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Binding energy of the positronium negative ion via dimensional scaling

Nikita Blinov[*] and Andrzej Czarnecki[†]
Department of Physics, University of Alberta, Edmonton, Alberta T6G 2E1, Canada

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We determine the binding energy of a negative positronium ion in the limits of one spatial dimension and of infinitely many dimensions. The numerical result for the one-dimensional ground-state energy seems to be a rational number, suggesting the existence of an analytical solution for the wave function. We construct a perturbation expansion around the infinitely dimensional limit to compute an accurate estimate for the physical three-dimensional case. That result for the energy agrees to five significant figures with variational studies.

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I. INTRODUCTION

The negative positronium ion Ps$^-$ is a bound state of two electrons and a positron. It is the simplest bound three-body system from a theoretical point of view, since it does not contain a hadronic nucleus. It provides an important testing ground for quantum electrodynamics (QED), which should be able to describe this purely leptonic bound state with a high precision.

Because of the e^+e^- annihilation, Ps$^-$ is unstable, with a lifetime about four times that of para-positronium. It decays predominantly into two or three photons, with one-photon decay possible but extremely rare. It is weakly bound and has no excited states in the discrete spectrum [1,2] (for a discussion of resonances, see [3] and [4]).

Following its prediction by Wheeler in 1946 [5] and experimental observation by Mills in 1981 [6], the positronium ion has been the subject of much theoretical study. Its nonrelativistic bound-state energy, its decay rate, the branching ratios of various decay channels, and its polarizabilities have been computed accurately using variational methods [7–14].

Recently, intense positronium sources have become available, opening new possibilities for experimental studies of Ps$^-$ [15]. The measured decay rate [16,17] agrees with the theoretical prediction. Improved measurements of the decay rate, the three-photon branching ratio, and the binding energy have been proposed [18].

A challenge in the theoretical study of this three-body system is that its wave function is not known analytically, even if only the Coulomb interaction is considered. Since all particle masses and magnitudes of their charges are equal, it is not possible to use the Born-Oppenheimer approximation. So far all precise theoretical predictions of Ps$^-$ properties have relied on variational calculations.

In the present paper we explore a different approach to computing the wave function and the binding energy of Ps$^-$. We use the dimensional scaling (DS) method, in which the dimensionality of space D is a variable. We focus on the limits $D \to 1$ and $D \to \infty$. A precise result for $D = 3$ may be obtained by interpolating between the two limits using perturbation theory in $1/D$. The advantage of DS is that the two limits of the Schrödinger equation often have relatively simple solutions. Full interparticle correlation effects are included at every order in the perturbation expansion in $1/D$. More information about DS and further references can be found in [19–24].

It is important to note that the dimensional limits considered here are not physical in the sense that the form of the potential energy is taken to be $1/r$, regardless of the dimension. A physical limit of a system would use an appropriate Coulomb potential that is the solution of a D-dimensional Poisson equation. For example, for $D = 1$ it is linear, is logarithmic for $D = 2$, and depends on the charge separation as $r^{-(D-2)}$ for $D > 2$. Since we are ultimately interested in $D = 3$ physics, it is useful to fix the potential to be the $D = 3$ Coulomb interaction. The $D \to 1$ limit used here offers the additional simplification that, after coordinate and energy rescaling, the potential takes the form $(D - 1)/r$, which can be formally replaced by a Dirac δ function [25].

We find that the DS provides a useful complement to the variational method. In the future, it can be employed to independently check matrix elements of operators needed in precise studies of Ps$^-$.

This paper is organized as follows. In Sec. II we consider the $D = 1$ limit of the Ps$^-$ system. We solve the Schrödinger equation numerically to find an eigenvalue that approaches a simple rational number, possibly hinting at the existence of an analytical solution.

In Sec. III we consider the $D \to \infty$ limit and describe the resulting $1/D$ expansion. We sum up the perturbation series for the ground-state energy and evaluate it at $D = 3$. The binding energy we find agrees with variational studies to five significant figures. We conclude in Sec. IV.

II. $D = 1$ LIMIT OF Ps$^-$

In the one-dimensional limit, the Coulomb potential is represented by the Dirac δ function [25]. The δ function models have also been used extensively in condensed matter physics. A simple analytical wave function exists for any number of identical particles interacting via attractive potentials [26]. The case of all repulsive potentials with periodic boundary conditions has been treated by Lieb and Liniger [27] and Yang [28]. More recent works have studied one-dimensional systems with both attractive and repulsive δ interactions. Craig *et al.* considered the dependence of the energy on the number of particles in a system of equal numbers of positively and

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[*] Theory Group, TRIUMF, 4004 Wesbrook Mall, Vancouver, British Columbia V6T 2A3, Canada.

[†] andrzejc@ualberta.ca

negatively charged bosons [29]. Li and Ma studied a system of N identical particles with an impurity with periodic boundary conditions [30].

The $D = 1$ limit of the Ps$^-$ quantum problem is a δ function model with two attractive and one repulsive δ functions with nonperiodic boundary conditions, which, to the best of our knowledge, has not yet been solved. We present a derivation of a one-dimensional integral equation for the solution to this problem, analogous to the helium case treated by Rosenthal [31].

The time-independent Schrödinger equation for the relative motion of Ps$^-$ takes the dimensionless form

$$\left(-\frac{1}{2}\left[\nabla_1^2+\nabla_2^2+\vec{\nabla}_1\cdot\vec{\nabla}_2\right]-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r}\right)\psi=\varepsilon\psi, \qquad (1)$$

where r_1 and r_2 are the electron-positron distances, r is the interelectron distance [in units of $2(m\alpha)^{-1}$ with $\hbar = c = 1$], and ε determines the energy eigenvalue, $E = \varepsilon m\alpha^2/2$. This choice of units helps us to compare intermediate results with Rosenthal's δ function model of helium [31].

In the limit $D \to 1$, we let $\vec{r}_1 \to x$ and $\vec{r}_2 \to y$, where $-\infty < x, y < \infty$; the gradients become partial derivatives and the Coulomb potentials are replaced by Dirac δ functions (this limit is described in detail in [32]). Equation (1) is replaced by

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial x\partial y}\right)\right.$$
$$\left.-\,\delta(x)-\delta(y)+\delta(x-y)\right]\psi=\varepsilon\psi. \qquad (2)$$

Using Fourier transformation, we rewrite this Schrödinger equation as a one-dimensional integral equation,

$$G(k_1,k_2)=\frac{F(k_1)+F(k_2)-H(k_1+k_2)}{\frac{1}{2}\left(k_1^2+k_2^2+k_1k_2+p^2\right)}, \qquad (3)$$

where the Fourier transforms of the wave function $\psi(x,y)$ are

$$G(k_1,k_2)=\iint e^{-ik_1x-ik_2y}\psi(x,y)dxdy, \qquad (4)$$

$$F(k)=\int e^{-ikx}\psi(x,0)dx, \qquad (5)$$

$$H(k)=\int e^{-ikx}\psi(x,x)dx, \qquad (6)$$

and $p^2/2 = -\varepsilon$. We now invert transformation (4) and use the resulting ψ in Eqs. (5) and (6) to obtain a system of two integral equations for $F(k)$ and $H(k)$. These are easily decoupled and yield

$$F(k)=\frac{2F(k)}{\sqrt{3k^2+4p^2}}+\frac{1}{\pi}\int\frac{F(k')dk'}{k^2+k'^2+kk'+p^2}$$
$$-\frac{2}{\pi^2}\int\frac{\sqrt{3k'^2+4p^2}}{2+\sqrt{3k'^2+4p^2}}\frac{1}{k^2+k'^2-kk'+p^2}$$
$$\times\left(\int\frac{F(k'')dk''}{k'^2+k''^2-k'k''+p^2}\right)dk' \qquad (7)$$

and

$$H(k)=\frac{2}{\pi}\frac{\sqrt{3k^2+4p^2}}{2+\sqrt{3k^2+4p^2}}\int\frac{F(k')dk'}{k^2+k'^2-kk'+p^2}. \qquad (8)$$

TABLE I. Binding energy of the one-dimensional model of the positronium ion, in units of $m\alpha^2/2$. For $N \geqslant 100$ the eigenvalue appears to converge to $-2/3$. For these large quadrature sizes the uncertainty in the energy is in the last digit due to the finite precision used in the calculation.

Quadrature size N	ε
10	−0.6666657902370426
20	−0.6666666661283767
50	−0.6666666666666257
100	−0.6666666666666660

Once $F(k)$ is found, one can compute $H(k)$. The two-dimensional eigenvalue problem is thus reduced to a one-dimensional integral equation (7), which we solve numerically. The integral equation is discretized using the Gauss-Legendre quadrature, casting it into a system of homogeneous linear equations for $F(k_i)$, where k_i are the abscissas. The system has a nontrivial solution when the determinant of the discretized integral kernel vanishes. This condition fixes the value of p and thus the $D = 1$ binding energy.

The wave function is then determined by solving the linear system for $F(k_i)$. One finds that $F(k_i)$ spans the null space of the discretized kernel and can be computed using its singular value decomposition. We used cubic spline interpolation on the set $\{F(k_i)\}$ to interpolate between the quadrature points and generate an approximation for $F(k)$.

Once $F(k)$ is known, the functions $H(k)$ and $G(k_1,k_2)$ are constructed using Eqs. (8) and (3). Finally, the wave function $\psi(x,y)$ is obtained by the inverse Fourier transformation of $G(k_1,k_2)$.

We performed this procedure for various quadrature sizes N, with the results summarized in Table I.

We see that as N increases, ε approaches $-2/3$. For $N = 100$ the 16-decimal-place precision limit of the *double* data type used in the calculation is almost reached. This simple numerical result suggests that the one-dimensional Schrödinger equation has an analytical solution. The wave function and its Fourier transform are plotted in Figs. 1 and 2. We observe that the wave function has ridges at $x = 0$, $y = 0$, and $x = y$ as expected from the δ function potential in Eq. (2). A simple numerical comparison of $H(k)$ with

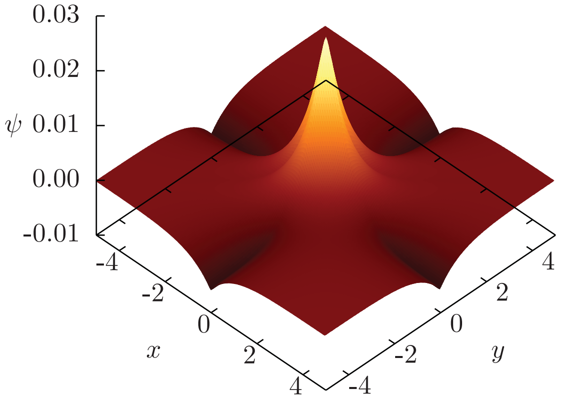

FIG. 1. (Color online) The unnormalized wave function $\psi(x,y)$ satisfying Eq. (2). Distances are in units of $2/(m\alpha)$.

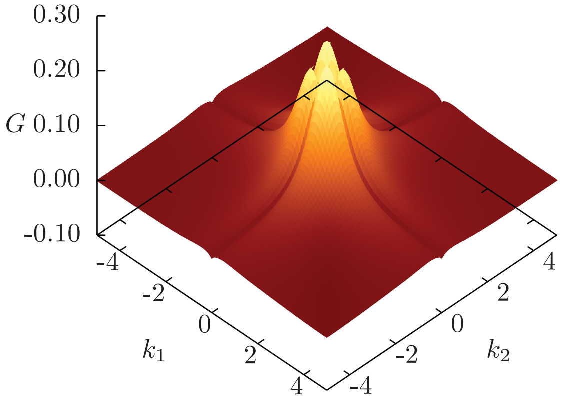

FIG. 2. (Color online) Fourier transform $G(k_1,k_2)$ of the ground-state position-space wave function $\psi(x,y)$ of Eq. (2) computed numerically. Fourier space coordinates have units of $m\alpha/2$.

the Fourier transform of $\exp(-a|x|)$ indicates that the wave function falloff in the $x = y$ direction is nearly exponential.

The result $\varepsilon = -2/3$ translates into the energy eigenvalue $E = -1/3$ a.u. of energy (1 a.u. $= m\alpha^2$) or -9.07 eV. This is in qualitative agreement with the actual value, which is about -0.26 a.u., just below $-1/4$ a.u. (this fraction is the binding energy of a positronium atom in the nonrelativistic approximation).

We note that the eigenvalue that can be obtained for the two-body problem (the positronium or the hydrogen atom) in the one-dimensional δ model coincides precisely with the physical value. This is the case because the wave function in the δ model has the same cusp at the origin as the radial wave function in the physical space. Thus the δ model reproduces that radial wave function exactly. For the three-body problem the agreement is only rough.

It would be interesting to determine the one-dimensional wave function analytically. We remark that the Schrödinger equation of the three-body problem, (2), can be rewritten, with a simple change of variables x,y, in the form of a one-particle motion in the external potential consisting of two attractive and one repulsive δ function ridges.

In the following section we focus on the opposite limit of very many dimensions. We find that an expansion around that limit can be constructed, giving a very accurate determination of the binding energy of Ps$^-$. Interestingly, the $D = 1$ method will again be useful: it will provide an important subtraction term that we use to accelerate the convergence of a perturbative expansion.

III. $D \to \infty$ AND DIMENSIONAL PERTURBATION THEORY

The first step in taking the $D \to \infty$ limit is to generalize the Ps$^-$ Schrödinger equation to D dimensions. We are interested in the ground state, which is completely described by the three interparticle distances $\rho_{ij} = |\vec{r}_i - \vec{r}_j|$. The Schrödinger equation takes the form

$$H\phi \equiv (T + U + V)\phi = E\phi, \tag{9}$$

where E is the energy in atomic units $m\alpha^2$ (note that it differs by a factor of $1/2$ from the ε used in $D = 1$ in the previous section) and

$$\begin{aligned} T &= -\frac{1}{2}\sum_{i\neq j}\left(\frac{\partial^2}{\partial\rho_{ij}^2} + \sum_{k\neq i,j}\frac{\rho_{ij}^2+\rho_{ik}^2-\rho_{jk}^2}{2\rho_{ij}\rho_{ik}}\frac{\partial^2}{\partial\rho_{ij}\partial\rho_{ik}}\right),\\ U &= \frac{(D-1)(D-5)}{8\Upsilon^2}\left(\rho_{13}^2+\rho_{23}^2+\rho_{12}^2\right), \qquad (10)\\ V &= \frac{1}{\rho_{12}} - \frac{1}{\rho_{13}} - \frac{1}{\rho_{23}}, \end{aligned}$$

and $\phi = \Upsilon^{(D-1)/2}\psi$ is the rescaled wave function with

$$\Upsilon = 2\sqrt{s(s-\rho_{12})(s-\rho_{13})(s-\rho_{23})}, \tag{11}$$

$$s = \tfrac{1}{2}(\rho_{12}+\rho_{13}+\rho_{23}). \tag{12}$$

Note that the characteristic D^2 dimensional dependence is confined to U. (The U term in the effective potential is the usual centrifugal contribution from the kinetic energy found by expressing the Laplacian in terms of ρ_{ij}.) In order to obtain a finite limit the coordinates and the energy must be rescaled, $\rho_{ij} = D^2 r_{ij}$ and $E = \epsilon/D^2$. This introduces a factor of $1/D^2$ in front of the kinetic energy term, Eq. (10), so in the limit $D \to \infty$ it is suppressed. In terms of the rescaled quantities, the Schrödinger equation is written as

$$(\delta^2 T + \delta^2 U + V)\phi = \epsilon\phi, \tag{13}$$

where $\delta = 1/D$.

In the limit $\delta \to 0$, terms containing derivatives vanish in Eq. (13). Since the ground-state energy is the smallest eigenvalue of the Hamiltonian, we seek to minimize the effective potential

$$V_{\text{eff}} = \delta^2 U + V \tag{14}$$

at $\delta = 0$, under the constraint that r_{ij} define a triangle. Unfortunately, in $D \to \infty$, the Ps$^-$ system described by the potential in Eq. (10) is unbound (even if the positron were very heavy, its charge would have to be larger than 1.228 for a bound state to exist [23]; see also [33,34]). The qualitative explanation of this is that even though we have increased the number of spatial dimensions, we have retained the $1/r$ behavior of the Coulomb potential. Thus it is relatively stronger at large distances than in three dimensions and the electron-electron repulsion plays a more important role even if the electrons are on the opposite sides of the positron.

However, the strict $\delta = 0$ regime is unphysical. We are interested in the $\delta = 1/3$ case, so we are free to modify the potential as long as it reduces to the correct form at $\delta = 1/3$. This can be done by reducing the strength of the electron-electron repulsion, as done for H$^-$ [23],

$$V = \frac{\lambda_0 + 3(1-\lambda_0)\delta}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{23}}, \tag{15}$$

where λ_0 is a free numerical parameter. Note that at $\delta = 1/3$, Eq. (15) reduces to Eq. (10), as required. We have used $\lambda_0 = 0.5$ throughout our computations since this value gave the best results for the H$^-$ system, but other values of λ_0 may

TABLE II. Results of summation of the $1/D$ expansion using Padé summation with first- and second-order poles removed. The first 21 nonzero terms were used in the summation.

	Known energy (1 a.u. $= m\alpha^2$)	$1/D$ expansion
He	-2.9037243770341196 [37]	$-2.90374(1)$
Ps^-	-0.2620050702329801 [11]	$-0.262005(2)$

result in better convergence of the perturbation series for Ps^-. The effective potential, Eq. (14), is minimized at

$$\bar{r}_{12} = 0.773603828324(1),$$
$$\bar{r}_{13} = \bar{r}_{23} = 0.5866862922582(4), \tag{16}$$

with the minimum value of $V_0 = -1.381325607963162(1)$. The errors are estimated by performing the calculation again with a higher precision and lower tolerances. Convergence is ensured by restarting the minimization from a slightly perturbed location. We note that this result corresponds to the energies rescaled by δ^2. Thus, to compare with the physical value, we have to divide this result by $3^2 = 9$, obtaining the first estimate of the binding energy, $\simeq -0.15$ a.u., to be compared with the known value (see Table II) of about -0.26 a.u.

The static $\delta = 0$ limit is the zeroth order in $1/D$ expansion, but without the kinetic energy, it does not allow us to generate further orders in the perturbation expansion. In order to construct such an expansion, we consider the next simplest case, the harmonic approximation to the potential. This will yield a complete set of states that can be used to generate an expansion. The natural expansion parameter for Eq. (13) is $\delta^{1/2}$. This follows from the dominant balance argument applied to the Schrödinger equation. One finds that, for $\delta^{1/2}$, the harmonic terms in the expansion of the potential are of the same order as the constant coefficient terms in the kinetic energy expansion.

Details of the procedure used to construct the expansion are described in the Appendix. The summation of the resulting series in powers of $\delta = 1/D$ is complicated by the fact that the expansion is divergent at high orders due to a singularity at $\delta = 0$ [35], so we expect the convergence of the naive summation,

$$E(\delta) = \delta^2 \sum_{k=0}^{\infty} E_k \delta^k, \tag{17}$$

to be slow. In the above expression, $E_0 = V_0$ and $E_k = \epsilon_{2k-2}$ for $k > 0$, where ϵ_k are expansion coefficients of the rescaled energy that appears in Eq. (13). There are also poles at $D = 1$ that slow down the asymptotic convergence of the expansion at low values of D. A better estimate for E can be obtained by subtracting these poles from the expansion. To this end, the residues of the poles must be determined. Following [23] and [35], we define

$$E(\delta) = \delta^2 \left[\frac{a_{-2}}{(1-\delta)^2} + \frac{a_{-1}}{1-\delta} + \sum_{k=0}^{\infty} E'_k \delta^k \right], \tag{18}$$

where

$$E'_k = E_k - (k+1) a_{-2} - a_{-1}. \tag{19}$$

The residue of the second order pole, a_{-2}, corresponds to the ground-state energy in the $D = 1$ limit (more precisely, $a_{-2} = 4E_{D=1}$). We have computed it again employing the method described in Sec. II, this time with the rescaled charges of electrons and the positron so as to satisfy Eq. (15). We find

$$a_{-2} = -1.102499999999999(1), \tag{20}$$

which again (see Table I) resembles a rational number, indicating that there are likely analytical solutions of the $D = 1$ model even for an arbitrary charge of the positron (not necessarily equal in magnitude to that of the electron). As in Table I, the uncertainty in this converged residue is due to finite precision, as checked by using larger quadrature sizes.

To find the residue of the single pole, a_{-1}, we subtract the double pole from both sides of Eq. (18) and multiply by $1 - \delta$. We get the condition

$$a_{-1} = \lim_{\delta \to 1} \sum_{k=0}^{\infty} (E_k - E_{k-1} - a_{-2}) \delta^k, \tag{21}$$

where $E_{-1} = 0$. In practice, we only have a finite number of terms in the sums in Eqs. (18) and (21). Padé approximants have been shown to work well for summing up $1/D$ expansions [22,23]. Using this method to compute the limit in Eq. (21), we get, for Ps^-,

$$a_{-1} = 0.427(2). \tag{22}$$

This result was obtained with the first 21 terms in the sum in Eq. (21). The uncertainty in the computed value was estimated by varying the order of the Padé approximant for a_{-1} as $[N/M] \to [(N-1)/(M+1)]$ [36]. If the result has converged, the order of the approximant should not matter (barring the introduction of spurious poles in the denominator of the approximant). We use this method to estimate the error for all quantities computed using Padé approximants. In our calculations we use the full unrounded result for a_{-1}, which gives a slightly worse result for the bound-state energy than Eq. (22). As noted in Ref. [22], this way of determining a_{-1} is not very accurate. An exact value for a_{-1} (in principle, obtainable from expansions about $D = 1$) would improve the convergence of the $1/D$ expansion. For He we used $a_{-2} = -3.15546$ [31] to get $a_{-1} = 0.313(1)$ using an identical calculation with 21 energy expansion coefficients. We then evaluated Eq. (18) (with the summation truncated again at 21 terms) at $\delta = 1/3$. For helium, this yields a ground-state energy that agrees with the variational calculation of [37] to five digits, which is consistent with the result of [21] for this summation method and perturbation expansion cutoff. The same calculation for the positronium ion yields a five-digit agreement with the results in [10,11], and [13]. These results are summarized in Table II.

Figure 3 shows the improvements to the energy that are obtained by summing more terms. Higher orders yield a better accuracy despite the poor behavior of the $1/D$ expansion coefficients (see Table III). In fact, the pole subtraction and Padé resummation described above are necessary to get a sensible answer.

Aside from computing higher orders in perturbation theory, the precision of the result may be improved by using a different summation method. For example, Ref. [21] found that

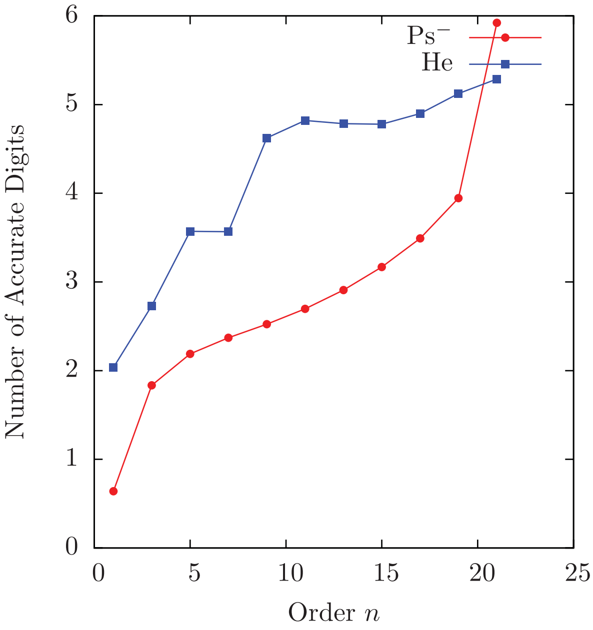

FIG. 3. (Color online) Number of accurate digits in the ground-state energy, defined as $-\log_{10}[(E - E_{\text{exact}})/E_{\text{exact}}]$ as a function of the number of terms in the summation of Eq. (18).

Padé-Borel summation gives better results for helium than Padé summation.

IV. CONCLUSIONS

We have investigated the viability of DS for making accurate predictions for the positronium ion system. Equal masses and correlation strengths make Ps^- a good candidate for the DS treatment. We considered the $D = 1$ limit and found that the Schrödinger equation can be reduced to a one-dimensional integral equation. The numerical solution for the energy eigenvalue approaches a simple rational number, suggesting the possibility of a completely analytical solution. While this energy is not physically relevant by itself, it can be used to accelerate the convergence of the $1/D$ perturbation series.

We constructed such a perturbative series by expanding the solution of the full Schrödinger equation about the $D \to \infty$ limit. Each coefficient was computed exactly in the harmonic basis. To obtain an accuracy of five significant figures required expanding up to order 41 in perturbation theory. While the accuracy of the energy expansion at this order is not yet competitive with variational calculations, the present method provides a valuable alternative approach to few-body systems. It can be used to check a variety of matrix elements that have previously been computed only variationally.

In the future, higher orders in the $1/D$ perturbation series can be determined without sacrificing speed if the analytical expansions can be replaced with numerical evaluations of series coefficients through finite differencing. It would also be very valuable to establish how the convergence of this expansion depends on the value of the parameter λ_0 introduced in Eq. (15). Finally, the accuracy of the obtained wave function should be determined by evaluating matrix elements of various operators and comparing them with the variational approach.

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APPENDIX: PERTURBATIVE EXPANSION IN 1/*D*

In this Appendix we describe how the coefficients of the $1/D$ expansion were determined. Our procedure follows the matrix method in Ref. [20]. In terms of the displacement coordinates x_i defined by

$$\begin{aligned} r_{12} &= \bar{r}_{12} + \delta^{1/2} x_1, \\ r_{13} &= \bar{r}_{13} + \delta^{1/2} x_2, \\ r_{23} &= \bar{r}_{23} + \delta^{1/2} x_3 \end{aligned} \tag{A1}$$

[$\bar{r}_{ij}$ are the coordinates of the minimum of the effective potential, Eq. (16)], the Schrödinger equation takes the form

$$(\delta T + V_{\text{eff}})\phi = \epsilon \phi. \tag{A2}$$

The Hamiltonian is expanded in powers of $\delta^{1/2}$ such that

$$T = \sum_{i=0}^{\infty} T_i \delta^{i/2}, \tag{A3}$$

$$V_{\text{eff}} = \sum_{i=0}^{\infty} V_i \delta^{i/2}. \tag{A4}$$

Since the expansion is about the minimum of V_{eff}, there is no linear term in its expansion and $V_1 = 0$. Also, the kinetic energy T starts contributing only in the second order in $\delta^{1/2}$, so the energy ϵ has the form

$$\epsilon = V_0 + \delta \sum_{i=0}^{\infty} \epsilon_i \delta^{i/2}. \tag{A5}$$

For second order in $\delta^{1/2}$ in Eq. (A2), we have

$$\begin{aligned} T_0 &= -\frac{1}{2} \sum_{i+j+k=2} t_{ijk} \left(\frac{\partial}{\partial x_1}\right)^i \left(\frac{\partial}{\partial x_2}\right)^j \left(\frac{\partial}{\partial x_3}\right)^k, \\ V_2 &= v_{000} + \sum_{i+j+k=2} v_{ijk} x_1^i x_2^j x_3^k, \end{aligned} \tag{A6}$$

where t_{ijk} and v_{ijk} are expansion coefficients that are functions of $\bar{r}_{ij}$. This order in perturbation theory corresponds to three coupled harmonic oscillators. To solve the Schrödinger equation, they need to be decoupled. This procedure yields normal mode frequencies ω_i and the corresponding normal coordinates q_i, related to x_i by a linear transformation S,

$$q_i = \sum_{j=1}^{3} (S^{-1})_{ij} x_j. \tag{A7}$$

In terms of coordinates q_i,

$$T_0 = -\frac{1}{2} \sum_{i=1}^{3} \frac{\partial^2}{\partial q_i^2}, \tag{A8}$$

$$V_2 = v_{000} + \frac{1}{2} \sum_{i=1}^{3} \omega_i^2 q_i^2. \tag{A9}$$

Defining

$$H_i = T_i + V_{i+2}, \tag{A10}$$

the Hamiltonian can be written as

$$H = \delta T + V_{\mathrm{eff}} = V_0 + \delta \sum_{i=0}^{\infty} H_i \delta^{i/2}. \tag{A11}$$

Next we consider the wave function expansion

$$\phi = \sum_{i=0}^{\infty} \phi_i \delta^{i/2}. \tag{A12}$$

Without loss of generality, ϕ_i can be normalized as

$$\langle \phi_0 | \phi_j \rangle = \delta_{0,j}. \tag{A13}$$

Collecting like powers of $\delta^{\frac{1}{2}}$ in Eq. (A2) yields

$$\sum_{i=0}^{p} (H_i - \epsilon_i)\phi_{p-i} = 0. \tag{A14}$$

The $p = 0$ order equation is a system of three independent harmonic oscillators with the solution

$$\phi_0 = h_{\nu_1}(q_1) h_{\nu_2}(q_2) h_{\nu_3}(q_3), \tag{A15}$$

$$\epsilon_0 = v_{000} + \sum_{i=1}^{3} \left(\nu_i + \frac{1}{2} \right) \omega_i, \tag{A16}$$

with

$$h_\nu(q_i) = \sqrt[4]{\frac{\omega_i}{\pi}} \frac{1}{\sqrt{2^\nu \nu!}} H_\nu(\sqrt{\omega_i} q_i) e^{-\omega_i q_i^2/2}, \tag{A17}$$

where H_ν is the νth Hermite polynomial. For the ground state, $\nu_i = 0$.

To compute further orders in the perturbation expansion, ϕ_j from Eq. (A12) are projected onto the harmonic oscillator basis,

$$\phi_j = \sum_{i_1,i_2,i_3} {}_j a^{i_1 i_2 i_3} h_{i_1}(q_1) h_{i_2}(q_2) h_{i_3}(q_3). \tag{A18}$$

Here ${}_j a^{i_1 i_2 i_3}$ are the expansion coefficients. The advantage of using the Hermite function basis is that only a finite basis at every order of perturbation theory is needed, since the perturbations are polynomials in q_i. Thus the perturbation expansion coefficients can be computed exactly. We note that ${}_0 a^{i_1 i_2 i_3} = \delta_{0,i_1}\delta_{0,i_2}\delta_{0,i_3}$. Equation (A13) then implies that, for any $p > 0$,

$${}_p a^{000} = 0. \tag{A19}$$

The matrix elements of the operators H_j defined in Eq. (A10) are computed by noting that each H_j is a sum of terms of the form

$$q_1^{i_1} q_2^{i_2} q_3^{i_3} \left(\frac{\partial}{\partial q_1} \right)^{\alpha_1} \left(\frac{\partial}{\partial q_2} \right)^{\alpha_2} \left(\frac{\partial}{\partial q_3} \right)^{\alpha_3}, \tag{A20}$$

where $\alpha_1 + \alpha_2 + \alpha_3 = 2$ for the kinetic terms and $\alpha_i = 0$ for terms coming from V_{eff}. The matrix elements of q_i and $\frac{\partial}{\partial q_i}$ are derived from the recurrence relations of the Hermite functions [20],

$$q_i = \frac{1}{\sqrt{2\omega_i}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \\ & & \vdots & & \ddots \end{pmatrix}, \tag{A21}$$

$$\frac{\partial}{\partial q_i} = \sqrt{\frac{\omega_i}{2}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & \\ 0 & -\sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & -\sqrt{3} & 0 & \\ & & \vdots & & \ddots \end{pmatrix}, \tag{A22}$$

so H_j is a linear combination of direct products of such matrices. We denote the matrix representation of H_j by $\mathbf{H}_j$, and the tensor with elements ${}_j a^{i_1 i_2 i_3}$ by $\mathbf{a}_j$ in the harmonic basis. Finally, we derive the recursion relations for computation of the energy and wave-function expansion coefficients. First, we rewrite Eq. (A14) in the harmonic basis

$$\sum_{i=0}^{p} (\mathbf{H}_i - \epsilon_i)\mathbf{a}_{p-i} = 0, \tag{A23}$$

and then contract with $\mathbf{a}_0$ and solve for ϵ_p, which yields

$$\epsilon_p = \mathbf{a}_0 \sum_{i=1}^{p} \mathbf{H}_i \mathbf{a}_{p-i}. \tag{A24}$$

To compute the wave-function expansion coefficients we need the pseudoinverse $\mathbf{K}$ of the operator $\mathbf{H}_0 - \epsilon_0$, defined component-wise as

$$\mathbf{K}^{k_1 k_2 k_3}_{i_1 i_2 i_3} = \begin{cases} 0 & i_\alpha = k_\alpha = 0 \forall \alpha; \\ \left(\sum_{j=1}^{3} \omega_j i_j \right)^{-1} \delta^{k_1 k_2 k_3}_{i_1 i_2 i_3} & \text{otherwise.} \end{cases} \tag{A25}$$

The operator $\mathbf{K}$ is defined such that $\mathbf{K}(\mathbf{H}_0 - \epsilon_0) = 1$ everywhere except for the subspace spanned by the harmonic ground-state wave function ϕ_0, where the inverse of $\mathbf{H}_0 - \epsilon_0$ would be undefined and it is convenient to choose $\mathbf{K} = 0$. Contracting $\mathbf{K}$ with Eq. (A23) gives

$$\mathbf{a}_p = \mathbf{K} \sum_{i=1}^{p} (\epsilon_i - \mathbf{H}_i)\mathbf{a}_{p-i}. \tag{A26}$$

Together Eqs. (A24) and (A26) allow us to compute the ground-state energy and wave function to any order.

We implemented the steps required to compute the $1/D$ expansion to arbitrary order in MATHEMATICA [38] and in C++. The determination of the Taylor expansion coefficients of the Hamiltonian is done with MATHEMATICA. The computation of the perturbation series Eqs. (A24) and (A26) is done in C++, for its speed of operations with large arrays (corresponding to the various tensor contractions in these equations). We have computed 20 $1/D$ expansion coefficients (which required expanding up to order 41 in perturbation theory). The results are presented in Table III. Also in this table are the corresponding coefficients for helium (from an identical calculation), which

TABLE III. $1/D$ energy expansion coefficients in Eq. (A5), in units of $m\alpha^2$. Terms with odd p vanish. Numbers in square brackets indicate the power of 10 multiplying the entry. The uncertainty in each coefficient (given in round brackets) was estimated using a similar calculation with 20 digits of precision as described in the text.

p	ϵ_p for Ps$^-$	ϵ_p for He
0	−1.185438078904337(1) [0]	−2.423036748379509(1) [1]
2	−2.78770519314798(1) [0]	−3.544873487874171(2) [1]
4	−7.2695509791874(1) [0]	−5.56025516084019(2) [1]
6	6.7347904088005(2) [1]	−2.174685942637(1) [1]
8	−2.1412953632562(1) [3]	−3.30958097736(1) [2]
10	7.8884951280128(7) [4]	5.2508188805(2) [2]
12	−3.519438146299(1) [6]	4.0504015254(2) [4]
14	1.842029153744(1) [8]	−1.7333557830(1) [6]
16	−1.107117203726(1) [10]	5.6857880174(1) [7]
18	7.51651405108(1) [11]	−1.77525788344(2) [9]
20	−5.69017274005(1) [13]	5.528541546(1) [10]
22	4.75290730575(1) [15]	−1.732045588(2) [12]
24	−4.34262756760(1) [17]	5.409411228(4) [13]
26	4.30867078063(3) [19]	−1.638399579(2) [15]
28	−4.6135902290(1) [21]	4.4914966(2) [16]
30	5.3029755999(1) [23]	−8.6523653(2) [17]
32	−6.512769125044(1) [25]	−1.289717(2) [19]
34	8.5114570184(2) [27]	3.152243(3) [21]
36	−1.17941098599(2) [30]	−2.796124(6) [23]
38	1.7272349225(1) [32]	2.031490(1) [25]
40	−3.253630209(1) [34]	−1.705787919969(3) [33]

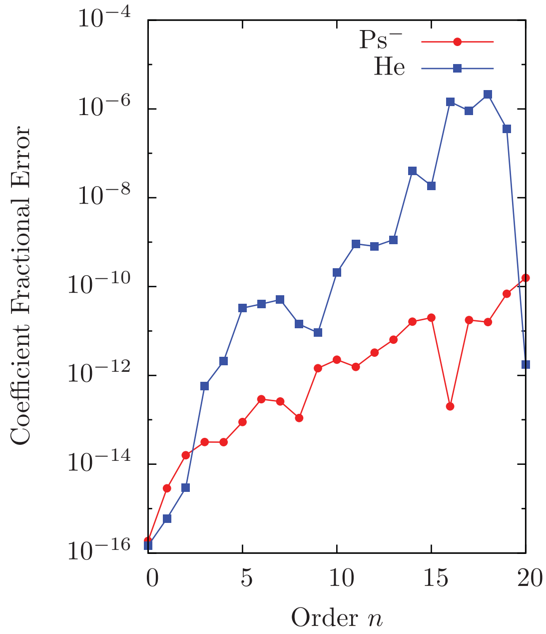

FIG. 4. (Color online) Fractional error in $1/D$ expansion coefficients defined as $|(E_n^{(16)} - E_n^{(20)})/E_n^{(20)}|$ as a function of the order n. Coefficients $E_n^{(16)}$ were obtained using the standard double-precision arithmetic (≈16 digits of precision), while $E_n^{(20)}$ were obtained using the ARPREC arbitrary-precision library (with 20 digits of precision).

agree to at least five significant figures with Table I of [21] (after accounting for a difference in units, which amounts to diving by $Z^2 = 4$) and serve as a check of our calculations. Note that the coefficients in Table III become large at high orders. This is due to the essential singularity at $\delta = 0$. The nature of this singularity was investigated in Ref. [21].

Due to the large number of algebraic operations required to generate the $1/D$ expansion, we need to check for roundoff error in our coefficients; one way to do this is to repeat the C++ computation at a higher precision (there should be no need to redo the MATHEMATICA part, since MATHEMATICA does arbitrary-precision computations by default, as long as one does not invoke numerical solvers). We have implemented a version of the C++ code using the arbitrary precision arithmetic package ARPREC [39].

The relative effect of roundoff error is shown in Fig. 4. We see that the error introduced by finite-precision arithmetic is much smaller than the accuracy of the final ground-state energy obtained by resumming the $1/D$ expansion. Higher order calculations will require better precision when the fractional error becomes of the same order as the accuracy required.

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