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Virial expansion of a quantum particle in a classical gas: Application to the orthopositronium decay rate

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Experiments measuring the decay of positrons and orthopositronium in gases show a complicated dependence of the annihilation rate on the gas density. Theoretical and experimental studies indicate that the nonlinear dependence of the decay rate on gas density is the result of local alterations in the gas density surrounding the decaying particle. In this paper the virial expansion of the decay rate of both free positrons and positronium atoms in powers of the gas density is developed. The temperature-dependent coefficients in the density expansion of the decay rate are expressed in terms of modified cluster integrals that are determined by the interaction of the free positron or positronium atom with the host gas. Explicit expressions are given for the decay rate through terms of order ρ^2 in the gas density. The term linear in the gas density is investigated analytically for the specific case of a hard-sphere interaction and its relevance to the decay of orthopositronium is demonstrated. Both the low- and high-temperature limits of the decay rate are determined analytically and the lack of temperature dependence observed in most experimental measurements of the decay rate at low density is explained. Finally, the results of path-integral Monte Carlo calculations for the decay rate over a wide temperature range are presented.

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I. INTRODUCTION

Positron and positronium decay in gases is an important experimental tool for studying the states of a quantum particle in a disordered environment. The quantum particle (QP) can be in a localized or extended state depending on the thermodynamic variables of the gas [1,2]. Since both the decay rate of free positrons and the pickoff decay rate of ortho-positronium atoms (o-Ps) are sensitive to the local electron density, they provide information concerning the local QP environment. Using theoretical models, this information can be related to the local gas structure and the quantum state of the QP, which ranges between localized and extended. Localized states are also available to an excess electron in a gas; however, their chief experimental manifestation is a reduction in the mobility [3]. Because the mobility is a transport property, its theoretical prediction involves the construction of a two-time correlation function, which is difficult to evaluate either analytically or computationally. In contrast, the decay rate is an equilibrium property that can be computed at a single fixed time and provides a direct connection with the equilibrium distribution of the gas.

Because the mean de Broglie wavelength of an electron or positron is of the order of 100 Å at room temperature, quantum mechanics is required to represent these particles. This also holds true for the positronium atom. However, the de Broglie wavelength of an atom or molecule at these temperatures is generally less than 1 Å and the translational degrees of freedom can be treated classically. Consequently, all theoretical models used to date to gain understanding of the system of an excess QP thermalized in a gas are a hybrid of both classical and quantum mechanics. The two primary theoretical methods that have been used to study this system are density-functional theory (DFT) and the path-integral method.

In DFT [4–9] the local gas density is represented as a continuum and the QP is represented by a single quantum state. A free-energy functional of the local density and the wave function is constructed and the null condition of its variation is used to obtain coupled equations for the optimal wave function of the QP and density profile of the classical gas. This theory is relatively easy to apply but, since it is a mean-field theory, it ignores fluctuations in the gas density and quantum states. It has been successfully used to study localized states in helium and supports the concept that the self-trapped state of the QP is dominant over a specific region of thermodynamic states [4,5]. The DFT produces an abrupt transition between self-trapped and extended QP states. This is consistent with the abrupt change in the decay rate that is observed experimentally in the decay of o-Ps in helium above its critical temperature [10]. However, experiments of o-Ps and positron decay in other noble gases, such as argon [6] and xenon [7], which have higher critical-point temperatures, indicate that the decay rate is a smooth continuous function of the gas density and temperature. This suggests that the localization of the QP occurs in a continuous fashion and is not consistent with the DFT results. The discrepancy between the experiments and theory are likely because DFT is a mean-field theory and neglects local fluctuations.

Recently, path-integral Monte Carlo (PIMC) calculations [11–13] of the full adiabatic model have succeeded in producing a continuous transition from an extended to a localized state that is expected for a thermalized positron or positronium atom in a gas as a function of density and temperature and accurately predicts the observed density dependence of the decay rate of positrons in xenon and o-Ps in argon and xenon. The PIMC calculations show the subtle relation between QP localization, cluster and bubble formation, and the decay rate. However, it is more difficult to obtain predictions from this model as its implementation

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generally requires the development of sophisticated "smart" Monte Carlo algorithms coupled with long runs on a supercomputer to obtain convergence. The situation is especially problematic in the extremes of high and low density, where convergence is slow.

The above theoretical and experimental results have demonstrated the importance of the many-body interaction between the QP and the classical gas. The physical manifestation of this interaction is a local increase in the gas density, i.e., cluster formation, around the positron and a local decrease in gas density, bubble formation, around the positronium atom. The alteration in density that is created results in a decay rate that is not simply a linear function of gas density. A systematic method of examining the deviation of the decay rate from a linear dependence on the gas density would provide important information about the effect of cluster and bubble formation on the decay rate. In addition, recent many-body calculations show that the anomalous rise in the positron decay rate with xenon density [7] may be the result of the transformation of a two-body (positron and single xenon atom) virtual level resonance to a real bound level for the positron in the three-body interaction (positron and two xenon atoms) [14]. The virial expansion of the decay rate in the gas density provides a framework for investigating the initial deviations from linearity and their origin. At the present time, these are all open questions.

The virial of the positron and o-Ps pickoff decay rate can be written as

$$\langle\hat{\lambda}\rangle = A(T)\rho + B(T)\rho^2 + C(T)\rho^3 + \cdots , \tag{1}$$

where coefficients $A(T)$, $B(T)$, and $C(T)$ are, in general, temperature dependent. The first coefficient $A(T)$ describes the two-body interaction of the QP and a single classical atom, $B(T)$ describes the three-body interaction of the QP with two interacting classical atoms, etc. From the virial expansion of the decay rate the temperature dependence of the coefficients that multiply the gas density can be calculated independently.

There is very little available information concerning the total potential energy of the system of a gas and a positron or o-Ps atom. In theoretical studies to date it is standard to treat the positron-gas interaction energy as a sum over two-body interactions. The first term in the density expansion of the positron decay rate depends only on the effective two-body potential $v(r)$, which describes the effective interaction between the QP and a single classical atom. Scattering experiments have yielded model potentials that accurately reproduce the low-density decay rate of positrons in most noble gases [15]. The situation is less clear for o-Ps [16]. If the experimental decay rate is known with sufficient accuracy and the onset of deviations from the linear dependence of the decay rate with density is isolated, the applicability of using pairwise two-body potentials could be evaluated using the virial expansion. This is not unlike the situation that exists for an atomic gas, where some success in determining two-body potentials for classical gases has been achieved by using the second term of the virial expansion for the pressure [17], and its limitations evaluated by examining the higher terms.

The region of density where the first deviations from linearity in the decay rate occur, i.e., $B(T)$, has received only modest theoretical and experimental attention. McNutt and Sharma [18] have attempted to explain the initial nonlinear dependence of the decay rate with a semi-phenomenological theory that depends on fluctuations in the gas density. In their model the QP passively samples energetically favorable local-density fluctuations. Calculations show, however, that fluctuations in the density of atoms in volumes of the order of the QP thermal wavelength are insufficient to explain the experimental results [19–21]. Deviations from the linear dependence of the positron decay rate in helium were considered in detail by Nieminen [22]; however, the method does not allow a systematic study of increasing gas density or of the temperature-dependent quantum effects. Polischuk [20] and Artem'ev, Polishchuk, and Khrapak [23] have used finite-temperature Green's functions to investigate the effects of temperature and many-particle scattering on the deviation from linearity, i.e., $B(T)$, of the decay rate. Their results are obtained under the severe approximation of a δ-function interaction potential and neglects the role of feedback of the positron on the gas. Within these approximations, their results suggest that the temperature dependence of $B(T)$ is determined by the increase in the role played by the attraction between atoms as the temperature is lowered.

The remainder of the paper is arranged as follows. A density expansion for the QP-atom correlation function in powers of the gas density is developed. We then use the correlation function to directly obtain a density expansion for the positron decay rate. The orthopositronium pickoff decay rate is also given in the approximation of treating the positronium atom as a composite quantum particle of mass $2m_e$. As an application of the viral expansion the term linear in the gas density is evaluated for a hard-sphere interaction. The hard-sphere interaction is a common model for the effective Ps-atom interaction potential [1,12]. Since the dominant contribution to the Ps-atom interaction is provided by fermionic repulsion between the Ps atom's electron and the atomic electrons, the hard-sphere potential is expected to offer a crude representation of this interaction. From this simple model for the decay rate of o-Ps in gases we are able to explain the experimentally observed temperature independence of the term that is linear in the gas density and discuss why this result is likely to be valid for a range of interaction potentials.

II. DEVELOPMENT OF THE DENSITY EXPANSION

In general, the experimental conditions are such that it is justifiable to assume that the QP's are sufficiently dispersed and screened by the surrounding gas that the interaction between them is negligible. Thus, we can consider a single QP interacting with a classical gas. In order to simplify the role played by the atomic electrons, in theoretical studies it is common to assume effective two-body potentials. The simplest microscopic Hamiltonian that contains the physics of a single quantum particle of mass m and momentum $\hat{\mathbf{p}}$ interacting with a gas of N classical particles is then

$$H = \hat{\mathbf{p}}^2/2m + \sum_i v(\mathbf{r}-\mathbf{R}_i) + \sum_{i<j} u(\mathbf{R}_i-\mathbf{R}_j) + \sum_i \mathbf{P}_1^2/2M, \tag{2}$$

where the effective interaction energy between the QP at $\mathbf{r}$ and the gas $V(\mathbf{r},\underline{\mathbf{R}})=\Sigma_i v(\mathbf{r}-\mathbf{R}_i)$ is assumed to be pairwise additive. The interaction between the gas atoms $U(\underline{\mathbf{R}})=\Sigma_{i<j}u(\mathbf{R}_i-\mathbf{R}_j)$ is also taken to be pairwise additive. The set of atomic positions $\{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N\}$ is represented by $\underline{\mathbf{R}}$. The momentum and mass of the ith classical atom are, respectively, $\mathbf{P}_i$ and M.

The thermal wavelength of the QP is of the order of 100 times larger than the thermal wavelength of a typical classical atom (say, for example, xenon) at the same temperature. Therefore, neglecting the quantum dispersion of the relatively massive classical atoms appears reasonable. The consequence of this approximation is that the trace over the atomic translational degrees of freedom in the partition function can be reduced to a classical phase-space integration [24]. Thus the partition function for a QP interacting with a classical gas of N atoms is

$$\begin{aligned} Z_{N,\mathrm{QP}}&=\mathrm{Tr}[\exp(-\beta H)]\\ &=1/(N!\Lambda_{\mathrm{CP}}^{3N})\int d\underline{\mathbf{R}}\,\exp[-\beta U(\underline{\mathbf{R}})]\\ &\quad\times\mathrm{Tr}[\exp(-\beta H')]. \end{aligned}\tag{3}$$

The N gas momenta have been integrated away producing the factor involving the thermal wavelength of a gas atom (classical particle) $\Lambda_{\mathrm{CP}}=\hbar\sqrt{2\pi\beta/M}$. The trace in the second expression is with respect to the QP states with $H'=\hat{\mathbf{p}}^2/2m+V(\mathbf{r},\underline{\mathbf{R}})$. The classical part consists of the integral over the translational coordinates of the gas $(\int d\mathbf{R}_1\cdots\int d\mathbf{R}_N\equiv\int d\underline{\mathbf{R}})$, which is weighted by the classical Gibbs factor $\exp[-\beta U(\underline{\mathbf{R}})]$. In thermal equilibrium, the mean value of a physical observable $O(\mathbf{r},\hat{\mathbf{p}},\underline{\mathbf{R}})$, which can depend on the QP coordinate and momentum, but only on the gas coordinates, is given by

$$\begin{aligned} \langle O\rangle&=(1/N!\Lambda_{\mathrm{CP}}^{3N}Z)\int d\underline{\mathbf{R}}\,\exp[-\beta U(\underline{\mathbf{R}})]\\ &\quad\times\mathrm{Tr}[O\,\exp(-\beta H')]. \end{aligned}\tag{4}$$

Physically the annihilation rate is proportional to the overlap of the positron and the electron density of the gas. If $f(\mathbf{r})$ is the quantum-averaged electron density of an atom fixed at the origin, then the quantum state $|\varphi\rangle$ and molecule i contribute $\int|\varphi(\mathbf{r})|^2 f(\mathbf{r}-\mathbf{R}_i)d\mathbf{r}$ to the decay rate. Thus the decay rate is represented by the quantum-mechanical operator

$$\hat{\lambda}=\sum_{1\leqslant i\leqslant N}f(\mathbf{r}-\mathbf{R}_i).\tag{5}$$

The equilibrium average of the decay rate operator of a thermalized positron is given in suitably scaled units by [1,24]

$$\langle\hat{\lambda}\rangle=\int d\mathbf{R}\int d\mathbf{r}\;f(|\mathbf{r}-\mathbf{R}|)n(\mathbf{r},\mathbf{R}),\tag{6}$$

where $n(\mathbf{r},\mathbf{R})$ is the configurational probability for finding a positron at $\mathbf{r}$ and a classical atom at $\mathbf{R}$ and $f(\mathbf{r})$ is the distribution of atomic electrons a distance r from the atomic nucleus. It should be noted that the use of the unperturbed electron distribution of the isolated atom for $f(\mathbf{r})$ in (6) may introduce a significant error. The ability of the positron to distort the atomic electron distribution is well documented [15].

Thus the virial expansion of the decay rate can be found from the density expansion of $n(\mathbf{r},\mathbf{R})$. The density expansion for the two-particle correlation function of a homogenous quantum gas was obtained by De Boer [25]. A straightforward extension of this method can be used for the mixed system of a QP in a classical gas. To obtain an expansion of $n(\mathbf{r},\mathbf{R})$ in the density of the gas it is convenient to introduce the diagonal element of the density matrix for the N atoms and the single QP,

$$W(\mathbf{r},\underline{\mathbf{R}})=\Lambda_{\mathrm{QP}}^{3}\langle\mathbf{r},N|\exp[-\beta H']|N,\mathbf{r}\rangle\exp[-\beta U(\underline{\mathbf{R}})],\tag{7}$$

where $|N,\mathbf{r}\rangle$ is a complete set of orthonormal states. In the limit of no interaction between the QP and the gas Eq. (7) reduces to $\exp[-\,\beta U(\underline{\mathbf{R}})]$. The partition function can now be expressed as

$$Z_{N,\mathrm{QP}}=1/(N!\Lambda_{\mathrm{CP}}^{3N}\Lambda_{\mathrm{QP}}^{3})\int d\underline{\mathbf{R}}\int d\mathbf{r}\;W(\mathbf{r},\underline{\mathbf{R}}).\tag{8}$$

In the canonical ensemble, the configurational probability density is given by

$$n(\mathbf{r},\mathbf{R}_1)=[1/Q_{N,\mathrm{QP}}(N-1)!]\int d\mathbf{R}_2\cdots\int d\mathbf{R}_N W(\mathbf{r},\underline{\mathbf{R}}),\tag{9}$$

where $Q_{N,\mathrm{QP}}=(\Lambda_N^{3N}\Lambda_{\mathrm{QP}}^{3})Z_{N,\mathrm{QP}}$. The density expansion for $n(\mathbf{r},\mathbf{R}_1)$ can now be obtained by one of two standard methods, i.e., either by finding an expansion for $n(\mathbf{r},\mathbf{R}_1)$ in terms of powers of the activity by introducing the grand canonical ensemble and using series reversion to convert to a density expansion or by introducing a sequence of Ursell functions [26]. In either case, we obtain

$$\begin{aligned} n(\mathbf{r},\mathbf{R}_1)=(1/V)\Big\{&\rho W(\mathbf{r},\mathbf{R}_1)+\rho^2\int d\mathbf{R}_2[W(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2)\\ &-W(\mathbf{r},\mathbf{R}_1)W(\mathbf{R}_1,\mathbf{R}_2)]+O(\rho^3)+\cdots\Big\} \end{aligned}\tag{10}$$

through second order in ρ^2, where $W(\mathbf{R}_1,\mathbf{R}_2)$ is the classical two-body distribution function. The decay rate can now be written as

$$\begin{aligned} \langle\hat{\lambda}\rangle=(1/V)\int d\mathbf{R}_1\int d\mathbf{r}\;f(|\mathbf{r}-\mathbf{R}_1|)\Big\{&\rho W(\mathbf{r},\mathbf{R}_1)\\ &+\rho^2\int d\mathbf{R}_2[W(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2)-W(\mathbf{r},\mathbf{R}_1)W(\mathbf{R}_1,\mathbf{R}_2)]\Big\}\\ &+O(\rho^3). \end{aligned}\tag{11}$$

The term linear in the gas density involves a simple integration over the function $f(\mathbf{r}-\mathbf{R}_1)W(\mathbf{r},\mathbf{R}_1)$. The two-body term $W(\mathbf{r},\mathbf{R}_1)$ can be reduced to quadrature [27] and the integral evaluated numerically or integrated directly by PIMC [28]. The three-body term $W(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2)$ is the density matrix for a quantum particle in an axially symmetric field created by the two classical particles at R_1 and R_2. The difference that appears in the term quadratic in the gas density is seen to go to zero in the limit that the gas atom at $\mathbf{R}_2$ is removed to infinity, thus indicating in this limit that the density dependence of the lifetime is linear. This is completely rigorous and we can say with certainty that any nonlinearity in the decay rate with gas density indicates the presence of a many-body interaction, i.e., greater than one gas atom simultaneously interacting with the quantum particle.

III. APPLICATION TO POSITRONIUM DECAY

The pickoff decay of the positronium atom in a gas represents a complex many-body problem of two quantum particles, the electron and positron of the Ps atom, interacting with a classical gas. The hard-sphere interaction is frequently used in theoretical studies of Ps decay in gases [1,12] to represent an effective interaction between the classical gas atoms and Ps atom. The Ps atom is represented as a single composite quantum-mechanical particle of mass $2m_e$ located at the Ps center of mass. This severe approximation is primarily motivated by the considerable complexity created by two quantum particles interacting with each other and a classical gas and the general lack of scattering data. The dominance of the short-range repulsion due to the Pauli exclusion between the Ps atom electron and the gas electrons is approximated by a hard-sphere interaction. In spite of the overall charge neutrality of the Ps atom, ignoring long-range polarization effects of the Ps is more difficult to justify.

However, some agreement with experiment has been obtained for Ps decay in noble gases by treating the Ps as a composite quantum particle [1,12]. Reese and Miller [12] have recently used the path-integral Monte Carlo technique to model the decay of positronium in xenon and argon. They were successful in roughly fitting the decay rate over a wide range of densities using a simple hard-sphere interaction between the positronium atom and the classical gas. The hard-sphere parameter characterizing the interaction was determined by looking for self-trapping near the critical point. In the following we will obtain an analytic expression for the positronium decay rate in the region linear in the gas density. This result can be used for determining potential parameters at low temperature and density and also demonstrates why the term is essentially temperature independent.

Reese and Miller [12] have shown that the pickoff decay rate of Ps in a gas can be expressed as

$$\langle\hat{\lambda}\rangle=[1/(\pi a_0^3)]\int d\mathbf{r}\,\exp[-2r/a_0]n(\mathbf{r}), \tag{12}$$

where r is now the relative coordinate $(\mathbf{r}-\mathbf{R})$ and a_0 is the Bohr radius. This expression is obtained by assuming that the internal state of the Ps atom is undisturbed by the presence of the gas molecules. In this approximation the electron distribution of the classical atom is represented as a δ function. The exponential term in the integrand simply represents the spread of the quantum-mechanical positron with respect to the Ps center of mass, i.e., it is the ground-state probability of the positron around the Ps center of mass.

The first term in (11) can be used to obtain the decay-rate linear in the gas density, i.e., the two-body term

$$\langle\hat{\lambda}\rangle=[\rho/(\pi a_0^3)]\int d\mathbf{r}\,\exp[-2r/a_0]W_2(\mathbf{r}). \tag{13}$$

For a hard-sphere interaction the diagonal density-matrix element $W_2(\mathbf{r})=\Lambda^3\langle\mathbf{r}|\exp[-\beta H']|\mathbf{r}\rangle$ has been calculated numerically by Larsen [27]. As expected, the function is a monotonically increasing function of temperature for any given value of $\mathbf{r}$ and approaches the classical result of a step function as $\sigma/\Lambda\to 0$, where σ is the hard-sphere diameter. Therefore, we expect that (13) is a monotonically increasing function of temperature, since it is essentially a measure of the overlap of the diagonal density-matrix element and the exponential term representing the positron probability density. This is not in agreement with the majority of experiments, where it is found that the decay rate is independent of temperature [7,10,18]. The absence of a temperature dependence for the o-Ps decay in the region that is linear with the gas density can be explained with the simple hard-sphere interaction. Below we will show that it results from the lack of temperature dependence of W_2 at low temperature for values of $\mathbf{r}$ close to the hard-sphere diameter, where the major contribution to the decay rate occurs.

In the following analysis the pickoff decay rate is reduced to quadrature and an exact result is obtained for the S wave $(l=0)$ contribution to the decay rate. For a hard-sphere interaction the square of the eigenfunctions of H' for $r\geqslant\sigma$, the hard-sphere diameter, is [27]

$$\Psi_{l,k}^2(r)=2\{j_l(k\sigma)n_l(kr)-n_l(k\sigma)j_l(kr)\}^2/\pi k^2[n_l(k\sigma)+j_l(k\sigma)], \tag{14}$$

where σ is the hard-sphere diameter. The phase shifts are $\delta_l=\tan^{-1}[j_l(k\sigma)/n_l(k\sigma)]$. The wave number k is related to the energy by $E_k=\hbar^2k^2/2m$ and $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively. The two-particle density matrix for the composite Ps atom and a single classical atom can now be expressed as

$$W_2(r)=(2\sigma\sqrt{\pi}/q_0^3)\sum_l(2l+1)\int_0^\infty dk\,\Psi_{l,k}^2(r)\times\exp(-\beta E_k),\quad r\geqslant\sigma, \tag{15}$$

where $\Lambda_{\mathrm{Ps}}=\hbar\sqrt{\pi\beta/m}$ is the Ps-atom thermal wavelength and $q_0^2=4\pi(\sigma/\Lambda_{\mathrm{Ps}})^2$. Thus $W_2(r)$ is reduced to quadrature. Unfortunately, even for this simple system an analytic solution is not possible.

The decay rate is determined by the overlap of the atomic charge distribution and the positron wave function. From Fig. 1, which shows the range of the probability density of the positron, it can be seen that this occurs primarily in the region where $r\approx\sigma$, i.e., when the positron is relatively close to the hard sphere. Therefore, the large-r behavior of $W_2(r)$ is irrelevant for determining the decay rate. The absence of a temperature dependence for the decay rate of the Ps can easily be shown by directly expanding $\Psi_{l,k}^2(r)$ about $r\approx\sigma$ in a Taylor series, which gives [27]

$$W_2(r)=\{(x-1)^2-(x-1)^3\}\{1+\tfrac{9}{2}q_0^2-\tfrac{55}{6}q_0^4+\cdots\} \tag{16}$$

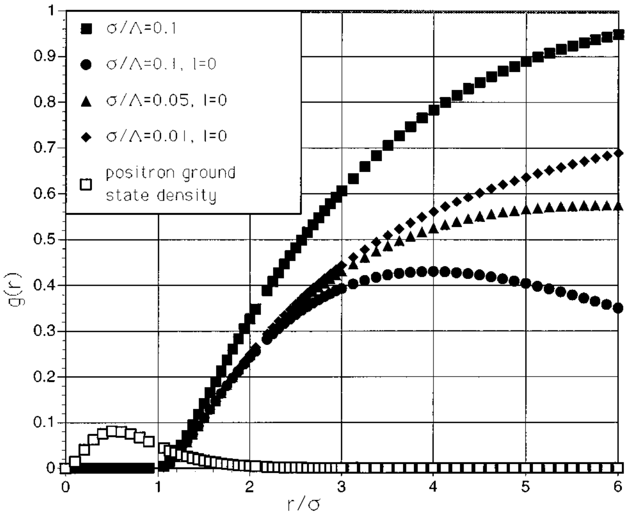

FIG. 1. QP-atom radial distribution function $W_2(r)$ plotted for different values of σ/Λ. The solid curve gives the complete function (including all angular-momentum states) whereas the dashed curves give the $l=0$ contribution. The dotted curve is the radial probability density of the positron wave function. It is seen that, where significant overlap occurs, all of the distributions are approximately equal, resulting in a temperature-independent annihilation rate.

in terms of the dimensionless coordinate $x=r/\sigma\geqslant 1$. This demonstrates that at sufficiently small q_0 the largest contribution to the decay rate is temperature independent. The above expression also shows that the first correction to the decay rate is linear with temperature.

At thermal energies, when $r\approx\sigma$ a back of the envelope estimate easily gives $L/\hbar\approx q_0$, where L is the orbital angular momentum of Ps. Thus, for the temperatures at which the majority of the experiments have been performed, corresponding to q_0 ranging from roughly 0.01 to 0.1, $L/\hbar\ll 1$ and we are justified in using only the $l=0$ term in (15). The S-wave ($l=0$) term can be evaluated analytically [27] and is given by

$$W_2(r)_{l=0}=(1/q_0^2x^2)\{1-\exp[-q_0^2(x-1)^2]\}, \quad x=r/\sigma\geqslant 1. \tag{17}$$

The S-wave contribution to the decay rate can now be written as

$$\begin{aligned}\langle\hat{\lambda}\rangle_{l=0}&=[4\rho\sigma^3/(a_0^3q_0^2)]\int_1^\infty dx\ \exp(-2x\sigma/a_0)\\ &\qquad\times\{1-\exp[-q_0^2(x-1)^2]\}\\ &=2\rho(\sigma/a_0q_0)^2\ \exp(-2\sigma/a_0)x\\ &\qquad\times[1-(\sigma\sqrt{\pi}/q_0a_0)\exp[(\sigma/q_0a_0)^2\mathrm{erfc}(\sigma/q_0a_0)],\end{aligned} \tag{18}$$

where erfc(x) is the complimentary error function [29]. This expression gives the experimentally observed temperature independence of the decay rate for small q_0.

This result is easily understood by examining Fig. 1, where it is seen that for $r\approx\sigma$ (i.e., $x\approx 1$) the function $W_2(r)_{l=0}$ is independent of temperature over a large range. Of course, this is not true for larger r, where higher-angular-momentum states contribute, which is evident from the deviation of the $l=0$ term from the exact result shown in Fig. 1. But, since the decay rate is determined by the behavior of $W_2(r)$ near the hard-sphere diameter, the higher-order terms, i.e., $l\neq 0$, have a negligible contribution to the decay rate.

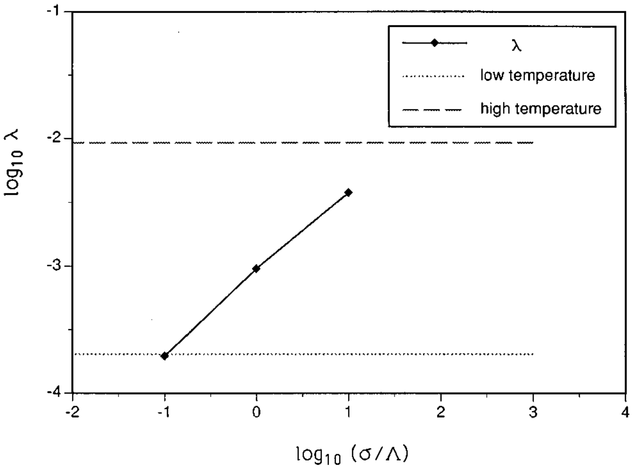

FIG. 2. Dependence of the coefficient of the linear term in the density expansion of the decay rate on σ/Λ over nearly the complete temperature range. The QP mass was chosen as $2m_e$, the mass of positronium, and σ=2.25 Å corresponding to xenon gas. The computations were performed using path-integral Monte Carlo theory. The computations are consistent with both the high- ($\sigma/\Lambda\rightarrow\infty$) and low- ($\sigma/\Lambda\rightarrow 0$) temperature limits determined from the analytical results (29). The smallest plotted value generated by PIMC at $\sigma/\Lambda=0.1$ is very close to the asymptotic $T=0$ limit obtained analytically.

To explore the behavior of $\langle\hat{\lambda}\rangle$ at higher temperatures, where the restriction to $l=0$ no longer applies, we have evaluated $W_2(r)$ using path-integral Monte Carlo. This is a useful technique for more structured interaction potentials that generally do not possess analytical solutions for $W_2(r)$. We will describe this approach in detail later when we report our results on positron annihilation. For the sake of comparison with the low-temperature calculations given above, in Fig. 2 we simply provide the complete dependence of the decay rate on $\sigma/\Lambda_{\mathrm{Ps}}$. This shows both the asymptotic behavior at long wavelength seen in most experiments and the approach to the classical limit at short wavelengths. In each extreme both $W_2(r)$ and $\langle\hat{\lambda}\rangle$ can be evaluated analytically: In the classical limit, $W_2(r)=\theta(r-\sigma)$, where θ is the usual step function, while in the quantum (zero-temperature) limit we see from (17) that $W_2(r)=(r-\sigma)^2\theta(r-\sigma)/r^2$. Substitution of these forms in (13) yields

$$\langle\hat{\lambda}\rangle=\begin{cases}\exp(-2\sigma/a_0) & (T\rightarrow 0)\\ [1+2(\sigma/a_0)+2(\sigma/a_0)^2]\exp(-2\sigma/a_0) & (T\rightarrow\infty),\end{cases} \tag{19}$$

which gives the exact high-temperature to low-temperature ratio of the decay rates for this model. Note that the Monte Carlo results are consistent with these limits.

IV. CONCLUSIONS

We have developed a virial expansion for the properties of a quantum particle that has thermalized in a disordered environment consisting of particles (atoms or molecules) having translational degrees of freedom that can be modeled classically. The method was applied to the problem of the QP-atom correlation function under circumstances where all the interactions are determined by pairwise additive coordinate-dependent interaction potentials. For the particular case where the QP-atom interaction can be approximated by a hard-sphere potential, the term of the correlation function linear in the density (the first term of the series) can be determined analytically. We have used the result to explicitly evaluate the temperature dependence of the annihilation rate of positronium in gases at low density. By investigating the contributions from different angular-momentum states we have verified and explained the apparent lack of temperature dependence in most experimental measurements of the decay rate in low-density gases. Although this was carried out for the explicit case of a hard-sphere interaction, the arguments for the S-wave dominance are general, so we expect that this result is generic to a wide variety of potentials. The results appear to be valid even for molecular gases, such as methane, but fails for ethane [30].

Although a hard-sphere interaction represents the crudest approximation of the interaction between the Ps atom and the atomic gas, this result is likely generic to a variety of interaction potentials, i.e., the decay rate is independent of temperature at low density. At higher density, where the onset of three-body effects become significant, we anticipate important qualitative differences in the decay rate depending on the form of the interaction potential. For instance, in xenon it is believed that a weak bound state exists for the three-body system [14]. In future work we will investigate more realistic potentials using the path-integral method, where analytic results are not available. We have also exhibited the results of a path-integral Monte Carlo calculation for the behavior of the linear contribution over the entire temperature range. The latter demonstrates the large variation in $\langle\hat{\lambda}\rangle$ that occurs when going from the extreme quantum to the classical limit.

When coupled with the path-integral representation of the QP, the virial expansion provides a powerful tool to investigate a number of interesting phenomena. The advantage is that Monte Carlo techniques can be employed to consider interaction potentials of arbitrary shape: The analytic solution for $W_2(r)$ is no longer required. Specific questions we can address concern the influence of the binding of the positron to small atomic clusters, the effect of virtual scattering resonances, and the role of the induced atomic polarization charge density on the decay rate of a thermalized positron. Some of this work is currently in progress.

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