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Corrections to the prevalent bubble model of positronium annihilation in liquids

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The prevalent bubble model to account for the medium dependent pick-off process for positronium (Ps) annihilation in liquids is based on the notion of a bubble (or cavity) in which Ps gets self-trapped. This description, however, suffers from several rather unrealistic features. The Ps atom is treated as a structureless point particle, the potential responsible for its entrapment (as well as the molecular density profile of the cavity) is taken to have a sharp and discontinuous boundary, and the expected change in the surface tension from its bulk value (due to the curvature effects in such microbubbles) is neglected. We demonstrate that all these *ad hoc* assumptions can be corrected for in a rather simple manner, without the introduction of any new free parameter. The finite size of the positronium atom taken in conjunction with the diffusivity of the bubble boundary plays a crucial role. As a consequence, the discrepancies in the prediction of the annihilation characteristics are removed and satisfactory agreement with observations is achieved.

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I. INTRODUCTION

The positronium atom (Ps) consists of an electron e^- and a positron e^+ bound in its lowest s state $(l=0)$, and exists as the spin-singlet para-positronium (p-Ps) and the spin-triplet ortho-positronium (o-Ps). These are formed in liquids and molecular solids, in the ratio 1:3 (in the absence of any spin polarization of the electrons in the medium). In vacuum the p-Ps, having charge conjugation parity plus $(C=+1)$, decays into two γ particles with a lifetime of 0.125 ns, while the o-Ps, with $C=-1$, cannot do so, and annihilates into three γ photons with a much larger lifetime of 140 ns. However, in the presence of matter o-Ps can decay into two γ photons through a process known as pick-off annihilation, whereby the positron in o-Ps senses electrons with opposite spin in the surrounding medium and annihilates through the two photon mode. This component of the positron annihilation spectrum is of great utility since it enables its use as a microprobe in the study of condensed matter, and hence a proper understanding of the underlying process is of paramount importance.

The rate for pick-off annihilation is observed to be considerably lower than what would be expected if the atoms (or molecules) of the liquid were close packed around the positronium. This led Ferrell[1] to propose that the repulsive electron exchange interaction between Ps and surrounding atoms could lead to a self-trapped localized state for the center-of-mass motion of Ps as it finds itself in a confining potential. The interaction energy between the positronium and the surrounding atom is dominated in the relevant range by the integral corresponding to the exchange of the electron in the positronium and the valence electron of the atom involving the Coulomb potential between the electron and the core of the atom. As a result the overlap of the probability density for finding the positron at the site of the electrons in the surrounding atoms (which are pushed away as it were) is reduced and this would lead to the desired increase in the lifetime.

The model was further developed,[2–13] but in its prevalent form the positronium is considered to be a point particle of mass $2m$ ($m=$mass of an electron) moving in a spherical well (SW) of depth U_0 and range R, and the density profile is taken to be of the same shape, viz., $\rho(r)=\rho_0\Theta(r-R)$, r being reckoned from the center of the cavity, where $\Theta(x)$ is the Heaviside step function, and ρ_0 is the number density of molecules in the bulk of the liquid. Henceforth R shall be called the bubble radius. The zero point motion of the positronium inside the bubble (existing in a localized state of energy E_0) exerts an outward "force" on the wall given by $\partial E_0/\partial R$ that is balanced by the inward (contractile) force due to the surface tension σ of the surrounding liquid, thus minimizing the total energy of Ps-bubble system,

$$\frac{\partial}{\partial R}(E_0+4\pi R^2\sigma)=0. \tag{1}$$

Since the pick-off annihilation involves the positron from the positronium and the electrons in the surrounding medium, the rate for the process is governed by the product of the probability of finding the positronium in the liquid (given through its wave function by $|\psi_{SW}|^2$) and the density of electrons in the medium. This factor is given in this model by

$$Z_{eff}\rho_0\mathcal{P}_0=Z_{eff}\rho_0 4\pi\int_R^\infty|\psi_{SW}(r)|^2r^2dr, \tag{2}$$

where the factor $\mathcal{P}_0$ shall be referred to as the overlap integral and Z_{eff} is the effective number of electrons available per molecule for pick-off annihilation (in effect the number of valence electrons, since the Ps atom is unable to penetrate the core of the surrounding atoms). Multiplying this with the annihilation rate given by Quantum electrodynamics, one arrives at the result,

$$\lambda_{pick-off}^{(0)}\equiv\lambda_p=4\pi r_0^2c\rho_0Z_{eff}\mathcal{P}_0, \tag{3}$$

for the pick-off rate, where $r_0 = e^2/mc^2$ is the classical electron radius, e being the charge of the electron and c the velocity of light. The normalized wave function for the positronium center-of-mass motion in the given spherical well[4] is

$$\psi_{SW}(r) = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{2\kappa_0}{1+R\kappa_0}}\begin{cases} \dfrac{\sin k_0 r}{r} & \text{for} \quad r<R \\ \sin k_0 R\dfrac{e^{-\kappa_0(r-R)}}{r} & \text{for} \quad r>R, \end{cases} \tag{4}$$

where $k_0 = \sqrt{4mE_0/\hbar^2}$ and $\kappa_0 = \sqrt{4m(U_0 - E_0)/\hbar^2}$, the energy E_0 being given by the eigenvalue condition,

$$k_0 \cot k_0 R = -\kappa_0 . \tag{5}$$

Apart from the influence of the bubble on the annihilation rate (and hence the lifetime), the bodily motion of the positronium confined in the bubble implies, via the uncertainty principle (and by virtue of momentum conservation) a nontrivial angular correlation (not back to back as for positronium decay at rest) for the two photons emitted through the annihilation of positronium in the bubble. The angular correlation curve $N(\theta)$ is determined from the momentum distribution $P(p)$ of the positronium that in turn is given in terms of the square modulus of the Fourier transform of the wave function, viz.,

$$P(p) = 4\pi p^2 |\tilde{\psi}(p)|^2, \tag{6a}$$

with

$$\tilde{\psi}(p) = \left(\frac{1}{2\pi\hbar}\right)^{3/2}\int \psi(r)\exp\left(-i\frac{\vec{p}\cdot\vec{r}}{\hbar}\right)d^3\vec{r}, \tag{6b}$$

and

$$\mathrm{N}(\theta) = \int_{mc\theta}^{\infty}\frac{1}{p}P(p)dp. \tag{6c}$$

The experimentally measured quantity $\theta_{1/2}$, the full width at half maximum of the narrow component (mainly due to p-Ps) of the angular correlation curve is readily determined from

$$\mathrm{N}(\tfrac{1}{2}\theta) = \tfrac{1}{2}\mathrm{N}(0). \tag{6d}$$

The same basic phenomenon also gives rise to Döppler broadening ΔE_γ of the decaying γ photons that is easily seen to be

$$\Delta \mathrm{E}_\gamma \simeq mc^2\theta_{1/2}. \tag{7}$$

The bubble model described above has been used extensively for the interpretation of the characteristics of positronium spectroscopy in liquids. If the parameters of the model (U_0 and R) are determined by using the observed values of surface tension σ, the balance condition [Eq. (1)] and the experimentally measured rate for pick-off annihilation λ_p, then $\theta_{1/2}$ (and ΔE_γ) can be predicted. Though the agreement appears superficially to be reasonably good it is found that $\theta_{1/2}$ is *systematically underpredicted*[12] sometimes by as much as 20% for some liquids. To bring this discrepancy into sharper relief another strategy is found to be more revealing.[13] The model parameters (U_0 and R) are determined on the one hand by fitting the lifetime data and on the other by using the angular correlation measurement, and then a comparison of the two sets is made. It is found that the potential U_0 obtained by using the former protocol can be as much as a factor of 2 smaller than that arrived at through the later methodology, while the range parameter R could be 10–15% smaller. This type of discrepancy was initially pointed out by Nakanishi and Jean[4] (Table I). This inability to provide a consistent set of parameters to fit the two measurements clearly underlines the need to modify the model.

Apart from the unsatisfactory nature of the prevalent bubble model revealed through the detailed comparison with data as discussed above, it should also be recognized, even from a purely theoretical point of view, that despite its popularity, it is difficult to accept a picture that (i) treats the positronium as a structureless point particle, (ii) considers the liquid-vapor interface as a sharp discontinuity, (iii) neglects the curvature dependence of the effective surface tension of such a microbubble and uses the bulk value.

II. CORRECTIONS TO THE PREVALENT MODEL

In view of the serious lacunae in the prevalent model of positronium annihilation in liquids, we go on to introduce corrections due to each of the neglected factors.

A. Correction due to finite size and structure of the positronium

In order to introduce the structure of the positronium[14] into the framework of the prevailing model we need to appreciate that Eq. (4) for $\psi(r)$ simply describes the motion of the center of mass of the positronium, where $\vec{r} = (\vec{r}_+ + \vec{r}_-)/2$, and $\vec{r}_+$ and $\vec{r}_-$ are the coordinates of the positron and the electron with respect to the center of the bubble. The complete wave function of the positronium is, however, $\psi(r)\phi(\varrho)$ where $\vec{\varrho} = \vec{r}_+ - \vec{r}_-$ is the relative coordinate between the positron and the electron, and the internal ground-state wave function of the positronium is given by

$$\phi(\varrho) = \sqrt{\frac{1}{\pi a^3}}e^{-\varrho/a}, \tag{8}$$

where $a = 2(\hbar^2/me^2)$. Here we have taken recourse to some simplifying and not unreasonable assumptions, to wit, the internal wave function of the positronium is not modified by the environment, and the solvent molecules being much heavier than the Ps atom allows the use of adiabaticity, and the center of mass and relative motions remain separable. The pick-off rate [in lieu of Eqs. (2) and (3)] is now given by

TABLE I. Parameters of the prevalent bubble model (without finite Ps size and diffusivity corrections) for various liquids taken mainly from the paper of Nakanishi and Jean (Ref. 4) however, the lifetime data of those marked with * are cited from that of Jerie (Ref. 24). The subscripts τ or $\theta_{1/2}$ designate values determined by fitting lifetime (τ) or angular correlation data ($\theta_{1/2}$), respectively. The last column shows percentage error in $\theta_{1/2}$ when bubble parameters are fitted using lifetime data.

Liquid	$[R]_\tau$ (Å)	$[R]_{\theta_{1/2}}$ (Å)	$[E]_\tau$ (eV)	$[E]_{\theta_{1/2}}$ (eV)	$[U_0]_\tau$ (eV)	$[U_0]_{\theta_{1/2}}$ (eV)	% err in $\theta_{1/2}$
n-pentane	4.85	5.36	0.42	0.44	0.75	1.44	−17
n-hexane	4.65	5.08	0.46	0.47	0.79	1.33	−15
n-heptane	4.55	4.97	0.48	0.49	0.84	1.44	−15
n-decane	4.33	4.81	0.52	0.42	0.90	1.72	−17
Iso-octane	4.66	5.53	0.46	0.49	0.83	4.78	−18
Cyclohexane	4.26	4.67	0.54	0.55	0.90	1.54	−16
Methylcyclohexane	4.36	4.83	0.52	0.54	0.92	1.78	−17
Benzene	4.11	4.53	0.58	0.59	0.96	1.69	−17
Toluene	4.14	4.58	0.57	0.59	0.97	1.81	−17
Ethylebenzene	4.08	4.39	0.58	0.59	0.96	1.40	−13
o-xylene	4.06	4.51	0.59	0.58	0.99	1.54	−15
m-xylene	4.11	4.45	0.58	0.59	0.98	1.50	−14
p-xylene	4.13	4.48	0.57	0.58	0.97	1.52	−14
Mesitylene	4.18	4.51	0.57	0.59	0.99	1.54	−13
Diethylether	4.75	5.25	0.44	0.45	0.78	1.50	−16
*Methanol	4.26	4.69	0.51	0.52	0.79	1.23	−17
*Ethanol	4.30	4.77	0.51	0.52	0.80	1.37	−18
Propanol	4.36	4.72	0.52	0.53	0.92	1.46	−13
Butanol	4.30	4.66	0.54	0.55	0.95	1.56	−14
Octanol	4.18	4.63	0.56	0.58	0.97	1.84	−15
Acetone	4.29	4.72	0.53	0.54	0.89	1.57	−16
Water	3.12	3.47	0.92	0.93	1.36	2.14	−19

$$\lambda_p = 4\pi r_0^2 c \int d^3\vec{r}_+ \int d^3\vec{r}_- \times \int d^3\vec{r}_e |\psi(r)|^2 |\phi(\varrho)|^2 \rho(r_e)\, \delta(\vec{r}_+ - \vec{r}_e), \tag{9}$$

where $\vec{r}_e$ gives the location of the picked-off electron (which is annihilated by the positron at that point) and $\rho(r_e)$ the density of these electrons given by $Z_{eff}\rho(r)$, where $\rho(r)$ is the number density of the surrounding molecules. Now it is possible for the center of mass of the positronium to be inside the bubble while the positron is outside and contributes to the pick-off rate and also vice versa (in contrast to the earlier description using a structureless positronium). The evaluation of the multiple integral is straight forward though tedious, and the details are relegated to Appendix A. As we shall see later the correction due to finite positronium size to the rate, using the bubble model with a sharp boundary, is small because the additional contribution arising from the positronium center of mass being inside and outside the bubble are of opposite sign and tend to cancel each other. However, this is not the case when the bubble boundary is made diffuse. Juxtaposition of the two corrections, it is seen, enhances the effect.

B. Correction due to diffuse bubble boundary and curvature dependence of surface tension

The picture of a sharp bubble boundary is at variance with the general notion of a liquid-vapor interface,[15] and even more so in the case of bubbles with such microscopic dimensions, as revealed through the numerical-simulation studies of small liquid drops.[16,17] This aspect too, in the present context, has been remarked upon by Roellig,[8] while addressing the pick-off process in liquid helium: "the agreement between the calculated values and the experimental data is surprising, for the bubble may not possess a definite radius, there very well may be a transition region between the cavity that has a helium atom density of zero and the bulk density of the liquid." The more realistic density profile $\rho(r)$ should contain a parameter R characterizing the "size" or "radius" of the cavity, as well as another quantity Δ characterizing the diffuseness of the transition layer.[12] A suitable form for the density profile as obtained from a molecular dynamics study of liquid drops[17] is

$$\rho(r) = \rho_0\left[1 - \frac{1+e^{-R/\Delta}}{1+e^{(r-R)/\Delta}}\right], \tag{10}$$

which smoothly interpolates between $\rho = 0$ at the center of the bubble $(r=0)$ and the bulk density ρ_0 as r becomes very large. The prevailing form of the bubble model results when $\Delta \rightarrow 0$ as in that limit $\rho(r) \rightarrow \rho_0 \Theta(r-R)$.

Since the repulsive exchange interaction between the Ps atom and the host molecules is short ranged, it is not too unreasonable to take the self-trapping potential (which binds the positronium to the bubble) to have the same radial dependence, and accordingly we adopt,

$$U_{WS} = U_0 \left[1 - \frac{1+e^{-R/\Delta}}{1+e^{(r-R)/\Delta}} \right], \tag{11}$$

which is the celebrated Woods-Saxon (WS) potential[18] (in vogue among nuclear physicists). The same symbols U_0 and R are used for the depth and the range for the WS as was used for the spherical well with the understanding that these are parameters that are fitted to reproduce the data. The Schrödinger equation for the center-of-mass motion of the positronium trapped in this potential will have to be solved for the lowest and only relevant state that has the orbital angular momentum $l=0$ (s wave) and the corresponding wave function can be found analytically in terms of Gauss's hypergeometric function (Appendix B). Since Δ/R is expected and found to be rather small, the diffuseness can be treated as a perturbation on the spherical-well potential (U_{SW}) with the same depth and range, and indeed the shift in the energy due to diffusivity may be obtained perturbatively as

$$\Delta E = 4\pi \int_0^\infty (U_{WS} - U_{SW}) |\psi_{SW}(r)|^2 r^2 dr, \tag{12a}$$

the only non-trivial part of the integral being $\int_0^\infty f_{WS} u_{SW}^2 dr$ where $f_{WS} = 1/(1+e^{(r-R)/\Delta})$, the Woods-Saxon function and $u_{SW} = r\psi_{SW}$. This integral for small Δ/R can be easily approximated by writing $u_{SW}^2 = (d/dr)F$, integrating by parts and expanding $F(r)$ in a Taylor series about $r=R$. The method employed is simply akin to what is done in statistical mechanics textbooks[19] in the calculation of the specific heat of a Fermi gas at low temperatures (Δ analogous to the temperature T and R analogous to E_F, the Fermi-energy). The result is

$$\begin{aligned} \Delta E &\simeq -\frac{U_0 \pi^2 \Delta^2}{6} 2 u_{SW}(R) u'_{SW}(R) \\ &= \frac{2U_0 \pi^2 \Delta^2}{3} \frac{\kappa_0^2}{1+\kappa_0 R} \frac{k_0^2}{k_0^2+\kappa_0^2} = E_0 \frac{2\pi^2 \Delta^2 \kappa_0^2}{3(1+\kappa_0 R)}. \end{aligned} \tag{12b}$$

The same correction (to lowest order) is also obtained when the eigenvalue condition for the Woods-Saxon potential is expanded in powers of Δ/R (Appendix B), providing thereby a cross check on the expression. To the same order of accuracy the perturbed wave function has the form of the unperturbed solution [Eq. (4)] except that k_0 and κ_0 are replaced by k and κ that solve the modified eigenvalue condition,

$$k \cot kR = -\kappa \left[1 + \frac{\pi^2 \Delta^2}{3} (k^2 + \kappa^2) \right]. \tag{13}$$

The introduction of diffusivity in the bubble surface enables us to incorporate, in a natural manner, the influence of its radius of curvature on the surface energy, leading to the notion of an effective surface tension σ_{eff} in place of its bulk value σ. This is because this finite-size effect necessitates, in view of the underlying theory, the introduction of not only the radius R of the surface of tension but also the distance Δ characterizing the diffusivity of the surface (which is the separation between the surface of tension and the equimolecular dividing surface). Indeed an approximate relation between σ_{eff} and σ, based on thermodynamic considerations, for a surface with radius of curvature r was put forward by Tolman[20] and by Koenig,[21]

$$\sigma_{eff}(r) = \sigma \frac{r}{r+\Delta}, \tag{14}$$

and, accordingly, the surface energy of the bubble, instead of being $4\pi R^2 \sigma$ [see Eq. (1)], will now be

$$\begin{aligned} E_S &= \int_0^R \frac{2\sigma_{eff}(r)}{r} 4\pi r^2 dr \\ &= 4\pi R^2 \sigma \left[1 - \frac{2\Delta}{R} + 2\frac{\Delta^2}{R^2} \ln\left(\frac{R+\Delta}{\Delta} \right) \right]. \end{aligned} \tag{15}$$

While the possible importance of this effect was emphasized long back by Nakanishi *et al.*,[22] as also by Byakov and Petuchov,[5] since they based their discussion on a model with a sharp bubble boundary, the diffusivity Δ was introduced by hand as a free adjustable parameter. In our version, on the contrary, the diffusivity of the bubble boundary has been organically included, and as such the energy E of the positronium in the bubble, vide Eq. (12b), depends on both R and Δ. As a consequence the total energy must be minimized with respect to both these parameters, and thus the single condition [Eq. (1)] is now replaced by two, namely,

$$\frac{\partial E_t}{\partial R} = \frac{\partial}{\partial R}(E + E_S) = 0, \tag{16a}$$

$$\frac{\partial E_t}{\partial \Delta} = \frac{\partial}{\partial \Delta}(E + E_S) = 0. \tag{16b}$$

Therefore, even though a new parameter Δ was introduced, the additional minimization conditions ensures that we have no more free parameters than the primitive model on which we are making the corrections.

III. RESULTS AND DISCUSSION

In comparing the consequences of incorporating our corrections in the primitive model of positronium annihilation in liquids, we have summarized the results through three tables.

The bubble parameters obtained from the prevailing spherical-well model, in which the bubble potential and the molecular density of the medium follow the sharp profile (and the curvature corrections to the surface tension ignored) is shown in Table I. The severe inadequacy of the model is clearly exposed through the glaring discrepancies in the val-

TABLE II. Same as Table I including finite size and diffusivity corrections.

Liquid	$[R]_\tau$ (Å)	$[R]_{\theta_{1/2}}$ (Å)	$[E]_\tau$ (eV)	$[E]_{\theta_{1/2}}$ (eV)	$[U_0]_\tau$ (eV)	$[U_0]_{\theta_{1/2}}$ (eV)	% err in $\theta_{1/2}$
n-pentane	5.04	5.03	0.47	0.47	1.19	1.28	−2.17
n-hexane	4.86	4.87	0.50	0.50	1.26	1.24	0.47
n-heptane	4.73	4.74	0.53	0.53	1.37	1.32	0.93
n-decane	4.54	4.52	0.58	0.58	1.45	1.51	−1.41
Iso-octane	4.81	4.79	0.52	0.54	1.40	1.55	−2.54
Cyclohexane	4.47	4.48	0.60	0.59	1.59	1.54	2.87
Methylcyclohexane	4.54	4.53	0.58	0.59	1.51	1.56	−1.08
Benzene	4.33	4.33	0.63	0.63	1.56	1.58	−0.39
Toluene	4.34	4.34	0.63	0.63	1.63	1.63	−0.25
Ethylebenzene	4.32	4.33	0.63	0.61	1.53	1.37	3.46
o-xylene	4.27	4.28	0.65	0.64	1.64	1.54	2.06
m-xylene	4.32	4.33	0.64	0.62	1.63	1.46	3.31
p-xylene	4.33	4.35	0.63	0.62	1.61	1.47	2.88
Mesitylene	4.34	4.36	0.64	0.61	1.74	1.48	5.05
Diethylether	4.94	4.93	0.50	0.50	1.26	1.32	−1.45
Methanol	4.63	4.62	0.52	0.54	1.10	1.21	−3.69
Ethanol	4.63	4.62	0.53	0.55	1.14	1.31	−4.76
Propanol	4.53	4.55	0.59	0.57	1.56	1.38	3.75
Butanol	4.45	4.47	0.61	0.59	1.65	1.46	3.70
Octanol	4.37	4.36	0.63	0.63	1.62	1.65	−0.59
Acetone	4.51	4.51	0.58	0.58	1.43	1.46	−0.79
Water	3.44	3.44	0.97	0.96	2.16	2.13	0.24

ues of the bubble parameters, viz., the depth of the confining potential U_0 and the range R obtained by fitting the lifetime τ, on the one hand, and the angular correlation $\theta_{1/2}$ on the other. The respective quantities are indicated through the corresponding subscripts. Note that there is a mismatch of about a factor of 2 between the values of U_0 determined through the two procedures (and a 15–20% difference in the values of the bubble radius R). The last column shows the percentage deviation in the predicted values of $\theta_{1/2}$ from its experimental value for a variety of liquids, with the bubble model parameters determined by fitting the lifetime data. It is important to observe that in all the cases there is a systematic underprediction.

In order to demonstrate the effect of inclusion of the finite size and internal structure of the positronium, the diffusivity of the bubble boundary (and the confining potential) and the curvature dependence of the surface tension, we employ the same procedure as described above, and the results are shown in Table II. It is clear that the errors in values of $\theta_{1/2}$ are no longer systematically underpredicted or overpredicted and that the errors have become significantly smaller. More importantly the values of the model parameters arrived at by fitting the lifetime and angular correlation data are no longer widely divergent, as was the case for the prevailing model, but are in fact rather close to each other. Indeed one may say that the model has become more robust as a consequence of the corrections that we have introduced.

In order to understand the relative importance of the different sources of correction, we have depicted, through Table III, the evolution in the values of the model parameters as the different corrections are introduced, and the attendant change in the percentage departure of the predicted value of $\theta_{1/2}$ from observations, in the case of three liquids for the sake of illustration. It is worth noticing that the effects of the finite positronium size and the diffusivity taken in isolation are each not quite as significant as when they are taken in conjunction. These corrections in fact reinforce each other coherently. The deepening of the well (refer Table III) with the introduction of diffusivity in the bubble boundary has led to the positronium center-of-mass wave function being drawn inwards and thereby the finite-size effects are also magnified, as the cancellation referred to at the end of Sec. II A is thereby offset. However, it is observed that the energy E due to the center-of-mass motion of the positronium in the well is not very sensitive to these changes. It is gratifying to observe *a posteriori* that the value of Δ, is generally small being ~ 0.15 Å, and what is more relevant, $\Delta/R \sim 0.03 \ll 1$. This is necessary or else the Tolman type of description would have been quite meaningless.

Thus we have demonstrated the inadequacies of the prevalent model of positronium decay in liquids, and have shown how the inclusion of the corrections that we have introduced brings the model in closer agreement with experiment, and most importantly makes the description more self-consistent. In particular, by expressing these as perturbative corrections to the existing spherical-well model we have been able to make these results easily accessible. We also emphasize that the modifications discussed are of particular importance in the case of high surface-tension liquids such as water and other associated liquids. We should stress, that

TABLE III. Bubble parameters determined using lifetime data for the representative three liquids water, *n*-heptane, and methanol, showing evolution of the parameters and errors as modification are introduced in steps: SW = spherical well; SWF = spherical well with finite-size correction; SWD = spherical-well with diffusivity correction; SWFD =spherical well with finite-size and diffusivity corrections.

	Water				*n*-heptane				Methanol			
Model	R (Å)	E (eV)	U_0 (eV)	% err in $\theta_{1/2}$	R Å	E (eV)	U_0 (eV)	% err in $\theta_{1/2}$	R (Å)	E (eV)	U_0 (eV)	% err in $\theta_{1/2}$
SW	3.13	0.92	1.36	−19	4.55	0.48	0.84	−15	4.26	0.51	0.79	−17
SWF	3.24	0.92	1.52	−13	4.63	0.48	0.91	−12	4.34	0.51	0.84	−14
SWD	3.43	0.88	1.49	−14	4.77	0.49	1.01	−9	4.62	0.50	0.88	−12
SWFD	3.44	0.97	2.16	+0.24	4.73	0.53	1.37	+0.93	4.63	0.52	1.1	−3.69

apart from the question of numerical comparison with observation, the corrections also represent removing some rather unphysical characteristics of the existing model. Furthermore, it may be worth remarking that there may very well be situations where the internal structure of the positronium plays an important part. Thus, for example, Goldanskii[23] had conjectured on the possibility of the swollen positronium to explain the apparent change in the hyperfine splitting between *o*-Ps and *p*-Ps in media as opposed to its value in the vacuum as revealed through effect of magnetic fields. Our inclusion of this aspect into the model permits a scope for such discussions, not possible with the prevalent version.

Although there have been certain simplifying assumptions made regarding (a) the unperturbed wave function of Ps, irrespective of the environment and that center of mass and relative coordinates remain separable (which may not be always applicable and, therefore, remains as fraility for the present), (b) that the self-trapping potential and the density profile of the host molecules have the same radial dependence, and (c) that the Tolman length (Δ) in Eq. (14) is used to be the same as the diffusivity parameter, nevertheless, the interpretation of a wide variety of experimental data may make the application of this model quite useful.

APPENDIX A

The effect of the internal structure of the positronium on the pick-off rate is given *vide* Eq. (9) as

$$\lambda_p = 4\pi r_0^2 c \rho_0 Z_{eff} \frac{1}{\pi a^3} \int d^3\vec{r} \int d^3\varrho \, e^{-2\varrho/a} |\psi(r)|^2,$$

choosing $\vec{r}$ as the temporary z axis and the angle made by $\vec{\varrho}$ as the polar angle θ, the problem is reduced to the integral,

$$\lambda_p = 4\pi r_0^2 c \rho_0 Z_{eff} \frac{1}{\pi a^3}(4\pi) \times (2\pi) \int_0^\infty r^2 dr |\psi(r)|^2 \int d(\cos\theta) \int d\varrho \, \varrho^2 e^{-2\varrho/a}, \tag{A1}$$

where the limits on the θ and ϱ integrals are discussed below. On the other hand if the positronium were treated as a point particle in a spherical well we would have

$$\lambda_p^{(0)} = 4\pi r_0^2 c \rho_0 Z_{eff} 4\pi \int_R^\infty r^2 dr |\psi(r)|^2 = (4\pi)^2 r_0^2 c \rho_0 Z_{eff} N^2 \sin^2 kR \frac{e^{-2kR}}{2\kappa}, \tag{A2}$$

where N is the normalization constant appearing in Eq. (4) of the text. Thus the correction factor,

$$\frac{\lambda_p}{\lambda_p^{(0)}} = \left(\frac{4\kappa e^{2\kappa R}}{a^3 \sin^2 kR} \right) \times \left[e^{-2\kappa R} \int_0^R dr \sin^2 kr \int d(\cos\theta) \int d\varrho \, \varrho^2 e^{-2\varrho/a} + \sin^2 kR \int_R^\infty dr e^{-2\kappa r} \int d(\cos\theta) \int d\varrho \varrho^2 e^{-2\varrho/a} \right]. \tag{A3}$$

For $r<R$, since the positron must lie outside the cavity to contribute to the pick-off rate, the range of the ϱ integral is from $2[\sqrt{R^2 - r^2 \sin^2\theta} - r\cos\theta]$ to ∞, for given θ going from 0 to π with r from 0 to R. Note that in the limit of a structureless positronium this region $(r<R)$ is unable to contribute at all.

For $r>R$, on the other hand, there are three regions that contribute, two of them with $0 \leqslant \varrho \leqslant 2(-r\cos\theta - \sqrt{R^2 - r^2\sin^2\theta})$ and $2(-r\cos\theta + \sqrt{R^2 - r^2\sin^2\theta}) \leqslant \varrho \leqslant \infty$, when $\cos\theta$ lies between -1 and $-\sqrt{r^2 - R^2}/r$, and one with ϱ ranging from 0 to ∞ with $-\sqrt{r^2 - R^2}/r \leqslant \cos\theta \leqslant 1$. The integrals can be carried out analytically except for some exponential integral functions of the form $\int_R^\infty e^{-\alpha r}/r dr$, etc., or the real part of such integrals for α complex that are easily evaluated numerically.

APPENDIX B

The corrections to the positronium center-of-mass wave function due to diffusivity of the bubble boundary is, as we have argued in the text, best approached by starting from the Schrödinger equation for a Woods-Saxon potential. The wave function for the lowest state $(l=0)$ may be obtained through a change of variables from the radial coordinate r to

$$y=\frac{1}{1+e^{(r-R)/\Delta}}, \tag{B1}$$

whence the reduced wave function $u(r)=r\psi(r)$ is found to satisfy the Gauss hypergeometric equation[25] and

$$u(r)=Ny^{\nu}(1-y)^{\mu}{}_2F_1(\mu+\nu,\mu+\nu+1,2\nu+1;y), \tag{B2a}$$

where N is the normalization constant and

$$\mu=i\left[\frac{4m\Delta^2}{\hbar^2}(E+U_0e^{-R/\Delta})\right]^{1/2}, \tag{B2b}$$

$$\nu=\left[\frac{4m\Delta^2}{\hbar^2}(U_0-E)\right]^{1/2}. \tag{B2c}$$

The eigenvalue condition for the energy E is given by the requirement $u(r=0)=0$ necessary for the well behavior of the wave function ψ at the origin, which implies

$$y_0^{\nu}(1-y_0)^{\mu}{}_2F_1(\mu+\nu,\mu+\nu+1,2\nu+1;y_0)=0, \tag{B3a}$$

where $y_0=y(r=0)$ is given by

$$y_0=\frac{1}{1+e^{-R/\Delta}}. \tag{B3b}$$

Since Δ/R is rather small, y_0 is very close to unity, and for such arguments of the hypergeometric function it is useful to use the identity,

$$F(a,b,c;z)=\frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)}F(a,b,a+b+c+1;1-z)+\frac{\Gamma(c)\Gamma(a+b-c)}{\Gamma(a)\Gamma(b)}(1-z)^{c-a-b}\times F(c-a,c-b,c-a-b+1;1-z),$$

and to translate the eigenvalue condition (B3a) into

$$\frac{\Gamma(-2\mu)}{\Gamma(\nu-\mu+1)\Gamma(\nu-\mu)}(1-y_0)^{\mu}F(\mu+\nu,\mu+\nu+1,2\mu+1;1-y_0)+\frac{\Gamma(2\mu)}{\Gamma(\nu+\mu+1)\Gamma(\nu+\mu)}(1-y_0)^{-\mu}F(\nu-\mu,\nu-\mu+1,-2\mu+1;1-y_0)=0. \tag{B3c}$$

In the limit $\Delta\rightarrow 0$ when the Woods-Saxon potential goes over into the spherical well, by virtue of the fact that $(1-y_0)^{\mu}\rightarrow e^{-ikR}$, and through use of identities such as $\Gamma(z)\Gamma(1-z)=\pi/\sin\pi z$, we can easily recover the eigenvalue condition for the spherical well, namely, $k\cot kR=-\kappa$. We can go on to find the next to leading order term, viz., corrections to order Δ^2 in the eigenvalue condition for which we shall need the expansion of the gamma function

$$\ln\Gamma(1+z)=-\gamma z+\sum_{k=1}^{\infty}(-1)^k\frac{z^k}{k}\zeta(k)\quad \text{for } |z|<1,$$

where γ is the Euler-Mascheroni constant and $\zeta(k)$ are the Bernoulli numbers. Actually we shall only need the term $\zeta(2)=\pi^2/6$, and shall arrive at the result

$$k\cot kR=-\kappa\left[1+\frac{\pi^2\Delta^2}{3}(k^2+\kappa^2)+\cdots\right], \tag{B4}$$

as the modified approximate eigenvalue condition. This is easily seen to be in agreement with the perturbation calculation given in the text [see Eq. (13)]. The modification in the wave function to the same order can similarly be obtained by implementing appropriate expansions of the hypergeometric function in the region $r<R$ and $r>R$. One readily arrives at the result that the form of the wave function, to the order with which we are concerned is the same, in a formal sense, with the solutions for the spherical well [see Eq. (4)] except that k_0 and κ_0 are replaced by k and κ modified in accordance with Eq. B4, with the normalization constant appropriately changed.

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