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Path integral method in quantum statistics problems: generalized ensemble Monte Carlo and density functional approach

P N Vorontsov-Velyaminov¹, M A Voznesenski¹, D V Malakhov¹,
A P Lyubartsev² and A V Broukhno³

¹ Faculty of Physics, St Petersburg State University, 198504 St Petersburg, Russia

² Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

³ Quantum Protein Centre, Technical University of Denmark, Building 309, DK-2800 Lyngby, Denmark

E-mail: voron.wgroup@pobox.spbu.ru and sasha@phycs.su.se

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Abstract

Three items related to path integrals in quantum statistics are discussed: (1) entropic sampling within Wang–Landau algorithm; (2) calculating partition function for a fermion system using expanded ensemble technique; (3) applying classical density functional theory to expressions in path integral form.

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1. Entropic sampling within Wang–Landau algorithm for calculation of quantum canonical averages

The path integral form of the canonical quantum partition function (PF) in the n -bead approximation is

$$Z_n(\beta) = \int dq \exp\left(-\frac{H_1(q)}{\beta} - \beta H_2(q)\right),$$

where q is a dNn -vector, d is the dimensionality, N and n are the number of particles and beads, respectively, $\beta = (kT)^{-1}$; $H_1(q) = \frac{n\mu}{2\hbar} \sum_{1 \leq t \leq n} (r_t - r_{t+1})^2$ and $H_2(q) = \frac{1}{n} \sum_{1 \leq t \leq n} V(r_t)$ account for kinetic and potential energy of the system (r_t is a dN -vector, μ is the particle mass, $r_{n+1} \equiv r_1$). β enters into two terms in $Z_n(\beta)$ of powers 1 and -1 , so the density of states, Ω , depends on two variables, E_1 and E_2 . For $Z_n(\beta)$, we get

$$Z_n(\beta) = \int dE_1 dE_2 \exp\left(-\frac{E_1}{\beta} - \beta E_2\right) \Omega(E_1, E_2),$$

$$\Omega(E_1, E_2) = \int dq \delta(E_1 - H_1(q)) \delta(E_2 - H_2(q)).$$

Table 1. Results for 1D harmonic oscillator. (...) * are for analytical data; $Z_{1D}(\beta; 8)$, $U_{1D}^{\text{pot}}(\beta; 8)$ due to [5] and $Z_{1D}(\beta; \infty) = (2 \sinh(\beta/2))^{-1}$, $U_{1D}^{\text{pot}}(\beta; \infty) = \coth(\beta/2)/4$; $(-R_{\text{cut}}, +R_{\text{cut}})$: interval of integration; N_{grid} : grid number; n : number of beads.

$\beta\hbar\omega$	$n = 2^{p+1}$	$Z_{1D}^3(\beta; n)$	$3 \times U_{1D}^{\text{pot}}(\beta; n)$	R_{cut}	N_{grid}	t_{CPU} (s)
8.0	8	9.6578×10^{-6}	0.671 429	6.0	300	2.0
–	(8	9.6578×10^{-6}	0.671 429)*			
–	1024	6.1506×10^{-6}	0.750 498	6.0	300	0.8
–	4096	6.1504×10^{-6}	0.750 503	6.0	300	0.6
–	(∞	6.1504×10^{-6}	0.750 503)*			
1.0	8	0.885 268	1.620 701	8.0	400	1.9
–	(8	0.885 268	1.620 701)*			
–	1024	0.883 402	1.622 965	8.0	600	3.6
–	(∞	0.883 402	1.622 965)*			

E_1 is always positive while E_2 can have both signs. Knowing Ω (or $S = \ln \Omega$), one gets the canonical distribution, $P(E_1, E_2; \beta) = \exp(-E_1/\beta - E_2\beta + S(E_1, E_2))$, to calculate equilibrium properties.

Simulations were carried out for a 3D quantum oscillator so that $V(r) = \frac{\mu\omega^2}{2}r^2 > 0$ (E_1, E_2 are both positive) with the number of beads $n = 5, 8$. A grid of boxes labelled as (i, k) , $1 \leq i \leq N_{b1}$, $1 \leq k \leq N_{b2}$, is introduced. Following the Wang–Landau (WL) algorithm [1] initial values of entropy distribution, S_{ik} , are set to zero. The MC step is an attempt to shift a bead to a new position with transition probability: $p(ik \rightarrow i'k') = \min(1, \exp(S_{ik} - S_{i'k'}))$; if it is satisfied the trial is accepted. Irrespectively, a constant Δs is added to the current entropy value (i.e., either to S_{ik} , or to $S_{i'k'}$) and 1—counter of visits ($nv(i, k)$ or $nv(i', k')$). The initial value of Δs , $\Delta s_0 = 1$, is used in most cases. A MC sweep included $\sim 10^7$ steps that provide $\sim 10^2$ visits to each box. Each next sweep starts with a decrease of Δs : $\Delta s \rightarrow a\Delta s$ ($a < 1$, we used $0.5 \leq a \leq 0.95$) that provides fine tuning of the values of S_{ik} .

Calculated function $S(E_1, E_2)$, figure 1(a), provides canonical distributions $P(E_1, E_2; \beta)$ shown for $\beta = \frac{1}{8}, \frac{1}{2}, 1, 2, 8$ in figures 1(b)–(d). For the highest T ($\beta = \frac{1}{8}$, classical regime) its maximum is stretched along the E_2 -axis in a narrow stripe. For $\beta = \frac{1}{2}, 1$ a strong shift of the maximum to the origin of the (E_1, E_2) -plane is observed, isolines are oblique to both axes and the steepness of slopes is much less. For $\beta = 2, 8$ the maximum is stretched along the E_1 -axis. The calculated potential energy $\langle U_p \rangle$ was compared (table 1 [2]) with the exact one, $U_p^{\text{ex}} = \frac{d}{4} \coth(\frac{\beta}{2})$, and with finite n -bead analytical expression [2].

2. Calculating partition function and averages for a fermion system using the expanded ensemble MC technique

For a system of N identical particles in 3D space, the partition function (PF) is expressed as a sum over permutations $\{P\}$ of PF for distinguishable particles [3]:

$$Z_N^{(A,S)} = \text{Tr}(\rho^{(A,S)}) = \frac{1}{N!} \sum_{\{P\}} \xi^{[P]} \int dx_1 \cdots dx_N \rho^{(D)}(x_1 \cdots x_N; P(x_1) \cdots P(x_N)).$$

x_i is a set of space and spin variables, $x_i = (\vec{r}, \sigma)$ and $\int dx = \sum_{\sigma} \int d\vec{r}$, $\xi = \pm 1$ for fermions and bosons and $[P]$ is the parity of permutation P . For the spin-independent Hamiltonian $Z_N^{(A,S)} = \frac{1}{N!} \sum_{\{P\}} \xi^{[P]} K_N^{(D)}(P) Z_N^{(D)}(P)$. $K(P) = \sum_{\sigma_1 \cdots \sigma_N = \pm 1/2} \delta(\sigma_1, P(\sigma_1)) \cdots \delta(\sigma_N, P(\sigma_N))$ is the spin PF; the coordinate PF for distinguishable particles is

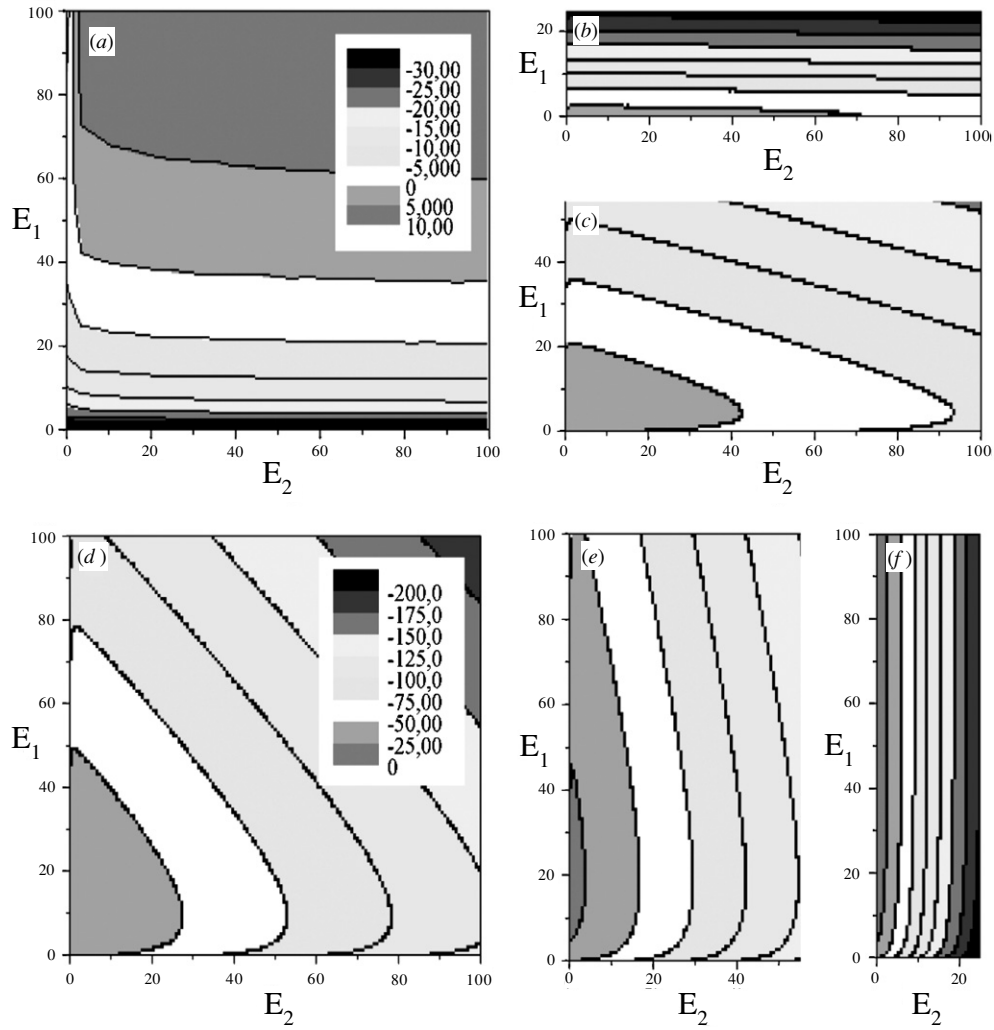


Figure 1. Entropy (a) and canonical distributions for $\beta = \frac{1}{8}, \frac{1}{2}, 1, 2, 8$ ((b), (c), (d), (e), (f)).

$Z_N^{(D)}(P) = \int d\vec{r}_1 \cdots d\vec{r}_N \rho_0^{(D)}[\vec{r}_1 \cdots \vec{r}_N; P(\vec{r}_1) \cdots P(\vec{r}_N)] = \int dq \rho_0^{(D)}(q, P(q))$. $Z_N^{(A,S)}$ can be presented as a sum over classes of permutations $\{G\}$. Then $\xi^{[P]} \rightarrow \xi^{[G]}$, $K_N^{(D)}(P) \rightarrow K_N^{(D)}(G) = 2^{\sum_\nu C_\nu(G)}$, where $C_\nu(G)$ is the number of cycles of length ν in class G , so that $\sum_\nu C_\nu(G)$ is the total number of cycles in class G . For $sp = 0$, $K(G) = 1$ for all G . $Z_D(P) = Z_D(G)$, since the value of an integral depends only on the cycle structure of P [4]. This way the PF becomes

$$Z_N^{(A,S)} = \frac{1}{N!} \sum_{\{G\}} \xi^{[G]} K(G) n(G) Z_N^{(D)}(G),$$

where $n(G)$ is the number of permutations in the given class G , $n(G) = N! / (\prod_{\nu=1}^N (\nu^{C_\nu(G)} C_\nu(G)!))^{-1}$.

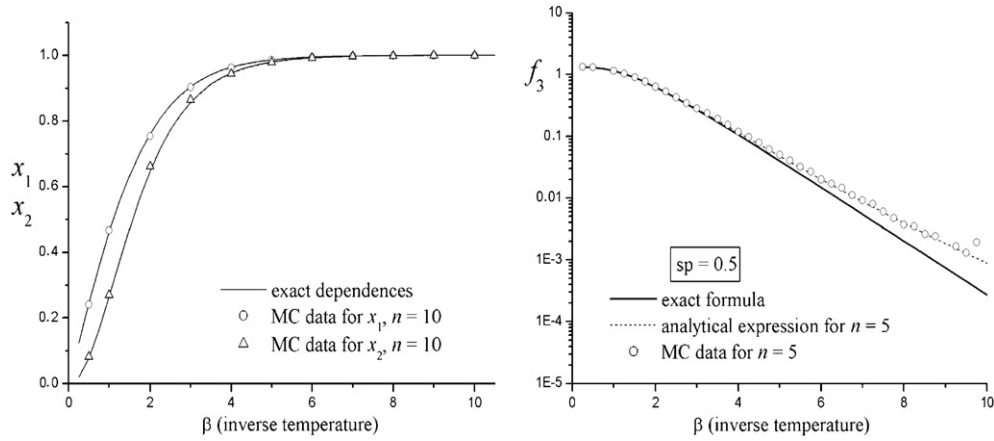


Figure 2. Ratios of partition functions x_1 , x_2 and factor f_3 .

For $N = 2$, PF is $Z_2^{(A)} = \frac{1}{2}[K(1^2)Z_{1^2} - K(2)Z_2]$, classes are designated as (1^2) , (2) and $n(1^2) = n(2) = 1$. For $sp = 1/2$, $K(1^2)$, $K(2) = 4, 2$. For $N = 3$, PF is $Z_3^{(A)} = \frac{1}{3!}[K(1^3)Z_{1^3} - 3K(12)Z_{12} + 2K(3)Z_3]$, $K(1^3)$, $K(12)$, $K(3) = 8, 4, 2$. $Z_2^{(A)}$ and $Z_3^{(A)}$ can be presented in the form $Z_2^{(A)} = Z_{1^2}f_2$; $Z_3^{(A)} = Z_{1^3}f_3$, where $f_2 = \frac{1}{2}((4) \cdot 1 - (2) \cdot x)$, $x = \frac{Z_2}{Z_{1^2}}$; $f_3 = \frac{1}{6}((8) \cdot 1 - (4) \cdot 3x_1 + (2) \cdot 2x_2)$, $x_1 = \frac{Z_{12}}{Z_{1^3}}$, $x_2 = \frac{Z_3}{Z_{1^3}}$; (factors (8) , (4) , (2) correspond to $sp = \frac{1}{2}$). Z_{1^N} is the PF for N distinguishable particles while factor f_N accounts for exchange. It is expressed through ratios of PF for certain classes to PF for 1^N . The energy can be derived from $E = -(\partial/\partial\beta)(\ln Z)$. $E_2^{(A)} = E_{1^2}f_E^{(2)}$, $f_E^{(2)} = \frac{(4) \cdot 1 - (2) \cdot xy}{(4) \cdot 1 - (2) \cdot x}$, $y = \frac{E_2}{E_{1^2}}$, $E_3^{(A)} = E_{1^3}f_E^{(3)}$, $f_E^{(3)} = \frac{(8) \cdot 1 - (4) \cdot 3x_1y_1 + (2) \cdot 2x_2y_2}{(8) \cdot 1 - (4) \cdot 3x_1 + (2) \cdot 2x_2}$, $y_1 = \frac{E_{12}}{E_{1^3}}$, $y_2 = \frac{E_3}{E_{1^3}}$.

We apply expanded ensemble (EE) MC [5] to calculate x , y , x_1 , y_1 , x_2 , y_2 for systems with $N = 2, 3$ noninteracting fermions in a harmonic field and compare our results with the exact data, figure 2. It is seen that x_1 and x_2 follow the exact curves very accurately. Data for f_3 , f_3^E , $sp = \frac{1}{2}$ are also consistent up to $\beta = 9$. Data for $sp = 0$ (not shown) already strongly deviate from theory at $\beta > 3$.

3. Applying classical density functional theory developed for polymers to quantum statistical expressions in path integral form

The density functional approach implies obtaining in some way the particle density $\rho(\mathbf{r})$, which is used for the calculation of PF, $Z = \int \rho(\mathbf{r}) d\mathbf{r}$, and related averages. Consider a quantum particle in an external field $\phi(\mathbf{r})$ at inverse temperature β presented by a closed trajectory of n beads $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_n)$. This trajectory can be treated as a phantom polymer ring chain of n monomers with springs dependent on temperature. $\rho(\mathbf{r})$ can be expressed as

$$\rho(\mathbf{r}) = \int \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{r}_i) \exp(-\beta V_b(\mathbf{R})) \exp(-\beta \Phi_{\text{ext}}(\mathbf{R})) d\mathbf{R}$$

with $V_b(\mathbf{R}) = K_f \sum_{i=1}^n (\mathbf{r}_{i+1} - \mathbf{r}_i)^2$; $\Phi_{\text{ext}}(\mathbf{R}) = \frac{1}{n} \sum_{i=1}^n \phi(\mathbf{r}_i)$; $K_f = \pi n / \beta \lambda^2$; $\lambda^2 = \frac{2\pi \hbar^2 \beta}{m}$; $\mathbf{r}_{n+1} = \mathbf{r}_1$.

Table 2. ORA-results for ground states of hydrogen, helium and lithium compared to exact values in eV: $E_g(\text{H}) = -13.606$, $E_g(\text{He}^+) = -54.4$, $E_g(\text{He}) = -79.1$, $E_g(\text{Li}^{2+}) = -121.8$, $E_g^{\text{ex}}(\text{Li}^+) = -197.4$.

	T (K)	n	U^{tot} (eV)	R_s (Å)	R_{cut} (Å)	N_{grid}	t_{CPU} (FFT) (m)
H	4 000	96 000	-13.607	0.001	10.24	4096	30.0
He ⁺	8 000	16 384	-54.608	0.001	15.36	4096	5.0
He	8 000	16 384	-78.150	0.001	15.36	4096	32.0
Li ²⁺	16 000	24 000	-122.725	0.001	15.36	4096	7.5
Li ⁺	16 000	24 000	-197.342	0.001	15.36	4096	45.0

3.1. Exact solution for a ring

For a ring $\rho(\mathbf{r})$ can be calculated exactly in the following way: $\rho_{\text{ring}}^{\text{(exact)}}(\mathbf{r}) = \exp(-\beta\phi(\mathbf{r})) \times \int \exp(-\beta\phi(\mathbf{r}')) [g_{n/2}(\mathbf{r}, \mathbf{r}')]^2 d\mathbf{r}'$, where $g_{n/2}(\mathbf{r}, \mathbf{r}')$ is the $n/2$ th order correlation function obtained from a p -stage procedure: $g_1^{(0)}(\mathbf{r}, \mathbf{r}') = \exp(-\beta K_f(\mathbf{r} - \mathbf{r}')^2)$; $g_2^{(1)}(\mathbf{r}, \mathbf{r}') = \int \exp(-\beta\phi(\mathbf{r}'')) g_1^{(0)}(\mathbf{r}, \mathbf{r}'') g_1^{(0)}(\mathbf{r}', \mathbf{r}'') d\mathbf{r}''$; \dots ; $g_{n/2}^{(p)}(\mathbf{r}, \mathbf{r}') = \int \exp(-\beta\phi(\mathbf{r}'')) g_{n/4}^{(p-1)}(\mathbf{r}, \mathbf{r}'') g_{n/4}^{(p-1)}(\mathbf{r}', \mathbf{r}'') d\mathbf{r}''$. The integral of $\rho_{\text{ring}}^{\text{(exact)}}(\mathbf{r})$ yields the PF. The problem reduces to evaluation of integrals over r'' for each pair (r, r') . Results for a quantum 1D oscillator and comparison with the analytic data (table 1) shows the striking accuracy of the numerical method in a wide range of T together with the great number of beads involved and extremely short computer times (compared with typical MC parameters).

3.2. Exact expression for an open chain and related approximation for a ring

For an open chain $\rho(\mathbf{r})$ is $\rho_{\text{open}}^{\text{(exact)}}(\mathbf{r}) \sim \sum_{i=1}^n \exp(-\frac{\beta}{n}\phi(\mathbf{r})) G^{(i)}(\mathbf{r}) G^{(n-i)}(\mathbf{r})$, where functions $G^{(i)}(\mathbf{r})$ are obtained from the following iteration procedure: $G^{(0)}(\mathbf{r}) = 1$; $G^{(i)}(\mathbf{r}) = \int G^{(i-1)}(\mathbf{r}') \exp(-\frac{\beta}{n}\phi(\mathbf{r}')) \exp(-\beta K_f(\mathbf{r} - \mathbf{r}')^2) \dots$

This equation is exact for open chains and can yield an open ring approximation (ORA) $\rho_{\text{ring}}^{\text{(approx)}}(\mathbf{r}) \sim n \exp(-\frac{\beta}{n}\phi(\mathbf{r})) [G^{(n/2)}(\mathbf{r})]^2$. That becomes more and more accurate with increasing n . ORA was used for a quantum particle in a 3D harmonic field, an electron in the H-atom and He⁺, Li²⁺ ions. In all the 3D cases the fast Fourier transform was used (table 2).

3.3. Interacting particles in a Coulomb field, no exchange

Particles are inserted into the external field one after another. The first one is treated within the ORA procedure while a self-consistent iteration for each newly added chain-particle interacting with a *temporarily fixed* distribution of all the rest is organized. This is done on the mean-field level by calculating the ‘correlation integral’ for an arbitrary pair of interacting beads: $\tilde{I}_{\text{corr}}(\mathbf{r}') = \int \frac{\rho_N(\mathbf{r}'')}{N} \exp[-\beta_n V_{\text{int}}(|\mathbf{r}' - \mathbf{r}''|)] d\mathbf{r}''$, which is incorporated into iteration ORA procedure: $\tilde{G}_N^{(i)}(\mathbf{r}) = \int \tilde{G}_N^{(i-1)}(\mathbf{r}') \tilde{I}_{\text{corr}}^{N-1}(\mathbf{r}') \exp(-\beta_n \phi(\mathbf{r}')) \exp(-\beta_n K_f(\mathbf{r} - \mathbf{r}')^2) d\mathbf{r}'$.

The overall distribution of N distinguishable quantum particles is then obtained as: $\tilde{\rho}_N(\mathbf{r}) \sim N n \exp(-\beta_n \phi(\mathbf{r})) [\tilde{G}_N^{(n/2)}(\mathbf{r})]^2$ (iteration is initialized with $\rho_N(\mathbf{r}) = \rho_{N-1}(\mathbf{r}) N / (N - 1)$, $N > 1$). The updated distribution is mixed with the previous one: $\tilde{\tilde{\rho}}_N(\mathbf{r}) = (4\tilde{\rho}_N(\mathbf{r}) + \rho_N(\mathbf{r})) / 5$, so that a few (< 10) iterations per added particle are needed.

The energy of a particle in the external field is calculated as $U_1^{\text{pot}}(\beta) = \int \phi(\mathbf{r}) \rho(\mathbf{r}; \beta_n) d\mathbf{r}$; the inter-particle interaction $U_N^{\text{int}}(\beta) = \frac{N(N-1)}{2} \int \frac{\rho_N(\mathbf{r}; \beta_n)}{N} d\mathbf{r} \int \frac{\rho_N(\mathbf{r}'; \beta_n)}{N} \exp(-\beta_n V_{\text{int}}(|\mathbf{r} -$

$\mathbf{r}'|))V_{\text{int}}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'$. Virial theorem gives for Coulomb interaction $U_N^{\text{kin}} = -\frac{1}{2}(U_N^{\text{pot}} + U_N^{\text{int}})$; so for total energy $U_N^{\text{tot}} = U_N^{\text{pot}} + U_N^{\text{int}} + U_N^{\text{kin}} = \frac{1}{2}(U_N^{\text{pot}} + U_N^{\text{int}})$.

Calculations were made for two electrons in the He atom and in the Li^+ ion (table 2).

4. Conclusion

We presented three different approaches to the treatment of quantum statistical problems. The entropic sampling and expanded ensemble Monte Carlo methods of sections 1 and 2 can readily be applied to more complicated systems than those considered above; though this would require much greater computer efforts. The density functional approach of section 3 appears to be much faster, though so far it has been restricted to low-dimensional cases or cases with spherical symmetry.

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