Quantum partition functions of composite particles in a hydrogen-helium plasma via path integral Monte Carlo

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We compute two- and three-body cluster functions that describe contributions of composite entities, like hydrogen atoms, ions H+, H2+, and helium atoms, and also charge-charge and atom-charge interactions, to the equation of state of a hydrogen-helium mixture at low density. A cluster function has the structure of a truncated virial coefficient and behaves, at low temperatures, like a usual partition function for the composite entity. Our path integral Monte Carlo calculations use importance sampling to sample efficiently the cluster partition functions even at low temperatures where bound state contributions dominate. We also employ a new and efficient adaptive discretization scheme that allows one not only to eliminate Coulomb divergencies in discretized path integrals, but also to direct the computational effort where particles are close and thus strongly interacting. The numerical results for the two-body function agree with the analytically known quantum second virial coefficient. The three-body cluster functions are compared at low temperatures with familiar partition functions for composite entities. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4900984]

I. INTRODUCTION

Internal partition functions for composite particles in a plasma, like atoms, molecules, or ions with inner degrees of freedom, determine reaction constants at equilibrium and are important ingredients in equation of state (EOS) calculations. Within the chemical picture, such functions are introduced on phenomenological grounds where the long-range Coulomb divergencies are removed via ad hoc regularizations, for example, in the Brillouin-Planck-Larkin partition function for the hydrogen atom.1,2,3 In this paper, we consider a hydrogen-helium mixture described in the physical picture as a Coulomb gas of point electrons, protons, and α particles, and we focus on the contributions to the EOS of composite entities, made with three elementary particles, namely, ions H+, H2+, and helium atoms.

The contributions of three particle effects are described at low densities by the third virial coefficient. Virial coefficients would naïvely be divergent in a system with long-range Coulomb forces, but are in fact convergent thanks to the screening provided by ionized charges.4–7 This screening erases in particular the contributions of infinitely extended Rydberg states. A proper estimation of internal partition functions for composite entities requires thus to deal simultaneously with recombination and screening effects. The Screened Cluster Representation (SCR),8 presented synthetically in Refs. 9 and 10, achieves precisely such a description within the physical picture. It establishes that the usual virial coefficients are replaced, in a system with long-range forces, by truncated virial coefficients, the so-called cluster functions, and further contributions associated with screened Coulomb interactions between these clusters of particles.

The cluster functions converge even in the vacuum, where particles interact via the bare Coulomb potential.8 The large-distance integrability is ensured by regularizing truncation terms whose origin can be traced back to screening. The cluster functions are entirely determined by the spectral properties of the associated few-body Coulomb Hamiltonians and depend, in the vacuum, solely on the inverse temperature β and on fundamental constants. They contain contributions from both bound and diffusive states. At low temperatures, a cluster function tends to the internal partition function of the entity described by the cluster, i.e., to the sum of Boltzmann weights e−βEj of all energy levels Ej of the composite entity identified by those bound states. The ground state, with energy E0 = min(Ej) < 0, provides, in the low temperature limit β → ∞, the most important contribution as it grows exponentially fast as exp(−βE0).

The Screened Cluster Representation has been used to study van der Waals interactions in the presence of free charges11 and to compute the first corrections to the Saha EOS for a partially ionized hydrogen plasma, in a low-density and low-temperature limit appropriate to describe the Saha regime.12 Those corrections involve the cluster functions in the vacuum for two-, three-, and four-body clusters, as well as further functions describing in particular atom-charge interactions. They have been computed numerically, in some approximations, in Ref. 13. Beyond the two-body function, the cluster functions are currently known only at very low temperatures. An accurate calculation of those functions at higher temperatures, where many states in the cluster are excited or it is even dissociated, is highly desirable to improve our knowledge of the thermodynamical properties of the hydrogen gas and of the hydrogen-helium mixture.13
The goal of the present paper is to calculate, from first principles, the three-body cluster functions, i.e., truncated quantum virial coefficients, appearing in the EOS of the hydrogen-helium mixture. We also compute the contributions to the EOS from atom-charge interactions. We employ Path Integral Monte Carlo (PIMC) methods, without introducing any other approximation than the use of discretized paths. The calculations are thus exact, apart from the statistical uncertainties/errors inherent to the Monte Carlo (MC) approach and from the finite discretization. PIMC methods have been applied previously to compute internal partition functions of model systems and of small to medium-size molecules. Our calculations differ from those works for several reasons. First, a cluster function is not a plain partition function, to which it reduces only at low temperatures. This prevents us from applying numerical methods specifically designed to compute free-energy differences. Second, those works aimed to calculate molecular partition functions and introduced therefore ad hoc cutoffs to restrict the path integral (PI) calculation to molecular states only, excluding diffusive states. No such cutoff appears in our calculations, which need to capture not only molecular contributions but also large-distance ionized contributions. Third, previous works used the Born-Oppenheimer approximation and an effective potential between the nuclei determined from density-functional theory, similar to Refs. 23 and 24 on calculations of the third virial coefficient in an atomic helium gas. Here, the electronic problem is neither solved separately, namely, no Born-Oppenheimer approximation is made, nor do we assume that the temperature is sufficiently low for the electrons to be in the ground state. Rather, we compute the partition function, or more generally the truncated virial coefficient, of the full three-body Coulomb system by sampling directly, at finite temperature, over both nuclei and electron paths interacting via the Coulomb potential. This increases significantly the computational cost, but the results are then approximation-free and also valid at high temperatures where electrons can be highly excited or even ionized, i.e., in states not described by a ground state potential energy surface.

An algorithm to compute few-body cluster functions must overcome several difficulties. The quantity of interest is not an expectation value over some probability distribution, since the cluster function has the structure of a virial coefficient, which is not necessarily positive. Thus, the standard Metropolis-Hastings Monte Carlo algorithm cannot be applied directly as in usual PIMC simulations. We employ a partially adaptive importance sampling approach, and well-chosen coordinates, to sample efficiently the high-dimensional configuration space of three mutually interacting paths. At the considered temperatures, electrons behave quantum mechanically and interact strongly with the surrounding particles, so that bound states can be formed. The aforementioned works used free-particle sampling since only the almost classical nuclear paths intervene, once the Born-Oppenheimer approximation has been used and the electronic problem is solved separately. For temperatures below the dissociation energy, free-particle sampling cannot capture properly bound state electronic paths. In our proposed algorithm, the sampling of electron paths is governed by a simple importance sampling function that mimics the exact two-body density matrix. This approach allows us to sample efficiently the truncated virial coefficient, and other functions if wished, even at quite low temperatures where contributions from bound states dominate.

The divergence of the Coulomb potential at the origin requires special care in discretized path integrals. Notice that this difficulty is not present if the Born-Oppenheimer approximation is used since the effective potential between nuclei is regular at the origin. The common solution to this problem consists in using an effective two-body potential. This potential can be derived from the analytically known two-body Coulomb density matrix or one can use high-temperature approximations. Paths need to be highly discretized in order to capture the correlations, beyond the two-body ones, between the various interacting particles. In PIMC simulations, paths are usually discretized uniformly up to a maximum level. The chosen discretization might be too low for strongly interacting close-by particles, while being too high for far-away particles. We avoid this by introducing an adaptive discretization scheme in which portions of paths that are strongly interacting are more discretized than portions where the interaction is weak, thereby concentrating the numerical effort in the region where it is most needed.

II. FEW-BODY CLUSTER FUNCTIONS

A. The hydrogen-helium mixture within the SCR

In the physical picture, the hydrogen-helium mixture is described as a quantum Coulomb system of point protons (p),
electrons (e), and α particles governed by the Coulomb Hamiltonian
\[ H_{N_p,N_e,N_\alpha} = - \sum_{i=1}^{N} \frac{\hbar^2}{2m_{\gamma_i}} \Delta_{\gamma_i} + \frac{1}{2} \sum_{i \neq j} e_{\gamma_i} e_{\gamma_j} |r_i - r_j|, \]  
(1)

Here, \( N = N_p + N_e + N_\alpha \) denotes the total number of particles and \( \gamma \), the species (e, p, or \( \alpha \)) of the \( i \)th particle with mass \( m_{\gamma_i} \), charge \( e_{\gamma_i} \), and spin \( \sigma_{\gamma_i} \). The particles are enclosed in a box with volume \( V \), in contact with a thermostat at temperature \( T \) and a reservoir of particles that fixes the chemical potentials \( \{ \mu_{\gamma_i} \} \), or equivalently the fugacities \( z_{\gamma_i} = \exp(\mu_{\gamma_i}/T) \).

For a short-ranged interaction, the second virial coefficient in the expansion of the pressure in terms of the fugacities would involve traces of the form\(^{12}\)
\[ \frac{1}{\Lambda} \text{Tr}[e^{-\beta H_{\gamma,N_{\gamma},N_e}}]_{\text{Mayer}}, \]  
(2)

over properly anti-symmetrized states, in, for instance, position and spin space, of Mayer virial operators \( [e^{-\beta H_{\gamma,N_{\gamma},N_e}}]_{\text{Mayer}} \). Examples of two-body Mayer operators are
\[ [e^{-\beta H_{\gamma,N}}]_{\text{Mayer}} = e^{-\beta H_{\gamma,N}} - e^{-\beta H_{\gamma}} e^{-\beta H_{N}}, \]  
(3)
\[ [e^{-\beta H_{\gamma}}]_{\text{Mayer}} = e^{-\beta H_{\gamma}} - \frac{1}{2} e^{-\beta H_{\gamma_1}} e^{-\beta H_{\gamma_2}}, \]  
(4)

with an obvious short-hand notation for Hamiltonians \( H_{N_p,N_e,N_\alpha} \). Analogous expressions hold for Mayer operators associated to other two-body clusters like \( (\alpha, e) \) or \( (2e) = (e_1, e_2) \). Similarly, the Mayer operator for the three-body cluster \( (2p,e) \) reads
\[ [e^{-\beta H_{\gamma,N}}]_{\text{Mayer}} = e^{-\beta H_{\gamma,N}} - e^{-\beta H_{\gamma}} e^{-\beta H_{N}} - \frac{1}{2} e^{-\beta H_{\gamma_1}} e^{-\beta H_{\gamma_2}} e^{-\beta H_{N}} - \frac{1}{2} e^{-\beta H_{\gamma_1}} e^{-\beta H_{\gamma_2}} + e^{-\beta H_{\gamma_3}}, \]  
(5)

where \( H_{\gamma_p} = H_{\gamma_p}^{(0)} = H_{p} + H_{e} + H_{\alpha} \) is the free Hamiltonian. In a system with long-range forces, the trace (2) is divergent. These divergences are suppressed by screening effects.

Three different techniques can be used to account for screening effects in a quantum plasma: the effective-potential formalism,\(^{12,23}\) and Abe-Meeron chain resummations in many-body perturbation theory within the thermodynamic Green function formalism,\(^1\) and Abe-Meeron chain resummations in the path integral representation of the system, known as the loop or polymer formalism.\(^{29}\) These formalisms, though quite different, lead to the same formula for the virial EOS, as it should.\(^4,7,30\) The SCR, derived in the polymer formalism, is a suitable technique able to deal simultaneously, and exactly, with recombination and screening effects at arbitrary orders in the fugacity series. This approach is efficient for handling recombination effects since it is not perturbative with respect to the interaction, contrary to the Green function formalism.

The SCR provides explicit formulas for all terms contributing at given order in the fugacity series for any thermodynamic quantity. The expressions of the SCR are represented by Mayer-like diagrams built with clusters of particles interacting via an effective screened interaction \( \phi \) resulting from chain resummations. All long-range Coulomb divergences are removed via the introduction of \( \phi \), which is the quantum analog of the Debye potential.\(^{31}\) A cluster \( C \) is a group of strongly interacting particles that may form bound states. In the zero-density limit, the contribution of a cluster in the SCR is given by a truncated virial coefficient, known as a cluster function \( Z_C(\beta) \). These functions can be interpreted, at temperatures below the dissociation temperature of the cluster, as an internal partition function of the cluster. They are finite thanks to truncation terms, inherited from screening effects, that ensure large-distance integrability. The truncation terms do not introduce any arbitrariness because the associated counter-terms are also included in the SCR: only the full contribution of \( Z_C(\beta) \) plus that of the corresponding counter-terms has an unambiguous sense. The counter-terms appear as diagrams describing screened interactions between all possible dissociation products of \( C \).

The SCR has been used to derive the first corrections to the ideal Saha EOS in a partially ionized hydrogen gas in a low-density and low-temperature limit appropriate to describe the Saha regime.\(^{12,13}\) In this limit, known as Scaled Low Temperature (SLT) limit, those corrections to the Saha equation can be ordered, providing the SLT equation of state.\(^{12,13}\) The terms in the SLT EOS involve the cluster functions in the vacuum for two-, three-, and four-body clusters, as well as further functions describing charge-charge, charge-atom, and atom-atom interactions (see Sec. II D in Ref. 13). We recall that only the sum of the three-body cluster functions and of the associated screened interactions between dissociated products has an intrinsic meaning, free of any arbitrariness. It is precisely this sum that appears in the SLT EOS.

The contribution of a cluster \( C(N_p,N_e,N_\alpha) \) can be written as a trace over a truncated Mayer operator
\[ Z_C(\beta) = \frac{(2\pi \lambda_{N_p,N_e,N_\alpha})^{3/2}}{\Lambda} \frac{1}{\text{Tr}[e^{-\beta H_{\gamma,N_{\gamma},N_e}}]_{\text{Mayer}}} \]  
(6)

The operators \( [\exp(-\beta H_{\gamma,N_{\gamma},N_e})]_{\text{Mayer}} \) are similar to plain Mayer operators, for instance, Eqs. (3)–(5), but involve further truncation terms (see formulas in Subsections II B–II C) that ensure large-distance integrability. The factor \( (2\pi \lambda_{N_p,N_e,N_\alpha})^{3/2} \), where \( \lambda_{N_p,N_e,N_\alpha} = (\hbar^2 \beta / (N_p m_p + N_e m_e + N_\alpha m_\alpha))^{1/2} \) is the de Broglie thermal wavelength associated with the center-of-mass motion of the cluster, is included in definition (6) so that \( Z_C(\beta) \) is dimensionless and linked to a sum over internal states only.

In the following, we study clusters build by two particles, namely, \( (p,e) \) and \( (\alpha,e) \), describing the formation of atoms \( H \) and ions \( He^+ \), as well as charge-charge interactions. Furthermore, we consider the three-body clusters \( (2p,e) \), \( (2p,e) \), and \( (\alpha,2e) \), which account for the formation of ions \( H^+ \), \( H^+_2 \) and atoms \( He \) and for interactions between their dissociation products.
B. Two-particle clusters

The proton-electron cluster function $Z_{p,e}(\beta)$, which describes free hydrogen atoms and ionized p-e interactions, is defined by

$$Z_{p,e}(\beta) = \frac{(2\pi \lambda^2_{H})^{3/2}}{\Lambda} \text{Tr}[e^{-\beta H_{p,e}}]_{Mayer}^{T},$$

where the truncation terms are generated according to the rules of the Screened Cluster Representation.\(^8\) The trace (10) can be split into a direct and an exchange term

$$Z_{2p,e}(\beta) = \frac{(2\pi \lambda^2_{H})^{3/2}}{\Lambda} \int dr_p \int dr_e [4D^T(0, r_p, r_e) - 2E^T(0, r_p, r_e)],$$

where we identify

$$D^T(r_1, r_2, r_3) = \langle r_1, r_2, r_3 | D^T | r_1, r_2, r_3 \rangle,$$

$$E^T(r_1, r_2, r_3) = \langle r_2, r_1, r_3 | E^T | r_1, r_2, r_3 \rangle.$$

The trace of the pure Mayer operator (5) (without long-range truncation terms), taken over globally anti-symmetrized states in position-spin space, leads to the identifications

$$D = e^{-\beta H_{p,e}} - e^{-\beta (H_{p,e} + H_{f})} - e^{-\beta (H_{p,e} + H_{f})}_{0} - e^{-\beta (H_{p,e} + H_{f})}_{1},$$

$$E = e^{-\beta H_{p,e}} - e^{-\beta (H_{p,e} + H_{f})},$$

The truncation manifests itself by the subtraction of further terms (see Eq. (4.10) in the SCR\(^8\)). The full expression of the truncated direct term $D^T$ is given in Appendix A. For the exchange contribution, we have

$$E^T = e^{-\beta H_{p,e}} - e^{-\beta H_{p,e}} \left(1 - \int dr_r V^1_{2p-e}(r_1) + \frac{1}{2!} \int dr_r dr_r T[V^1_{2p-e}(r_1) V^1_{2p-e}(r_2)] - \frac{1}{3!} \int dr_r dr_r dr_r T[V^1_{2p-e}(r_1) V^1_{2p-e}(r_2) V^1_{2p-e}(r_3)] \right),$$

where $H_{p,e} = H_{p} + H_{e}$ (the electron does not interact with the 2 protons), $V_{2p-e} = V_{p,e} + V_{p,e}$ and $V^1_{2p-e}(\tau) = \exp(\tau H_{2p,e}) V_{2p-e} \exp(-\tau H_{2p,e}).$

2. Clusters (p,2e) and (\(\alpha,2e\))

The cluster functions $Z_{p,2e}(\beta)$ and $Z_{\alpha,2e}(\beta)$ are defined in the same way as $Z_{2p,e}(\beta)$ [Eq. (10)] with obvious substitutions for particle species, taking into account the zero spin of the p\-particle.

D. Path integral formula for cluster functions

In the genuine Screened Cluster Representation, the statistical weights and bonds are expressed in terms of functional integrals over the paths associated with the particles forming the clusters. The expressions for $Z_{\alpha}(\beta)$ as traces (6) over truncated Mayer operators are obtained by applying backwards the Feynman-Kač formula.\(^32\) The original expressions in terms of path integrals are written explicitly in the following for two- and three-particle clusters.

1. Proton-electron cluster function

The matrix element (8) that appears in (7) is obtained from the path integral expression

$$D^T(r_p, r_e) = \frac{1}{(2\pi \lambda^2_{p})^{3/2}(2\pi \lambda^2_{e})^{3/2}} \int D(\xi_{1}) D(\xi_{2}) \left[ \left( e^{-\beta V(\xi_{1}, \xi_{2})} - 1 + \beta V - \frac{(\beta V)^2}{2} + \frac{(\beta V)^3}{3!} \right) \right]^{0}_{(\xi_{1}, \xi_{2})},$$

where $\int D(\xi)$ denotes path integration over a Brownian bridge $\xi(s), s \in [0, 1], (\xi(0), \xi(1)) = 0$ with normalized
Gaussian measure $D(\xi)$. Here, $\mathcal{L}_p (\mathcal{L}_e)$ is a loop made up of a single proton (electron), characterized by its position $r_p (r_e)$ and by its shape $\xi_p (s)$ ($\xi_e (s)$). The attractive Coulomb interaction between these two one-particle loops is given by

$$V(\mathcal{L}_p, \mathcal{L}_e) = -e^2 \int_0^1 ds \frac{1}{|r_e + \lambda_e \xi_e (s) - r_p - \lambda_p \xi_p (s)|}. \quad (18)$$

### 2. Three-particle cluster function

The genuine path integral expression of the direct function $D_T (r_1, r_2, r_3)$ [Eq. (12)] is

$$D_T (r_1, r_2, r_3) = \frac{1}{(2\pi \lambda^2)^3/2} \int D(\xi_1)D(\xi_2)D(\xi_3) B_T^0 (\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3), \quad (19)$$

where $B_T^0 (\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3)$ is identical to expression (A1) of $D_T$ in Appendix A in which one sets

$$a = -\beta V(\mathcal{L}_1, \mathcal{L}_2), \quad b = -\beta V(\mathcal{L}_1, \mathcal{L}_3), \quad \text{and} \quad c = -\beta V(\mathcal{L}_2, \mathcal{L}_3). \quad (20)$$

The function $D_T (r_1, r_2, r_3)$ takes a quite simple form in the path integral language (it involves some combination of loop-loop interactions as expressed by Eqs. (20) and (A1)), in contrast to the operatorial language in which each truncation term involves more cumbersome time ordered Coulomb interactions, for example, in Eq. (A3). The exchange term [Eqs. (13) and (16)] of the three-particle cluster function is given by

$$E_T (r_1, r_2; r_3) = \frac{1}{(2\pi \lambda^2)^3/2} \int D(\xi_1)D(\xi_2)D(\xi_3) \times e^{-i(\xi_1 - \xi_2 - \xi_3)} \mathcal{B}_T (\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3). \quad (21)$$

Here, $\mathcal{L}_{12}$ is a 2-particle closed loop made with the two open paths $[r_{12}(s) = (1-s)r_1 + sr_2 + \lambda_1 \xi_1 (s)$ and $r_{21}(s) = (1-s)r_2 + sr_1 + \lambda_2 \xi_2 (s)]$ of the exchanged particles 1 and 2. The interactions between the particles along their paths which appear in (21) are $V_{\text{self}} (\mathcal{L}_{12}) = \int_0^1 ds e^{-i[r_{12}(s) - r_{21}(s)]^{-1}}$ and

$$V(\mathcal{L}_{12}, \mathcal{L}_3) = \int_0^1 ds \left[ \frac{e_a e_a}{|r_{12}(s) - r_3(s)|} + \frac{e_a e_a}{|r_{21}(s) - r_3(s)|} \right], \quad (22)$$

with $r_3 (s) = r_3 + \lambda_3 \xi_3 (s)$.

### III. ALGORITHM

#### A. Position of the problem

A numerical method for computing few-particle cluster functions must overcome several difficulties. We underline that both short and long distance effects of the Coulomb potential must be treated simultaneously when computing $Z_C (\beta)$. A first difficulty arises because the cluster functions do not have the standard form of an expectation value, as required for using the Metropolis-Hastings algorithm. Instead, $Z_C (\beta)$ takes the form of an integral over the whole phase space, like a partition function, whose calculation is significantly more challenging. The cluster functions are moreover virtual partition functions that differ from plain partition functions, the integrand being not a pure exponential, but a truncated exponential. The subtracted terms, arising either from the Mayer truncation or from the long-range truncation inherited from screening effects, can cause $Z_C (\beta)$ to become negative. Standard methods for computing partition functions, such as free energy perturbation, Bennett’s Monte Carlo or thermodynamic integration are not applicable to such virial partition functions. The free-energy perturbation method can be used to sample Mayer integrals in classical systems, but its generalization to a quantum system poses the problem of the choice of the reference system for which the exact cluster function needs to be known and to be similar to that of the system of interest. A thermodynamic integration approach is possible in the two-particle case, where one can compute $Z_{\text{free}} (\beta)$ by sampling efficiently the bond $B_T^0 (\mathcal{L}_p, \mathcal{L}_e)$ at any temperature via a Markov chain random walk, but such an approach does not generalize conveniently to three-particle clusters because the truncated Mayer function $B_T^0 (\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3)$ is not always positive and therefore cannot be used as equilibrium probability distribution of a Markov chain. Without the benefit of importance sampling brought by Markov chain Monte Carlo, one must develop a numerical method that is able to sample sufficiently well the integrand, in particular at low temperatures where small regions in configuration space can lead to exponentially large contributions arising from the exponentials in Eqs. (17), (19), and (21). Those large contributions at low temperatures occur due to the formation of bound states, and capturing them correctly in a numerical path integral calculation is not trivial.

#### B. Adaptive discretization and effective action of paths

Paths integrals are usually discretized uniformly in the imaginary time interval $[0, \beta]$ by using the convolution property of the density matrix at times $\beta_k = k \tau$ with $k = 1, \ldots, M$ and $\tau = \beta/M$. For a single particle of mass $m$ in a potential $V(r)$, the density matrix $\rho(r, r; \beta) = \langle r | \exp(-\beta (H_0 + V)) | r \rangle$ is rewritten, for instance, as an integration over products of density matrices at a higher temperature $\tau$,

$$\rho(r, r; \beta) = \int dr_1 \cdots dr_{M-1} \rho(r, r_1; \tau) \cdots \rho(r_k, r_{k+1}; \tau) \cdots \rho(r_{M-1}, r; \tau). \quad (23)$$

The Feynman-Kač formula provides the PI representation

$$\rho(r_1, r_2; \tau) = \rho_{\text{free}} (r_1, r_2; \tau) \int D(\xi) e^{-\int_0^\tau d\tau^' V(r_{12}(\xi_{12}(\tau^')))}, \quad (24)$$

where $\rho_{\text{free}} (r_1, r_2; \tau) = (2\pi \lambda^2)^{-3/2} \exp(-i(r_1 - r_2)^2/2\lambda^2)$ is the free particle density matrix. $r_{12}(s) = (1-s)r_1 + sr_2$ is the straight-line path, and $\lambda^2 = \hbar^2 \tau / m$. Expressing the average of the exponential in (24) with the cumulant expansion, the high-temperature behavior of the density matrix is seen...
to be
\[
\rho(r_1, r_2; \tau) \approx \rho_{\text{free}}(r_1, r_2; \tau) \exp \left[ -\tau V_{\text{eff}}(r_1, r_2; \tau) + O(\tau^3) \right],
\]
where the effective potential
\[
V_{\text{eff}}(r_1, r_2; \tau) = \int D(\xi) \int_0^1 ds \ V(r_{1,2}(s) + \lambda \xi(s))
\]
corresponds to the average of the genuine potential over free paths connecting \(r_1\) to \(r_2\). For the Coulomb interaction, the cumulant effective potential reads\(^\dagger\)
\[
V_{\text{eff}}(r_1, r_2; \tau) = \int_0^1 ds \ e_{\gamma \gamma'} e_{rr'} |r_{1,2}(s)| / \sqrt{2 \lambda s (1-s)},
\]
Combining (23) and (25) yields the well known discretized path integral
\[
\rho(r, r'; \beta) \approx (2\pi L)^{-2} \int dr_1 \ldots dr_{M-1} \times \exp \left[ -\sum_{k=0}^{M-1} (r_{k} - r_{k+1})^2 / 2\lambda^2 - \tau \sum_{k=0}^{M-1} V_{\text{eff}}(r_k, r_{k+1}; \tau) \right].
\]
If the Trotter decomposition
\[
e^{-\beta(H_0 + V)} = \lim_{M \to \infty} (e^{-\beta H_0} e^{-\beta V})^M
\]
had been used to discretize the PI, Eq. (28) would have been obtained but with the smoothed potential \(V_{\text{eff}}\) replaced by the genuine Coulomb potential. It would then be divergent since the exponentiated Coulomb singularity is not integrable. By contrast, \(V_{\text{eff}}\) remains bounded everywhere and Eq. (28) converges towards the continuous result as \(1/M^2\).\(^\dagger\) Other bounded effective potentials have been proposed for performing path integral simulations of coulombic systems, such as partially averaged potentials\(^\dagger\) and also the exact effective pair potential \(V_{\text{eff}}^{\text{pair}}\). The latter potential is inferred from the exact two-body density matrix via
\[
\rho(r_1, r_2; \tau) = \rho_{\text{free}}(r_1, r_2; \tau) e^{-\tau V_{\text{eff}}^{\text{pair}}(r_1, r_2; \tau)}. \tag{29}
\]
When discretizing the PI for the density matrix of a many-particle system using \(V_{\text{eff}}^{\text{pair}}\), errors still scale as \(1/M^2\), due to the correlations between the paths beyond the two-body ones.\(^\dagger\) To capture those correlations, a large number \(M\) of time slices needs to be used, the exact potential reducing then to the cumulant potential.

In this paper, we introduce a new way of discretizing Coulombic path integrals that does not require the effective potential to remain bounded thanks to an adaptive non-uniform discretization of paths. Note that the \(M\) time intervals in Eq. (23) need not all have the same length \(\tau\). In the limit \(M \to \infty\), where Eq. (28) becomes exact, the thermal wavelength \(\lambda_\tau\) tends to 0 and the cumulant potential (26) reduces to the semi-classical straight-line potential
\[
V_{\text{line}}(r_1, r_2) = \int_0^1 ds \ V(r_{1,2}(s)) = e_{\gamma \gamma'} \arctanh \left( |r_1 - r_2| / |r_1 + r_2| \right),
\]
which is integrable but unbounded. The unphysical exponentiated \(1/r\) singularity can be avoided by discretizing the paths, via recursive bisectations, until
\[
-r_{k+1}\ V_{\text{line}}(r_k, r_{k+1}) \leq \epsilon
\]
for all path segments where one fixes in practice a threshold value \(\epsilon \ll 1\). Here, \(r_k = \beta L^{k+1}\) is the length of the time interval associated to the path segment \(k\) (\(L\) is the discretization level). Notice that the stopping criterion (31) relies on \(V_{\text{line}}\) rather than on the cumulant potential to ensure that the discretization of the paths is not stopped prematurely. The absolute value \(|V_{\text{line}}|\) is indeed an upper bound for \(|V_{\text{eff}}|\). If one uses the primitive action
\[
-r_{k+1}(V(r_k) + V(r_{k+1})) / 2
\]
the cumulant potential in the criterion, the algorithm could stop refining paths early even though the particle passes right next to the Coulomb singularity (see Fig. 1). Portions of paths that approach the singularity are thus discretized to a degree that is inversely proportional to the closest distance of approach to the singularity. The Coulomb divergence, which does not exist in the continuous path integral, is effectively eradicated via this adaptive discretization, even in the case where the genuine Coulomb potential is used in Eq. (28). Most importantly, the computational effort is directed, as it should, in regions where the potential is strong. The adaptive discretization avoids furthermore the systematic error associated to a uniform discretization. This adaptive scheme is simple to implement, provides accurate results (see Sec. IV A) and agrees with the physical discussion of how a collapse of paths on the Coulombic singularity is prevented by the entropy associated with highly discretized paths.\(^\dagger\)

When the paths are discretized adaptively, a good accuracy is obtained by computing the path actions with the simple effective potential \(V_{\text{line}}\), i.e., the high-temperature limit of the cumulant potential. The choice of this action allows one not only to reuse the value of \(V_{\text{line}}\) already computed when checking the stopping criterion (31), but, more importantly, it provides results with the same accuracy as with the full cumulant potential. To understand this surprising result, which is a

---

Fig. 1. A path segment \((r_0, r_i)\) of an electron (blue circle) near a proton (red circle). The use of the cumulant potential instead of \(V_{\text{line}}\) in the stopping criterion would lead to such a path segment not being further refined, because of the smoothing embedded in the cumulant potential, even though the potential is large in-between the path segment’s end points.
discretization level \( (\lambda_s \to 0) \). When evaluating the action \(-\tau V_{\text{line}}\) instead of \(-\tau V_{\text{eff}}\), one neglects terms of order \( O(1/M^2) \) since \( \lambda_s^2 = O(1/M) \) assuming a uniform discretization. Since this error is made \( M \) times, once in each slice, the resulting global error is \( O(1/M) \) when paths actions are computed with \( V_{\text{line}} \). However, this argument no longer holds in the case of the Coulomb potential because the coefficient in the \( O(\lambda_s^2) \) term vanishes everywhere, except at the origin, since it involves the Laplacian of the potential. The errors decay therefore faster than \( 1/M \). When the paths are discretized adaptively, the argument of the error function in the Coulombic cumulant potential (27) is almost always large. Indeed, \( \beta \epsilon^2 r(s) < \epsilon \) (adaptive discretization) implies \( \lambda_s \epsilon r(s) < \sqrt{\epsilon} \epsilon r a_0 r(s) \) and hence \( \lambda_s \epsilon r(s) < 1 \) if \( r(s) \geq \epsilon a_0 \) (the latter condition is satisfied most of the time in molecular systems). The Coulombic cumulant potential can then be expanded as

\[
V_{\text{cumul.}} \approx \int_0^1 ds \frac{e r_i e r_j}{|r_{1,2}(s)|} \left( 1 - \exp \left[ -\frac{|r_{1,2}(s)|^2}{2 \lambda_s^2 s (1-s)} \right] \right) P \left( \frac{\sqrt{2 \lambda_s^2 s (1-s)}}{|r_{1,2}(s)|} \right),
\]

where the polynomial \( P(x) = \frac{x}{\sqrt{\pi}} - \frac{x^3}{3 \sqrt{\pi}} + \cdots \) arises from the large-\( x \) expansion of \( \text{erf}(x) \). From Eq. (33), \( V_{\text{line}} \) deviates from the cumulant potential only by exponentially small terms which have no impact on the order of the errors (recall that they scale as \( 1/M^2 \) when using the cumulant potential). When using \( V_{\text{line}} \) together with the adaptive discretization, the errors are therefore expected to scale as \( 1/M^2 \) thanks to the vanishing Laplacian of the Coulomb potential. The effective potential associated to the exact pair-action could be used in place of \( V_{\text{line}} \), but it is more expensive to evaluate and provides errors that scale similarly as \( 1/M^2 \), for matrix elements involving three and more particles.

### C. Importance sampling of paths at low temperatures

After discretization of the particle paths \( r_i(s) \) (\( i = 1, \ldots, N_p + N_e + N_a \)) into their root point \( r_{i,0} = r_i(0) = \hat{R}_i \) and \( M_i - 1 \) intermediate points \( r_{i,k} \) (\( k = 1, \ldots, M_i - 1 \)), a cluster function \( Z_{\beta}(\hat{R}_i) \) becomes a multidimensional integral of a function \( f((\hat{R}_i), (r_{i,k}); (\tau_{i,k})) \). The number of points \( M_i \geq 1 \) in the discretized path for particle \( i \) is determined by the stopping criterion (31) and \( \tau_{i,k} = \beta/(2^{M_i-1}) \) is the length of the time interval between points \( r_{i,k} \) and \( r_{i,k+1} \). For instance, the discretization of quantity (17) expressed in relative coordinates takes the form

\[
f(R; \beta) = \int D(\xi) \, f(R, \xi; \beta)
\]

\[
\approx \int dr_1 \cdots dr_{M-1} \, f(R, (r_k); (\tau_k)),
\]

with

\[
f(R, (r_k); (\tau_k)) = \prod_{k=0}^{M-1} \left( \frac{1}{2 \pi \lambda_s^2} \right)^{3/2} e^{-\frac{1}{2 \lambda_s^2 \tau_{k+1}^2} - \frac{\tau_{k+1}}{2 \lambda_s^2}} (V_{\text{line}}(r_{i,k+1}) - \cdots),
\]

where \( r_0 = r_M = \hat{R}, \lambda_s \hat{R} = \hat{R}_0 r_{i,k}/m_{\text{pe}}, \) and the dots stand for the truncation terms \( \sum_{n=0}^{3} (-\tau_{i,n} V_{\text{eff}})^n/ n! \). In (34), function \( f(R; \beta) \) is equivalent to the matrix element \( \langle 2 \pi \lambda_s^2 \rangle \langle e^{-\beta H_{\text{eff}}} + \cdots \rangle \) of the Hamiltonian \( H_{\text{eff}} \) describing relative motion of a proton-electron pair.

The integrand (35) is sampled at low temperatures from a well chosen sampling function \( P_{[\hat{R}_i]}(r_{i,k}) \) for fixed root points \( [\hat{R}_i] \) and temperature \( \beta \), while the remaining integrations over those root points are performed by an adaptive importance sampling scheme. At fixed \( [\hat{R}_i] \), the integration over the inner path points \( (r_{i,k}) \),

\[
\int f([\hat{R}_i], (r_{i,k}); (\tau_{i,k})) \prod_{i,k} dr_{i,k} = f([\hat{R}_i]; \beta),
\]

is performed by rewriting the integral as an average

\[
f([\hat{R}_i]; \beta) = \left( f([\hat{R}_i], (r_{i,k}); (\tau_{i,k})) \right) N_{[\hat{R}_i], \beta} \frac{P_{[\hat{R}_i]}(r_{i,k})}{P_{[\hat{R}_i], \beta}(r_{i,k})},
\]

over a well chosen probability distribution \( P_{[\hat{R}_i], \beta}(r_{i,k}) \), with known normalization constant \( N_{[\hat{R}_i], \beta} \), and by evaluating this average by direct importance sampling according to the distribution \( P \).

The simplest choice for \( P \) is the free-particle distribution,\(^{15}\) i.e., Eq. (35) where \( V_{\text{eff}} \) is set to zero, from which one can sample efficiently, since it is Gaussian, using a Lévy construction.\(^{14}\) Free-particle sampling is adequate at high temperatures, but fails to sample the integrand sufficiently well at low temperatures, due to the formation of bound states. The extension \( \lambda \propto \sqrt{\beta} \) of the free Brownian paths becomes very large at low temperatures whereas the size of bound states is of the order of the Bohr radius \( a_B \ll \lambda \), leading to undersampling of the dominating region. By this undersampling, the variance of the MC estimator grows quickly when the temperature is decreased, so that the MC calculation converges extremely slowly. We recall that this problem is avoided in usual PIMC simulations by the Metropolis-Hastings algorithm in which the most contributing regions are explored preferentially, but such an approach does not seem to be applicable to the computation of virial partition functions as stated previously.

Since the truncation terms in (35) are well sampled by free-particle paths, we focus on the sampling of the exponential terms. Several approaches, in particular matrix squaring and direct summation over eigenfunctions, see Ref. 15, allow to compute efficiently the two-body Coulomb density.
matrix (35), but they are limited to the two-particle case. We introduce here a sampling of paths, based on a Lévy construction, that is adequate to compute, even at quite low temperatures, few-body virial partition functions. The Lévy construction consists in generating paths via bissections. One begins with the two fixed end points, for instance, \( r_0 \) at “time” \( 0 \) and \( r_M = r_0 \) at “time” \( \beta \), and samples a bisecting point \( r_1 \) at time \( \beta/2 \) according to some distribution \( T_{r_0,r_0,L=1}(r_1) \) given below.

Once that point has been chosen, one bisects the two new intervals \([0, \beta/2]\) and \([\beta/2, \beta]\), generating points at “times” \( \beta/4 \) and \( 3\beta/4 \). In our implementation, one recursively bisects all intervals for which \( \beta |V_{\text{lin}}(r_k, r_{k+1})|/(2E) \) is not small in comparison to \( \epsilon < 1 \).

The optimal sampling distribution for a point \( r \), for given end-points points \( x_1 \) and \( x_2 \) of a path segment at recursion level \( L \), is, in the two-particle case,

\[
T^*_{x_1,x_2,L}(r) \propto \langle x_1 | e^{-\beta H/2} | r \rangle \langle r | e^{-\beta H/2} | x_2 \rangle.
\]

Sampling from this optimal distribution is not feasible since the normalization constant cannot be computed quickly. The idea is to sample from a simple, easily normalizable, approximation for \( T^*(r) \) that mimics, at all temperatures, the optimal distribution (38). The low-temperature behavior of \( T \) follows from inserting the spectral decomposition of \( \exp(-\beta H) \) in (38) and from discarding all excited state contributions,

\[
T_{x_1,x_2,L}(r) \propto e^{-\beta H/2} |\Psi_0(r)|^2, \quad \beta \to \infty,
\]

where \( |\Psi_0(r)|^2 = \exp(-r/a_B)/(\sqrt{\pi}a_B^{3/2}) \) is the ground-state wave function and \( E_0 = E_H \) is the ground-state energy of the hydrogen atom. The probability distribution \( T^*(r) \) behaves at high temperatures (or \( L \to \infty \)) as

\[
T^* \approx T_{x_1,x_2,L}(r) - \frac{1}{N} e^{-\beta E_0} \left( 1 + e^{-\beta H} |\Psi_0(r)|^2 \right).
\]

Expression (42) illustrates our sampling scheme in the case of a single path associated to the relative motion of an electron-proton pair.

D. Sampling paths in a few-particle cluster

The previously described algorithm can be adapted to sample simultaneously paths of several interacting charged particles. Protons are much smaller than electron paths, \( \lambda_p \ll \lambda_e \), due to the large mass difference. For the electrons being more mobile, it is their paths that arrange themselves around the proton paths. Inspired by such a Born-Oppenheimer-like picture, one generates first proton and \( \alpha \) particle paths by free-particle sampling. The electron paths are then generated, by a mixture of the two-body importance sampling function (41) which involves the hydrogen ground-state. This method for sampling few-particle partition functions \( Z_{\alpha}(\beta) \) turns out to be quite effective. To generate an inner point \( r_{i,k} \) of electron path \( i \), one therefore first chooses a particle \( j \), among the \( N_p + N_{\alpha} \) heavy particles and samples the bisection point \( r_{i,k} \) according to (41). Close-by particles are favored by setting the probability to pick particle \( j \) to be

\[
N_j/N \delta_j
\]

where \( N_j \) is the normalization constant introduced earlier. The probability distribution for point \( r_{i,k} \) is hence the weighted mean of two-body sampling distributions,

\[
\frac{1}{\sum_j N_j} \sum_j N_j T_j \left( L, \frac{x_1 + x_2}{2}, r_{j,k} \right)
\]

where the normalized probability distribution \( T_j \) introduced in Sec. III C includes the factor \( 1/N_j \). The integrand is eventually rewritten, similar to (42), with factors that are the inverse of (43) for each bisected interval in the Lévy
construction. The importance sampling distribution \( P_{(r, \phi)}(\{r_{i,k}\}) \) in Eq. (37) is hence built with free-particle Gaussian distributions for the intermediate points in proton and \( \alpha \)-particle paths and with products of distributions (43) for electron paths for each bisected path interval.

E. Integration over root points

Sampling over the root points is carried out by an adaptive importance sampling scheme that presents similarities with the Vegas algorithm.\(^36\) Regions in root-points coordinate-space where the variance of the MC estimate of the path integral is large, are sampled with higher probability. In a two-particle cluster, the integration over the root point of the second particle reduces, by rotational symmetry, to a one-dimensional integral over the relative distance \( r \). In a three-particle cluster, the two integrals over root points \( R_1 = r_1 \) and \( R_2 = \{r_2, r'\} \) reduce, thanks to rotational symmetry and to the specific form of the integrand \( f(r_1, r_2) = F(r_1, r_2, r') \), to an integration over three distances \( r_1 = |r_1|, r_2 = |r_2| \) and \( r' = |r_1 - r_2| \).

\[
\int dr_1 \int dr_2 F(r_1, r_2, r') = 8\pi^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr' r_1 r_2 r' F(r_1, r_2, r'). \tag{44}
\]

Notice that the phase space volume element \( r_1 r_2 r' dr_1 dr_2 dr' \) makes the integrand much smoother in these coordinates than with coordinates \( r_1, r_2, \theta \) where \( \theta \) is the angle between vectors \( r_1 \) and \( r_2 \). With the latter variables, sharp peaks would indeed be generated at large distances when \( r_1 \approx r_2 \) and \( \theta \approx 0 \). The three distances are not treated on an equal footing in Eq. (44), but this drawback can be circumvented. Summing over distances \( r_1, r_2, r' \) corresponds to summing over all possible triangles. Since a triangle can be parametrized by the radii \( x_1, x_2, x_3 \) of three circles touching each other (see Fig. 2), one can convert (44) into an integration over all radii,

\[
\int dr_1 dr_2 F(r_1, r_2, r') = (4\pi^2) \int_0^\infty dx_1 dx_2 dx_3 (x_1 + x_2)(x_1 + x_3)x_2 + x_3) \times F(x_1 + x_2, x_1 + x_3, x_2 + x_3), \tag{45}
\]

where each radius can vary without constraint. These new radii variables reflect the full symmetry of the problem. The integral (45) is then rescaled to the unit cube via a change of variable

\[
x_i = a \frac{y_i}{(1 - y_i)^2}, \quad y_i \in [0, 1], \quad i = 1, 2, 3, \tag{46}
\]

where \( a \) is a length scale, chosen in practice to be \( \min(a_B, \lambda_e) \). This particular choice is motivated by the observation that the relevant length scale is the Bohr radius at low temperatures, whereas it is the thermal de Broglie wavelength at high temperatures.

The unit cube, or unit interval in the case of \( Z_{p,e}(\beta) \), is then discretized evenly on a grid. To initialize the adaptive imp-

FIG. 2. A triangle with sides of lengths \( r_1, r_2, r_3 = |r_1 - r_2| \) can be characterized by the radii \( x_1, x_2, x_3 \) of three circles that touch each other. The simple relations \( r_1 = x_1 + x_2, r_2 = x_1 + x_3, \) and \( r_3 = x_2 + x_3 \) hold. The contact points between the three circles are the same as the contact points between a circle inscribed in the triangle and the three sides.

IV. NUMERICAL RESULTS

First, we test our sampling method by computing the hydrogen internal partition function \( Z_{p,e}(\beta) \) (Sec. IV A) and apply it then to partition function of three-particle clusters (Sec. IV B). As the three-body truncated virial coefficient (A1) contains large compensating terms at low temperatures, the evaluation of this function is done in our implementation using arithmetics with a precision of 40 digits\(^{37,38}\) rather than with 15 digits as provided by usual double precision numbers. Error bars in all plots are standard deviations evaluated over 8 independent calculations.

A. Proton-electron cluster function

The proton-electron cluster function \( Z_{p,e}(\beta) \) [Eq. (7)] can be considered as a benchmark and is known analytically. It can be expressed in terms of Ebeling’s second virial function \( Q(x) \) for which an exact series representation is available.\(^3,39\) One can write\(^40\)

\[
Z_{p,e}(\beta) = 2 \sum_{n=4}^{\infty} \frac{\zeta(n-2)}{\Gamma\left(\frac{n}{2} + 1\right)} \left(\frac{\lambda_e}{2}\right)^n \tag{47}
\]
\begin{equation}
2 \sum_{n=1}^{\infty} \left( n^2 e^{-\frac{x}{2n}} \left[ 1 + \text{erf} \left( \frac{x}{2n} \right) \right] \right) - n^2 - \frac{x^2}{\sqrt{\pi}} - \frac{x^3}{4} - \frac{x^4}{6n\sqrt{\pi}},
\end{equation}

with \( x = x_{pe} = \sqrt{2\beta E^2/\lambda_{pe}} \). The second equality is derived by inserting the definition \( \zeta(s) = \sum_{m=1}^{\infty} m^{-s} \) and carrying out the sum over \( n \) in (47). The series in the l.h.s. of (48) converges rapidly at high temperatures (small \( x \)), while the new series representation in the second line converges rapidly at any temperature (including large \( x \)).

We use atomic units, and measure thus energies in Hartrees (1 Hartree = 2 Ry). Let \( \beta^* = \beta |E_H| \) and notice that \( x_{pe} = 2\beta^* \). The dimensionless parameter \( \beta^* \) is very close to the inverse temperature measured in Hartree\(^{-1} \) since \( |E_H| \approx 1 \) Ry, where the corresponding difference \( E_H - 1 \) Ry is due to the finite mass of the proton.

At low temperatures, the most important contribution in \( Z_{p,e}(\beta^*) \) arises from the exponentially growing Boltzmann factor \( \exp(-\beta E_H) \) associated to the ground-state energy. This behavior is apparent in Eq. (48) since \( Z_{p,e}(\beta^*) \sim 4\exp(\beta^*/2) \) when \( \beta^* \to \infty \) with a factor \( 4 \) accounting for spin degeneracy.

We computed \( Z_{p,e}(\beta^*) \) by sampling the functional integral (17) over \( 10^7 \) particle paths. The adaptive discretization of the paths was stopped if the break-up condition with \( \epsilon = 0.1 \) (see Sec. III B) is fulfilled, providing the discretization level \( L \) is at least 4. This cutoff represents the only small source of systematic error in our calculation. Our results for \( Z_{p,e} \) are shown in Fig. 3. The numerical calculations are in excellent agreement with the analytical result (48) from high down to quite low temperatures (\( \beta^* \sim 40 \) corresponds to \( T \approx 8000 \) K). If we had used plain free particle sampling instead of our importance sampling method, the MC calculations would show large deviations for temperatures below \( \beta^* \approx 1 \) because bound state paths would not be sampled properly. The sum over states embedded in trace (7) is clearly well captured by our PIMC calculation. At high temperatures (\( \beta^* \to 0 \)), the numerical results display the asymptotic behavior \( Z_{p,e}(\beta^*) \sim \pi/\beta \pi^2 \beta^2 \) as expected.

The average number \( \langle M \rangle \) of time slices in our calculations is plotted in Fig. 4, for three different temperatures, as a function of the electron-proton distance at time zero (i.e., relative electron-proton distance between the paths’ root points). The number of slices decreases, as expected, when the two particles are far away from each other. The accuracy of the adaptive discretization method can be compared with that of a fixed uniform discretization in \( M = 2^L \) time slices. Fixing \( M \) to be close to \( \langle M \rangle \) (in fact slightly larger), the accuracies of both the adaptive and non-adaptive approaches are reported in Table I. For the same numerical effort, the adaptive discretization provides a better accuracy than a fixed discretization (recall that \( M > \langle M \rangle \)). The accuracy gain is noticeable especially at low temperatures. This gain is brought by the fact that the adaptive algorithm concentrates the numerical effort where it is most needed, i.e., in regions where the potential is strong. Portions of paths that explore those regions can be discretized effectively more finely in the adaptive method than they are in the fixed discretization method. Table I also shows that the straight-line effective potential provides results essentially as accurate as those computed with the cumulant effective potential, as expected from the theoretical analysis (see Sec. III B).

\begin{figure}[h]
\includegraphics{fig3}
\caption{Numerical results (crosses) and analytical result (red solid line, Eq. (48)) for the cluster function \( Z_{p,e} \) in units of \( 4\exp(\beta E_H) \). The phenomenological Brillouin-Planck-Larkin partition function \( Z_{BPL}(\beta) \) \( = \sum_{n=1}^{\infty} n^4 \exp(-\beta E_H/n^2) - 1 + \beta E_H/n^2 \) is also shown.}
\end{figure}

\begin{figure}[h]
\includegraphics{fig4}
\caption{Average number of time slices used in the computation of \( Z_{p,e}(\beta) \), as a function of distance, for 3 different temperatures. The dimensionless distance variable \( y \) is defined by Eq. (46).}
\end{figure}

\textbf{B. Three-body cluster functions}

We computed the three-body cluster functions for ions \( H^- , H^+ \) and for the helium atom by sampling over \( 10^7 \) paths. Notice that all paths are independent in our direct sampling approach. The direct (D) and exchange (E) terms appearing in Eq. (11) are plotted each time separately and the results are compared with simple models for the partition functions of those entities that hold at low temperatures (\( k_B T \ll \text{dissociation energy} \)).
The high temperature behavior of the cluster functions is a polynomial in $\sqrt{\beta}$. We extracted the exponent $n$ and the prefactor $a$ of $Z_{\text{c}}(\beta) \sim a \beta^n$ by fitting the results of eight calculations for two high temperatures $\sqrt{\beta} \sim (1 \text{ Hartree}) = \{2.5 \times 10^{-3}, 5.0 \times 10^{-3}\}$, for each considered cluster (see Table II). The fitted exponents agree well with their theoretical values: $n = 7$ for the direct and $n = 4$ for the exchange term.

1. $\text{H}^-$ cluster

The results for the cluster function $Z_{\text{p,2e}}(\beta)$ are shown in Fig. 5. The exchange term is always positive, while the direct term is negative at high temperatures and changes sign at around $\beta = 19 \text{ Hartree}^{-1}$ ($T \simeq 17000 \text{ K}$). It is not surprising that $D$ becomes negative at high temperatures because some subtracted terms in (A1) are negative and provide the leading contribution.

At low temperatures, the ground-state of ion $\text{H}^-$ dominates exponentially the matrix elements $D$ and $E$, leading to the low-temperature asymptotic behavior $Z_{\text{GS}}(\beta) = 2 \exp(-\beta E_{\text{H}})$, with a degeneracy factor of 2 due to proton spin. The numerical results are compared in Figs. 5(b) and 6 with $Z_{\text{GS}}(\beta)$. Both functions grow approximately with the same rate, but the former is about five times smaller than the latter. This difference is caused by truncation terms in (A1) associated to interactions between an ionized electron and a hydrogen atom, namely, terms of the form $(e^b - 1 + b - b^2/2 + b^3/3)!a(a+c)^{3!}(a+b)^{4!}h!$ (with $n = 2$ or 3), where $a = -\beta V_{e_i-e_{-p}}$, $b = -\beta V_{e_i-e_p}$ and $c = -\beta V_{e_{-p}}$. Notice that these terms are zero by charge symmetry and translational invariance in imaginary time when $n = 1$. The factors $e^b$ and $e^c$, which describe a hydrogen atom formed by the pair $e_1 - p$ or $e_2 - p$, can be exponentially large at low temperature (their magnitude is controlled by the binding energy $|E_{\text{H}}|$ of the atom which is not much smaller than the energy $|E_{\text{H}^-}|$), while factors $(a+c)^{3!}$ and $(a+b)^{4!}$ can also be significant. The term $(a+b)^{4!}$ takes large positive values when the ionized electron is close to the proton, since the attractive proton-ionized electron interaction dominates indeed the repulsive electron-ionized electron interaction at short distances, the proton path being more localized. The subtraction of the atom-charge interactions lowers $Z_{\text{p,2e}}(\beta)$ with respect to a partition function defined by summing only over bound states of the three-body Hamiltonian. The sum of the atom-charge interaction terms can be identified with the opposite of function $W(1,1|0,1)$ defined in Ref. 12 if one replaces the screened Coulomb potential in $W$ by the bare Coulomb potential. Those interactions are excluded (subtracted) in the definition of particle clusters, but the full contribution of three-particle effects to the thermodynamic properties involve not only the contributions of the 3-body particle clusters but also those of the counter-terms that generate the functions $W$ (see Eq. (4.10) of Ref. 12). By subtracting the atom-charge interactions for all relative distances of the particles, unphysical negative contributions have appeared in $Z_{\text{p,2e}}$ at short distances. Those are compensated by the counter-terms in $W_{\text{H}^-e}$ which have eventually to be added. We therefore consider the sum $Z_{\text{p,2e}} + W_{\text{H}^-e}$, which is the combination appearing in the function $R(\beta)$ of the SLT expansion. Notice that the function $Z_{\text{p,2e}} + W_{\text{H}^-e}$ accounts simultaneously for the atom-electron interactions at large distances as well as the formation of a $\text{H}^-$ ion at short distances, without any approximate treatment for configurations at intermediate distances. The numerical results for electron-atom interactions $W_{\text{H}^-e}$ and for the sum $Z_{\text{p,2e}} + W_{\text{H}^-e}$ are shown in Figs. 5(b) and 6. The atom-charge contribution $W_{\text{H}^-e}$ is calculated in practice with a Mayer bond $B_{ij} = \beta^{-3/2}(\beta V(\mathcal{L}_i, \mathcal{L}_j))^{-4}$ between the proton and electron paths. At low temperatures, the sum $Z_{\text{p,2e}} + W_{\text{H}^-e}$ approaches $Z_{\text{GS}}(\beta)$ faster than $Z_{\text{p,2e}}$ alone. Fitting $Z_{\text{p,2e}} + W_{\text{H}^-e}$ to $2\exp(-\beta E)$ at low temperatures yields the energy $-0.525 \text{ Hartree}$, in good agreement with the known value $E_{\text{H}^-} \simeq -0.527 \text{ Hartree}$. We recall that the present work does not aim for spectroscopic accuracy of the ground state energy, but we study the low temperature

<table>
<thead>
<tr>
<th>$\beta$ (Ha$^{-1}$)</th>
<th>Exact Value</th>
<th>Exact Error</th>
<th>$\langle M \rangle_{\text{max}}$</th>
<th>Uniform discretization Value</th>
<th>Uniform Error</th>
<th>Effective potential $M$</th>
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<tr>
<td>36</td>
<td>$6.50 \times 10^7$</td>
<td>$6.39 \times 10^7$</td>
<td>$1.8%$</td>
<td>$453$</td>
<td>$5.84 \times 10^7$</td>
<td>$10%$</td>
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<td>16</td>
<td>$2.98 \times 10^1$</td>
<td>$2.96 \times 10^1$</td>
<td>$0.6%$</td>
<td>$222$</td>
<td>$2.86 \times 10^8$</td>
<td>$4.0%$</td>
</tr>
<tr>
<td>1</td>
<td>$1.519 \times 10^{-1}$</td>
<td>$1.511 \times 10^{-1}$</td>
<td>$0.4%$</td>
<td>$42$</td>
<td>$1.521 \times 10^{-1}$</td>
<td>$0.1%$</td>
</tr>
</tbody>
</table>

TABLE II. Coefficients of the high temperature behavior $a \beta^n$ for the direct and exchange contributions for the various particle clusters.

<table>
<thead>
<tr>
<th>$Z_{\text{p,2e}}$</th>
<th>Direct</th>
<th>$6.999 \pm 0.002$</th>
<th>$-0.144 \pm 0.001$</th>
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<tbody>
<tr>
<td>Exchange</td>
<td>$4.00 \pm 0.02$</td>
<td>$0.40 \pm 0.04$</td>
<td></td>
</tr>
<tr>
<td>$Z_{\text{u,2e}}$</td>
<td>Direct</td>
<td>$6.999 \pm 0.003$</td>
<td>$-0.59 \pm 0.06$</td>
</tr>
<tr>
<td>Exchange</td>
<td>$4.000 \pm 0.002$</td>
<td>$6.57 \pm 0.08$</td>
<td></td>
</tr>
<tr>
<td>$Z_{\text{u,3e}}$</td>
<td>Direct</td>
<td>$6.978 \pm 0.009$</td>
<td>$-(1.8 \pm 0.1) \times 10^3$</td>
</tr>
</tbody>
</table>
behavior of our path integral calculations, well suited for high temperatures, in order to connect to known low temperature asymptotics.

2. H$_2^+$ cluster

The results for the cluster function $Z_{2p,e}(\beta)$ are shown in Fig. 7. Again, $Z_{2p,e}(\beta)$ is negative at high temperatures. The exchange term (not shown) is negligible at all considered temperatures because of the large mass of the protons. The direct contribution is also not shown since it reduces to $Z_{2p,e}(\beta)/4$. At low temperatures, the contributions from bound states grow exponentially fast. Since the energy quanta $k_B T_{H_2}^{\text{rot}}$ and $k_B T_{H_2}^{\text{vib}}$ for rotations and vibrations of the molecular ion H$_2^+$ are small ($T_{H_2}^{\text{rot}} \approx 41.87$ K and $T_{H_2}^{\text{vib}} \approx 3150.78$ K), many rotational-vibrational states are excited at the considered temperatures. We compare in Fig. 7, for temperatures lower than the dissociation energy ($T < (E_{H_2^+} - E_H)/k_B \approx 30000$ K), the cluster function $Z_{2p,e}(\beta)$ with two different models for the partition function of ion H$_2^+$. In the first model, the molecular states are described in the simple picture where the electron is in its ground state, while global rotations and vibrations are taken into account with a rigid rotor model and a harmonic oscillator, respectively. When $T \gg T_{H_2}^{\text{rot}}$, the partition function for this model is given by

$$Z_{\text{rot-vib}}(\beta) \approx 2 \exp(-\beta E_{H_2^+}) \frac{2T}{T_{H_2}^{\text{rot}}} \frac{1}{1 - \exp(-T_{H_2}^{\text{vib}}/T)}. \quad (49)$$

In the second model, the partition function is calculated via a direct sum over all (423) electronic ground state rotational-vibrational levels whose energies are determined by solving the radial nuclear Schrödinger equation within the Born-Oppenheimer approximation (using an effective potential obtained by a density functional theory calculation). The latter model provides the more refined partition function $Z_{\text{Stancil}}(\beta)$ which accounts for rotation-vibration coupling. $Z_{\text{Stancil}}(\beta)$ is about 1.5 times larger than $Z_{\text{rot-vib}}(\beta)$ (see Fig. 7). The rotational and vibrational partition functions in (49) depend only weakly on the temperature, in contrast to the exponential growth of the electronic partition function $Z_{\text{GS}}(\beta) = 2 \exp(-\beta E_{H_2^+})$ as $\beta \to \infty$. They provide a slowly varying factor whose magnitude is about 1500 when $T \approx 10000$ K.
FIG. 7. Cluster function $Z_{2p,e}(\beta)$: (a) in absolute values in a logarithmic scale; (b) in units of $Z_{\text{rot-vib}}(\beta)$ in a linear scale. The partition functions $Z_{\text{rot-vib}}(\beta)$ and $Z_{\text{Stancil}}(\beta)$, and the atom-proton interactions $W_{H-p}(\beta)$ are defined in the main text. In plot (b), $Z_{2p,e}(\beta)$ and $|W_{H-p}(\beta)|$ are divided by 20 for visualization purposes.

Fig. 7 shows that $Z_{2p,e}(\beta)$ is about 50 times larger than the Stancil partition function when $T < 20000$ K. The difference arises from the subtracted atom-ionized proton interactions $W(1,1|1,0) = W_{H-p}(\beta)$ in the truncation of $Z_{2p,e}(\beta)$, similar to the case of $Z_{c,2p}(\beta)$. When the ionized proton is close to the other proton bound in a hydrogen atom, $W_{H-p}$ takes large negative values, which lead to an increase of $Z_{2p,e}(\beta)$ since those interactions are subtracted in the cluster function. One considers therefore the sum $Z_{2p,e} + W_{H-p}$, which is the relevant quantity for thermodynamics. Notice that $Z_{2p,e} + W_{H-p}$ accounts exactly for the effects of ionized proton-hydrogen atom interactions at large distances and for molecular states of $H_2^+$ at short-distances, without any arbitrariness in how configurations at intermediate distances are treated. The numerical results for $W_{H-p}$ and for the sum $Z_{2p,e} + W_{H-p}$ are shown in Fig. 7. The atom-ionized proton interaction $W_{H-p}$ does compensate the large contributions in $Z_{2p,e}$ in such a way that the sum $Z_{2p,e} + W_{H-p}$ is close, for temperatures below the dissociation energy of $H_2^+$, to the partition function $Z_{\text{Stancil}}(\beta)$. The fact that $Z_{2p,e} + W_{H-p}$ is slightly larger, at low temperatures, than the partition function of Stancil is probably due to the fact that our calculations are not restricted to bound molecular states, but also includes contributions from dissociated states, such as atom-charge interactions at large distances.

FIG. 8. Cluster function $Z_{\alpha,2e}(\beta)$: (a) in absolute values (logarithmic scale); (b) in units of $Z_{\text{GS}}(\beta) = \exp(-\beta E_{He})$ (linear scale). The direct and exchange contributions and the ground state partition function $Z_{\text{GS}}(\beta) = \exp(-\beta E_{He})$ are also shown.
3. He cluster

The cluster function $Z_{u,\alpha}(\beta)$ is shown in Fig. 8. Since the difference $|E_{\text{He}} - E_{\text{He}}^{\beta}| = 0.903$ Ha is large, the ground state contribution of the helium Hamiltonian quickly dominates all other terms in $Z_{u,\alpha}(\beta)$ at low temperatures ($T < 60 000$ K). Fitting the data at low temperatures to $\exp(-\beta E)$, one finds $E_{\text{He}}^{\beta} \approx -2.905$ Hartree, which is close to the ground state energy $E_{\text{He}} = -2.9034$ Hartree of the helium atom. Below $30 000$ K, $Z_{u,\alpha}(\beta)$ can safely be approximated by $\exp(-\beta E_{\text{He}})$.

V. CONCLUSIONS

This work reports two new developments for the numerical calculations of Coulomb path integrals, as well as their application to cluster functions, appearing in equations of state at low densities.

First, we have devised an efficient importance sampling strategy to compute few-body cluster functions. It relies on the knowledge of the solution of the two-particle Coulomb problem and enables us to overcome to a large extent the exponential variance increase of the MC estimator at low temperatures originating from the formation of bound states. Second, an adaptive discretization procedure is introduced which removes all short-distance Coulomb divergences that would be present at fixed discretization when working with the bare Coulomb potential. This adaptive discretization exempts us from using more sophisticated and computationally demanding effective potentials such as the pair-action potential. With this self-adapting discretization, correlations between the particle paths are not approximated by pair-actions, but are accounted for by discretizing sufficiently. Notice that in the limit of finely discretized paths, as required to capture all correlations, the pair-action effective potential reduces to the plain Coulomb straight-line potential employed in our calculations. The direct discretization is efficient because it directs the computational effort where it is most needed, in regions where particles are close and therefore strongly interacting. Numerical tests have shown that our approach combining the adaptive discretization with the straight-line Coulomb action provides results that are more accurate at low temperatures than those computed with the usual uniform discretization and the cumulant action.

We have applied our algorithm to calculate two- and three-body cluster functions, which include bound and diffusive states. Our calculation of the two-body function agrees well with its known series representation, even at low temperatures where bound state contributions dominate, underlining the efficiency of our importance sampling approach. The uncertainties on our numerical results for the three-body cluster functions are very high at small and intermediate temperatures. At a low temperature like $T \approx 8000$ K, the error on function $Z_{u,\alpha}(\beta)$ is about 1%. The three-body cluster functions reduce at low temperatures to known atomic, ionic, or molecular partition functions determined by other means, so that they are now known in the whole temperature regime. Ground state energies can be extracted with relatively small errors, at most 1%, highlighting the accuracy and reliability of our computations. For ion $\text{He}^+$, the cluster function agrees at low temperatures with Stancil’s partition function obtained by summing explicitly over many rotational-vibrational energies. We stress that the aim of the present work is not extracting ground state energies with spectroscopic accuracy, but determining precisely the three-body cluster partition functions at temperatures $T \geq 8000$ K where the considered clusters are significantly excited and possibly even dissociated. The application of the present results in the extension of the SLT EOS to a partially ionized hydrogen-helium mixture, as well as the computation of four-body cluster functions describing $\text{H}_2$ molecules and interactions between its dissociation products is foreseen.

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APPENDIX A: DIRECT TERM IN A 3-BODY CLUSTER

The direct term in a 3-body cluster [Eq. (12)] involves the following operator $D^3$:

$$D^3 = e^{a+b+c} - e^a - e^b - e^c + 2$$

$$\quad + 2(a + b + c) + a^2 + b^2 + c^2 + 2(ab + ac + bc)$$

$$\quad + \frac{1}{3}(a^3 + b^3 + c^3) + a^2(b + c) + b^2(a + c)$$

$$\quad + c^2(a + b) + 2abc$$

$$\quad + \frac{1}{4}(a^2b^2 + a^2c^2 + b^2c^2) + \frac{1}{6} [a^3(b + c)$$

$$\quad + b^3(a + c) + c^3(a + b)] + a^2bc + ab^2c + abc^2$$

$$\quad + \frac{1}{12} [a^3(b^2 + c^2) + b^3(a^2 + c^2) + c^3(a^2 + b^2)]$$

$$\quad + \frac{1}{4}(ab^2c^2 + a^2bc^2 + a^2b^2c)$$

$$\quad + \frac{1}{36} (a^3b^3 + a^3c^3 + b^3c^3) - \frac{1}{8} a^2b^2c^2$$

$$\quad - e^a(b + c) - e^b(a + c) - e^c(a + b) - \frac{1}{2} e^a(b + c)^2$$

$$\quad - \frac{1}{2} e^b(a + c)^2 - \frac{1}{2} e^c(a + b)^2$$

$$\quad - e^a \left( \frac{1}{6} b^3 + \frac{1}{6} c^3 + \frac{1}{2} b^2c + \frac{1}{2} bc^2 \right) - e^b \left( \frac{1}{6} a^3 + \frac{1}{6} c^3$$

$$\quad + \frac{1}{2} a^2c + \frac{1}{2} c^2a \right) - e^c \left( \frac{1}{6} a^3 + \frac{1}{6} b^3 + \frac{1}{2} a^2b + \frac{1}{2} ab^2 \right)$$

(A1)

where kinetic operators are implicit and where we have set

$$a = -\beta V_{p_1p_2}, \quad b = -\beta V_{p_1e}, \quad c = -\beta V_{p_2e}.$$  (A2)
In the first line of (A1), one recognizes the Mayer operator (14), while the truncation terms (besides those of the Mayer truncation) involve one or more time-evolved Coulomb operator(s) possibly associated with a Gibbs operator $e^{\beta H}$ or $e^{\beta H}$ for a sub-set of particles inside the cluster. Truncation term $a \rho^b$ stands for, instead of the expression

$$
\int_0^\beta d \tau_1 \int_0^{\tau_1} d \tau_2 e^{-\beta H_{\rho^b}} \left[ V_{\rho^a} - e^{-\beta H_{\rho^b}} \left( \tau_1 \right) V_{\rho^a} - e^{-\beta H_{\rho^b}} \left( \tau_2 \right) \right] + V_{\rho^a} - e^{-\beta H_{\rho^b}} \left( \tau_1 \right) V_{\rho^a} - e^{-\beta H_{\rho^b}} \left( \tau_2 \right),
$$

where Hamiltonian $H_{\rho^b}$ is the sum of 3 kinetic terms and of the Coulomb operator $V_{\rho^a}$ and where the time-ordering of the time-evolved operators has been taken into account. By construction, operator $D^\tau$ remains integrable when any of the three particles is sent to infinity. This can be performed by a Dyson expansion of (A1). The terms of lowest order in the interaction potential are indeed $\frac{1}{\lambda^3} (a^2 b^2 c^2 + a^2 b^2 c^2 + a^2 b^2 c^2) + \frac{1}{\lambda^3} (a^2 b^2 c + a^2 b c + a^2 b c)$, which are all integrable.

**APPENDIX B: NORMALIZATION OF THE SAMPLING DISTRIBUTION**

The norm of the second distribution in Eq. (41) is $N_\Psi$

$$
N_\Psi = \int d \tau e^{-\beta E_\rho/M} |\Psi_0(\tau)|^2
$$

$$
= \frac{2}{a^b} \int_0^\infty d r e^{-\beta \int_0^1 d \tau (a^2 \tau^2 + b^2 \tau^2 + c^2 \tau^2) / \lambda^2} e^{-2 \beta r/a^b}
$$

$$
= \frac{\lambda^2_M}{\lambda^2_M} \left[ 1 - \frac{\lambda^2_M}{\lambda^2_M} \right] \left[ 1 + \frac{\lambda^2_M}{\lambda^2_M} \right]
$$

with $\lambda^2_M = \lambda^2 / M = 2^\beta$.


35. In the most contributing region, when $s$ is close to zero or 1, the argument is moreover always large.
Denoting Euler’s constant by \( \gamma \approx 0.577 \), function \( Q(x) \) is defined, for \( x > 0 \), as

\[
Q(x) = \lim_{R \to \infty} \left\{ \int_{r < R} \left[ \left( \frac{2\pi\lambda^2}{2} \right)^{3/2} r e^{-\beta r} \right] \, dr + 2\pi \left( \frac{\sqrt{\beta}}{3} \right) \ln(3\sqrt{2}) + \gamma \right\}.
\]

Notice that \( Q(x) \) and Eq. (7) are both truncated traces over the density matrix \( \langle r | e^{-\beta H} | r \rangle \) of a (relative) particle in an attractive Coulomb potential, but differ in the subtracted terms, which involve the first three powers of the Coulomb potential (thus subtracting non-integrable contributions at large distances) are not the same at short distances. Since the truncation in (9) amounts to subtracting exactly the first terms in the Dyson expansion of \( e^{-\beta H} \), function \( Z_{pe}(\beta) \) does not contain any term of order lower than \( (\sqrt{\beta})^4 = \beta^2 \) (recall that \( \lambda \propto \sqrt{\beta} \)). All terms of order \( (\sqrt{\beta})^n \) with \( n \geq 4 \) coincide in both formulas, except for a trivial factor \( 2/\sqrt{\pi} \). We have thus \( Z_{pe}(\beta) = \frac{2}{\sqrt{\pi}} \tilde{Q}(x_{pe}) \) where \( \tilde{Q}(x) \) is equal to \( Q(x) \) in which one discards terms of order \( x^n \) with \( n < 4 \).