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Does Quantum Mechanical Tunneling Affect the Validity of Hole Volume Distributions Obtained from Positron Annihilation Lifetime Measurements?

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ABSTRACT: Positron annihilation lifetime spectroscopy, which is applied to measure distributions of hole volume sizes in polymers, uses a model to relate the positronium (Ps) lifetime to hole volume dimensions. It is assumed in this model that the Ps remains in one site until annihilation. Recently, the validity of this last assumption has been questioned by Yu et al. (Yu, Z.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1995**, *28*, 6268.), who calculated the tunneling rate between sites and concluded that the rate was rapid enough that a Ps would typically sample many hole volumes before annihilating. To investigate this question we calculated the rate for Ps in one potential well to transfer to a second. We found for appropriate, equal wells, that the rate is comparable with that of Yu et al., while for only slightly unequal wells the transfer is cut off. This cutoff is a consequence of the removal of the degeneracy of the single well energies. For multiple wells it is found that *Anderson localization* applies so that quite generally a Ps is trapped at only a single hole volume until it decays. Thus Ps-lifetime hole-size-distribution measurements should be unaffected by tunneling.

Introduction

The lifetimes of positrons in condensed matter provide information on local electron densities. When a positron forms *para*-positronium (*p*-Ps) with an electron, its vacuum lifetime is about 0.125 ns. When it forms *ortho*-positronium (*o*-Ps), its lifetime is about 142 ns. This much longer lifetime is a consequence of the requirement that *ortho*-positronium must decay into 3 γs since the electron and positron spins are coupled to one unit of angular momentum. In solids *o*-Ps interacts with other electrons in the material so that *o*-Ps becomes *p*-Ps and quickly decays. The rate at which this occurs is sensitive to the local environment, e.g., the presence of hole volume defects. The dependence of this rate on material characteristics has been calculated; for example, Brandt et al.[1] considered a model in which the hole volumes accessible to Ps are located on a periodic lattice. The calculated annihilation rate is proportional to the overlap of the wave functions of the lattice electrons and the positron in Ps, which in turn is affected by the field of the lattice electrons and the electron to which it is bound. The overlap depends on the characteristics of the hole volume and the lattice, so the rate reflects these characteristics.

For some systems, polymers in particular, it has been thought the Ps would be localized in one site for its entire lifetime. The lifetimes from different sized holes can then be used to determine the hole size distribution through a model proposed in 1971 by Tao.[2] A premise of the Tao model is that the lack of positive nuclear charge in the hole volume can be approximated as an infinitely deep spherical potential well which acts as a trap for *o*-Ps. The annihilation rate of *o*-Ps inside the electron layer is assumed to be 2.0/ns, which is one-fourth of the bulk annihilation rate of *p*-Ps. The probability of finding *o*-Ps in the electron layer can then be used to calculate the annihilation rate and thus the lifetime of Ps in the void. Eldrup et al.[3] derived the relation below for what is usually designated as τ_3, the *o*-Ps lifetime in a single volume. R_o is the radius of the potential well, R is the radius of the volume measured, and $R_o - R$ is the thickness of the electron cloud layer inside the well.

$$\tau_3 = \frac{1}{2.0}\left(1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_o}\right)^{-1} \qquad (1)$$

Yu et al.[4] have questioned the assumption that the Ps will remain localized for its lifetime. Using a model much like the tunneling model for α-decay, they estimated that the tunneling rates between wells are sufficiently high that a Ps samples many wells in its lifetime. If this is the case, Ps lifetime measurements would only determine the average well size and not carry much, if any, information on hole-size distributions.

We investigate this question by studying in one and three dimensions the behavior of Ps in an isolated two-well system. We then extend this study to multiple wells by comparing the transfer matrix elements and on-site energy variations of a Ps in multiple wells with the criteria for *Anderson localization*. We describe below the calculation of the probability that *o*-Ps will remain localized for its lifetime to a single volume in a two-well and a multiwell system. The parameters used in this calculation are derived from experimental data for various polymer systems measured by positron annihilation lifetime spectroscopy.

Positronium in Two Wells

One Dimension. The eigenstates for this system are symmetric and antisymmetric with respect to the midpoint between the wells. The lowest energy solutions of each type are shown in Figure 1. The time dependent wave function for a particle assumed to be in the left well at $t = 0$ is

$$\Psi(L@t = 0,t) = \frac{1}{\sqrt{2}}(e^{-iE_S t}\Psi_S + \mathrm{e}^{-iE_S t}\Psi_A) \qquad (2)$$

where we have used $\hbar = 1$. The time to transfer to the right well is then the time such that $|<\Psi_R|\Psi(L@t=0,t)>|^2 = 1$, that is $t = \pi/(E_S - E_A)$. Therefore, the difference

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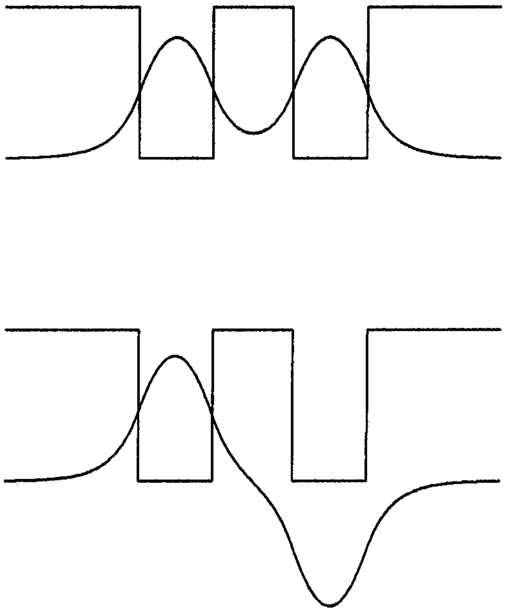

Figure 1. Symmetric and antisymmetric solutions to the two equal well problem in one dimension.

in the symmetric and antisymmetric energies, ($E_S - E_A$), can be used to calculate the time to transfer between wells.

We used:

$$\Psi = Ae^{\kappa x}, \quad B\cos(kx - \gamma), \quad C_1e^{\kappa x} + C_2e^{-\kappa x}, \quad D\cos(kx + \epsilon), \quad F_e^{-\kappa x} \tag{3}$$

for the wave function in the respective regions and then applied boundary conditions to find k, κ, the amplitudes $A-F$, and the phases ϵ and γ.

The depth of the potential well (V_o) is chosen to attain the positronium binding energies that are found for the three-dimensional case, which will be discussed below. The values of the width of the potential well are twice the experimental hole volume radii reported by Jean et al.[5,6] for various polymer systems. For example, Jean et al. found volume radii of around 3 Å for polypropylene[5] and 6 Å for epoxy−diamide systems.[6] The distance between the holes was calculated to be 10 Å for 5% hole volume fraction. The energies were calculated using numbers in these ranges.

For wells of exactly equal dimension, the symmetric and antisymmetric solutions have energy differences on the time scale of picoseconds. Thus a Ps which is initially trapped in one of two equal wells will oscillate back and forth very rapidly. This time scale is comparable to that given by Yu et al.[4]

However, a small difference in the radii of the two neighboring wells results in markedly different behavior. The Ps eigenfunctions become predominantly localized in one well or the other so that a Ps starting in one well is already in an approximate eigenstate and does not oscillate between wells. Localization of the eigenfunctions is shown in the probability curve in Figure 2. The half-widths of the two wells are 3 and 3.05 Å, the distance between the wells was 10 Å, and the well depth was 1.1 eV.

Visualization in Transition Space. When slightly different wells are considered, we can present a geometrical representation of our results.[7] We consider as basis functions the lowest energy eignefunctions of each well separately. So long as the overlap of one of these functions with the other is small, orthogonality issues are neglectable. The full Hamiltonian with both wells may then be written in matrix form as

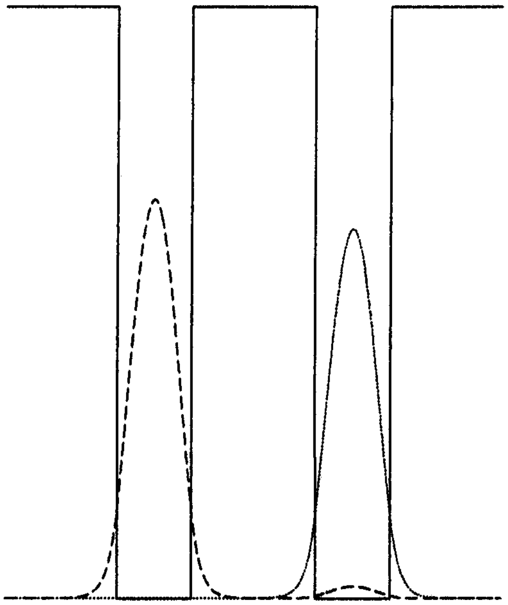

Figure 2. Probability distributions for the unequal two-well problem in one dimension. The left well has a half-width of 3 Å, while the right well has a 3.05 Å half-width. The barrier width is 10 Å and the potential is 1.1 eV.

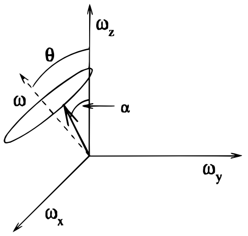

Figure 3. A state vector precessing about a pseudomagnetic field ω. The on-site energy differences are represented by ω_z and the coupling between wells by ω_x. The amplitudes of the spin up (left well) and spin down (right well) states cos $\alpha/2$ and sin $\alpha/2$, respectively, to within a phase factor.

$$\begin{pmatrix} \langle\Psi_L|H|\Psi_L\rangle & \langle\Psi_L|H|\Psi_R\rangle \\ \langle\Psi_R|H|\Psi_L\rangle & \langle\Psi_R|H|\Psi_R\rangle \end{pmatrix} = \begin{pmatrix} E_L & J \\ J & E_R \end{pmatrix} \tag{4}$$

If we subtract the average diagonal elements from the individual diagonal elements we can then write the Hamiltonian as

$$\mathbf{H} = \begin{pmatrix} \omega_z/2 & \omega_x/2 \\ \omega_x/2 & -\omega_z/2 \end{pmatrix} \tag{5}$$

where we have made the obvious identifications. This Hamiltonian describes the precession of a spin 1/2 object in a pseudomagnetic field, as shown in Figure 3. If the spin is up, then the particle is in the left well, while if it is down, then it is in the right well. If the wells are equal, then the precession is about the x axis and complete transfer occurs. If the wells are unequal, the pseudospin precesses primarily around the original direction. Using θ to denote the angle between vector ω and the z axis, the long time average probability of being in the initial well is $(1 + \cos^2\theta)/2$ and the long time average probability of being in the other well is $(\sin^2\theta)/2$. The results for typical wells are given in Table 1. For equal wells, $(\sin^2\theta)/2$ is 0.5, indicating that

Table 1. Two 1-D Wells Separated by 10 Å with V_o = 1.1 eV[a]

δ radii (Å)	ω ($\times 10^{12}$ Hz)	θ (deg)	($\sin^2\theta$)/2
3 → 3	0.725	90.0	0.5
3 → 3.05	1.303	3.4	0.002
3 → 3.1	2.563	2.7	0.001

[a] The time average probability of being in the right well after starting in the left well is ($\sin^2\theta$)/2.

Table 2. Interaction Integral and Isolated Well Energies for a Ps in Two 3-D Wells Separated by 10 Å with Different Potential Well Depths[a]

δ radii (Å)	V_o (eV)	E_L (eV)	E_R (ev)	($E_L - E_R$) (eV)	J (eV)
3 → 3	1.5	0.49	0.49	0	1.74×10^{-4}
3 → 3.05	1.5	0.49	0.51	0.02	1.74×10^{-4}
3 → 3.1	1.5	0.49	0.53	0.04	1.74×10^{-4}
3 → 3	2.0	0.89	0.89	0	2.94×10^{-5}
3 → 3.05	2.0	0.89	0.91	0.02	2.94×10^{-5}
3 → 3.1	2.0	0.89	0.93	0.04	2.94×10^{-5}

[a] Since the interaction integral, J, has only a weak dependence on the well radii, the interaction integral was calculated between two equal 3 Å wells.

there is an equal probability of being in either well. For only slightly unequal wells, 3 and 3.05 Å, the probability of being in the other well drops to 0.002, demonstrating the cutoff of transfer.

Three-Dimensions. We could treat the two-well three-dimensional problem exactly by solving the Schrödinger equation numerically for the full Hamiltonian. Rather than do this, we start with solutions for the single well problem for a spherical well of radius R and depth V_o

$$\Psi = \begin{Bmatrix} A\dfrac{\sin \kappa r}{\kappa r} & r \le R \\ B\dfrac{e^{-kr}}{kr} & r > R \end{Bmatrix}$$

[This is in contrast to the infinitely deep well assumed by Eldrup. We compared the overlap of the Ps wave function with the bulk in the finite well case and found that this was in qualitative agreement with that for the shell of charge assumed by eq 1.] The constants A and B are obtained from the boundary conditions at R and by normalization. The energy of positronium is determined by $\tan \kappa R = \kappa/k$. The well potential was calculated to be between 1.5 and 2 eV by considering the limiting hole volume for formation of o-Ps.

Note that so long as the two wells are reasonably separated the lowest energy solutions of each separate well are approximately orthogonal to each other and we can write the Hamiltonian as

$$\mathbf{H} = \begin{pmatrix} E_L & J \\ J & E_R \end{pmatrix} \tag{6}$$

in which the interaction or transfer integral is

$$J = \int A_L \frac{\sin \kappa_L r_L}{\kappa_L r_L} V_L(r) B_R \frac{e^{-k_R r_R}}{k_R r_R}\, dV \tag{7}$$

and, e.g., r_L is the distance from the left well center to the point of integration. Since J depends only weakly on the well radii, the interaction integral is calculated between two wells of equal 3 Å radius. Typical values of E_L, E_R, and J are shown in Table 2. These values of J, when compared with the differences in diagonal energies, ($E_L - E_R$), indicate that here too the Ps becomes localized in one of the two wells. Having introduced the interaction between neighboring wells, J, we can now make a natural transition to the multiple well case which we consider next.

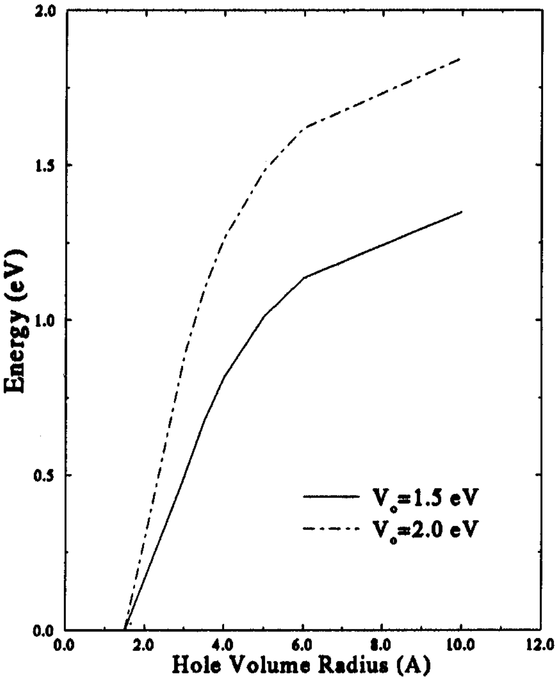

Figure 4. Dependence of the energy on the radius in three dimensions for potential well depths of 1.5 and 2 eV.

Multiple Wells

The problem of a Ps in a lattice of all equal wells is the same as that of an electron in a periodic potential. The solutions are then of the usual completely delocalized Bloch form, $e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{u}_k(\mathbf{r})$, where $u_k(\mathbf{r})$ is a periodic function. This is the case discussed by Brandt et al.[1] If multiple sites having equal isolated well energies are distributed throughout a volume, it would not be unexpected if the eigenfunctions of the total Hamiltonian involved sums over large numbers of isolated well eigenfunctions. A Ps initially in one site would then diffuse away with a rate proportional to J, the interaction integral discussed above.

In the case at hand however, we not only have wells randomly distributed throughout the volume but also have wells of different sizes. A similar problem was considered by Anderson[8] in 1958. Anderson considered a particle moving in a disordered system of sites of varying on-site energies. He found that for sufficient on-site energy variation, δV, the particle becomes localized for a given coupling to nearby sites expressed as BW = $2zJ$, where z is the coordination number or number of near neighbors. Although the intersite coupling is expressed as a bandwidth, BW, which is equal to that which is obtained in the tight binding limit for a periodic lattice, e.g. ref 9, Anderson's approach makes no use of periodicity and thus is applicable to the case of holes in polymers. Anderson found that for a coordination number of $z = 6$, δV/BW greater than 5.5 leads to localization. Values of δV/BW as low as 2 for the same z-value have been shown to lead to localization, as shown by Edwards and Thouless.[10]

The one-site energy variations may be described as

$$\delta V = \langle (E - \langle E \rangle)^2 \rangle^{1/2} = \frac{\partial E}{\partial R} \langle (R - \langle R \rangle)^2 \rangle^{1/2} \tag{8}$$

where we use the numerical relation linking the on-site

Table 3. Values of the Anderson Ratio Calculated for Radii Values Taken From Experimental Polypropylene Data[a]

δ radii (Å)	V_o (eV)	δV (eV)	BW (eV)	δV/BW
3 → 3.05	1.5	0.14	1.04×10^{-3}	134
3 → 3.05	2.0	0.17	1.76×10^{-4}	964

[a] The hole volume fraction is 5%.

energy with the radius. Figure 4 shows $E(R)$, which is obtained from the boundary conditions, for potential well depths of 1.5 and 2 eV. The coupling between sites is the interaction integral, J, described above. We use a z-value of 3, which falls between the minimum of 1 and 6 of a cubic lattice. Values for these parameters are shown in Table 3.

Of course, localized Ps states in Anderson's sense need not be restricted to a single well. The ratio of δV/BW is a measure of the extent of localization. We present in Table 3 values that we calculated for δV/BW. These range from 134 to 964. Since these values are orders of magnitude higher than the threshold predicted by Anderson, we can clearly infer that even for multiwell systems, localization of the Ps states to a single well can be expected.

Discussion and Conclusions

For the case of Ps in two wells, we have used parameters appropriate to polymers to demonstrate that variations of on-site energies associated with small changes in hole radii are sufficient to cause the lowest energy eignefunctions to be predominantly in one well or the other. This is in contradistinction to the degenerate case for which particles starting in one well tunnel rapidly between the two wells, on the time scale of the Ps lifetime. The extension to multiwell systems has been made by showing that *Anderson localization* of the Ps to a single well is expected. Thus, we conclude that tunneling does not significantly affect the validity of positron annihilation lifetime spectroscopy measured hole-volume distributions in polymers.

References and Notes

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