Positron-electron annihilation in the proximity of a second electron in a dense medium

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Annihilation rates for a positron interacting with two unpaired-spin electrons in a dense environment have been calculated in terms of parameters having the physical meaning of electron-positron contact densities. The influence on annihilation rates of an external magnetic field has been explicitly taken into account. The results of the theory have been fitted to recent experimental data showing the formation in some polymers of a positron bound state with "anomalous" spin characteristics.

I. INTRODUCTION

In the study of positron annihilation in condensed matter, modifications of lifetime spectra and of momentum distributions depending on an applied magnetic field demonstrate the interaction of a positron with an electron ensemble having nonzero magnetic moment, and are generally taken as the evidence for the existence of a bound state of the positron with an electron (see examples in Refs. 1 and 2). The basis of this assumption is the extension to condensed matter of well known properties of positronium (Ps) in vacuum or in a dilute medium; the effect of the magnetic field on Ps is to mix singlet and triplet spin states, thereby producing the increase of probability of two-quantum annihilation, which is a forbidden mode for pure triplet states (for reviews on Ps, see for instance Refs. 3 and 4). In fact, predictions based on a straightforward extension of the theory[5] of the magnetic effect on unperturbed Ps to e^+-e^- bound states in a dense environment[2,6] often given satisfactory agreement with experiment. In these cases, the theoretical curves can be fitted to experimental data by adjusting a parameter proportional to the effective unpaired-spin electron density at the positron position (here called internal contact density). For this reason, measurements of magnetic effects on annihilation are not only helpful for identifying positron-electron bound systems, but also probe the internal structure of these systems (a systematic discussion on this subject can be found in Ref. 7).

Recently, however, a series of experiments revealed the existence of cases where the Ps scheme is inadequate.[8–13] This is certainly not a surprise. A positron in a dense medium interacts with many indistinguishable mobile electrons in an external fixed field; under these conditions, the spin alignment of the annihilating pair can be defined, and is a conserved observable, only in restricted cases,[7] i.e., when (a) no other electron with unpaired spin is in the proximity of the pair, (b) spin coupling to the field seen by the pair in motion is negligible, and (c) the relative motion of the two particles bound in the pair is described by a wave function with s character (no spin-orbit interaction). Condition (c) is not severe: since only s states contribute to annihilation, the very fact that the effects of internal annihilation of the pair can be observed ensures that the internal pair wave function has at least partial s character; thus, the effect of the spin-spin interaction, typical of s states, is always present and is likely to be dominant over spin-orbit terms (for instance, the energy splitting between different spin states in the positronium $2p$ state is ony 5% of the hyperfine splitting, i.e., the spin-spin contribution, in the $1s$ state.[14] On the contrary, effects connected to a violation of conditions (a) and (b) need to be evaluated with reference to specific situations.

Unfortunately, a first-principles approach to a complicated many-body system, as a positron in a dense environment actually is, remains intractable in this case. We are thus left with treatments based on simplified models. Along this direction, in a previous work[15] we have presented an approximate treatment dealing with violations of condition (b); here, we address violations of condition (a) by discussing the case of a positron interacting at the same time with two unpaired electrons and, possibly, with a dense environment in a closed-shell configuration. There are founded arguments against the stability of the simplest example of a system of this class, i.e., an excited state of the negative positronium ion (Ps^-) in vacuum,[16,17] but, on the other hand, it is easy to imagine more practical situations. Here are a few examples: (1) free electrons coming from the positron excitation spur are trapped in neighboring sites in the medium (e.g., on the same polymer molecule) and, in turn, trap the positron (see Fig. 1, borrowed from Ref. 18); (2) positronium formed in a liquid medium reacts by forming an additive complex with a paramagnetic solute; (3) an energetic positron excites a neutral atom or molecule by promoting an

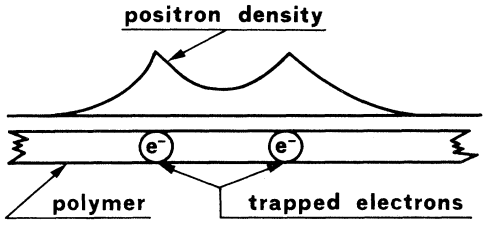

FIG. 1. Positron bound to two unpaired-spin electrons trapped in adjacent sites on a polymer chain. The cusps of the positron density do not need to be equal (from Ref. 15).

electron from a filled to an unoccupied shell, and sticks to it, thus forming a positive complex; (4) an energetic positron in an insulating crystal promotes an electron from the valence to the conduction band, and forms with it, and with the hole left in the valence band, a more or less mobile positron-exciton complex.[6] A somewhat different situation occurs when the positron is bound to one electron only, and the interaction with a second unpaired electron can be described as a collision. Collisions with possibility of spin exchange are included in the Mills theory of Ps magnetic quenching,[19] but neither this theory nor any of the existing treatments of magnetic quenching (see references in Ref. 19) applies to bound states of a positron with two unpaired electrons. The problem is solved, under some restrictive hypotheses, in the present work.

In Sec. II we develop the mathematical formalism enabling us to calculate the annihilation rates of the eight possible states of lowest energy in the presence of a static magnetic field. We obtain numerical results in some exemplificative cases (Sec. III), and compare predictions based on our model with the experimental data given by Bisi *et al.*[9] (Sec. IV).

II. FORMALIZATION OF THE PROBLEM

We attack the problem of calculating the annihilation rates for the system "positron+two unpaired electrons+environment" by looking for the eigenvalues of a suitable Hamiltonian formed by real terms, which account for energy contributions due to spin-spin and spin-magnetic field interactions, as well as by imaginary terms, which account for different annihilation channels. We do not include spin-orbit terms in the Hamiltonian; this is a crucial simplification, as it enables us to separate spatial and spin variables and to diagonalize the Hamiltonian by taking into account only the spin-dependent part of the eigenfunctions. As far as it goes, a justification for this approximation comes from the considerations made in Sec. I on the smallness of spin-orbit terms when annihilation is observable.

We thus assume a Hamiltonian H given by the sum of the following terms:

(i) A "positional" term H_0, accounting for the kinetic energy and for the electrostatic interaction between mobile particles and between each one of these and the environment; we do not include in H_0 the Coulomb terms giving energy splitting between eigenstates of even or odd symmetry under electron position exchange, but we introduce afterwards an "exchange" term to correct for this [see point (vi) below]; we assume that the only eigenstates of H_0 energetically accessible to the system correspond to the lowest eigenvalue (taken as the ground level for the energy scale).

(ii) A term H_a accounting for the spin interaction between the positron and one of the unpaired-spin electrons (labeled as electron a), and for the annihilation with this electron:

$$H_a = 8\pi a_0^3 \delta(\mathbf{r}_p - \mathbf{r}_a) \left[\frac{\Sigma_a + 1}{2} \left(\Delta_{\rm hf} - i\hbar \frac{\lambda_t}{2} \right) + \frac{\Sigma_a - 1}{2} i\hbar \frac{\lambda_s}{2} \right] . \quad (1)$$

In this equation, the δ function takes into account the quasi-contact character of the interaction, the factor $8\pi a_0^3$ is the reciprocal of the electron-positron contact density in Ps, Σ_a is the operator that interchanges the spin states of the positron and of electron a, $\Delta_{\rm hf}$ is the hyperfine splitting in Ps , λ_t and λ_s are the triplet and singlet annihilation rates for Ps. [An equivalent expression of H_a, reminiscent of the Fermi contact operator, can be written in terms of the dot product of the Pauli spin matrices σ. Note that $\Sigma_a = (\sigma_a \cdot \sigma_p + 1)/2$];

(iii) A term H_b, similar to H_a, to account for spin-dependent interactions of the positron with a second unpaired electron (electron b).

(iv) A term $H_{\text{pick-off}}$ accounting for annihilation with the $2N$ electrons forming the closed-shell environment:

$$H_{\text{pick-off}} = -i\hbar\lambda_{\text{pick-off}}/2 . \quad (2)$$

(v) A term H_m accounting for the interaction of the external magnetic field B with the spin magnetic moments:

$$H_m = \mu_B B(\sigma_{a_z} + \sigma_{b_z} - \sigma_{p_z}) , \quad (3)$$

where the σ's are Pauli spin operators along the direction of B.

(vi) A term accounting for the energy separation $\Delta_{\rm ex}$ between singlet and triplet states of the electron pair, which combines the Coulomb effects that we have not included in H_0 with that of the magnetic interaction between electron spins; due to the Pauli principle, which couples spatial eigenfunctions with spin eigenfunctions of reversed electron exchange symmetry, this term can be expressed as function of the electron spin exchange operator $\Sigma_{\rm el}$ in the form

$$H_{\rm ex} = \Delta_{\rm ex}(1 - \Sigma_{\rm el})/2 . \quad (4)$$

The effect of the terms listed above is to remove the 8-fold spin degeneracy of each level of the spatial Hamiltonian H_0. In order to find the spectrum of the octet corresponding to the ground level of H_0, we express the complete Hamiltonian in matrix form by taking as a basis a complete set of space and spin eigenfunctions, belonging to the eigenvalue $E_0 = 0$ of H_0. The Pauli principle

dictates that the chosen eigenfunctions need to be antisymmetrical for the exchange of any pair of electrons. We shall assume that this condition is implicitly satisfied as far as it concerns the $2N$ electrons occupying closed-shell orbitals,[20] while we take it explicitly into account for the electron-a–electron-b pair by choosing the following basis:

$$\begin{aligned}
\xi_1&=\Phi_+\chi_{00}(a,b)\alpha(p)\ ,\\
\xi_2&=\Phi_+\chi_{00}(a,b)\beta(p)\ ,\\
\xi_3&=\Phi_-\chi_{11}(a,b)\alpha(p)\ ,\\
\xi_4&=\Phi_-\chi_{11}(a,b)\beta(p)\ ,\\
\xi_5&=\Phi_-\chi_{10}(a,b)\alpha(p)\ ,\\
\xi_6&=\Phi_-\chi_{10}(a,b)\beta(p)\ ,\\
\xi_7&=\Phi_-\chi_{1-1}(a,b)\alpha(p)\ ,\\
\xi_8&=\Phi_-\chi_{1-1}(a,b)\beta(p)\ .
\end{aligned}\tag{5}$$

The symbols used in Eq. (5) have the following meaning:

(a) Φ_+ and Φ_- are ground-state eigenfunctions of H_0; the symmetry under coordinate exchange between a and b is even for Φ_+ and odd for Φ_-.

(b) $\chi_{jm}(a,b)$ is an eigenfunction of the modulus and of the z component of the electron spin operator for the a-b pair, corresponding to the total spin quantum number j and to the azimuthal quantum number m.

(c) $\alpha(p)$ and $\beta(p)$ are the spin eigenfunctions for the positron alone.

For obtaining concise expressions for the Hamiltonian matrices, it is convenient to adopt the following compact notation:

$$\alpha=2\left[\Delta_{\rm hf}-i\hbar\lambda_t/2\right]\ ,\tag{6}$$

$$\beta=\Delta_{\rm hf}-i\hbar(\lambda_t+\lambda_s)/2\ ,\tag{7}$$

$$\gamma=\Delta_{\rm hf}-i\hbar(\lambda_t-\lambda_s)/2\ .\tag{8}$$

We also define the "symmetrized" electron-positron contact densities as follows:

$$\kappa_{++}=8\pi a_0^3\langle\Phi_+|\delta(\mathbf{r}_p-\mathbf{r}_a)|\Phi_+\rangle\ ,\tag{9}$$

$$\kappa_{--}=8\pi a_0^3\langle\Phi_-|\delta(\mathbf{r}_p-\mathbf{r}_a)|\Phi_-\rangle\ ,\tag{10}$$

$$\kappa_{+-}=8\pi a_0^3\langle\Phi_+|\delta(\mathbf{r}_p-\mathbf{r}_a)|\Phi_-\rangle\ ,\tag{11}$$

$$\kappa_{-+}=8\pi a_0^3\langle\Phi_-|\delta(\mathbf{r}_p-\mathbf{r}_a)|\Phi_+\rangle\ .\tag{12}$$

In the next section we shall discuss how the symmetrized contact densities are related to the contact densities defined in Refs. 7 and 18. Here we limit ourselves to noting that, due to the electron indistinguishability, the value of $\kappa_{++},\kappa_{--},\kappa_{+-},\kappa_{-+}$ would not change using $\delta(\mathbf{r}_p-\mathbf{r}_b)$ instead of $\delta(\mathbf{r}_p-\mathbf{r}_a)$ in Eqs. (9)–(12). The second point to be noted is that we are free to assume $\kappa_{+-}=\kappa_{-+}$ since Φ_+,Φ_- can be taken real without loss of generality.

Using the above notation, one obtains

(i) $H_0=0$, (13)

(ii) $$H_a=\frac{1}{2}\begin{pmatrix}
\kappa_{++}\frac{\alpha+\beta}{2} & 0 & 0 & -\frac{\kappa_{+-}}{\sqrt{2}}\gamma & \frac{\kappa_{+-}}{2}\gamma & 0 & 0 & 0\\
0 & \kappa_{++}\frac{\alpha+\beta}{2} & 0 & 0 & 0 & -\frac{\kappa_{+-}}{2}\gamma & \frac{\kappa_{+-}}{\sqrt{2}}\gamma & 0\\
0 & 0 & \kappa_{++}\alpha & 0 & 0 & 0 & 0 & 0\\
-\frac{\kappa_{+-}}{\sqrt{2}}\gamma & 0 & 0 & \kappa_{--}\beta & \frac{\kappa_{--}}{\sqrt{2}}\gamma & 0 & 0 & 0\\
\frac{\kappa_{-+}}{2}\gamma & 0 & 0 & \frac{\kappa_{--}}{\sqrt{2}}\gamma & \kappa_{--}\frac{\alpha+\beta}{2} & 0 & 0 & 0\\
0 & -\frac{\kappa_{-+}}{2}\gamma & 0 & 0 & 0 & \kappa_{--}\frac{\alpha+\beta}{2} & \frac{\kappa_{--}}{\sqrt{2}}\gamma & 0\\
0 & \frac{\kappa_{-+}}{\sqrt{2}}\gamma & 0 & 0 & 0 & \frac{\kappa_{--}}{\sqrt{2}}\gamma & \kappa_{--}\beta & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \kappa_{--}\alpha
\end{pmatrix}\ ,\tag{14}$$

(iii) $H_b=H_a$, (15)

(iv) $H_{\text{pick-off}}=-i\hbar\frac{\lambda_{\text{pick-off}}}{2}\,\text{diag}(1,1,1,1,1,1,1,1)$, (16)

(v) $H_m=\mu_B B\,\text{diag}(-1,1,1,3,-1,1,-3,-1)$, (17)

(vi) $H_{\rm ex}=\Delta_{\rm ex}\,\text{diag}(1,1,0,0,0,0,0,0)$. (18)

In the above equations, diag$(a,b,c,\ldots)$ indicates a diagonal matrix with elements $(a,b,c\ldots)$. The sum of the terms from (i) to (vi) gives the complete Hamiltonian H for the functional space associated with the ground state of H_0. If the proper values are assigned to the various parameters, the eight complex eigenvalues ε_i of H can be determined by using a numerical procedure. The annihilation rates are then simply given by the relationship

$$\lambda_j = -2\,\mathrm{Im}(\varepsilon_j)/\hbar \ . \tag{19}$$

Several examples of numerical calculations are presented below.

III. NUMERICAL CALCULATIONS

The aim of this section is to demonstrate how the formalism developed in the previous section can be adapted to different physical situations, and to show the effect of the different parameters of H on the annihilation rates. It is important, at this point, to have a clear idea of the values to be assigned to the symmetrized contact densities. This is easy for the simple situation occurring when the two electrons of the system are confined in nonoverlapping space regions A and B, as qualitatively shown in Fig. 1. In this case, we do not need to worry about electron indistinguishability. We may describe the system with a wave function Ψ, where the labels a and b are assigned to the electrons according to the region where they are found. We then obtain the contact density of the positron with each one of these electrons according to the definition given in Refs. 7 and 18, i.e.,

$$\kappa_a = 8\pi a_0^3 \langle \Psi | \delta(\mathbf{r}_a - \mathbf{r}_p) | \Psi \rangle \tag{20}$$

and

$$\kappa_b = 8\pi a_0^3 \langle \Psi | \delta(\mathbf{r}_b - \mathbf{r}_p) | \Psi \rangle \ . \tag{21}$$

The physical meaning of the electron-positron contact density, and its importance in determining annihilation rates, has been thoroughly discussed in Refs. 7 and 18. The relationships with the less familiar "symmetrized" contact densities can be found by observing that

$$\Phi_+ = \frac{1}{\sqrt{2}}(1+X)\Psi \tag{22}$$

and

$$\Phi_- = \frac{1}{\sqrt{2}}(1-X)\Psi \ , \tag{23}$$

where X indicates the operator that exchanges electron coordinates bringing electron a into region B and vice versa. By combining Eqs. (9)–(12) with (20)–(23), and taking into account that an equivalent way of writing κ_b is

$$\kappa_b = 8\pi a_0^3 \langle X\Psi | \delta(\mathbf{r}_a - \mathbf{r}_p) | X\Psi \rangle \ , \tag{24}$$

one obtains

$$\kappa_{++} = \tfrac{1}{2}(\kappa_a + \kappa_b) + \kappa_{ab} \ , \tag{25}$$

$$\kappa_{--} = \tfrac{1}{2}(\kappa_a + \kappa_b) - \kappa_{ab} \ , \tag{26}$$

and

$$\kappa_{+-} = \kappa_{-+} = \tfrac{1}{2}(\kappa_a - \kappa_b) \ . \tag{27}$$

Here κ_{ab} is defined by

$$\kappa_{ab} = 8\pi a_0^3 \langle \Psi | \delta(\mathbf{r}_a - \mathbf{r}_p) | X\Psi \rangle \ . \tag{28}$$

The physical meaning of κ_{ab} is that of a "mixed" contact density, related to the overlap of two different electrons in the position occupied by the positron. In the situation we are discussing now (electrons confined in nonoverlapping regions) κ_{ab} is zero. The general case with $\kappa_{ab} \neq 0$ will be treated below, but we want to begin here with more familiar situations.

A free Ps atom in vacuum can be framed in our formalism, if one includes in the system a second unpaired electron very far from the atom, acting as an inert spectator. In this case, the contact density is $\kappa_a = 1$ for the electron in the atom and $\kappa_b = 0$ for the dummy electron. We then assume $\Delta_{\mathrm{ex}} = 0$, $\lambda_{\text{pick-off}} = 0$ (no exchange interaction between electron a and electron b, no pick-off annihilation), and keep the magnetic field as a variable. The result of the numerical calculation of the annihilation rates, reported in Fig. 2(a), is essentially coinciding with the outcome of the Halpern theory, apart from the obvious difference of a doubling of the degeneracy, due to the inclusion in our model of the dummy electron with two possible spin orientations. It can be shown that the difference between our calculation and that of Halpern is of second order in the ratio $\hbar(\lambda_s + \lambda_t)/2\Delta_{\mathrm{hf}} = 3 \times 10^{-3}$, and comes from different approximations in the quantum mechanical treatment of a system with finite lifetime (on this point, see also Mills[19]).

Let us now imagine that the Ps atom is inside a medium giving pick-off annihilation. We can account for this new annihilation channel by taking $\lambda_{\text{pick-off}} \neq 0$ in our Hamiltonian. The result of the numerical calculation with that of the annihilation rates versus magnetic field with $\lambda_{\text{pick-off}} = 0.2\lambda_s$ are shown in Fig. 2(b). This is identical to Fig. 1(a) but for a rigid upward shift of all annihilation rates by $0.2\lambda_s$.

However, the interaction of the Ps atom with a medium does not give only pick-off annihilation, but also a distortion of the wave function of the bound electron-positron pair. This means that the contact density κ_a is no longer 1. In Fig. 2(c) we have reduced κ_a to 0.5; this is a case representing the so-called "relaxed Ps", often invoked for the interpretation of the "normal" magnetic effect on annihilation in condensed media. The result of reducing κ_a is to decrease the annihilation rate differences and to increase the sensitivity to the magnetic field. Actually, Fig. 2(c) could be made identical to Fig. 2(b) by rescaling the horizontal axis by the factor κ_a and the vertical axis by the factor $1/\kappa_a$. We have also considered the case of a "compressed Ps" with $\kappa_a = 2$ [Fig.

2(d)], hypothetically possible in a medium where the particles respond to the mutual attraction with effective masses larger than the bare electron mass.

For the situations included in Fig. 2, our model is unnecessarily complicated. The modifications to the Halpern scheme discussed in Ref. 7 would be sufficient for obtaining essentially the same results with much less labor. The need for the new formalism presented in this paper arises if we want to take into account the possibility that the positron touches a second unpaired electron ($\kappa_b \neq 0$), and that there is an exchange interaction between the first and second electron ($\Delta_{ex} \neq 0$).

In order to illustrate with an example the consequences of the contact of the positron with the second electron, let us assume that $\kappa_b = 0.1$, and leave for the moment all other parameters the same as in the five cases of Fig. 2. One has now eight states, with three distinct annihilation rates at $B = 0$ and seven at $B \neq 0$ (the lowest rate, which is not affected by the external field, refers to the two states with total spin $\pm 3/2$ along the field direction). The graphs of the annihilation rates versus magnetic field are reported in Fig. 3 side by side with the corresponding cases of Fig. 2; in spite of the greater complication of Fig. 3, the two figures appear to be similar. Of course, this is only a consequence of the small value of κ_b chosen in our examples. With this choice, an approximated classification of the states according to the spin alignment of the positron with electron a is still possible, although this alignment is no more a true constant of motion. This helps us to regard the effect of the second electron as a small perturbation. At $B = 0$, this effect is to split the rate of the original ortho-Ps state in a doublet well separated from the rate of the original para-Ps state; in turn, this is increased but not split. The effect of the magnetic field takes place in two stages, the first one due to the mixing within the doublet, the second interconnecting the two groups of lines. In Fig. 4, we present an enlargement of Fig. 3 in the low-field region giving a detailed view of the first stage of the magnetic field effect.

Our model can be extended to represent a positron bound to an exciton, a possibility that was mentioned in Ref. 6. All we have to do is to take into account that an electron hole gives a negative contribution to annihilation, and this is simply done by assuming $\kappa_b < 0$. In Fig. 5 we present an example with $\kappa_a = 0.5$ and $\kappa_b = -0.1$.

Our next step is to include in our model the exchange interaction between the two unpaired electrons by assuming $\Delta_{ex} \neq 0$. Even in the absence of direct contact of the positron with the second electron ($\kappa_b = 0$), this interaction affects annihilation with electron a via the spin exchange process taking place between the two electrons.

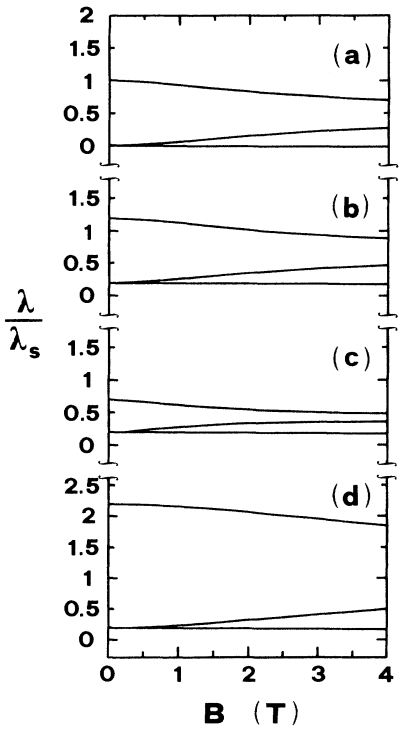

FIG. 2. Evolution of annihilation rates under the action of the applied field with $\Delta_{ex} = 0$, $\kappa_{ab} = 0$ and the following choices for the internal contact densities (κ_a, κ_b) and external contact density ($\lambda_{pick\text{-}off}$):
(a) $\kappa_a = 1$, $\kappa_b = 0$, $\lambda_{pick\text{-}off} = 0$;
(b) $\kappa_a = 1$, $\kappa_b = 0$, $\lambda_{pick\text{-}off} = 0.2\lambda_s$;
(c) $\kappa_a = 0.5$, $\kappa_b = 0$, $\lambda_{pick\text{-}off} = 0.2\lambda_s$;
(d) $\kappa_a = 2$, $\kappa_b = 0$, $\lambda_{pick\text{-}off} = 0.2\lambda_s$.

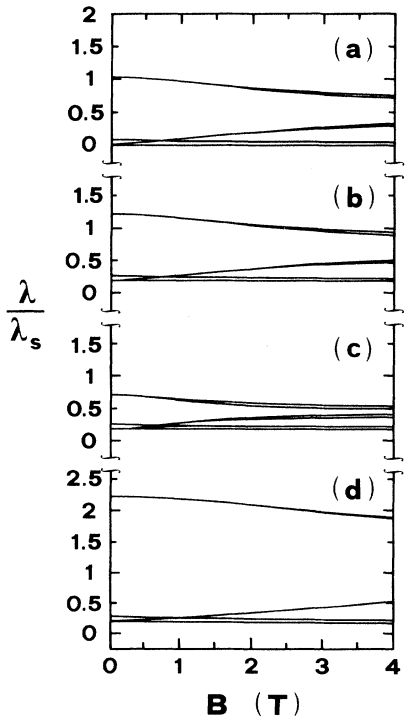

FIG. 3. Evolution of annihilation rates under the action of the applied field with the same κ_a and $\lambda_{pick\text{-}off}$ of the corresponding sections a,b,c,d of Fig. 2, and $\kappa_b = 0.1$.

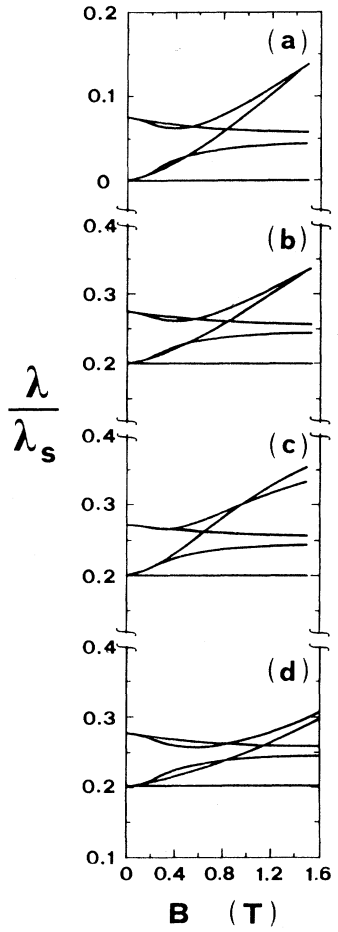

FIG. 4. Enlarged view of the region of Fig. 3 showing details of the evolution of the lowest annihilation rates.

We show in Fig. 6 the dependence of the annihilation rates vs Δ_{ex} in the absence of other perturbations (i.e., $\kappa_a=1$, $\kappa_b=0$, $\lambda_{pick\text{-}off}=0$, $B=0$). In this figure, we have limited the range of Δ_{ex} to a few meV; in the present context, we are not interested in too large values of Δ_{ex}, which would imply to freeze the electrons in the triplet

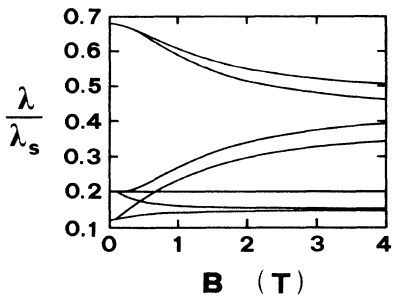

FIG. 5. Annihilation rates vs magnetic field with the choice $\kappa_a=0.5$, $\kappa_b=-0.1$, $\lambda_{pick\text{-}off}=0.2\lambda_s$.

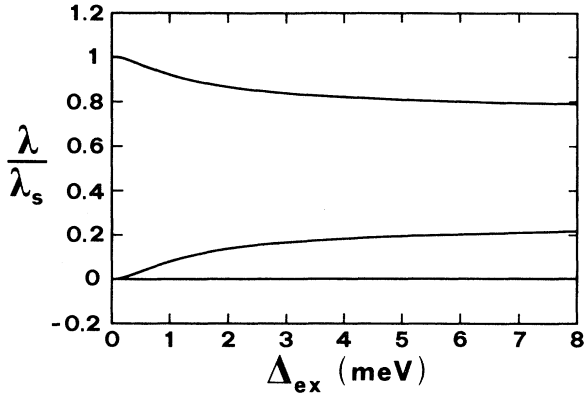

FIG. 6. Annihilation rates vs exchange energy Δ_{ex} without other perturbations ($\kappa_a=1$, $\kappa_b=0$, $\lambda_{pick\text{-}off}=0$, $B=0$).

state, thereby reducing the numbers of available spin states of the whole system.

The presence of an exchange interaction comparable with the hyperfine splitting is sufficient to modify the effect of the magnetic field on the annihilation rates in a very remarkable way. This is shown in Fig. 7, presenting the annihilation rates vs B, as calculated for $\kappa_a=1$, $\kappa_b=0$, $\lambda_{pick\text{-}off}=0$, $\Delta_{ex}=1$ meV.

Finally, in our last example, we consider the most general situation, including a mixed contact density $\kappa_{ab}\neq 0$. This implies also electron-electron overlap ($\Delta_{ex}\neq 0$) as well as contact of the positron with both electrons taken separately ($\kappa_a\neq 0$, $\kappa_b\neq 0$). Actually, some simple algebra shows that $\kappa_{ab}\leq\sqrt{\kappa_a\kappa_b}$. We thus combine all our ingredients, making the following choice: $\kappa_a=0.8$, $\kappa_b=0.4$, $\lambda_{pick\text{-}off}=0.2\lambda_s$, $\Delta_{ex}=1$ meV. In Fig. 8 we present our results for the alternative: $\kappa_{ab}=0$ (broken lines) and 0.04 (continuous lines).

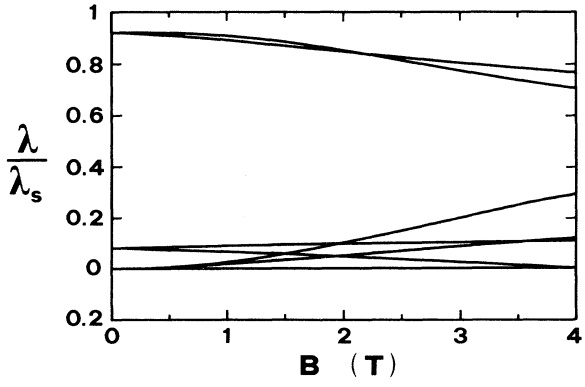

FIG. 7. Annihilation rates vs magnetic field with $\kappa_a=1$, $\kappa_b=0$, $\lambda_{pick\text{-}off}=0$, $\Delta_{ex}=1$ meV.

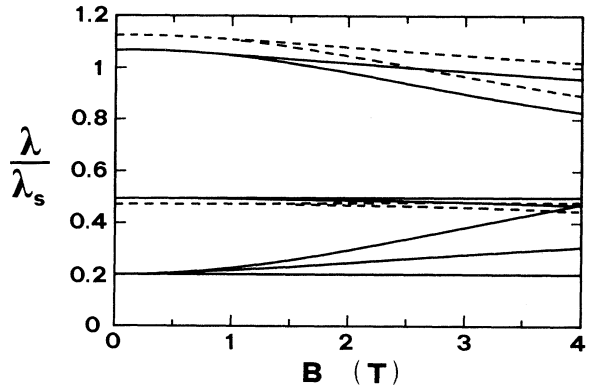

FIG. 8. Annihilation rates vs magnetic field with $\kappa_a=0.8$, $\kappa_b=0.4$, $\lambda_{\text{pick-off}}=0.2\lambda_s$, $\Delta_{\text{ex}}=1$ meV, $\kappa_{ab}=0$ (broken lines), and $\kappa_{ab}=0.04$ (continuous lines).

IV. CONTACT WITH MAGNETIC QUENCHING EXPERIMENTS

Because we are able to calculate annihilation rates for any possible interaction among the positron, two electrons and a medium, we can make contact with experiment in the cases that cannot be easily interpreted using the "relaxed" Ps model. We recall that the experimental results of Bisi *et al.*[9] show the existence of two stages of magnetic quenching of the positron lifetimes in several plastic materials, a behavior that might suggest the presence of two different Ps-like objects coexisting in the same sample. However, even combining this hypothesis with the relaxed Ps model, the above-mentioned authors did not obtain a fair fit of their data, without forcing the theory by adjusting a larger number of parameters than compatible with the model itself (they assumed the singlet-triplet energy splittings to be independent of the contact density). The calculations reported in the previous section suggest, as an alternative explanation for a magnetic quenching occurring in two stages, the presence of a second electron located somewhere near a bound positron-electron pair. We discuss here the compatibility of this second hypothesis with experiment.

Fortunately, the data of Ref. 9 are expressed in terms of a purely experimental shape parameter R (the area of the spectrum between two specified time limits t_1 and t_2, divided by the same area measured at $B=0$), which does not imply any assumption on the number of components forming the spectrum. This is an advantage, since it gives us the possibility of an immediate comparison with the predictions of our model. No similar opportunity is provided by the data reported in Refs. 11–13.

The mathematical expression of R for a multicomponent spectrum is

$$R=\frac{\sum_j w_j(e^{-\lambda_j t_1}-e^{-\lambda_j t_2})_{B\neq 0}}{\sum_j w_j(e^{-\lambda_j t_1}-e^{-\lambda_j t_2})_{B=0}}, \tag{29}$$

where w_j indicate the probability that state j is formed. The sums of Eq. (29) include eight terms, corresponding to the eight eigenstates of H; the terms corresponding to eigenstates with the same lifetime are repeated. We thus assume $w_j\equiv 1$ for all j; this is consistent with the experimental arrangement of Ref. 9, which gives no net spin polarization of the positron flux injected into the sample. It also implies that the energy differences among the states, which are of the order of $\kappa_a\Delta_{\text{hf}}$ and of Δ_{ex}, are small in comparison with the formation energy; this is confirmed *a posteriori* by the best-fit values reported below.

We have fitted expression (29) to the experimental data of Ref. 9 using κ_a, κ_b, κ_{ab}, Δ_{ex} as adjustable parameters and fixing the pick-off rate at the experimental value for the long-living component of the spectrum. Figure 9 shows the experimental points of Ref. 9 and our best-fit curves. The corresponding parameters are given in Table I. In most cases, the best-fit values of κ_{ab} and Δ_{ex} are less than 10^{-2}. In fact, acceptable fits can be obtained with κ_{ab} and Δ_{ex} fixed at 0 in all cases. This indicates that the interaction between the two electrons is not a very important factor.

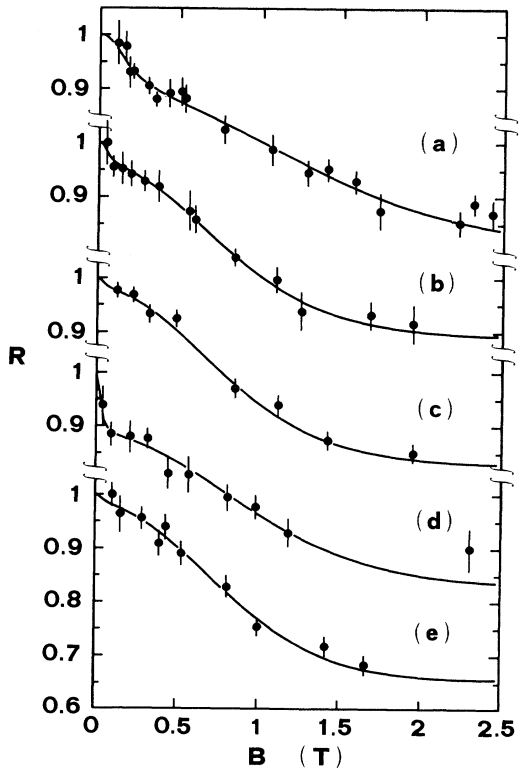

FIG. 9. Magnetic quenching of positron lifetime spectra in some polymers. The experimental points are from Ref. 9. The curves are obtained from our model by leaving $\kappa_a,\kappa_b,\kappa_{ab},\Delta_{\text{ex}}$ as adjustable parameters (best-fit values are given in Table I): (a) Mylar; (b) Nylon; (c) polystyrene; (d) Terfane; (e) Teflon.

Some of the κ_a values reported in Table I are larger than 1. As explained in the previous section, a contact density above 1 might indicate effective masses larger than the bare electron mass, as the result of binding to a substratum. However, we would take any physical interpretation of the values in Table I with caution, owing to the following reasons: (i) with the modest statistical quality of the available experimental data, fairs fits can be obtained even with the constraint $\kappa_a < 1$; (ii) we cannot exclude that the experimental data reflect a superposition of effects due to coexisting positronic complexes of a different structure.

The important point shown by our calculations is that the hypothesis of the perturbation of a Ps-like object due to spin of a second unpaired electron gives all the necessary flexibility for retrieving a two-stage magnetic quenching curve. The truth can even be more complicated, but the idea of simultaneous spin correlation of the positron with more than one electron really seems the easy key to interpret the so-called anomalous magnetic quenching.

TABLE I. Internal contact densities, "mixed" contact density, and exchange energy, as obtained from the best fit to the experimental data of Ref. 9.

Sample	κ_a	κ_b	κ_{ab}	Δ_{ex} (meV)	χ^2/degrees of freedom
Mylar	1.95	0.05	$<10^{-2}$	$<10^{-2}$	0.62
Nylon	0.81	0.02	$<10^{-2}$	$<10^{-2}$	0.40
polystyrene	0.92	0.01	$<10^{-2}$	$<10^{-2}$	0.50
Teflon	1.33	0.01	$<10^{-2}$	$<10^{-2}$	0.62
Terfane	1.06	0.05	0.01	$<10^{-2}$	0.90

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