Enhancement factors for positron annihilation studies

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Electron and positron densities for a number of positron binding atoms and ions are used to benchmark methods used to compute positron annihilation rates in solids. The electron and positron densities from *ab initio* calculations are multiplied by some commonly used enhancement factors and integrated to give the annihilation rate. These are then compared with the close to exact annihilation rate calculation using the fully correlated positronic atom wave functions. The results reveal deficiencies in the one-component local-density approximation (LDA) and the Boronski-Nieminen two-component LDA. A simple modification of the one-component LDA leads to an enhancement factor that predicts annihilation rates more reliably for some positronic systems with a minimal increase in complexity. An approach based on an existing version of the generalized gradient approximation tends to underestimate the annihilation rate with the valence electrons.

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I. INTRODUCTION

Experimental methods based on positron annihilation spectroscopy give valuable information on the electronic and ionic structures of condensed media, especially defects in solids.[1,2] However, the outcomes of such experiments give indirect information about the structure of the solid, typically the lifetime of the positron or data related to the momentum distribution of the annihilating electron positron pair. The fundamental question in the analysis of the positron annihilation data concerns the extent to which the positron-electron attraction distorts the medium under investigation. The attractive interaction leads to a pile up of electron density at the position of the positron, resulting in an increase in the annihilation rate. There have been many studies of a single positron immersed in a homogeneous electron gas, and for many purposes the annihilation characteristics of this system are reasonably well understood.[3–16] These analyses are used as the basis of the local-density approximation (LDA) that has often been used to compute positron annihilation rates in solids.

More accurate descriptions of positron annihilation require a more sophisticated analysis that goes beyond simple applications of density functional theory (DFT). The DFT reduces the quantum-mechanical many-body problem in a computationally tractable mean field approach.[17] It solves the ground state of a given system so that the particle densities are the basic quantities. For this reason DFT is often used to describe the behavior of electrons and positrons interacting in condensed matter systems.[18–20] In the simplest application of DFT, one solves the Kohn-Sham equations for the electron, uses this solution to construct a mean field for the positron, and then computes the annihilation rate with some enhancement factor. In two-component theories, the electron and positron densities are given by self-consistent solutions of the Kohn-Sham equations. (Two component theories are most important in situations where the positron is localized, e.g., at an open volume defect.) Irrespective of the approach used, the DFT formalism provides explicit density functionals to calculate the annihilation rate of the electron-positron pairs. Recent implementations of the DFT have given good agreement between the theoretical and experimental results for a large number of materials.[21,22] Nevertheless studies of positron trapping at As vacancies in GaAs (Ref. 15,20) indicate that better DFT approximations are needed to correctly predict the positron annihilation characteristics. One problem with the DFT calculations of positron annihilation is that the density functionals are largely derived from electron gas (or electron-positron gas) models and so far it has not been possible to rigorously test the assumptions inherent in these models.

However, it has been shown recently that positrons can form electronically stable bound states with a number of atoms and atomic ions. For example, recent calculations have shown the following systems: e^+Li,[23–26] e^+He($^3S^e$),[27,28] e^+Be,[25,29] e^+Na,[25,26] e^+Mg,[25,29] e^+Ca,[30] e^+Cu,[31,32] e^+Zn,[33] e^+Ag,[34,35] e^+Cd,[36] LiPs,[25,29] NaPs,[25,29] KPs,[37] and CuPs,[36] to be electronically stable. Most of these calculations were performed with the stochastic variational method (SVM).[25,38–41] This is a variational method which uses a trial wave function constructed from a linear combination of explicitly correlated Gaussians. The ability to compute relatively accurate wave functions for a number of small systems provides another line of investigation into the positron-annihilation problem. The calculations on a number of these systems give wave functions and annihilation rates that are sufficiently accurate to benchmark the different procedures that are commonly used to compute annihilation rates in solids. Since the positron is bound to an isolated atom, it might be possible to apply the insights derived from these calculations to an improved understanding of vacancy annihilation.

In this paper, SVM electron and positron densities from selected systems are used to calculate the corresponding annihilation rates within the DFT scheme. These calculated rates are then compared to their SVM values. The present study focuses on approaches within the one- and two-component LDA,[18,19] but the effects of the generalized gradient approximation (GGA) (Refs. 21,22) are discussed as

well. Specifically, the standard LDA annihilation rate formula by Boronski-Nieminen (BN),[19] which is based on the hypernetted chain approximation (HNC),[9,10] is tested against a set of SVM annihilation rates. Finally, qualities and limitations of the existing DFT schemes are exhibited and possible improvements are briefly discussed from an atomic physics perspective.

II. DESCRIPTION OF CALCULATIONS

A. Atomic states with a bound positron

It is the aim of this article to use existing bound-state wave functions to validate enhancement factors commonly used in condensed matter studies. Therefore it is important that the wave functions and derived annihilation rates for the atomic type systems be reasonably accurate. All the atomic wave functions used for benchmarking were computed with the SVM or the fixed core SVM (FCSVM).[25,42]

The SVM diagonalizes the positron-atom Hamiltonian in a basis set

$$\Psi=\sum_i^K C_i\psi_{SM_S}(\mathbf{x},A^i)=\sum_i^K C_i G(\mathbf{x},A^i)\chi_{SM_S}, \qquad (1)$$

where $\mathbf{x}$ is the matrix of Jacobi coordinates for the system and χ_{SM_S} contains the spin dependence. The spatial part of basis functions were written as explicitly correlated Gaussians (ECG's), i.e.,

$$G(\mathbf{x},A^i)=\exp\left(-\frac{1}{2}\sum_{\mu,\nu=1}^{N-1}A^i_{\mu\nu}\mathbf{x}_\mu\mathbf{x}_\nu\right)=\exp\left(-\frac{1}{2}\mathbf{x}^\dagger A^i\mathbf{x}\right). \qquad (2)$$

These basis functions include the interparticle coordinate between every pair of particles as a quadratic term. Since the ECG basis functions do not have the correct form to represent the Kato cusp condition exactly, they were long regarded as inferior to a basis with $\exp(-\alpha r_{ij})$ correlation factors. However, a major advantage of an ECG basis is that the Hamiltonian matrix elements are very simple and can be computed very quickly. This can compensate for the fact that generally more terms are required in an ECG basis set than for a Hylleraas type basis.

The ability of variational methods using ECG's to obtain accurate wave functions and precise energies depends crucially on the proper optimization of the nonlinear parameters, i.e., the exponents of the ECG's. Classical optimization techniques are not effective for an energy functional than can have between 100 and 10 000 free parameters. In the SVM,[25,38–41] the search for the optimal set of exponents is performed stochastically, i.e., via a trial and error procedure.

The ECG basis is very effective for positron binding complexes since the interactions between every pair of particles are given equal prominence in the variational expansion. The electron-positron correlations are really no more harder to incorporate than the electron-nucleus correlations. Therefore reasonably accurate estimates of the annihilation rate can be obtained without too much difficulty.

The fixed core stochastic variational method (FCSVM) was developed in order to investigate positron binding to larger atoms. The electrons are partitioned into two groups, the core electrons and the valence electrons. The core electrons are described by a Hartree-Fock calculation and are spectators apart from the influence they have on the active particles. The FCSVM core potential treats direct and exchange interactions with the core exactly, correctly incorporates the Pauli principle into the calculation and includes one and two-body polarization interactions with the core. The FCSVM allows for correlations between the positron and the valence electrons and therefore the annihilation rate with the valence electrons can be expected to be reliable. The annihilation rate with the core electrons is likely to be an underestimate since the FCSVM wave function makes no allowance for correlations between positron and the core electrons.

A number of systems have been used for benchmarking purposes. They are e^+Li,[26] e^+He($^3S^e$),[28], e^+Be,[29] e^+Na,[26] e^+Mg,[29] PsH,[28] LiPs,[29] and NaPs.[29] The present investigations are based on the existing basis sets for these systems and so there is no point in describing the calculations details for any of these systems. However, a brief description of the structure of these systems and an assessment of the accuracy of the calculated wave functions is useful in the context of the present work.

The PsH, LiPs, and NaPs systems consist of a positronium atom bound to the parent H, Li, or Na atom by exchange and van der Waals forces.[37] All three systems have annihilation rates slightly larger than that of the Ps ground state. The Ps cluster (a Ps cluster is something approximating the ground state of Ps that is bound to the rest of the system) tends to be located in the outer valence region for each system and therefore is largely shielded from the strong nuclear interaction which would otherwise tend to break up the cluster.

The structure of the e^+A systems can be understood in terms of a Heuristic model.[34,42] The wave function is written as

$$\Psi=\alpha\Phi(\text{atom}^*)\phi(e^+)+\beta\Omega(\text{atom}^+)\omega(\text{Ps}), \qquad (3)$$

with the relative size of α and β largely determined by the ionization potential of the parent atom. The first of these terms represents a positron moving in the field of a polarized atom while the second term represents a Ps cluster attached to the residual ion. The relative strength of these two configurations is determined by the ionization potential of the atomic parent. When the ionization potential is less than 0.250 Hartree (the Ps binding energy) the most loosely bound electron is attached to the positron forming a Ps cluster. The e^+Li, e^+Na, and e^+He(e^+S^e) systems are good examples of such systems. However, when the ionization potential is greater than 0.250 Hartree, the tendency to form a Ps cluster is disrupted by the stronger attraction of the electrons to the parent atom. The electron is more strongly attracted to the nucleus and the repulsive positron-nucleus interaction tends to break up the cluster. Positronic beryl

TABLE I. Estimates errors in the electron and positron densities of the SVM and FCSVM wave functions. Estimated uncertainties in the annihilation rates are also given.

System	Error in n	Error in Γ	Structure type
e^+He($^3S^e$) (SVM)	<1%	<1%	Ps+He$^+$
e^+He($^3S^e$) (FCSVM)	<1%	<1%	Ps+He$^+$
e^+Li (SVM)	<1%	<1%	Ps+Li$^+$
e^+Li (FCSVM)	<1%	<1%	Ps+Li$^+$
e^+Be	<1%	<1%	e^++Be*
e^+Na	<1%	<1%	Ps+Na$^+$
e^+Mg	<2%	<5%	50%(e^++Mg*), 50%(Ps+Mg$^+$)
PsH	<1%	<1%	Ps+H
LiPs	<1%	<1%	Ps+Li
NaPs	<2%	<2%	Ps+Na

lium, e^+Be is a good example of such a system (the ionization potential for neutral beryllium is about 0.34 Hartree). Positronic magnesium, i.e., e^+Mg provides an example of a system in which neither of the configurations tends to dominate.

The estimated error in the derived electron densities, and annihilation rates for all systems are listed in Table I. These estimates are based upon visual examination of the convergence patterns of the energy, annihilation rates, and other expectation values as the wave functions for these systems have been optimized. To a certain extent they obviously represent subjective judgements, but some estimate of the uncertainty is better than none. For a long time ECG basis sets were regarded as inferior to exponential Hylleraas type basis sets when it came to representing short-range correlations. However, recent investigations have shown that an ECG basis set can reliably estimate expectation values for operators such as the electron-positron δ function.[25,38,43,44] In the course of many SVM calculations it has been noted that the annihilation rate usually converges quickly to a value about 5% smaller than the correct value. Then the annihilation rate steadily increases during the final stage of the wave function optimization. For example, the expectation value of $\delta(\mathbf{r}_e-\mathbf{r}_p)$ for Ps^- as calculated in the correlation-function hyperspherical-harmonic method was 0.02073320.[43] An SVM wave functions with 800 ECG's gives 0.02073105 (Ref. 43) while another SVM wave function with only 150 ECG's gave 0.02068323.[44] The estimates of the annihilation rates in Table I are quite conservative considering the accuracy achievable for Ps^-. There is no experimental information on the annihilation rates for these systems since apart from PsH,[45] none of the systems has been isolated in the laboratory.

B. Positron annihilation

The total rate (with implicit spin averaging) for positron annihilation is

$$\Gamma=\pi r_e^2 c\int d^3\tau|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{r}_N)|^2, \tag{4}$$

where $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{r}_N)$ is the total wave function for the system with the positron co-ordinate set to $\mathbf{r}_N$. For purposes of comparison the spin-averaged annihilation rate for the Ps ground state is 2.008 ns^{-1}.

The expression for Γ is the expression that is commonly called the 2γ annihilation rate in the literature. Equation (4) does not give the transition rate between a well defined initial and final state. This equation is a sum rule which adds up the individual transition rates over all possible final states.

In a two-component DFT the annihilation rate is often written as a matrix element involving the electron density, the positron density and an enhancement factor that is a function of the electron and positron densities, viz.

$$\Gamma=\pi r_e^2 c\int d^3r n_-(\mathbf{r})n_+(\mathbf{r})\gamma(n_-,n_+), \tag{5}$$

where $n_-(\mathbf{r})$ is the total electron density, $n_+(\mathbf{r})$ is the positron density, and $\gamma(n_+,n_-)$ is the enhancement factor, respectively. The partial annihilation rate for annihilation with a particular electron shell (e.g., the core electrons), is given by

$$\Gamma_i=\pi r_e^2 c\int d^3r n_-^i(\mathbf{r})n_+(\mathbf{r})\gamma(n_-,n_+), \tag{6}$$

where $n_-^i(\mathbf{r})$ is the electron density for that shell.

The independent particle model (IPM) assumes that electron-positron correlations have no impact upon the annihilation rate, therefore

$$\gamma_{\mathrm{IPM}}=1. \tag{7}$$

In the LDA, the enhancement factor is just a function of the electron density. It is derived from calculations of the electron-positron contact factor for a single positron immersed in an electron gas. A number of different parameterizations of the enhancement factor exist.[18,19,46–48] We use a parametrization derived from the algebraic bosonization calculations of Arponen and Pajanne (AP).[12,21]

$$\gamma_{\mathrm{LDA}}=1+1.23r_s-0.0742r_s^2+\frac{1}{6}\,r_s^3, \tag{8}$$

where r_s is the electron gas parameter given by

$$r_s=\left(\frac{3}{4\pi n_-}\right)^{1/3}. \tag{9}$$

The only fitting parameter in this equation is the factor in the front of the quadratic term. The first two terms are fixed to reproduce the high-density RPA limit[11] and the last term the low-density positronium (Ps) atom limit. This expression implicitly assumes that the electron density is always larger than the positron density. While this is likely to be true in the condensed matter environment, it is not always true in an atomic environment. Therefore, a symmetrized LDA may be advanced as

$$\gamma_{\mathrm{SLDA}}=\gamma_{\mathrm{LDA}}(n_>), \tag{10}$$

where $n_>=\max(n_+,n_-)$.

More sophisticated treatments use an enhancement factor that depends on both the electron and positron densities. Boronski and Nieminen[19] devised an enhancement factor based upon the electron-positron gas HNC calculations of Lantto.[9] The BN enhancement factor consists of two parts. The first part consists of a functional form for the electron-positron contact factors at density ratios $x=n_+/n_-$ of 0, 0.5, and 1. The rest of the $\gamma_{\rm BN}$ enhancement factor consists of a two-dimensional interpolating formula to compute $\gamma_{\rm BN}$ for arbitrary densities. Their procedure for computing the enhancement factor can be summarized as follows:

$$\gamma_{\rm BN}=a(n_>)n_<^3+b(n_>)n_<^2+c(n_>)n_<+\gamma_0(n_>), \quad (11)$$

where

$$a(n)=\frac{1}{n^3}[2k(n)-6\gamma_1(n)+8\gamma_2(n)-2\gamma_0(n)],$$

$$b(n)=\frac{1}{n^2}[-3k(n)+11\gamma_1(n)-16\gamma_2(n)+5\gamma_0(n)],$$

$$c(n)=\frac{1}{n}[k(n)-4\gamma_1(n)+8\gamma_2(n)-4\gamma_0(n)], \quad (12)$$

and $\gamma_0(n)$, $\gamma_1(n)$, and $\gamma_2(n)$ are parametrizations of the enhancement factor for $x=n_+/n_-=0$, 1, and 1/2, respectively. These functions were defined as

$$\gamma_0^{\rm BN}=1+1.23r_s+0.8295r_s^{3/2}-1.26r_s^2+0.3286r_s^{5/2}+\frac{1}{6}r_s^3, \quad x=0,$$

$$\gamma_1^{\rm BN}=1+0.51r_s+0.65r_s^2-0.51r_s^{5/2}+\frac{1}{6}r_s^3, \quad x=1,$$

$$\gamma_2^{\rm BN}=1+0.60r_s+0.63r_s^2-0.48r_s^{5/2}+\frac{1}{6}r_s^3, \quad x=1/2. \quad (13)$$

The formulas are interpolation of Lantto results preserving the proper behavior for the $r_s\to\infty$ (Ps limit). The function $k(n)$ is defined as

$$k(n)=\frac{1}{2}n\frac{d\gamma_1}{dn}=-\frac{r_s}{6}\frac{d\gamma_1}{dr_s}. \quad (14)$$

At a given value of r_s, the enhancement factors γ_1 and γ_2 are smaller than γ_0. It will be seen later that there are problems with the values of $\gamma_2^{\rm BN}$ and $\gamma_1^{\rm BN}$ (they are too small for large $r_s>10$). A tabulation of $\gamma_i^{\rm BN}$ and $\gamma^{\rm LDA}$ at selected values of r_s is given in Table II.

In the generalized gradient approximation (GGA) (Ref. 21,22) 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 $1/q_{TF}$ where $q_{TF}=\sqrt{4k_F/\pi}$ and $k_F=(3\pi^2 n_-)^{1/3}$ is the local Fermi momentum. The lowest order gradient correction to the LDA correlation hole density is proportional to the parameter

$$\epsilon=|\nabla n|^2/(nq_{\rm TF})^2=|\nabla \ln n|^2/q_{\rm TF}^2=\left|\frac{dn}{dr}\right|^2/(nq_{\rm TF})^2. \quad (15)$$

This parameter also describes the reduction of the screening cloud close to the positron. For the HEG $\epsilon=0$, whereas in the case of rapid density variations ϵ approaches infinity. At the former limit the LDA result for the induced screening charge is valid and the latter limit should lead to the IPM result with vanishing enhancement. An enhancement factor of the form

$$\gamma_{\rm GGA}=1+(\gamma_{\rm SLDA}-1)\exp(-\alpha\epsilon) \quad (16)$$

is used to interpolate between these limits. The parameter α was set to 0.22. This value had been chosen previously in order to ensure that the calculated and experimental lifetimes agree for a large number of different types of solids.[21,22]

With one exception (PsH), all the calculations using Eqs. (5) and (6) were done with FCSVM electron and positron densities since this permitted the separation of the valence and core annihilation rates. For some systems, e^+Li, e^+He($^3S^e$) and LiPs, electron and positron densities are also available from *ab initio* SVM calculations. The electron/positron densities for the SVM and FCSVM wave functions are very similar and give annihilation rates that are for all practical purposes identical.

TABLE II. The electron-positron contact factors for the Boronski-Nieminen (BN) and Arponen-Pajanne (AP) parametrizations of the homogeneous electron-positron electron gas.

$r_s(a_0)$	LDA	BN		
		$\gamma_0: x=0$	$\gamma_2: x=0.5$	$\gamma_1: x=1$
1	2.32	2.29	1.92	1.82
2	4.50	3.96	3.34	3.07
3	8.52	7.28	5.49	4.93
4	15.4	13.6	8.79	7.79
5	26.1	24.1	13.8	12.1
6	41.7	40.2	21.0	18.5
10	173	184	84.9	76.5
15	565	633	296	273
20	1329	1517	739	692
40	10 598	12 235	6842	6567

III. COMPARISONS WITH POSITRONIC ATOM DATA

A. Valence electron annihilation

The importance of incorporating an enhancement factor into the calculations of the annihilation rate is very noticeable from Table III. The total IPM annihilation rate is more than an order of magnitude smaller than the actual annihilation rate for every system in Table III.

TABLE III. Annihilation rates for a number of positronic atoms and ions. The SVM and FCSVM annihilation rates are computed from the correlated wave functions describing these systems without making any approximations. All the other annihilation rates where computed from Eq. (6) with the designated enhancement factor. All annihilation rates are given in units of 10^9 s^{-1}.

System	SVM	FCSVM	IPM	LDA	SLDA	DFT-BN	GGA
				Valence			
e^+He($^3S^e$)	1.900	1.899	0.002 07	2.00	1.89	1.08	1.68
e^+Li [a]	1.748	1.743	0.006 39	2.03	1.77	0.924	1.46
e^+Be		0.418	0.0316	2.14	0.720	0.455	0.264
e^+Na		1.896	0.001 72	1.98	1.88	1.09	1.68
e^+Mg		0.955	0.0437	2.21	1.32	0.765	0.657
PsH	2.472		0.324	3.15	2.95	1.83	1.69
LiPs [a]	2.151	2.156	0.0466	2.24	2.24	1.18	1.63
NaPs		2.083	0.0330	2.16	2.16	1.14	1.58
				Core			
e^+He($^3S^e$)	8.3^{-4}	3.5^{-4}	3.5^{-4}	5.39^{-3}	5.39^{-3}	4.41^{-3}	1.34^{-3}
e^+Li		0.001 58	0.001 58	0.009 02	0.009 02	0.007 80	0.002 79
e^+Be		0.002 22	0.002 22	0.005 56	0.005 56	0.005 31	0.003 19
e^+Na		0.001 69	0.001 69	0.0131	0.0131	0.0109	0.003 46
e^+Mg		0.0121	0.0121	0.0349	0.0349	0.0325	0.0198
LiPs		0.007 32	0.007 32	0.0278	0.0278	0.0249	0.0128
NaPs		0.0157	0.0157	0.0608	0.0608	0.0541	0.0291

[a]The rate for the SVM wave function is the total annihilation rate and contains a contribution from the core.

When the initial calculations were done one of the most striking features of Table III was the value of $\Gamma_{\mathrm{LDA}} = 2.03$ ns^{-1} for e^+Li. It did not seem credible that the annihilation rate could exceed that of the Ps ground state. A detailed scrutiny of the integrand of Eq. (6) revealed that the local annihilation rate per unit electron density was greater than that of Ps when the electron density was less than the positron density. Such a result is not physical at large r_s and provided the primary motivation for introducing a symmetrized version of the LDA. The symmetrized version of the LDA gives accurate annihilation rates for the e^+Li, e^+Na, and e^+He($^3S^e$) systems.

Another noticeable feature of Table III was the tendency for the BN-DFT to underestimate the annihilation rate for systems such as e^+Li and e^+Na. A casual examination of the γ_1^{BN} and γ_2^{BN} showed that these enhancement factors were about 50% smaller than γ_0^{BN} at $r_s=20$. At these large electron-electron separations there is effectively no impediment to Ps formation and therefore the respective contact factor should be about the same size as γ_0^{BN}.

The next class of system evaluated were the APs systems. Here the LDA and SLDA enhancement factors tend to produce annihilation rates that are too large with the effect being most noticeable for PsH. The PsH system is actually the most compact of these systems. With respect to the two-component theory, the BN factor underestimates annihilation rate by a substantial amount.

The GGA enhancement factor tends to underestimate the annihilation rate by about 16% for the e^+Li and e^+Na systems. For the APs systems the underestimate is more severe, ranging from 25% for LiPs to 35% for PsH. It even underestimates the annihilation rates for e^+Be and e^+Mg which are generally overestimated in all the other approximations. One should keep in mind that the GGA was initially introduced to cure the exaggerated annihilation with core and semicore electrons in solids,[21,22] and the primary parameter α was fixed empirically. For the valence electrons in solids the density gradient is rather flat in the interstitial region between the ions and therefore one recovers automatically the LDA limit for valence electrons away from the ions. However, in atomic systems the electron density is an exponential function of the distance, and at large distances the logarithmic derivative is constant. Therefore the density gradient can have an impact even in the outer valence region of the atom. The γ_{GGA} factor was about 15–20% smaller than γ_{SLDA} at very large distances from the nucleus. In order to apply GGA type corrections to atoms reliably it will probably be necessary to reevaluate the foundations of the GGA from first principles.

The e^+Be and e^+Mg systems were able to expose the limitations of most of the LDA type approximations. The simple LDA formula grossly overestimates the annihilation rate by a factor of 5 for e^+Be and a factor of 2 for e^+Mg. Using the symmetric form γ_{SLDA} leads to much improved estimates although they are still too large. Not too much credence should be placed in the apparently good agreement of the BN-LDA and FCSVM annihilation rates for e^+Be. The general tendency for LDA type enhancement factors to overestimate the annihilation rate with tightly bound electrons is compensated by the fact that the BN contact factors for $x>0$ are much too small for $r_s>5$.

B. Annihilation with core electrons

The only system for which a separate core annihilation rate has been calculated with full consideration of electron-

positron correlations was the e^+He($^3S^e$) systems. (The SVM calculations of e^+Li and LiPs do incorporate fully correlated calculations of the positron annihilation with the core electrons but the core annihilation rate itself has not been calculated as a separate quantity.) However, the e^+He($^3S^e$) system consists of a Ps atom orbiting the He^+ core at a rather large distance (the mean positron-nucleus distance was about $17a_0$). This type of configuration is not likely to be a common one in condensed matter systems and these results are most likely to be of interest in describing pick-off annihilation in Ps-atom scattering.[49]

The FCSVM core annihilation rates for all the other systems are equivalent to the IPM which assume an enhancement factor of unity and so cannot give much insight into the influence of electron-positron correlations upon the annihilation rate. The valence annihilation rates for the e^+Be system and to a lesser extent the e^+Mg system can be regarded as the systems giving the most insight into the core annihilation problem. Both systems have a closed ns^2 subshell, and the electron distribution in e^+Be is very similar to that of neutral Be, i.e., it can be regarded as an analog of a core state, albeit rather weakly bound. As mentioned earlier, the LDA type approximations overestimate the annihilation rate for e^+Be while the GGA with $\alpha=0.22$ underestimates the annihilation rate. The tendency for the nuclear interaction to disrupt the electron screening by an amount that is difficult to estimate makes the core annihilation rate hard to reliably calculate.

The results in the second part of Table III are mainly of interest for atomic physics purposes. They give some indication of the extent with which the existing FCSVM calculations are likely to underestimate the core annihilation rate. The LDA and SLDA factors can be expected to give overestimates of the annihilation rate while comparisons with the valence rates for e^+Be and e^+Mg suggest that the GGA with an interpolating factor of $\alpha=0.22$ will tend to underestimate the core annihilation rate. Taken together, the two sets of rates give some indicative bound of the expected annihilation rate enhancement for the core electrons of positronic atoms.

IV. CONCLUSION

We have examined the accuracy of some enhancement factors commonly used for the calculation of positron annihilation in solids. The simple one-component LDA is not accurate when the positron density exceeds the electron density, a circumstance that does not occur often in solids, but which can be expected to occur in atomic-type systems. A simple correction gives a enhancement factor which is much more reliable. The two-component DFT parametrization of Boronski-Nieminen is seen to systematically underestimate the enhancement factor at large interparticle separations. It is desirable the Boronski-Nieminen contact factors be replaced by a new parametrization that is more reliable for low electron (positron) densities. One important qualification about the use of the two-component BN parametrization must be be made. This parametrization was derived from calculations of an electron-positron fluid with multiple electrons and positrons and it should be used with caution for systems with just one positron. However, the problems associated with this point are probably of minor significance when compared to the existing problems with the BN parametrization at large r_s.

It is probably not a coincidence that LDA type approximations give an overestimate for the two systems with the most tightly bound valence electrons. The LDA does not take into consideration the influence that the nuclear interaction will have in disrupting the pile-up of electronic charge around the position of the positron. The LDA can be expected to overestimate the annihilation rate when the positron is detached from its screening cloud. More general approaches, such as the generalized gradient approximation are needed in such circumstances. However, the application of a particular form of the GGA that was developed to compute positron annihilation rates in solids[21,22] resulted in annihilation rates that were too small.

The present investigation is only addressed to one half of the positron-annihilation problem. It is of course necessary to compute the overlap of the electron and positron densities accurately and this requires solutions of the Kohn-Sham equations that reproduce the actual electron and positron densities. The present success of the SLDA enhancement factors in describing the annihilation rates for a number of systems suggests that it might be worthwhile attempting to compute the structure of systems such as e^+Li and e^+Na from first principles using DFT. Some earlier attempts to calculate the structures of positron binding atoms using DFT have given very inaccurate results.[50,51] However, these earlier calculations were hampered by the absence of any reliable information about the structure of the positronic atoms and ions. A renewed attempt to use DFT to describe positronic atoms is probably justified since the detailed information now available about the interactions of positrons with a number of atomic systems increases the chance for success.

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[1] P.J. Schultz and K.G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).

[2] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors*, Springer Series in Solid-State Sciences, No. 127 (Springer Verlag, Berlin 1999).

[3] R.A. Ferrell, Rev. Mod. Phys. **28**, 308 (1956).

[4] S. Kahana, Phys. Rev. **129**, 1622 (1963).

[5] J.P. Carbotte, Phys. Rev. **144**, 309 (1966).

[6] P.F. Maldague, Phys. Rev. B **20**, 21 (1979).

[7] T. Jarlborg and A.K. Singh, Phys. Rev. B **36**, 4660 (1987).
[8] H. Stachowiak, Phys. Rev. B **41**, 12 522 (1990).
[9] A. Kallio, P. Pietiläinen, and L.J. Lantto, Phys. Scr. **25**, 943 (1982).
[10] L. Lantto, Phys. Rev. B **36**, 5160 (1987).
[11] J. Arponen, J. Phys. C **11**, L739 (1978).
[12] J. Arponen and E. Pajanne, Ann. Phys. (N.Y.) **121**, 343 (1979).
[13] A. Harju, B. Barbiellini, S. Siljamäki, R.M. Nieminen, and G. Ortiz, Phys. Rev. Lett. **79**, 1173 (1997).
[14] X. Zhu, M.S. Hybertsen, and P.B. Littlewood, Phys. Rev. B **54**, 13 575 (1996).
[15] L. Gilgien, R. Car, and D.M. Ceperley, Mater. Sci. Forum **255-257**, 52 (1997); L. Gilgien, Ph. D. thesis, Ecole Polytechnique Fédérale de Lausanne, 1997.
[16] B. Barbiellini, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic Publishers, The Netherlands, 2001)
[17] R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
[18] M.J. Puska and R.M. Nieminen, Rev. Mod. Phys. **66**, 841 (1994).
[19] E. Boronski and R.M. Nieminen, Phys. Rev. B **34**, 3820 (1986).
[20] M.J. Puska, A.P. Seitsonen, and R.M. Nieminen, Phys. Rev. B **52**, 10 947 (1995).
[21] B. Barbiellini, M.J. Puska, T. Torsti, and R.M. Nieminen, Phys. Rev. B **51**, 7341 (1995).
[22] B. Barbiellini, M.J. Puska, T. Korhonen, A. Harju, T. Torsti, and R.M. Nieminen, Phys. Rev. B **53**, 16 201 (1996).
[23] G.G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. **79**, 4124 (1998).
[24] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).
[25] G.G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, 3965 (1998).
[26] J. Mitroy and G.G. Ryzhikh, J. Phys. B **32**, L621 (1999).
[27] G.G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, 3465 (1998).
[28] G.G. Ryzhikh and J. Mitroy, J. Phys. B **32**, 4051 (1999).
[29] J. Mitroy and G.G. Ryzhikh, J. Phys. B **34**, 2001 (2001).
[30] M.W.J. Bromley and J. Mitroy, J. Phys. B **33**, L325 (2000).
[31] G.G. Ryzhikh and J. Mitroy, J. Phys. B **31**, 4459 (1998).
[32] V.A. Dzuba, V.V. Flambaum, G.F. Gribakin and C. Harabati, Phys. Rev. A **60**, 3641 (1999).
[33] G.G. Ryzhikh and J. Mitroy, J. Phys. B **32**, 1375 (1999).
[34] G.G. Ryzhikh and J. Mitroy, J. Phys. B **31**, 5013 (1998).
[35] V.A. Dzuba, V.V. Flambaum, and C. Harabati, Phys. Rev. A **62**, 042504 (2000).
[36] M.W.J. Bromley, J. Mitroy, and G.G. Ryzhikh, Nucl. Instrum. Methods Phys. Res. B **171**, 47 (2000).
[37] J. Mitroy and G.G. Ryzhikh, J. Phys. B **32**, 3839 (1999).
[38] Y. Suzuki and K. Varga, *Stochastic Variational Approach to Quantum-Mechanical Few-Body Problems*. (Springer, New York 1998).
[39] V.I. Kukulin and V.M. Krasnopolsky, J. Phys. G **3**, 795 (1977).
[40] K. Varga and Y. Suzuki, Phys. Rev. C **52**, 2885 (1995).
[41] K. Varga and Y. Suzuki, Comput. Phys. Commun. **106**, 157 (1997).
[42] J. Mitroy, M.W.J. Bromley, and G.G. Ryzhikh, in *New Directions in Antimatter Chemistry and Physics*, edited by C.M. Surko and F.A. Gianturco (Kluwer Academic Publishers, The Netherlands, 2001)
[43] R. Krivec, V.B. Mandelzweig, and K. Varga, Phys. Rev. A **61**, 062503 (2000).
[44] J. Mitroy, J. Phys. B **33**, 5307 (2000).
[45] D.M. Schrader, F.M. Jacobsen, N-P. Frandsen, and U. Mikkelsen, Phys. Rev. Lett. **69**, 57 (1992).
[46] W. Brandt and J. Reinheimer, Phys. Lett. **35A**, 109 (1971).
[47] P.A. Sterne and J.H. Kaiser, Phys. Rev. B **43**, 13 892 (1991).
[48] H. Stachowiak and J. Lach, Phys. Rev. B **48**, 9828 (1993).
[49] J. Mitroy and I. A. Ivanov, Phys. Rev. A **65**, 034709 (2002).
[50] J.G. Harrison, J. Chem. Phys. **84**, 1659 (1986).
[51] K. Kim, Helv. Phys. Acta **69**, 81 (1996).