and $\rho(p)$ depends sensitively on the product of the electron and positron wavefunctions. Therefore it is important that equation (10) is evaluated without any approximation. This is possible using the LSO representation of the positron wavefunction: the three-dimensional integration over the cell can be performed by direct numerical computation and, therefore, accurate results are obtained. Applications of this method to lithium and other materials (e.g. higher alkali metals) are in work and a detailed description of the results will be given elsewhere.

4. Summary

In the present paper, the LCAO method is applied to the calculation of positron wavefunctions in crystalline solids. The wavefunction is expressed by a superposition of localized spherical orbitals (LSO) centred at atomic sites. This *ansatz* is exact around the nuclei (like a Wigner–Seitz approximation), but it is also able to describe the anisotropies of ψ^+ in the interstitial region. Unlike to previous work (Stroud and Ehrenreich 1968, Sundararajan *et al* 1988, etc), we use numerical functions as basis-set for the LCAO expansion of the orbitals in order to optimize convergency. Due to this fact and due to its simple mathematical representation, our LSO expansion of ψ^+ is very well qualified for numerical computations of expectation values like annihilation rates etc. Another advantage of the application of the LCAO method to the problem

of calculating positron wavefunctions is that one is not restricted to use special forms of the positron potentials like, for example, a muffin-tin approximation.

The problem of the numerical evaluation of the Wigner–Seitz cell integration, which is a key problem for all LCAO electron calculations, is very much softened by the fact that we are only interested in the positron Γ_1 Bloch state which has the full symmetry of the lattice. For simple materials with one or two atoms per unit cell, the integrand can be expressed in polar or elliptic coordinates, respectively, in order to remove the Coulomb singularities. For more complicated structures, standard integration routines or the techniques known from electron LCAO calculations (see, e.g., Freeman and Zunger 1977, 1978 and references therein) may be used.

Acknowledgments

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