Thermal dissociation of dipositronium: Path-integral Monte Carlo approach

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Path-integral Monte Carlo simulation of the dipositronium "molecule" Ps_2 reveals its surprising thermal instability. Although, the binding energy is ~ 0.4 eV, due to the strong temperature dependence of its free-energy Ps_2 dissociates, or does not form, above ~ 1000 K, except for high densities where a small fraction of molecules are in equilibrium with Ps atoms. This prediction is consistent with the recently reported first observation of stable Ps_2 molecules by Cassidy and Mills, Jr., [Nature (London) **449**, 195 (2007); Phys. Rev. Lett. **100**, 013401 (2008)] at temperatures below 1000 K. The relatively sharp transition from molecular to atomic equilibrium, which we find, remains to be experimentally verified. To shed light on the origin of the large entropy factor in free-energy, we analyze the nature of interatomic interactions of these strongly correlated quantum particles. The conventional diatomic potential curve is given by the van der Waals interaction at large distances; but due to the correlations and high delocalization of constituent particles, the concept of potential curve becomes ambiguous at short atomic distances.

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Dipositronium or positronium molecule Ps_2 is a four-body system consisting of two electrons and two positrons. The dynamical stability of dipositronium was established in 1947 by Hylleraas and Ore [1]. However, the molecule was not observed experimentally until recently [2], even though a lot of knowledge had been provided by a number of theoretical studies (see Refs. [3–9] and references therein). In addition to the fundamental issues of physics, Ps_2 is of interest also in astrophysical applications and in solid-state physics [10,11].

In laboratory conditions, Ps_2 formation has recently been observed resulting from implantation of intense pulses of positrons into porous silica films [2,12].

The positronium molecule, with all the four particles of the same mass, sets challenges to modeling since quantum calculations are to be performed fully nonadiabatically [13]. This, however, can be realized with quantum Monte Carlo (QMC) methods [14–16]. It should be pointed out that also for other systems, approaches that are not restricted by the Born-Oppenheimer or other adiabatic approximations are gaining more attention [16–23].

Among the QMC methods, the path-integral Monte Carlo (PIMC) offers a finite-temperature approach together with a transparent tool to trace the correlations between the particles involved. Though computationally challenging, with the carefully chosen approximations PIMC is capable of treating low-dimensional systems, such as small molecules or clusters, accurately enough for good quantum statistics for a finite-temperature mixed state [24–29].

In this study, using PIMC, we evaluate the density matrix of the full four-body quantum statistics in temperature-dependent stationary states. Thus, the temperature-dependent distributions of structures and energetics of Ps_2 are established. The main focus here is to find the preferred configuration of the four-body system at each temperature—Ps_2 molecule or two Ps atoms.

According to the Feynman formulation of the statistical quantum mechanics [30], the partition function for interacting distinguishable particles is given by the trace of the density matrix $\hat{\rho}(\beta) = e^{-\beta \hat{H}}$,

$$Z = \text{Tr }\hat{\rho}(\beta) = \int dR_0 dR_1 \ldots dR_{M-1} \prod_{i=0}^{M-1} e^{-S(R_i, R_{i+1}; \tau)},$$

where S is the action, $\beta = 1/k_B T$, $\tau = \beta/M$, and M is called the Trotter number ($R_M = R_0$). In present simulations, we use the pair approximation of the action and matrix squaring for the evaluation of the Coulomb interactions [25,31]. Sampling of the paths in the configuration space is carried out using the Metropolis algorithm [32] with the bisection moves [33]. The Coulomb potential energy is obtained as an expectation value from sampling and the kinetic energy is calculated using the virial estimator [34].

The error estimate for the PIMC scheme is commonly given in powers of the imaginary time step τ [25]. Therefore, in order to determine comparable thermal effects on the system, we have carried out the simulations with similar sized time steps regardless of the temperature. This way the temperature-dependent properties can be compared avoiding temperature-dependent systematic errors. The standard error of the mean with two-sigma limits is used to indicate the statistical uncertainty, where relevant. The average of the chosen time step is $\langle \tau \rangle \approx 0.0146 E_H^{-1}$, where E_H denotes the atomic unit of energy, hartree (≈ 27.2 eV). The other atomic unit we use here is Bohr radius for the length a_0 (≈ 0.529 Å).

The total energy of positronium "atom" Ps is -0.25 at 0 K and the binding energy of the molecule Ps_2 is 0.0160 (≈ 0.435 eV) [8]. We find these values as zero Kelvin extrapolates from our simulations at low temperatures. We point out that with PIMC we evaluate energetics as statistical expectation values from sampling with less accuracy than that from conventional solutions of wave functions and the zero Kelvin data we obtain as extrapolates only.

In Fig. 1 we present the "apparent dissociation energy" of Ps_2 at several different temperatures. In each temperature, this is the negative total energy of the molecule with respect to two atoms as $D_T = -[\langle E_{\text{tot}}^{Ps_2} \rangle_T - 2\langle E_{\text{tot}}^{Ps} \rangle_T]$. At $T \leq 900$ K, we find for the average over shown temperatures $\bar{D}_T$
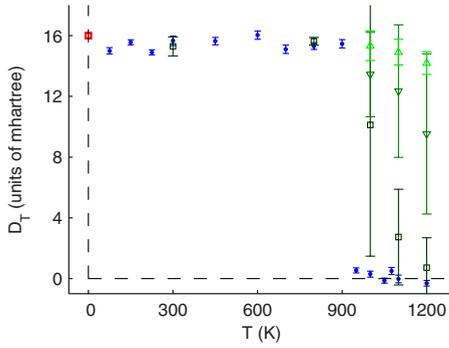
FIG. 1. (Color online) Apparent temperature-dependent disso-ciation energy of dipositronium in units of mhartree: zero Kelvin reference (square without error bars, red) and finite-temperature simulation results at the low-density limit (blue dots). Data from higher Ps density simulations are also shown (green): 0.50 ($\square$), 14 ($\triangledown$), and 100×10^{24} m^{-1} ($\triangle$).

$=0.0154(5)$, which is very close to the dissociation energy at 0 K, D_0. However, at higher temperatures the apparent dis-sociation energy vanishes because $\langle E_{tot}^{Ps_2} \rangle_T$ and $2\langle E_{tot}^{Ps} \rangle_T$ be-come the same. This is because of molecular dissociation, or to be more exact, the two atoms do not bind in our equilib-rium state simulation at $T \geq 900$ K and the predominant con-figuration is that of two separate positronium atoms.

Simulations in a well-defined Ps density are time consum-ing and, therefore, studies of this kind have been carried out at the transition region around 1000 K only. Using the peri-odic boundary conditions and the cubic supercells of sizes from $(300a_0)^3$ to $(50a_0)^3$ with two Ps atoms, we have simu-lated three densities from 0.5 to 100×10^{24} m^{-1}, respec-tively. We see that with increasing density, the equilibrium shifts to the molecular direction making the transition smoother and raising it to higher temperatures compared to the more sharp low-density limit.

For completeness, we should point out that in equilibrium at any finite temperature the zero density limit consists of Ps atoms only. Correspondingly, increasing density will eventu-ally smoothen the transition away.

In the recent experiment cited above [2,12], the formation of Ps$_2$ molecules was observed below 900 K in about two orders of magnitude lower densities than our lowest, above (Fig. 1). Formation was not observed at higher temperatures, however, because the Ps atoms desorbed from the confining porous silica surface with the activation energy k_BT ~ 0.074 eV (~ 850 K). Thus, our prediction of thermal dis-sociation of Ps$_2$ above 900 K in the experimentally achiev-able densities remains to be verified in forthcoming experi-ments in higher temperatures.

Next, we compare our finite-temperature Ps$_2$ data to the published zero Kelvin results, discuss the details of Ps-Ps interaction and, finally, conclude with the explanation of the higher-temperature instability.

The conventional zero Kelvin like Ps$_2$ state of the system is confirmed below 900 K from the distributions in Fig. 2 and related data in Table I. The pair-correlation functions for like and opposite charged particles are essentially identical with those reported elsewhere [6], and the expectation values of various powers of these distributions match with other
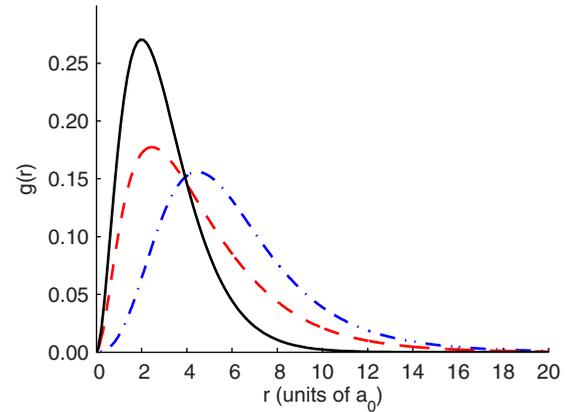

FIG. 2. (Color online) Temperature averaged pair-correlation functions for different particle pairs ($T \leq 900$ K): $e^- \, e^-$ and $e^+ \, e^+$ (dash dotted) and $e^- \, e^+$ (dashed). The ground-state ($T=300$ K) ra-dial distribution of the free positronium atom is given as a reference (solid line). The pair-correlation functions are averaged over tem-peratures below 900 K. The distributions include the r^2 weight and normalization to one to allow direct comparison to other published data (see Table I).

published reference data. At higher temperatures, where D_T ≈ 0 K, the corresponding distributions and data become that of the free Ps atoms.

At 900 K, the thermal energy $k_BT = 0.0030E_H \approx 0.08$ eV only. Therefore, the obvious question arises: why the Ps$_2$ molecule with binding energy 0.44 eV is unstable above 900 K? Is there a temperature dependence hidden in the interac-tions? What does the potential energy curve of this diatomic molecule look like?

It is the van der Waals interaction or so called dispersion forces that are expected to contribute to the potential curve at larger atomic distances. These arise from the "dynamic dipole-dipole correlations," as usually quoted. Now, within our approach we have a transparent way to consider these interactions: the dipoles and their relative orientations. Thus, we monitor the dipole-dipole orientation correlation func-tion,

$$\left\langle \frac{\mathbf{p}_I \cdot \mathbf{p}_J}{p_I p_J} \right\rangle, \tag{1}$$

as a function of interatomic distance R, where $\mathbf{p}_I$ and $\mathbf{p}_J$ are the two $e^- e^+$ dipoles. This function assumes values from -1

TABLE I. Simulated and reference data [3,6,9,10,15] in atomic units. Our data are given as averages from temperatures T ≤ 900 K. Apart from the energy, the values are calculated using the averaged pair-correlation functions shown in Fig. 2. Electrons are labeled 1 and 2; positrons are 3 and 4. Because of symmetry $\langle r_{12} \rangle$ $= \langle r_{34} \rangle$ and $\langle r_{13} \rangle = \langle r_{23} \rangle = \langle r_{14} \rangle = \langle r_{24} \rangle$.

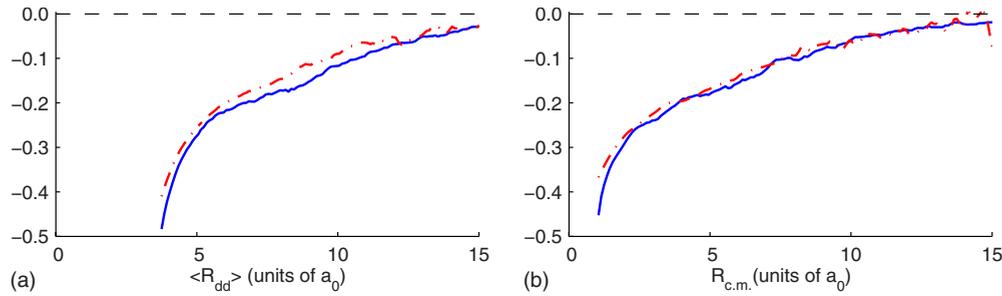|	$\langle E_{tot} \rangle$	$\langle r_{12} \rangle$	$\langle r_{13} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle r_{12}^2 \rangle$	$\langle r_{13}^2 \rangle$
Refs.	−0.5160	6.033	4.487	0.221	0.368	46.375	29.113
PIMC	−0.5154(5)	6.02	4.48	0.22	0.37	45.67	28.78

FIG. 3. (Color online) Dipole-dipole correlation functions [Eq. (1)]. The upper (dash dotted, red) and lower (solid, blue) curves correspond to 1000 K and 800 K, respectively. See the two definitions of the interatomic distances R_{dd} and $R_{c.m.}$ in text.

to 0, corresponding orientations from perfectly opposite to fully random.

The concept of interatomic distance needs to be defined for evaluation. We should note that at the "equilibrium distance" the centers-of-mass (c.m.) of all four particles are superimposed on the same location, as evaluated from their one-particle distributions (or wave functions). However, the particles do have well-defined (correlated) average distances (see Table I). Thus, the definition is not trivial.

We can define the center-of-mass interatomic distance $R_{c.m.}$ using the expectation value of the c.m. of one $e^- e^+$ pair and that of the other pair. An alternative (correlated) definition is the expectation value of the separation of the two $e^- e^+$ dipoles R_{dd}. At large distances, these two coincide; but at the opposite limit, in Ps_2 molecule, the former becomes zero whereas the latter remains at about $4\, a_0$.

Another problem is that in an equilibrium simulation we are not able to choose or fix the interatomic distance R ($R_{c.m.}$ or R_{dd}). Therefore, evaluation of R-dependent quantities presumes that sampling in the chosen temperature includes the relevant R with good enough statistics. This kind of data hunting turns out to be computationally challenging.

To overcome this, we have used a "close-to-equilibrium" technique by starting from 800 K distribution and rising the temperature to 1000 K, and then, applying the reverse change in temperature to obtain another estimate. In the former case, we are able to follow the increase in R from the molecular region to "dissociation," while the latter follows "recombination."

In Fig. 3 we show the estimates from these two temperatures to the correlation function with respect to the interatomic distances R_{dd} and $R_{c.m.}$. We emphasize that these are estimates, only, because at different temperatures the equilibrium sampling regions of R are very different. However, we see that the difference between these two estimates is very small and the equilibrium simulation correlation function between these two is easily conceived. Thus, we conclude that the dipole-dipole correlation is not temperature dependent.

Using the same close-to-equilibrium technique, we evaluate the van der Waals interaction energy next. This is shown in Fig. 4. There too, the true equilibrium curve can be estimated as the average of the two shown ones. Simple fit reveals that the large distance limit ($R_{dd} > 12 a_0$) shows the asymptotic $R^{-\alpha}$ behavior (α roughly 6) as expected.

Sampling all the energy contributions with the same close-to-equilibrium technique allows us to evaluate the total

energy or the diatomic potential energy curve as a function of interatomic distance $E_{tot}^{Ps_2}(R)$, where $R = R_{dd}$ or $R_{c.m.}$. It shows the same temperature-independent behavior, though the statistics is not good enough to allow showing the curve here. As expected, we find that the true dissociation energy is not temperature dependent, as is the apparent dissociation energy D_T shown in Fig. 1.

Now, the "thermal dissociation" can be explained by the strong temperature dependence of the Ps_2 free-energy. With the rising temperature, the free-energy of the two atoms decreases below that of the molecule, leading to transition from the molecular dominance to the atomic one. This is not a surprise, but the usual behavior of the conventional molecules. From our simulations, we find, however, the following surprising features: (i) the low temperature, where the transition takes place, (ii) sharpness of the transition, and (iii) almost negligible density dependence at the experimentally relevant densities.

The transition temperature is usually estimated by matching the thermal energy $k_B T$ with the dissociation energy. This is where the entropic contribution in free-energy $-TS$ becomes comparable with the dissociation energy. In the present case, this gives about 5000 K. Conventionally, the transition is smooth following from the equilibrium between molecular dissociation and formation, where the former depends on the temperature and, the latter, on the density, the density being the main factor in the entropy.

The Ps_2 molecule lacking in the heavy nuclei is peculiar. All of its constituents are strongly delocalized, barely fitting into the binding regime of the molecular potential curve. This is what they do below 900 K in experimentally relevant densities, but not above 1000 K. This is a consequence from
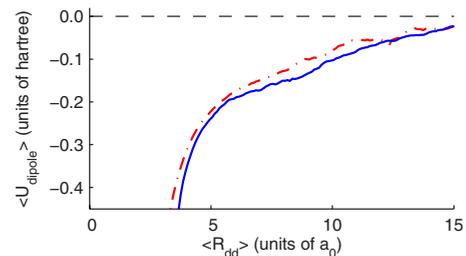

FIG. 4. (Color online) Dipole-dipole interaction energy with the same notations as in Fig. 3. The upper (dash dotted, red) and lower (solid, blue) curves correspond to 1000 K and 800 K, respectively.

the exceptionally large entropy factor originating from the strong quantum delocalization more than the density.

In summary, with path-integral Monte Carlo simulations of the dipositronium molecule Ps_2, we have found and explained its surprising thermal instability. Due to the strong temperature dependence of the free-energy of the considered four particle system, the molecular form is less stable than two positronium atoms above about 900 K, though the molecular dissociation energy is $\sim$0.4 eV. The transition in equilibrium from molecules to atoms is sharp in temperature

and only weakly density dependent. This can be understood by the large entropy factor originating from strong delocalization of all of the molecular constituents. Our prediction remains to be experimentally verified.

[1] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).

[2] D. B. Cassidy and A. P. Mills, Jr., Nature (London) **449**, 195 (2007).

[3] D. B. Kinghorn and R. D. Poshusta, Phys. Rev. A **47**, 3671 (1993).

[4] R. D. Poshusta and D. B. Kinghorn, Int. J. Quantum Chem. **60**, 213 (1996).

[5] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A **55**, 200 (1997).

[6] J. Usukura, K. Varga, and Y. Suzuki, Phys. Rev. A **58**, 1918 (1998).

[7] J. Usukura and Y. Suzuki, Phys. Rev. A **66**, 010502(R) (2002).

[8] D. M. Schrader, Phys. Rev. Lett. **92**, 043401 (2004).

[9] D. H. Bailey and A. M. Frolov, Phys. Rev. A **72**, 014501 (2005).

[10] S. Bubin and L. Adamowicz, Phys. Rev. A **74**, 052502 (2006).

[11] M. Emami-Razavi, Phys. Rev. A **77**, 042104 (2008).

[12] D. B. Cassidy and A. P. Mills, Jr., Phys. Rev. Lett. **100**, 013401 (2008).

[13] P. M. Kozlowski and L. Adamowicz, Phys. Rev. A **48**, 1903 (1993).

[14] C. A. Traynor, J. B. Anderson, and B. M. Boghosian, J. Chem. Phys. **94**, 3657 (1991).

[15] D. Bressanini, M. Mella, and G. Morosi, Chem. Phys. Lett. **272**, 370 (1997).

[16] I. Kylänpää, M. Leino, and T. T. Rantala, Phys. Rev. A **76**, 052508 (2007).

[17] A. K. Bhatia and R. J. Drachman, Phys. Rev. A **59**, 205 (1999).

[18] J. M. Taylor, A. Dalgarno, and J. F. Babb, Phys. Rev. A **60**, R2630 (1999).

[19] V. I. Korobov, Phys. Rev. A **63**, 044501 (2001).

[20] T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. **86**, 2984 (2001).

[21] Y. Ohta, J. Maki, H. Nagao, H. Kono, and Y. Fujimura, Int. J. Quantum Chem. **91**, 105 (2003).

[22] A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, Phys. Rev. Lett. **101**, 153001 (2008).

[23] T. Kreibich, R. van Leeuwen, and E. K. U. Gross, Phys. Rev. A **78**, 022501 (2008).

[24] X.-P. Li and J. Q. Broughton, J. Chem. Phys. **86**, 5094 (1987).

[25] D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).

[26] M. Pierce and E. Manousakis, Phys. Rev. B **59**, 3802 (1999).

[27] Y. Kwon and K. B. Whaley, Phys. Rev. Lett. **83**, 4108 (1999).

[28] L. Knoll and D. Marx, Eur. Phys. J. D **10**, 353 (2000).

[29] J. E. Cuervo and P.-N. Roy, J. Chem. Phys. **125**, 124314 (2006).

[30] R. P. Feynman, *Statistical Mechanics* (Perseus Books, Reading, Massachusetts, 1998).

[31] R. G. Storer, J. Math. Phys. **9**, 964 (1968).

[32] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[33] C. Chakravarty, M. C. Gordillo, and D. M. Ceperley, J. Chem. Phys. **109**, 2123 (1998).

[34] M. F. Herman, E. J. Bruskin, and B. J. Berne, J. Chem. Phys. **76**, 5150 (1982).