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A two-particle model for Positronium confined in sub-nanometric cavities

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INTRODUCTION

In the last years, the electron-positron bound state, namely the **positronium atom** (Ps), has been widely used as a **probe** to test structural properties of porous materials. This is possible thanks to the strong connection between Ps annihilation rate and the electronic structure of the confining medium.
Accessible experimental measurements concern **annihilation rates** by pickoff processes and contact densities (the electron density at the positron position).
While the pickoff process is well understood, existing models describing Ps properties in nanometric or sub-nanometric cavities **fail** to justify the lowering of the contact density with respect to that of Ps in vacuum, as found in most materials.
For this reason we formulated a **new two-particle model** in which only the electron is confined in the cavity by exchange forces, while the positron is moving freely and feels the medium via a positive work function.
We show that this model explains experimental data for a large class of materials and suggests a way to gain information on pore sizes and positron work functions.

ANNIHILATION IN MATTER: basic concepts

There are two main annihilation processes that affect Ps in matter.
Pickoff annihilation rate depends on the **electron density** of the material

$$\lambda_{pickoff} = \pi r_0^2 c \iiint |\psi_{Ps}(\vec{r}_+, \vec{r}_-)|^2 n(\vec{r})\, \delta^3(\vec{r}_+ - \vec{r}) d^3\vec{r}_+ d^3\vec{r}_- d^3\vec{r}$$

Intrinsic annihilation rate depends on the **relative contact density**: the probability of finding the positron at the electron position inside Ps, normalized with respect to its vacuum value.

$$k_r = \frac{1}{k_0} \iiint |\psi_{Ps}(\vec{r}_+, \vec{r}_-)|^2 \delta^3(\vec{r}_+ - \vec{r}_-) d^3\vec{r}_+ d^3\vec{r}_-$$

The total annihilation rate for Ps in matter can be written as:

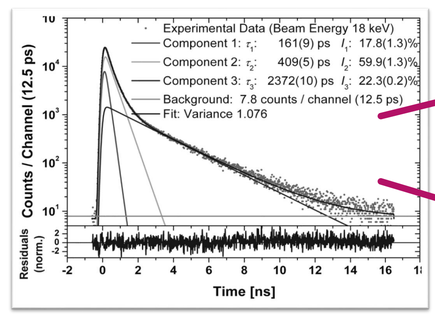
$$\lambda_{para} = \kappa_r \lambda_{2\gamma} + \lambda_{\text{pickoff}}$$

$$\lambda_{ortho} = \kappa_r \lambda_{3\gamma} + \lambda_{\text{pickoff}}$$

PALS

Positron annihilation lifetime spectroscopy is a non-destructive spectroscopy technique that allows studying a variety of phenomena and material properties on an atomic scale.
PALS measures the elapsed time between the implantation of the positron into the material and the emission of annihilation radiation.
In combination with a **magnetic field**, it can be used to obtain information about the pickoff annihilation rate and the contact density of Ps in matter.

This technique is especially useful for the geometric characterization of free spaces inside **nanoporous** materials.



Without magnetic field: λ_{pickoff}

With magnetic field: κ_r

THEORETICAL MODEL

A new **two-particle** model[1] is formulated in order to describe the **internal** structure of the confined Ps.
The key concept behind the model is that the strong **confining potential** is mainly due to the Pauli exclusion principle and as such it is felt only by the electron.
In this picture, the complex interactions between the positron and both bulk electrons and nuclei can be collected into a **bulk potential** which acts only on the positron and which to a first approximation is related only to the value of the **positron work function** ϕ_+(minimum energy needed to remove the positron from the solid).

Because of the spherical symmetry of the system, the ground-state wave function depends on three independent scalar variables only:

r_e is the electron distance from the cavity center,
R is the interparticle distance and
a is the angle between them.

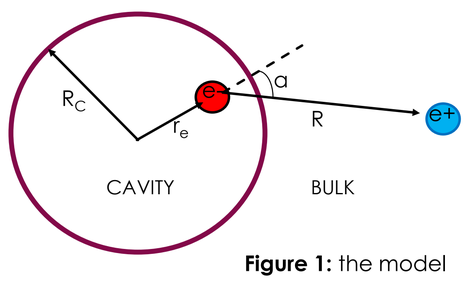


Figure 1: the model

In terms of these variables, the Hamiltonian operator reads:

$$H = \left(\frac{\partial^2}{\partial r_e^2} + 2\frac{\partial^2}{\partial R^2} + \frac{2r_e^2 + R^2 + 2r_e R\cos\alpha}{r_e^2 R^2} \frac{\partial^2}{\partial \alpha^2} - 2\cos\alpha \frac{\partial^2}{\partial r_e \partial R} + 2\frac{\sin\alpha}{R}\frac{\partial^2}{\partial r_e \partial \alpha} + 2\frac{\sin\alpha}{r_e}\frac{\partial^2}{\partial R \partial \alpha} + \frac{2}{r_e}\frac{\partial}{\partial r_e} + \frac{4}{R}\frac{\partial}{\partial R} + \frac{2r_e^2\cos\alpha + R^2\cos\alpha + 2r_e R}{r_e^2 R^2 \sin\alpha}\frac{\partial}{\partial \alpha} \right) - \frac{1}{R} + V_{bulk}[\phi_+]$$

The Hamiltonian is not separable and does not contain a small parameter on which a perturbation expansion might be based, therefore we perform a numerical calculation.

NUMERICAL SOLUTION

Expansion of the ground state wave function on a **trial** basis set:

$$\psi_\varepsilon(r_e, R, \alpha) = \sum_{i,j,k} C_{ijk} (R_C^2 - r_e^2)^i (R^{j-1} e^{-\frac{R}{\varepsilon}}) (\cos\alpha)^{k-1}$$

(with $k \le j$)

Which satisfy $|\psi_\varepsilon(r_e, R, \alpha)|_{r_e = R_C} = 0$
Energy minimization with respect to the expansion coefficients C_{ijk} and ε, an additional parameter which represents a variation of the Bohr radius of Ps

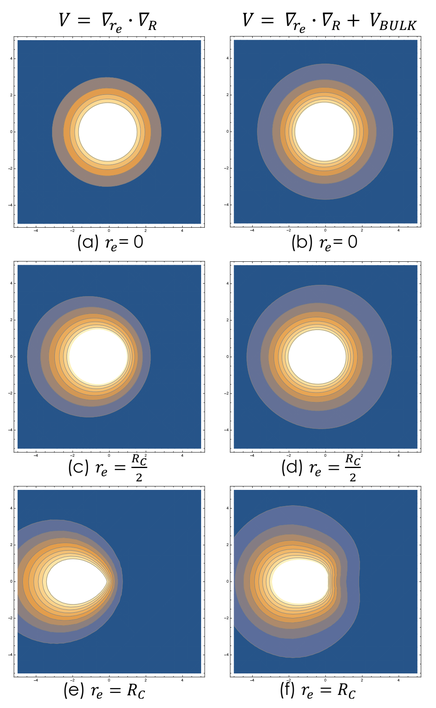


Figure 2: the distortion of the relative wavefunction of the positron around the electron, for a cavity $R_C = 5\ au$. On the left column we used $\phi_+ = 0\ eV$ (no Bulk Potential) to stress the confining contribution, while on the right we used $\phi_+ = 6\ eV$. In all pictures, the nearest cavity wall is on the right side.
It is clear that when the electron is in the center of the cavity (a,b), radial symmetry is recovered. At half the cavity radius (c,d) some deformation effects begin to show up till the maximum deformation is reached at the cavity walls (e,f).

RESULTS

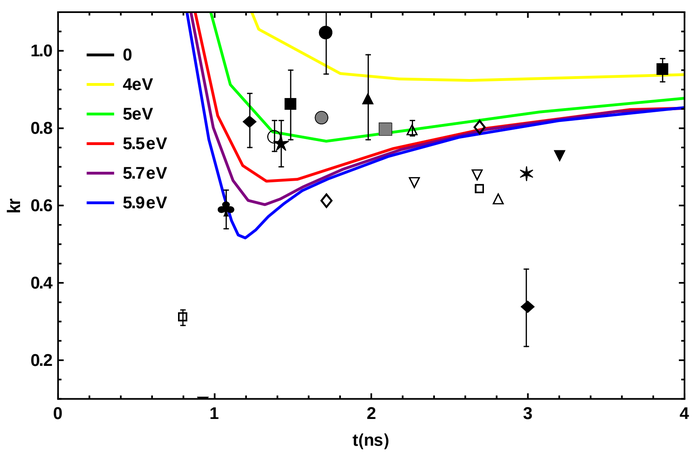


Figure 4: the relative contact density k_r as a function of the lifetime τ, for some values of the positron work function ϕ_+. The lines are calculated with a $N = 216$ basis set. Available experimental data (symbols) are also shown.

Using the simple relations

$$\lambda = 2p_{out} + (1 - p_{out})\frac{1}{142}[ns]^{-1}$$

$$\tau = \frac{1}{\lambda}[ns]$$

where p_{out} is the probability of finding the positron outside the confining cavity:

$$p_{out} = \int_{|\vec{r}_e + \vec{R}| > R_C} |\psi(r_e, R, \alpha)|^2 d\Omega$$

we are able to establish a **new useful relation** between the relative contact density and the lifetime, which can be used to experimentally determine the value of the positron work function.

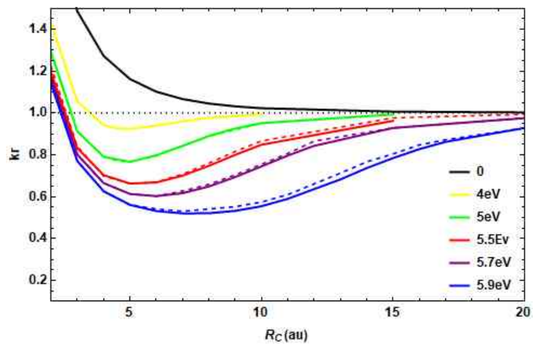


Figure 3: the relative contact density k_r as a function of the confining radius R_C, for some values of the positron work function ϕ_+. Full lines are calculated with a $N = 216$ basis set, while the dashed lines are calculated with a smaller $N = 125$ set. The distance between those lines can be considered as a raw error estimation.

References: [1]G. Marlotti Tanzi, F. Castelli, and G. Consolati, Phys. Rev. Lett. **116**, 033401(2016)