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The three-electron harmonium atom: The lowest-energy doublet and quadruplet states

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Calculations of sub-μhartree accuracy employing explicitly correlated Gaussian lobe functions produce comprehensive data on the energy $E(\omega)$, its components, and the one-electron properties of the two lowest-energy states of the three-electron harmonium atom. The energy computations at 19 values of the confinement strength ω ranging from 0.001 to 1000.0, used in conjunction with a recently proposed robust interpolation scheme, yield explicit approximants capable of estimating $E(\omega)$ and the potential energy of the harmonic confinement within a few tenths of μhartree for any $\omega \geq 0.001$, the respective errors for the kinetic energy and the potential energy of the electron-electron repulsion not exceeding 2 μhartrees. Thanks to the correct $\omega \to 0$ asymptotics incorporated into the approximants, comparable accuracy is expected for values of ω smaller than 0.001. Occupation numbers of the dominant natural spinorbitals and two different measures of electron correlation are also computed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4717461]

I. INTRODUCTION

Electronic structures of N-electron harmonium atoms, described by the nonrelativistic Hamiltonian,[1–5]

$$\hat{H} = -\frac{1}{2}\sum_{p=1}^{N}\hat{\nabla}_p^2 + \frac{1}{2}\omega^2\sum_{p=1}^{N}r_p^2 + \sum_{p>q=1}^{N}r_{pq}^{-1}\,, \qquad (1)$$

are governed by the magnitude of the confinement strength ω that measures the extent of electron correlation. At the strong-confinement (or the weak-correlation) limit of $\omega \to \infty$, harmonium atoms can be regarded as systems of independent harmonic oscillators weakly perturbed by the electron-electron repulsion. Consequently, their energies $E(\omega)$ are given by the series expansion[3,6–8]

$$E(\omega) = \sum_{j=0}^{\infty} A_j\,\omega^{(2-j)/2}\,, \qquad (2)$$

where the coefficients $\{A_j\}$ depend upon N and the electronic state under consideration. The corresponding electron densities of low-energy states decrease monotonically with the distance from the origin of the coordinate system, making harmonium atoms at the weak-correlation limit very much alike their ordinary counterparts (except for the absence of the nuclear cusp).

What sets apart harmonium atoms from the fully Coulombic systems is the strong-correlation (or the weak-confinement) limit of $\omega \to 0$. While ordinary atoms undergo autoionization below critical values of nuclear charge, the Hamiltonian (1) admits bounded eigenstates for all values of ω. Therefore, upon the confinement strength becoming vanishingly small, the harmonium atoms evolve into the so-called Wigner molecules,[4,5,9,10] which are spherical Coulomb crystals[11] weakly perturbed by the kinetic energy of their constituent electrons. In the relevant series expansion for the energy,[3,4,6]

$$E(\omega) = \sum_{j=0}^{\infty} B_j\,\omega^{(2+j)/3}\,, \qquad (3)$$

the first two terms are simply the electrostatic energy of the pertinent Coulomb crystal and the zero-point energy of harmonic vibrations about the equilibrium geometry determined by the balance between the harmonic confinement and the electron-electron repulsion. Whereas the dynamical electron correlation dominates at the strong-confinement limit, the Wigner molecules are perfect examples of systems involving the nondynamical correlation with the consequent electron localization and the asymptotic vanishing of occupation numbers of *all* the natural spinorbitals.[10]

It is the infinite tunability of the absolute magnitudes and relative extents of the dynamical and nondynamical electron correlations that makes harmonium atoms ideal tools for calibration, testing, and benchmarking of approximate electronic structure methods of quantum chemistry and solid-state physics. In this respect, thanks to their realistic electron densities and smooth variation of electronic properties between the $\omega \to 0$ and $\omega \to \infty$ limits, these systems hold a definite advantage over the homogeneous electron gas, in which the constant-density ground state is abruptly replaced by the Wigner crystal due to crossing of energy levels at some critical value of the electron density (which in this case serves the role analogous to that of ω).

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Despite the availability of exact wavefunctions and energies for certain values of ω[1–3] that has prompted several studies assessing accuracies of diverse methods of quantum chemistry,[12–20] the trivial nature of electron correlation in the two-electron harmonium atom limits its usefulness, especially in research on electron-pair and density-matrix functional theories. In contrast, the three-electron species, for which only numerical and asymptotic solutions of the Schrödinger equations are possible, offers insights into more intricate interplays between the same- and opposite-spin correlation effects.

Thus far, the three-electron harmonium atom has been the subject of relatively few investigations. The study of the $\omega \to \infty$ limit has resulted in closed-form expressions for the coefficients A_0, A_1, and A_2,

$$A_0 = \frac{11}{2}\,, \tag{4}$$

$$A_1 = \frac{5}{2}\sqrt{\frac{2}{\pi}}\,, \tag{5}$$

and

$$A_2 = \frac{49}{9} + \frac{1}{6\pi}\left[-88 + 2\sqrt{3} - 173\ln 2 + 98\ln(1+\sqrt{3})\right] \approx -0.176654 \tag{6}$$

for the $^2P_-$ doublet ground state, and

$$A_0 = \frac{13}{2}\,, \tag{7}$$

$$A_1 = 2\sqrt{\frac{2}{\pi}}\,, \tag{8}$$

and

$$A_2 = \frac{23}{9} + \frac{8}{3\pi}\left[-4 + \sqrt{3} - 7\ln 2 + 4\ln(1+\sqrt{3})\right] \approx -0.0756103 \tag{9}$$

for the $^4P_+$ quartet first excited state.[6] The analysis of the strong-correlation limit of $\omega \to 0$ has yielded

$$B_0 = \frac{1}{2}\,3^{5/3} \tag{10}$$

and

$$B_1 = \frac{1}{2}\left(3 + \sqrt{3} + \sqrt{6}\right) \tag{11}$$

for both of the aforementioned states.[4,6]

Numerical computations of the ground- and excited-state energies of the three-electron harmonium atom have also been carried out, involving methods ranging from the Hartree-Fock approximation[21] and low-level electron-correlation approaches [22] to Monte Carlo calculations [23] and the full configuration interaction (FCI) employed in conjunction with extrapolation to the complete basis set (CBS).[24] The FCI/CBS study, in which approximate energies of the $^2P_-$ and $^4P_+$ states have been computed for 12 values of ω between 0.1 and 1000.0, has uncovered both advantages and disadvantages of using uncorrelated Gaussian basis sets in electronic structure calculations on harmonium atoms. On one hand, unlike those relying upon explicitly correlated basis sets, such calculations produce not only the actual energies but also their corresponding limits for specific angular momenta that are of much value in assessment of the accuracy of approximate methods involving finite basis sets. On the other hand, they afford energies of inferior accuracy and, due to the emergence of linear dependencies among the basis functions, are not feasible for smaller values of ω.

Prompted by those observations, we have recently embarked upon large-scale calculations that aimed at obtaining highly accurate energies and other electronic properties of the lowest-energy $^2P_-$ and $^4P_+$ states of the three-electron harmonium atom for a wide range of the confinement strengths. The results of these definitive calculations are reported in this paper.

II. NUMERICAL METHODS

Variational energies of the lowest-energy $^2P_-$ and $^4P_+$ states of the three-electron harmonium atom have been computed with accuracy exceeding 1 μhartree for 19 values of ω belonging to the set $\{0.001, 0.002, 0.005, 0.1, \ldots, 1000.0\}$ using the ansatz

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \sigma_1, \sigma_2, \sigma_3) = \sum_{I=1}^{M} C_I\, \hat{A}\left[\Theta(\sigma_1, \sigma_2, \sigma_3)\; \hat{P}\, \chi_I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\right], \tag{12}$$

where $\Theta(\sigma_1, \sigma_2, \sigma_3)$ is the appropriate spin function, $\hat{A}$ is the three-electron antisymmetrizer that ensures proper permutational symmetry, $\hat{P}$ is the spatial symmetry projector, and

$$\chi_I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \exp\left[-\sum_{p=1}^{3} \alpha_{Ip}\,(\mathbf{r}_p - \mathbf{R}_{Ip})^2 - \sum_{p>q=1}^{3} \beta_{Ipq}\,(\mathbf{r}_p - \mathbf{r}_q)^2\right] \tag{13}$$

is the Ith explicitly correlated Gaussian lobe primitive. Since their introduction over half a century ago,[25,26] such primitives have found numerous applications in nonrelativistic electronic structure studies, including those yielding the currently most accurate energies of atoms and molecules containing between two and five electrons.[27–31] Their popularity stems from the fact that, despite satisfying neither the nucleus-electron nor electron-electron cusp conditions, they are flexible enough to recover most of the correlation energy even with relatively short expansions (12) while allowing for rapid computations of all the necessary integrals.

The wavefunctions of the harmonium atoms are eigenfunctions of both the $\hat{L}^2$ and $\hat{L}_z$ operators with the respective eigenvalues of $L(L+1)$ and m_L. The primitives (13) do not correspond to any particular value of L, except for the case when all the vectors $\{\mathbf{R}_{Ip}\}$ vanish (which yields $L = 0$). In principle, the multiplication of these primitives by either respective angular functions[23] or polynomials in $\{x_p\}$, $\{y_p\}$, and $\{z_p\}$ $(p = 1, 2, 3)$[32] would produce their counterparts pertaining to higher angular momenta. However, the lobe primitives are numerically expedient and efficient when the energies are minimized with respect to all the variational parameters $\{C_I, \mathbf{R}_{Ip}, \alpha_{Ip}, \beta_{Ipq}\}$.[33]

The spatial symmetry projector

$$\hat{P} = \sum_{m=1}^{N_{sym}} a_m \, \hat{p}_m \, , \tag{14}$$

where the index m runs over all the operations $\{\hat{p}_m\}$ belonging to a finite symmetry point group and the coefficients $\{a_m\}$ depend on the chosen irreducible representation, acts upon the primitive χ_I in the following manner:

$$\hat{P} \, \chi_I(\mathbf{R}_{I1}, \mathbf{R}_{I2}, \mathbf{R}_{I3}) = \sum_{m=1}^{N_{sym}} a_m \, \chi_I(\hat{p}_m \mathbf{R}_{I1}, \hat{p}_m \mathbf{R}_{I2}, \hat{p}_m \mathbf{R}_{I3}) \, . \tag{15}$$

While lower than K_h, the spatial symmetries employed in the actual calculations (A_{2g} of the D_{4h} point group for the $^4P_+$ state and Σ_u of the $D_{\infty h}$ point group for the $^2P_-$ state), conserve the correct parities.[34] In order to minimize the numbers of primitives, the symmetries have been enforced with simple expedients. Thus, for the $^4P_+$ state, the vectors $\{\mathbf{R}_{Ip}\}$ were constrained to the xy plane, yielding the A_2 symmetry of the C_{4v} point group and the corresponding projector

$$\hat{P} = \hat{E} + \hat{C}_4 + \hat{C}_2 + \hat{C}_4^3 - \hat{\sigma}_{v1} - \hat{\sigma}_{v2} - \hat{\sigma}_{d1} - \hat{\sigma}_{d2} \, . \tag{16}$$

Similarly, for the $^2P_-$ state, the A_u symmetry of the C_i point group, corresponding to the projector

$$\hat{P} = \hat{E} - \hat{i} \, , \tag{17}$$

has been enforced by restricting the vectors $\{\mathbf{R}_{Ip}\}$ to the z axis. However, for the three smallest values of ω, where the Wigner molecule with its off-center maximum in electron density[4,5,10] emerges, such symmetry restriction results in exceedingly long expansions (12). Lowering the symmetry to A_{2u} of the D_{4h} point group and removing all the constraints on the vectors $\{\mathbf{R}_{Ip}\}$ rectifies this problem.

Stitching of the expansions (2) and (3) while accurately reproducing the computed energies is possible with the newly developed robust interpolation scheme.[35] The appropriate $[\frac{K}{1+2}]$ approximants read

$$E(\omega) = \sum_{k=0}^{K} C_{K,k} \, (1-t)^{K-k-2} \, t^{k+2} \, , \tag{18}$$

where t is the real-valued solution of the equation

$$\omega = \omega_0 \, t^3 \, (1-t)^{-2} \, . \tag{19}$$

The parameters $C_{K,0}$, $C_{K,1}$, $C_{K,K-2}$, $C_{K,K-1}$, and $C_{K,K}$ are entirely determined by the coefficients A_0, A_1, A_2, B_0, and B_1 [Eqs. (4)–(11)],

$$C_{K,0} = \omega_0^{2/3} \, B_0 \, , \tag{20}$$

$$C_{K,1} = \frac{3K-2}{3} \, \omega_0^{2/3} \, B_0 + \omega_0 \, B_1 \, , \tag{21}$$

$$C_{K,K-2} = \frac{(K-1)(K-2)}{2} \, \omega_0 \, A_0 + \frac{2K-1}{2} \, \omega_0^{1/2} \, A_1 + A_2 , \tag{22}$$

$$C_{K,K-1} = (K-1) \, \omega_0 \, A_0 + \omega_0^{1/2} \, A_1 \, , \tag{23}$$

and

$$C_{K,K} = \omega_0 \, A_0 \, , \tag{24}$$

whereas the remaining parameters $\{C_{K,2}, \ldots, C_{K,K-3}\}$ are obtained with the least-square fit of the computed energies. Finally, the parameter ω_0 follows from minimization of the maximum absolute difference between the computed energies and those produced by the respective approximant.

The availability of differentiable approximants $E(\omega)$ allows accurate estimation of not only the total energy for any value of ω but also its components, namely[3] the kinetic energy

$$T(\omega) = \frac{3}{2} \, \omega E'(\omega) - E(\omega) \, , \tag{25}$$

the potential energy of the harmonic confinement

$$V(\omega) = \frac{1}{2} \, \omega E'(\omega) \, , \tag{26}$$

and the potential energy of the electron-electron repulsion

$$W(\omega) = 2E(\omega) - 2 \, \omega E'(\omega) \, , \tag{27}$$

where

$$\omega E'(\omega) \equiv \omega \frac{dE(\omega)}{d\omega} = \sum_{k=0}^{K} C_{K,k} \, (k+2-Kt) \, (3-t)^{-1} (1-t)^{K-k-2} \, t^{k+2} . \tag{28}$$

Natural spinorbitals and their occupation numbers $\{n_i(\omega)\}$ have been obtained by diagonalization of the finite-matrix representations $\{\Gamma_{IJ}\}$ of the respective 1-matrices. These representations have been computed with accurate Gaussian quadratures of the multiple integrals

$$\Gamma_{IJ} = \sum_{\sigma} \int \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \sigma_1, \sigma_2, \sigma_3) \, \Psi(\mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}_3, \sigma_1, \sigma_2, \sigma_3) \times \phi_I(\mathbf{r}_1) \, \phi_J(\mathbf{r}'_1) \, d\mathbf{r}_1 \, d\mathbf{r}'_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 , \tag{29}$$

where $\sum_\sigma$ denotes the appropriate collective spin summations and

$$\phi_I(\mathbf{r}) = \zeta^{3/4} \, H_{I_x}(\sqrt{\zeta} \, x) \, H_{I_y}(\sqrt{\zeta} \, y) \, H_{I_z}(\sqrt{\zeta} \, z) \, \exp(-\zeta \, r^2/2) \, . \tag{30}$$

In Eq. (30), $H_k(x)$ is the kth normalized Hermite polynomial and $I \equiv (I_x, I_y, I_z)$. The quality of the projection (29) has been optimized by maximizing the trace of Γ with respect to ζ. In practice, employment of the basis functions (30) with $0 \le I_x, I_y, I_z \le 10$ (for the total of $11^3 = 1321$ functions) has been found to produce sufficiently accurate natural spinorbitals and their occupation numbers.

Occupation numbers of natural spinorbitals enter formulae for various measures of electron correlation.[36–38] Two of such measures, namely the index of almost

idempotency,[36,38]

$$\mathcal{I}(\omega) = \sum_i n_i(\omega)\,[\,1 - n_i(\omega)\,]\,, \tag{31}$$

and the correlation entropy[37,38]

$$S(\omega) = -\sum_i n_i(\omega)\ \ln\ n_i(\omega)\,, \tag{32}$$

have been computed. Analysis of the occupation numbers at the weak- and strong-correlation limits[10] leads to the conclusion that the proper approximant for $\mathcal{I}(\omega)$ has the form

$$\mathcal{I}(\omega) = \sum_{k=0}^{K} c_{K,k}\,(1-t)^{K-k+2}\ t^k\,, \tag{33}$$

where $c_{K,0}$ equals the number of electrons in question and t is defined by Eq. (19). On the other hand, since the analogous asymptotic series for $S(\omega)$ involves logarithmic terms, they are not amenable to stitching with the aforedescribed interpolation.

III. RESULTS AND DISCUSSION

Among all the three-electron Slater determinants built from one-particle wavefunctions of a harmonic oscillator with a given ω, those corresponding to the configurations $s\bar{s}p_m$ ($m = -1, 0, 1$) possess the lowest energy. However, according to the present calculations, the triply-degenerate $^2P_-$ doublet is the ground state of the three-electron harmonium atom for all the values of ω rather than only at the weak-correlation limit. Inspection of the computed energies (Table I) reveals that the strong-confinement expansion (2) truncated at three terms yields values of $E(\omega)$ accurate to within 1% for $\omega > 0.4$.

TABLE I. The total energy and its components of the $^2P_-$ ground state of the three-electron harmonium atom.[a]

ω	M[b]	E(ω)	T(ω)	V(ω)	W(ω)
1000.0	131	5562.9024148	2734.4057549	2765.7693899	62.7272701
500.0	198	2794.4275166	1364.0240136	1386.1505100	44.2529929
200.0	148	1128.0345088	543.1213467	557.0519518	27.8612103
100.0	162	569.7728341	270.1857383	279.9861908	19.6009050
50.0	139	288.9314294	134.1446524	141.0253606	13.7614163
20.0	150	118.7492107	52.9374089	57.2288732	8.5829286
10.0	152	61.1385255	26.0870108	29.0751788	5.9763360
5.0	136	31.7939128	12.7939735	14.8626287	4.1373105
2.0	116	13.6600905	4.9446231	6.2015712	2.5138962
1.0	131	7.3397411	2.3916874	3.2438095	1.7042443
0.5	148	4.0132179	1.1507610	1.7213263	1.1411306
0.2	149	1.8582001	0.4358712	0.7646904	0.6576385
0.1	166	1.0594492	0.2095449	0.4229980	0.4269063
0.05	180	0.6138518	0.1012844	0.2383787	0.2741886
0.02	225	0.3048014	0.0391424	0.1146479	0.1510111
0.01	457	0.1819359	0.0192012	0.0670457	0.0956890
0.005	145[c]	0.1096579	0.0094614	0.0397065	0.0604901
0.002	223[c]	0.0568472	0.0037303	0.0201925	0.0329244
0.001	318[c]	0.0348458	0.0018500	0.0122319	0.0207639

[a]All energies in hartree.
[b]The number of basis functions in the expansion (12).
[c]Calculations within the D_{4h} point group, see the text for explanation.

TABLE II. The individual-spin components of the kinetic and confinement energies of the $^2P_-$ ground state of the three-electron harmonium atom.[a]

ω	$T_\alpha(\omega)$	$T_\beta(\omega)$	$V_\alpha(\omega)$	$V_\beta(\omega)$
1000.0	1989.0767832	745.3289717	2011.0317772	754.7376127
500.0	992.3095874	371.7144262	1007.7985630	378.3519470
200.0	395.1777625	147.9435842	404.9295799	152.1223719
100.0	196.6228859	73.5628524	203.4835539	76.5026369
50.0	97.6441971	36.5004554	102.4609812	38.5643794
20.0	38.5492641	14.3881448	41.5534626	15.6754106
10.0	19.0041401	7.0828707	21.0959042	7.9792746
5.0	9.3242298	3.4697437	10.7721644	4.0904643
2.0	3.6051012	1.3395219	4.4845316	1.7170395
1.0	1.7434928	0.6481946	2.3392439	0.9045656
0.5	0.8379286	0.3128324	1.2362435	0.4850828
0.2	0.3159915	0.1198797	0.5446321	0.2200583
0.1	0.1509211	0.0586238	0.2985682	0.1244298
0.05	0.0722512	0.0290333	0.1663939	0.0719849
0.02	0.0274846	0.0116578	0.0787618	0.0358861
0.01	0.0133217	0.0058795	0.0455753	0.0214704
0.005	0.0064979	0.0029635	0.0267825	0.0129240
0.002	0.0025374	0.0011929	0.0135392	0.0066533
0.001	0.0012522	0.0005977	0.0081826	0.0040494

[a]All energies in hartree.

Conversely, the two-term weak-confinement expansion (3) produces energy estimates of such accuracy only for $\omega < 0.02$.

At large values of ω, $E(\omega)$ is dominated by the kinetic energy and the potential energy of the harmonic confinement. For these energy components, it is possible to compute the individual-spin contributions $T_s(\omega)$ and $V_s(\omega)$ ($s = \alpha, \beta$, Table II). At the $\omega \to \infty$ limit, both the $T_\alpha(\omega)/T_\beta(\omega)$ and $V_\alpha(\omega)/V_\beta(\omega)$ ratios tend to $\frac{(5/4)+(3/4)}{(3/4)} = 8/3$ (Fig. 1). On the other hand, at the limit of $\omega \to 0$, where a classical description becomes valid, the ratios become equal to 2, simply reflecting the totalities of particles with individual spins.

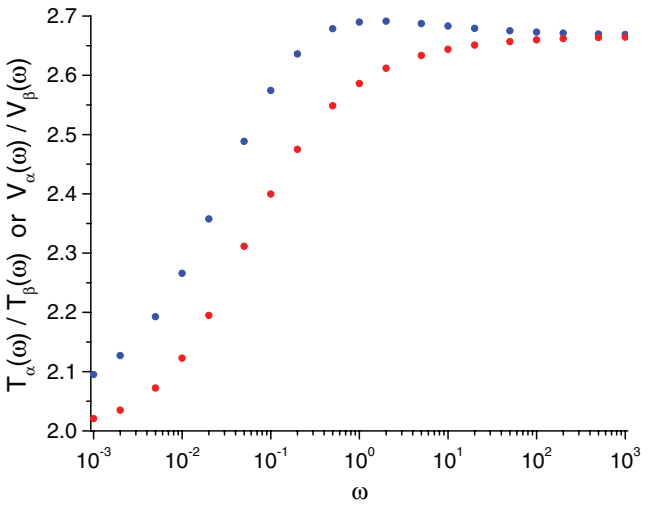

FIG. 1. The dependence of the ratios $T_\alpha(\omega)/T_\beta(\omega)$ (blue dots) and $V_\alpha(\omega)/V_\beta(\omega)$ (red dots) on the confinement strength for the $^2P_-$ state of the three-electron harmonium atom.

TABLE III. The total energy and its components of the $^4P_+$ first excited state of the three-electron harmonium atom.[a]

ω	M[b]	E(ω)	T(ω)	V(ω)	W(ω)
1000.0	250	6550.3872366	3237.4596057	3262.6156141	50.3120168
500.0	216	3285.6071494	1616.1545067	1633.9205520	35.5320907
200.0	173	1322.4924099	644.4329526	655.6417875	22.4176698
100.0	148	665.8826969	321.0851132	328.9892700	15.8083137
50.0	137	336.2090496	159.7531499	165.3207331	11.1351666
20.0	124	137.0622507	63.2891151	66.7837886	6.9893470
10.0	131	69.9725716	31.3107229	33.7610982	4.9007505
5.0	125	35.9953228	15.4289150	17.1414126	3.4249951
2.0	107	15.1853142	6.0042894	7.0632012	2.1178236
1.0	107	8.0259277	2.9168822	3.6476033	1.4614421
0.5	81	4.3106903	1.4052467	1.9053123	1.0001313
0.2	108	1.9498681	0.5278552	0.8259078	0.5961051
0.1	186	1.0947376	0.2493872	0.4480416	0.3973088
0.05	221	0.6266728	0.1173191	0.2479973	0.2613564
0.02	243	0.3079190	0.0434012	0.1171067	0.1474111
0.01	313	0.1829731	0.0206388	0.0678706	0.0944637
0.005	565	0.1100055	0.0099264	0.0399773	0.0601017
0.002	691	0.0569337	0.0038356	0.0202565	0.0328417
0.001	880	0.0348783	0.0018844	0.0122542	0.0207396

[a]All energies in hartree.
[b]The number of basis functions in the expansion (12).

The $sp_m p_{m'}$ ($m \neq m' = -1, 0, 1$) configurations of the $\omega \to \infty$ limit give rise to the triply-degenerate $^4P_+$ quartet that remains the first excited state of the three-electron harmonium atom for all the values of ω (Table III). As in the case of the ground state, the truncated weak- and strong-correlation expansions for $E(\omega)$ perform rather poorly, producing energy estimates accurate to within 1% only for $\omega > 0.14$ and $\omega < 0.008$, respectively. The doublet-quartet energy splitting, which is significant at strong confinements, vanishes as the confinement strength tends to zero.[4]

It is instructive to compare the highly accurate energies of the present study with those published previously.[23,24] In general, excellent (sub-μhartree) agreement with the Monte Carlo results[23] is observed except for the energy of the $^2P_-$ state at $\omega = 0.5$, where the present value is lower by 6 μhartree (Table I). Despite judicious extrapolation employed, the FCI/CBS energies[24] fare much worse, the energy errors steadily rising with a decreasing confinement strength: 2 μhartree at $\omega = 1000.0$, 8 μhartree at $\omega = 10.0$, 35 μhartree at $\omega = 0.5$, and 44 μhartree at $\omega = 0.1$ for the $^2P_-$ state; 1 μhartree at $\omega = 1000.0$, 1 μhartree at $\omega = 10.0$, 8 μhartree at $\omega = 0.5$, and 13 μhartree at $\omega = 0.1$ for the $^4P_+$ state.

The quality of the data compiled in Tables I and III is readily assessed by analysing the behavior of the $[\frac{K}{1+2}]$ approximants (18) and (19) that smoothly interpolate energies between the weak- and strong-correlation limits (Fig. 2). It is found that, after initially decreasing with K in a steady fashion, the maximum absolute deviations of the approximate energies from their "exact" computed counterparts reach temporary plateaus at $K = 10$, where they amount to 0.3 and 0.4 μhartree for the $^2P_-$ and $^4P_+$ states, respectively. This extent of numerical noise is consistent with the convergence

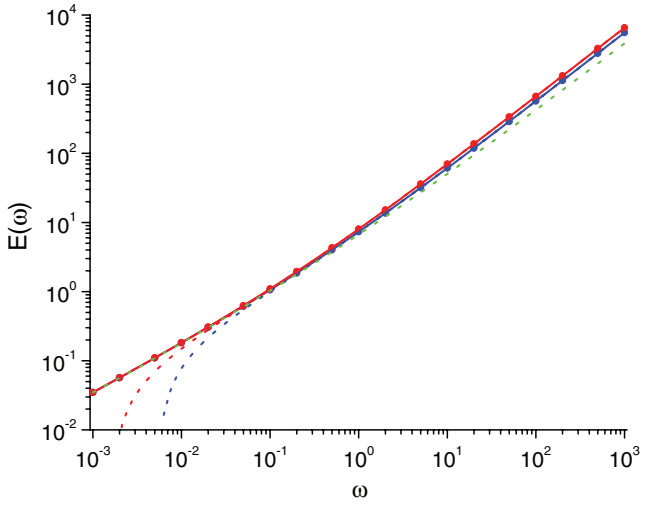

FIG. 2. The dependence of the total energy on the confinement strength for the three-electron harmonium atom. The blue dots and lines: the $^2P_-$ state, the red dots and lines: the $^4P_+$ state; the dots, the solid and the dotted lines denote the computed data, the approximants, and the large-ω expansion (2), respectively, whereas the dotted green line denotes the small-ω expansion (3) that is common to both the states.

of energies observed in the variational calculations that is suggestive of their accuracy in the order of 0.1 μhartree.[39] The high quality of the computed energies and wavefunctions is independently confirmed by the impressive agreement between the "exact" expectation-value energy components and their counterparts calculated according to Eqs. (25)–(28) from the $[\frac{10}{1+2}]$ energy approximant (with the parameters listed in Table IV) and its first derivative, the maximum absolute deviations amounting to 1.4 (1.4) μhartree for $T(\omega)$, 0.4 (0.5) μhartree for $V(\omega)$, and 2.0 (1.9) μhartree for $W(\omega)$ of the $^2P_-$ ($^4P_+$) state.

In calibration and benchmarking of approximate electron correlation methods, the knowledge of accurate occupation numbers of natural spinorbitals is as important as that of energies. The computed occupation numbers of dominant natural spinorbitals, compiled in Tables V–VII are expected to be accurate to within ca. 10^{-5}. In both the cases of the strongly

TABLE IV. The parameters of the $[\frac{10}{1+2}]$ approximants for the total energies of the $^2P_-$ and $^4P_+$ states of the three-electron harmonium atom.[a]

State	$^2P_-$	$^4P_+$
ω_0	0.06065557442	0.08602151109
$C_{10,0}$	0.4816733024	0.6080091855
$C_{10,1}$	4.713417723	5.983635883
$C_{10,2}$	20.69834808	26.45130240
$C_{10,3}$	53.77973749	69.26555948
$C_{10,4}$	91.11439973	118.1960178
$C_{10,5}$	105.8686226	139.1568142
$C_{10,6}$	84.65349282	114.5061120
$C_{10,7}$	46.18853978	65.12956009
$C_{10,8}$	16.50016288	24.49970722
$C_{10,9}$	3.493715488	5.500288290
$C_{10,10}$	0.3336056593	0.5591398221

[a]See Eqs. (18) and (19).

TABLE V. The occupation numbers of the strongly occupied natural spinorbitals of the $^2P_-$ and $^4P_+$ states of the three-electron harmonium atom.

	$^2P_-$			$^4P_+$	
ω	p_0	s	$\overline{s}$	s	$p_{\pm1}$
1000.0	0.999988	0.999985	0.999977	0.999997	0.999995
500.0	0.999975	0.999971	0.999954	0.999995	0.999989
200.0	0.999939	0.999928	0.999886	0.999988	0.999973
100.0	0.999878	0.999856	0.999773	0.999975	0.999946
50.0	0.999758	0.999714	0.999548	0.999951	0.999892
20.0	0.999404	0.999296	0.998884	0.999878	0.999734
10.0	0.998830	0.998613	0.997801	0.999759	0.999475
5.0	0.997723	0.997289	0.995695	0.999527	0.998968
2.0	0.994606	0.993532	0.989704	0.998858	0.997508
1.0	0.989848	0.987749	0.980456	0.997805	0.995207
0.5	0.981362	0.977364	0.963807	0.995841	0.990930
0.2	0.960535	0.951816	0.922792	0.990604	0.979656
0.1	0.933923	0.919518	0.871078	0.983078	0.963877
0.05	0.895183	0.873845	0.798618	0.970410	0.938488
0.02	0.823845	0.795040	0.676685	0.941210	0.885157
0.01	0.756550	0.727114	0.576149	0.905577	0.828089
0.005	0.681922	0.657702	0.479648	0.855174	0.758461
0.002	0.580567	0.568655	0.368830	0.765160	0.655808
0.001	0.507569	0.504063	0.300161	0.683940	0.578544

TABLE VII. The occupation numbers of the dominant weakly occupied natural spinorbitals of the $^4P_+$ first excited state of the three-electron harmonium atom.

ω	$d_{\pm2}$	$d_{\pm1}$	p_0
1000.0	0.000003	0.000002	0.000002
500.0	0.000006	0.000003	0.000003
200.0	0.000016	0.000008	0.000008
100.0	0.000032	0.000016	0.000016
50.0	0.000064	0.000031	0.000031
20.0	0.000158	0.000078	0.000077
10.0	0.000313	0.000154	0.000153
5.0	0.000616	0.000302	0.000300
2.0	0.001493	0.000731	0.000724
1.0	0.002884	0.001409	0.001392
0.5	0.005489	0.002673	0.002630
0.2	0.012424	0.006018	0.005885
0.1	0.022234	0.010711	0.010429
0.05	0.038154	0.018257	0.017727
0.02	0.071719	0.033973	0.033058
0.01	0.107169	0.050411	0.049510
0.005	0.148609	0.069591	0.069584
0.002	0.202465	0.094986	0.098500
0.001	0.233679	0.110298	0.118166

(Table V) and the dominant weakly occupied (Tables VI and VII) natural spinorbitals, the occupation numbers vary smoothly with ω, the leading asymptotic term beyond the constant of zero or one being proportional to ω^{-1} at the weak-correlation limit. The vanishing of the occupation numbers at certain values of ω, encountered previously in the case of the two-electron harmonium atom,[3] is not observed. It is not clear at present whether this vanishing is peculiar to the two-electron species or it is not found in the present study because of the limited range of ω considered.

Both the index of almost idempotency [Eq. (31)] and the correlation entropy [Eq. (32)] decrease monotonically with ω (Figs. 3 and 4). In the case of the $^2P_-$ ground state, this behavior is also observed for individual spin components of these measures of electron correlation. The computed values of $\mathcal{I}(\omega)$ are consistent with their $\omega \to 0$ limits that equal the respective numbers of electrons (we note in passing that the "linear entropies" of the two-electron harmonium atom displayed in Fig. 1 of Ref. 38 violate such asymptotics and thus are obviously in error). The approximants (33) with $K = 8$

TABLE VI. The occupation numbers of the dominant weakly occupied natural spinorbitals of the $^2P_-$ ground state of the three-electron harmonium atom.

ω	$p_{\pm1}$	s	$d_{\pm1}$	$\overline{p}_{\pm1}$	$\overline{p}_0$	$\overline{s}$	$\overline{d}_{\pm1}$
1000.0	0.000006	0.000004	0.000003	0.000007	0.000004	0.000001	0.000001
500.0	0.000013	0.000008	0.000007	0.000015	0.000008	0.000002	0.000001
200.0	0.000031	0.000019	0.000017	0.000037	0.000019	0.000006	0.000004
100.0	0.000062	0.000038	0.000033	0.000074	0.000037	0.000012	0.000007
50.0	0.000124	0.000076	0.000066	0.000147	0.000074	0.000024	0.000014
20.0	0.000307	0.000186	0.000163	0.000364	0.000182	0.000059	0.000036
10.0	0.000606	0.000365	0.000320	0.000720	0.000357	0.000115	0.000072
5.0	0.001193	0.000711	0.000623	0.001414	0.000695	0.000225	0.000144
2.0	0.002879	0.001685	0.001476	0.003408	0.001642	0.000531	0.000357
1.0	0.005518	0.003167	0.002776	0.006516	0.003075	0.000990	0.000706
0.5	0.010344	0.005794	0.005090	0.012168	0.005593	0.001780	0.001378
0.2	0.022498	0.012138	0.010750	0.026246	0.011564	0.003539	0.003221
0.1	0.038137	0.020047	0.017972	0.044075	0.018768	0.005387	0.005836
0.05	0.060243	0.031199	0.028533	0.068797	0.028439	0.007308	0.009930
0.02	0.096639	0.050563	0.048316	0.108301	0.043963	0.008916	0.017701
0.01	0.124206	0.066989	0.067377	0.136944	0.056146	0.009291	0.024774
0.005	0.146562	0.082347	0.088474	0.158465	0.067061	0.011739	0.032023
0.002	0.163958	0.096941	0.115007	0.171020	0.077250	0.016848	0.040833
0.001	0.168097	0.102231	0.130364	0.168675	0.080708	0.020934	0.046345

TABLE VIII. The parameters of the approximants (33) for the index of almost idempotency of the $^2P_-$ and $^4P_+$ states of the three-electron harmonium atom.

	$^2P_-$ (α)	$^2P_-$ (β)	$^2P_-$ (*all*)	$^4P_+$ (*all*)
ω_0	0.01484874089	0.01530072302	0.01413903705	0.004896250478
$c_{8,0}$	2.000000000	1.000000000	3.000000000	3.000000000
$c_{8,1}$	20.24421304	12.12803986	33.33619779	16.33346031
$c_{8,2}$	60.15209407	20.84392444	75.94978756	148.8331478
$c_{8,3}$	207.3145352	168.6699549	388.4239730	195.8369088
$c_{8,4}$	207.2133717	58.39362443	262.3008601	438.9297534
$c_{8,5}$	285.4437247	270.7200045	554.3720075	341.7734661
$c_{8,6}$	135.6185831	113.1232035	264.9911628	188.8322466
$c_{8,7}$	34.83841331	30.12866095	68.47998523	49.79905454
$c_{8,8}$	3.648558054	3.001496875	7.092185256	5.508184935

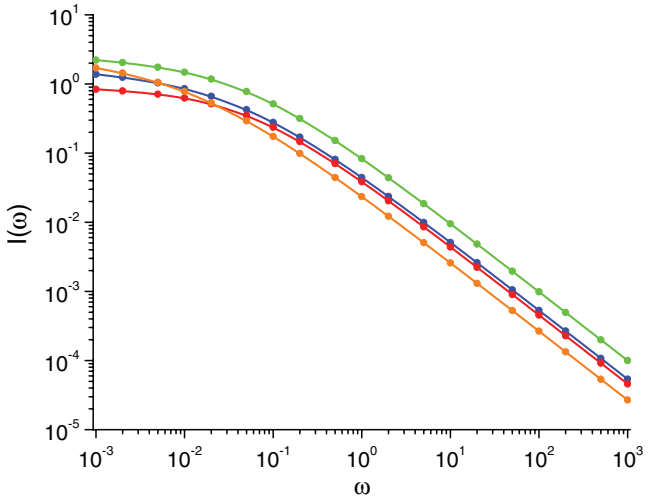

FIG. 3. The dependence of the index of almost idempotency on the confinement strength for the three-electron harmonium atom. Blue dots and lines: the α electrons of the $^2P_-$ state, red dots and lines: the β electrons of the $^2P_-$ state, green dots and lines: all the electrons of the $^2P_-$ state, orange dots and lines: all the electrons of the $^4P_+$ state; the dots and the solid lines denote the computed data and the approximants, respectively.

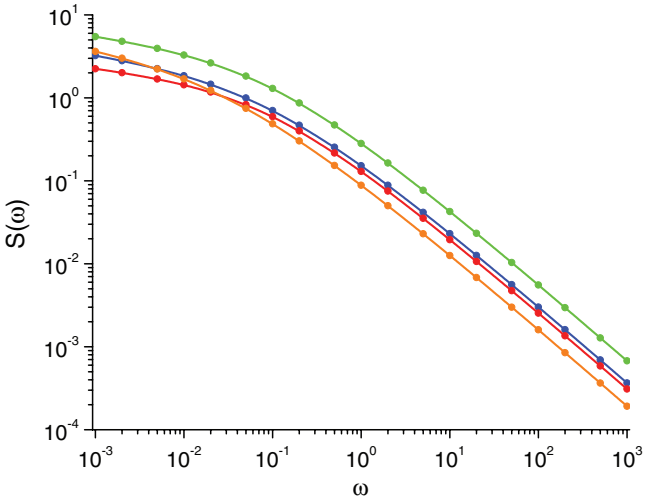

FIG. 4. The dependence of the correlation entropy on the confinement strength for the three-electron harmonium atom. Blue dots: the α electrons of the $^2P_-$ state, red dots: the β electrons of the $^2P_-$ state, green dots: all the electrons of the $^2P_-$ state, orange dots: all the electrons of the $^4P_+$ state; the lines are drawn for guidance only.

and the parameters listed in Table VIII reproduce the "exact" values of $\mathcal{I}(\omega)$ within $4 \cdot 10^{-6}$ in all cases.

IV. CONCLUSIONS

The present calculations of sub-μhartree accuracy produce data on the energy $E(\omega)$, its components, and the one-electron properties of the two lowest-energy states of the three-electron harmonium atom that are both comprehensive and definitive. When employed in conjunction with the recently proposed[35] robust interpolation scheme, the energy computations at 19 values of the confinement strength ω ranging from 0.001 to 1000.0 yield explicit approximants capable of estimating $E(\omega)$ and the potential energy of the harmonic confinement $V(\omega)$ within a few tenths of μhartree for any $\omega \geq 0.001$, the respective errors for the kinetic energy $T(\omega)$ and the potential energy of the electron-electron repulsion $W(\omega)$ not exceeding 2 μhartrees. Thanks to the correct $\omega \to 0$ asymptotics incorporated into the approximants, comparable accuracy is expected for values of ω smaller than 0.001. It is also worth mentioning that all the coefficients $\{C_{K,k}\}$ of the energy approximant are positive, which eliminates round-off errors due to partial term cancellations. The same is true about the respective approximants for the index of almost idempotency.

Comparison of the computed energies with those previously published reveals some discrepancies that apparently stem from the substandard performance of the extrapolation employed in the workout of the FCI/CBS data[24] and an error of unknown origin in one instance of the results of Monte Carlo calculations.[23] Overall, the excellent performance of both the explicitly correlated Gaussian lobe functions and the robust interpolation scheme in calculations on the three-electron harmonium atom bode well for analogous studies of systems with larger numbers of particles.

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[34]The extent of symmetry breaking by the computed wavefunctions is readily assessed with the expectation values of the $\hat{L}^2$ operator for the individual natural spinorbitals that are expected to approach $L(L+1), L = 0, 1, 2, \ldots$ at the limit of $\omega \to \infty$. For example, one obtains the expectation values of 0.000006, 2.000000, and 2.000000 for the strongly occupied natural spinorbitals pertaining to the $^4P_+$ state of the three-electron harmonium atom with $\omega = 1000$.
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[39]The convergence of the computed energies is illustrated by the following examples: For the $^2P_-$ state, one obtains $E(10.0) = 61.13852568$, 61.13852556, and 61.13852553, for $M = 39$, 69, and 152, respectively, which yields the extrapolated value of 61.13852552 based upon a [1/1] Padé approximant. Similarly, one obtains $E(0.1) = 1.05944965$, 1.05944933, and 1.05944923 (for $M = 36$, 71, and 166), and $E(0.001) = 0.03484805$, 0.03484604, and 0.03484583 (for $M = 39$, 100, and 225), which results in the respective extrapolated energies of 1.05944918 and 0.03484571. For the $^4P_+$ state, the analogous data for $E(0.001)$ read 0.03488111, 0.03487876, and 0.03487830 (for $M = 225$, 572, and 880), which corresponds to the extrapolated energy of 0.03487750.