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## Positronium contact density in ferrocene

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### Abstract

In a medium where positronium (Ps) is formed, a lowering of the electron density at the positron (contact density) with respect to vacuum is generally observed. The effect is usually attributed to the interaction with the medium, which induces Ps polarization. Such a reduction, explainable in polar media due to Debye forces, can be expected also in non-polar media, where London forces are present. To investigate this subject we measured the Ps contact density in ferrocene, an organometallic compound whose molecule does not have intrinsic dipole moment; therefore, only induced dipole-induced dipole interactions may be present. Contact density was obtained by means of two different experimental techniques. A lowering by 23 % with respect to vacuum value was observed, which allowed us a simple estimation of the order of magnitude of the effective microscopic electric field mimicking the Ps-ferrocene interaction.

### 1. Introduction

Once injected into a solid, a positron loses its energy in a very short time interval (a few ps) owing to inelastic scatterings with neighboring atoms or molecules of the medium. The thermalized positron diffuses through the medium until annihilation with one of the surrounding electrons occurs. A positron can also form an unstable bound positron-electron system (positronium, Ps), when favorable energetic conditions exist. In vacuum, ground state Ps is found in two sublevels: para-Ps (*p*-Ps, anti-parallel spins of the electron and the positron) and ortho-Ps (*o*-Ps, parallel spins), characterized by very different lifetimes: 125 ps (*p*-Ps) and 142 ns (*o*-Ps). The energy separation between the two sublevels (hyperfine splitting) amounts to  $8.45 \cdot 10^{-4}$  eV [1]. Positronium in condensed matter shows properties similar to those of Ps in vacuum. However, Ps lifetimes are changed with respect to those in vacuum due to possible annihilation with external electrons. This process, called ‘pickoff’ [2], has a negligible influence on *p*-Ps, whose intrinsic lifetime is very short, but can greatly reduce *o*-Ps lifetime, up to two orders of magnitude with respect to vacuum, depending on the electron density around Ps. When Ps is hosted in a cavity, this effect allows one to get insights on the typical size of the hole, by modeling this last according to a suitable geometry [3-7]. Furthermore, the surrounding molecules reveal their influence on Ps by modifying the hyperfine splitting and the intrinsic decay rates, sometimes to a considerable extent. A key quantity

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of Ps in matter is the electron density at the positron ('contact density'), represented by  $|\psi(0)|^2$ , where  $\psi$  is the Ps wavefunction. The perturbing effect of the molecules surrounding Ps on its wavefunction can be taken into account in a phenomenological way by defining a relative contact density  $\eta$ :

$$\eta = \frac{|\psi(0)|_{matter}^2}{|\psi(0)|_{vacuum}^2} \quad (1)$$

This parameter, firstly introduced by Goldanskii [8], can be measured by means of various experimental techniques [9]. The most popular one uses the Zeeman effect on Ps: the Ps lifetime of the triplet sublevel with magnetic quantum number  $m = 0$  is progressively quenched by a magnetic field. For this reason the method is known as "magnetic quenching" [10]. The results obtained by different research groups in various classes of materials (polymers, molecular solids, insulators, aqueous solutions) point out that  $\eta < 1$ ; in some cases anomalous magnetic quenching effects were found [11-13]. The common interpretation of the contact density reduction with respect to vacuum is that Ps is polarized by effective microscopic electric fields, which have an opposite effect on the positron and the electron [14]. The spacing out of the two particles swells Ps and the contact density decreases. This effect seems to overcome the squeezing of the Ps wavefunction due to spatial confinement in a cavity, which should increase the contact density [15]. Polarization of Ps can be expected in polar compounds, where Debye forces due to dipole (medium) – induced dipole (Ps) interaction occur [16]. Furthermore, an effect can be guessed even in non-polar compounds, where London forces due to induced dipole (medium) – induced dipole (Ps) interaction may be present. The aim of the present paper was to explicitly investigate this possible interaction. To this purpose, we needed a material whose molecule does not show a permanent electric dipole moment, in order to consider only London forces on Ps, by excluding Debye forces. Of course, the medium should allow Ps formation. We focused on bis( $\eta^5$ -cyclopentadienyl)iron (ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ ), an organometallic compound which satisfies the two requirements. Indeed, Ps is formed in it [17] and ferrocene molecule has no electric dipole moment [18]. A magnetic quenching experiment allowed us to obtain the Ps contact density in this material. Another independent estimate of the contact density was supplied by means of a three quantum yield measurement. Knowledge of the contact density allowed us to get insight on the effective microscopic electric field acting on Ps and responsible of its polarization, with the aid of a simple model for Ps swelling.

## 2. Experimental

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3 The positron source,  $^{22}\text{Na}$  from a carrier free neutral solution, was deposited between two identical  
4  $7.5\ \mu\text{m}$   $^{\text{®}}$ Kapton foils (in which Ps is not formed [19]), glued together and inserted in the specimen  
5 to be studied in the usual sandwich configuration. Care was taken to prevent the glue from reaching  
6 the region involved in annihilation. The samples of ferrocene from Sigma-Aldrich (essay 98%)  
7 were prepared without special caution, being air-stable [20]. Crystalline samples were compressed  
8 into a cylindrical aluminum cell used as a container; the thickness of each sample was sufficient to  
9 stop the positrons before reaching the walls of the container. Our study started with the analysis of  
10 the lifetime spectra in ferrocene. They were obtained by means of a fast-fast coincidence system,  
11 with a cylindrical plastic scintillator (NE111 24x10 mm) on the start channel and a  $\text{BaF}_2$  scintillator  
12 (identical in size to the former) on the stop. The scintillators were coupled to photomultipliers  
13 Philips XP2020Q. The resolution of the spectrometer was about 220 ps. The fraction of positrons  
14 annihilating in the Kapton was estimated to be about 11% [21-23]; after subtraction of this  
15 contribution the spectra were analyzed in three components by means of the LT program [24]. Each  
16 spectrum contained at least  $2 \cdot 10^6$  counts. The normalized chi-square tests were found in every case  
17 to be acceptable, being in the range 0.98 – 1.06 .

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30 Then, we carried out a magnetic quenching experiment. To this purpose, the cell containing the  
31 sample was placed in the gap of an electromagnet. The gamma rays were collected by a couple of  
32 two identical cylindrical plastic scintillators (Pilot U 38x25 mm), placed near the gap and coupled  
33 to photomultipliers Philips XP2020 through poly(methyl methacrylate) light guides coming out of  
34 the magnet. The photomultipliers were protected against stray fields by cylindrical mu-metal  
35 shields. In this configuration the spectrometer had of course a worse resolution (440 ps), but still  
36 sufficient to discriminate the longest component due to *o*-Ps from the shorter ones. The lifetime  
37 spectra, taken in the presence as well as in the absence of the magnetic field, could be directly  
38 compared without any correction. Indeed, we checked that the centroid of ‘prompt’ curves, as  
39 obtained from the coincidences of the two gamma rays emitted from a  $^{60}\text{Co}$  source, shifted less than  
40 8 ps in the presence of the highest magnetic field with respect to zero field.

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The three quantum yield was obtained by means of an apparatus already described [25], able to  
measure simultaneously the three quantum annihilation events and the background. It consisted of  
three identical channels, each one formed by a cylindrical 51x51 mm  $\text{NaI}(\text{TI})$  scintillator coupled to  
a photomultiplier tube and a preamplifier, followed by an amplifier and a timing single channel  
analyzer. Four outgoing, identical signals from this last stage fed the same number of coincidence  
units, whose output triggered a counter and timer. The scintillators were arranged at  $120^\circ$  each  
other; their symmetry axes were coplanar and in the same plane of the source. Each scintillator was  
surrounded by a truncated conical lead shield. The gamma rays collected by the scintillators were

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3 processed through the timing single channel analyzer, in order to accept quanta in the range 280–  
4 420 keV, that is, a region centered around 340 keV (one third of the total annihilation energy, 1022  
5 keV). The resolving time interval  $\Delta T$  of each coincidence unit could cover a range from 25 to 110  
6 ns. The measurements were carried out at some fixed values of  $\Delta T$ , in order to simultaneously get  
7 the three quantum true coincidences and the background. Details on the procedure can be found in  
8 [25]. Each run in ferrocene was alternated to one in beryllium, where Ps does not form, in order to  
9 obtain the relative three quantum annihilation rate in the organometallic compound, by using the  
10 metal as a reference.  
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### 21 3. Results and discussion

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23 The time annihilation spectra in ferrocene obtained with resolution of 220 ps show the following  
24 lifetimes (in ns) and intensities:  
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$$26 \tau_1 = 0.14 \pm 0.02 ; I_1 = 0.18 \pm 0.03$$

$$27 \tau_2 = 0.34 \pm 0.01; I_2 = 0.53 \pm 0.05$$

$$28 \tau_3 = 1.22 \pm 0.02; I_3 = 0.29 \pm 0.02$$

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35 The longest component can be ascribed to *o*-Ps formation: the best proof of this contention is given  
36 by the fact that this component undergoes magnetic quenching, as it will be explained below. The  
37 shortest component has a lifetime compatible with a *p*-Ps decay; its intensity is higher than that  
38 expected (indeed it should amount to 1/3 of that of *o*-Ps), in the absence of ortho-para conversion  
39 processes. A ratio  $I_3/I_1 > 3$  is generally ascribed to the limited resolution of the lifetime  
40 spectrometer. In polymers, it was attributed [26] to neglect a distribution of free positrons and *o*-Ps  
41 lifetimes. Anyway, we ascertained that in ferrocene we are not in the presence of ortho-para  
42 conversion, as discussed later. The second component comes from free positrons, that is, not  
43 forming Ps. If we compare our results with those by Kang et al. [17], who also resolved the  
44 spectrum in three components, we note a good agreement concerning the lifetimes. We find a  
45 higher *o*-Ps intensity, but this is probably due to the different concentration of defects hosting Ps.  
46 Lifetime data are needed to set a correct time interval for the evaluation of the quenching ratio  
47 defined below.  
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59 Before showing the magnetic quenching results it is useful to recall the main features of the  
60 Zeeman effect on ground state Ps. A static magnetic field does not influence the  $m = \pm 1$  ortho  
states, but it mixes the  $m = 0$  sublevels. The resulting ‘mixed *o*-Ps’ contains an amount of *p*-Ps

equal to  $\frac{y^2}{1+y^2}$ , where  $y = \frac{(\sqrt{1+x^2}-1)}{x}$ ,  $x = \frac{4\mu_B B}{\Delta W}$ ,  $\mu_B$  is the Bohr magneton,  $B$  the magnetic field,  $\Delta W$  the hyperfine splitting [10]. Consequently, the lifetime of the mixed ortho state is progressively decreased by increasing the magnetic field. Indeed, in vacuum the decay rates become [10]:

$$\lambda_3 = \lambda_{t,v} \quad J = 1, m = \pm 1 \quad (2a)$$

$$\lambda'_3 = \frac{\lambda_{t,v} + y^2 \lambda_{s,v}}{1+y^2} \quad J = 1, m = 0 \quad (2b)$$

$$\lambda'_0 = \frac{\lambda_{s,v} + y^2 \lambda_{t,v}}{1+y^2} \quad J = 0, m = 0 \quad (2c)$$

where  $\lambda_{s,v}$  and  $\lambda_{t,v}$  are the intrinsic decay rates in the para and ortho state at zero field, respectively.

Both  $\lambda_{s,v}$  and  $\lambda_{t,v}$ , as well as the hyperfine splitting  $\Delta W$ , are proportional to  $|\psi(0)|^2$  [1]:

$$\lambda_{s,v} = \frac{\alpha^2 h^2}{\pi m^2 c} |\psi(0)|^2; \quad \lambda_{t,v} = \frac{4}{9\pi^2} (\pi^2 - 9) \frac{\alpha^3 h^2}{m^2 c} |\psi(0)|^2; \quad \Delta W = \frac{56}{3} \pi \mu_B^2 |\psi(0)|^2 \quad (3)$$

where  $\alpha$  is the fine structure constant,  $m$  is the electron mass.

In the presence of matter the perturbing effect of the molecules surrounding Ps on the intrinsic decay rates and hyperfine splitting is taken into account through eq. (1). It follows that we can write the total decay rates in a medium in terms of the same quantities in vacuum and of the relative contact density  $\eta$ :

$$\lambda_t = \eta \lambda_{t,v}; \quad \lambda_s = \eta \lambda_{s,v} \quad (4)$$

The total decay rate of each sublevel in matter can be written:

$$\lambda_3 = \eta \lambda_{t,v} + \lambda_p \quad (5a)$$

$$\lambda'_3 = \eta \frac{\lambda_{t,v} + y^2 \lambda_{s,v}}{1+y^2} + \lambda_p \quad (5b)$$

$$\lambda'_0 = \eta \frac{\lambda_{s,v} + y^2 \lambda_{t,v}}{1+y^2} + \lambda_p \quad (5c)$$

where the pickoff decay rate  $\lambda_p$  has been added. In our case it can be assumed equal to  $0.82 \pm 0.01$  ns<sup>-1</sup>, the inverse of the *o*-Ps lifetime (the longest component of the spectra). The dependence of the

decay rates on the relative contact density is evident; furthermore,  $\eta$  is also contained in the  $y$  factor, through the hyperfine splitting.

By comparing the lifetime spectra in the presence as well as in the absence of the magnetic field  $B$  it is possible to extract a ‘quenching ratio’  $R$ , defined as:

$$R = \frac{F(t_1, t_2, B)}{F(t_1, t_2, 0)} \quad (6)$$

where:

$$F(t_1, t_2, B) = \sum_k \int_{t_1}^{t_2} I_k \lambda_k \exp(-\lambda_k t) dt \quad (7)$$

and the sum includes all the meaningful components in the time interval  $t_2 - t_1$ . In particular, if  $t_1$  is chosen so that the contribution of the shorter lifetime components is negligible, while in the instant  $t_2$  the counting rate is still statistically meaningful, the ratio  $R$  for the  $o$ -Ps component alone is obtained:

$$R = \frac{2}{3} + \frac{1}{3} \frac{\exp(-\lambda'_3 t_1) - \exp(-\lambda'_3 t_2)}{\exp(\lambda_3 t_1) - \exp(\lambda_3 t_2)} \quad (8)$$

In the case of ferrocene a possible choice for the values of  $t_1$  and  $t_2$  which satisfy these requirements is 4.5 and 9.0 ns respectively. Indeed, in this time interval the contribution of the middle component is completely negligible. The measured values for  $R$  are reported in figure 1. Since  $R$  depends on  $\eta$  through  $\lambda_s$ ,  $\lambda_t$  and  $\Delta W$ , a least squares adjustment enables one to obtain the values of the relative contact density as a quantitative measurement of the influence of the medium on Ps. We found that  $\eta = 0.77 \pm 0.04$ , corresponding to the dashed line. The continuous line is obtained for  $\eta = 1$  and would correspond to an ‘unperturbed’ Ps. Uncertainty on  $\eta$  was obtained from the propagation of the uncertainties of the experimental quenching ratios.

We obtained another determination of the relative contact density in ferrocene by using the three quantum yield method. It is based on the fact that the rate of three quantum annihilations,  $P$ , in a medium where Ps is formed is raised with respect to a metal,  $P_0$ , where no Ps occurs. In a metal, the relative three quantum yield is  $\frac{3\lambda_t}{\lambda_s} = \frac{1}{372}$ , by using eq. (3) (the factor 3 results from the average over

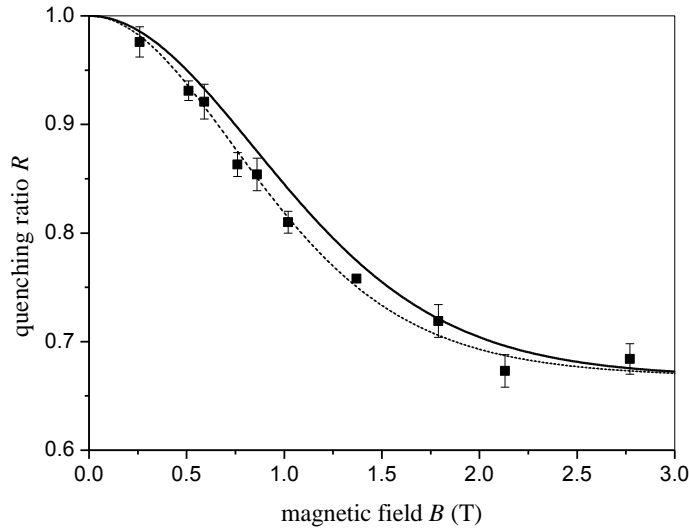


Figure 1 – Quenching ratio  $R$  versus the magnetic field in ferrocene. The continuous curve is calculated for a Ps with  $\eta = 1$ ; the dashed curve results from a best fit to the experimental  $R$  values and corresponds to  $\eta = 0.77$ .

the relative spin populations [27]). In a medium which allows for Ps formation the relative three quantum yield is the sum of three terms. The first one is due to  $o$ -Ps and is equal to the formation probability multiplied by the probability that  $o$ -Ps decays in three quanta through the intrinsic decay rate,  $\eta\lambda_{t,v}/(\eta\lambda_{t,v} + \lambda_p)$ , or by pickoff,  $\frac{(\lambda_p/372)}{\eta\lambda_{t,v} + \lambda_p}$ ; the two contributions sum each other. It results:

$I_3 \left( \frac{\eta\lambda_{t,v} + \lambda_p/372}{\eta\lambda_{t,v} + \lambda_p} \right)$ . A second contribution is due to  $p$ -Ps, which decays only in two quanta in a

vacuum, but in a medium it can decay in three quanta by means of the pickoff process:  $\frac{I_3}{3} \frac{\lambda_p/372}{\eta\lambda_{s,v} + \lambda_p}$ .

The last contribution comes from positrons not forming Ps and annihilating in three quanta:

$\left(1 - \frac{4}{3}I_3\right)/372$ . Therefore, the ratio  $P/P_0$  results [9]:

$$\frac{P}{P_0} = 372I_3 \left( \frac{\eta\lambda_{t,v} + \lambda_p/372}{\eta\lambda_{t,v} + \lambda_p} + \frac{1}{3} \frac{\lambda_p/372}{\eta\lambda_{s,v} + \lambda_p} \right) + \left(1 - \frac{4}{3}I_3\right) \quad (9)$$

The above formula is obtained by assuming that all the positrons emitted from the source annihilate in the material surrounding it. If  $k$  is the fraction of the positrons annihilated in the  $^{\text{®}}$ Kapton support, the previous equation is modified as follows:

$$\frac{P}{P_0} = \left[ 372I_3 \left( \frac{\eta\lambda_{t,v} + \lambda_p/372}{\eta\lambda_{t,v} + \lambda_p} + \frac{1}{3} \frac{\lambda_p/372}{\eta\lambda_{s,v} + \lambda_p} \right) + \left(1 - \frac{4}{3}I_3\right) \right] (1 - k) + k \quad (10)$$



From eq. (10) the relative contact density  $\eta$  can be determined by treating it as a free parameter and by adjusting the ratio  $P/P_0$  to the measured value, the other quantities  $k$ ,  $I_3$  and  $\lambda_p$  being known. The measured ratio  $P/P_0$  for ferrocene is  $1.58 \pm 0.03$ , which gives  $\eta = 0.80 \pm 0.04$ , in agreement with the results supplied by the magnetic quenching experiment. We conclude that the Ps contact density in ferrocene is smaller than in vacuum; in other words, Ps is ‘relaxed’.

Comparison of our result with some existing theoretical models is hard, since the number of papers discussing the subject of the contact density is scanty. Urbanovich [28] modeled the interaction between Ps and surrounding medium in terms of an effective electric field, assumed constant and uniform. Using a variational method, an interaction energy between Ps and medium, which can be expressed in terms of the relative contact density, was obtained. But this result should be considered cautiously, because of the unrealistic assumption of a complete spherical symmetry. McMullen and Stott [29] proposed an exactly soluble model, in which the electron-positron interaction, as well as external fields acting on the particles, are expressed in terms of harmonic potentials. Relative contact density turns out to be a function of three elastic constants. Unfortunately, according to the authors, the model is not able to give a quantitative description of Ps contact density in a real solid.

Swelling of Ps wavefunction in ferrocene can be attributed to Van der Waals interactions between Ps and molecules of the medium. Although Ps does not have an electric dipole moment in its ground state, in a non-polar medium instantaneous induced dipole-induced dipole forces (London dispersion forces) occur. Such forces are generally weaker than the Debye forces (permanent dipole-induced dipole forces) which turn up in polar media, but in the case of ferrocene these could play a significant role. Indeed, by using the Tao-Eldrup equation [3, 4, 30] we estimate a typical size for the cavity hosting Ps of about 0.20 nm. This is also the average distance between the Ps center of mass and external electrons of the surrounding molecules. At such small distances dispersion interactions, which scale as  $r^{-6}$ , may become rather intense. We can estimate the order of magnitude of the interaction energy  $u$  between Ps and ferrocene molecule. It is given by [31]:

$$u = -\frac{3}{2} \frac{\alpha_{Ps} \alpha_{frc}}{(4\pi\epsilon_0)^2 r^6} \frac{I_{Ps} I_{frc}}{I_{Ps} + I_{frc}} \quad (11)$$

where  $\alpha_{Ps}$  and  $\alpha_{frc}$  are the polarizabilities of Ps and ferrocene, respectively;  $I$  the corresponding ionization potential and  $r$  is the distance between the center of mass of Ps and ferrocene molecule. It results  $I_{frc} = 9.78$  eV [32]. Concerning Ps we can assume  $I_{Ps} = 6.8$  eV, that is, the value in vacuum, although in a medium the value is expected to be different (but in any case of the order of

a few eV [33]). Ps polarizability is eight times the one of hydrogen [14], which is equal to  $0.74 \cdot 10^{-40} \text{ C m}^2\text{V}^{-1}$  [34]; therefore  $\alpha_{Ps} = 5.94 \cdot 10^{-40} \text{ C m}^2\text{V}^{-1}$ . We did not find in the literature the value of ferrocene polarizability; however, it can be estimated as  $\alpha_{frc} = \sum \alpha_i$ , where  $\alpha_i$  is the contribution to the polarizability of the atom – or group of atoms – forming the molecule [31]. For an aromatic C – C bond it results  $1.19 \cdot 10^{-40} \text{ C m}^2/\text{V}$ , for a C – H bond  $0.72 \cdot 10^{-40} \text{ C m}^2/\text{V}$  [31], while for Fe  $9.3 \cdot 10^{-40} \text{ C m}^2/\text{V}$  [34]. Therefore, it results  $\alpha_{frc} = 28.4 \cdot 10^{-40} \text{ C m}^2/\text{V}$ . At last,  $r$  can be assumed of the order of 0.4 nm, that is, the sum of the distance between Ps centre of mass and external electrons of ferrocene (0.2 nm, as reported above) and the distance C – Fe in the ferrocene molecule, equal to 0.2 nm [35]. By inserting the above values in eq. (11) we find  $u = -0.2 \text{ eV} = -4.5 \text{ kcal/mol}$ . It seems a reasonable value, by taking into account that cohesive energies due to Van der Waals interactions typically span a range of values between 2 and 30 kcal/mol [31].

Knowledge of the Ps contact density allows us to get insight on the instantaneous microscopic electric field acting on Ps. Ps polarizability can be visualized as a displacement of the electron orbital by a small quantity  $b$  along the polarization axis, with respect to the unperturbed Ps. Given

the ground state Ps wavefunction in vacuum as  $\psi_{vac}(x, y, z) = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{\sqrt{x^2+y^2+z^2}}{a_0}\right) =$

$\frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right)$  ( $a_0$  being the Bohr radius of Ps, twice that of hydrogen), using this simple model for

polarized Ps we can write:  $\psi_{matter}(x, y, z) = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{\sqrt{x^2+y^2+(z-b)^2}}{a_0}\right)$ , by assuming that the

displacement occurs along the  $z$  axis. Therefore:  $\eta = \frac{|\psi(0)|_{matter}^2}{|\psi(0)|_{vac}^2} \cong \exp\left(-\frac{2b}{a_0}\right)$  and we find  $b = 0.014$  nm. Then, the Ps induced dipole moment results:  $p = qb = 2.2 \cdot 10^{-30} \text{ C m}$ ,  $q$  being the electron charge and the effective electric field acting on Ps, responsible of its induced polarization, can be estimated as:  $E = p/\alpha_{Ps} = 3.7 \cdot 10^9 \text{ V/m}$ . This value is compatible with microscopic dipolar electric fields produced at distances of a few tenth of nm.

Although in our discussion we used a rather naïve model of Ps polarization, nevertheless, we found reasonable results, at least in terms of order of magnitude.

At last, another conclusion that can be drawn from the analysis of the magnetic quenching of Ps in ferrocene is that we can exclude the presence of ortho-para conversion processes. Indeed, in the absence of such processes the quenching ratio  $R$  must reach the value  $2/3$  at high fields, as it is clear from eq. 8. On the other hand, ortho-para conversion processes induce transitions also between the ortho sublevels with  $m = \pm 1$  and the para sublevel, as well as reorientation transitions among the triplet sublevels [36-38]. The result is a drop of  $R$  below the asymptotic limit. A mathematical expression of  $R$  in the presence of ortho-para conversion is reported in ref. [36]. In figure 2 we show

the different behavior of  $R$  in the absence (full line) and in the presence (dashed line) of ortho-para conversion, by assuming, as an example, a small conversion rate, equal to 1/10 of the pickoff decay rate in ferrocene. For simplicity, the curves refer to a Ps with  $\eta = 1$ . The dotted line represents the asymptotic limit of  $R$  in the absence of conversion. Data in fig. 1 clearly show that even at the highest fields  $R$  does not fall below the expected limiting value.

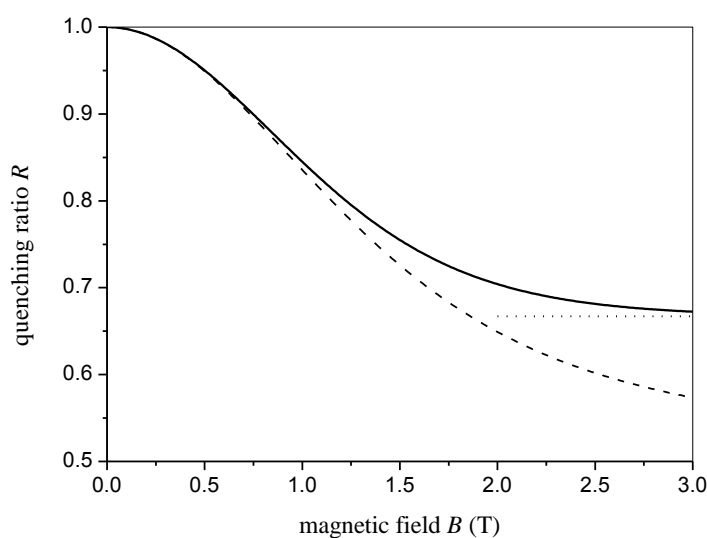


Figure 2 – Magnetic quenching of an unperturbed Ps (with  $\eta = 1$ ) in the absence (full line) and in the presence (dashed line) of ortho-para conversion. The conversion rate is taken equal to 10% of the pickoff decay rate in ferrocene. The horizontal, dotted line evidences the limit ( $2/3$ ) reached by the quenching ratio at high magnetic fields.

## Conclusions

Before being annihilated, a positron in ferrocene can form, with a surrounding electron, a bound system, whose lifetime in the ortho state is 1.22 ns. This system can be described as a ‘swollen’ Ps: its contact density is reduced to about 77% of that characterizing an unperturbed Ps, owing to the interactions with the medium. This diminution accounts for the reduction of the intrinsic decay rates as well as of the hyperfine splitting. We attributed the swelling of the Ps wavefunction to London dispersion forces, which are the only Van der Waals interactions occurring between Ps and ferrocene molecules. Although weak, these interactions may be responsible of the reduction of the contact density due to the small distance involved in the interaction. Our data allowed us to estimate the order of magnitude of the Ps-ferrocene molecule interaction as well as the effective microscopic electric field acting on Ps trapped in a cavity of the host medium.

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