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Benchmark calculations on the lowest-energy singlet, triplet, and quintet states of the four-electron harmonium atom

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For a wide range of confinement strengths ω , explicitly-correlated calculations afford approximate energies $E(\omega)$ of the ground and low-lying excited states of the four-electron harmonium atom that are within few μ hartree of the exact values, the errors in the respective energy components being only slightly higher. This level of accuracy constitutes an improvement of several orders of magnitude over the previously published data, establishing a set of benchmarks for stringent calibration and testing of approximate electronic structure methods. Its usefulness is further enhanced by the construction of differentiable approximants that allow for accurate computation of $E(\omega)$ and its components for arbitrary values of ω . The diversity of the electronic states in question, which involve both single- and multideterminantal first-order wavefunctions, and the availability of the relevant natural spinorbitals and their occupation numbers make the present results particularly useful in research on approximate density-matrix functionals. The four-electron harmonium atom is found to possess the $^3P_+$ triplet ground state at strong confinements and the $^5S_-$ quintet ground state at the weak ones, the energy crossing occurring at $\omega \approx 0.0240919$. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891301>]

I. INTRODUCTION

The ongoing quest for methods enabling accurate but computationally inexpensive estimation of correlation energies in Coulombic systems has produced a variety of quantum-chemical approaches that range from straightforward wavefunction-based formalisms to those relying on reduced density matrices or densities themselves. Despite many partial successes, the ultimate goal of uncovering a formalism capable of describing dynamical and nondynamical correlation effects with equal fidelity has not yet been attained and thus novel approaches, such as those based upon the density matrix functional theory (DMFT)¹ and breaking/restoring symmetry of the electronic wavefunctions,² continue to appear in chemical literature. The process of developing such approaches invariably involves not only formulation of new approximations and derivation of the respective energy expressions but also testing them against suitable benchmarks. Consequently, the availability of benchmarking and calibration tools for electronic structure methods is as important to quantum chemistry as the knowledge of diverse approximations to the solutions of the Schrödinger equation.

One of the model systems commonly employed in testing of approximate electron correlation theories is the two-electron harmonium atom, i.e., the species described by the

nonrelativistic Hamiltonian

$$\hat{H} = \frac{1}{2} \sum_{i=1}^N (-\hat{\nabla}_i^2 + \omega^2 r_i^2) + \sum_{i>j=1}^N \frac{1}{r_{ij}} \quad (1)$$

with $N = 2$. Electronic properties of this model atom have been thoroughly elucidated with a combination of mathematical analysis and numerical methods.^{3,4} At the weak correlation limit, i.e., for large values of the confinement strength ω , the two-electron harmonium atom closely resembles helium-like systems. On the other hand, its strong-correlation limit of $\omega \rightarrow 0$ is characterized by purely nondynamical correlation and a complete spatial localization of electrons (i.e., Wigner crystallization). Thus, electron correlation effects with arbitrary relative strengths of the dynamical and nondynamical components can be modeled with a proper choice of ω – a fine tuning impossible to attain with ordinary atoms that, prior to the onset of Wigner crystallization, undergo spontaneous ionization upon their nuclear charges falling below certain critical values.

Together with the availability of exact wavefunctions and energies for select values of ω (such as $\frac{1}{2}$, $\frac{1}{10}$, etc.), the continuous tunability of electron correlation effects makes the two-electron harmonium atom a convenient benchmark that has been already applied to a multitude of electronic structure methods, including those based on DFT^{5–15} and other formalisms.^{16–18} Unfortunately, its general usefulness is severely limited by its failure to provide any new information for those approximate electron correlation methods that are already exact for two-electron systems.

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Harmonium atoms with $N > 2$ do not suffer from such a limitation and, due to the abundance of electronic states with diverse spin multiplicities and characters (single- or multideterminantal),^{19,20} provide a much richer testing ground for approximate electronic structure formalisms. As in the case of the two-electron system, properties of these atoms possess well-defined asymptotic expansions at the $\omega \rightarrow 0$ and $\omega \rightarrow \infty$ limits. Thanks to the absence of unbound states, the coefficients that appear in the individual terms of these expansions are rigorously evaluable in closed forms.

Despite the obvious usefulness of many-electron harmonium atoms in testing, calibration, and benchmarking of approximate methods of quantum chemistry, their properties have not been investigated in sufficient detail. Thus far, only the two lowest-energy $^2P_-$ and $^4P_+$ states of the three-electron species have been exhaustively studied, the values of their total, kinetic, confinement, and electron-electron repulsion energies being currently known within $1 \mu\text{hartree}$ for arbitrary values of ω .²¹⁻²³

The data currently available for the four-electron harmonium atom are limited to the asymptotic energy expressions valid at the $\omega \rightarrow \infty$ ²⁰ and $\omega \rightarrow 0$ ²⁴ limits, and the results of two independent Monte Carlo studies that are in disagreement on the nature of its ground state.^{19,25} Prompted by this unsatisfactory state of knowledge, we report in this paper on highly accurate explicitly-correlated calculations on the lowest-energy singlet, triplet, and quintet states of this species.

II. NUMERICAL METHODS

At the weak-correlation limit of $\omega \rightarrow \infty$, the four-electron harmonium atom possesses the single-determinantal $^3P_+$ ground state, whereas the lowest-lying singlet and quintet excited states are the multideterminantal $^1D_+$ and the single-determinantal $^5S_-$, respectively, their energies bracketing that of another singlet state (a multideterminantal $^1S_+$).^{19,20} The asymptotic expressions for their energies read²⁰

$$E(\omega) = A_0 \omega + A_1 \omega^{1/2} + A_2 + \dots, \quad (2)$$

where

$$\begin{aligned} A_0 &= 8, & A_1 &= \frac{14}{3} \sqrt{\frac{2}{\pi}}, \\ A_2 &= \frac{370}{27} - \frac{1204}{27\pi} + \frac{40}{9\pi} \sqrt{3} - \frac{848}{9\pi} \ln 2 + \frac{520}{9\pi} \ln(1 + \sqrt{3}) \\ &\approx -0.344\,824\,960 \end{aligned} \quad (3)$$

for the $^3P_+$ ground state,

$$\begin{aligned} A_0 &= 8, & A_1 &= \frac{143}{30} \sqrt{\frac{2}{\pi}}, \\ A_2 &= \frac{10274}{675} - \frac{300647}{6750\pi} + \frac{407}{225\pi} \sqrt{3} - \frac{43751}{450\pi} \ln 2 \\ &\quad + \frac{13391}{225\pi} \ln(1 + \sqrt{3}) \\ &\approx -0.370\,649\,862 \end{aligned} \quad (4)$$

for the $^1D_+$ excited state, and

$$\begin{aligned} A_0 &= 9, & A_1 &= 4\sqrt{\frac{2}{\pi}}, \\ A_2 &= \frac{62}{9} - \frac{320}{9\pi} + \frac{32}{3\pi} \sqrt{3} - \frac{208}{3\pi} \ln 2 + \frac{128}{3\pi} \ln(1 + \sqrt{3}) \\ &\approx -0.195\,514\,553 \end{aligned} \quad (5)$$

for the $^5S_-$ excited state. At the strong-correlation limit of $\omega \rightarrow 0$, the three states share the same energy asymptotics of Ref. 24,

$$E(\omega) = \frac{9}{2} 2^{1/3} \omega^{2/3} + \frac{1}{4} (6 + 4\sqrt{3} + 3\sqrt{6}) \omega + \dots \quad (6)$$

The individual energy components are given by simple expressions involving $E(\omega)$ and its first derivative with respect to the confinement strength ω , namely,⁴

$$T(\omega) = \frac{3}{2} \omega E'(\omega) - E(\omega), \quad (7)$$

$$V(\omega) = \frac{1}{2} \omega E'(\omega), \quad (8)$$

and

$$W(\omega) = 2E(\omega) - 2\omega E'(\omega), \quad (9)$$

where $T(\omega)$, $V(\omega)$, and $W(\omega)$ stand for the kinetic energy, the potential energy of the harmonic confinement, and the potential energy of the electron-electron repulsion, respectively. For each of the three states under study, differentiable approximants to $E(\omega)$ are provided by the robust interpolation scheme,²⁶ which allows for stitching of the asymptotics (2) and (6) with the results of numerical calculations carried out for 19 values of ω belonging to the set $\{0.001, 0.002, 0.005, 0.1, \dots, 1000.\}$. The ansatz

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \sigma_1, \sigma_2, \sigma_3, \sigma_4) \\ = \sum_{I=1}^M C_I \hat{A} [\Theta(\sigma_1, \sigma_2, \sigma_3, \sigma_4) \hat{P} \chi_I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)] \end{aligned} \quad (10)$$

employed in these calculations has several computational advantages that have been discussed in Ref. 21. In Eq. (10),

$$\begin{aligned} \chi_I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ = \exp \left[- \sum_{p=1}^4 \alpha_{Ip} (\mathbf{r}_p - \mathbf{R}_{Ip})^2 - \sum_{p>q=1}^4 \beta_{Ipq} (\mathbf{r}_p - \mathbf{r}_q)^2 \right] \end{aligned} \quad (11)$$

is the I th explicitly correlated Gaussian lobe primitive, $\Theta(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$ is the appropriate spin function, \hat{A} is the four-electron antisymmetrizer that ensures proper permutational symmetry, and \hat{P} is the spatial symmetry projector pertaining to the B_{1g} and A_{2g} irreducible representations of the D_{4h} point group for the $^1D_+$ and $^3P_+$ states, respectively, and to the A_{1u} irreducible representation of the O_h point group for the $^5S_-$ state. While admittedly lower than the proper K_h spatial symmetry, these symmetries retain transformation properties

(such as parities) of the states under study. In particular, they are compatible with the wavefunctions of the ${}^3P_+$ and ${}^5S_-$ states that are eigenfunctions of the \hat{L}_z operator with vanishing eigenvalues and with the wavefunction of the ${}^1D_+$ state that is a symmetric combination of the eigenfunctions with the eigenvalues of -2 and 2 .

The extraction of natural spinorbitals and their occupation numbers $\{n_i(\omega)\}$ from the approximate wavefunctions [Eq. (10)], and the subsequent derivation of the correlation measures, namely, the index of almost idempotency,^{27,28}

$$\mathcal{I}(\omega) = \sum_i n_i(\omega) [1 - n_i(\omega)] \quad (12)$$

and the correlation entropy,^{28,29}

$$S(\omega) = - \sum_i n_i(\omega) \ln n_i(\omega), \quad (13)$$

have been described previously.²¹

III. RESULTS AND DISCUSSION

The computed coefficients of the $[\frac{10}{1+\omega}]$ approximants to the total energies of the ${}^1D_+$, ${}^3P_+$, and ${}^5S_-$ states of the four-electron harmonium atom are compiled in Table I. A straightforward calculation employing these approximants leads to the conclusion that the energy crossing between the ${}^3P_+$ and ${}^5S_-$ states occurs at $\omega \approx 0.0240919$, clarifying the ambiguities in the results of the previously published Monte Carlo studies.^{19,25} The present data are somewhat less accurate than those for the three-electron species²¹ as reflected in the estimated errors in the energies and their components, which are listed in Table II. At the strong-correlation regime, these estimates exceed those resulting from the classical expression $\Delta E = \Delta L^2/(2I) = 2^{-7/3} \omega^{4/3} \Delta L^2$, where ΔL^2 is the deviation of the computed expectation value of the \hat{L}^2 operator from its proper value of $L(L+1)$, and I is the moment of inertia of the Wigner molecule.

TABLE I. The parameters of the $[\frac{10}{1+\omega}]$ approximants to the total energies of the ${}^1D_+$, ${}^3P_+$, and ${}^5S_-$ states of the four-electron harmonium atom.^a

State	${}^1D_+$	${}^3P_+$	${}^5S_-$
ω_0	0.020837321596	0.0095556769847	0.039649962858
$C_{10,0}$	0.42932262426	0.25530744893	0.65925136175
$C_{10,1}$	4.1126390460	2.4313088564	6.3540050372
$C_{10,2}$	17.703618870	10.303296117	27.423119807
$C_{10,3}$	44.368197117	26.274357679	70.015450876
$C_{10,4}$	74.170955794	42.140607200	115.73260488
$C_{10,5}$	82.451343963	47.292048867	130.46516336
$C_{10,6}$	63.490904514	35.670718308	101.36538137
$C_{10,7}$	32.848794334	18.189191433	53.784579499
$C_{10,8}$	10.846040153	5.8650204262	18.688405297
$C_{10,9}$	2.0492915124	1.0519887866	3.8471556108
$C_{10,10}$	0.16669857277	0.076445415877	0.35684966572

^aSee Refs. (21) and (26) for details.

TABLE II. The estimated errors in the total energies and their components of the ${}^1D_+$, ${}^3P_+$, and ${}^5S_-$ states of the four-electron harmonium atom.^a

State	$E(\omega)$	$T(\omega)$	$V(\omega)$	$W(\omega)$
${}^1D_+$	0.6	3.8	1.1	5.4
${}^3P_+$	1.3	5.8	1.9	7.7
${}^5S_-$	0.6	1.8	0.5	2.5

^aAll values in μ hartree; see Ref. (21) for the details of computation.

A. The ${}^1D_+$ state

The lowest-energy singlet state of the four-electron harmonium atom possesses the ${}^1D_+$ symmetry. At the weak-correlation limit, it originates from a combination of the $|s\bar{s}p_m\bar{p}_m|$ ($m = -1, 0, 1$) Slater determinants and remains an excited state for all the magnitudes of the coupling strength ω , always lying above its ${}^3P_+$ triplet counterpart. Inspection of Table III reveals its energies at the confinement strengths of 0.01, 0.5, and 10 being more than 1 mhartree lower than those previously published.¹⁹

The multideterminantal nature of the ${}^1D_+$ state is confirmed by the calculated occupation numbers of its dominant natural spinorbitals, and the asymptotic values of $1/2$ and $\ln 2$, respectively, for the index of almost idempotency and the correlation entropy at the $\omega \rightarrow \infty$ limit (Table IV).

B. The ${}^3P_+$ state

At the weak-correlation limit, the ${}^3P_+$ triplet ground state arises from a single $|s\bar{s}p_m p_{m'}|$ ($m \neq m' = -1, 0, 1$) Slater determinant. It remains the lowest-energy state down to $\omega \approx 0.0240919$, where it becomes the first excited state. As in the case of its singlet counterpart, its previously published energies turn out to be quite inaccurate, their deviations from the

TABLE III. The total energy and its components of the ${}^1D_+$ state of the four-electron harmonium atom.^a

ω	M^b	$E(\omega)$	$T(\omega)$	$V(\omega)$	$W(\omega)$
1000.0	611	8119.9004256	3970.3002484	4030.0668913	119.5332859
500.0	422	4084.6750828	1979.1055020	2021.2601949	84.3093859
200.0	361	1653.4193378	786.9173063	813.4455480	53.0564835
100.0	347	837.6673638	390.8529205	409.5067614	37.3076819
50.0	375	426.5301504	193.6339012	206.7213505	26.1748987
20.0	370	176.6501573	76.0974516	84.2492030	16.3035028
10.0	361	91.6732887	37.3346292	43.0026393	11.3360201
5.0	351	48.1573585	18.2040579	22.1204721	7.8328285
2.0	226	21.0442762	6.9647054	9.3363272	4.7432436
1.0	286	11.4822275	3.3373399	4.9398558	3.2050318
0.5	318	6.3855432	1.5894359	2.6583263	2.1377809
0.2	314	3.0266216	0.5945009	1.2070408	1.2250799
0.1	433	1.7555753	0.2839576	0.6798443	0.7917735
0.05	1013	1.0334602	0.1370008	0.3901537	0.5063057
0.02	644	0.5224807	0.0533003	0.1919270	0.2772534
0.01	765	0.3153516	0.0264376	0.1139297	0.1749843
0.005	757	0.1917953	0.0131939	0.0683297	0.1102717
0.002	1173	0.1003551	0.0052648	0.0352066	0.0598837
0.001	1211	0.0618543	0.0026199	0.0214914	0.0377429

^aAll energies in hartree.

^bThe number of basis functions in the expansion (10).

TABLE IV. The index of almost idempotency $\mathcal{I}(\omega)$, the correlation entropy $S(\omega)$, and the occupation numbers of the dominant natural spinorbitals of the $^1D_+$ state of the four-electron harmonium atom.

ω	$\mathcal{I}(\omega)$	$S(\omega)$	Occupation numbers ^a				
			s	$P_{\pm 1}$	P_0	d_0	$d_{\pm 1}$
1000.0	0.50005	0.69359	0.999980	0.499994	0.000009	0.000007	0.000003
500.0	0.50011	0.69399	0.999959	0.499987	0.000018	0.000015	0.000006
200.0	0.50027	0.69508	0.999898	0.499968	0.000045	0.000037	0.000015
100.0	0.50053	0.69677	0.999797	0.499937	0.000090	0.000074	0.000030
50.0	0.50105	0.69990	0.999597	0.499875	0.000179	0.000147	0.000060
20.0	0.50260	0.70830	0.999006	0.499694	0.000445	0.000362	0.000147
10.0	0.50511	0.72078	0.998040	0.499401	0.000882	0.000712	0.000289
5.0	0.50997	0.74286	0.996161	0.498840	0.001740	0.001392	0.000564
2.0	0.52369	0.79833	0.990805	0.497278	0.004230	0.003321	0.001346
1.0	0.54464	0.87349	0.982511	0.494925	0.008174	0.006280	0.002552
0.5	0.58176	0.99271	0.967499	0.490779	0.015512	0.011557	0.004731
0.2	0.67074	1.24334	0.930047	0.480695	0.034639	0.024314	0.010208
0.1	0.77891	1.51634	0.881720	0.467678	0.060527	0.039945	0.017449
0.05	0.92387	1.86080	0.811599	0.447984	0.099334	0.061033	0.028459
0.02	1.14924	2.40334	0.687274	0.408909	0.165900	0.094423	0.049879
0.01	1.31426	2.85144	0.580867	0.369919	0.211478	0.120145	0.070296
0.005	1.45405	3.30621	0.478661	0.326754	0.235644	0.142820	0.090860
0.002	1.59395	3.89164	0.365675	0.271307	0.231272	0.161755	0.110809
0.001	1.67215	4.32114	0.299137	0.234161	0.211397	0.164765	0.117320

^aAll values for the individual spin components; the designations of the natural spinorbitals refer to their weak-correlation limits.

present data (Table V) amounting to, respectively, at least 0.2 and 0.6 mhartree at the confinement strengths of 0.5 and 10,¹⁹ and 0.1, 0.3, and 0.6 mhartree at the those of 0.01, 0.02, and 0.5.²⁵

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 $V_s(\omega)$ ($s = \alpha, \beta$). At

TABLE V. The total energy and its components of the $^3P_+$ state of the four-electron harmonium atom.^a

ω	M^b	$E(\omega)$	$T(\omega)$	$V(\omega)$	$W(\omega)$
1000.0	633	8117.4029616	3970.9054802	4029.4361473	117.0613341
500.0	498	4082.9165625	1979.5260945	2020.8142190	82.5762490
200.0	395	1652.3164348	787.1741850	813.1635399	51.9787098
100.0	375	836.8948122	391.0274246	409.3074123	36.5599753
50.0	361	425.9910924	193.7503306	206.5804743	25.6602875
20.0	377	176.3180690	76.1627215	84.1602635	15.9950840
10.0	424	91.4452738	37.3745214	42.9399317	11.1308206
5.0	444	48.0026379	18.2265023	22.0763801	7.6997555
2.0	502	20.9539730	6.9726772	9.3088834	4.6724124
1.0	382	11.4237455	3.3390236	4.9209230	3.1637989
0.5	534	6.3488297	1.5877329	2.6455209	2.1155760
0.2	326	3.0079189	0.5914319	1.1997836	1.2167034
0.1	436	1.7448805	0.2812461	0.6753756	0.7882589
0.05	618	1.0275760	0.1350600	0.3875453	0.5049707
0.02	808	0.5199411	0.0522200	0.1907204	0.2770007
0.01	906	0.3140686	0.0257466	0.1132718	0.1750503
0.005	960	0.1911873	0.0127690	0.0679854	0.1104328
0.002	1046	0.1001534	0.0050830	0.0350788	0.0599916
0.001	1284	0.0617723	0.0025390	0.0214371	0.0377961

^aAll energies in hartree.

^bThe number of basis functions in the expansion (10).

the $\omega \rightarrow \infty$ limit, both the $T_\alpha(\omega)/T_\beta(\omega)$ and $V_\alpha(\omega)/V_\beta(\omega)$ ratios tend to $\frac{(3/4)+(5/4)+(5/4)}{(3/4)} = 13/3$ (Table VI). On the other hand, at the limit of $\omega \rightarrow 0$, where a classical description becomes valid, the ratios become equal to 3, simply reflecting the totalities of particles with individual spins.

The single-determinantal character of the $^3P_+$ state implies vanishing of both $\mathcal{I}(\omega)$ and $S(\omega)$ at the limit of $\omega \rightarrow \infty$, which is indeed the case for both spin components of these

TABLE VI. The individual spin components of the kinetic and confinement energies of the $^3P_+$ state of the four-electron harmonium atom.^a

ω	$T_\alpha(\omega)$	$T_\beta(\omega)$	$V_\alpha(\omega)$	$V_\beta(\omega)$
1000.0	3227.1288022	743.7766780	3273.1150550	756.3210923
500.0	1608.9021676	370.6239269	1641.3406816	379.4735374
200.0	639.9114327	147.2627524	660.3294318	152.8341081
100.0	317.9390382	73.0883864	332.2996134	77.0077988
50.0	157.5785497	36.1717809	167.6570153	38.9234590
20.0	61.9741676	14.1885539	68.2554209	15.9048426
10.0	30.4264880	6.9480334	34.7965942	8.1433375
5.0	14.8461730	3.3803293	17.8681109	4.2082692
2.0	5.6829885	1.2896887	7.5151618	1.7937216
1.0	2.7214206	0.6176030	3.9604875	0.9604355
0.5	1.2926241	0.2951088	2.1193977	0.5261232
0.2	0.4790473	0.1123846	0.9521064	0.2476772
0.1	0.2258607	0.0553854	0.5304092	0.1449664
0.05	0.1069720	0.0280879	0.3004479	0.0870974
0.02	0.0403678	0.0118522	0.1452791	0.0454413
0.01	0.0195680	0.0061786	0.0854595	0.0278123
0.005	0.0096009	0.0031681	0.0510464	0.0169390
0.002	0.0038029	0.0012801	0.0262963	0.0087825
0.001	0.0018991	0.0006399	0.0160703	0.0053668

^aAll energies in hartree.

TABLE VII. The individual spin components of the index of almost idempotency $\mathcal{I}(\omega)$ and the correlation entropy $S(\omega)$ of the ${}^3P_+$ state of the four-electron harmonium atom.

ω	$\mathcal{I}_\alpha(\omega)$	$\mathcal{I}_\beta(\omega)$	$S_\alpha(\omega)$	$S_\beta(\omega)$
1000.0	0.00008	0.00006	0.00055	0.00037
500.0	0.00016	0.00011	0.00104	0.00070
200.0	0.00041	0.00028	0.00240	0.00163
100.0	0.00081	0.00055	0.00449	0.00305
50.0	0.00161	0.00110	0.00836	0.00570
20.0	0.00395	0.00271	0.01876	0.01285
10.0	0.00776	0.00534	0.03418	0.02353
5.0	0.01509	0.01046	0.06146	0.04261
2.0	0.03567	0.02501	0.13001	0.09119
1.0	0.06696	0.04736	0.22316	0.15816
0.5	0.12242	0.08714	0.37190	0.26624
0.2	0.25679	0.18201	0.68979	0.49722
0.1	0.42465	0.29391	1.04453	0.74753
0.05	0.65950	0.43326	1.50264	1.04768
0.02	1.05189	0.61380	2.23836	1.45256
0.01	1.36695	0.71259	2.85694	1.71652
0.005	1.66141	0.77690	3.50541	1.94436
0.002	1.99367	0.83271	4.39097	2.22855
0.001	2.19649	0.86423	5.07238	2.44546

indices (Table VII). It is also consistent with the computed occupation numbers of the dominant natural spinorbitals (Table VIII).

C. The ${}^5S_-$ state

The relatively high energy of the ${}^5S_-$ state at strong confinements stems from its limiting $|sp_{-1}p_0p_{+1}|$ configuration. Consequently, for large values of ω this quintet is the third excited state that lies above the ${}^1D_+$ and ${}^1S_+$ pair of sin-

TABLE IX. The total energy and its components of the ${}^5S_-$ state of the four-electron harmonium atom.^a

ω	M^b	$E(\omega)$	$T(\omega)$	$V(\omega)$	$W(\omega)$
1000.0	133	9100.7304499	4474.9630312	4525.2311604	100.5362583
500.0	131	4571.1703874	2232.3526381	2267.8410085	70.9767408
200.0	128	1844.9411295	888.9091464	911.2834253	44.7485579
100.0	127	931.7219502	442.2130409	457.9783304	31.5305790
50.0	126	472.3750021	219.5485170	230.6411730	22.1853120
20.0	123	194.0820778	86.6192936	93.5671238	13.8956605
10.0	84	99.9034609	42.6612528	47.5215712	9.7206368
5.0	98	51.9499808	20.8959374	24.2819727	6.7720707
2.0	112	22.3318759	8.0435671	10.1251477	4.1631611
1.0	119	12.0151005	3.8656076	5.2935694	2.8559235
0.5	100	6.5871908	1.8384768	2.8085559	1.9401581
0.2	125	3.0698659	0.6776810	1.2491823	1.1430026
0.1	138	1.7634952	0.3158878	0.6931277	0.7544798
0.05	141	1.0315840	0.1471183	0.3929008	0.4915649
0.02	141	0.5196516	0.0542163	0.1912893	0.2741461
0.01	144	0.3135847	0.0259327	0.1131725	0.1744795
0.005	141	0.1908993	0.0126314	0.0678435	0.1104243
0.002	142	0.1000523	0.0049939	0.0350154	0.0600430
0.001	140	0.0617312	0.0024979	0.0214097	0.0378236

^aAll energies in hartree.

^bThe number of basis functions in the expansion (10).

glets. However, the weaker electron-electron repulsion [compare Eqs. (3)–(5)] imparted by its higher multiplicity results in a steeper decrease of its energy upon weakening of the confinement. Therefore, it becomes the ground state of the four-electron harmonium atom for values of ω less than ca. 0.0240919 (Table IX). Again, the computed energies are significantly lower (by as much as 0.6 mhartree) than their previously published counterparts.^{19,25}

In contrast to those of the two other states under study, the occupation numbers of the dominant natural spinorbitals

TABLE VIII. The occupation numbers of the dominant natural spinorbitals of the ${}^3P_+$ state of the four-electron harmonium atom.^a

ω	s	$p_{\pm 1}$	$d_{\pm 2}$	p_0	$d_{\pm 1}$	\bar{s}	\bar{p}_0	$\bar{p}_{\pm 1}$	\bar{s}	$\bar{d}_{\pm 1}$
1000.0	0.999990	0.999985	0.000008	0.000008	0.000004	0.999972	0.000010	0.000006	0.000002	0.000001
500.0	0.999979	0.999969	0.000016	0.000015	0.000008	0.999944	0.000020	0.000012	0.000003	0.000002
200.0	0.999948	0.999924	0.000041	0.000037	0.000021	0.999862	0.000049	0.000031	0.000008	0.000004
100.0	0.999897	0.999848	0.000081	0.000075	0.000041	0.999724	0.000098	0.000061	0.000015	0.000008
50.0	0.999795	0.999700	0.000161	0.000149	0.000082	0.999451	0.000195	0.000121	0.000031	0.000016
20.0	0.999495	0.999263	0.000395	0.000371	0.000201	0.998644	0.000485	0.000297	0.000076	0.000041
10.0	0.999003	0.998557	0.000773	0.000737	0.000394	0.997325	0.000962	0.000583	0.000149	0.000082
5.0	0.998045	0.997197	0.001501	0.001460	0.000766	0.994752	0.001900	0.001135	0.000291	0.000167
2.0	0.995301	0.993390	0.003532	0.003584	0.001809	0.987395	0.004623	0.002678	0.000688	0.000431
1.0	0.991014	0.987611	0.006593	0.007011	0.003394	0.975961	0.008941	0.005003	0.001284	0.000893
0.5	0.983136	0.977353	0.011946	0.013571	0.006212	0.955189	0.016976	0.009041	0.002301	0.001864
0.2	0.962860	0.952219	0.024562	0.031618	0.013125	0.903220	0.037873	0.018289	0.004481	0.004940
0.1	0.935510	0.919895	0.039639	0.057860	0.022041	0.836558	0.065876	0.028606	0.006559	0.010113
0.05	0.893901	0.872076	0.059642	0.100177	0.035337	0.742374	0.106813	0.040576	0.008290	0.019618
0.02	0.816365	0.781983	0.092017	0.178012	0.060932	0.588869	0.172959	0.054749	0.010702	0.039980
0.01	0.746468	0.697044	0.120120	0.233592	0.085540	0.475545	0.215008	0.062656	0.015028	0.057528
0.005	0.671914	0.606171	0.150132	0.264815	0.111211	0.382247	0.236984	0.069189	0.019629	0.071360
0.002	0.566802	0.491007	0.185018	0.263835	0.138770	0.291634	0.234993	0.076279	0.025619	0.080683
0.001	0.484257	0.414331	0.200341	0.243180	0.150177	0.241567	0.217775	0.079331	0.029661	0.082265

^aThe designations of the natural spinorbitals refer to their weak-correlation limits.

TABLE X. The index of almost idempotency $\mathcal{I}(\omega)$, the correlation entropy $S(\omega)$, and the occupation numbers of the dominant natural spinorbitals of the ${}^5S_-$ state of the four-electron harmonium atom.

ω	$\mathcal{I}(\omega)$	$S(\omega)$	Occupation numbers ^a		
			s	p	d
1000.0	0.00006	0.00039	0.999998	0.999991	0.000005
500.0	0.00011	0.00073	0.999997	0.999982	0.000010
200.0	0.00028	0.00170	0.999992	0.999956	0.000024
100.0	0.00056	0.00318	0.999985	0.999912	0.000047
50.0	0.00111	0.00594	0.999969	0.999825	0.000094
20.0	0.00273	0.01339	0.999924	0.999569	0.000232
10.0	0.00538	0.02454	0.999850	0.999152	0.000456
5.0	0.01052	0.04445	0.999706	0.998343	0.000893
2.0	0.02511	0.09528	0.999289	0.996039	0.002138
1.0	0.04769	0.16592	0.998622	0.992468	0.004073
0.5	0.08866	0.28188	0.997344	0.985959	0.007604
0.2	0.19225	0.54168	0.993714	0.969342	0.016620
0.1	0.32956	0.85010	0.987980	0.946950	0.028725
0.05	0.53704	1.27807	0.977161	0.912277	0.047279
0.02	0.93462	2.04136	0.948122	0.842749	0.083472
0.01	1.31770	2.75867	0.907630	0.771389	0.118653
0.005	1.73861	3.57365	0.844980	0.687080	0.156521
0.002	2.28010	4.75275	0.726568	0.567295	0.199741
0.001	2.63245	5.68362	0.619388	0.480580	0.218984

^aThe designations of the natural spinorbitals refer to their weak-correlation limits. The occupation numbers are identical for the p_0 and $p_{\pm 1}$ natural spinorbitals, whereas for their d counterparts they deviate (due to the O_h symmetry employed in the calculations) by less than 10^{-5} from the average values listed in the table.

of the lowest-energy quintet fall into very simple patterns as their ordering does not vary with ω (Table X). This behavior is undoubtedly related to both the totally symmetric nature of this state (which implies that all the natural spinorbitals are eigenfunctions of both the \hat{L}^2 and \hat{L}_z operators) and the absence of the opposite-spin correlation.

IV. CONCLUSIONS

For a wide range of confinement strengths ω , the calculations reported in this paper afford approximate energies $E(\omega)$ of the ground and low-lying excited states of the four-electron harmonium atom that are within few μ hartree of the exact values, the errors in the respective energy components being only slightly higher. This level of accuracy constitutes an improvement of several orders of magnitude over the previously published data,^{19,25} establishing a set of benchmarks for stringent calibration and testing of approximate electronic structure methods. Its usefulness is further enhanced by the construction of differentiable approximants that allow for accurate computation of $E(\omega)$ and its components for arbitrary values of ω . The diversity of the electronic states in question, which involve both single- and multideterminantal first-order wavefunctions, and the availability of the relevant natural spinorbitals and their occupation numbers make the present

results particularly useful in research on approximate density-matrix functionals.

This methodology, which works equally well within both the weak- and strong-correlation regimes, can be readily applied (though at a much higher computational cost) to harmonium atoms involving more than four electrons. One expects such calculations to clarify the ordering of electronic states in those species and generate further benchmarks.

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