Formal calculation of the pick-off annihilation rate for ortho- and parapositronium

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The annihilation of a positronium atom in matter is often described as occurring through two alternative channels; self-annihilation (involving the electron in the atom itself) and pick-off annihilation (involving an external electron). For many years it has been debated if it is correct to assume the same pick-off annihilation rate for orthopositronium and for parapositronium. We address this problem with a formal calculation that takes into full account the spin variables of all the electrons involved in the process as well as the indistinguishability of the electrons. On the basis of our results, we make clear the conditions leading to a definition of the pick-off rate independent of the spin state of the positronium atom.

I. INTRODUCTION

Pick-off annihilation of positronium (Ps), a familiar concept for anyone in the field of low-energy positron physics, is based on the following simple model: in a chemically inert medium, annihilation for positrons that have formed Ps atoms may occur through two alternative channels, namely, (a) annihilation with the electron bound in the Ps atom itself (self-annihilation); (b) annihilation with an electron of the medium (pick-off annihilation). Correspondingly, the overall annihilation rate should be given by the sum of two contributions: for self-annihilation, the same rates of Ps in vacuo [$\lambda_{2\gamma}=(125.2\ \text{ps})^{-1}$ for parapositronium (p-Ps) and $\lambda_{3\gamma}=(142.1\ \text{ns})^{-1}$ for orthopositronium (o-Ps)], and, for the pick-off process, a rate $\lambda_{\text{pick-off}}$ proportional to the encounter probability of the Ps atom with external electrons.

Clearly, the above formulation of a two-channel model does not take into the proper account either the modification of the Ps wave function due to the interaction with the medium or the indistinguishability of the electrons. Nevertheless, as long as the model is applied to gases, where the overlap of the Ps electron with any other electron of the medium is small, these weaknesses have limited practical consequences. However, the pick-off model has been applied to condensed matter since early investigations on annihilation in solids and liquids (for reviews, see Refs. 1 and 2), and maintains all its importance for modern developments in this fields. For instance, it turns out to be crucial for the quantitative interpretation of magnetic quenching experiments in liquids and solids, leading to the identification and to the characterization of positroniumlike complexes.[3,4] Several authors (Hodges *et al.*,[5] Mogensen,[6] Mogensen and Eldrup,[7] Dupasquier, Schrader[8]) have discussed the problem of a definition of the pick-off rate consistent with electron indistinguishability and with the Pauli principle. Unfortunately, their conclusions are in part conflicting. The main point of discrepancy is whether the pick-off annihilation rate is, or is not, the same for ortho and para states.

In this paper we address this question with additional arguments. In Sec. II we make clear the terms of the problem with a discussion of the different viewpoints; in Sec. III we present a formal calculation of the annihilation rates for a system formed by a positron interacting with one unpaired electron and, at the same time, with a pair of electrons in a closed shell. This is the simplest example of a positron-multielectron complex containing at least one unpaired electron.[3] The results guide us to a correct evaluation of the assumptions that have to be made in order to simplify calculations in more general cases.

II. DIFFERENT VIEWPOINTS ON PICK-OFF ANNIHILATION

The Mogensen treatment of the annihilation rates for an unperturbed Ps atom embedded in a diamagnetic medium[6] is based on a formalism consistent with the electron indistinguishability and the Pauli principle. In the framework of the Hartree-Fock approximation, the wave function of the system is taken by Mogensen as an antisymmetrized linear combinations of products of the Ps wave function with electron wave functions representing closed-shell orbitals of the medium. The result of the calculation shows that the annihilation rate is the sum of four terms. One of these terms coincides with the intrinsic annihilation rate of Ps. The sum of the other three terms represents the overall effect of the interaction with the medium; it contains two terms specifically connected to electron exchange, which depend on the spin state of the system.

Mogensen's calculation thus demonstrates that the net difference between the annihilation rates of Ps in a medium and in a vacuum depends on the spin. One might take this difference as a definition of pick-off rate, which

would certainly be in line with the original two-channel model mentioned in the previous section. We are, however, against this choice, which includes in the pick-off rate two exchange terms that cannot be properly connected to annihilation of the positron with the electrons of the medium. This is not only disturbing for the formulation of interpretative models, but is also a serious complication for applications related to magnetic quenching experiments. We shall see below that a more convenient definition is possible.

The approach of Hodges *et al.*[5] is very similar to that of Mogensen. The main difference is that the overall antisymmetric wave function is built up as a combination of terms which are mutually orthogonal in the electron space. The advantage of this choice, which does not limit the generality of the approach, is that the exchange terms in the annihilation rate expression disappear. The treatment of Ref. 5 has been extended by Dupasquier[3,4] to a more general case, including the distortion of the Ps wave function due to the interaction of the bound electron-positron pair with the medium. Brusa *et al.*[9] have recently shown that the same formalism can also be applied to a system with two unpaired electrons.

According to Dupasquier,[3,4] the final expression of the annihilation rates for para and ortho states of a bound electron-positron pair, including any possible disturbance of the internal wave function due to exchange as well as to electric forces, can be expressed in the form

$$\lambda_{\text{para}}=\kappa\lambda_{2\gamma}+\lambda_{\text{pick-off}}\ , \tag{1}$$

$$\lambda_{\text{ortho}}=\kappa\lambda_{3\gamma}+\lambda_{\text{pick-off}}\ . \tag{2}$$

where κ is the contact density of the positron with an electron occupying the unpaired state, in units of the contact density in unperturbed Ps; λ_{para} and λ_{ortho} are, respectively, the annihilation rates of *p*-Ps and *o*-Ps in vacuo; $\lambda_{\text{pick-off}}$ is defined by the equation

$$\lambda_{\text{pick-off}}=(\tfrac{1}{4}\lambda_{2\gamma}+\tfrac{3}{4}\lambda_{3\gamma})2\sum_i \eta_i\ . \tag{3}$$

Here, η_i is the positron-electron contact density evaluated for the electron in the ith full orbital, in the same units as κ.

The above equations are not in contrast with Mogensen's results. They imply, however, a new definition of the pick-off rate. The advantage is that one obtains an expression which (a) is the same for ortho and para states; (b) is directly related to the probability of encounter of the positron with electrons in closed-shell orbitals. It becomes also explicit that self-annihilation rates, represented in (1) and (2) by the term containing the parameter κ (internal contact density), are not the same in a medium and in a vacuum. The difference comes from the dependence of κ on many body interactions, including exchange. As discussed in Refs. 3 and 4, $\lambda_{\text{pick-off}}$ and κ are experimentally accessible by combining lifetime and magnetic quenching measurements,[10] also by lifetime measurements alone, if the short-living para component can be isolated with sufficient accuracy.[11]

The treatments of Mogensen, Hodges *et al.*, and Dupasquier refer to the same physical situation, i.e., full closed-shell symmetry for all electrons but one. On the basis of this assumption, all the above authors limit the antisymmetrization of the wave function to exchange between spatial electron states. This means that the spin of the electrons occupying full orbitals is not taken explicitly into account in the wave function; in the calculation of the annihilation rate, a "spin-averaged" state is assumed for these electrons. According to Mogensen[6] and to Mogensen and Eldrup,[7] this is only an approximation, and not necessarily a good one. Their argument can be presented as follows. Owing to the Pauli principle, electrons repel other electrons of the same spin orientation. Therefore, the electron of *p*-Ps should screen the positron from those electrons which are more effective for annihilation, i.e., those with the correct orientation for giving fast 2γ annihilation; on the contrary, the *p*-Ps electron should repel only the electrons oriented for the less probable 3γ annihilation. According to this picture, full orbitals should contribute to annihilation more effectively for *o*-Ps than for *p*-Ps.

We do not agree with the above argument. One has to remember that we are discussing a system that includes one unpaired electron and many other electrons occupying filled orbitals. The mathematical consequence of this hypothesis, according to the Pauli principle, is the orthogonality in the position space of the wave function of the unpaired electron to the wave function of any other electron, independently of its spin orientation. Physically, this means that the "Pauli repulsion" mentioned by Mogensen and Eldrup acts in the same way on both electrons of a filled orbital. In a formal calculation of the pick-off rate, the delicate point is to take into account the orthogonalization of electron states in the proper way. This is shown in detail in the next section.

Schrader[8] presents an evaluation of pick-off annihilation rates, based on a representation of the electron orbitals of the medium in terms of eigenfunctions of unperturbed Ps. This approach gives the pick-off rate as a sum of terms proportional to $1/n^3$, where n is the principle quantum number of the Ps eigenfunctions. On the grounds of the same argument of Mogensen and Eldrup cited above, and on the assumption that the $n=1$ level is already occupied by the Ps electron, the $n=1$ term of the sum is included in the calculation of 2γ pick-off annihilations for *o*-Ps only; on the contrary, for *p*-Ps the same term, contributing only to 3γ annihilations, is neglected. Clearly, the result is a much larger value of the pick-off rate for *o*-Ps than for *p*-Ps.

Schrader's approach is interesting. Indeed, it can be shown that the calculation of an upper limit to the effective electron density at the positron as a sum of Ps-like terms is based on the orthonormality and the completeness of the set of Ps eigenfunctions (the only remark we can make is that, in order to satisfy the requirement of completeness, the sum should include also the contribution of the continuum states, whose weight we are unable to estimate). However, the idea that the dominant contribution to pick-off for the ortho state comes from an electron of the medium with a large projection on the Ps $n=1$ eigenstate is not convincing. According to Schrader's picture, this eigenstate is already occupied by

the Ps electron; in our view, the presence of a second electron with a large projection onto the same eigenstate is justifiable only as the result of a redox reaction between the medium, donating an electron, and the Ps atom. Here, however, we are discussing pick-off, not chemical reactions. In an inert medium (e.g., liquids like water and hydrocarbons, or solid insulators like quartz, ice, alkali halides) the transfer of an electron from a filled orbital of the medium to an unfilled orbital correlated to the positron is energetically impossible, independently from the spin orientation. If we identify approximately the empty orbital with the $n=1$ eigenstate, as Schrader suggests, we see that the corresponding term should in no case be included in Schrader's sum.

III. MATHEMATICAL TREATMENT

The mathematical proof of the arguments, that in the previous section we have brought against the conclusion that the pick-off rate must be different for *o*-Ps and *p*-Ps, can be given in the most direct way by calculating the annihilation rates of a positroniumlike system on the basis of an antisymmetrical wave function with full account of spin variables. This has never been done before, for the labor it may cost with complicated algebra. However, the task is not impossible if we consider a system with four particles only: a positron, an unpaired electron, and two electrons occupying the same orbital. For fixing ideas, one may think of the collisional complex PsHe or of the system $PsLi^+$. Actually, it is not important at this point to consider a specific system. We are interested only in bringing out the dependence of annihilation rates on the spin state, and for this we do not need to specify the forces that keep together the four particles. In this respect, the present approach is very general; we assume, however, the absence of spin-orbit interactions, and this restricts our treatment to nonrelativistic energies. Noting that pick-off annihilation occurs after thermalization, and that it involves with high probability only external atomic shells, the restriction to the nonrelativistic case is not a severe sacrifice. On the other hand, neglecting spin-orbit interaction is a necessary assumption for us: otherwise, total spin would not be a conserved observable and the distinction of ortho and para states would be meaningless. An approximate treatment of spin-orbit effects on spin states can be found in Ref. 12.

We proceed as follows. As a first step we define an operator Λ whose expectation value is the annihilation rate. The next step is to write the wave functions of the different spin states of the four-particle system. Finally, we calculate the expectation values of Λ for these wave functions, and comment on the result.

The operator Λ is assumed to be a contact operator, i.e., a linear combination of δ functions of the positron-electron relative positions. This is a widely accepted approximation, that we do not discuss here (see, for instance, Ref. 6). As selection rules on annihilation require that antisymmetric spin states (para states) of positron-electron pairs annihilate essentially via 2γ emission, whereas symmetric spin states (ortho states) annihilate in 3γ's, we find it convenient to express Λ in terms of the positron-electron spin exchange operator $\Sigma_{p,e}$. Of course, since in our system the positron may annihilate with anyone of the three electrons, Λ is a sum of three formally identical terms Λ_i. We thus write

$$\Lambda=\sum_{i=1,3}\Lambda_i \ , \tag{4}$$

where

$$\Lambda_i=8\pi\alpha_0^3\delta(\mathbf{r}_p-\mathbf{r}_i)\left[\frac{1-\Sigma_{p,i}}{2}\lambda_{2\gamma}+\frac{1+\Sigma_{p,i}}{2}\lambda_{3\gamma}\right] . \tag{5}$$

The factor $8\pi\alpha_0^3$ is the reciprocal of the positron-electron contact density in unperturbed Ps. It is easy to check that the rate operator Λ_i is diagonal with the energy and spin eigenfunctions of Ps, with expectation values $\lambda_{2\gamma}$ for *p*-Ps and $\lambda_{3\gamma}$ for *o*-Ps in the $n=1$ energy level.

The wave functions we need for our calculation are supposed to be energy eigenfunctions belonging to the same eigenvalue of the spatial Hamiltonian, as well as eigenfunctions of $|\mathbf{S}|^2$ and of S_z, where $\mathbf{S}$ is the total spin of the system. We thus label these wave functions Ψ_{jm} with the total spin quantum number j and the azimuthal quantum number m; the limitation $j\leq 1$ comes from the assumption that there is one unpaired electron only. Due to the requirement of full exchange antisymmetry, Ψ_{jm} is not factorable in a spatial and a spin part; the simplest possible form is

$$\begin{aligned}\Psi_{jm}=&\frac{1}{\sqrt{3}}\phi(\mathbf{r}_p,\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)\chi_{jm}(p,1)\chi_{00}(2,3)\\&+\frac{1}{\sqrt{3}}\phi(\mathbf{r}_p,\mathbf{r}_2;\mathbf{r}_3,\mathbf{r}_1)\chi_{jm}(p,2)\chi_{00}(3,1)\\&+\frac{1}{\sqrt{3}}\phi(\mathbf{r}_p,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2)\chi_{jm}(p,3)\chi_{00}(1,2) \ ,\end{aligned} \tag{6}$$

where the positron is indicated by p and the electrons by numbers. The symbols χ indicate two-particle eigenfunctions of $|\mathbf{S}|^2$ and S_z. The spatial part is represented by the function ϕ; a semicolon in the list of variables separates the unpaired electron from the two electrons in the filled orbital; for these two electrons, the spin factor is always the singlet eigenfunction χ_{00}. This spin factor ensures the antisymmetry under exchange of the electrons in the same orbital; of course ϕ must be invariant for this exchange, i.e.,

$$\phi(\mathbf{r}_p,\mathbf{z};\mathbf{x},\mathbf{y})=\phi(\mathbf{r}_p,\mathbf{z};\mathbf{y},\mathbf{x}) \ . \tag{7}$$

In accordance with the limits of the present treatment, which concerns the interaction of a positron-electron pair with an electron pair frozen in a singlet state, we have not included in (6) terms with reversed spatial and spin symmetry for the last pair of electrons, that may come from electron exchange even in the absence of a direct spin interaction. The same simplification is adopted in the classical treatment of pick-off in He by Frazer and Kreidy.[13] Physically, terms with reversed symmetry correspond to virtual triplet excitation of the electron pair initially prepared in the singlet state. In a real situation, triplet terms would contribute to the complete wave function

with an amplitude of the order of the ratio between the gain in electrostatic energy obtained with the excitation and the energy required for the excitation. The gain in electrostatic energy is approximately 75% of the London dispersion energy for the interaction of a Ps atom in contact with a polarizable system containing the other electrons. According to this evaluation, we expect a triplet amplitude of $<7\times10^{-3}$ for Ps-He.

We come now to a crucial point of the present theory, consisting in a specific condition to be imposed on the spatial wave function in order to obtain an expression of the annihilation rate free from exchange terms. What we require is a sort of "internal orthogonality"; we mean here the orthogonality, in the presence of the positron, of electron states which correspond to position variables separated by a semicolon in the list of variables of ϕ. This is expressed by the equations

$$\int_\Omega \phi^*(\mathbf{r}_p,\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)\delta(\mathbf{r}_p-\mathbf{r}_1)\phi(\mathbf{r}_p,\mathbf{r}_2;\mathbf{r}_3,\mathbf{r}_1)d\mathbf{r}_p d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3=0\ , \tag{8}$$

$$\int_\Omega \phi^*(\mathbf{r}_p,\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)\delta(\mathbf{r}_p-\mathbf{r}_1)\phi(\mathbf{r}_p,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_p d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3=0\ . \tag{8'}$$

The integration domain Ω is the normalization 12D-volume of the wave function ϕ. For scattering situations, where the wave function may not be entirely contained in a limited space region, normalization in a box is required. In this case, the normalization box needs to coincide with a Wigner-Seitz cell centered on the closed-shell scatterer.

Similar relationships, obtained from Eqs. (8) and (8′) by permuting electron indexes, are implicitly satisfied when (7), (8) and (8′) are satisfied. Conditions (8) and (8′) are equivalent, within our more general formalism, to the orthogonality of the Ps electron to filled electron orbitals mentioned in Refs. 3–5. These conditions are automatically ensured in the independent particle approximation, if ϕ is written as the product of eigenfunctions belonging to different eigenvalues of the same one-electron Hamiltonian. However, we do not need to restrict here the generality of our approach; in the Appendix we show that Eqs. (7), (8), and (8′) can be satisfied by a proper choice of ϕ which does not imply any limitation on the interaction between the four particles of our system.

The rate operator Λ is diagonal with the wave functions Ψ_{jm}. The expectation values of Λ depend only on the quantum number j; for $j=1$, one has the ortho annihilation rate λ_{ortho} and, for $j=0$, the para annihilation rate λ_{para}. From the symmetry of Ψ_{jm} it follows that

$$\begin{aligned}\langle\Psi_{jm}|\Lambda_1|\Psi_{jm}\rangle&=\langle\Psi_{jm}|\Lambda_2|\Psi_{jm}\rangle\\&=\langle\Psi_{jm}|\Lambda_3|\Psi_{jm}\rangle\\&=\tfrac{1}{3}\langle\Psi_{jm}|\Lambda|\Psi_{jm}\rangle\ .\end{aligned} \tag{9}$$

We thus can obtain the annihilation rates from the equations

$$\lambda_{\text{ortho}}=3\langle\Psi_{11}|\Lambda_1|\Psi_{11}\rangle \tag{10}$$

and

$$\lambda_{\text{para}}=3\langle\Psi_{00}|\Lambda_1|\Psi_{00}\rangle\ . \tag{11}$$

The explicit calculation of (10) and (11), which in turn implies the calculation of the expectation values of the positron-electron spin exchange operator $\Sigma_{p,1}$, can be carried out by expressing all spin factors in (6) in terms of eigenfunctions of $\Sigma_{p,1}$. One can use the following relationships:

$$\chi_{11}(p,2)\chi_{00}(3,1)=\tfrac{1}{2}[\chi_{00}(p,1)+\chi_{10}(p,1)]\chi_{11}(2,3)-\tfrac{1}{2}[\chi_{00}(2,3)+\chi_{10}(2,3)]\chi_{11}(p,1)\ , \tag{12}$$

$$\chi_{11}(p,3)\chi_{00}(1,2)=-\tfrac{1}{2}[\chi_{00}(p,1)+\chi_{10}(p,1)]\chi_{11}(2,3)+\tfrac{1}{2}[-\chi_{00}(2,3)+\chi_{10}(2,3)]\chi_{11}(p,1)\ , \tag{12'}$$

$$\chi_{00}(p,2)\chi_{00}(3,1)=\tfrac{1}{2}[-\chi_{10}(p,1)\chi_{10}(2,3)+\chi_{00}(p,1)\chi_{00}(2,3)-\chi_{11}(p,1)\chi_{1-1}(2,3)-\chi_{1-1}(p,1)\chi_{11}(2,3)]\ , \tag{13}$$

$$\chi_{00}(p,3)\chi_{00}(1,2)=\tfrac{1}{2}[-\chi_{10}(p,1)\chi_{10}(2,3)-\chi_{00}(p,1)\chi_{00}(2,3)+\chi_{11}(p,1)\chi_{1-1}(2,3)+\chi_{1-1}(p,1)\chi_{11}(2,3)]\ . \tag{13'}$$

It is also convenient to have a concise notation for the space integrals implicitly contained in (10) and (11). Consistently with the definitions given in Ref. 3, leading to Eqs. (1) and (3) we thus write the internal (κ) and the external (η) contact density parameters as

$$\kappa=8\pi\alpha_0^3\int_\Omega|\Phi(\mathbf{r}_p,\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)|^2\delta(\mathbf{r}_p-\mathbf{r}_1)d\mathbf{r}_p d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ , \tag{14}$$

$$\begin{aligned}\eta&=8\pi\alpha_0^3\int_\Omega|\Phi(\mathbf{r}_p,\mathbf{r}_2;\mathbf{r}_3,\mathbf{r}_1)|^2\delta(\mathbf{r}_p-\mathbf{r}_1)d\mathbf{r}_p d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\\&=8\pi\alpha_0^3\int_\Omega|\Phi(\mathbf{r}_p,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2)|^2\delta(\mathbf{r}_p-\mathbf{r}_1)d\mathbf{r}_p d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ .\end{aligned} \tag{15}$$

As for Eqs. (8) and (8′), the integration domain of the integrals in the above equations concides with the normalization volume. It may be interesting to note that, in the

case of scattering situations requiring normalization in a Wigner-Seitz cell, the dependence on the normalization volume is canceled by integration in Eq. (14) but not in Eq. (15). This leads to a linear dependence of η on the density of the scatterers.

Taking into account that the exchange terms in (10) and (11) are suppressed by conditions (8) and (8′), one obtains the annihilation rates as sums of three terms. The first one comes from the first term of (6), and corresponds to annihilation with the unpaired electron (self-annihilation of quasi-Ps); the other two, coming from the remaining terms of (6), are identical, and correspond to annihilation with electrons in the filled orbital (pick-off annihilation). The final result is

$$\lambda_{\text{ortho}}=\kappa\lambda_{3\gamma}+2\eta(\tfrac{1}{4}\lambda_{2\gamma}+\tfrac{3}{4}\lambda_{3\gamma}) , \tag{16}$$

$$\lambda_{\text{para}}=\kappa\lambda_{2\gamma}+2\eta(\tfrac{1}{4}\lambda_{2\gamma}+\tfrac{3}{4}\lambda_{3\gamma}) . \tag{17}$$

We thus retrieve, for the case of a single filled orbital, the result of Refs. 3 and 4, reported above in Eqs. (1)–(3). However, the important difference of the present treatment compared to Refs. 3 and 4 is that we have not adopted any simplification concerning the contribution of filled orbitals to annihilation. This shows that the identity of the pick-off rate for ortho and for para states is not an artifact due to a cavalier approximation, but the consequence of the proper symmetry and orthogonality requirements of the spatial wave function.

The four-particle system discussed in the present work reproduces, at a reduced level of formal complexity, all the important features of the interaction of a bound electron-positron pair with a system with an arbitrary number of paired electrons. Thus, in the nonrelativistic limit, in agreement with Refs. 3 and 4 we confirm that

(i) a definition of the pick-off annihilation rate consistent with the electron indistinguishability is possible even by taking full account of the spin of all the electrons;

(ii) the above definition implies the calculation of the pick-off rate on the basis of a wave function of the system chosen in accordance with specific conditions [Eqs. (7), (8), and (8′) in the case of a four-particle system] which suppress exchange terms;

(iii) with this definition, and if the closed-shell symmetry of the interacting system is not perturbed by the Ps atom, the pick-off rate does not depend on the spin state;

(iv) the final result coincides with that obtained by taking an average spin state for electrons occupying filled orbital;

(v) the effect of exchange forces is implicitly present in the conditions (7), (8), and (8′) (or their equivalent) for the wave function; therefore it affects the overall annihilation rate (self-annihilation as well as pick-off);

(vi) in consequence of (v), the variations of the overall annihilation rates due to the presence of an environment depend on the spin state, in agreement with Mogensen's result[6]; our Eqs. (1) and (2) give

$$\lambda_{\text{ortho}}-\lambda_{3\gamma}=(\kappa-1)\lambda_{3\gamma}+\lambda_{\text{pick-off}} , \tag{18}$$

$$\lambda_{\text{para}}-\lambda_{2\gamma}=(\kappa-1)\lambda_{2\gamma}+\lambda_{\text{pick-off}} , \tag{19}$$

APPENDIX

As anticipated in Sec. III, Eqs. (7), (8), and (8′) do not limit the generality of our approach. Indeed, the four-particle ground-state eigenfunction ϕ of the spatial Hamiltonian H can be obtained from another generical ground-state eigenfunction ξ as explained below.

Let us define the following operators:

R is a rotation of electron position by one step in a list

and

E is an exchange of the position of the last two electrons in a list .

Taking into account the electron exchange degeneracy of the ground level, we use R and E for obtaining a complete set of ground-state eigenfunctions:

$$\begin{aligned}&\zeta_1=(1+E)\xi,\quad \zeta_1'=(1-E)\xi ,\\ &\zeta_2=R(1+E)\xi,\quad \zeta_2'=R(1-E)\xi ,\\ &\zeta_3=R^2(1+E)\xi,\quad \zeta_3'=R^2(1-E)\xi .\end{aligned} \tag{A1}$$

A properly chosen linear combination of these eigenfunctions gives the final wave function ϕ. According to (7), however, the eigenfunctions $\zeta_1',\zeta_2',\zeta_3'$, which are antisymmetric for the exchange of the last two electrons in the list of variables, are not to be included in the linear combination. We are thus left with the expression

$$\phi=\sum_{i=1,3} C_i\zeta_i . \tag{A2}$$

The three equations to be used for determining the coefficients C_i are the normalization condition, and Eqs. (8) and (8′), i.e.,

$$\langle\phi|\phi\rangle=1 , \tag{A3}$$

$$\langle\phi|\delta(\mathbf{r}_p-\mathbf{r}_1)|R\phi\rangle=0 , \tag{A4}$$

$$\langle\phi|\delta(\mathbf{r}_p-\mathbf{r}_1)|R^2\phi\rangle=0 . \tag{A5}$$

For writing explicitly these equations in terms of the coefficients C_i, we adopt the following concise notation:

$$\langle\zeta_i|\zeta_j\rangle=\alpha_{ij} , \tag{A6}$$

$$\langle\zeta_i|\delta(\mathbf{r}_p-\mathbf{r}_1)|\zeta_j\rangle=\beta_{ij} . \tag{A7}$$

We thus obtain

$$\sum_{i,j} C_i^*C_j\alpha_{i,j}=1 , \tag{A3′}$$

$$\sum_{i,j} C_i^*C_j\beta_{i,j+1}=0 , \tag{A4′}$$

$$\sum_{i,j} C_i^*C_j\beta_{i,j+2}=0 . \tag{A5′}$$

where, of course, the indexes are to be counted modulo 3.

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