PHYSICAL REVIEW B **96**, 085135 (2017)

Application of the weighted-density approximation to the accurate description of electron-positron correlation effects in materials

Vincent Callewaert,[1,*] Rolando Saniz,[1] Bernardo Barbiellini,[2] Arun Bansil,[2] and Bart Partoens[1]
[1]*Department of Physics, Universiteit Antwerpen, Antwerpen 2020, Belgium*
[2]*Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA*

(Received 16 May 2017; revised manuscript received 28 July 2017; published 24 August 2017)

We discuss positron-annihilation lifetimes for a set of illustrative bulk materials within the framework of the weighted-density approximation (WDA). The WDA can correctly describe electron-positron correlations in strongly inhomogeneous systems, such as surfaces, where the applicability of (semi-)local approximations is limited. We analyze the WDA in detail and show that the electrons which cannot screen external charges efficiently, such as the core electrons, cannot be treated accurately via the pair correlation of the homogeneous electron gas. We discuss how this problem can be addressed by reducing the screening in the homogeneous electron gas by adding terms depending on the gradient of the electron density. Further improvements are obtained when core electrons are treated within the LDA and the valence electron using the WDA. Finally, we discuss a semiempirical WDA-based approach in which a sum rule is imposed to reproduce the experimental lifetimes.

DOI: 10.1103/PhysRevB.96.085135

I. INTRODUCTION

Positron-annihilation spectroscopy (PAS) is widely accepted as a sensitive method to characterize vacancy type defects in bulk solids [1]. The sensitivity of the method arises from the strong repulsion of the positron by the positive ions in the material. Hence, open volumes, such as vacancies and voids, act as efficient positron traps. If a positron gets trapped prior to annihilation, the radiation carries information on the electronic properties of the overlapping electronic states and thus gives PAS the atomic resolution required to identify the chemical environment of the defect. In this way, one can also understand how positrons can be used to probe surface properties. In fact, most materials have a positive positron work function and hence when a positron diffuses to the surface, it can either get expelled into the vacuum, or get trapped in its image potential well [2–4]. This trapping mechanism of positrons is exploited in positron-annihilation-induced Auger electron spectroscopy (PAES), where the surface bound positron annihilates with a core electron at the surface to trigger an Auger process [5]. The surface sensitivity of positrons has been demonstrated via, e.g., monitoring submonolayer coverages with adatoms on various surfaces [6,7].

There is a renewed interest in exploiting positrons in surface studies. Recent examples include: Observation of surface segregation of Cu in Pd through time-resolved PAES [8], annihilation-induced O^+ desorption from $TiO_2(110)$ surfaces [9], and angle-resolved spectroscopy of positronium (Ps) emission from Cu(110) [10]. Moreover, advances in slow positron techniques now allow direct deposition of very low-energy positrons (<5 eV) in a bound surface state through a process called Auger mediated positron sticking [11]. These advances have been used to demonstrate multielectron emission in Auger processes [12] to determine the binding energy of positrons to the surface of Bi_2Te_2Se [13], and directly measure Auger emission from holes created in the valence band of graphene [14]. Finally, positrons have been shown to act as self-seeking probes for the surface of colloidal quantum dots [15] to enable a detailed characterization of their surface properties [16,17].

First-principles modeling is widely recognized as a valuable tool for understanding and interpreting PAS results [1]. Such computations are normally carried out within the framework of the two-component density function theory (2CDFT) [18,19]. For bulk PAS properties, the local density approximation (LDA) and generalized gradient approximations (GGA) have proven to yield reliable results. In the case of surfaces, however, these (semi-)local approximations fail to correctly describe the correct behavior of the correlation potential in the vacuum far away from the surface. At very low densities, the LDA predicts Ps^- formation. This strongly negative correlation potential ($V_c = -7.13$ eV with respect to the vacuum level) prohibits the formation of a surface bound state. A positive charge far away from a surface, however, experiences an image potential $V_c \sim -1/(z - z_0)$, where z denotes the distance to the surface and z_0 is the so-called image potential reference plane [20]. The failure of the LDA/GGA to reproduce this long-range correlation is an inherent limitation of (semi-)local approximations.

An accurate description of positron states and their annihilation properties near surfaces has, for this reason, been a theoretical challenge for which a satisfactory solution remains elusive. The most widely applied model is the corrugated mirror model, originally proposed by Nieminen and Puska [21], in which the bulk LDA or GGA correlation potential is matched to the $\sim 1/[z - z_0(\mathbf{r})]$ potential outside the surface, where the image potential reference plane is position dependent. The latter is determined in such a way that the isocontours of the density and the image potential still coincide (at different values in general), as is the case for the LDA potential. Stated differently, the image potential $\sim 1/(z - z_0)$ is parametrized as a function of the density along a reference line perpendicular to the surface. In the linear response theory, the image potential reference plane z_0 is determined by the charge induced due to the presence of an external point charge [20]. This quantity can then be calculated by directly solving the electronic problem in the presence of an electrical field perpendicular to the surface.

---

[*] vincent.callewaert@uantwerpen.be

The corrugated mirror model suffers from a number of flaws even though its results agree reasonably with experiments [13,22–25]. In particular, while it is straightforward to construct the corrugated image potential for perfect surfaces, this quickly becomes unfeasible for more complex surfaces. For example, imagine a molecule adsorbed on a surface, a problem relevant to the study of positron states in colloidal quantum dots [17]. In this case, one can expect that, depending on the position of the positron, the induced image charge will be distributed over the molecule and/or the surface. Several issues now arise. First, the idea of an image potential assumes that the induced charge is spread out over a perfect, infinite surface. With the molecule in place, this is no longer the case and, in general, the simple $\sim 1/(z - z_0)$ form would no longer apply. Second, z_0 is in principle defined by the center of the induced charge density. Since the screening properties of the surface and the molecule will differ, a single value will likely not be sufficient for an accurate description of the whole system. Another limitation of the corrugated mirror model is that the LDA/GGA potential, which is reasonably accurate in the bulk, is matched continuously to the image potential, which is the correct limiting behavior only far away from the surface. In general this matching happens in the vacuum region close to the surface where neither the LDA/GGA nor the image potential are expected to give accurate results. Also, even though the potential is continuous, its derivative is not and in some systems this leads to unrealistically narrow or wide wells at the surface. The matching procedure can thus have a large influence on the predicted binding energy of the positron surface state and, in the end, become critical for determining whether or not a given surface can support the formation of a bound state.

A full first-principles alternative is provided by the weighted-density approximation (WDA) [26–30]. In this approach, which is inherently nonlocal as opposed to the LDA/GGA, the screening cloud is modeled using the electron-positron pair-correlation function of the homogeneous electron gas. The correlation potential is then determined by the Coulomb interaction with the screening cloud. The main advantage of the WDA is that it reasonably captures the effects of the screening cloud localized at the surface when the positron is in the vacuum region, which in turn gives rise to the characteristic $\sim 1/z$ behavior of the potential [14,28]. This should be contrasted with the LDA/GGA where the screening cloud is implicitly assumed to be centered around the positron. The detachment of the screening cloud as the positron leaves the surface is correctly described by the WDA, and thus the transition between the bulk potential and the asymptotic image potential takes place smoothly, so that the WDA does not suffer from the limitations we listed above of the corrugated mirror model.

The application of the WDA for modeling electron-positron correlations has been discussed previously in connection with jellium surfaces [27–29] as well as bulk materials [30]. Here we revisit the problem and construct a new WDA scheme based on more recent quantum Monte Carlo (QMC) results [31]. A necessary first step towards establishing the efficacy of our new WDA scheme is to investigate its performance in bulk materials where extensive experimental data is available for testing and benchmarking, and accurate LDA results are readily available for comparison. It is only when the new functional can be shown to yield reasonable positron lifetimes in bulk materials that we could expect it to also yield improved results for positrons at surfaces.

The paper is organized as follows. In Sec. II we present the theory behind the WDA. Section III discusses the parameters used in the computations. In Sec. IV we undertake a detailed study of WDA-based positron-annihilation lifetimes. A naive application of the WDA scheme is shown to yield poor positron lifetimes. We pinpoint the reasons for this failure, and discuss modifications of the WDA for obtaining improved results. We conclude with a summary of our most important results in Sec. V.

II. THEORY

A good introduction to the WDA can be found in Ref. [28], although for the sake of completeness, we reproduce the most important ideas here. Throughout this paper we will use atomic units ($e = \hbar = m_e = 1$), unless stated otherwise.

In this paper, our main concern is the zero positron-density limit of the 2CDFT [19], which applies when there is a single, delocalized positron present in the system (e.g., in perfect bulk crystals or at perfect surfaces). In this case, the ground state electron density remains unperturbed by the presence of the positron. The Kohn-Sham potential for the positron in the absence of external fields is then given by the sum of the ionic potential, the Hartree interaction with the ground state electron density, and the electron-positron correlation potential. In the rest of this section, we will focus on the electron-positron correlation contribution.

An exact expression for the electron-positron correlation energy can be written in terms of a coupling constant (or adiabatic) integration [27,32]

$$E_c^{e-p}[n_e,n_p] = -\int_0^1 d\lambda \iint d\mathbf{r}_e d\mathbf{r}_p \times \frac{n_e(\mathbf{r}_e)n_p(\mathbf{r}_p)\{g(\mathbf{r}_e,\mathbf{r}_p;[n_e,n_p];\lambda) - 1\}}{|\mathbf{r}_e - \mathbf{r}_p|}, \tag{1}$$

where n_e and n_p are the electron and positron densities, respectively. The pair-correlation function $g(\mathbf{r}_e,\mathbf{r}_p;[n_e,n_p];\lambda)$ describes the relative increase of the electron density n_e at $\mathbf{r}_e$ given a positron density n_p at $\mathbf{r}_p$. The pair-correlation function is itself a functional of the electron and positron densities, and thus, unknown *a priori*. The coupling constant λ takes the electron-positron interaction from the noninteracting $\lambda = 0$ to the fully interacting limit $\lambda = 1$.

In the 2CDFT, the electron-positron correlation potentials experienced by the electrons and the positrons are obtained by the functional derivatives of the correlation energy with respect to the densities,

$$V_{e,c}^{e-p}(\mathbf{r}) = \frac{\delta E^{e-p}}{\delta n_e(\mathbf{r})}, \quad V_{p,c}^{e-p}(\mathbf{r}) = \frac{\delta E^{e-p}}{\delta n_p(\mathbf{r})}. \tag{2}$$

In the zero-density limit, the positron density approaches zero at every point in space $n_p(\mathbf{r}_p) \to 0\ \forall \mathbf{r}_p$, such that electrons do not experience a correlation potential due to the presence of the positron. Note that the term

$$-\int_0^1 d\lambda \int d\mathbf{r}_e \frac{n_e(\mathbf{r}_e)n_p(\mathbf{r}_p)}{|\mathbf{r}_e-\mathbf{r}_p|}\frac{\delta g}{\delta n_p(\mathbf{r})} \tag{3}$$

gives no contribution to the positron's correlation potential. We thus have

$$V_{p,c}^{e-p}(\mathbf{r}_p) = -\int_0^1 d\lambda \int d\mathbf{r}_e \frac{\Delta n(\mathbf{r}_e|\mathbf{r}_p;\lambda)}{|\mathbf{r}_e-\mathbf{r}_p|}, \tag{4}$$

where

$$\Delta n(\mathbf{r}_e|\mathbf{r}_p;\lambda) = n_e(\mathbf{r}_e)\{g(\mathbf{r}_e,\mathbf{r}_p;[n_e,n_p];\lambda)-1\} \tag{5}$$

is the screening charge for a positron at $\mathbf{r}_p$ at a given interaction strength λ. This potential can be easily interpreted as the Coulomb interaction of the positron with its coupling constant averaged induced screening cloud, to which we will refer in the reminder of this paper as "the screening cloud". Also, we will denote the electron-positron correlation potential experienced by the positron by V_c, unless otherwise specified.

The expressions (4) and (5) are formally exact but do not provide a scheme for practical calculations. The pair-correlation function g is an unknown, system-dependent function, and in order to proceed, the true pair-correlation function must necessarily be approximated. In fact, the LDA is obtained by replacing both the pair-correlation function and the electron-density prefactor in Eq. (5) by the corresponding quantities from the homogeneous electron gas at the local density $n_e(\mathbf{r}_p)$ as follows:

$$\Delta n^{\mathrm{LDA}}(\mathbf{r}_e|\mathbf{r}_p;\lambda) = n_e(\mathbf{r}_p)\{g^h(|\mathbf{r}_e-\mathbf{r}_p|;n_e(\mathbf{r}_p);\lambda)-1\}, \tag{6}$$

where the pair-correlation function for the homogeneous electron gas g^h depends only on the distance from the positron. Note that in the zero-density limit, the pair-correlation function does not depend on the local positron density. Since the resulting potential then only depends on the local electron density at $\mathbf{r}_p$, one can immediately parametrize the correlation energy as a function of the local electron density. In the WDA, the idea is to keep the pair-correlation function of the homogeneous electron gas, but restore the proper electron density prefactor in the equation for the screening cloud. In order to retain some of the favorable properties of the LDA, one additionally imposes conditions on the screening cloud in the form of a sum rule, e.g., on the net induced screening charge.

We comment on the question of generalizing the theory beyond the zero-density limit, which is our focus in this paper, to consider the case of finite positron densities. One important difference here is that we will need to take into account the correlation potential obtained from the functional derivative of Eq. (2) in the Kohn-Sham equation for the electrons. Next, the term of Eq. (3) will now give a finite contribution to the positron correlation potential, and finally, the pair-correlation function of the homogeneous electron-positron gas will depend on both the local electron and positron densities.

Before developing our practical WDA scheme for the zero-density limit below, we will discuss the matter of an important sum rule. Next, we will examine more closely the nature of the pair-correlation function and derive some constrains that it should satisfy. This will be followed by the discussion of the WDA approach [28] in the subsequent sections of this paper.

A. Sum rule

An important reason why the LDA approximation for electron-electron correlations works well for a large variety of systems is that it is in principle the *exact* functional for the homogeneous electron gas. It thus also satisfies all exact conditions that can be imposed on the functional in the homogeneous case. In order to construct reliable functionals that go beyond the LDA, it is important in this spirit to satisfy known exact constrains and limits as far as possible. In this connection, Gunnarsson *et al.* realized that the sum rule on the electron-electron exchange-correlation hole, which states that the hole corresponds to the removal of one electron worth of charge, is a key reason for the success of the LDA [26].

Note that the preceding sum rule arises because the interaction involves indistinguishable particles (electrons), so that the exchange-correlation energy cancels the self-interaction of the Hartree term. Since electrons and positron are different particles, there is no formal reason for this sum rule to hold for the electron-positron correlation cloud. In fact, the Coulomb correlation can now only cause a redistribution of the electron charge, suggesting that the positron's correlation cloud should integrate to zero [33].

Despite these remarks, some statements can be made about the short-range part of the correlation cloud. In a very dilute homogeneous electron gas, one expects the formation of Ps$^-$, indicating that a charge equal to twice the electron charge is accumulated in the screening cloud. With this motivation, we assume that the screening cloud can be written as $\Delta n = \Delta n_{\mathrm{sr}} + \Delta n_{\mathrm{lr}}$, where the first term is to capture the short-range part and the second for the long-range part of the screening cloud. From electron-positron pair-correlation data, we expect that the short-range part can be described roughly by an exponentially decaying function, while the long-range part resembles Friedel oscillations [31,34,35]. If we make the further assumption that the charge in the short-range part is compensated by the long-range part, i.e., $\int d\mathbf{r}_e\, \Delta n_{\mathrm{sr}}(\mathbf{r}_e|\mathbf{r}_p;\lambda) = -\int d\mathbf{r}_e\, \Delta n_{\mathrm{lr}}(\mathbf{r}_e|\mathbf{r}_e;\lambda)$, we can write

$$\int d\mathbf{r}_e\, \Delta n_{\mathrm{sr}}(\mathbf{r}_e|\mathbf{r}_p;\lambda) = \mathcal{Q}(\mathbf{r}_p;n_e;\lambda). \tag{7}$$

It is important to recognize that, in general, the screening charge $\mathcal{Q}$ depends on the screening properties of a specific system and thus does not provide a sum rule that holds for all systems. Indeed, going back to the case of Ps$^-$ formation, we have $\lim_{n_e\to 0}\mathcal{Q}(\mathbf{r}_p;n_e;1)=2$ for the homogeneous electron gas. On the other hand, for metallic systems, we generally expect $\mathcal{Q}(\mathbf{r}_p;n_e;1)\approx 1$, whereas for good insulators, it seems reasonable to assume $\mathcal{Q}(\mathbf{r}_p;n_e;1)\ll 1$.

We would already like to emphasize that there is a large difference between the "true" screening charge $\mathcal{Q}$, i.e., the one we would obtain from the true pair-correlation function and ground state densities, and the screening charge Q, which is used in the sum rule of the WDA. We will show below, for example, that even though for insulators $\mathcal{Q}$ is expected to be small, a large Q has to be imposed in order to obtain reasonable results within the WDA. The reason for the counterintuitive behavior will become apparent in the rest of the paper.

In order to construct a WDA functional for the electron-positron problem, Jensen and Walker [27] imposed the charge-neutrality condition, which states that the screening and positron charge should be exactly equal. Stated differently, they assumed that the positron charge is always perfectly screened by the electrons. Their charge-neutrality condition takes the form

$$\int_0^1 d\lambda \int d\mathbf{r}_e\, \Delta n(\mathbf{r}_e|\mathbf{r}_p;\lambda) = 1. \tag{8}$$

Rubaszek [28,30], on the other hand, interpreted the coupling constant λ as the scaled charge of the positron, and hence concluded that the charge neutrality condition should hold for any λ. This slightly different interpretation yields the sum rule

$$\int d\mathbf{r}_e\, \Delta n(\mathbf{r}_e|\mathbf{r}_p;\lambda) = \lambda, \quad \forall\, \lambda \in [0,1]. \tag{9}$$

From our discussion above, it is clear that these sum rules should not be interpreted as exact conditions on the electron-positron screening cloud but merely represent an *ad hoc* assumption on the screening properties of the system. In fact, *a priori* there is no guarantee that imposing either of these conditions will yield improved results.

B. Electron-positron pair-correlation function

If the electron-positron pair-correlation function is known exactly for a given system, we could obtain the exact Kohn-Sham potential for the positron through Eq. (4). As mentioned before, however, the exact pair-correlation function is in general not known and an essential step in the WDA is the replacement of the true pair-correlation function by the one for the homogeneous electron gas (in the zero-density limit)

$$g(\mathbf{r}_e,\mathbf{r}_p;[n_e,n_p];\lambda) \to g^h(r;n_e(\mathbf{r}_e);\lambda), \tag{10}$$

where $r = |\mathbf{r}_e - \mathbf{r}_p|$. Also, the pair-correlation g^h is not known in closed form, and additional assumptions have to be made to obtain a useful expression. In the remainder of this section, we first discuss the known part of the pair-correlation function, then introduce a reasonable general form based on the exact limit at low electron densities, and finally, we impose additional exact conditions which will be seen to almost completely determine g^h.

Especially important in the calculation of positron annihilation properties is the enhancement of the electron density at the positron position given by the enhancement factor γ. The expression for, e.g., the positron-annihilation lifetime τ, is given by

$$\lambda_a = \frac{1}{\tau} = \pi r_e^2 c \int d\mathbf{r}\, n_e(\mathbf{r}) n_p(\mathbf{r}) \gamma(\mathbf{r}), \tag{11}$$

where r_e is the classical electron radius, c is the speed of light, and λ_a is the annihilation rate (subscript a is to avoid confusion with the coupling constant). The independent particle model (IPM) neglects the enhancement term ($\gamma = 1$), but its inclusion is well known to be necessary for obtaining any reasonable agreement with experiments. In the LDA, the enhancement term can be approximated by the value of the pair-correlation function at $r = 0$ of the homogeneous electron gas evaluated at the local electron density, i.e., $\gamma(\mathbf{r}) \to \gamma(n_e(\mathbf{r})) = g^h(0;n_e(\mathbf{r});1)$. Several parametrizations of the enhancement term derived from many-body calculations are available in the literature, see, e.g., Refs. [19,31,36].

The $g^h(0;n_e;1)$ dependence of the pair-correlation function alone is not sufficient to obtain a useful form of the pair-correlation function. One can make progress, however, by assuming that the short-range part of the screening cloud resembles the Ps atom

$$g^h(r;n_e(\mathbf{r}_e);\lambda) = 1 + \alpha(n_e(\mathbf{r}_e);\lambda)e^{-\beta(n_e(\mathbf{r}_e);\lambda)r}, \tag{12}$$

where several choices for α and β can be made. Interestingly, a number of parametrizations of the LDA correlation energy and the enhancement factor γ assume that $g(r;n_e;1) = 1 + e^{-r}/(8\pi n_e)$ is an exact limit for $n_e \to 0$ as it yield the Ps contact density [19,36]. Recent quantum Monte Carlo data furthermore confirm that this is a reasonable assumption for the short-range part of the screening cloud over a wide range of electron densities [31].

We now discuss additional constraints on the pair-correlation function. Two obvious conditions are $\lim_{r\to\infty} g^h(r;n_e(\mathbf{r}_e);\lambda) = 1$ and $g^h(r;n_e(\mathbf{r}_e);0) = 1$. The first condition tells us that the electron density remains unperturbed far away from the positron and it is satisfied by the Ps form for any reasonable choice of α and β. The second condition simply states that electrons remain unperturbed by the presence of the positron, if there is no interaction between them, so that $\alpha(n_e(\mathbf{r}_e);0) = 0$. Next, we should recover the LDA enhancement term in the fully interacting case, which poses the condition $\alpha(n_e(\mathbf{r}_e);1) = \{\gamma(n_e(\mathbf{r}_e)) - 1\}$. A final condition comes from the Coulomb interaction between the particles, namely the Kimball cusp condition [35,37]

$$\left(\frac{\partial g^h}{\partial r}\right)_{r=0} = -g^h(0), \tag{13}$$

from which one can easily derive that

$$\beta(n_e(\mathbf{r}_e);\lambda) = \frac{1 + \alpha(n_e(\mathbf{r}_e);\lambda)}{\alpha(n_e(\mathbf{r}_e);\lambda)}. \tag{14}$$

Note that, with the exception of the scaling of α with λ, the Ps form of the pair-correlation function is thus completely determined by the enhancement term $\gamma(n_e(\mathbf{r}_e))$.

C. The WDA approximation

We now present the WDA approximation developed by Rubaszek [28]. In this approach, the starting point is the sum rule (9), which is imposed to hold for all $\mathbf{r}_p$. The pair-correlation function is assumed to take the form

$$g^h(r;n_e(\mathbf{r}_p);\lambda) = 1 + \lambda\{\gamma(n_e(\mathbf{r}_p)) - 1\}e^{-a(n_e(\mathbf{r}_p))r}, \tag{15}$$

where the decay length a is derived from the sum rule (9) for the homogeneous electron gas

$$a^3(n_e(\mathbf{r}_p)) = 8\pi n_e(\mathbf{r}_p)\{\gamma(n_e(\mathbf{r}_p)) - 1\}. \tag{16}$$

For inhomogeneous systems, the sum rule is, using the pair-correlation function for the homogeneous electron gas, generally not satisfied. In order to restore it, one introduces an effective (weighted) electron density $n_e^*(\mathbf{r}_p)$ at each point, i.e., one determines $n_e^*(\mathbf{r}_p)$ such that

$$\{\gamma(n_e^*(\mathbf{r}_p))-1\}\int d\mathbf{r}_e n_e(\mathbf{r}_e)e^{-a(n_e^*(\mathbf{r}_p))|\mathbf{r}_e-\mathbf{r}_p|}=1, \tag{17}$$

where the coupling constant dependence drops out due to the linear scaling of g^h with λ, and as a result the adiabatic integration in the expression for the correlation potential (4) can be performed analytically to obtain

$$\begin{aligned} V_c(\mathbf{r}_p) &= -\frac{1}{2}\{\gamma(n_e^*(\mathbf{r}_e))-1\} \\ &\quad\times\int d\mathbf{r}_e\,\frac{n_e(\mathbf{r}_e)e^{-a(n_e^*(\mathbf{r}_p))|\mathbf{r}_e-\mathbf{r}_p|}}{|\mathbf{r}_e-\mathbf{r}_p|}. \end{aligned} \tag{18}$$

For the calculation of positron lifetimes, the local density n_e in the enhancement factor has to be replaced by the effective density n_e^*,

$$\lambda_a=\frac{1}{\tau}=\pi r_e^2 c\int d\mathbf{r}\,n_e(\mathbf{r})n_p(\mathbf{r})\gamma(n_e^*(\mathbf{r})). \tag{19}$$

We note that the pair-correlation function in this approach does not satisfy the Kimball cusp condition (13), and as discussed earlier, there is no formal reason why the sum rule should hold. We will return to investigate the effect of modifying the sum rule below. It will be interesting to examine positron lifetimes with a pair-correlation function that satisfies the cusp condition, which we hope to take up elsewhere.

Despite these shortcomings, the pair-correlation function defined by Eqs. (15) and (16) has some favorable properties. The first is that the correlation potential for the homogeneous electron gas obtained within this approach

$$V_c=-\frac{3\{\gamma(n_e)-1\}^{1/3}}{2\times 6^{2/3}\times r_s} \tag{20}$$

results in the correct Ps limit $V_c=-1/4$ Ha for the dilute electron gas, if the enhancement factor has the correct limiting $\gamma\sim r_s^3/6$ behavior. In the limit $r_s\to 0$, on the other hand, the potential goes as $\sim r_s^{-2/3}$ and does not reduce to the RPA limit [38] $\sim r_s^{-1/2}$. A second advantage is that the adiabatic integration can be performed analytically, which reduces the required computational resources.

Figure 1 shows a comparison between the LDA parametrizations of Refs. [19,31] and the WDA potential for the homogeneous electron gas. Note that the WDA predicts a correlation potential which is generally more negative than the LDA. Only at very high densities ($r_s<0.9$), the Drummond LDA is more negative than the WDA. The agreement between the LDA and WDA is reasonable for the Boronski-Nieminen parametrization [19], whereas the WDA is substantially more negative for the Drummond parametrization [31]. It is important to point out that in the present study of bulk positron annihilation lifetimes, only the relative values of the positron correlation potential in different parts of the unit cell can influence the results, i.e., our results do not depend on the absolute value of the potential.

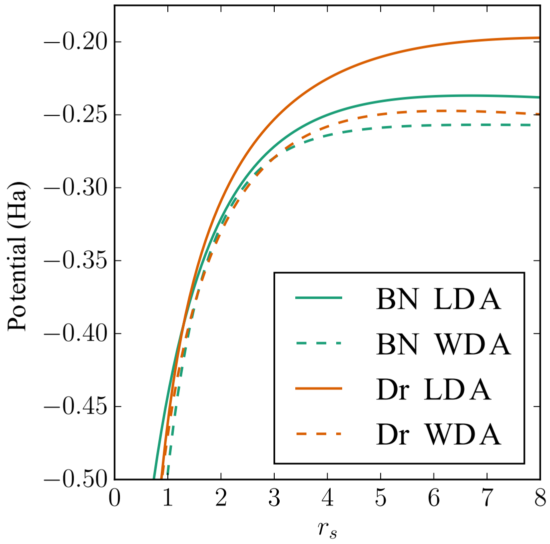

FIG. 1. Comparison of the LDA potentials as parametrized by Boronski and Nieminen (BN) [19], and Drummond *et al.* (Dr) [31] with the corresponding WDA potentials of Eq. (20) for the homogeneous electron gas. For the enhancement factors, we took the parametrizations from the same references.

III. COMPUTATIONAL DETAILS

The electronic densities used in this work were obtained with the PAW method [39] as implemented in the VASP *ab initio* package [40–42]. All parameters in the calculation were checked until the positron lifetimes were converged to within 1 ps. Due to the sensitivity of the positron lifetimes to the lattice constant of the material, we used experimental lattice parameters [43] for all systems. In the following discussion, we will distinguish between the core and valence electrons in each system for which we take the same partitioning as in the electronic ground state calculation. The electrons taken as valence electrons are summarized in Table I.

We compared the lifetimes obtained with the ground state LDA [44,45] and PBE [46] electron densities (using experimental lattice parameters) but in none of the considered cases, we found a difference in the lifetime larger than 1 ps. Therefore, the uncertainty in positron lifetimes due to electronic and structural properties depends mainly on the accuracy with which the electron correlation functional used can predict lattice constants. Accordingly, in the remainder of this paper, we will only report our results obtained with the LDA. Positron lifetime calculations were performed with the MIKA/doppler package [47]. Details of our WDA implementation are given in the Appendix.

TABLE I. Electrons treated as valence electrons in the ground state calculations and in the shell-partitioning of Sec. IV C.

Li	C	Na	Al	Si
$2s$	$2s^2\,2p^2$	$3s$	$3s^2\,3p$	$3s^2\,3p^2$
Fe	Cu	Nb	W	Pt
$3d^6\,4s^2$	$3d^{10}\,4s$	$4p^6\,4d^4\,5s$	$5d^4\,6s^2$	$5d^9\,6s$

TABLE II. Overview of the elemental materials considered. The third to fifth columns give positron-annihilation lifetimes using an LDA derived from the Brandt-Reinheimer expression,[a] the Boronski-Niemenen LDA, and the Drummond LDA. The last column gives experimental lifetimes taken from Ref. [48] and references therein.

System	Structure	BR	BN	Dr	Expt.
Li	bcc	295.914	300.287	304.261	291
C	diamond	81.152	92.862	94.569	98
Na	bcc	315.587	328.082	342.821	338
Al	fcc	157.749	164.743	161.128	160
Si	diamond	204.313	210.620	207.929	216
Fe	bcc	86.373	100.263	101.355	105
Cu	fcc	87.604	104.518	105.596	110
Nb	bcc	111.738	121.280	120.760	120
W	bcc	102.742	111.951	111.641	105
Pt	fcc	83.716	96.089	97.380	99

[a] This expression can be derived from the Brandt-Reinheimer enhancement factor by solving the WDA correlation potential equation (18) for the homogeneous electron gas. The result is $V_c(r_s) = -0.25(1 + 10/r_s^3)^{1/3}$.

IV. BULK TESTS

Here we consider a set of elemental bulk materials for which experimental positron-annihilation lifetimes are available [48]. Table II gives the experimental and LDA lifetimes, obtained with the Brandt-Reinheimer (BR) expression [28,49,50], the Boronski-Nieminen (BN) parametrization [19], and the Drummond (Dr) parametrization [31] of the LDA. In principle, the Drummond parametrization is the most accurate one currently available but the BN is still in wide use. The BR does not involve a very accurate parametrization of the enhancement term, including the fact that it does not satisfy the RPA limit, but we consider it nonetheless because it was used in early WDA work [27,28,51].

A. Rubaszek WDA

We now apply the WDA of Rubaszek as explained in Sec. II C for different parametrizations of the enhancement factor to a set of elemental bulk materials. Figure 2(a) shows the results of our calculations. Our WDA based on the BN and Drummond enhancements is seen to result in a systematic overestimation of the lifetime. The BR expression for the enhancement term gives somewhat better results, although it does not satisfy the RPA limit, and that the BN and Drummond parametrizations are more accurate. We expect the BR-based WDA to benefit from a fortunate cancellation of errors.

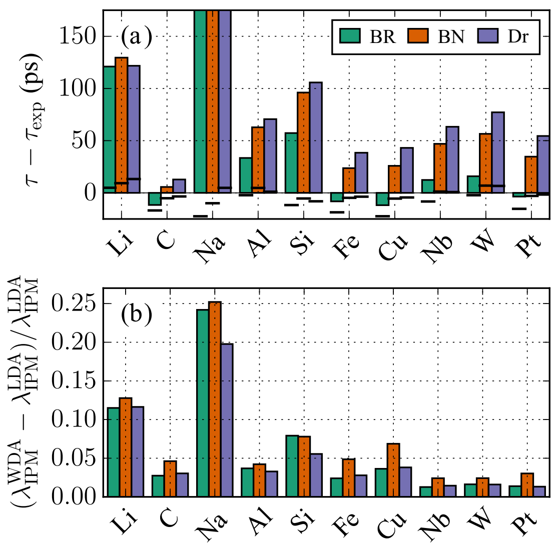

FIG. 2. Results of (a) positron annihilation lifetime calculations and (b) the relative change in the electron positron overlap with respect to the LDA for various elemental materials using Rubaszek's [28] approach. Horizontal black lines denote the LDA lifetimes for each system. Different colors are used to distinguish the results for various choices of the enhancement factor γ: BR (Brandt-Reinheimer), BN (Boronski-Nieminen), and Dr (Drummond).

Insight into the failure of the present WDA approach is obtained by considering the expression of the annihilation rate [Eq. (19)] which shows that the decrease of the annihilation rate (increase of the lifetime) with respect to the LDA could result from two different factors: (1) a decrease of the electron-positron overlap or (2) a decrease of the enhancement factor. The first factor is driven by the change in the correlation potential between the LDA and WDA. This effect can be quantified by comparing the lifetimes obtained within the IPM [setting $\gamma(\mathbf{r}) = 1$] from the LDA and WDA positron densities. More specifically, we examine the relative increase of the electron-positron overlap for the WDA, i.e., $(\lambda_{\mathrm{IPM}}^{\mathrm{WDA}} - \lambda_{\mathrm{IPM}}^{\mathrm{LDA}})/\lambda_{\mathrm{IPM}}^{\mathrm{LDA}}$. The results are displayed in Fig. 2(b). The WDA is seen to systematically predict a larger electron-positron overlap compared to the LDA. This implies that the WDA correlation potential is more attractive near the cores compared to the interstitial region. Since an increase of the overlap will lead to an increased annihilation rate, our lifetime results can only be explained through a decrease of the enhancement factor.

In this connection, it is interesting to examine the behavior of the effective density n^* in the vicinity of a local minimum and maximum [52]. For the minimum case, consider the model density

$$n_e(\mathbf{r}_e) = \tfrac{1}{2}[1 + \sin^2(r)], \tag{21}$$

where $r = |\mathbf{r}_e|$, and we take $\mathbf{r}_p = 0$. In the LDA, the screening charge is given by

$$\Delta n(r) = n_e(0)\{\gamma(n_e(0)) - 1\}e^{-a(n_e(0))r}, \tag{22}$$

which, by the choice of a [Eq. (16)], satisfies the sum rule. The dependence is plotted (green line) in Fig. 3(b). In the WDA we take into account the inhomogeneity of the electron density around $\mathbf{r}_p$,

$$\Delta n(r) = n_e(r)\{\gamma(n^*) - 1\}e^{-a(n^*)r}, \tag{23}$$

where n^* has to be determined such that $\Delta n(r)$ integrates to one. If one takes $n^* = n_e(0)$ around a local minimum, the screening charge will be overestimated, see the orange curves in Figs. 3(b) and 3(c). For this simple model, one can easily solve (17) to find $n^* \approx 1.59\, n_e(0)$, where we used the enhancement factor parametrized by Boronski and Nieminen [19], see the blue curves in Figs. 3(b) and 3(c). The

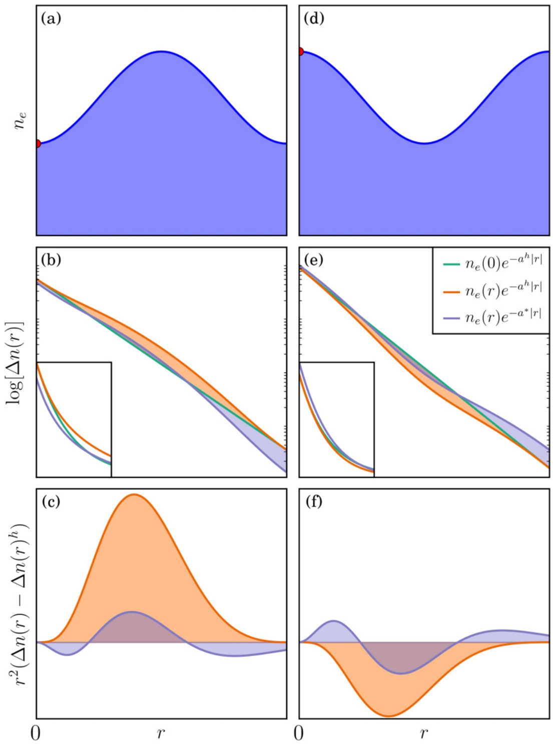

FIG. 3. Results of a simple model (discussed in the text) to illustrate the behavior of WDA screening in the vicinity of a local minimum (left column of panels) and maximum (right column of panels) of the electron density. The position of the positron $\mathbf{r}_p$ is taken at $r = 0$ (red dots in topmost figures). The second row plots the radial dependence of the screening cloud for the LDA (green), the WDA using the local electron density (orange), and the WDA using an effective density that satisfies the sum rule (blue). The insets show the same quantities on a linear scale. Figures in the bottom row show the radially integrated differences between the WDA and LDA screening clouds; in order to satisfy the sum rule, this quantity should integrate to zero.

final result is that the local contribution to the annihilation rate decreases due to a decrease in the enhancement term $g(0,n^*) \approx 0.94\, g(0,n_e(0))$. Around a local maximum, the opposite conclusion holds. Indeed, consider

$$n_e(\mathbf{r}_e) = \tfrac{1}{2}[1 + \cos^2(r)], \tag{24}$$

for which the effective density is found to be $n^* \approx 0.70\, n_e(0)$, which yields a relative increase of the enhancement term $g(0,n^*) \approx 1.05\, g(0,n_e(0))$. The corresponding curves are given in Figs. 3(d)–3(f).

These results explain why the average enhancement factor decreases. The reason is that even though there is a shift of the positron density towards the core regions in the WDA, the positron is still mostly localized in the interstitial region due to the large Coulomb repulsion from the ions. In the interstitial region, the effective density will generally decrease due to the large contributions of the cores to the screening charge, leading to a decrease in the enhancement factor and, hence, the annihilation rate.

We note that physically the charge of the positron will mostly be screened by the valence electrons, so that core electrons should not contribute significantly to the screening charge. If we can reduce the contribution of the cores to the screening charge, we expect an increase in the annihilation rate. In the next sections we will explore two such approaches, which are motivated by these observations.

B. Gradient correction

One obvious way to reduce the screening effect of core electrons is to introduce a correction based on the gradient of the electron density. Since the density varies rapidly near the ions but more smoothly in the valence region, the density gradient provides a convenient handle for selective reduction of the core contribution to the screening cloud. In fact, the GGA correction to the LDA positron correlation potential is derived from a gradient correction to the induced contact charge density [53]

$$\Delta n_e^{\mathrm{GGA}}(\mathbf{r}_p|\mathbf{r}_p) = \Delta n_e^{\mathrm{LDA}}(\mathbf{r}_p|\mathbf{r}_p)e^{-\alpha\epsilon(\mathbf{r}_p)}, \tag{25}$$

with $\epsilon = |\nabla n_e|^2/q_{\mathrm{TF}}^2$, where $1/q_{\mathrm{TF}}$ is the Thomas-Fermi screening length. The parameter α can be chosen phenomenologically [53,54], though recently a connection with the LDA potential was found [48].

In the nonlocal case we could apply the gradient correction to the pair-correlation function at the positron position, i.e.,

$$\begin{aligned} g(r;n_e(\mathbf{r}_p);\lambda) = 1 + \lambda\{\gamma(n_e(\mathbf{r}_p)) - 1\} \\ \times\, e^{-a(n(\mathbf{r}_p))r}e^{-\alpha\epsilon(\mathbf{r}_p)}, \end{aligned} \tag{26}$$

but this would not reduce the relative contribution of the core electrons to the screening cloud. Note that the form above is equivalent to imposing the position dependent sum rule

$$\int d\mathbf{r}_e\, \Delta n_e(\mathbf{r}_e|\mathbf{r}_p) = e^{\alpha\epsilon(\mathbf{r}_p)}, \tag{27}$$

which would imply that the screening charge is larger near the cores, which seems unphysical. We will return to discuss this point below. Instead, let us look at a modification of the screening charge of the form

$$\begin{aligned} \Delta n_e(\mathbf{r}_e|\mathbf{r}_p) = \{\gamma(n_e^*(\mathbf{r}_p)) - 1\} \\ \times\, n_e(\mathbf{r}_e)e^{-\alpha\epsilon(\mathbf{r}_e)}e^{-a(n_e^*(\mathbf{r}_p))|\mathbf{r}_e-\mathbf{r}_p|}. \end{aligned} \tag{28}$$

This means that we replace the true electron density by the modified form $n_e(\mathbf{r})e^{-\alpha\epsilon(\mathbf{r})}$ that takes into account the local ability of the electron density to screen external charges. The modified pair-correlation function is then given by

$$\begin{aligned} g(\mathbf{r}_e,\mathbf{r}_p;n_e(\mathbf{r}_p);\lambda) = 1 + \lambda\{\gamma(n_e(\mathbf{r}_p)) - 1\} \\ \times\, e^{-a(n(\mathbf{r}_p))r}e^{-\alpha\epsilon(\mathbf{r}_e)}, \end{aligned} \tag{29}$$

where the gradient correction is evaluated at the electron position $\mathbf{r}_e$ instead of the positron position $\mathbf{r}_p$, as is the case in Eq. (26). The resulting lifetime formula is

$$\lambda_a = \frac{1}{\tau} = \int d\mathbf{r}\, n_e(\mathbf{r})n_p(\mathbf{r})(1 + \{\gamma(n_e^*(\mathbf{r})) - 1\}e^{-\alpha\epsilon(\mathbf{r})}), \tag{30}$$

which, with exception of the effective density n_e^* in the enhancement term, has the same form as the GGA correction to the lifetime formula [53].

An important difference between the gradient correction proposed here and the GGA correction to the LDA should be

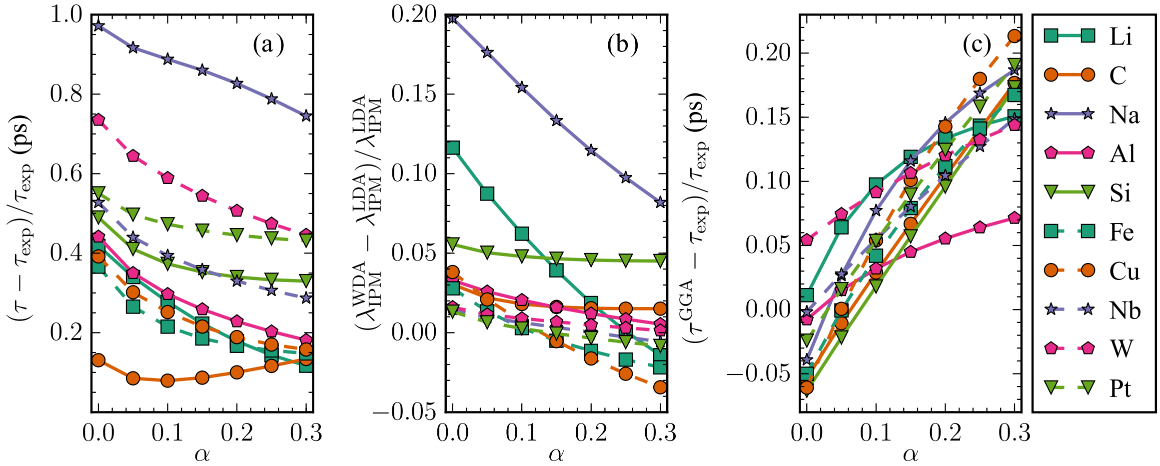

FIG. 4. Scaling of (a) the relative error of the lifetime and (b) the relative change in the electron-positron overlap with respect to the LDA with the gradient correction parameter α applied to the WDA. (c) Lifetimes obtained via Eq. (30) where the local density is inserted in the enhancement factor instead of the effective density [unlike the results in (a)]. Only results obtained with the Drummond enhancement term are shown. Markers indicate calculated results and lines serve as guides to the eye.

emphasized. In the LDA, the potential is too attractive and the enhancement factor is overestimated in the core region due to an overestimation of the *local* screening of the core electrons. As a result, positron lifetimes are generally slightly underestimated. By introducing a local gradient correction [53] both these effects are corrected, leading to an *increase* in the lifetime because the gradient corrections dominate in the core regions. In our proposed gradient correction to the WDA, we attempt to correct for the overestimation of the *nonlocal* screening of the core densities, i.e., the contribution of the core charges to the screening cloud of the positron at a (possibly) different position. Since the density participating in the screening is decreased with respect to the true electron density, the screening length must be increased with respect to the unmodified WDA in order to accumulate the same amount of total screening charge. An increase of the screening length is obtained via a decrease of the effective density and, as a consequence, the enhancement term is increased everywhere. Since the correction will again dominate in the core regions, we would expect a shift of the positron density away from the ions. If the gradient correction to the annihilation rate is neglected, these effects will always lead to a *decrease* of the lifetime. In reality, however, the results depend on the balance between the decreased effective density and the gradient correction to the enhancement term.

Our results for this approach with the Drummond enhancement are shown in Fig. 4 as a function of the parameter α, which controls the strength of the gradient correction. We start our evaluation of the gradient correction by discussing the change in the electron-positron overlap, shown in Fig. 4(b), which results from the change in the correlation potential. In most cases, we see a slight, nearly linear decrease in the overlap with increasing α. For diamond and Si, the change in the overlap quickly saturates and the gradient correction has a relatively small effect. On the other hand, this correction is much more pronounced for the alkali metals Li and Na. Note that the gradient correction decreases the electron density participating in the screening cloud mainly in the core regions. As a result, it yields a correlation potential that is less attractive in the core regions relative to the valence region when compared to the uncorrected WDA, hence explaining the observed decrease in the overlap.

Next, we discuss the decrease in annihilation rate caused by the gradient correction to the enhancement factor. For this purpose, we replace the effective electron density n_e^* in the enhancement factor γ in Eq. (30) by the true electron density n_e. The results are shown in Fig. 4(c). Note that the gradient correction has the largest effect on the lifetime in those regions where the positron density is large. This explains why the gradient correction has a more pronounced effect in systems such as Si and diamond, where there are larger inhomogeneities in the valence electron density due to covalent bonding, than in metals like Al and W.

The final lifetime results are shown in Fig. 4(a). The gradient correction to the WDA is seen to decrease the lifetime with increasing α for all metals considered. This implies that the effect of the decrease of the effective density n^* in the interstitial regions dominates over that of the decrease in the electron-positron overlap and the gradient correction to the enhancement factor. On the other hand, for Si and diamond, the opposite scenario holds, leading to a slight increase of the lifetime. These results show that we cannot expect accurate lifetimes from the gradient correction to the WDA proposed in this section. Despite a slight improvement for the metallic systems, we do not obtain acceptable lifetimes with reasonable values of the parameter α, which for the Boronski-Nieminen LDA is set to $\alpha = 0.22$ [53] and for the Drummond LDA to $\alpha = 0.05$ [54]. (For systems with larger inhomogeneities, worse results are obtained.) It is clear that another approach is needed for screening the core electrons.

C. Shell partitioning

The idea of shell partitioning is as old as the WDA itself and in connection with electron-electron exchange, it provides a scheme to correct the (erroneous) large exchange interaction involved in the WDA between spatially well separated electron shells [26]. Rubaszek *et al.* [30,55] proposed such a scheme for electron-positron correlation in which the electron density is separated into core and valence parts. The latter is again split into its s, p, d, and f components in a sphere around each ion, and the part in the remainder of the unit cell. The idea is that each of these electrons will in general contribute differently to the screening cloud around the positron [56–62]. One can then introduce a specific enhancement factor γ_t for each type of electron density $n_{e,t}$. For instance, for the core electrons we expect $\gamma_c \approx 1$, whereas for the valence electrons in the interstitial region the LDA enhancement factor is likely a reasonable approximation. Next, for each contribution, a sum rule is imposed, which in the work of Rubasek *et al.* is assumed to take the form

$$\int d\mathbf{r}_e\, n_{e,t}(\mathbf{r}_e)\{g_t^h(|\mathbf{r}_e-\mathbf{r}_p|,\tilde{n}_{e,t}(\mathbf{r}_p),\lambda)-1\} = Q\frac{\{g_t^h(0,n(\mathbf{r}_p),\lambda)-1\}n_t(\mathbf{r}_p)}{\sum_{t'}\{g_{t'}^h(0,n(\mathbf{r}_p),\lambda)-1\}n_{t'}(\mathbf{r}_p)}, \tag{31}$$

where

$$\tilde{n}_{e,t}(\mathbf{r}_e) = n_e(\mathbf{r}_e) + [n_{e,t}^*(\mathbf{r}_e) - n_{e,t}(\mathbf{r}_e)] \tag{32}$$

is the effective density for a given type of electron t. The preceding sum rule states that various electrons contribute to the screening charge depending on the ratios of their local densities to the total electron density. Though, note that each electron type is weighted by its local enhancement term $g_t^h - 1$, and not the bare density. As a result, valence electrons, for example, can contribute a larger fraction to the screening cloud than d electrons, even though their local density can be smaller. As required, this form reproduces the LDA in the homogeneous electron gas [30].

Although excellent results for positron lifetimes have been obtained within this shell-partitioning approach [30], a number of technical issues arise. One is that there is no unique way to split the electron density into interstitial part and its angular momentum components around each ion. It is also not clear what form for the enhancement factor should be used for each l channel. Rubaszek *et al.* [30] used a Kahana-type enhancement factor $\epsilon(E_l/E_F, n_e(\mathbf{r}_p))$, where E_l are the l-dependent linearization energies used in the LMTO method and E_F is the Fermi energy. Even though the results obtained are excellent, this choice is arbitrary and depends on method-specific computational parameters, which do not carry over easily to our present approach. In order to address these difficulties, we investigate a simpler shell partitioning scheme in this study in which we distinguish only between the valence and core electrons. The latter are treated within the LDA and the former within the WDA. We expect that the essence of the problems in the previous sections will be solved by removing the core electrons from the nonlocal screening. The introduction of l-dependent enhancement factors can be expected to provide a further improvement of the results, but are likely only of secondary importance.

We now turn to present details of our shell-partitioning approach, which is based on Refs. [63,64]. We start by writing the (total) effective electron density as

$$\tilde{n}_e(\mathbf{r}) = n_{e,v}^*(\mathbf{r}) + n_{e,c}(\mathbf{r}), \tag{33}$$

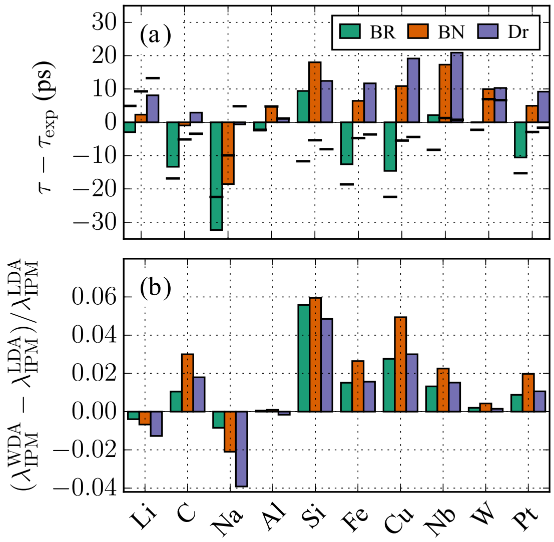

FIG. 5. Results of (a) positron annihilation lifetime calculations and (b) the relative change in the electron positron overlap with respect to the LDA for various elemental materials using the WDA with shell partitioning. Horizontal black lines denote the LDA lifetimes for each system. Different colors are used to distinguish the results for various choices of the enhancement factor γ: BR (Brandt-Reinheimer), BN (Boronski-Nieminen), and Dr (Drummond).

where $n_{e,c}$ is the core electron density and $n_{e,v}^*$ is an effective valence electron density, which is determined by solving the modified sum rule

$$\int d\mathbf{r}_e\, \Delta n(\mathbf{r}_e|\mathbf{r}_p) = \{\gamma(\tilde{n}_e(\mathbf{r}_p)) - 1\} \times \int d\mathbf{r}_e\, n_{e,v}(\mathbf{r}_e) e^{-a(\tilde{n}_e(\mathbf{r}_p))|\mathbf{r}_e-\mathbf{r}_p|} = \frac{n_{e,v}(\mathbf{r}_p)}{n_e(\mathbf{r}_p)}. \tag{34}$$

The correlation potential is given by

$$V_c(\mathbf{r}_p) = \frac{n_{e,c}(\mathbf{r}_p)}{n_e(\mathbf{r}_p)}\epsilon_c^{e-p}(n_e(\mathbf{r}_e)) + \frac{1}{2}\int d\mathbf{r}_e \frac{\Delta n_e(\mathbf{r}_e|\mathbf{r}_p)}{|\mathbf{r}_e - \mathbf{r}_p|}, \tag{35}$$

where ϵ_c is the LDA correlation potential. Lifetimes are given by

$$\lambda = \frac{1}{\tau} = \pi r_e^2 c \int d\mathbf{r}\, n_e(\mathbf{r}) n_p(\mathbf{r}) \gamma(\tilde{n}_e(\mathbf{r})). \tag{36}$$

The electrons taken as valence electrons are listed in Table I.

This approach, even though somewhat arbitrary as it depends on the chosen partitioning between core and valence electrons, leads to substantially improved lifetime results, see Fig. 5. In particular, Li and Na now give better lifetimes than the LDA, whereas WDA results without shell partitioning were poor. We attribute this striking improvement to the fact that valence electrons of alkali metals are quite free-electron-like. These electrons are very efficient in screening the positron charge, so that the core electrons contribute little to screening. For the five materials in our test set that do not have d valence orbitals, we obtain results comparable to the LDA using the Drummond parametrization of the LDA potentials and enhancement factors. The results for transition metals are notably poorer due to an overestimation of the effect of d electrons in the screening process. Overall, our analysis indicates that WDA with shell partitioning yields reasonable results. An l-dependent shell partitioning should provide further improvement.

Our tests of shell partitioning indicate that the LDA is generally more reliable than the WDA, although the WDA appears to work well when all valence electrons are sufficiently free-electron-like. This is a consequence of the local nature of the LDA, which prevents localized non-free-electron-like electrons from strongly influencing the overall potential.

D. Effect of the sum rule

In Sec. II A we pointed out that in the treatment of electron-electron correlation, the sum rule expresses that electrons should not experience self-interaction. We also commented that such a self-interaction is not involved in treating electron-positron correlation effects, and we argued that there is no real reason why the short-ranged part of the screening cloud should have a value of one. In fact, as we showed in Sec. IV B on the gradient correction [Eqs. (26) and (27)], the charge of the screening cloud determines the screening length, which is expected to be system dependent.

In this section we discuss, within the framework of the shell-partitioning scheme of the preceding section, effects of the imposed screening charge on the positron lifetime, i.e., we now determine the effective electron density by solving the modified sum rule:

$$\int d\mathbf{r}_e\, \Delta n(\mathbf{r}_e|\mathbf{r}_p) = \{\gamma(\tilde{n}_e(\mathbf{r}_p)) - 1\} \times \int d\mathbf{r}_e\, n_{e,v}(\mathbf{r}_e) e^{-a(\tilde{n}_e(\mathbf{r}_p))|\mathbf{r}_e-\mathbf{r}_p|} = Q\frac{n_{e,v}(\mathbf{r}_p)}{n_e(\mathbf{r}_p)}. \tag{37}$$

In particular, we determine which value of the screening charge Q reproduces the experimental lifetime. In order to accumulate more charge in the screening cloud, the effective density n_e^* must decrease, and thus we expect the lifetime to decrease monotonically with increasing Q. The scaling of the lifetime with respect to the imposed value of the sum rule is displayed in Fig. 6 and the related values which reproduce experimental lifetimes are given in Table III.

Table III reveals interesting trends. The experimental lifetimes in free-electron-like materials (Li, Na, and Al) are all reproduced with $Q \approx 1$. The d-electron materials, on the other hand, require significantly larger values of Q, especially Cu and Nb. We attribute this to the presence of the $3d$ shell in Cu and the $4p$ shell in Nb, both of which are physically expected to contribute little to the screening of the positron. For Si and diamond, which have strong covalent bonds, we also find an optimal value of Q slightly larger than one. This again is in line with the expectation that screening in these materials is less effective than in metals, a point to which we return in the next paragraph. The sensitivity of the lifetime with respect to changes in Q, see Fig. 6, is related to the density n_e which enters in the sum rule, where lower densities yield greater sensitivity to the choice of Q.

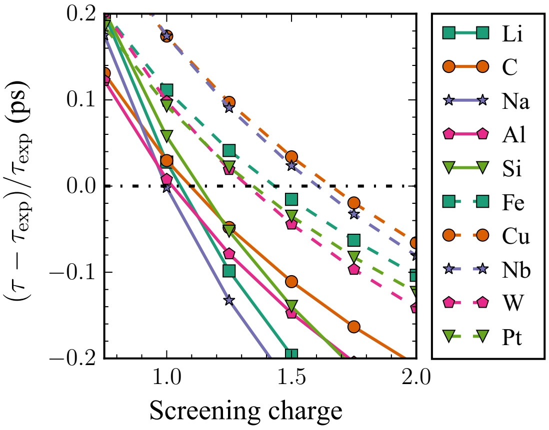

FIG. 6. Scaling of the calculated positron annihilation lifetimes with an imposed screening charge in the sum rule. The results have been obtained with shell partitioning and the Drummond enhancement factor.

Values of $Q > 1$ discussed above seem counterintuitive and deserve further explanation. Physically, we expect the true screening cloud to have $Q < 1$ in a good insulator. Even so, we need to impose $Q > 1$ in the WDA because, like the core electrons, the electron density in the sum rule involves electrons which do not participate efficiently in the screening process, at least not as efficiently as free electrons, which is implicit through the use of the pair-correlation function of the homogeneous electron gas. In order to understand how this plays out technically, assume that the positron is located at a point where the local electron density screens the positron like free electrons, even though there may be some electrons in the neighborhood that are very ineffective in screening, such as the those forming strong covalent bonds. The enhancement effect in this case is described correctly by the LDA evaluated at the local electron density. In the WDA, however, the effective density will generally be higher than the local electron density since the regions where electrons do not participate significantly in screening are often characterized by large local electron densities. Thus, the (approximately) free electrons in the material are located close to local minima, and the conclusions from our simple model of Sec. IV A hold. These considerations also lead to an underestimation of the local enhancement factor. There are two ways to address this problem, as was already indicated in our discussion of the gradient correction in Sec. IV B above. The first approach is to replace the true electron density in the sum rule with a modified value (generally reduced) that takes into account its screening capacity. We investigate this approach within the

TABLE III. Screening charge values that reproduce experimental lifetimes using the WDA scheme with Drummond enhancement term and shell-partitioning.

Li	C	Na	Al	Si	Fe	Cu	Nb	W	Pt
1.06	1.10	1.00	1.02	1.13	1.43	1.66	1.60	1.33	1.35

gradient correction and shell-partitioning schemes. The second approach is to allow the screening cloud to accumulate more than one electron to approximately account for the fact that too many electrons are contained in the electron density that enters in the sum rule equation.

With all this in mind, it is natural to wonder if the results could be improved by applying the gradient correction of Sec. IV B in combination with the shell partitioning. We have investigated this possibility but did not find any improvement. The reason is that the decrease in the effective density turns out to be too small to compensate for the gradient correction to the enhancement term in the lifetime formula, Eq. (30).

The screening charge Q can, in principle, be used as a phenomenological parameter in WDA calculations. (As we have already pointed out, Q defines a material-dependent screening length.) In this vein, we could fit the Q value to reproduce the experimental lifetime in a specific material. This value of Q can then be employed to investigate PAS properties at defects and surfaces/interfaces more generally. This approach will be in the spirit of the hybrid functionals in electronic structure calculations, where a part of the exact exchange is used to correct the band gap. We do not claim that this approach is guaranteed to give a reliable description of the positrons properties and tests will have to point out whether it is useful. Such tests are, however, outside the scope of the current paper.

V. SUMMARY AND OUTLOOK

We have carried out an in-depth study of the WDA approach for describing electron-positron correlations as a basis for constructing a functional, which is suitable for modeling PAS properties of strongly inhomogeneous systems such as surfaces. We critically examined the general theory behind the WDA and the approximations and assumptions underlying earlier related work in the literature [27,28,30]. Positron annihilation lifetimes obtained from the WDA of Ref. [28] were shown to yield poor results due to the (unphysical) involvement of core electrons in the screening of the positron charge. This lead us to consider a gradient correction for removing the large core-electron contribution to the screening cloud, but this approach fails to obtain accurate lifetimes. A shell-partitioning scheme, on the other hand, was shown to yield excellent results for positron lifetimes in free-electron-like materials. The results are somewhat worse for insulators and d-electron systems, though, where not all valence electrons participate in the screening of the positron as free electrons. We have attempted to account for this by combining the gradient correction with the shell partitioning but, unfortunately, found no further improvement of the results. It is expected that more sophisticated versions of the shell partitioning, such as the one from Ref. [30] can further improve the results. Finally, we considered a semiempirical scheme in which the screening charge is described in terms of a single material-specific parameter, which is fitted to reproduce experimental lifetimes; the scheme will then allow effective treatment of positron properties more generally in strongly inhomogeneous regions such as surfaces and large voids. Future tests will have to point out, though, if a realistic description of positron properties in strongly inhomogeneous environments can be obtained in this way.

Notably, we do not expect the WDA and its modifications discussed in this paper to provide more accurate functionals (compared to the standard LDA or GGA schemes) for treating relatively homogenous bulk systems and small defects. Instead, their usefulness lies in the treatment of strongly inhomogeneous systems where the semilocal approximations are known to fail.

Recent work has shown that incorporation of exact constraints on electron-electron correlation functionals can yield improved results in a wide variety of diversely bonded systems [65–67]. It will be interesting to explore the extent to which improvements in WDA-based electron-positron correlation functionals could be obtained along similar lines. A specific example will be the imposition of the Kimball cusp condition [35,37] on the WDA-based electron-positron functional. A different approach to achieve better results would be to move away from results for the homogeneous gas, and instead calculate a pair-correlation function directly from the electronic structure of the material.

ACKNOWLEDGMENTS

V.C. and R.S. were supported by the FWO-Vlaanderen through Project No. G. 0224.14N. Computational resources and services used in this work were in part provided by the VSC (Flemish Supercomputer Center) and the HPC infrastructure of the University of Antwerp (CalcUA), both funded by the FWO-Vlaanderen and the Flemish Government (EWI Department). The work at Northeastern University was supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences Grant No. DE-FG02-07ER46352 (core research), and benefited from Northeastern University's Advanced Scientific Computation Center (ASCC), the NERSC supercomputing center through DOE Grant No. DE-AC02-05CH11231, and support (applications to layered materials) from the DOE EFRC: Center for the Computational Design of Functional Layered Materials (CCDM) under DE-SC0012575.

APPENDIX: DETAILS OF IMPLEMENTATION

This Appendix provides some details of the WDA implementation used in this work. We determine the effective electron density $n_e^*(\mathbf{r})$ and the correlation potential $V_c(\mathbf{r})$ on a regular three-dimensional real space grid. The value of the effective density $n_e^*(\mathbf{r}_p)$ is determined at all grid points by searching for the roots of the sum rule equation. Our algorithm uses an implementation of Brent's method.

Because it is not feasible to accurately integrate the contribution of core and valence charges on the same grid, we separate the total charge density as $n_e(\mathbf{r}) = n_v(\mathbf{r}) + n_c(\mathbf{r})$, where n_v and n_c are the valence and core charge distributions, respectively. The valence electron density is represented on a regular three-dimensional real-space grid, while the core charges are stored on logarithmic radial grids, which are centered around ionic positions. The screening charge is thus calculated as

$$Q = Q^v + \sum_\alpha Q^\alpha, \tag{A1}$$

where Q^v and Q^α are valence and core contributions, respectively. The former can be readily obtained as a weighted sum over all grid points within a selected cutoff radius $R^{\max}$:

$$Q^v = \sum_{r^i \leqslant R^{\max}} w^i n_v^i e^{-ar^i}, \tag{A2}$$

with $n_v^i = n_v(\mathbf{r}_e^i)$, $r^i = |\mathbf{r}_e^i - \mathbf{r}_p|$, and the w^i are the integration weights. Core contributions are taken into account for all ions for which $d^\alpha = |\mathbf{R}^\alpha - \mathbf{r}_p| < R^{\max} + R^{c,\alpha}$, where $\mathbf{R}^\alpha$ denotes the position of the ion and $R^{c,\alpha}$ is its core radius. The contribution of an ion labeled α to the sum rule is given by

$$Q^\alpha = 4\pi \sum_i w^i r^i \left(n_c^\alpha\right)^i f^i \tag{A3}$$

where, for $d \neq 0$,

$$f^i = \frac{1}{2ad^\alpha}\left[\left(\frac{1}{a} + |d^\alpha - r^i|\right)e^{-a|d^\alpha - r^i|} - \left(\frac{1}{a} + |d^\alpha + r^i|\right)e^{-a|d^\alpha + r^i|}\right], \tag{A4}$$

and, for $d = 0$,

$$f^i = r^i e^{-ar^i}. \tag{A5}$$

For the correlation potential, we apply the same partitioning of the valence and core charges. In this case the relevant formulas are

$$V_c^v = \sum_{r^i \leqslant R^{\max}} w^i n_v^i \frac{e^{-ar^i}}{r_i} \tag{A6}$$

and

$$V_c^\alpha = 4\pi \sum_i w^i r^i \left(n_c^\alpha\right)^i f^i, \tag{A7}$$

where

$$f^i = \frac{1}{2ad^\alpha}\left(e^{-a|d^\alpha - r^i|} - e^{-a|d^\alpha + r^i|}\right) \tag{A8}$$

for $d \neq 0$ and

$$f^i = e^{-ar^i} \tag{A9}$$

for $d^\alpha = 0$.

[1] F. Tuomisto and I. Makkonen, Rev. Mod. Phys. **85**, 1583 (2013).

[2] A. P. Mills, Solid State Commun. **31**, 623 (1979).

[3] A. P. Mills, Science **218**, 335 (1982).

[4] K. G. Lynn, W. E. Frieze, and P. J. Schultz, Phys. Rev. Lett. **52**, 1137 (1984).

[5] A. Weiss, R. Mayer, M. Jibaly, C. Lei, D. Mehl, and K. G. Lynn, Phys. Rev. Lett. **61**, 2245 (1988).

[6] K. H. Lee, G. Yang, A. R. Koymen, K. O. Jensen, and A. H. Weiss, Phys. Rev. Lett. **72**, 1866 (1994).

[7] J. H. Kim, S. Wheeler, A. Nangia, E. Jung, and A. H. Weiss, Appl. Surf. Sci. **116**, 324 (1997).

[8] J. Mayer, C. Hugenschmidt, and K. Schreckenbach, Phys. Rev. Lett. **105**, 207401 (2010).

[9] T. Tachibana, T. Hirayama, and Y. Nagashima, Phys. Rev. B **89**, 201409 (2014).

[10] A. C. L. Jones, H. J. Rutbeck-Goldman, T. H. Hisakado, A. M. Piñeiro, H. W. K. Tom, A. P. Mills, B. Barbiellini, and J. Kuriplach, Phys. Rev. Lett. **117**, 216402 (2016).

[11] S. Mukherjee, M. P. Nadesalingam, P. Guagliardo, A. D. Sergeant, B. Barbiellini, J. F. Williams, N. G. Fazleev, and A. H. Weiss, Phys. Rev. Lett. **104**, 247403 (2010).

[12] S. F. Mukherjee, K. Shastry, and A. H. Weiss, Phys. Rev. B **84**, 155109 (2011).

[13] V. Callewaert, K. Shastry, R. Saniz, I. Makkonen, B. Barbiellini, B. A. Assaf, D. Heiman, J. S. Moodera, B. Partoens, A. Bansil, and A. H. Weiss, Phys. Rev. B **94**, 115411 (2016).

[14] V. A. Chirayath, V. Callewaert, A. J. Fairchild, M. D. Chrysler, R. W. Gladen, A. D. Mcdonald, S. K. Imam, K. Shastry, A. R. Koymen, R. Saniz, B. Barbiellini, K. Rajeshwar, B. Partoens, and A. H. Weiss, Nat. Commun. **8**, 16116 (2017).

[15] S. W. H. Eijt, A. T. van Veen, H. Schut, P. E. Mijnarends, A. B. Denison, B. Barbiellini, and A. Bansil, Nat. Mater. **5**, 23 (2006).

[16] S. W. H. Eijt, P. E. Mijnarends, L. C. van Schaarenburg, A. J. Houtepen, D. Vanmaekelbergh, B. Barbiellini, and A. Bansil, Appl. Phys. Lett. **94**, 091908 (2009).

[17] W. Shi, S. W. H. Eijt, C. S. Suchand Sandeep, L. D. A. Siebbeles, A. J. Houtepen, S. Kinge, E. Brück, B. Barbiellini, and A. Bansil, Appl. Phys. Lett. **108**, 081602 (2016).

[18] B. Chakraborty and R. W. Siegel, Phys. Rev. B **27**, 4535 (1983).

[19] E. Boronski and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).

[20] N. D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973).

[21] R. M. Nieminen and M. J. Puska, Phys. Rev. Lett. **50**, 281 (1983).

[22] N. G. Fazleev, J. L. Fry, and A. H. Weiss, Phys. Rev. B **70**, 165309 (2004).

[23] N. G. Fazleev and A. H. Weiss, J. Phys. Conf. Ser. **443**, 012038 (2013).

[24] S. Hagiwara, C. Hu, and K. Watanabe, Phys. Rev. B **91**, 115409 (2015).

[25] S. Hagiwara and K. Watanabe, J. Phys. Soc. Jpn. **85**, 114703 (2016).

[26] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

[27] K. O. Jensen and A. B. Walker, J. Phys. F **18**, L277 (1988).

[28] A. Rubaszek, Phys. Rev. B **44**, 10857 (1991).

[29] A. Rubaszek, A. Kiejna, and S. Daniuk, J. Phys.: Condens. Matter **5**, 8195 (1993).

[30] A. Rubaszek, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **58**, 11285 (1998).

[31] N. D. Drummond, P. López Ríos, R. J. Needs, and C. J. Pickard, Phys. Rev. Lett. **107**, 207402 (2011).

[32] I. Makkonen, M. M. Ervasti, T. Siro, and A. Harju, Phys. Rev. B **89**, 041105 (2014).

[33] Formally, this statement is correct only for finite systems. In an infinite system, the integral over the correlation hole could strictly take a finite value [35].
[34] H. Stachowiak, Phys. Rev. B **41**, 12522 (1990).
[35] N. D. Drummond, P. López Ríos, C. J. Pickard, and R. J. Needs, Phys. Rev. B **82**, 035107 (2010).
[36] H. Stachowiak and J. Lach, Phys. Rev. B **48**, 9828 (1993).
[37] J. C. Kimball, Phys. Rev. A **7**, 1648 (1973).
[38] J. Arponen, J. Phys. C **11**, L739 (1979).
[39] P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).
[40] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[41] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[42] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[43] R. W. G. Wyckoff, *Crystal Structures 1* (Interscience, New York, 1963), pp. 7–83.
[44] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[45] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[46] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[47] I. Makkonen, M. Hakala, and M. J. Puska, Phys. Rev. B **73**, 035103 (2006).
[48] B. Barbiellini and J. Kuriplach, Phys. Rev. Lett. **114**, 147401 (2015).
[49] W. Brandt and J. Reinheimer, Phys. Rev. B **2**, 3104 (1970).
[50] W. Brandt and J. Reinheimer, Phys. Lett. A **35**, 107 (1971).
[51] G. M. Dunn, K. O. Jensen, and A. B. Walker, J. Phys.: Condens. Matter **3**, 2049 (1991).
[52] Here we assume that the electron density varies smoothly on the length scale of the decay length $1/a$.
[53] B. Barbiellini, M. J. Puska, T. Torsti, and R. M. Nieminen, Phys. Rev. B **51**, 7341 (1995).
[54] J. Kuriplach and B. Barbiellini, Phys. Rev. B **89**, 155111 (2014).
[55] A. Rubaszek, Z. Szotek, and W. M. Temmerman, Acta Phys. Pol. A **95**, 652 (1999).
[56] M. J. Puska and R. M. Nieminen, J. Phys. F **13**, 333 (1983).
[57] K. O. Jensen, J. Phys.: Condens. Matter **1**, 10595 (1989).
[58] T. Jarlborg and A. K. Singh, Phys. Rev. B **36**, 4660 (1987).
[59] F. Plazaola, A. P. Seitsonen, and M. J. Puska, J. Phys.: Condens. Matter **6**, 8809 (1994).
[60] B. Barbiellini, M. J. Puska, T. Korhonen, A. Harju, T. Torsti, and R. M. Nieminen, Phys. Rev. B **53**, 16201 (1996).
[61] A. Rubaszek, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **63**, 165115 (2001).
[62] J. Laverock, T. D. Haynes, M. A. Alam, and S. B. Dugdale, Phys. Rev. B **82**, 125127 (2010).
[63] H. Przybylski and G. Borstel, Solid State Commun. **49**, 317 (1984).
[64] H. Przybylski and G. Borstel, Solid State Commun. **52**, 713 (1984).
[65] J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015).
[66] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, Nat. Chem. **8**, 831 (2016).
[67] I. G. Buda, C. Lane, B. Barbiellini, A. Ruzsinszky, J. Sun, and A. Bansil, Sci. Rep. **7**, 44766 (2017).