Thermal dissociation of dipositronium: path integral Monte Carlo approach

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Path integral Monte Carlo simulation of the dipositronium "molecule" \( \text{Ps}_2 \) reveals its surprising thermal instability. Although, the binding energy is \( \sim 0.4 \) eV, due to the strong temperature dependence of its free energy \( \text{Ps}_2 \) dissociates, or does not form, above \( \sim 1000 \) K, except for high densities where a small fraction of molecules are in equilibrium with \( \text{Ps} \) atoms. This prediction is consistent with the recently reported first observation of stable \( \text{Ps}_2 \) molecules by Cassidy & Mills Jr., Nature 449, 195 (07), and Phys.Rev.Lett. 100, 013401 (08); at temperatures below 1000 K. The relatively sharp transition from molecular to atomic equilibrium, that 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, \( \text{Ps}_2 \), 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, 4, 5, 6, 7, 8, 9] and references therein. In addition to the fundamental issues of physics, \( \text{Ps}_2 \) is of interest also in astrophysical applications and solid state physics [10, 11].

In laboratory conditions, \( \text{Ps}_2 \) 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 non-adiabatically [13]. This, however, can be realized with quantum Monte Carlo (QMC) methods [14, 15, 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, 17, 18, 19, 20, 21, 22, 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, 25, 26, 27, 28, 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 \( \text{Ps}_2 \) are established. The main focus here is to find the preferred configuration of the four-body system at each temperature — \( \text{Ps}_2 \) molecule or two \( \text{Ps} \) atoms.

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

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

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 evaluation of the Coulomb interactions [23, 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 time-step \( \tau \) [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 (SEM) with two-sigma limits is used to indicate the statistical uncertainty, where relevant. The average of the chosen time-step is \( \langle \tau \rangle \approx 0.0146 E_{\text{H}}^{-1} \), where \( E_{\text{H}} \) denotes the atomic unit of energy, Hartree \( (\approx 27.2 \text{ eV}) \). The other atomic unit we use here is Bohr radius for the length, \( a_0 \) \( (\approx 0.529 \text{ Å}) \).

The total energy of positronium "atom" \( \text{Ps} \) is \( -0.25 \) at 0 K and the binding energy of the molecule \( \text{Ps}_2 \) is 0.0160 \( (\approx 0.435 \text{ eV}) \) [3]. We find these values as zero Kelvin extrapolates from our simulations at low temper-
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 wavefunctions and the zero Kelvin data we obtain as extrapolates, only.

In Fig. 2, we present the "apparent dissociation energy" of Ps2 at several different temperatures. In each temperature this is the negative total energy of the molecule with respect to two atoms as $D_T = -\langle E_{\text{tot}}^{\text{Ps}_2} \rangle_T - 2\langle E_{\text{tot}}^{\text{Ps}} \rangle_T$. At $T \leq 900$ K we find for the average over shown temperatures $D_T = 0.0154(5)$, which is very close to the dissociation energy at zero Kelvin, $D_0$. However, at higher temperatures the apparent dissociation energy vanishes, because $\langle E_{\text{tot}}^{\text{Ps}_2} \rangle_T$ and $2\langle E_{\text{tot}}^{\text{Ps}} \rangle_T$ become the same. This is because of molecular dissociation, or to be more exact, the two atoms do not bind in our equilibrium state simulation at $T \geq 900$ K and the predominant configuration is that of two separate positronium atoms.

Simulations in a well-defined Ps density are time consuming, and therefore, these kind of studies have been carried out at the transition region around 1000 K, only. Using the periodic boundary conditions and the cubic supercells of sizes from $(300a_0)^3$ to $(50a_0)^3$ with two Ps atoms we have simulated three densities from 0.5 to $100 \times 10^{24}$ m$^{-1}$, respectively. 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 eventually smoothen the transition away.

In the recent experiment, cited above \cite{2,12}, formation of Ps2 molecules was observed below 900 K in about two orders of magnitude lower densities than our lowest, above (Fig. 2). Formation was not observed at higher temperatures, however, because the Ps atoms desorbed from the confining porous silica surface with the activation energy $k_BT \sim 0.074$ eV ($\sim 850$ K). Thus, our prediction of thermal dissociation of Ps2 above 900 K in the experimentally achievable densities remains to be verified in forthcoming experiments in higher temperatures.

Next, we compare our finite-temperature Ps2 data to the published zero Klevin results, discuss the details of Ps–Ps interaction, and finally, conclude with the explanation of the higher temperature instability.

The conventional zero Kelvin like Ps2 state of the system below 900 K is confirmed 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 \cite{6} and the expectation values of various powers of these distributions match with other published reference data. At higher temperatures, where $D_T \approx 0$ 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 Ps2 molecule with binding energy 0.44 eV is unstable above 900 K? Is there a temperature dependence hidden in the interactions? What does the potential energy curve of this diatomic molecule look like?

It is the van der Waals interaction or sc. 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 function

$$\langle p_I \cdot p_J \rangle$$

as a function of interatomic distance $R$, where $p_I$ and $p_J$ are the two $e^-e^+$ dipoles. This function assumes values from $-1$ 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 (CM) of all four particles are superimposed on the same location, as evaluated from their one particle distributions (or wavefunctions). 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 $R_{\text{CM}}$ using the expectation value of the CM of one $e^-e^+$
Figure 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) radial distribution of the free positronium atom is given as a reference (solid line). The pair correlation functions are averaged over temperatures 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.

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 $R$ ($R_{CM}$ 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 wrt. the interatomic distances $R_{dd}$ and $R_{CM}$. 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.

Table I: Simulated and reference data [3, 6, 9, 10, 15] in atomic units. Our data is given as averages from temperatures $T \leq 900$ 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 $\langle r_{13} \rangle = \langle r_{24} \rangle = \langle r_{14} \rangle = \langle r_{23} \rangle$.

| $(E_{tot})$ | $\langle r_{12} \rangle$ | $\langle r_{13} \rangle$ | $\langle r_{12}^{-1} \rangle$ | $\langle r_{13}^{-1} \rangle$ | $\langle r_{12}^2 \rangle$ | $\langle r_{13}^2 \rangle$ |
|------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 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                |

Figure 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 $R_{CM}$ in text.

Figure 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.
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 \( R_{\text{td}} > 12 \alpha_0 \) shows the asymptotic \( R^{-\alpha} \) behavior (\( \alpha \) 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 \( E_{\text{tot}}^{\text{PS}^2} (R) \), where \( R = R_{\text{td}} \) or \( R_{\CM} \). 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 \( \text{Ps}_2 \) 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 (ii) 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 \( -T S \) 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 \( \text{Ps}_2 \) 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 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" \( \text{Ps}_2 \) 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 \( \sim 0.4 \text{ eV} \). The transition in equilibrium from molecules to atoms is sharp in temperature and only weekly 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.

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