Screening of a positron in an inhomogeneous electron gas

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Most calculations of positron annihilation characteristics in metals avoid direct determination of the effect of electron-positron interaction and use heuristic approaches such as the local density, generalized gradient, or weighted density approximations, benefitting in this way of enhancement factors calculated for an electron gas. As shown in the paper these approaches lead to quite different values of the local annihilation rates. In this work these last are computed for a spherical inhomogeneity in jellium by solving quantum mechanical equations obtained along the lines of the theory of liquids in the difficult but extremely important case when the surrounding of the positron is anisotropic. It is shown that, at least for the model investigated in this paper, the weighted density approximation shows the smallest deviations from our results for a large interval of amplitudes and sizes of the inhomogeneity. We do not treat situations when electrons are described by wave functions having nodes in the present work. However, the formalism developed in this paper is a necessary step in solving this problem also. A vacancy in Al is investigated as an example.

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I. INTRODUCTION

The electron-positron interaction (EPI) has always been a challenging many-body problem in positron annihilation studies.[1,2] Several approaches to EPI in an electron gas have been developed (for a review see Ref. 3), basing, e.g., on the Bethe-Goldstone equation,[4,5] the Sawada boson approach,[2] and the Lippmann-Schwinger equation.[6] Recently Gilgien *et al.*[7] performed extensive Quantum Monte Carlo (QMC) studies of EPI in a homogeneous electron gas, including Diffusion Monte Carlo (DMC) calculations, which, at least in principle, should give information on the exact ground state of the system. There is an opinion that DMC calculations should constitute a ''benchmark'' in many-body studies. It is obvious, and this is also apparent in Ref. 7 that such calculations have problems of their own. The importance of EPI studies is due to the numerous applications of the positron annihilation method in investigations of condensed matter.[8]

The approach to EPI developed by Kallio, Pietiläinen, and Lantto[9,10] and labeled HNC (hypernetted-chain) benefits of the achievements of the theory of liquids. In its form proposed by Gondzik and Stachowiak[11] (also conventionally labeled HNC) it proved to be particularly efficient and leading to reasonable results as well for positron lifetime, EPI correlation energy and partial annihilation rates. The partial annihilation rates, however, are obtained after development of the theory,[12–14] (labeled PHNC) by perturbing the Jastrow type trial function of HNC in order to allow for momentum dependence in electron-positron scattering.[12] The simplicity of the HNC-like approach of Ref. 11 makes it a useful one while investigating EPI in an inhomogeneous medium, e.g., a metal lattice. Also, Ladanyi *et al.*[15] presented a simple approach basing on the Thomas-Fermi-Weizsäcker theory, however, their method does not properly take into account $e^- - e^-$ correlations.

Indeed, EPI in inhomogeneous media is still an unsolved theoretical problem. In spite of quite a few attempts to understand the mechanism of screening the positron in a metal, the subject remains very controversial. The classical approach is the independent particle model (IPM) still used with success in most experimental Fermi surface studies. If EPI enhances the contact density of all electronic states on the positron by the same factor independent of the positron coordinates IPM [or rather constant enhancement approach (CEA)] is a better approximation than would follow from its name, at least as concerns the angular correlation experiment.

Many theoretical works used the local density approximation (LDA) to EPI.[16–18] This approach was generalized by Barbiellini *et al.*[19] who proposed the generalized gradient approximation (GGA) and by Rubaszek *et al.* who used the weighted density approximation (WDA).[20] Works using the constant density potential approximation should be mentioned,[21,22] as well as their generalizations.[23] The common defect of all these approaches is that self-consistency of EPI is not controlled, i.e., it is not known whether the potential used in the formalism leads to exact screening of the positron. If it does not, then the electron density on the positron obtained in this way is not reliable.

As concerns deviations from the local density approximation in metal lattices, this problem according to Ref. 24 is of lesser importance, at least in Al. But this conclusion follows from experimental considerations and means that a satisfactory theory of $e^+ - e^-$ interaction in metal lattices is not existing. Note also that the conclusion of Ref. 24 differs in this regard from other studies both experimental and theoretical[19] also (Refs. 25,20,26).

The HNC approach in the form of Ref. 11 has been used for studying EPI in inhomogeneous media,[25] including metal lattices (for the case of a positron in lithium).[27,26] However, technical reasons prevented the authors of Refs. 25,27, and 26 from treating cases where the medium surrounding the positron is anisotropic, so one single one-dimensional function cannot describe the screening.

In the present work a formalism is developed in which the local annihilation rates are computed for a positron inside a

spherical inhomogeneity in an electron liquid. Since the positron is more or less delocalized, all its positions with regard to the inhomogeneity must be taken into account, particularly those where the positron coordinates do not coincide with its center. Remark that a spherical inhomogeneity is a quite good model of a real metal (at least from the point of view of EPI), since far away from the positron the metal can be treated as homogeneous as concerns screening the positron. So a single spherical inhomogeneity includes most of the problem. On the other hand, nodes of the density amplitude introduce singularities in the equations. In Refs. 27,26 a problem of this kind was solved in the isotropic case (i.e., for the positron on the Li nucleus). In the present work we decided to overcome only one still unsolved problem, namely, screening of a noncentral positron, leaving aside the problem of nodes in the anisotropic case (for earlier attempts in this direction see Ref. 28).

II. BASIC ASSUMPTIONS

We derived the equation for the enhancement amplitude w in a metal lattice in Ref. 26:

$$\chi[-\nabla^2+W(\mathbf{r}_p,\mathbf{r})]w-2\nabla\chi\nabla w=0. \tag{1}$$

$\chi(\mathbf{r})$—the density amplitude of conduction electrons in the absence of the positron—is a known function. We will assume that it has spherical symmetry. $\mathbf{r}_p$—the positron coordinate—differs from zero. The derivatives are taken with regard to $\mathbf{r}$.

Equation (1) is obtained in the following way: $\chi(\mathbf{r})$ obeys the Euler-Lagrange type equation

$$[-\tfrac{1}{2}\nabla^2+V^0(\mathbf{r})]\chi(\mathbf{r})=\eta\chi(\mathbf{r}), \tag{2}$$

where $V^0(\mathbf{r})$ is the self-consistent lattice potential [self-consistent in the meaning of Eq. (2)] and η is the Lagrange multiplier. It is shown in Refs. 29,26,30 that in lithium and in other alkalis, $\chi(\mathbf{r})$ obtained from Eq. (2) reproduces quite well the main features of the distribution of conduction electrons. In presence of the positron at $\mathbf{r}_p$ the density amplitude takes the form $\zeta(\mathbf{r}_p,\mathbf{r})$ and it is logical to assume that it obeys the equation

$$[-\tfrac{1}{2}\nabla^2+V^0(\mathbf{r})+\tfrac{1}{2}W(\mathbf{r}_p,\mathbf{r})]\zeta(\mathbf{r}_p,\mathbf{r})=\eta\zeta(\mathbf{r}_p,\mathbf{r}), \tag{3}$$

where $W(\mathbf{r}_p,\mathbf{r})$ is the screened electron-positron potential. Substituting

$$\zeta(\mathbf{r}_p,\mathbf{r})=w(\mathbf{r}_p,\mathbf{r})\chi(\mathbf{r}) \tag{4}$$

into Eq. (3) one gets Eq. (1).

The screened potential of electron-positron interaction W is consisted of three parts:

$$W(\mathbf{r}_p,\mathbf{r})=-\frac{1}{|\mathbf{r}-\mathbf{r}_p|}+W_p(\mathbf{r}_p,\mathbf{r})+W_{\mathrm{xc}}(\mathbf{r}_p,\mathbf{r}), \tag{5}$$

where the Coulomb potential of the screening cloud is expressed as

$$W_p(\mathbf{r}_p,\mathbf{r})=\int d\mathbf{r}'\frac{w^2(\mathbf{r}_p,\mathbf{r}')-1}{|\mathbf{r}-\mathbf{r}'|}\chi^2(\mathbf{r}'), \tag{6}$$

the exchange-correlation contribution is assumed as

$$W_{\mathrm{xc}}(\mathbf{r}_p,\mathbf{r})=V_{\mathrm{HL}}\{w^2(\mathbf{r}_p,\mathbf{r})\chi^2(\mathbf{r})\}-V_{\mathrm{HL}}\{\chi^2(\mathbf{r})\}, \tag{7}$$

where $V_{\mathrm{HL}}\{\rho\}$ has the form proposed by Hedin and Lundqvist.[31]

We intend to solve in this work the problem of positron screening in an inhomogeneous electron gas in which the spherical inhomogeneity is isolated and is described by the electron density in absence of the positron expressed as

$$\rho(r)=\chi^2(r)=\rho_0\left\{1+\sigma\exp\left[-\left(\frac{r}{s_0}\right)^2\right]\right\}. \tag{8}$$

σ and s_0 are parameters ($\sigma>-1$) that allow one to describe both the amplitude and the size of the inhomogeneity. ρ_0 is the density of the electron gas. In most of our calculations we will use for ρ_0 the value of the density of conduction electrons in lithium corresponding to $r_s=3.248$.

Let us note that for $\sigma=0$ (i.e., for a homogeneous electron gas), Eq. (1) takes the well-known form of Ref. 11

$$[-\nabla^2+W(\mathbf{r})]w=0. \tag{9}$$

A similar model has already been investigated for the positron in the center of the inhomogeneity.[26] Here we will consider the problem of a non central positron. The positron, of course, is a delocalized particle, so all its possible positions must be considered.

III. EQUATION FOR THE ENHANCEMENT AMPLITUDE

The enhancement amplitude can be written as an expansion in Legendre polynomials:

$$w(\mathbf{r}_p,\mathbf{r})=A(r_p)e^{-\alpha s}+\tau(\mathbf{r}_p,\mathbf{r}), \tag{10}$$

where

$$\tau(\mathbf{r}_p,\mathbf{r})=\sum_{n=0}^{\infty}\varphi_n(r_p,r)P_n(\cos\vartheta) \tag{11}$$

vanishes at $\mathbf{r}=\mathbf{r}_p$ and is devoid of the cusp occurring in w at the positron.

$$s=|\mathbf{r}-\mathbf{r}_p|=(r^2+r_p^2-2rr_p\cos\vartheta)^{1/2}. \tag{12}$$

From the assumption $\tau(\mathbf{r}_p,\mathbf{r}_p)=0$ it follows that $\alpha=1/2$.

Note that the above assumption is not the only way of avoiding the cusp in τ at the positron. In general we can assume

$$\tau(\mathbf{r}_p,\mathbf{r}_p)=D(r_p) \tag{13}$$

and then the value of α equal to

$$\alpha=\frac{D(r_p)+A(r_p)}{2A(r_p)} \tag{14}$$

takes care of the cusp. Of course, the substitution $D=0$ is the simplest one, since it leads to a constant value of α (independent of r_p).

TABLE I. Dependence of $A(r_p)$ as obtained from Eqs. (20), (21) for a homogeneous electron gas on the positron coordinate r_p ($r_s=3.248$).

r_p in atomic units	$A(r_p)$
0.011 25	3.250 04
0.0525	3.250 05
0.1125	3.250 06
0.2250	3.250 23
0.30	3.250 51
0.45	3.251 51
0.60	3.253 42
0.75	3.256 89
0.90	3.262 00
1.05	3.268 51
1.20	3.276 15
1.35	3.284 58
1.50	3.293 67
1.65	3.302 87
1.80	3.312 10
1.95	3.320 83
2.10	3.329 10

The value of $A(r_p)$ gives information about the local annihilation rate. ϑ is the angle between $\mathbf{r}$ and $\mathbf{r}_p$. The smoothness of τ allows to limit ourselves, at least in this work, to two terms in Eq. (11).

The exponential term in formula (10) includes the cusp contribution to χ_i. Reproducing the cusp with a series in Legendre polynomials would need including many terms in the expansion. Of course, describing τ with only two spherical harmonics requires the screening cloud around the positron to be large in comparison to the distance of the positron from the nucleus. Table I shows that such an assumption is reasonable up to $r_p=2.1$ a.u. (at least for $r_s=3.248$ corresponding to lithium) and leads to the right values of the enhancement factors for a positron in an electron gas. It is also remarkable that for r_p approaching zero the solution approaches continuously the result for $r_p=0$ obtained by solving an infinitely simpler equation.

With two components left in the expansion (11) and a nodeless unperturbed density amplitude $\chi(r)$, Eq. (1) takes a more specific form

$$
\begin{aligned}
&-\varphi_0''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\varphi_0'+W(\mathbf{r}_p,\mathbf{r})\varphi_0\\
&\quad+\left[-\varphi_1''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\varphi_1'+\left(W(\mathbf{r}_p,\mathbf{r})+\frac{2}{r^2}\right)\varphi_1\right]\cos\vartheta\\
&\quad+\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta\right.\\
&\quad\left.+W(\mathbf{r}_p,\mathbf{r})\right]Ae^{-\alpha s}=0. \qquad (15)
\end{aligned}
$$

We solve Eq. (15) as usual by way of successive linearizations, substituting for φ_0, φ_1, and A the forms

$$
\varphi_0=\varphi_0^0+\delta\varphi_0,\quad \varphi_1=\varphi_1^0+\delta\varphi_1,\quad A=A_0+\delta A, \qquad (16)
$$

where φ_0^0, φ_1^0, and A_0 are assumed to be known and $\delta\varphi_0$, $\delta\varphi_1$, and δA to be small, so terms nonlinear in these quantities can be omitted. Usually five successive linearizations are sufficient to obtain a satisfactory solution of such equations.

In this way we get from Eq. (15) the linearized equation for $\delta\varphi_i$ and δA

$$
\begin{aligned}
&-\delta\varphi_0''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_0'+W_0(\mathbf{r}_p,\mathbf{r})\delta\varphi_0+\varphi_0^0\delta W(\mathbf{r}_p,\mathbf{r})\\
&\quad+\left[-\delta\varphi_1''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_1'+\left(W_0(\mathbf{r}_p,\mathbf{r})+\frac{2}{r^2}\right)\delta\varphi_1\right.\\
&\quad\left.+\varphi_1^0\delta W(\mathbf{r}_p,\mathbf{r})\right]\cos\vartheta+\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)\right.\\
&\quad\left.-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta+W_0(\mathbf{r}_p,\mathbf{r})\right]\delta Ae^{-\alpha s}\\
&\quad+A_0e^{-\alpha s}\delta W(\mathbf{r}_p,\mathbf{r})=-F(\mathbf{r}), \qquad (17)
\end{aligned}
$$

where

$$
\begin{aligned}
F(\mathbf{r})&=-\varphi_0^{0\prime\prime}-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\varphi_0^{0\prime}+W_0(\mathbf{r}_p,\mathbf{r})\varphi_0^0\\
&\quad\times\left\{-\varphi_1^{0\prime\prime}-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\varphi_1^{0\prime}+\left[W_0(\mathbf{r}_p,\mathbf{r})+\frac{2}{r^2}\right]\varphi_1^0\right\}\\
&\quad\times\cos\vartheta+\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta\right.\\
&\quad\left.+W_0(\mathbf{r}_p,\mathbf{r})\right]A_0e^{-\alpha s}, \qquad (18)
\end{aligned}
$$

where

$$
W(\mathbf{r}_p,\mathbf{r})=W_0(\mathbf{r}_p,\mathbf{r})+\delta W(\mathbf{r}_p,\mathbf{r}). \qquad (19)
$$

W_0 is obtained by substituting w_0 for w in Eqs. (5)–(7). W_0 and δW are treated in detail in the Appendixes.

Following the way described in Appendixes A–E we finally get the set of equations

$$
\begin{aligned}
&-\delta\varphi_0''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_0'+(\tilde{\mathcal{W}}_1+\zeta_{00})\delta\varphi_0+(\tilde{\mathcal{W}}_2+\zeta_{01})\delta\varphi_1\\
&\quad+(\mathcal{B}_1+\tilde{\mathcal{W}}_4+\zeta_{0A}+\Sigma^0)\delta A+8\pi\int_0^\infty r'^2dr'\chi^2(r')\\
&\quad\times[\sigma_0^0\delta\varphi_0(r')+\sigma_1^0\delta\varphi_1(r')]=-F_0, \qquad (20)
\end{aligned}
$$

$$-\delta\varphi_1''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_1'+(3\tilde{\mathcal{W}}_2+\zeta_{10})\,\delta\varphi_0$$
$$+\left(\frac{2}{r^2}+3\tilde{\mathcal{W}}_3+\zeta_{11}\right)\delta\varphi_1$$
$$+(3\mathcal{B}_2+3\tilde{\mathcal{W}}_5+\zeta_{1A}+\Sigma^1)\,\delta A+8\pi\int_0^\infty r'^2dr'\chi^2(r')$$
$$\times[\sigma_0^1\delta\varphi_0(r')+\sigma_1^1\delta\varphi_1(r')]=-F_1, \tag{21}$$

where

$$F_0(r)=-(\varphi_0^0)''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)(\varphi_0^0)'+\tilde{\mathcal{W}}_1\varphi_0^0+\tilde{\mathcal{W}}_2\varphi_1^0$$
$$+(\mathcal{B}_1+\tilde{\mathcal{W}}_4)A_0, \tag{22}$$

$$F_1(r)=-(\varphi_1^0)''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)(\varphi_1^0)'+3\tilde{\mathcal{W}}_2\varphi_0^0$$
$$+\left(3\tilde{\mathcal{W}}_3+\frac{2}{r^2}\right)\varphi_1^0+3(\mathcal{B}_2+\tilde{\mathcal{W}}_5)A_0. \tag{23}$$

The above equations form the basis for the solution of the problem. The meaning of the quantities appearing in them is also given in the Appendixes.

IV. COMPUTATIONS

In order to solve Eqs. (20), (21) it is assumed that a sufficiently good description of the functions $\delta\varphi_k(r)$ is given by their values at a discrete set of points $r_i, i=1,\ldots,N$. Under this assumption, Eqs (20), (21), which in fact form a set of two integrodifferential equations, can be written in the form of a set of linear algebraic equations for the unknown quantities $\delta\varphi_k(r_i)$ and δA.

The boundary conditions are obvious:

$$\varphi_0'(r_p,0)=0,\ \ \varphi_0(r_p,\infty)=1,\ \ \varphi_1(r_p,0)=0,\ \ \varphi_1(r_p,\infty)=0. \tag{24}$$

The quantity δA rises the necessity of introducing an additional equation that gives the criterion for the choice of A in the formula (10). In practice here is a major source of the uncertainties occurring in the solution.

The additional condition should be

$$\tau(\mathbf{r}_p,\mathbf{r}_p)=0. \tag{25}$$

However, describing τ with two spherical harmonics only, we are unable to reproduce the zero. For this reason we used in our calculations the additional condition in the form

$$\varphi_0(r_p,r_p)+\varphi_1(r_p,r_p)=v(r_p), \tag{26}$$

where the way of choosing $v(r_p)$ is described below.

For a given system defined by the formula (8) the conditions (24) and (26) lead to a unique solution, inasmuch as the final results do not depend on the starting values of $\varphi_0^0(r_p,r)$, $\varphi_1^0(r_p,r)$, and A_0 as far as they are not too different from the ground state function.

A major problem was to estimate the function $v(r_p)$ in Eq. (26). Our first attempt to solve Eqs. (20), (21) was performed for a homogeneous electron gas. Here we are in the advantageous situation that the exact solution of the problem is known. It is obtained for the positron at $\mathbf{r}_p=0$. Transferring the positron from the central point of the coordinate system to $\mathbf{r}_p$ we can compute the functions $\varphi_k^j(r_p,r)$ from the formulas

$$\varphi_0^j(r_p,r)=\frac{1}{2}\int_0^\pi \sin\vartheta\,d\vartheta\,\tau(0,|\mathbf{r}-\mathbf{r}_p|), \tag{27}$$

$$\varphi_1^j(r_p,r)=\frac{3}{2}\int_0^\pi \sin\vartheta\,d\vartheta\,\tau(0,|\mathbf{r}-\mathbf{r}_p|)\cos\vartheta, \tag{28}$$

where $\tau(\mathbf{r}_p,\mathbf{r})$ is defined by Eqs. (10), (11).

The function $v(r_p)$ is obtained in analogy to Eq. (26) as

$$v^j(\rho_0,r_p)=\varphi_0^j(r_p,r_p)+\varphi_1^j(r_p,r_p), \tag{29}$$

where ρ_0 is the density of the electron gas. We remark that the function $\tau(0,s)$ is the exact value that should result from solving Eq. (1) for a homogeneous electron gas while $v^j(\rho_0,r_p)$ is the exact value of the function $v(r_p)$ for this particular case.

Let us now solve Eqs. (20), (21) with the boundary conditions (24)–(26) with $v(r_p)$ given by Eq. (29), but assuming a value of σ in Eq. (8) equal 0. We solve in this way the problem of screening the positron in a homogeneous electron gas, but using a coordinate system displaced with regard to the positron. The results for $A(r_p)$ are given in Table I. It is visible that for not very large values of r_p the formalism developed in this work leads to quite reliable figures for the annihilation rate, provided appropriate values for $v(r_p)$ are used in Eq. (26).

While solving Eqs. (20), (21) for the inhomogeneous electron gas described by the formula (8) we will simply use for $v(r_p)$ the local density approximation, assuming that $v(r_p)$ is a function of r_p and of the electron density at r_p in absence of the positron, i.e.,

$$\varphi_0(r_p,r_p)+\varphi_1(r_p,r_p)=v^j[\rho(r_p),r_p], \tag{30}$$

where $\rho(r_p)$ is given by Eq. (8). This approach is based on numerical studies showing that the function $v(r_p)$ has a more local character than the screening cloud around the positron.

V. LDA, GGA, AND WDA

We shall compare the results obtained in this work to the predictions of the local density approximation, the generalized gradient approximation (GGA),[19] the weighted density approximation (WDA),[20] and the constant enhancement approximation (CEA) for the same system [described by Eq. (8)]. Since this work is the generalization of the approach of Gondzik and Stachowiak[11] labeled HNC, we will assume while applying LDA, GGA, and WDA the values of the en-

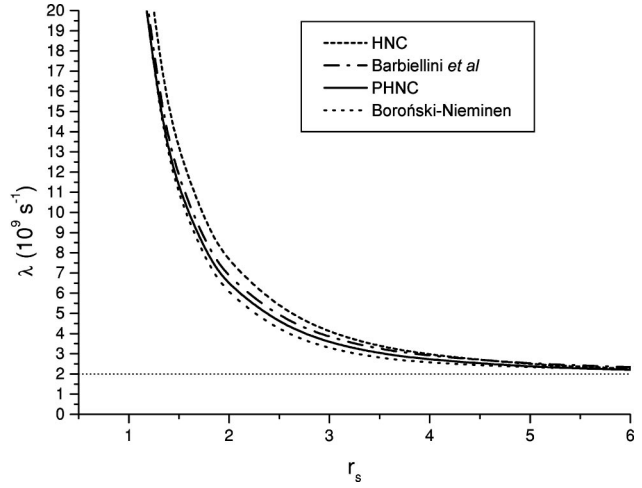

FIG. 1. Enhancement factors for jellium according to different approaches. In order of increasing enhancement the figure shows the enhancements proposed in Ref. 33 (*bn*), Ref. 12 (*phnc*), and Ref. 19 (*ap*). The highest enhancement corresponds to the solution of Eq. (9) (*hnc*).

hancement factors for a homogeneous electron gas obtained according to Ref. 11. Comparison of the enhancement factors of Ref. 11 with the ones obtained in other approaches to e^+-e^- interaction in jellium is given in Fig. 1 (for comments see Ref. 32). The approach of Ref. 11 is very simple and leads to results not very different from the ones obtained in Refs. 2,5, or 6. Since the purpose of LDA, GGA, and WDA is to describe the influence of inhomogeneities on the effect of electron-positron interaction, it is appropriate to assume in all cases the same values of the jellium enhancement. Let us remind the reader that assumptions concerning enhancement factors in jellium do not constitute an integral part of the three approaches (LDA, GGA, and WDA; as for GGA, the phenomenological constant α should depend, however, on the choice of the jellium enhancement). In their case the choice of jellium enhancement is a question of taste (or convenience). The approach used in the present work differs from them in this regard: for a homogeneous electron gas it reduces to the formalism of Gondzik and Stachowiak.[11]

The local density approximation has been widely used in positron physics both for determining the theoretical annihilation rates and the angular correlation functions.[17,18,3] It consists in assuming that the local annihilation rate $\lambda(r_p)$ (in units of 10^9 s^{-1}) is determined uniquely by the local value of the electron density in absence of the positron, i.e., it is expressed by the formula

$$\lambda_{\mathrm{LDA}}(r_p)=\frac{12}{r_s^3(r_p)}\gamma[r_s(r_p)], \tag{31}$$

where γ is the enhancement factor and the electron density $\rho(r)$ is connected with the local value of the r_s parameter by the formula

$$\rho(r)=\frac{3}{4\pi r_s^3(r)}. \tag{32}$$

Here we will determine γ on the base of $w_j(r_s,0)$, the value on the positron of the solution of Eq. (9) for an electron gas ($\sigma=0$) characterized by the appropriate value of the r_s parameter [$r_s(r)$ in the case of Eq. (32)]. Since the values of $w_j(r_s,0)$ for the electron gas (according to the formalism of Gondzik and Stachowiak[11]) have never been published we present them here in the following form:

$$\begin{aligned}\gamma_{hnc}(r_s)&=w_j^2(r_s,0)\\&=1.019\,06+1.336\,96r_s+0.136\,51r_s^2+0.081\,12r_s^3\\&\quad+0.008\,63r_s^4-3.2491\times10^{-4}r_s^5\\&\quad+4.414\,54\times10^{-6}r_s^6\end{aligned} \tag{33}$$

[the formula describes $w_j^2(r_s,0)$ correctly in the range of r_s from 0.1 to 25]. Referring to the correlation function (33) we shall label it with small letters *hnc*, while the self-consistent approach expressed by Eq. (3) will be called HNC.

We will also use in this paper other formulas that have been proposed in the literature. When referring to them we will assume a similar convention as above. The formula resulting from the PHNC approach[13] is

$$\gamma_{phnc}(r_s)=1+1.23r_s-0.1375r_s^2+r_s^3/6 \tag{34}$$

and the formula of Boroński and Nieminen is[33]

$$\gamma_{bn}(r_s)=1+1.23r_s+0.8295r_s^{3/2}-1.26r_s^2+0.3286r_s^{5/2}+r_s^3/6. \tag{35}$$

The local annihilation rates used in this work are determined from the formula

$$\lambda(r_p)=\frac{12}{r_s^3(r_p)}A^2(r_p), \tag{36}$$

where A is given by Eq. (10).

The generalized gradient approximation (GGA) has been proposed by Barbiellini *et al*.[19] In their approach the local enhancement factor depends both on the electron density and the absolute value of the local gradient of this density. It is made to obey the formula

$$\gamma_{\mathrm{GGA}}(r_p)=1+\{\gamma[r_s(r_p)]-1\}\exp(-\alpha\epsilon), \tag{37}$$

where

$$\epsilon=\left|\frac{\nabla\rho(\mathbf{r})}{\rho(\mathbf{r})q_{\mathrm{TF}}}\right|^2, \tag{38}$$

and $\gamma(r_s)$ in Ref. 19 was given by the formula interpolating the results of Arponen and Pajanne (AP) for the homogeneous electron gas[2]

$$\gamma_{ap}(r_s)=1+1.23r_s-0.0742r_s^2+r_s^3/6. \tag{39}$$

q_{TF}^{-1} is the local Thomas-Fermi screening length and α is a phenomenological constant chosen equal to 0.22 in order to fit experimental positron lifetimes in metals. Because of the reasons presented at the beginning of this section we used in Eq. (37) the formula (33) for $\gamma(r_s)$ [in Sec. VII we use also

the formulas (34), (35), and (39)]. In this situation the corresponding coefficient α should be different. We considered, however, that the appropriate change would introduce only minor quantitative corrections to γ_{GGA}. This is why we applied the value of α proposed by Barbiellini *et al*.

The weighted density approximation applied to positrons by Rubaszek *et al.*[20] (earlier applications can be found in Refs. 34 and 35) replaces the local electron density by an effective density taking account of the whole behavior of the electron density within the range of the e^+-e^- interaction. The correlation function $g^{\mathrm{WDA}}(\mathbf{r}_e,\mathbf{r}_p)$ is approximated by its analog in an electron gas $g^h[|\mathbf{r}_e-\mathbf{r}_p|,\rho^*(\mathbf{r}_p)]$, where $\rho^*(\mathbf{r}_p)$ is an effective WDA density for electrons.

Conventionally, one assumes an exponential distribution of the screening charge

$$g^h[|\mathbf{r}_e-\mathbf{r}_p|,\rho^*(\mathbf{r}_p)]=1+\{\gamma[r_s^*(r_p)]-1\}\exp(-\alpha|\mathbf{r}_e-\mathbf{r}_p|), \tag{40}$$

where $\alpha=\sqrt[3]{8\pi\{\gamma[r_s^*(r_p)]-1\}\rho^*}$.

In our calculations the density $\rho^*(\mathbf{r}_p)$ is found for any positron position $\mathbf{r}_p$ on the base of the charge neutrality condition for the screening cloud:

$$\int d\mathbf{r}_e\rho(\mathbf{r}_e)\{g^h[|\mathbf{r}_e-\mathbf{r}_p|,\rho^*(\mathbf{r}_p)]-1\}=1 \tag{41}$$

[for given positron coordinates $\mathbf{r}_p$, one seeks such a density value ρ^* that the formula (41) is fulfilled].

VI. RESULTS

We present here results obtained for $\sigma=-0.9$ and 2 and different values of s_0 and compare them to the results of different approaches used previously in the literature in order to estimate annihilation characteristics in metals. Equations (20), (21) are solved in two cases. Namely, writing Eq. (1) in the form

$$\chi[-\nabla^2+W(\mathbf{r}_p,\mathbf{r})]w-2c\nabla\chi\nabla w=0 \tag{42}$$

we should put $c=1$. However, in order to study the importance of the gradient term in the above equation we computed the solution also for $c=0$.

First-principles computations of the enhancement amplitude for $r_p>0$ performed in this way allow one to check the reliability of earlier guesses concerning this quantity which can be found in the literature. The annihilation rates obtained from solving Eqs. (20), (21) are shown in Figs. 2 and 3, together with the predictions following from LDA, GGA, WDA, and CEA. The results of our calculations approach LDA only for quite large dimensions of the inhomogeneity (i.e., of the order of the lattice constant of lithium). Calculations performed for the positron at $r=0$ (Ref. 26) have already shown that (a) the contact values of the enhancement amplitudes for both cases ($\sigma<0$ and $\sigma>0$) are not monotonic functions of s_0, (b) for narrow inhomogeneities ($s_0<1$) the screening charge around the positron (and the contact value) resembles the corresponding figures for the bulk, the inhomogeneity is too narrow for the screening cloud to build up inside of it, and (c) for wider inhomogeneities ($s_0>1$) the screening charge builds up inside the inhomogeneity and the charge distribution (and the contact value) starts to approach the expectations of LDA. The wider is the inhomogeneity the closer is the enhancement to the LDA values.

Comparison of the annihilation rates obtained in this paper with the predictions of earlier works leads to the following conclusions. As concerns LDA the conclusions obtained in Ref. 26 concerning the case of a positron at $r_p=0$ are confirmed. Only for $s_0>1$ the annihilation rates begin to approach LDA expectations.

GGA improves to a certain degree agreement with the results of the present work in comparison to LDA, but only for $\sigma<0$. This is connected with the fact that the sign of the gradient correction does not change with the sign of σ.

The WDA predictions are closer to our results than those of GGA. In many cases WDA reproduces quite well the results obtained from solving Eq. (42) especially if c is put equal to 0. This last feature is presented in Fig. 4.

The annihilation rates obtained in this work are also compared to the constant enhancement approximation (CEA) which as concerns angular correlation is equivalent to the independent particle model (IPM). According to CEA the enhancement factor depends neither on the electronic state nor on the positron coordinate [γ in Eq. (31) is given for the constant value of r_s corresponding to the bulk value of the electron density]. In surprisingly many cases the behavior of the annihilation rate obtained in our work is closer to CEA than to LDA. Remark that WDA is still closer to CEA than the results of the present paper.

Note that in Fig. 2 the annihilation rates drop quite often below 2 (i.e., below the spin averaged positronium value). This agrees with the results obtained earlier.[25]

VII. CALCULATIONS FOR A VACANCY IN AL

In order to show how the methods presented above work for particular cases, we performed calculations for a vacancy in Al. This vacancy was modelled by a spherical hole in jellium with r_s corresponding to the electron density of aluminum and equal 2.07. The electron density distribution in the vacancy has been calculated self-consistently according to the conventional scheme used in Ref. 33. It can be described quite well by a Gaussian with parameters $\sigma=-0.84$ and $s_0=3$. We preferred to use, however (this presents no difficulty), exactly the same profile as obtained from calculations.

We calculated the enhancement factors corresponding to this density distribution according to formulas (31), (37), (40), (36) corresponding to LDA, GGA, WDA, and the present approach, respectively. Additionally, we calculated the enhancement according to the Boroński and Nieminen (BN) two-component approach[33] by applying the corresponding numerical code.

In order to make all the approximations comparable we had to (a) replace the enhancement factors obtained from our theory by the LDA result for $r_p>3$ [the reason was that we were able to solve reliably Eq. (42) only up to 3.0 a.u. for the r_s value of Al] and (b) renormalize the enhancement calculated self-consistently according to the BN[33] two-

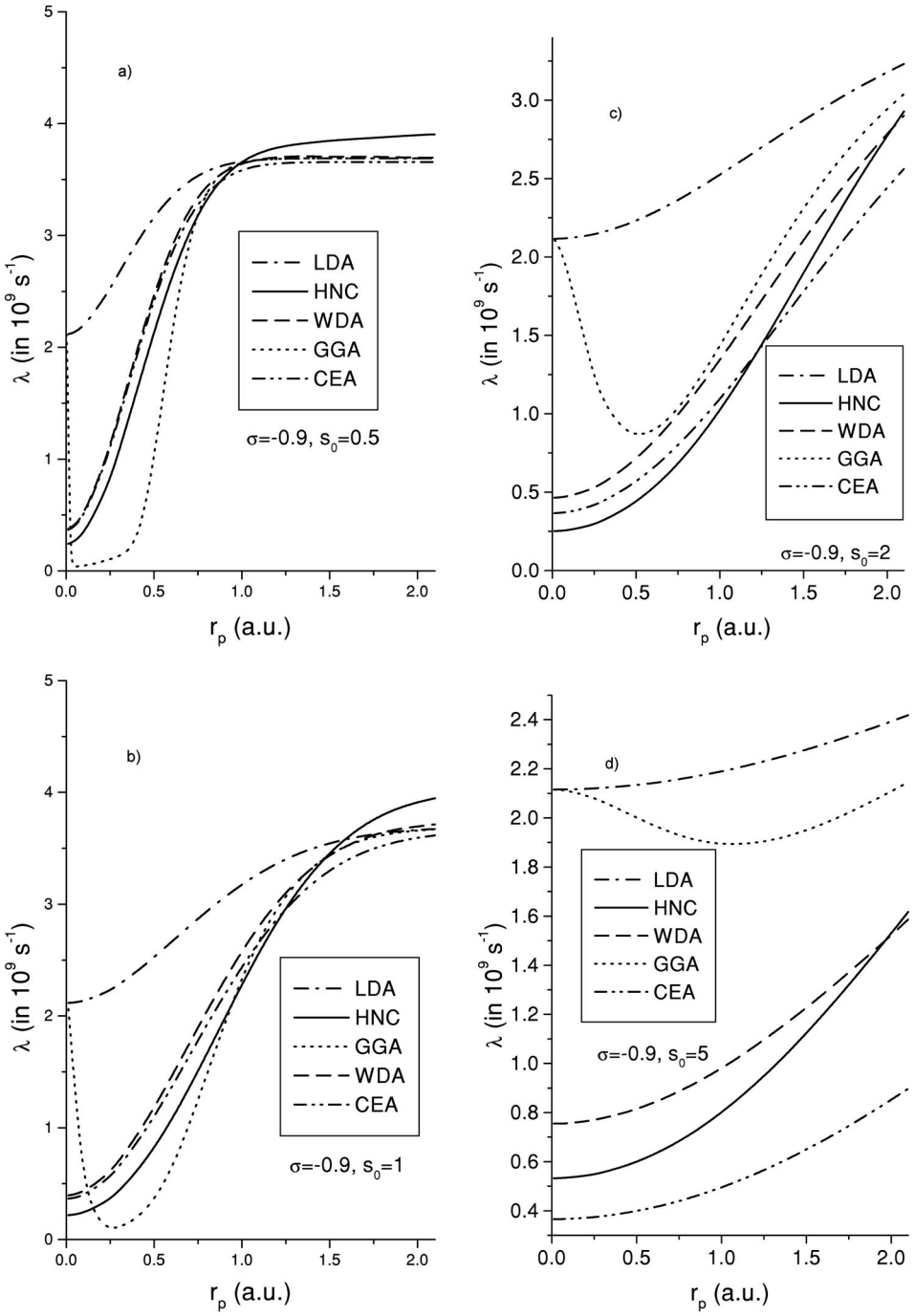

FIG. 2. Local annihilation rate $\lambda(r_p)$ according to this work and labelled HNC, according to the local density approximation (LDA), the weighted density approximation (WDA), the generalized gradient approximation (GGA), and the constant density approximation (CEA). σ is equal to -0.9 and s_0 is given on the figures in atomic units.

component approach in the whole region of interest in order to account for the difference between the Boroński and Nieminen formula (35) for the correlation function and the HNC formula (33) applied in the present calculations.

The results are presented in Fig. 5. Again, the WDA approximation agrees best with our results unlike LDA and GGA that are quite far both from WDA and the solution of Eq. (42). The BN enhancement in the vacancy (according to the two-fluid approach) is also smaller for $r \to 0$ than follows from pure LDA or GGA. Let us remark that in the approach used in Ref. 33 an effective electron density in presence of the positron trapped in the vacancy is calculated using the two-fluid model. Then the local values of this density are applied for determining the local annihilation rates in LDA approximation. The application of the two-component scheme required very complicated many-body calculations for electron-positron mixtures that have been carried out by Lantto.[36] In our opinion, the present approach that determines directly the electron density amplitude for any positron position is superior to the method used in Ref. 33.

We also computed positron lifetimes for the vacancy in Al. The experimental values range from 240,[37], 246,[38] to 253 psec.[39] Calculations were performed in LDA, GGA, and WDA and according to the self-consistent approach presented in this work. The positron wave function was calculated using the LDA approximation for the correlation poten-

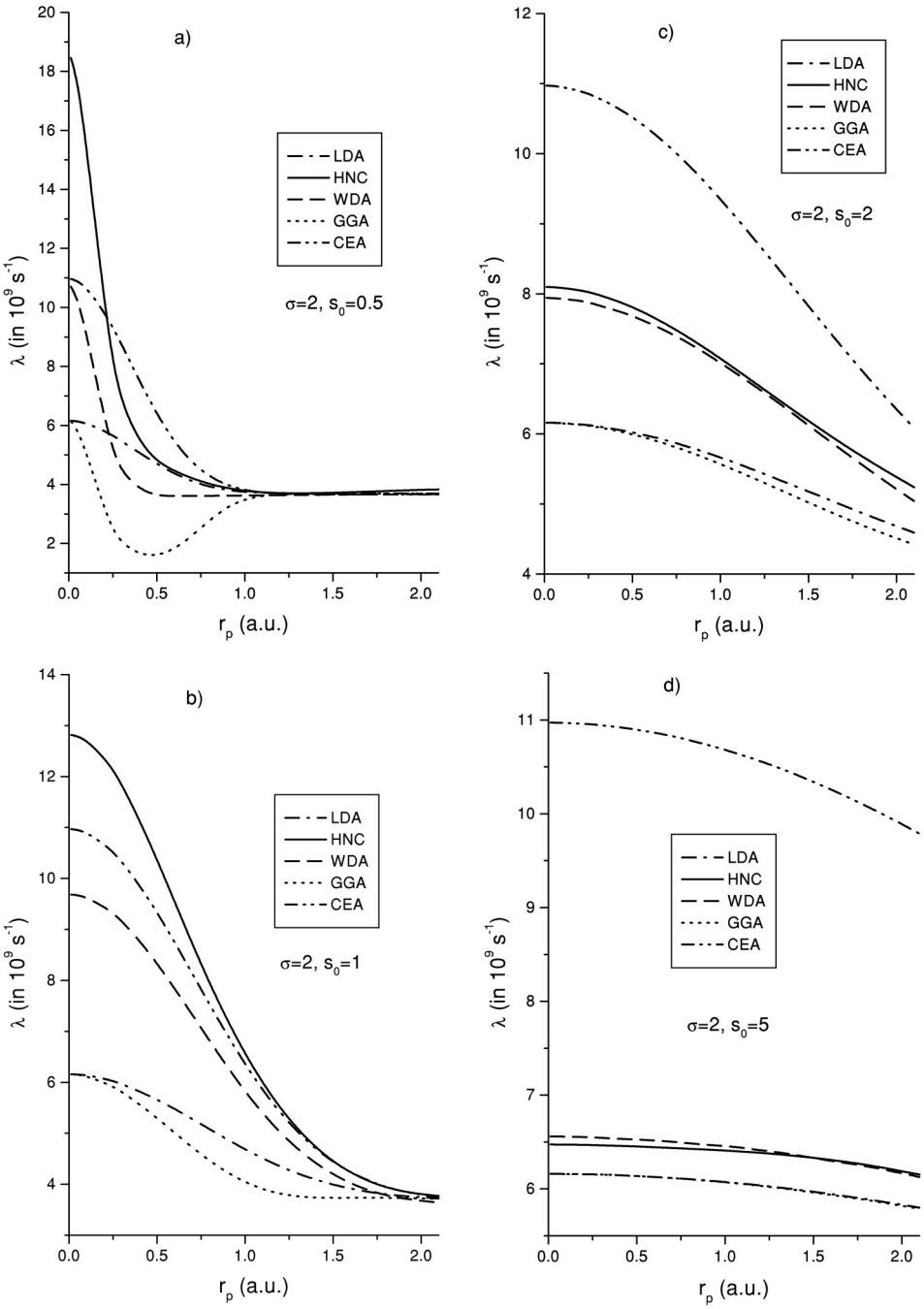

FIG. 3. The same as in Fig. 2 but for $\sigma=2$.

tial. The results are presented in Table II in the first column.

Of course, the convenient and simple HNC-type approximation to the enhancement used in this paper cannot be considered as the best and conclusive one when comparing our results to experiment. One should then apply rather the PHNC approximation (elaborated for the electron gas in Refs. 12 and 13) that takes into account scattering of electrons in different states on the positron. So, in order to see the trends we applied the *phnc* formula (34) in LDA, GGA, and WDA approximations. The corresponding results are given in the third column in Table II. Unfortunately, it is impossible at the moment to get self-consistent results for the inhomogeneous electron gas according to PHNC. Therefore we simply renormalized the results obtained using Eq. (42). We did it in such a way that we found with the *hnc* formula (33) the electron density corresponding to the HNC enhancement in the positron position and then used this value again in the *phnc* formula (34). The corresponding lifetime is presented in the fourth row in the third column of Table II (the abbreviation renorm. is added). We repeated a similar procedure using the formulas of Arponen-Pajanne (39) and of Boroński-Nieminen (35) for the enhancement in jellium. The corresponding results are presented in the second and fourth columns in Table II. Note that the positron lifetime resulting from calculations in Ref. 33 is 240 psec.

As can be seen from Table II the HNC approach gives [as

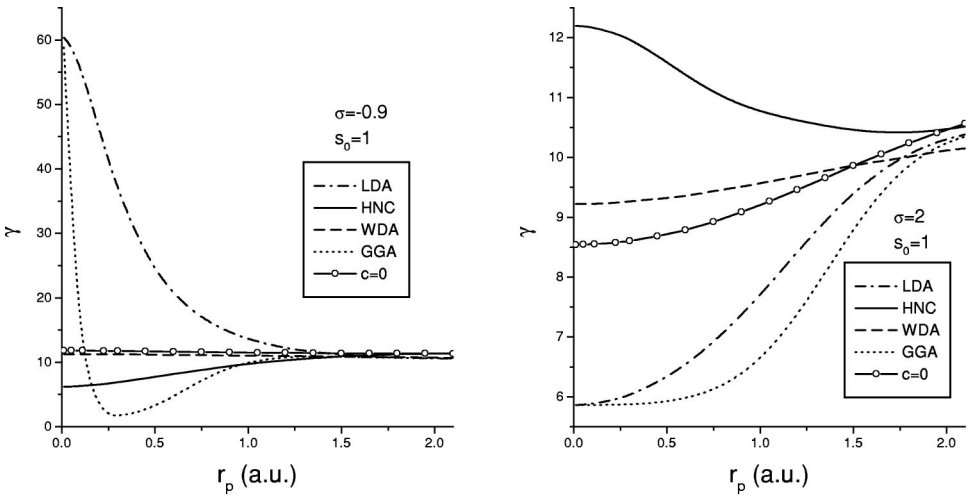

FIG. 4. Enhancement factors for two values of the σ and s_0 parameters. The case when c is put equal 0 in Eq. (42) is also shown (full curve with circles).

should be expected (cf see Fig. 1)] too low a value of positron lifetime when comparing to experiment. The best agreement can be observed for *ap* (WDA and HNC renormalized) and *phnc* (GGA and HNC renormalized) enhancements. Also, the *bn* LDA and GGA values are close to experimental figures. However, according to the discussion contained in the paper (in Sec. VI) and our criticism towards LDA and GGA one should put confidence rather in the HNC and WDA results. In this respect the *ap* formula gives the values that fit the experiment the best. Because of the general reasons expressed earlier in the paper and in Ref. 32, we give our confidence and priority to the PHNC approach.

VIII. CONCLUSIONS

It has been shown that the problem of e^+-e^- interaction in an inhomogeneous electron system can be solved from first-principles by generalizing the approach proposed by Gondzik and Stachowiak[11] for a homogeneous electron gas. Unlike in earlier first-principles calculations[21–23] self-consistency of the solution is controlled. This makes the results more reliable. Calculations have been performed for a model. They give the possibility to appreciate the reliability of such intuitive guesses concerning this problem as the local density approximation, the generalized gradient approach, the weighted density approximation, and the constant enhancement model (often referred to as IPM). It is shown that all these approaches lead to local annihilation rates differing drastically as well from each other as from most of the results of first-principles calculations performed in this work.

The model assumes a spherical inhomogeneity of gaussian shape, characterized by two parameters describing its amplitude and its size, respectively. This allows to study e^+-e^- interaction in any spherical inhomogeneity with regular behavior of the electron density. The two parameters make possible a classification of inhomogeneities and are in no way a limitation of the generality of the approach. In this paper, however, we were unable to treat the inhomogeneities that play the most important role in metals, namely, those connected with atoms where singularities occur, connected with the nucleus and the nodes in the wave functions of conduction electrons. This problem was solved in Ref. 26 for the positron on the nucleus. Generalizing the solution on arbitrary positions of the positron with regard to the nucleus needs further studies that are under way. However, the formalism developed in the present work (i.e., computing the accumulation of electrons on the positron for the positron in an anisotropic surrounding) is a necessary first step in this direction.

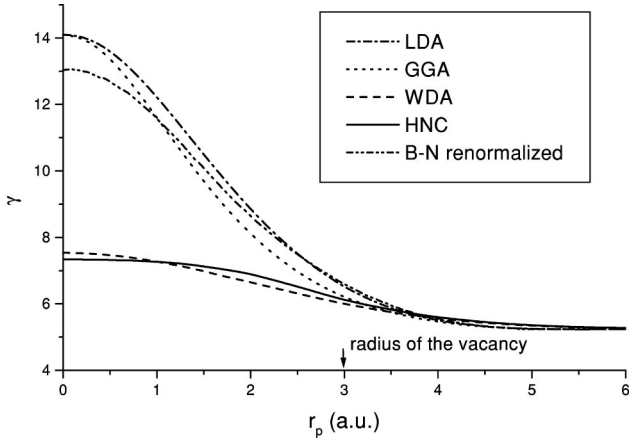

FIG. 5. The enhancement factors for different positions of the positron inside the Al vacancy calculated with the formula (33) in LDA, GGA, WDA, and HNC. The results obtained within the BN two-component approach have been renormalized as explained in the text.

TABLE II. Positron lifetimes in an Al vacancy according to different approximations (in psec). The abbreviations *hnc*, *phnc*, *ap*, and *bn* refer here to formulas (33), (34), (39), and (35) used when applying LDA, GGA, WDA, and HNC. Original self-consistent BN calculations within the two-fluid model give 240 pse.

	hnc	*ap*	*phnc*	*bn*
LDA	198	216	230	250
GGA	208	225	241	261
WDA	222	251	269	292
HNC	227	247 renorm.	263 renorm.	285 renorm.

In general LDA, GGA, and WDA lead to results for the local enhancement very different from each other. WDA seems to deviate less from the results of our computations in the whole range of values of the size and the amplitude (positive or negative) of the inhomogeneity. This conclusion, however, concerns only the kind of inhomogeneities investigated in this work.

As concerns inhomogeneities corresponding to vacancies, we were able to perform full calculations of positron lifetimes. We used the example of an Al vacancy treated in detail quite long ago by Boroński and Nieminen.[33]

Comparison of theoretical values of lifetime with experiment (and in principle this is the only experimental information available) is not very conclusive, since a single value can be easily adjusted to one's needs. So we would like to emphasize rather methodological problems that are solved in the present work in comparison to Ref. 33.

Boroński and Nieminen compute the electron and positron distributions in the vacancy by using the two-fluid approach. The electron distribution obtained in this way is then enhanced on the positron using LDA.

Let us point out that applying the two-fluid model is in this case a controversial assumption, since only one positron is present in the system. And LDA for e^+-e^- interaction is just an approximation that can be contested on base of quantum mechanics.

In the present paper the electron distribution around the positron in the vacancy is computed directly for each position of the positron by solving the appropriate Euler-Lagrange equation. This last is a generalization of the approach proposed by Gondzik and Stachowiak[11] on the base of the work of Kallio, Lantto, and Pietiläinen.[9]

In order to perform the calculations it was necessary to elaborate numerical methods of solving integrodifferential equations for systems devoided of spherical symmetry. These methods, of course, have a more general applicability.

ACKNOWLEDGMENTS

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APPENDIX A: SPHERICAL HARMONICS OF THE EQUATION FOR THE ENHANCEMENT AMPLITUDE

By expressing Eq. (17) in terms of spherical harmonics we could obtain from it an infinite series of one-dimensional equations describing the angular behavior of the solution. However, since we limit ourselves to two terms in the expansion, the same must be done while solving Eq. (17). Namely, we must expand both sides of Eq. (17) into spherical harmonics, limiting ourselves to the first two terms. for example, we have

$$F_0(r)=\frac{1}{2}\int_0^\pi \sin\vartheta d\vartheta F(\mathbf{r})=\frac{1}{2}\int_0^\pi \sin\vartheta d\vartheta F(\mathbf{r})P_0(\cos\vartheta), \tag{A1}$$

$$F_1(r)=\frac{3}{2}\int_0^\pi \sin\vartheta d\vartheta F(\mathbf{r})\cos\vartheta = \frac{3}{2}\int_0^\pi \sin\vartheta d\vartheta F(\mathbf{r})P_1(\cos\vartheta). \tag{A2}$$

From Eq. (17), we obtain in this way the set of equations

$$-\delta\varphi_0''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_0'+\langle W_0(\mathbf{r}_p,\mathbf{r})\rangle\delta\varphi_0+\langle W_0(\mathbf{r}_p,\mathbf{r})\cos\vartheta\rangle\delta\varphi_1+\varphi_0^0\langle\delta W(\mathbf{r}_p,\mathbf{r})\rangle+\varphi_1^0\langle\delta W(\mathbf{r}_p,\mathbf{r})\cos\vartheta\rangle$$
$$+\left\langle\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta+W_0(\mathbf{r}_p,\mathbf{r})\right]e^{-\alpha s}\right\rangle\delta A+A_0\langle\delta W(\mathbf{r}_p,\mathbf{r})e^{-\alpha s}\rangle=-F_0(r), \tag{A3}$$

$$-\delta\varphi_1''-2\left(\frac{1}{r}+\frac{\chi'}{\chi}\right)\delta\varphi_1'+3\langle W_0(\mathbf{r}_p,\mathbf{r})\cos\vartheta\rangle\delta\varphi_0+3\varphi_0^0\langle\delta W(\mathbf{r}_p,\mathbf{r})\cos\vartheta\rangle+\left[3\langle W_0(\mathbf{r}_p,\mathbf{r})\cos^2\vartheta\rangle+\frac{2}{r^2}\right]$$
$$\times\delta\varphi_1+3\varphi_1^0\langle\delta W(\mathbf{r}_p,\mathbf{r})\cos^2\vartheta\rangle+3\left\langle\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta+W_0(\mathbf{r}_p,\mathbf{r})\right]e^{-\alpha s}\cos\vartheta\right\rangle\delta A$$
$$+3A_0\langle\delta W(\mathbf{r}_p,\mathbf{r})e^{-\alpha s}\cos\vartheta\rangle=-F_1(r), \tag{A4}$$

where $\langle\cdots\rangle$ means averaging over directions of $\mathbf{r}$.

We introduce the notation

$$\tilde{\mathcal{W}}_i=\langle W_0H_i\rangle \tag{A5}$$

and

$$\tilde{\mathcal{S}}_i=\langle\delta WH_i\rangle, \tag{A6}$$

where

$$H_1=1,\ H_2=\cos\vartheta,\ H_3=\cos^2\vartheta,\ H_4=e^{-\alpha s},$$
$$H_5=e^{-\alpha s}\cos\vartheta. \tag{A7}$$

We also define the function $B(\mathbf{r}_p,\mathbf{r})$ as

$$B(\mathbf{r}_p,\mathbf{r})=\left[-\alpha^2+\frac{2\alpha}{s}\left(1+\frac{\chi'}{\chi}r\right)-\frac{2\alpha}{s}\frac{\chi'}{\chi}r_p\cos\vartheta\right]e^{-\alpha s} \tag{A8}$$

and its averages

$$\mathcal{B}_1=\langle B\rangle,\ \ \mathcal{B}_2=\langle B\cos\vartheta\rangle. \tag{A9}$$

The expressions $\mathcal{G}^i$ are defined as

$$\mathcal{G}^0=\varphi_0^0\tilde{\mathcal{S}}_1+\varphi_1^0\tilde{\mathcal{S}}_2+A_0\tilde{\mathcal{S}}_4, \tag{A10}$$

$$\mathcal{G}^1=3(\varphi_0^0\tilde{\mathcal{S}}_2+\varphi_1^0\tilde{\mathcal{S}}_3+A_0\tilde{\mathcal{S}}_5). \tag{A11}$$

The way of computing the functions $\tilde{\mathcal{W}}_i$, $\tilde{\mathcal{S}}_i$, and $\mathcal{B}_i$ is shown in Appendixes B and D. In Appendix E it is shown that the expressions $\mathcal{G}^i$ can be written as

$$\mathcal{G}^i=\zeta_{i0}\delta\varphi_0(r)+\zeta_{i1}\delta\varphi_1(r)+(\zeta_{iA}+\Sigma^i)\delta A$$
$$+8\pi\int_0^\infty r'^2dr'\chi^2(r')[\sigma_0^i\delta\varphi_0(r')+\sigma_1^i\delta\varphi_1(r')]. \tag{A12}$$

The way of computing the quantities ζ_{ij}, Σ^i, and σ_j^i is also shown in Appendix E.

APPENDIX B: NOTATION FOR THE AVERAGES

The quantities $\tilde{\mathcal{W}}_i$ and $\tilde{\mathcal{S}}_i$ of Eqs.(A5) and (A6) are computed from the formulas

$$\tilde{\mathcal{W}}_i=-\mathcal{U}_i+\mathcal{V}_i+\mathcal{W}_i \tag{B1}$$

and

$$\tilde{\mathcal{S}}_i=\mathcal{X}_i+\mathcal{S}_i, \tag{B2}$$

where

$$\mathcal{U}_i=\left\langle\frac{H_i}{s}\right\rangle,\ \ \mathcal{V}_i=\langle W_{xc}^0H_i\rangle,\ \ \mathcal{X}_i=\langle\delta W_{xc}H_i\rangle,$$
$$\mathcal{W}_i=\langle W_p^0H_i\rangle,\ \ \mathcal{S}_i=\langle\delta W_pH_i\rangle. \tag{B3}$$

δW_p is obtained from Eq. (6) and has the form

$$\delta W_p(\mathbf{r}_p,\mathbf{r})=2\int d\mathbf{r}'\frac{w_0(\mathbf{r}_p,\mathbf{r}')\delta w(\mathbf{r}_p,\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\chi^2(r'). \tag{B4}$$

Let us introduce the notation

$$f_1=(\varphi_0^0)^2-1,\ \ f_2=2\varphi_0^0\varphi_1^0,\ \ f_3=(\varphi_1^0)^2,$$
$$f_4=(A_0)^2,\ \ f_5=2A_0\varphi_0^0,\ \ f_6=2A_0\varphi_1^0, \tag{B5}$$

$$g_1=\varphi_0^0\delta\varphi_0,\ \ g_2=\varphi_1^0\delta\varphi_0+\varphi_0^0\delta\varphi_1,\ \ g_3=\varphi_1^0\delta\varphi_1,$$
$$g_4=A_0\delta A,\ \ g_5=A_0\delta\varphi_0+\varphi_0^0\delta A,\ \ g_6=A_0\delta\varphi_1+\varphi_1^0\delta A. \tag{B6}$$

We can write $\mathcal{W}_i$ and $\mathcal{S}_i$ in the form

$$\mathcal{W}_i=\sum_{j=1}^6\mathcal{W}_i^j,\ \ \mathcal{S}_i=\sum_{j=1}^6\mathcal{S}_i^j, \tag{B7}$$

where

$$\mathcal{W}_i^j=4\pi\int_0^\infty r'^2dr'f_j(r_p,r')\chi^2(r')T_i^j(r_p,r,r'), \tag{B8}$$

$$\mathcal{S}_i^j=8\pi\int_0^\infty r'^2dr'g_j(r_p,r')\chi^2(r')T_i^j(r_p,r,r'). \tag{B9}$$

In this way the problem of computing the averages $\mathcal{W}_i$ and $\mathcal{S}_i$ has been reduced to computing the functions T_i^j. Computation of $\mathcal{U}_i$ and $\mathcal{B}_i$ presents no special additional problem. In Appendix D some indications are given about how to express the T_i^j functions through the functions I_n and D_n defined in Appendix C.

APPENDIX C: THE FUNCTIONS I_n AND D_n

The functions $I_n(r,r')$ and $D_n(\alpha,r_p,r)$ are defined as

$$I_n(r_1,r_2)=\frac{1}{2}\int_{-1}^1dt\frac{P_n(t)}{(r_1^2+r_2^2-2r_1r_2t)^{1/2}}, \tag{C1}$$

$$D_n(\alpha,r_p,r)=\frac{1}{2}\int_{-1}^1dte^{-\alpha(r_p^2+r^2-2r_prt)^{1/2}}P_n(t). \tag{C2}$$

The analytical computation of the integral in Eq. (C1) starts with the substitution

$$s=(r_1^2+r_2^2-2r_1r_2t)^{1/2} \tag{C3}$$

leading to

$$dt=-\frac{sds}{r_1r_2},\ \ t=\frac{1}{2r_1r_2}(r_1^2+r_2^2-s^2). \tag{C4}$$

In this way we get

$$I_n(r_1,r_2)=\frac{1}{2r_1r_2}\int_b^ads P_n\left[\frac{1}{2r_1r_2}(r_1^2+r_2^2-s^2)\right], \tag{C5}$$

where

$$a=r_1+r_2,\ \ b=|r_1-r_2|. \tag{C6}$$

Using the notation

$$P_n(x)=\sum_{m=0}^{n} a_{nm}x^m \tag{C7}$$

we obtain $I_n(r_1,r_2)$ in the form of polynomials. The functions $D_n(\alpha,r_p,r)$ are computed by direct numerical integration, though their analytical form is known.

APPENDIX D: THE FUNCTIONS T_i^j

We define the functions $T_i^j(r_p,r,r')$ as

$$T_i^j=\frac{1}{4\pi}\left\langle \int d\Omega' \frac{F_j(r_p,r',\cos\vartheta')}{|\mathbf{r}-\mathbf{r}'|}H_i(r_p,r,\cos\vartheta)\right\rangle, \tag{D1}$$

where $d\Omega'$ means integration over directions of $\mathbf{r}'$. We have

$$F_1=1,\ F_2=\cos\vartheta',\ F_3=\cos^2\vartheta',\ F_4=e^{-2\alpha s'},$$
$$F_5=e^{-\alpha s'},\ F_6=e^{-\alpha s'}\cos\vartheta', \tag{D2}$$

H_i are defined in Eq. (A7). The angles are expressed in the coordinate system connected with $\mathbf{r}'$:

$$\mathbf{r}_p=r_p(\sin\vartheta',0,\cos\vartheta'),$$
$$\mathbf{r}'=r'(0,\ 0,\ 1),$$
$$\mathbf{r}=r(\sin\Theta\cos\Phi,\sin\Theta\sin\Phi,\cos\Theta). \tag{D3}$$

T_i^j can be written in the form

$$T_i^j=\frac{1}{2}\int \sin\vartheta' d\vartheta' F_j(r_p,r',\cos\vartheta')\left\langle \frac{H_i(r_p,r,\cos\vartheta)}{|\mathbf{r}-\mathbf{r}'|}\right\rangle. \tag{D4}$$

Our aim is to express the functions T_i^j according to the general formula

$$T_i^j=\sum_{n=-1}^{\infty} D_n(\alpha,r_p,r)\sum_{n'=0}^{\infty}\sum_{n''=-1}^{\infty} c_{nn'n''}^{ij} I_{n'}(r,r')\times D_{n''}(\alpha_j,r_p,r'), \tag{D5}$$

where D_{-1} is assumed to be equal to unity.

Four formulas are particularly useful while performing the computations. These are[40]

$$\int_0^{2\pi} d\Phi\, P_n(\sin\vartheta\sin\Theta\cos\Phi+\cos\vartheta\cos\Theta) = 2\pi P_n(\cos\vartheta)P_n(\cos\Theta), \tag{D6}$$

the second

$$(2n+1)zP_n(z)=(n+1)P_{n+1}(z)+nP_{n-1}(z), \tag{D7}$$

the third

$$e^{-\alpha(r_1^2+r_2^2-2r_1r_2\cos\vartheta)^{1/2}} = \sum_{n=0}^{\infty}(2n+1)D_n(\alpha,r_1,r_2)P_n(\cos\vartheta). \tag{D8}$$

The fourth formula will be particularly useful when averaging over directions of $\mathbf{r}$ expressions which depend both on the angle ϑ between $\mathbf{r}$ and $\mathbf{r}_p$ and on the angle Θ between $\mathbf{r}$ and $\mathbf{r}'$. The three vectors occurring in this case are expressed by Eq. (D3).

Using the formulas (D6) and (C1) we have

$$\left\langle \frac{P_n(\cos\vartheta)}{(r^2+r'^2-2rr'\cos\Theta)^{1/2}}\right\rangle = I_n(r,r')P_n(\cos\vartheta'). \tag{D9}$$

We adopt the convention that I_n is a function of r and r' and D_n situated after I_n depends on r' while situated before I_n it depends on r. The prime at D_n' indicates that the value α is replaced by 2α [see Eq. (C2)]. We get, e.g.,

$$T_5^6=\sum_{n=0}^{\infty} D_n\left\{\frac{n+1}{2n+3}I_{n+1}[(n+2)D_{n+2}+(n+1)D_n] + \frac{n}{2n-1}I_{n-1}[nD_n+(n-1)D_{n-2}]\right\}. \tag{D10}$$

It follows from numerical calculations that for low values of r_p which are for us of particular interest the magnitude of D_n decreases rapidly with increasing n. So in the following we will put $D_n=0$ for $n\rangle 1$. In this case the functions T_i^j take the following form which is used subsequently in the computations:

$$T_1^1=I_0,\ T_1^2=0,\ T_1^3=\tfrac{1}{3}I_0,\ T_1^4=I_0D_0',\ T_1^5=I_0D_0,$$
$$T_1^6=I_0D_1, \tag{D11}$$

$$T_2^1=0,\ T_2^2=\tfrac{1}{3}I_1,\ T_2^3=0,\ T_2^4=I_1D_1',\ T_2^5=I_1D_1,$$
$$T_2^6=\frac{I_1}{3}D_0, \tag{D12}$$

$$T_3^1=\tfrac{1}{3}I_0,\ T_3^2=0,\ T_3^3=\tfrac{1}{9}I_0+\tfrac{4}{15}I_2,\ T_3^4=\tfrac{1}{3}I_0D_0',$$
$$T_3^5=\tfrac{1}{3}I_0D_0,\ T_3^6=\tfrac{1}{3}I_0D_1+\tfrac{4}{15}I_2D_1, \tag{D13}$$

$$T_4^1=D_0I_0,\ T_4^2=D_1I_1,\ T_4^3=\tfrac{1}{3}D_0I_0,$$
$$T_4^4=D_0I_0D_0'+3D_1I_1D_1',\ T_4^5=D_0I_0D_0+3D_1I_1D_1,$$
$$T_4^6=D_0I_0D_1+D_1I_1D_0, \tag{D14}$$

$$T_5^1=D_1I_0,\ T_5^2=\tfrac{1}{3}D_0I_1,\ T_5^3=\tfrac{1}{3}D_1(I_0+\tfrac{4}{5}I_2),$$
$$T_5^4=D_0I_1D_1'+D_1I_0D_0',\ T_5^5=D_0I_1D_1+D_1I_0D_0,$$
$$T_5^6=\tfrac{1}{3}D_0I_1D_0+D_1I_0D_1+\tfrac{4}{5}D_1I_2D_1. \tag{D15}$$

APPENDIX E: DISENTANGLEMENT OF THE $\mathcal{OG}^i$ FUNCTIONS

In Eqs. (A3) and (A4) the unknown quantities $\delta\varphi_0$, $\delta\varphi_1$ and δA appear either *explicit* or they are entangled in δW. In order to solve these equations, the unknown quantities must appear openly. We will treat now the terms $\mathcal{G}^i$ as defined by Eqs. (A10) and (A11).

From Eq. (5) it follows that

$$\delta W = \delta W_p + \delta W_{\rm xc}. \tag{E1}$$

From Eq. (7) we have

$$\delta W_{\rm xc} = 2w_0\chi^2 V'_{\rm HL}(\delta\varphi_0 + \cos\vartheta\,\delta\varphi_1 + e^{-\alpha s}\delta A). \tag{E2}$$

We will use the notation from Eq. (B3)

$$\mathcal{X}_i = \xi_{i0}\delta\varphi_0 + \xi_{i1}\delta\varphi_1 + \xi_{iA}\delta A \tag{E3}$$

and also [in analogy to Eq. (E1)]

$$\mathcal{G}^i = \mathcal{G}^i_p + \mathcal{G}^i_{\rm xc}. \tag{E4}$$

We have

$$\mathcal{G}^i_{\rm xc} = \zeta_{i0}\delta\varphi_0 + \zeta_{i1}\delta\varphi_1 + \zeta_{iA}\delta A, \tag{E5}$$

where

$$\zeta_{0i} = \varphi^0_0\xi_{1i} + \varphi^0_1\xi_{2i} + A_0\xi_{4i}, \tag{E6}$$

$$\zeta_{1i} = 3(\varphi^0_0\xi_{2i} + \varphi^0_1\xi_{3i} + A_0\xi_{5i}). \tag{E7}$$

We would like to present $\mathcal{G}^i_p$ in the same form.

We remark, however, that $\mathcal{G}^i_{\rm xc}$ has the same form as the remaining terms in Eqs. (A3) and (A4) inasmuch as it does not contain nonlocal contributions. $\mathcal{G}^i_p$ is different. We have [see Eqs. (B7), (B9), (A10), (A11)]

$$\mathcal{G}^0_p = 8\pi\int_0^\infty r'^2 dr'\chi^2(r')\sum_{j=1}^6 g_j(\varphi^0_0 T^j_1 + \varphi^0_1 T^j_2 + A_0 T^j_4), \tag{E8}$$

$$\mathcal{G}^1_p = 24\pi\int_0^\infty r'^2 dr'\chi^2(r')\sum_{j=1}^6 g_j(\varphi^0_0 T^j_2 + \varphi^0_1 T^j_3 + A_0 T^j_5). \tag{E9}$$

Let us call

$$\tau^0_j = \varphi^0_0(r)T^j_1 + \varphi^0_1(r)T^j_2 + A_0 T^j_4,$$
$$\tau^1_j = 3[\varphi^0_0(r)T^j_2 + \varphi^0_1(r)T^j_3 + A_0 T^j_5]. \tag{E10}$$

We have

$$\sum_{j=1}^6 g_j\tau^i_j = \sigma^i_0\delta\varphi_0 + \sigma^i_1\delta\varphi_1 + \sigma^i_A\delta A, \tag{E11}$$

where

$$\sigma^i_0 = \varphi^0_0(r')\tau^i_1 + \varphi^0_1(r')\tau^i_2 + A_0\tau^i_5,$$
$$\sigma^i_1 = \varphi^0_0(r')\tau^i_2 + \varphi^0_1(r')\tau^i_3 + A_0\tau^i_6\ ,$$
$$\sigma^i_A = \varphi^0_0(r')\tau^i_5 + \varphi^0_1(r')\tau^i_6 + A_0\tau^i_4. \tag{E12}$$

So the terms containing δW_p in Eqs. (A3), (A4) can be written in the form

$$\mathcal{G}^i_p = 8\pi\int_0^\infty r'^2 dr'\chi^2(r')[\sigma^i_0\delta\varphi_0(r') + \sigma^i_1\delta\varphi_1(r')] + \Sigma^i\delta A, \tag{E13}$$

where

$$\Sigma^i = 8\pi\int_0^\infty r'^2 dr'\chi^2(r')\sigma^i_A. \tag{E14}$$

Summarizing we have

$$\mathcal{G}^i = \zeta^i_0\delta\varphi_0(r) + \zeta^i_1\delta\varphi_1(r') + (\zeta^i_A + \Sigma^i)\delta A + 8\pi\int_0^\infty r'^2 dr'\chi^2(r')[\sigma^i_0\delta\varphi_0(r') + \sigma^i_1\delta\varphi_1(r')]. \tag{E15}$$

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