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A.L.R. Bug, M. Muluneh, J. Waldman, and P.A. Sterne

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

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Positronium in Solids:
Computer Simulation of Pick-Off and Self-Annihilation

Amy L.R. Bug[1], Melaku Muluneh[1], Jillian Waldman[1] and P.A. Sterne[2]
[1] *Swarthmore College, Swarthmore, Pennsylvania 19081, U.S.A.*
[2]*Lawrence Livermore National Laboratory, Livermore, CA 94550, U.S.A.*

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Positronium (Ps) is simulated using Path Integral Monte Carlo (PIMC). This method can reproduce the results of previous simple theories in which a single quantum particle is used to represent Ps within an idealized pore. In addition, our calculations treat the e^- and e^+ of Ps exactly and realistically model interactions with solid atoms, thereby correcting and extending the simpler theory. We study the pick-off lifetime of o-Ps and the internal contact density, κ, which controls the self-annihilation behavior, for Ps in model voids (spherical pores), defects in a solid (argon), and microporous solids (zeolites).

I. Introduction: Positron annihilation lifetime spectroscopy (PALS), and ACAR, which measures the momentum distribution of annihilating electrons, are capable of measuring void dimensions in a material. The low self-annihilation rate, $\Gamma_0 = 142ns$ in vacuum, of the spin triplet o-Ps state, makes it an excellent probe of void spaces in insulating solids. Theory is needed in order to convert a lifetime or momentum spectrum into an estimation of the free volume fraction or distribution of pore spaces. While the "holy grail" would be a theory based on a quantum chemical calculation of the dynamics of all electrons in a given material, plus an injected positron, practical constraints require us to perform simplified calculations. This paper presents a computational model of positronium (Ps) within an insulating solid. In contrast to most previous work, we explicitly treat Ps as a two-particle electron-positron state bound by the Coulomb interaction. This allows us to access the accuracy of existing methods that treat Ps as a single quantum particle, and to look at experimental observables that depend explicitly on the two-particle nature of Ps, such as the internal contact density, κ.

II. Methods and Theory: PIMC is a method for sampling from the canonical density matrix, $\hat{\rho}(\beta) = exp(-\beta\hat{H})$, for systems of light particles. It thus allows calculation of thermal averages of observables: $<\hat{A}> = \frac{1}{Q}Tr\hat{\rho}\hat{A}$, where $Q \equiv Tr\hat{\rho}$. Here, $\hat{H}$ is the Hamiltonian, β the inverse temperature, and $\hat{A}$ is an observable of interest. Our PIMC method for simulating Ps is described in detail in Ref. [1]. PIMC has been used e.g. by Miller and Reese to investigate self-trapped Ps states in fluids[2]. In our calculation, the e^+ and e^- are represented as polymeric chains of entities known as "beads". The two chains of beads interact through the Coulomb interaction, which we treat using a numerical interpolation of the exact Coulombic propagator[3] (an improvement on the Yukawa propagator of Ref. [1].) The calculation also requires terms in the propagator of the form $exp(-\beta(V_+ + V_-))$ to describe interactions of e^+ and e^- with the material. We use an effective hard sphere potential for Ps within spherical pores, enabling a comparison with the commonly used Tao-Eldrup[4] and related models. For comparison, we have also calculated the lifetimes in a finite-temperature version of the PIB model by summing the appropriate Bessel function contributions for the given sphere size and temperature, following Goworek et al.[5]. For realistic systems such as argon, we use a Hartree potential V_+ calculated from overlapping atomic charges obtained from local Density Functional Theory (LDA-DFT), and a potential V_- fit to scattering data[6], in a superposed atom approximation. Correlation from atomic polarization is not included; more on this below.

We assume that the annihilation rate (inverse lifetime) of Ps in a solid can be written as[9]

$$\Gamma = \kappa\Gamma_0 + \Gamma_{\text{p.o.}}, \tag{1}$$

with the self-annihilation rate, $\kappa\Gamma_0$, and the pick-off annihilation rate, $\Gamma_{\text{p.o.}}$, operating in parallel. In materials simulated here, electronic densities $n_-(\mathbf{r})$ are given by LDA-DFT and the pick-off rate is obtained by standard Monte Carlo sampling of:

$$\Gamma_{\text{p.o.}} = \pi r_e^2 c \int n_-(\mathbf{r}) n_+(\mathbf{r}) \gamma[n_-(\mathbf{r})] d^3r \ . \tag{2}$$

The enhancement factor, γ, is a functional which can be calculated from theory[7]. Schmitz and Muller-Plathe used a similar approach in their PIMC simulation of Ps lifetimes in polymers[8]. Eq. 2 is an alternative to simpler model annihilation calculations[4] in which a uniform rate of $\Gamma_{\text{p.o.}} = 2ns^{-1}$ (the rate of annihilation of free Ps$^-$) is assumed to exist within a shell on the pore surface.

The internal contact density, κ, is the factor by which the square of the Ps orbital, $\phi(\mathbf{r}_+, \mathbf{r}_-)$, in a material differs from its vacuum value for coincident particles. Thus, $\kappa = 8\pi a_0^3 \int |\phi(\boldsymbol{r}_+, \boldsymbol{r}_-)|^2 \, \delta(\boldsymbol{r}_+ - \boldsymbol{r}_-) d^3\boldsymbol{r}_+ d^3\boldsymbol{r}_-$. Changes in κ can alter the lifetime of the shorter-lived singlet state p-Ps; a high-resolution spectrometer is required to see this effect. Normally for o-Ps, the second term of Eq. 1 is dominant. However, an applied magnetic field ("magnetic quenching") allows one to deduce κ in both PALS and ACAR experiments. Both dielectric screening and polarization should reduce κ from unity. Indeed, experiments find values from $\kappa \approx 1$ (some silaceous zeolites, polymers, and noble fluids) to $\kappa < 0.1$ (some ionic crystals)[9]. Ironically, the prevalent spherical "particle-in-a-spherical-box" (PIB) model[4], widely used to interpret data on micropores in molecular solids, would result in an increase in κ due to spherical confinement[10, 11]. Competition between effects of compression (spherical or asymmetrical) and polarization, and their net effect on κ, are calculable with our PIMC method.

III. Spherical Pores: Table I shows the calculated annihilation rate, $\Gamma \approx \Gamma_{\text{p.o.}}$, for o-Ps in a small, spherical pore (infinite potential well) as the probability of the e^+ lying within a distance of $\Delta = 1.656\mathring{A}$ multiplied by the rate $2ns^{-1}$. A temperature of $0.01\ au$ was chosen for swift convergence; pore radii R_c are sufficiently small that the system is approximately in its ground state. $P = 600$ beads and approximately $500K$ MC passes (several thousand uncorrelated configurations) were used.

Single-particle PIMC simulations in micropores reproduce the analytical, ground-state single-PIB results precisely, but the two-particle model gives smaller rates/longer lifetimes[1] so that, for example, pores of radii $5\ au$ and $10\ au$ have lifetimes that under the single-PIB theory correspond to radii of around $5.3\ au$ and $11.4\ au$ respectively. We are also able to study mesopores at finite temperature, as suggested by Gidley et al.[5] for application to thin films. Fig. 1 shows the distribution of e^+ density at $T = 600K$ within Δ of the wall for $R_c = 46.9\ au$. A PIMC simulation of a single particle of mass m_e reproduces single-PIB theory, confirming the accuracy of our method. From Fig. 1 and Eq. 1 lifetimes are $\Gamma^{-1} = 68$ (PIMC) and $67\ ns$ (single-PIB). But for Ps, as in the case of micropores, the e^+ of Ps avoids the wall as compared with a calculation involving a single particle of mass $2m_e$. The latter yields $\Gamma^{-1} = 50\ ns$ (less than for mass m_e since a higher mass allows more excited states, hence higher angular momenta, to participate at a given temperature). This lifetime is in reasonable agreement with same-volume cube data at this temperature[5]. However, the two-particle PIMC calculation yields a significantly higher value of $\Gamma^{-1} = 83\ ns$ due to the reduction in positron density near the cavity wall.

R_c (au)	Γ (ns^{-1})	Γ_{SPIB} (ns^{-1})	κ
∞	-	-	1.0
10	0.23	0.33	1.05
8	0.41	0.58	1.10
6	0.92	1.09	1.20
5	1.36	1.48	1.45
4.75	1.48	1.59	1.50

Table I: Calculated o-Ps annihilation rates and contact densities in cavity of radius R_c. "SPIB" denotes single particle-in-a-box model for Ps[4].

Our PIMC method also allows calculations of the internal contact density, κ. Although a hydrogen atom in a hard spherical cavity can be solved exactly[10, 11], the case of electron and positron wavefunctions vanishing on a sphere is different. (PIMC can reproduce the former, exact result for Ps. E.g. $\kappa(R = 6) = 0.744 \pm 0.10$ from PIMC, compared with an exact answer of 0.748.) Table I shows $\kappa(R_c)$, affirming the idea[10] that only tiny pore radii will increase κ significantly. Yet, for example, the confinement of a spherical bubble of radius $R_c = 8$ au (typical in a molecular liquid) increases κ by 10%, a meaningful contribution given that the net experimental change (a reduction) tends to be 20% or less in many liquids and solids of interest [9, 12]. Our PIMC model exhibits the correct electrostatic polarizability of $\alpha = 36$ au. Calculated values of κ decrease with electric field, E, as 1 - $\kappa(E) \propto E^2$, consistent with analytical theory. A future simulation of a polar solid is planned.

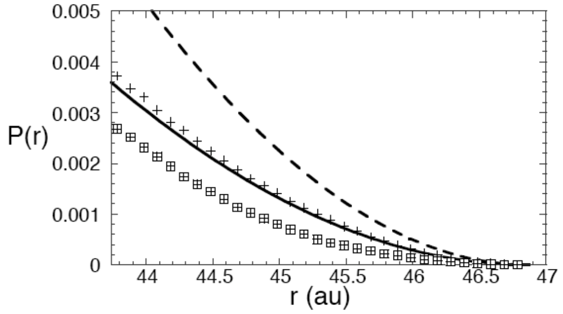

FIG. 1: Probability density, P(r), within outermost layer of $R_c = 46.9$ au cavity. Shown are lone e^+ (solid line: PIB theory; + : simulation) and e^+ of Ps (dashed line: PIB theory, ⊞ : simulation).

IV. Solid Argon: We simulate Ps within a rigid lattice (unfortunately precluding any self-trapped behavior in this solid[13]) with cubic cell lattice constant of 10.04 au. We model a perfect FCC crystal and also remove a single atom to model a crystal with an unrelaxed monovacancy. In the perfect crystal, quantities like Ps orbitals, annihilation rates, and bead-fluid correlation functions seem to vary little with simulation temperature $T = 0.01 - 0.00025$ au (the melting temperature of argon). Fig. 2 shows the bead-Ar pair correlation function, $g(r)$. In the perfect crystal, Ps exists in a delocalized, Bloch-type state. Its DeBroglie wavelength is on average somewhat less than that of a free particle; but Ps is not confined in any interstitial site. The first peak in $g(r)$ is consistent with a location equidistant between two adjacent Ar atoms, but this does not imply binding at this site since successive peaks in $g(r)$ do not conform to the distribution that would result. Valleys in $g(r)$ are well-correlated with locations of peaks in an Ar-Ar pair correlation function, giving rise to a picture of an e^+ fairly-well distributed in the interstitial spaces, and avoiding the atomic centers.

Thermal equilibrium has not been simulated in the defected crystal to date; the path integral would need to sample a volume roughly 20 au on a side, the unit cell size for the monovacant crystal; as opposed to 7 au in the perfect crystal. Preliminary data suggests that Ps is not localized in our model defect, although it is metastable there. Fig. 2 shows $g(r)$ for Ps localized within the defect during a $50K$ step sampling run at $T = 0.01\ au$. This form is typical of Ps localized in a cavity. The first peak is located at 7 au, the distance between the center of the cavity and the first surrounding layer of atoms. While successive features are indistinct, the next peak corresponds to what would be a strong peak at $12.2\ au$ for a particle centered in a monovacancy. Whether Ps, though delocalized, is able to remain in the vacancy for a time long compared to its lifetime (hence produce a distinct signal in the PALS spectrum) remains an open question, solvable via Path Integral Transition State Theory.

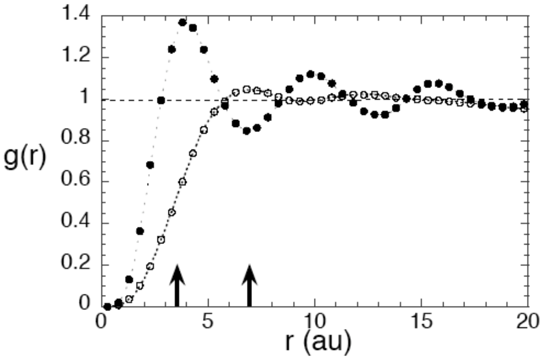

FIG. 2: Pair correlation function g(r), where r is the distance from a bead to an Ar atom. Runs with $P = 400$ averaged over $200K$ passes, for $T = 0.01\ au$. Filled circles: Perfect crystal. Open circles: Monovacant crystal. Arrows denote expected peaks from locations in tetrahedral interstitial site and center of monovacancy.

The calculated (pick-off) annihilation rates were $\Gamma = 1.9 \pm 0.1\ ns^{-1}$ and $0.53 \pm 0.05\ ns^{-1}$ for Ps thermalized in the perfect crystal and for Ps transiently located within the monovacancy. To our knowledge, separate experimental annihilation rates in bulk Ar for e^+ and Ps have not been reported, but the value of $\tau_2^{-1} = 2.3\ ns^{-1}$[14] might be compared with our perfect crystal rate. A rate of $\tau_3^{-1} = 0.4\ ns^{-1}$[13, 15] has been attributed to Ps annihilation in defects. Defects larger than a monovacancy, and ones that are annealed with Ps present, might well produce smaller simulated rates. On the other hand, we have not modeled the effect of solid polarizability. For the case of e^+ annihilation, polarization was found to increase a calculated annihilation rate for bulk Ar[16]. While one knows how to model the polarization attraction for an e^+-Ar interaction[17], a two-particle model of Ps presents a new challenge. A simple superposition of e^+ and e^- polarization potentials would tend to over-stabilize the system[18].

V. Zeolites: Zeolites, both dry and filled with water and other adsorbents, have frequently been the subject of positron annihilation experiments in which multiple lifetimes were determined. To simulate Ps within zeolites, a simple atomistic potential was adopted, with e^+ and e^- repelled from a zeolitic oxygen at a distance r with a potential proportional to $A(\sigma/r)^{12}$ where A = 0.22 au and $\sigma = 1.87\ au$. While this model might be embellished to include polarization, Si and Al, counterions and adsorbates; it provides a starting point from which to consider various cage structures. We have simulated Ps within silica sodalite and faujasite. Eq. 1, with an insulator model of electron correlation using $\gamma = 4.3$, gives a lifetime of $\Gamma^{-1} = 2.7\ ns$ for sodalite, which is consistent with experiment and previous calculations, both single-PIB and PIMC. But as pointed out previously [18, 19], though these two types of calculation yield similar lifetimes, the predicted physical details are rather different.

For faujasite in vacuum, experimental values in the range of $5 - 15\ ns$ have been reported in association with α-caged o-Ps[20]. In faujasite, the simulated lifetime for Ps is found to be $\Gamma^{-1} = 4.6\ ns$ for $T = 0.01\ au$. Interestingly, the single-PIB prediction suggests that temperature makes a large difference for α cages of radius $R_c - \Delta = 6.5\mathring{A}$. At $T = 0.01\ au$ and $0.001\ au$ (room temperature) the lifetimes would be $5.0\ ns$ and $9.2\ ns$, respectively. During a 200K step simulation at $T = 0.01$, Ps is seen to sample a region spanning more than one α cage and is not observed in the β cages. As before, the timescale for Ps to move to various locations (β vs. α cages, or between neighboring cages, for example) for such a large ($46\ au$) unit cell is left open for future study.

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University of California
Lawrence Livermore National Laboratory
Technical Information Department
Livermore, CA 94551