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Gradient correction for positron states in solids

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First-principles calculations of positron-annihilation characteristics in solids are usually based on the local-density approximation (LDA) for positron-electron correlation. The LDA systematically overestimates the annihilation rate. As a remedy we introduce a generalized gradient approximation (GGA). Our results for several metals and semiconductors show that the GGA systematically improves the predictive power of positron lifetime calculations over those based on the LDA. We compare also the resulting positron energy levels in solids with data from slow-positron experiments.

Experimental techniques based on positron annihilation have established their status among the important methods for probing the electronic and atomic structures of solids.[1-3] For a thorough understanding and interpretation of the experimental results an accompanying theory is needed.[4] As a matter of fact, the first-principles calculations of positron-annihilation characteristics in solids are a unique testing ground for electronic structure theories, as theoretical quantities can be directly compared with accurate experimental data arising, for example, from high-resolution positron lifetime spectroscopy, two-dimensional angular correlation (ACAR) measurements, or slow-positron beam experiments. The basis of the modern materials modeling by electronic structure calculations is the density-functional theory (DFT).[5] The DFT within its generalization[6] to two-component systems is also the basis for calculating positron states and annihilation characteristics in solids.

The success of the DFT in the electronic structure calculations stems from the fact that the effects due to exchange and correlation can be handled simply but with often sufficient accuracy using the local-density approximation (LDA), which is based on accurate calculations[7] for the homogeneous electron gas. The results obtained with the LDA for the properties of atoms, molecules, and solids have been surprisingly good if one takes into account that the LDA should, in the first place, be valid only for systems with slowly varying electron densities. However, as the accuracy of the numerical methods has improved the deficits of the LDA have become visible. For example, the LDA systematically overbinds atoms in molecules and solids and underbinds electrons in atoms.

Improvements of the LDA have become possible with the advent of the generalized gradient approximation (GGA),[8] which has been tested in many total-energy calculations. The LDA can also be improved by substituting the local electron density at a given point by a properly weighted density around that point.[9] This weighted density approximation (WDA) has also been applied in the case of positron-electron correlation for a description of the image-potential-induced positron surface state on metals and the corresponding positron lifetime.[10]

In this paper we introduce a GGA approach for calculating *positron*-annihilation characteristics in condensed matter. We propose a method for accurate calculations of the total

annihilation rate. The GGA correction is also used to improve estimates of positron energetics and electron-positron momentum densities.

In a solid, the positron is screened by an electron cloud. The positron-electron contact density, which is substantially higher than the unperturbed electron density, determines the positron lifetime. The ratio is the enhancement factor. In principle, one has to determine self-consistently the electron $n_-(\mathbf{r})$ and positron $n_+(\mathbf{r})$ densities using the two-component density-functional formalism.[6] The density of a positron delocalized in a perfect bulk crystal vanishes at every point and the electron density is, therefore, not affected by positron. Then only the correlation part in the positron screening remains, and it depends only on the unperturbed electron density. For the limit of vanishing positron density, there are several calculations for the correlation energy and the annihilation rate[11-13] in a homogeneous electron gas.

The results for a positron in a homogeneous electron gas constitute the basis of the LDA calculations for positron states in real solids. The positron-annihilation rate λ, which is the inverse of the positron lifetime τ, is calculated from the overlap of the positron and electron densities as

$$\lambda = \pi r_e^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(\mathbf{r}) d^3 r, \tag{1}$$

where r_e is the classical electron radius, c is the speed of light, and $\gamma(\mathbf{r})$ is the enhancement factor. The LDA has also been used to calculate the momentum content in ACAR spectra.[14] An important quantity related to the positron energetics in a solid is the positron affinity A_+.[15] It is defined as the sum of the electron and positron chemical potentials, i.e., the position of the Fermi level and the bottom of the lowest positron band, respectively, measured with respect to the common crystal zero. The positron affinity can be directly measured using the slow positron beam techniques.[16,17]

The various LDA calculations[18,19] show that the positron lifetimes for bulk transition metals are systematically too short in comparison with the experimental values. Sterne and Kaiser[19] suggested the use of the constant enhancement factor of unity for core electrons, i.e., the independent particle model (IPM). Plazaola, Seitsonen, and Puska[20] concluded that the positron lifetimes calculated for II-VI compound semiconductors are too short due to the LDA overestimation

of the annihilation rate with d electrons the group-II atom. Puska et al.[21] introduced a phenomenological model, containing the high-frequency dielectric constant, to explain the positron-annihilation rate in semiconductors and insulators. Also the comparison of the theoretical and experimental ACAR curves at high momenta indicates that the annihilation with the d electrons is overestimated in the calculations.[14,3,22] All this experience show that the LDA does not work quantitatively in the case of positron annihilation with the core and semicore electrons.

For the LDA correlation energy and the enhancement factor we use the results by Arponen and Pajanne.[11] For the former there exists a practical interpolation form due to Boroński and Nieminen.[6] For the enhancement the widely used form of Ref. 6 is based on Lantto's[12] hypernetted chain approximation calculations. However, in order to use an enhancement factor *consistent* with the correlation energy, we introduce the function

$$\gamma_{LDA}(r_s) = 1 + 1.23 r_s - 0.0742 r_s^2 + \tfrac{1}{6} r_s^3 \qquad (2)$$

based on the data by Arponen and Pajanne.[11] Moreover, these data are more accurate than the hypernetted chain results.[12] The only fitting parameter in Eq. (2) is the factor in the front of the square term. The first two terms are fixed to reproduce the high-density random-phase approximation limit and the last term the low-density positronium limit. In the fitting procedure we have used the original data points only up to $r_s = 5$ because the data at lower densities are less reliable [the Friedel sum rule is not obeyed for $r_s = 6$ and 8 (Ref. 11)]. The form (2) gives at high electron densities a larger enhancement than the Boroński-Nieminen one, and at low electron densities it avoids the unphysically high enhancement of the latter form. The positron lifetimes calculated in the LDA with the new form (2) are systematically lower than the experimental ones.

In electronic structure calculations the LDA overestimates the correlation energies, for example, in the case of free atoms.[8] This error has been traced back to the shape of the correlation hole close to the electron. In the GGA the depth of the correlation hole is reduced which decreases the correlation energy. Similarly, the gradient correction for the electron-positron correlation should reduce the electron density near the positron and thereby decrease the enhancement factor and increase the positron lifetime.

In the GGA the effects of the nonuniform electron density are described in terms of the ratio between the local length scale $n/|\nabla n|$ of the density variations and the local Thomas-Fermi screening length $1/q_{TF}$. The lowest order gradient correction to the LDA correlation hole density is proportional to the parameter[8]

$$\epsilon = |\nabla n|^2 / (n q_{TF})^2 = |\nabla \ln n|^2 / q_{TF}^2. \qquad (3)$$

We use this parameter to describe the reduction of the screening cloud close to the positron. For a uniform electron gas $\epsilon = 0$ whereas in the case of rapid density variations $\epsilon \rightarrow \infty$. At the former limit the LDA result for the induced screening charge is valid and the latter limit leads to the IPM result. When $\epsilon \rightarrow \infty$ the electrons are tightly bound core electrons and therefore nearly insensitive to the positron. The core enhancement factor close to unity is in accord with the

work by Lynn et al.[23] In order to interpolate between the limits $\epsilon = 0$ and $\epsilon \rightarrow \infty$, we use for the induced contact charge density Δn

$$\Delta n_{GGA} = \Delta n_{LDA} e^{-\alpha \epsilon}, \qquad (4)$$

whereby the corresponding enhancement factor reads

$$\gamma_{GGA} = 1 + (\gamma_{LDA} - 1) e^{-\alpha \epsilon}. \qquad (5)$$

Above α is an adjustable parameter, to be determined so that the calculated and experimental lifetimes agree as well as possible for a large number of different types of solids. We have found that the universal choice $\alpha = 0.22$ gives lifetimes for different types of metals and semiconductors in good agreement with experiment. The dependence of the positron lifetime on the α parameter is almost linear between the values $\alpha = 0$ (the LDA limit) and $\alpha = 0.22$.

The electron-positron correlation energy is obtained by integrating the Coulomb energy between the positron and its screening cloud over the coupling constant for the interaction. Only the spherical average of the screening cloud is needed in this calculation. Modeling it by the scaled positronium approximation,[10] modified by GGA reduction for the contact density with the appropriate normalization, we can relate the correlation energy to the annihilation rate by the scaling relation[24]

$$E^{corr} \sim (\lambda - \lambda_{IPM})^{1/3}, \qquad (6)$$

where λ and λ_{IPM} are the annihilation rates with and without the enhancement, respectively. The correlation energies calculated by Arponen and Pajanne[11] obey a similar dependence with a small constant term. In practice, one can therefore use in GGA calculations the correlation energy E_{GGA}^{corr}, which is obtained from electron-gas result (E_{LDA}^{corr}) through the scaling

$$E_{GGA}^{corr}(\mathbf{r}) = E_{LDA}^{corr}(n_-(\mathbf{r})) \left(\frac{\lambda_{GGA} - \lambda_{IPM}}{\lambda_{LDA} - \lambda_{IPM}} \right)^{1/3}$$

$$= E_{LDA}^{corr}[n_-(\mathbf{r})] \; e^{-\alpha \epsilon / 3}, \qquad (7)$$

where λ_{LDA} and λ_{GGA} are the annihilation rates in a homogeneous electron gas and in the GGA, respectively. We use for E_{LDA}^{corr} the interpolation form of Ref. 6.

We have performed calculations for positron states and annihilation rates in solids using the linear-muffin-tin-orbital method (LMTO) within the atomic-spheres approximation (ASA).[25] The potentials and charge densities are spherical around the nuclei and in the case of diamond-type lattices also around interstitial tetrahedral sites. First the electronic structure is calculated self-consistently. Then the positron potential is constructed in the LDA as a sum of the Coulomb potential and the correlation energy $E^{corr}(\mathbf{r})$. The positron state is then calculated using also the LMTO-ASA method and the annihilation rate is determined.

The effects of the GGA are demonstrated in Fig. 1 in the case of Cu. Figures 1(a) and 1(b) show the radial charge density and the positron density. The d-electron density reaches far into the interstitial region where the positron density is large. Therefore the annihilation with the d electrons makes an important contribution to the total annihilation rate. Figure 1(c) gives the radial behavior of the parameter ϵ and
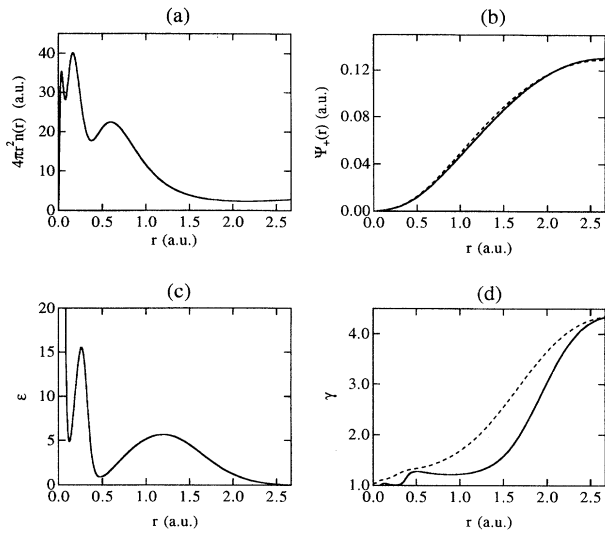
FIG. 1. (a) Spherically averaged radial electron density within the Wigner-Seitz sphere in Cu. (b) The corresponding positron wave function, (c) parameter ϵ [Eq. (3)], and (d) the enhancement factor in the LDA (dashed line) and in the GGA (solid line).

Fig. 1(d) that of the enhancement factor γ in the LDA and the GGA. The quantum-mechanical shell structure appears very clearly in the radial behavior of the GGA enhancement factor. The reduction of the enhancement factor in the interstitial region due to the GGA is not large. On the contrary, the GGA reduces strongly the enhancement factor across the d electrons. The resulting enhancement factor for the d electrons is nearly constant. In fact, this gives credence to the old scheme,[26,27] in which the annihilations with different atomic shells are separated and constant enhancement factors are used for the d and core shells. Now, this intuitively appealing model is obtained in the spirit of the DFT: One uses in the construction only the total electron density, which is the relevant quantity and not the densities and energies of the electron eigenfunctions.

Because the annihilation with the d electrons is important, the GGA increases positron lifetime for Cu as much as 21%. For comparison, the GGA increases the positron lifetime for Al only by 5%. This reflects the fact that Al has a compact core without d electrons. Most of the lifetime increase is due to the improved description of the screening cloud. The correlation potential has a minor effect on the positron wave function and thus the lifetime.

The GGA for positron states is clearly more sensitive to the atomic shell structure than the LDA. This is a common feature of some approaches beyond the LDA. For example, the effective electron potentials calculated in the GGA and in the optimized potential model[28] exhibit as a function of the distance from the nucleus bumb structures, which are absent in the LDA. On the other hand, in the WDA (Refs. 9 and 10) the effects of the shell structure can be less clear, because the treatment of the nonlocality smoothes out local variations of the charge density.

The calculated positron lifetimes are compared with experiment in Table I. In choosing the experimental lifetimes for comparison we have tried to make a collection which

represents many types of solids. On the other hand, we have tried to restrict to as few sources as possible in order to get reliable trends between different materials also when the lifetime differences are small. The LDA underestimates the positron lifetimes consistently. With the exception of Al, the GGA results agree well with the experiment. Our calculations for several other materials support these notions for the LDA and GGA.

The positron affinities calculated within the LDA and the GGA for the positron correlation energy and their experimental counterparts are also shown in Table I. The electron chemical potentials needed are calculated in all cases within the LDA,[15] because we want to study the effects of the GGA for positron states only. The effect of the GGA (Ref. 8) on electron states is, according to our calculations, to raise the Fermi level and decrease the magnitude of the positron affinity by $\sim$ 0.3 eV. The affinities calculated in the GGA for positron states are up to 0.8 eV smaller in magnitude than the corresponding LDA results. Compared to the experimental results, the LDA overestimates the magnitude of the affinity in the $3d$ series, and the GGA is there a clear improvement. For the metals in the $4d$ and $5d$ series the LDA results are generally in good agreement with experiments and the GGA results are too small in magnitude.

We have implemented the GGA also in the superimposed atom method[27] which retains the true three-dimensional geometry of the crystal lattice but the electronic structure is not self-consistent. The test calculations for the positron lifetime

TABLE I. Positron bulk lifetimes τ and affinities A_+ in solids. The theoretical results are obtained with the LMTO-ASA method using the LDA enhancement factor of Eq. (2) and the corresponding GGA with $\alpha = 0.22$.

Material	τ^{LDA} (ps)	τ^{GGA} (ps)	$\tau^{expt.}$ (ps)	A_+^{LDA} (eV)	A_+^{GGA} (eV)	$A_+^{expt.}$ (eV)
Na	279	329	338[a]	-7.59	-7.21	
K	329	392	397[a]	-7.55	-7.18	
Al	144	153	170[b]	-4.66	-4.49	
V	103	119		-4.29	-3.78	-3.7[d]
Fe	91	108	112[b]	-4.26	-3.62	-3.3[d]
Co	89	106		-4.24	-3.62	-3.3[e]
Ni	88	107	107[b]	-4.72	-3.99	-4.0,[d]-3.9[e]
Cu	96	118	120[b]	-5.05	-4.35	-4.3[e]
Nb	109	122		-3.82	-3.43	-3.8[e]
Mo	101	112		-2.78	-2.39	-2.45,[d]-2.4[e]
Pd	94	114		-5.31	-4.61	-5.1[e]
Ta	108	117		-3.39	-3.12	-3.5[e]
W	93	101		-1.89	-1.59	-1.8[e]
Pt	88	101		-3.78	-3.20	-3.8[d]
Si	186	210	216[b]			
Ge	191	228	228[b]			
GaAs	190	231	231[b]			
InP	201	248	244[b]			
CdTe	228	290	285[c]			

[a]Reference 29.
[b]Reference 30.
[c]Reference 31.
[d]Reference 16.
[e]Reference 17.

by using the superimposed atom method as well as calculations with non-self-consistent electron densities in the LMTO-ASA show that the GGA results are more sensitive to the approximations in the electronic structure than the LDA results, which are quite insensitive due to a feedback mechanism.[27,18] However, it is gratifying to note that the result calculated with the self-consistent electronic structures are systematically closer to the experiments than those obtained using the non-self-consistent electron densities. Using the superimposed atom method we have tested the GGA model also in the case of positrons trapped by vacancies in solids. Calculations for different metals as well as for semiconductors show that the lifetime increase relative to the bulk state is similar as in the LDA model for positron annihilation.

In conclusion, we have introduced a general-purpose formula for the calculation of positron characteristics in solids.

The correction has one empirically determined parameter. The gradient correction improves systematically the too large annihilation in the LDA and it accounts well for the positron energetics in solids. The GGA results are in good agreement with existing experimental positron lifetimes for many different types of electronic environments, including the simple metals, transition metals, and elemental group-IV semiconductors as well as the III-V and II-VI compound semiconductors. However, the GGA approach is sensitive to the quantum-mechanical shell structure and to the self-consistency of the electron density. We expect that the method is powerful in predicting positron lifetimes for perfect and defected solids and in calculating the ACAR maps to be quantitatively compared with experiments.

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