On LCAO positron wavefunctions in crystals

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Abstract. In this work we deal with the construction of delocalized positron wavefunctions in crystalline solids within the linear combination of atomic orbitals (LCAO) scheme. The present method leads to an accurate wavefunction of a positron, both in the core and in the interstitial region of a crystal. Furthermore, its representation by a superposition of atomic orbitals is simple enough for the application to calculations of expectation values, like e.g. of accurate electron-positron annihilation rates (high momentum components). The representation of the positron wavefunction can be optimized with respect to the two points of view: firstly, the number of orbitals in the LCAO representation can be minimized (e.g. within the localized spherical orbitals (LSO) method) or, secondly, the orbitals can be chosen to be well-localized around their atoms and vanishing near all others: this leads to the computational advantage, that three- or multicenter integrals arising during numerical calculations can be replaced by one- and two-center integrals which are treated using standard numerical techniques in spherical polar or elliptic coordinates. The transformation from the first into the second representation can be performed via a "fuzzy" cellular partitioning of the crystal volume via an analytically continuous shape-function. Finally we demonstrate our method in the case of a positron in lithium.

1. Introduction

Measurements of positron annihilation radiation are a valuable method to obtain information about the electronic and atomic structures of solids. For a thorough understanding and for reliable interpretations of experimental results an accompanying theory is needed [1].

For the determination of the electronic structure and of the spatial distribution of the positron the two-component density-functional theory (2C-DFT) [2, 3] is widely used. For the electronic part many methods of band structure calculations have been developed, like for example the expansion of the electron wavefunction in terms of symmetrized plane waves, the pseudopotential theory, the augmented-plane-wave approach, Green-function techniques in the KKR method, their full-potential linearized versions, the linear combination of atomic orbitals (LCAO) method, numerical methods using finite-element techniques and others. Many of these methods have been adapted also to the determination of positron wavefunctions [4, 5, 6]. For these methods two aspects are of importance: they should lead to accurate wavefunctions, so that precise expectation values as – for example – high momentum components of annihilation rates can be derived and secondly, the mathematical representation of the positron wavefunction should be simple enough for a direct use in the calculation of expectation values.
2. Basic equations as derived via the 2C-DFT and method of calculation

The 2C-DFT and the application of both, the Kohn-Sham method [7] and the local density approximation (LDA) in the case of one positron in a delocalized state, leads to the set of equations

\[ H^\sigma \psi^\sigma_i(r) = \varepsilon^\sigma_i \psi^\sigma_i(r) \quad (\sigma = +, -) \]

with

\[
H^+ = -\frac{1}{2} \nabla^2 + V^+(r) - \int \frac{n^-(r')}{|r - r'|} d^3r' + \epsilon^+_{c;n^+\rightarrow0}(n^-(r)) \\
H^- = -\frac{1}{2} \nabla^2 + V^-(r) + \int \frac{n^-(r')}{|r - r'|} d^3r' + \delta \frac{\delta n^-(r)}{\delta r} \{ n^-(r)[\epsilon_{\text{ex}}(n^-(r)) + \epsilon_c(n^-(r))] \}
\]

\[ n^-(r) = \sum_{i=1}^{N^-} |\psi_i^-(r)|^2, \quad n^+(r) = |\psi_i^+(r)|^2. \]

We use atomic units, \( \sigma = - \) or \(+\) denotes electrons and positrons, respectively, \( H^\sigma \) is the Hamiltonian and \( \psi^\sigma_i \) the crystal wavefunction associated with the energy \( \varepsilon^\sigma_i \). \( n^\sigma(r) \) is the particle density, \( N^- \) is the number of occupied electron states, \( V^\sigma(r) \) is the external potential, \( \int n^{-}(r')/|r - r'| d^3r' \) contains the Hartree part of the Coulomb energy, \( \epsilon_{\text{ex}}(n^-(r)) \) and \( \epsilon_c(n^-(r)) \) are the exchange and correlation energy of an homogeneous electron gas of the density \( n^-(r) \) and \( \epsilon^+_{c;n^+\rightarrow0}(n^-(r)) \) is the effective electron-positron correlation potential. The exchange energy is given by \(-3/4(3\pi/n)^{1/3}\) a.u. in energy per particle. For the correlation energy \( \epsilon_c(n^-(r)) \) the results of Arponen and Pajanne [8] as interpolated by Boroński and Nieminen [3] can be used.

3. Application of the LCAO method to the calculation of positron wavefunctions

3.1. Optimization of the LCAO positron wavefunction with respect to a minimum number of orbitals

For the following discussion we choose, for the sake of clarity, a metal which contains one atom per unit cell; but this is not a restriction on the method described, it can be generalized easily to more complex solids. In this case the external potential \( V^+(r) \) of the Hamiltonian (2) can be written as \( V^+(r) = \sum_{R} Z/|r - R| \), where \( Z \) is the atomic number of the atoms and the \( R \)'s are the vectors of the translation lattice of the metal and, in our case, also the positions of the atomic nuclei.

Furthermore we assume, that the positron is thermalized [11] and thus in the ground-state at \( k = \Gamma \) with energy \( \varepsilon^+(\Gamma_1) \). For this special case it follows from the Schrödinger equation that the positron wavefunction \( \psi^+ \) has the symmetry of the crystal lattice. Then the positron wavefunction can be written within the LCAO scheme as

\[ \psi^+(r) = \sum_{R} \chi(r - R) \]

and a suitable function \( \chi(r) \) has to be determined. \( \chi(r) \) is not uniquely defined [12] and it can be thus optimized with respect to several points of view.

In the following we expand \( \chi(r) \) in spherical harmonics \( Y_{lm}(r) \)

\[ \chi(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm}(r) Y_{lm}(r) \]

where the radial functions \( c_{lm}(r) \) are the expansion coefficients. Applying the symmetry operations of the crystal lattice to the wavefunction, the symmetry conditions can easily be
derived: for example, in the case of a cubic crystal lattice only orbitals with $l = 0, 4, 6, \ldots$ contribute to the expansion.

In the next step we determine an appropriate $\chi(r)$ in such a way, that a minimum number of functions $c_{lm}(r)$ is necessary in the expansion (5) for the representation of the positron wavefunction. For this purpose we expand it in terms of functions $\varphi_{ln}(r)$

$$c_{lm}(r) = \sum_n c_{lmn} \varphi_{ln}(r). \quad (6)$$

Theoretically, each function set $\{\varphi_{ln}(r)\}$ that is complete in $(0, \infty)$ may be used. Like in electron band-structure methods analytical functions like Gaussian and Slater-type orbitals may be used, in the present work we determine the $\varphi_{ln}(r)$ numerically \[13, 6\]: they are chosen as the solutions of a central-field one-particle atomic-like Schrödinger equation. The coefficients $c_{lmn}$ are found by the minimum principle for the positron ground-state energy. As an example we apply the method to a positron in BCC lithium: the function $c_{00}(r)$ is already sufficient for a very accurate representation of the positron wave function in both, the core and interstitial region of the crystal (LSO approximation). The numerical results are shown in figure 1.

![Figure 1. The functions $\chi(r)$ (-----), $\psi^+_{\text{loc}}(r)$ along the symmetry directions $[1,0,0]$ (---), $[1,1,0]$ (-----), and $[1,1,1]$ (--- ---), and the resulting positron wavefunction $\psi^+(r)$ in BCC lithium along these symmetry directions (thin solid lines). The positron wavefunction is normalized to one in the unit cell, $a$ is the lattice constant.](image)

### 3.2. Optimization of the LCAO positron wavefunction with respect to well-localized orbitals

For practical calculations it is often very useful to choose in the ansatz (4) the orbitals $\chi(r)$ such that their tails are negligible or exactly zero for $r$ larger than the distance to the nearest neighbouring atomic site. An increase of the complexity of $\chi(r)$ in the representation (5) is then rewarded by a reduction of the numerical effort e.g. in the calculation of expectation values, since multi-centre integrals can be avoided by replacing them by one- or two-center integrals which are treated accurately \[9\] by standard integration techniques in spherical polar or elliptic coordinates, respectively.

In the following we describe the transformation of the positron wavefunction into a representation with well-localized orbitals $\chi(r)$. For this purpose we first perform a partition of unity into a sum of localized functions $f(r)$ centered at the atomic sites $\mathbf{R}$

$$1 \equiv \sum_{\mathbf{R}} f(r - \mathbf{R}). \quad (7)$$

Thereby the shape function $f(r)$ has the value unity in the vicinity of its center and decreases in a continuous and well-behaved manner with increasing $r$: $1 \geq f(r) \geq 0$ and $f(r) \sim 0$ for $r$ larger than the distance to the nearest neighbours. $f(r)$ is not uniquely defined \[12, 14, 15, 16\];
as an example we show a smooth shape function for a BCC lattice in figure 2. In this case the crystal volume is divided not into conventional discrete cells, but into *fuzzy, overlapping, and analytically continuous* ones.

![Figure 2](image.png)

**Figure 2.** A shape function $f(r)$ for a BCC lattice along the symmetry directions: $[1,0,0]$ (——), $[1,1,0]$ (– – –), and $[1,1,1]$ (— · —). $a$ is the lattice constant.

Next we apply the function $f(r)$ with its property (7) to the partition of a periodic function $g(r)$ into well-localized orbitals $g_{\text{loc}}(r)$:

$$g(r) = g(r) \sum_{\mathbf{R}} f(r - \mathbf{R}) = \sum_{\mathbf{R}} g_{\text{loc}}(r - \mathbf{R})$$

with

$$g_{\text{loc}}(r) = g(r) f(r).$$

(8)

For further calculations it is useful to expand $g_{\text{loc}}(r)$ in terms of spherical harmonics. As an example for $g(r)$ we choose the positron wavefunction $\psi^+(r)$ for a positron in BCC lithium. We show the results obtained for the localized orbitals $\psi_{\text{loc}}^+(r)$ in figure 1.

This procedure (8) can be applied to any periodic function: for example, to the electron and positron densities, to effective potentials in the Hamiltonians (2) and (3), etc. The representations may then be well suited for an efficient calculation of expectation values like, for example, electron positron annihilation rates [17].

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