Pick-off annihilation in positronium scattering from alkali-metal ions

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When orthopositronium collides with a closed-shell atom or ion the “pick-off” process is the dominant process for positron annihilation. In pick-off annihilation the positron annihilates with electrons in the target but not with the electron that is part of the positronium atom. The rate for pick-off annihilation, expressed in terms of the dimensionless parameter $^{1}Z_{\text{eff}}$, for orthopositronium scattering from Li$^+$, Na$^+$, and K$^+$ was computed with an $L^2$ variant of the fixed-core stochastic variational method. The threshold $^{1}Z_{\text{eff}}$ for Li$^+$ and Na$^+$, which can form a stable bound state with Ps were found to be 0.067 and 0.73, respectively, while that for K$^+$, which does not bind Ps, was 0.064.

I. INTRODUCTION

When orthopositronium collides with an atom or ion, one of the possible annihilation processes is called pick-off annihilation. It is not possible for the positron to experience a 2γ decay with the electron-forming part of the orthopositronium atom since the electron and positron are in a spin-triplet state. In the pick-off annihilation process, the positron annihilates with one of the target electrons by the 2γ process. When the target atom has a closed electron shell or subshell, pick-off annihilation via collision is the dominant collision-induced decay process. The pick-off annihilation rate is often expressed in terms of the dimensionless parameter $^{1}Z_{\text{eff}}$. This is related to the cross section for annihilation, $\sigma_{\gamma}(k)$, by the identity [1,2]

\[ \sigma_{\gamma}(k) = 4\pi r_0^2(c/\nu)^{1}Z_{\text{eff}}(k), \]

where $r_0$ is the classical electron radius, $c$ is the speed of light, and $k$ is the momentum of the Ps atom.

The $^{1}Z_{\text{eff}}$ parameter has been measured for various gases [2–4], with the typical values ranging from 0.125 for He to 1.26 for Xe. One of the salient features of the experiments has been the fact that the values of $^{1}Z_{\text{eff}}$ for the most part are relatively small. Although the analogous parameter $Z_{\text{eff}}$ describing positron annihilation in gases can sometimes be very large [2–4] most of the values of $^{1}Z_{\text{eff}}$ are smaller than 1 [2–4].

Although there have been many experimental determinations of $^{1}Z_{\text{eff}}$, there have been few calculations. Until very recently [5], the only calculations reported for $^{1}Z_{\text{eff}}$ had all been for Ps-He collisions. One reason for the paucity of calculations is the difficulty in actually doing Ps-atom scattering calculations. The Ps projectile and the target atom are composite objects with an internal structure. The evaluation of the interaction matrix elements involve multicentre integrals, which are notoriously difficult and time consuming to evaluate [6]. Recently, the stochastic variational method (SVM) and its fixed-core variant (the FCSVM) [7,8] have been applied to the Ps-atom scattering problem [5,9,10]. Scattering lengths and the close-to-threshold phase shifts have been reported for Ps scattering from H, He, Ne, Ar, Li$^+$, Na$^+$, K$^+$, and Ps. In addition, the pick-off parameter $^{1}Z_{\text{eff}}$ was computed for He, Ne, and Ar. The calculated $^{1}Z_{\text{eff}}$ for He, Ne, and Ar generally underestimated the accepted experimental values by a factor of about 3. This was regarded as reasonable since the annihilation matrix element was calculated without the inclusion of short-range electron-positron correlations, which can be expected to increase the matrix element.

Given the shortage of calculations for $^{1}Z_{\text{eff}}$ we have decided to report this coefficient for Li$^+$, Na$^+$, and K$^+$. This effectively doubles the number of systems for which $^{1}Z_{\text{eff}}$ has been reported. Given that two of these systems (Li$^+$ and Na$^+$ [8,11,12]) can bind Ps it was interesting to see whether the $^{1}Z_{\text{eff}}$ was also small for these systems.

II. CALCULATIONS AND RESULTS

The present calculations are based on a modified version of the FCSVM that was recently developed to handle scattering problems. The essential idea of the approach is to diagonalize the system Hamiltonian in a large basis of square-integrable states designed to provide a reasonable representation of a typical scattering state. The phase shifts and other information are then extracted from the positive-energy pseudostates by projecting them with $\Phi_{p_i}(r_0-r_1)$ and fitting to the asymptotic form of the wave function, i.e., $\sin(k(r_0+r_1)/2+\delta)$, at large distances from the nucleus. A full description of the method has been given recently [5,9,10].

Recently, this method was used to give estimates of the phase shifts close to threshold for Ps scattering from He, Ne, Ar, Li$^+$, Na$^+$, and K$^+$ [5]. The actual calculations that are used to determine the scattering wave function were identical to those of [5]. Therefore, no details of the scattering calculation are presented apart from a brief description of the scattering Hamiltonian.

The FCSVM [8] has been used to describe the interaction of the projectile with the atom or ion. The FCSVM replaces the full Hamiltonian for the $N_e$ electrons and a positron by a model Hamiltonian with the core electrons removed, viz.,

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\[ H = -\frac{1}{2} \nabla_0^2 - \frac{1}{2} \nabla_1^2 - V_{\text{dir}}(\mathbf{r}_0) + V_{\text{dir}}(\mathbf{r}_1) + V_{\text{p1}}(\mathbf{r}_0) + V_{\text{p1}}(\mathbf{r}_1) + V_{\text{exc}}(\mathbf{r}_1) - \frac{1}{r_{01}} + V_{\text{p2}}(\mathbf{r}_1, \mathbf{r}_0) + \lambda \hat{P}. \]  

(2)

The direct potential \(V_{\text{dir}}\) for the core is taken from a Hartree-Fock wave function and is the same (although opposite in sign) for the electron and the positron. The exchange potential \(V_{\text{exc}}\) between the scattering electron and the Hartree-Fock core was computed exactly. The operator

\[ \lambda \hat{P} = \sum_{i=1}^{N} \lambda |\phi_i\rangle \langle \phi_i| \]  

is an orthogonalizing pseudopotential that acts to produce wave functions orthogonal to the occupied core orbitals provided \(\lambda\) is a large positive number [13,14].

The polarization potential \(V_{\text{p1}}\) is defined with the functional form

\[ V_{\text{p1}}(r) = -\frac{\alpha_d g^2(r)}{2r^4}. \]  

(4)

The factor \(\alpha_d\) is the static dipole polarizability of the core and \(g^2(r)\) is a cutoff function designed to make the polarization potential finite at the origin. The same cutoff function was adopted for both the positron and electrons. Its form was chosen as

\[ g^2(r) = 1 - \exp(-r^6/\rho^6), \]  

where \(\rho\) is an adjustable parameter. The two-body polarization potential \(V_{\text{p2}}\) is defined as

\[ V_{\text{p2}}(\mathbf{r}_0, \mathbf{r}_1) = \frac{\alpha_d}{r_{01}^3} \langle \mathbf{r}_0 \rangle g(\mathbf{r}_0) g(\mathbf{r}_1). \]  

(6)

Inclusion of the two-body potential ensures that the polarization interaction reduces to a Van der Waals–type interaction when the Ps is at large distances from the nucleus. The exact values of \(\alpha_d\) and \(\rho\) are given elsewhere [5].

In terms of the scattering wave function, the pick-off annihilation parameter \(1Z_{\text{eff}}\) for a collision between a Ps atom and an \(N\)-electron atom is defined as [1]

\[ 1Z_{\text{eff}} = \sum_{i=1}^{N+1} \int \Phi_i(\tau)^2 \delta(\mathbf{r}_0 - \mathbf{r}_i) d\tau. \]  

(7)

In this expression \(\Phi_i(\tau) = (\chi_{i}(\mathbf{s}_0, \mathbf{s}_i) | \Psi(\tau)\rangle\) is a projection of the scattering wave function onto a singlet state of the electron-positron pair, and the summation includes all electrons of the system. The positron coordinate is \(\mathbf{r}_0, \mathbf{r}_1, i > 0\) refers to the electron coordinates and \(\tau\) refers to the collective set of electron coordinates. The scattering wave function in this expression should be normalized to unit positronium density of incoming positronium atoms prepared in a singlet state. For an orthopositronium atom colliding with a closed-shell system, this expression simplifies to

\[ 1Z_{\text{eff}} = \frac{1}{4} \int d^3r d^3x \rho(\mathbf{r}) |\Psi(\mathbf{r}, \mathbf{x})|^2. \]  

(8)

Here \(\rho(\mathbf{r})\) is the electron density of the closed-shell target and \(\Psi(\mathbf{r}, \mathbf{x})\) is the Ps-scattering wave function, normalized to unit density of incoming Ps atoms (with \(r\) as the positron coordinate). The factor of \(\frac{1}{4}\) reflects the fact that only electrons in a spin-singlet state with the positron contribute to the decay process (assuming all annihilation events are \(2\gamma\) decays.) This expression is simpler than Eq. (7) since the inclusion of the \(\lambda \hat{P}\) operator into the scattering Hamiltonian means that the wave function has been constructed so that the overlap integral between the scattering wave function and any of the doubly occupied core orbitals is effectively zero. In the plane-wave Born approximation (PWBA), \(1Z_{\text{eff}}\) reduces to \(N/4\), where \(N\) is the number of target electrons.

### III. RESULTS

Prior to discussing the results of the calculations it is instructive to use effective-range theory (ERT) to make some estimates of the expected threshold \(1Z_{\text{eff}}\) for \(\text{Na}^+\) and \(\text{Li}^+\). Both of these systems have bound states, therefore it is possible to use the bound-state energy and core-annihilation rate [12] to make an estimate of the scattering length and also the threshold \(1Z_{\text{eff}}\).

Briefly, the lowest-order ERT for the phase shift is

\[ k \cot(\delta) = -\frac{1}{A}, \]  

where \(A = A_R - iA_I\) is the complex scattering length. When the system has a bound state, Eq. (9) can be used to estimate the scattering length since \(\cot(\delta) = i\) at the bound-state energy. The bound-state energy is

\[ E = E_R + iE_I = E_R - i\Gamma/2, \]  

where \(\Gamma\) is the rate for positron annihilation of the Ps-Li\(^+\) or Ps-Na\(^+\) systems with one of the core electrons. Using \(k^2 = -1/A^2\) and assuming \(|E_R| > |E_I|\) the complex energy and scattering length can be related as

\[ E_R \approx -\frac{1}{4A_R^2}, \]  

\[ E_I \approx -\frac{A_I}{2A_R^3}. \]  

(12)

The absorption cross section can be related to the imaginary part of the scattering length using [15]

\[ \sigma_{\text{abs}} = \frac{\pi}{k\tau} \{ 1 - \exp(-4 \text{ Im } \delta(k)) \} \approx \frac{4\pi}{k} A_I. \]  

(13)

Using Eq. (1) for \(1Z_{\text{eff}}(k)\) gives

\[ 1Z_{\text{eff}}(0) = \frac{A_I}{2\tau_0^3} \approx \frac{A_R^3 \Gamma}{2\tau_0^3}. \]  

(14)
In Table I values of $|e_R|$ presented in Fig. 1 for Ps-Li$^+$ those for Li$^+$ virtual state lying close to the $E^\text{scattering}$ length is big. This occurs when there is a real or
The approximation is likely to be most accurate when the $A_R \text{ and } |Z_{eff}(0)|$ deduced from the bound-state energy and annihilation rate using Eqs. (12) and (15) are given under the ERT heading.

| System     | $|e_R|$ | $\Gamma$ | $A_R$ | $|Z_{eff}(0)|$ | $A_R$ | $|Z_{eff}(0)|$ |
|------------|--------|----------|-------|---------------|-------|---------------|
| Ps-Li$^+$  | 0.002477 | 0.00157  | 12.9  | 0.067         | 10.1  | 0.049         |
| Ps-Na$^+$  | 0.000473 | 0.00167  | 28.5  | 0.73          | 23.0  | 0.62          |
| Ps-K$^+$   | No bound state | −1.93  | 0.064 |

In Eq. (14) all quantities are expressed in atomic units. Expressing $\Gamma$, in units of of nsec$^{-1}$, leads to

$$|Z_{eff}(0)| = 3.045 \times 10^{-2} A_R^{1/2} \Gamma \approx \frac{3.81 \times 10^{-3} \Gamma}{|e_R|^{3/2}}.$$  

(15)

In Table I values of $|Z_{eff}$ and $A_R$ computed from Eqs. (12) and (15) are listed for Li$^+$ and Na$^+$. The values obtained for both systems are smaller than the value expected from the PWBA. 0.5 and 2.5, respectively.

Plots of FCSVM values of $Z_{eff}$ versus momentum are presented in Fig. 1 for Ps-Li$^+$ and Ps-K$^+$ scattering and Fig. 2 for Ps-Na$^+$ scattering. The curve for K$^+$ is rather flat while those for Li$^+$ and Na$^+$ are strongly peaked at $k=0$. The strong peaking in $Z_{eff}$ can be easily explained in terms of effective-range theory. Applying Eq. (9) to nonzero energies leads to the result [17]

$$Z_{eff}(k) = \frac{Z_{eff}(0)}{1 + A_R^{1/2} k^2}.$$  

(16)

The approximation is likely to be most accurate when the scattering length is big. This occurs when there is a real or virtual state lying close to the $E=0$ threshold. The dashed curves for $Z_{eff}$ in Figs. 1 and 2 for Ps-Li$^+$ and Ps-Na$^+$ were computed with Eq. (16) using the values of $A_R$ taken from the FCSVM column of Table I. The threshold values $|Z_{eff}(0)|$ were estimated by extrapolation assuming that $\frac{Z_{eff}(k)}{Z_{eff}(0)} = 1 + bk + c k^2$ near threshold. There is reasonable agreement between the values of $Z_{eff}(0)$ derived from the scattering calculations and those derived from the bound-state data using ERT. Equation (16) does provide a qualitative description of the momentum dependence of $Z_{eff}$ for the Ps-Li$^+$,Ps-Na$^+$ systems. No curve is shown for K$^+$ since the scattering length, $-1.9a_0$ for this system, is small and, therefore, not likely to cause large variations in $Z_{eff}$. It is possible to add refinements to Eq. (16) to take into account polarization and other corrections [17] but this is not done for reasons of brevity.

The present FCSVM $Z_{eff}$ are expected to underestmate the actual $Z_{eff}$ by a factor of about 2–3. Correlations between the positron and the electrons in the target ion are taken into account (by means of the polarization potentials) when the the scattering equations are solved. However, such correlations were not taken into account when the annihilation matrix elements were computed. Previous calculations of $Z_{eff}$ for He, Ne, and Ar underestimated those of experiment by factors of about 3. Furthermore, the structure and annihilation rates for $e^+\text{He}(^3\text{S}^\text{c})$ have been calculated using the FCSVM and fully ab initio SVM methods [16]. The FCSVM annihilation rate with the He$^+(1s)$ core electron was 2.5 times smaller than the SVM annihilation rate.

FIG. 1. The pick-off annihilation rates $|Z_{eff}$ versus momentum (in terms of $a_0^{-1}$) for Ps-K$^+$ and Ps-Li$^+$ scattering are shown as the two solid lines. The values for Li$^+$ are multiplied by 2. The dashed line shows the result of using Eq. (16) for Ps-Li$^+$.

FIG. 2. The pick-off annihilation rate $|Z_{eff}$ versus momentum (in terms of $a_0^{-1}$) for Ps-Na$^+$ scattering is shown as the solid line. The dashed line shows the result of using Eq. (16).
The present results double the number of systems for which \( Z_{\text{eff}} \) has been explicitly calculated. All of the values of \( Z_{\text{eff}} \) are small, and it is interesting to speculate on the underlying dynamical reasons for this. First it must be mentioned that \( Z_{\text{eff}} \) is defined differently from \( Z_{\text{eff}} \). In the plane-wave Born approximation \( Z_{\text{eff}} \) should reduce to the number of electrons divided by 4 unlike \( Z_{\text{eff}} \), which collapses to the number of electrons. Second, all of the calculations have been done on target atoms or ions with a closed-shell core. Therefore, the short-range interaction of Ps with the target is likely to be repulsive due to the influence of the Pauli principle. A repulsive interaction will exclude the Ps projectile from overlapping the target charge distribution and thereby reduce \( Z_{\text{eff}} \). Third, Ps is electrically neutral and, therefore, the pileup of target electrons around the positron that occurs for positron-atom scattering is not so pronounced.

One notable feature of Table I is the result that the zero-energy values of \( Z_{\text{eff}} \) are almost the same for Li\(^+\), Na\(^+\), and K\(^+\) and about ten times smaller than \( Z_{\text{eff}} \) for Na\(^+\). A simple geometric argument based on the size of the target ions would suggest that \( Z_{\text{eff}} \) should increase moderately when going from Li\(^+\) to Na\(^+\) to K\(^+\). Certainly the experimental \( Z_{\text{eff}} \) increases for the He (0.125), Ne (0.235), and Ar (0.314) sequence. (Note, the theoretical values computed in [5] also increase with a similar progression although the absolute values are a factor of 3 smaller). While the scattering lengths for He, Ne, and Ar are all roughly the same [5], this is not true for Li\(^+\), Na\(^+\), and K\(^+\). Recent research on the related topic of positron annihilation in positron-atom (molecule) scattering has shown that the scattering length can act to increase the size of the threshold \( Z_{\text{eff}} \). In effect, the normalization conditions that relate the amplitude of the wave function in the inner interaction or annihilation region to the asymptotic region act to increase the amplitude of the inner wave function when \( A_R \) becomes very large [17–20].

IV. CONCLUSION

The FCSVM has been used to investigate pick-off annihilation for Ps scattering from Li\(^+\), Na\(^+\), and K\(^+\) targets. The values of \( Z_{\text{eff}} \) are of order unity or smaller and this is compatible with experiments and calculations done with other atoms and molecules. The strong energy dependence of \( Z_{\text{eff}} \) for Li\(^+\) and Na\(^+\) complements research undertaken on the positron-atom annihilation problem, which has shown that \( Z_{\text{eff}} \) decreases rapidly as the energy increases from threshold for systems with a large scattering length [17–20].

The omission of short-range electron-positron correlations during the evaluation of the annihilation matrix element means that the present \( Z_{\text{eff}} \) probably underestimates the true \( Z_{\text{eff}} \) by a factor of about 2–3. The enlargement of the calculation to incorporate these short-range correlations would increase the technical difficulties of any calculation enormously. The present calculations and earlier calculations of He, Ne, and Ar [5] can be regarded as a step towards the solution of a rather exacting two-center scattering problem.

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