First-Principles Study of a Positron Immersed in an Electron Gas

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Calculations of the relaxation energy, contact pair-correlation function, and annihilating-pair momentum density for a single positron immersed in a homogeneous electron gas are presented. We achieve an accurate description of the electron-positron correlation effects by working in the reference frame in which the positron is stationary and using a mean-field approach based on single-component density functional theory. Our positron relaxation energies and annihilation rates are similar to those from the best existing many-body calculations. Our annihilating-pair momentum densities are significantly different from previous data, and include a “tail” beyond the Fermi edge.

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Quantum impurity problems are of widespread interest in condensed matter physics. Here we study a positron in a homogeneous electron gas (HEG) as an example of an impurity problem in which a particle of one species is immersed in a fluid of another species, and where quantum effects are important for both the host and impurity. Examples of other problems of this type are the Mahan exciton in semiconductor physics, in which a hole in the valence band interacts with an electron gas in the conduction band (or an electron interacts with a hole gas), and an impurity atom in a Bose-Einstein condensate. Our approach requires knowledge of the explicit interaction between the host and impurity particles and the availability of a reasonably accurate mean-field description of the host, such as the Kohn-Sham density functional theory (DFT) of electrons or the Gross-Pitaevskii equation for Bose-Einstein condensates. An important characteristic of our approach is the inclusion of nonadiabatic impurity-host effects. We have chosen to present results for the positron problem, firstly, because they can be compared with data in the literature to gauge their accuracy and, secondly, because nonadiabatic effects are expected to be important as the electron and positron are of equal mass. Applications of our method to other problems such as those mentioned above require only straightforward modifications.

On entering condensed matter, a low-energy positron thermalizes rapidly and may be trapped by open-volume
defects such as vacancies, where the nuclear repulsion is weak. The positron lifetime is measured as the time interval between the detection of a photon emitted in the $\beta^+$ radioactive decay that produces the positron and the detection of the two 0.511 MeV photons emitted when the positron annihilates an opposite-spin electron. The lifetime is characteristic of the defect at which the positron settles, and positron annihilation spectroscopy is an important, non-destructive technique for characterizing open-volume defects. Measuring the Doppler broadening of the annihilation radiation or the angular correlation between the two 0.511 MeV photons yields information about the momentum density of the electrons in the presence of the positron. Modeling is then required to extract information about the unperturbed system from the experimental data.

The most widely used method for modeling positrons in real materials is two-component DFT, in which the interaction between the electrons and the positron is described by a functional of the densities of the electron and positron components. Within the local density approximation (LDA), this functional is obtained directly from the relaxation energy $\Delta \Omega$ of a positron in a HEG, which is the difference between the energy of a HEG with and without a positron immersed in it. Equivalently, $\Delta \Omega$ is the electron-positron correlation energy.

Two-component DFT can lead to accurate electron and positron densities, but the DFT orbitals yield very poor annihilating-pair momentum densities (MDs) $\rho(p)$ and electron-positron pair-correlation functions (PCFs) $g(r)$ because they do not include the full effects of the strong electron-positron correlation. The results can, however, be substantially improved by correcting the calculated PCFs and MDs using accurate data for a positron in a HEG. The effective electron density felt by the positron, and hence the annihilation rate, is proportional to the contact PCF between the positron and the electrons, $g(0)$. The annihilation rate for a positron immersed in a paramagnetic HEG is $\lambda = 3g(0)/(4c^3r_s^3)$, where $r_s$ is the electron density parameter, and $c$ is the speed of light in vacuo. If the electron and positron motions were uncorrelated then $g(0)$ would be unity, but the strong Coulomb attraction leads to much larger values, particularly at low densities, where a bound state may be formed. Together, our results for $\Delta \Omega$, $g(0)$, and $\rho(p)$ permit the construction of a two-component DFT within the LDA for a positron in a HEG, which in turn will enable the calculation of the annihilation rates and MDs used to interpret the results of positron annihilation experiments.

We follow the suggestion of Leung et al. that it is useful to describe a positron in a HEG using the set of electron positions relative to the position of the positron, $\{x_i\}$. Neglecting the center-of-mass motion, which is zero in the
ground state, the Hamiltonian becomes

$$\hat{H} = -\sum_i \left[ \nabla_i^2 - v_1(x_i) \right] + \sum_{j>i} \left[ v(x_i - x_j) - \nabla_i \cdot \nabla_j \right],$$

(1)

where $v_1$ is the interaction between the positron impurity and the electrons and $v$ is the interaction between the electrons. In this reference frame the Hamiltonian describes interacting fermions of mass $1/2$ a.u. and charge $-1$ a.u. with a fixed positive charge of magnitude $1$ a.u. at the origin, and an extra attractive interaction $\hat{V}_e = -\sum_{j>i} \nabla_i \cdot \nabla_j$, which resembles the mass-polarization term encountered in atomic physics when transforming to the center-of-mass frame. The advantage of this formulation is that the mean-field single-determinant approximation for the solution to Eq. (1) includes explicit electron-positron correlation via the $v_1$ term, whereas in the laboratory frame the ground state consists of a completely delocalized positron and a HEG. Leung et al. [9] did not, however, calculate the single-determinant approximation to the solution of Eq. (1), but instead they neglected $\hat{V}_e$ and noted that the resulting Hamiltonian is the same as for a fixed “proton” in an “electron gas” with particle mass $1/2$ a.u. Unfortunately this approximation is a gross violation of the properties of the system, as the magnitude of the expectation value of the neglected term is approximately equal to the kinetic energy of the system in the laboratory frame.

We have formulated a mean-field theory for the problem in which the ground-state charge density of the Hamiltonian of Eq. (1) is approximated by that arising from a single determinant of orbitals $\phi_i(x)$, and the exchange-correlation effects between the electrons are described by a density functional $E_{xc}[n]$. The resulting mean-field equations are

$$\left[ -\nabla^2 + \int n(x') v(x - x') \, dx' + v_1(x) + \frac{\delta E_{xc}[n]}{\delta n(x)} \right] \phi_i(x) + \sum_j f_j \langle \phi_j | \nabla \phi_i \rangle \cdot \nabla \phi_j(x) = E_i \phi_i(x),$$

(2)

where $n(x)$ is the electron density, $f_i$ is the occupation of orbital $i$ and $E_i$ is the orbital eigenvalue. All our DFT calculations were performed with orbitals at zero wave vector and with closed-shell configurations, in which case (i) the center-of-mass kinetic energy is zero in the ground state and (ii) the direct term in the expectation value of the extra interaction $\hat{V}_e$ is zero, which has been assumed to be the case in Eq. (2).

The plane-wave DFT code Castep [10] was modified to allow the solution of Eq. (2). We have used the LDA exchange-correlation functional in all our calculations. It was verified that the results were essentially unchanged when a generalized-gradient-approximation functional was used instead. To minimize finite-size effects, the density at the edge of the cell should be close to the target density, but the screening of the positron implies that an additional electron is attracted to the center of the cell. To reduce the finite size effects we therefore define the $r_s$ parameter via
\( \frac{4}{3} \pi r_s^3 = V/(N - 1) \), where \( V \) is the volume of the cell and \( N \) is the number of electrons. Our calculations were performed in simple cubic cells and we used the Ewald interaction to describe the Coulomb interactions. We have also restricted our attention to paramagnetic HEGs, although it is straightforward to apply our method to spin-polarized HEGs.

Our relaxation energies were extrapolated to basis-set completeness using the empirically derived expression
\[
\Delta \Omega_{E_{\text{cut}}} = \Delta \Omega_\infty + \kappa E_{\text{cut}}^{-4/3},
\]
where \( \kappa \) is a fitting parameter and \( E_{\text{cut}} \) is the plane-wave cutoff energy. We estimate the residual finite-size errors in our DFT relaxation energies to occur in the third significant figure. The fit to our data shown in Fig. 4 is
\[
\Delta \Omega(r_s) = \frac{A_{-1}r_s^{-1} + A_0 + A_1r_s - 0.262005B_2r_s^2}{1 + B_1r_s + B_2r_s^2},
\]
where \( A_{-1} = -0.28877, A_0 = -0.22339, A_1 = 0.011536, B_1 = 0.012331, \) and \( B_2 = 0.020016 \). This fitting form tends to the energy of the Ps\(^-\) ion at low density \([11]\) and could be used as the LDA electron-positron correlation functional in a two-component DFT calculation for a positron in a real system. Equation 3 does not yield the exact high-density behavior calculated within the random phase approximation, although this is only relevant for \( r_s < 0.1 \) \([12]\).

Our relaxation-energy results are in reasonable agreement with the many-body-theory results of Refs. \([13] \) and \([15] \), but are in clear disagreement with the quantum Monte Carlo (QMC) data of Ref. \([16] \). The orbitals in the trial wave functions used in the QMC calculations reported in Refs. \([16] \) and \([17] \) were single plane waves for the electrons and the positron, which do not allow for the strong pairing that occurs between the electrons and the positron at low density. In common with the most accurate many-body-theory results, our relaxation energy is higher than the energy of a Ps atom at the lowest density considered of \( r_s = 8 \). Neglecting the extra interaction \( \hat{V}_e \) as suggested by Leung et al. \([9] \) leads to relaxation energies that increase monotonically towards the DFT-LDA energy of a Ps atom.

The annihilating-pair MD depends sensitively on the accuracy of the correlated electron-positron pairing \( \phi_i(x) \) and we expect that our fully self-consistent treatment of the pairing orbitals will be more accurate than previous approaches \([18, 19] \). The MD at each momentum \( p \) was extrapolated to basis-set completeness using the empirically determined expression
\[
\rho_{E_{\text{cut}}}(p) = \rho_\infty(p) + \alpha(p)/E_{\text{cut}} + \beta(p)/E_{\text{cut}}^{3/2},
\]
where \( \alpha(p) \) and \( \beta(p) \) are fitting parameters. As the system size is increased, the momenta at which the MD is defined become more finely spaced and the finite-size errors at each point are reduced. We have therefore fitted a model curve to our MD data obtained at the largest system size available at each density. We have verified that our results are well-converged with respect to system size. Below the
FIG. 1: (Color online) Relaxation energy against density parameter. Results obtained with $N = 114, 162,$ and $246$ electrons for $1 \leq r_s \leq 3.5$, with $N = 54, 114,$ and $162$ electrons for $4 \leq r_s \leq 6.5$, and with $N = 14, 54,$ and $114$ electrons for $7 \leq r_s \leq 8$ were averaged to obtain the final results. Also shown are the relaxation energies obtained by other authors [13–16]. The dashed line following the data of Arponen and Pajanne [13] is the widely used fit of Boronski and Nieminen [6]. The energy of the Ps$^-$ ion is taken from Ref. [11].

Fermi wave vector $k_F$ we fit $\rho(p) = w_0 + w_2 p^2 + w_4 p^4$ to our MD data, where $w_0$, $w_2$, and $w_4$ are fitting parameters. Above $k_F$ the DFT-calculated MD falls off exponentially and so we fit $\rho(p) = W \exp(-sp)$ to our data, where $W$ and $s$ are fitting parameters.

Electron-positron annihilating-pair MDs at different densities are plotted in Fig. 2. The normalization is chosen such that $\int_0^\infty 4\pi p^2 \rho(p) \, dp = (4/3)\pi k_F^3$. Our results clearly show the enhancement of the annihilating-pair MD at the Fermi edge predicted by Kahana [18], but our MD data differ quantitatively from the previous results [18, 19] for $1 \leq r_s \leq 8$. In this range, we find the greatest enhancement of the MD at the Fermi edge at $r_s = 1$, whereas the previous works [18, 19] found the enhancement of the MD to increase when the density is lowered. The previous works [18, 19] did not report the weight in the MDs above the Fermi edge. In our calculations the exponential tail of the MD above the Fermi edge carries an increasing amount of weight as the density is lowered, which is responsible
for the decrease in the enhancement that we find at the Fermi edge. We find the exponent $s$ to be of the order of $r_s$ over the range of densities we have studied. It is essential to include the extra interaction when calculating the MD: omitting it results in a dramatic increase in the enhancement at the Fermi edge and substantial transfer of weight beyond the Fermi edge, as shown in Fig. 2. The Kohn-Sham orbitals do not describe the electron-electron correlation. Such correlation effects (i) tend to oppose the enhancement at the Fermi edge, particularly at low densities, and (ii) introduce an algebraically decaying tail in the MD.

The electron-positron PCF $g(r)$ is proportional to the charge density in the frame in which the positron is stationary. However, the fact that we used a plane-wave basis set for our orbitals results in a significant finite-basis error near $r = 0$, because the Kimball cusp condition [20] is not satisfied. We therefore extrapolated the contact PCF to basis-set

\[ \rho(p) \]

**FIG. 2:** (Color online) Annihilating-pair MDs $\rho(p)$ for different densities. $k_F$ is the Fermi wave vector. The solid lines show the MDs calculated with the extra interaction included; the dotted line shows the MD calculated at $r_s = 8$ without the extra interaction. Model functions have been fitted to the results obtained with $N = 406$ electrons at $r_s = 1$, $N = 246$ electrons for $2 \leq r_s \leq 7$, and $N = 162$ electrons at $r_s = 8$. MD data calculated by Kahana [18] and Stachowiak [19] using other approaches are also shown.
FIG. 3: (Color online) Electron-positron contact PCF $g(0)$ against density parameter $r_s$. The results were obtained by averaging the $g(0)$ values obtained in cells with $N = 114, 162,$ and 246 electrons for $1 \leq r_s \leq 7$ and $N = 114$ and 162 at $r_s = 8$. Various contact PCF results from the literature are also shown.

Completeness by fitting our data to the empirically determined expression $g_{E_{\text{cut}}}(0) = g_{\infty}(0) + a/E_{\text{cut}}^{1/2} + b/E_{\text{cut}}$, where $a$ and $b$ are fitting parameters. The residual finite-size error in $g(0)$ is less than about 1%.

The electron-positron contact PCF is plotted in Fig. 3. Adapting the fitting form of Ref. [6] slightly, we represent our contact PCF data by

$$g(0) = 1 + 1.23r_s + a_{3/2}r_s^{3/2} + a_2r_s^2 + a_{7/3}r_s^{7/3} + a_{8/3}r_s^{8/3} + 0.173694r_s^3,$$  

where $a_{3/2} = -1.56672$, $a_2 = 4.16983$, $a_{7/3} = -3.579$, and $a_{8/3} = 0.836389$. Equation (4) satisfies both the high-density (random phase approximation) [12] and low-density (Ps$^-$) limiting behavior [11].

The extra interaction reduces the contact PCF at all the densities we have studied, by about 8% at $r_s = 1$, rising to about 15% at $r_s = 8$. Our electron-positron PCF results are in reasonably good agreement with the many-body-theory results of [13, 14, 21, 22], but are in strong disagreement with the QMC results [16, 17], which give much smaller
values for the reasons discussed earlier.

In summary we have used a modified one-component DFT code to calculate the relaxation energy, contact PCF, and annihilating-pair MD of a single positron in a HEG by working in the frame in which the positron is stationary. It is interesting to observe that the data required to parameterize a two-component exchange-correlation density functional can be obtained using one-component DFT calculations. Our results for the positron relaxation energies and annihilation rates are in broad agreement with earlier theoretical work based on many-body-theory results. The annihilating-pair MDs are particularly sensitive to the description of the electron-positron correlation. We have reported MDs for a wider range of densities than previous studies, and our calculations extend above the Fermi edge where we find an exponential decay of the MD with momentum.

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