

# Stability of four-unit-charge systems: A quantum Monte Carlo study

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The family of four-particle systems ( $M^+m^+M^-m^-$ ) has been studied by means of Monte Carlo techniques. Nonadiabatic explicitly correlated wave functions for different values of the mass ratio  $M/m$  have been obtained using a variational Monte Carlo optimization method. These wave functions have been used in diffusion Monte Carlo simulations of ( $M^+m^+M^-m^-$ ) to compute exact ground-state energies. Our results enlarge the stability range of the mass ratio for these and for similar less symmetric systems and address the problem of the stability of the hydrogen-antihydrogen system. For the special case of the dipositronium molecule ( $M=m$ ) we report the ground-state energy, consistent with previous accurate calculations, and average values of various observables. [S1050-2947(97)05901-5]

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## I. INTRODUCTION

In the last few years attention has been paid to the stability problem of three [1–3] and four [4–15] unit-charge systems. Accurate results for the energy and other expectation values have been computed using a nonadiabatic description. These results helped to clarify the structure of these systems and to understand matter-antimatter annihilation. Investigations in this field are also concerned with the mass dependence of the complex mechanism driving the matter to build large aggregates of particles instead of splitting into smaller pieces [2,4,14].

In molecular physics stability is usually defined in the framework of the Born-Oppenheimer approximation, exploiting the small ratio between electronic and nuclear masses. This possibility is lost if the mass ratio is close to one, and in such a case it is necessary to adopt a nonadiabatic description of the motion of the particles. Furthermore, explicitly correlated wave functions are required to obtain accurate values of the observables. The matrix elements between explicitly correlated wave functions are not easy to compute for systems containing more than three particles, unless one resorts to use Gaussian type basis sets [5,6,10,11,13,14]. Since a correlated Gaussian does not reproduce the cusp conditions, i.e., the behavior of the exact wave function at small interparticle distances, very large basis sets must be employed, and also a careful and computationally expensive optimization of the nonlinear parameters of the trial wave function is required in order to obtain an accurate description.

Few papers have been published on four-particle systems owing to the difficulty of studying these systems both theoretically and numerically [4–15]. Recently an analytical proof of the stability of hydrogenlike molecules

( $M^+M^+m^-m^-$ ) was given by Richard [4]. His proof relies on the already established stability of the ground state of the Dipositronium system  $Ps_2$  [5,6,9–11,13,14], i.e., two electrons and two positrons, and on the fact that the binding energy (BE) is a concave function of  $m/M$ . In the same paper Richard extended the stability domain to less symmetric systems like ( $M^+m^+M^-m^-$ ), exploiting symmetry arguments about the kinetic part of the Hamiltonian. These systems remain stable as long as  $0.70 < \sigma < 1.43$ ,  $\sigma$  being the mass ratio  $M/m$ : this range was obtained using an estimate of the binding energy of the Dipositronium molecule. A numerical study on the stability of the same family of systems ( $M^+M^+m^-m^-$ ) had been previously given by Lee, Vashista, and Kalia [12] using diffusion Monte Carlo simulations. These results were used to discuss the effective mass ratio between an electron pair and a hole pair in some materials. For the same systems, Frolov and Smith [14] discussed the charge-mass-permutation invariance, proposing interpolation formulas for their ground-state mean energy as a function of the mass ratio  $M/m$ : these allow us an approximate computation of the bound-state spectra for the whole family.

In this paper we present a numerical study of the stability of the class of systems having the form ( $M^+m^+M^-m^-$ ). Our main goal is to extend the stability range previously determined by Richard [4] by optimization of approximate nonadiabatic wave functions by a variational Monte Carlo technique and subsequent diffusion Monte Carlo simulations. Since simple scaling arguments based on the variational principle allow one to prove that the stability of the systems having  $m=1$  and any  $M$  implies the stability of the family of systems with the same mass ratio  $\sigma=M/m$ , we restrict our computations to the case  $m=1$  without any loss of generality.

## II. TRIAL WAVE-FUNCTION FORM

In the following a numerical subscript denotes a positively charged particle, while an alphabetical subscript denotes a negatively charged one.

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The Hamiltonian operator for these systems has the form

$$\mathcal{H} = -\frac{1}{2} \left( \frac{\nabla_1^2}{M} + \frac{\nabla_2^2}{m} + \frac{\nabla_a^2}{M} + \frac{\nabla_b^2}{m} \right) + V(\mathbf{R}), \quad (1)$$

where  $V(\mathbf{R})$  is the Coulomb interaction potential

$$V(\mathbf{R}) = +\frac{1}{\mathbf{r}_{ab}} + \frac{1}{\mathbf{r}_{12}} - \frac{1}{\mathbf{r}_{1a}} - \frac{1}{\mathbf{r}_{1b}} - \frac{1}{\mathbf{r}_{2a}} - \frac{1}{\mathbf{r}_{2b}} \quad (2)$$

between the four-unit-charge particles,  $M$  and  $m$  are the masses of the particles, and  $\mathbf{R}$  is a point in configuration space.

The breakup of these systems in a three-particle cluster plus a free particle is not possible because the Coulomb attraction between the two fragments binds them together. This means that the energy dissociation threshold for this class of systems, when  $m=1$ , is given by [4]

$$E_{thr}(M) = -\frac{M}{4} - \frac{1}{4} \quad (3)$$

corresponding to the splitting in the two species ( $M^+ M^-$ ) and ( $m^+ m^-$ ). The alternative breakup in ( $M^+ m^-$ ) and ( $M^- m^+$ ) has a higher threshold energy of ( $-M/1+M$ ).

To approximate the nonadiabatic ground-state wave function for these systems we propose to use a linear combination of explicitly correlated functions [16]

$$\Psi_T = \sum_{i=1}^L c_i \Phi_i, \quad (4)$$

where

$$\begin{aligned} \Phi_i(\mathbf{R}, \mathbf{k}_i, \mathbf{p}_i) = & \mathcal{A}\{O_{sym} e^{-k_{i,1}r_{1a}-k_{i,2}r_{1b}-k_{i,3}r_{2a}-k_{i,4}r_{2b}} \\ & \times f(r_{12}, r_{ab}, \mathbf{p}_i) \Theta_{0,0}^{1,2} \Theta_{0,0}^{a,b}\}. \end{aligned} \quad (5)$$

In this equation  $\mathcal{A}$  is the antisymmetrization operator,  $O_{sym}$  is an operator used to fix the symmetry of the state,  $\Theta_{0,0}^{1,2}$  and  $\Theta_{0,0}^{a,b}$  are the spin eigenfunctions with quantum number  $S=0$  and  $M_s=0$  for the particles of equal charge. In the spin free formulation of quantum mechanics, Eq. (5) can be written as a linear combination of spatial terms with particle indices exchanged, i.e.,

$$\begin{aligned} \Phi_i(\mathbf{R}, \mathbf{k}_i, \mathbf{p}_i) = & \sum_{j=1}^{N_p} \mathcal{P}_j^{sym} e^{-k_{i,1}r_{1a}-k_{i,2}r_{1b}-k_{i,3}r_{2a}-k_{i,4}r_{2b}} \\ & \times f(r_{12}, r_{ab}, \mathbf{p}_i), \end{aligned} \quad (6)$$

where  $\mathcal{P}_j^{sym}$  are the exchange operators generated by acting with  $\mathcal{A}$  and  $O_{sym}$  on the spatial part of Eq. (5) and collecting all the terms with the same spin function.

The term  $f(r_{12}, r_{ab}, \mathbf{p}_i)$  is the correlation factor used to describe the repulsion between particles having the same charge and has the analytical form

$$f(r_{12}, r_{ab}, \mathbf{p}_i) = e^{-p_{i,1}r_{12}-p_{i,2}r_{ab}}, \quad (7)$$

where

$$p_{i,12} = e^{-p_{i,3}r_{12}} \quad (8)$$

and

$$\rho_{i,ab} = e^{-p_{i,3}r_{ab}}. \quad (9)$$

In the above equations  $\mathbf{p}_i$  and  $\mathbf{k}_i$  are vectors of parameters for the  $i$ th term of the linear expansion. This analytical form has the correct spin and space symmetry and allows the trial wave function to mimic the correct behavior of the exact wave function at the coalescence point for equal and opposite sign charges. Satisfying the cusp condition usually accelerates the convergence [17] of the linear expansion and reduces its length for a given accuracy. This is useful in order to reduce the effort needed to optimize the nonlinear parameters, usually a quite heavy task. Since the trial wave function depends only on the interparticle distances, the mean value of the center-of-mass kinetic energy for a given linear combination is always zero. This means that the computed energy is only the internal energy of the systems, and there is no need to subtract the contribution of the overall motion of the system in space.

### III. MONTE CARLO SIMULATION

The chosen form for the trial wave function makes it impossible to compute analytically the matrix elements of the Hamiltonian operator of the system and a numerical method must be used to obtain the energy mean value for a given trial wave function. The variational Monte Carlo method (VMC) [18] is well suited for this goal since it requires only the evaluation of the wave function, its gradient, and its Laplacian. Since this and others Monte Carlo methods are well described [18] in the literature, we only summarize the main points and equations.

VMC computes expectation values employing the steady-state distribution  $f = \Psi_T^2$  that can be obtained simulating the Fokker-Planck differential equation [18]

$$\begin{aligned} -\frac{\partial f(\mathbf{R}, t)}{\partial t} = & -\sum_{i=1,2,a,b} D_i \nabla_i^2 f(\mathbf{R}, t) \\ & + \sum_{i=1,2,a,b} D_i \nabla_i \cdot f(\mathbf{R}, t) \mathbf{F}_i(\mathbf{R}), \end{aligned} \quad (10)$$

where

$$\mathbf{F}_i(\mathbf{R}) = \nabla_i \ln[\Psi_T(\mathbf{R})^2] \quad (11)$$

is called the quantum force and  $D_i = (2m_i)^{-1}$  is the diffusion coefficient for a given particle. The simulation is realized using the Langevin equation

$$\mathbf{r}'_i = \mathbf{r}_i + D_i \tau \mathbf{F}_i(\mathbf{R}) + \boldsymbol{\chi}, \quad (12)$$

where  $\boldsymbol{\chi}$  is a three-dimensional Gaussian random variable with zero mean and  $\tau/m_i$  variance. This equation is used to select an attempted displacement for each particle, but since this is a discretization of the corresponding Fokker-Planck equation the mean values obtained from the steady-state distribution have an error dependent on the value of the time step  $\tau$  and are correct only in the zero time step limit. To avoid an extrapolation the attempted displacement is accepted with probability

$$P(\mathbf{R} \rightarrow \mathbf{R}') = \min \left[ 1, \frac{T(\mathbf{R}' \rightarrow \mathbf{R}, \tau) \Psi_T(\mathbf{R}')^2}{T(\mathbf{R} \rightarrow \mathbf{R}', \tau) \Psi_T(\mathbf{R})^2} \right], \quad (13)$$

where  $T(\mathbf{R} \rightarrow \mathbf{R}', \tau)$  is the transition matrix for the particles to move from  $\mathbf{R}$  to  $\mathbf{R}'$ . The transition matrix corresponding to the Langevin equation is

$$T(\mathbf{R} \rightarrow \mathbf{R}', \tau) = \prod_{i=1,2,a,b} \frac{1}{(4D_i \tau)^{3/2}} e^{-\{[\mathbf{r}'_i - \mathbf{r}_i - D_i \tau \mathbf{F}_i(\mathbf{R})]^2 / 4D_i \tau\}}. \quad (14)$$

The mean energy is computed using

$$\langle \mathcal{H} \rangle = \frac{\int \Psi_T^2(\mathbf{R}) E_{loc}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}}, \quad (15)$$

where

$$E_{loc}(\mathbf{R}_j) = \frac{\mathcal{H} \Psi_T(\mathbf{R}_j)}{\Psi_T(\mathbf{R}_j)}. \quad (16)$$

To optimize the linear and nonlinear parameters in the trial wave function we minimized the functional

$$\mu(E_r) = \frac{\sum_{j=1}^{N_{conf}} w_j [E_{loc}(\mathbf{R}_j) - E_r]^2}{\sum_{j=1}^{N_{conf}} w_j}, \quad (17)$$

$\{\mathbf{R}_j\}$  being a set of fixed configurations sampled from  $\Psi_T^2$ . All the weights  $w_j$  were set equal to one, while  $E_r$  is an approximation of the true value of the energy for the system. This method has been described in detail by Umrigar, Wilson, and Wilkins [19] and by Mushinski and Nightingale [20] and has been proved to be much more stable than the optimization of the energy.

The mean energy values of the optimized trial wave functions are upper bounds to the exact value. In order to obtain the exact ground-state energy, the diffusion quantum Monte Carlo method (DMC) [21,18] is employed to simulate the time-dependent Schrödinger equation (TDSE) as a diffusion equation having source and sink terms. In the DMC simulation the TDSE, in imaginary time, has the form

$$-\sum_{i=1,2,a,b} D_i \nabla_i^2 f(\mathbf{R}, t) + \sum_{i=1,2,a,b} D_i \nabla_i \cdot f(\mathbf{R}, t) \mathbf{F}_i(\mathbf{R}) \\ + [E_r - E_{loc}(\mathbf{R})] f(\mathbf{R}, t) = -\frac{\partial f(\mathbf{R}, t)}{\partial t}, \quad (18)$$

where the only difference with the Fokker-Planck equation, used in VMC, is the additional term  $[E_r - E_{loc}(\mathbf{R})] f(\mathbf{R}, t)$ . This is simulated varying the population of the configurations during the simulation. The formal solution of the TDSE in imaginary time can be written using the eigenfunctions  $\phi_i$  of the Hamiltonian, i.e.,

$$f(\mathbf{R}, t) = c_0 \Psi_T \phi_0 e^{-(E_0 - E_r)t} + \sum_{i=1}^{\infty} c_i \Psi_T \phi_i e^{-(E_i - E_r)t}. \quad (19)$$

The formal solution shows that the only long term surviving contribution is due to the ground state of the system. This can be used to estimate the energy by means of the mixed estimator

$$E(\sigma) = \frac{\int f(\mathbf{R}, \infty) E_{loc}(\mathbf{R}) d\mathbf{R}}{\int f(\mathbf{R}, \infty) d\mathbf{R}}. \quad (20)$$

The wave function optimized using the minimization of the variance of the local energy was used to guide the walk of the configurations in the space, to reduce the fluctuation of the population simulating the birth-death process described by  $[E_r - E_{loc}(\mathbf{R})] f(\mathbf{R}, t)$ , and to compute the energy value by means of the mixed estimator.

#### IV. VARIATIONAL AND DIFFUSION MONTE CARLO RESULTS

To test the capabilities of our analytical ansatz to correctly describe Coulomb clusters, the dipositronium molecule has been chosen as a nontrivial test case, since for this system there are several accurate nonadiabatic results, computed using explicitly correlated Gaussian basis sets [5,6,10,11,13,14], to compare with. As total symmetry operator we assumed

$$\sum_{j=1}^{N_p} \mathcal{P}_j^{sym} \approx 1 + \mathcal{E}(+, -), \quad (21)$$

where  $\mathcal{E}(+, -)$  is one of the exchange operators between particles having the same mass and opposite charges. As shown by Kinghorn and Poshusta [5] this operator is not the complete symmetry operator for the ground state of the Dipositronium molecule. Using their theory for the permutation symmetry of Dipositronium it is possible to prove that our right-hand term in Eq. (6), using the approximate Eq. (21), is a mixture of states having  $A_1$ ,  $B_1$ , and  $E$  symmetry,  $A_1$  being the correct ground-state symmetry. This means that the finite expansion in Eq. (4) could have different mean properties for particles with the same mass and equal charge.

A two-term trial wave function was optimized using a fixed sample of 4000 configurations for dipositronium. The starting set of parameters was forced to have the full correct symmetry under the exchange between two particles of equal charge, but constraints were not imposed during the optimization. In every two to three steps of the optimization process the fixed sample was updated using a VMC run, useful also to monitor the behavior of the optimization process.

The dipositronium molecule VMC mean energy and its binding energy, defined as  $E_{thr}(\sigma) - E(\sigma)$ , obtained using the optimized two-term expansion, are shown in Table I and Fig. 1, together with the results for the systems having mass ratio  $\sigma \leq 2.2$ . Comparing our variational value for the dipositronium energy,  $-0.509\ 67(1)$  hartree, with the best variational value  $-0.516\ 002\ 1$  hartree obtained by Frolov and Smith [14], we note that our short expansion is able to recover more than 98% of the internal energy and that this trial wave function is roughly equivalent to a 16 term explicitly correlated Gaussian wave function [6]. To assess the contamination from excited states with different symmetries we calculated some expectation values for dipositronium by

TABLE I. VMC energy and binding energy (BE) using a two-term linear expansion. Standard deviations of the mean values are given in parentheses.

$\sigma$	Energy (hartree)	BE (hartree)
1.0	-0.509 67(1)	0.009 67(1)
1.1	-0.536 97(3)	0.011 97(3)
1.2	-0.559 61(4)	0.009 61(4)
1.3	-0.582 65(4)	0.007 65(4)
1.4	-0.605 79(4)	0.005 79(4)
1.6	-0.652 03(3)	0.002 03(3)
1.7	-0.674 87(3)	-0.000 13(3)
1.8	-0.699 34(3)	-0.000 66(3)
1.9	-0.724 01(2)	-0.000 99(2)
2.0	-0.748 98(2)	-0.001 02(2)
2.1	-0.772 22(1)	-0.002 78(1)
2.2	-0.793 30(2)	-0.006 70(2)

means of a VMC simulation, using the two-terms trial wave function. These results, reported in Table II together with the accurate results from Refs. [5,15,6], and [13] as comparison, clearly show this contamination. To eliminate the problem, the full symmetry operator set of dipositronium must be used, at least if short linear expansions are employed together with VMC techniques. DMC does not suffer from this problem, being capable of projecting out all the components of the excited states. As our work is mainly concerned with the study of the dissociation threshold of  $(M^+m^+M^-m^-)$ , DMC is our preferred method, giving the “exact” ground-state energy.

From Eq. (2) of Ref. [10] the two-photon annihilation rate  $\Gamma_{2\gamma}$  for dipositronium can be written as

$$\Gamma_{2\gamma} = 4\pi\alpha c a_0^{-1} \langle \delta(\mathbf{r}_{+-}) \rangle = 201.234 961 8 \times 10^9 \langle \delta(\mathbf{r}_{+-}) \rangle s^{-1}, \quad (22)$$

where  $\langle \delta(\mathbf{r}_{+-}) \rangle = \frac{1}{4}\{\langle \delta(\mathbf{r}_{1a}) \rangle + \langle \delta(\mathbf{r}_{1b}) \rangle + \langle \delta(\mathbf{r}_{2a}) \rangle + \langle \delta(\mathbf{r}_{2b}) \rangle\}$ . Using mean values for  $\langle \delta(\mathbf{r}_{+-}) \rangle$  from Table II we obtain  $\Gamma_{2\gamma} = 4.5(2) \times 10^9 s^{-1}$ , a value in fair agreement with the results given by Frolov, Kryuchkov, and Smith [10]  $4.441 \times 10^9 s^{-1}$ , and by Rebane and Zotev [13] of  $4.17 \times 10^9 s^{-1}$ .

The variational results for the systems having mass ratio  $\sigma \leq 2$  were obtained starting each optimization from the

wave function obtained for the system with the nearest mass ratio available. The resulting wave functions show the tendency of the systems to separate into the two subsystems ( $M^+M^-$ ) and ( $m^+m^-$ ) on increasing the particle mass ratio. This behavior was confirmed also by plotting the interparticle distributions obtained during a VMC simulation. Due to this fact we were not able to optimize trial wave functions for the two systems with  $\sigma=2.1$  and 2.2: the variational results reported in Table I were obtained using the wave function optimized for  $\sigma=2.0$ , but including the correct mass ratio.

The DMC simulations were performed using these trial wave functions to project out the remaining components of the excited states for these systems. The dipositronium molecule is an optimal test case to check the ability of our DMC code to compute the energy of the systems although the guiding function does not possess the correct total symmetry. The resulting values for the energy are shown in Table III and Fig. 1. The DMC result for dipositronium molecule and for systems having  $\sigma \leq 2$  were obtained using a time step of 0.005 hartree<sup>-1</sup>. The accuracy of the energy values was checked using different time steps for the dipositronium molecule and for other systems. We estimate that for all the values presented the difference to the exact eigenvalue of the Hamiltonian for a given mass ratio is less than the statistical error associated with the computed value. For  $\sigma=2.1$  and 2.2 a complete extrapolation to  $\tau=0$  was carried out to avoid systematic errors due to the inaccuracy of the trial wave function.

## V. DISCUSSION

In this work we have computed the ground-state energy for the family of systems  $(M^+m^+M^-m^-)$  ( $m=1$ ) for  $1 \leq \sigma \leq 2.2$ , using both VMC and DMC simulations. The least accurate variational result is for the dipositronium molecule, an easily explained outcome as the symmetry operator does not contain the full symmetry for the ground state.

Our DMC simulations, using different time steps, show that the time step bias is negligible for the given statistical accuracy, i.e., it is smaller than the standard deviation of the mean value of the energy. Our DMC energy value for the dipositronium molecule, -0.516 06(7) hartree, is in optimal agreement with both the best variational estimate -0.516 002 1 hartree [14], and the old DMC calculation by Lee, Vashista, and Kalia of -0.515(1) hartree [12]. Recently El-Gogary *et al.* [8] have published a much lower

TABLE II. VMC mean values of various physical properties for the dipositronium system (in atomic units).

	This work	Ref. [13]	Ref. [5]	Refs. [15] and [6]
$\langle r_{1a} \rangle$	3.765(5)	4.428	4.483	
$\langle r_{12} \rangle = \langle r_{ab} \rangle$	6.009(9)	5.916	6.025	
$\langle r_{1b} \rangle = \langle r_{2a} \rangle$	5.093(7)	4.428	4.483	
$\langle r_{1a}^2 \rangle$	17.59(8)	27.72	29.01	28.88
$\langle r_{12}^2 \rangle = \langle r_{ab}^2 \rangle$	45.5(2)	43.61	46.17	45.91
$\langle r_{1b}^2 \rangle = \langle r_{2a}^2 \rangle$	36.9(1)	27.72	29.01	28.88
$\delta(\mathbf{r}_{+-})$	0.0222(9)	0.020 65	0.021 85	0.021 95
$\delta(\mathbf{r}_{12}) = \delta(\mathbf{r}_{ab})$	0.000 64(6)	0.000 68	0.000 634 7	0.000 638

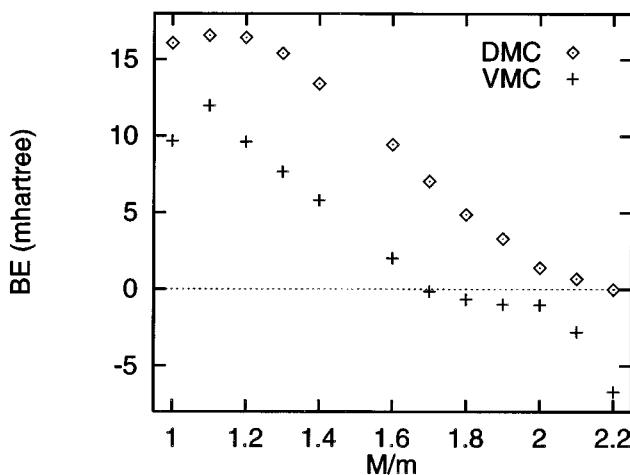


FIG. 1. Variational and diffusion Monte Carlo binding energy.

$E = -0.521\ 05$  hartree. Quantum Monte Carlo (QMC) methods are able to get the exact energy for nodeless systems like the dipositronium, so this is a puzzling result. Neither our two-term trial wave function, nor the much simpler one by Lee, Vashista, and Kalia [12] present nodal surfaces that might give an upper limit to the exact energy value, so both calculations should give the exact energy within the statistical accuracy. We are performing more accurate VMC and DMC calculations on this system trying to settle this problem: preliminary results [22] are still in agreement with the present one and with the results by Lee, Vashista, and Kalia [12], so the results by El-Gogary *et al.* [8] should be regarded with some caution.

The DMC results show a small increase of the value of the binding energy for the mass ratios 1.1 and 1.2 compared with the dipositronium system, followed by a decrease for a larger mass ratio.

The small increase for  $\sigma \leq 1.3$  can be rationalized invoking the Hellmann-Feynman theorem. Putting  $m=1$  in Eq. (1) we obtain

$$\frac{\partial E(M)}{\partial M} = -\frac{1}{M}(\langle T_a \rangle + \langle T_1 \rangle). \quad (23)$$

TABLE III. DMC energy and binding energy (BE). Standard deviations of the mean values are given in parentheses.

$\sigma$	Energy (hartree)	BE (hartree)
1.0	-0.516 06(7)	0.016 06(7)
1.1	-0.541 56(5)	0.016 56(5)
1.2	-0.566 43(5)	0.016 43(5)
1.3	-0.590 38(5)	0.015 38(5)
1.4	-0.613 40(4)	0.013 40(4)
1.6	-0.659 44(5)	0.009 44(5)
1.7	-0.682 04(4)	0.007 04(4)
1.8	-0.704 87(4)	0.004 87(4)
1.9	-0.728 30(4)	0.003 30(4)
2.0	-0.751 40(4)	0.001 40(4)
2.1	-0.775 69(4)	0.000 69(4)
2.2	-0.799 99(5)	-0.000 01(5)

For the dipositronium system ( $M=1$ )  $T_a+T_1=(T/2)$ , but for the virial theorem  $T=-E$  and

$$\left( \frac{\partial E(M)}{\partial M} \right)_{M=1} = \frac{E(1)}{2}, \quad (24)$$

where  $E(1)$  is the energy for the ground state of the Dipositronium system. Using the best variational estimate for this quantity the derivative of the energy is  $-0.258\ 001$  hartree amu $^{-1}$ , larger in modulus than the derivative of the threshold energy Eq. (3) for the same mass value ( $-0.25$  hartree amu $^{-1}$ ). This means that the slope of the binding energy for the dipositronium system is positive, explaining its increase for  $\sigma \geq 1$ .

The monotonous decrease of the binding energy for  $\sigma \geq 1.3$  can be explained by the reduction of the instantaneous dipole moment of the fragment ( $M^+M^-$ ) on increasing the mass. As a consequence its ability to polarize the lighter ( $m^+m^-$ ) system decreases.

Using simple symmetry arguments related to the variational approach, Richard [4] proved that the systems ( $M^+m^+M^-m^-$ ) are stable in the range  $0.7 \leq \sigma \leq 1.4$ . Our VMC results show that using a simple ansatz for the approximated wave function it is possible to extend this range to

$$0.625 \leq \sigma_{VMC} \leq 1.6. \quad (25)$$

Using the DMC results of Table III this range can be further extended to

$$0.476 \leq \sigma_{DMC} \leq 2.1. \quad (26)$$

Our numerical results for the total energy of this symmetric family of four-body Coulombic clusters can be exploited to obtain information about the stability of less symmetric systems. For the more general family ( $m_a^+m_b^+m_1^-m_2^-$ ) it is possible to define two new quantities [4]

$$\frac{2}{\Delta} = \frac{1}{m_a} + \frac{1}{m_1},$$

$$\frac{2}{\delta} = \frac{1}{m_b} + \frac{1}{m_2}, \quad (27)$$

where, without loss of generality, we impose  $m_a \geq m_b$  and  $m_1 \geq m_2$ . In his work Richard [4] proved that if the ratio  $\Delta/\delta$  is within the range of stability of the systems ( $M^+m^+M^-m^-$ ), the variational principle implies the stability for the general four-body Coulombic cluster. If we choose  $m_b=m_1=m_2=m$  and  $m_a=M$ , i.e., ( $M^+m^+m^-m^-$ ), then one can write the ratio between  $\Delta$  and  $\delta$  as

$$\frac{\Delta}{\delta} = \frac{2M}{m+M}. \quad (28)$$

Since this is always less than 2, the stability for this system is assured for any value of the masses. A well studied example of this family of systems is the positronium hydride which is known to be weakly bound. Another example of the applicability of our results is the possibility to show that the class of systems having the form ( $m_a^+m_b^+m_1^-m_1^-$ ) where

$m_a^+ \geq m_1^-$  and  $m_b^+ \geq m_1^-$  is stable against the dissociation in two neutral subsystems for all the values of the mass  $m_b$ . This proves the correctness of Richard's guess about the stability of this particular class of clusters [4], connecting the hydrogen molecule to the positronium hydride if  $m_1 = 1$ .

The value  $\sigma \approx 1836$  corresponds to the hypothetical molecule composed of an hydrogen atom and an antihydrogen atom. Few papers have been devoted to studying this interesting system using both numerical methods [23–25], within the Born-Oppenheimer approximation, and analytical techniques [7] without resolving the issue of whether the system is bound or not. Our numerical values show a reduction of the binding energy with increasing mass ratio for  $(M^+m^+M^-m^-)$ , and our extrapolated DMC simulations for mass ratio equal to 2.2 give results in agreement with the energy value for the dissociation threshold. An analysis of the distribution of the configurations representing this system during the simulation shows the tendency toward the dissociation of the cluster. Although not definitive, both these evidences strongly support the idea that the hydrogen-antihydrogen system is not bound, i.e., it does not exist as a bound stationary state, as suggested by Richard [4]. This conclusion has some analogies with the results obtained for the model system composed of a dipole and an electron [26,27]. This system has a stable ground state only if the modulus of the dipole moment is larger than a threshold value. As already stressed, by increasing  $M$ , the instanta-

neous dipole moment of  $(M^+M^-)$  decreases and this might lead to the dissociation of the composed three- and four-particle systems. These results are not in agreement with the assertion made by Abdel-Raouf and Ladik [7] in the hydrogen-antihydrogen system, but it is worth noting that they failed to recognize the correct dissociation threshold, assuming a dissociation into two subsystems  $(M^+m^-)$  and  $(M^-m^+)$  instead of  $(M^+M^-)$  and  $(m^+m^-)$ .

## VI. CONCLUSIONS

We have performed very accurate numerical calculations on the family of systems  $(M^+m^+M^-m^-)$ . Using VMC and DMC methods we extend the stability range of these systems, showing also that Monte Carlo techniques are well suited for the investigation of these exotic systems, as they do not pose restrictions on the mass values, potential form and trial wave function. Our study strongly suggests that the hydrogen-antihydrogen system is not bound.

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