Benchmark Full Configuration Interaction Calculations on the Lowest-Energy ^{2}P and ^{4}P States of the Three-Electron Harmonium Atom

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ABSTRACT: Full configuration interaction calculations carried out in conjunction with careful optimization of basis sets and judicious extrapolation schemes for 12 values of the confinement strength ω ranging from 0.1 to 1000.0 provide benchmark energies for the ^{2}P ground state and the ^{4}P first excited state of the three-electron harmonium atom, allowing for numerical verification of the recently obtained second-order energy coefficients and confirming the few available results of Monte Carlo studies. The final energy values, obtained by correcting the extrapolated data for residual errors in the low-order energy coefficients, possess accuracy of ca. 20 μHartree for the doublet state and ca. 10 μHartree for the quartet one, making them suitable for calibration and testing of approximate electron correlation methods of quantum chemistry. The energy limits for individual angular momenta ranging from 1 to 4 are also available, facilitating comparisons with results of calculations involving finite basis sets. An example of application involving the BLYP and B3LYP functionals is provided.

1. INTRODUCTION

The two-electron harmonium atom, described by the Hamiltonian:

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

with $N = 2$,[1−3] has been repeatedly employed in calibration and benchmarking of approximate electronic structure methods of quantum chemistry, including those based on the density functional theory (DFT).[4−12] However, although the availability of exact wave functions and energies for certain values of the confinement strength ω greatly facilitates accuracy assessments, the trivial nature of electron correlation in the two-electron species limits its usefulness in such test calculations. In contrast, the three-electron harmonium atom is of potentially greater interest as it allows for infinite tunability of the extent of the correlations between electrons of both same and opposite spins within a single electronic state.

Only very limited data have been accumulated on the three-electron harmonium atom until now. Relatively low-level electronic structure calculations have been carried out, and their results have been compared with the predictions of a pair model valid at the limit of $\omega \to 0$[13] that has also been investigated from the asymptotic point of view.[14] In addition, a study involving the Hartree−Fock approximation has been published.[15] Thus far, the most accurate energies of several low-energy states of the three-electron harmonium atom have been obtained with Monte Carlo calculations for three values of ω, namely 1/100, 1/2, and 10.[16]

In a recent pilot study, the ground-state energies of the two-electron harmonium atom have been computed with a few μHartree accuracy for 20 values of ω ranging from 0.03 to 1000.[17] The full configuration interaction (FCI) approach has been used in conjunction with even-tempered Gaussian basis sets and judicious extrapolations to both the individual angular momentum and the complete basis set (CBS) limits. As basis sets with only few angular momenta are employed in actual calculations, the availability of both these limits is of crucial importance to testing of approximate approaches of the electronic structure theory.

Encouraged by the performance of this computational scheme, we have recently performed analogous benchmark calculations for the two lowest-energy states of the three-electron harmonium atom. Results of these calculations are presented in this paper.

2. DETAILS OF CALCULATIONS

The calculations described here have been carried out for the ^{2}P and ^{4}P lowest-energy states of the three-electron harmonium atom that arise, respectively, from the $\bar{s}\bar{s}p_z$ and sp_xp_y configurations of the weak-correlation limit. The FCI energies have been computed for 12 values of ω, namely 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 5.0, 10.0, 100.0, and 1000.0, with a modified program of Knowles and Handy.[18] The respective one- and two-electron integrals, generated with the Gaussian09 suite of programs,[19] have involved uncontracted basis sets that, for each value of the angular momentum between 0 and L ($1 \leq L \leq 4$), comprise equal numbers N ($4 \leq N \leq 8$) of spherical Gaussian primitives with exponents $\zeta_{L,N}^k(\omega)$ even-tempered[20] according to the formula:

$$\zeta_{L,N}^k(\omega) = \frac{\omega}{2}\alpha_{L,N}(\omega)[\beta_{L,N}(\omega)]^{k-1}, \qquad 1 \leq k \leq N \qquad (2)$$

While depending on N, the maximum angular momentum L and the electronic state in question, the optimized parameters

Table 1. Optimized Basis Set Parameters $\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ [eq 2] and Corresponding FCI energies $E_{L,N}(\omega)$ of the ^{2}P State of the Three-Electron Harmonium Atom with $\omega = 1/2$

N	$\alpha_{1,N}(1/2)$	$\beta_{1,N}(1/2)$	$E_{1,N}(1/2)$	$\alpha_{2,N}(1/2)$	$\beta_{2,N}(1/2)$	$E_{2,N}(1/2)$	$\alpha_{3,N}(1/2)$	$\beta_{3,N}(1/2)$	$E_{3,N}(1/2)$
4	0.916687	1.546208	4.0436825	0.918520	1.559219	4.0169503	0.916222	1.588256	4.0143476
5	0.923655	1.502709	4.0436488	0.925382	1.512923	4.0169019	0.923432	1.536571	4.0142866
6	0.929189	1.466172	4.0436378	0.930788	1.475097	4.0168859	0.929089	1.494644	4.0142661
7	0.933634	1.435840	4.0436336	0.935130	1.443885	4.0168797	0.933653	1.460256	4.0142580
8	0.937386	1.410345	4.0436318	0.938764	1.417514	4.0168770	0.937502	1.431465	4.0142544
∞			4.0436301			4.0168744			4.0142510

$\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ that minimize the FCI energies $E_{L,N}(\omega)$ have been kept equal for individual Gaussian primitives irrespective of their angular momenta. The quantities $-\ln[-N\omega^{1/2}\ln\alpha_{L,N}(\omega)]$ and $N\ln\beta_{L,N}(\omega)$ have been found accurately approximated by quadratic polynomials in $\omega^{-1/2}$, which aids in the choice of the initial values for $\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ and speeds up the energy minimizations.

For $1 \leq L \leq 3$, the previously employed extrapolations to the $N \to \infty$ limits $E_L(\omega)$, based upon fitting of the parameters of the approximate equation:[17]

$$E_{L,N}(\omega) = E_L(\omega) + A_{1,L}(\omega)e^{-\lambda_{1,L}(\omega)N} + A_{2,L}(\omega)e^{-\lambda_{2,L}(\omega)N} \tag{3}$$

have been used. However, for $L = 4$, an alternative extrapolation scheme:

$$E_4(\omega) = E_{4,5}(\omega) + \frac{E_{4,5}(\omega) - E_{4,4}(\omega)}{E_{3,5}(\omega) - E_{3,4}(\omega)}[E_3(\omega) - E_{3,5}(\omega)] \tag{4}$$

which does not require the values of $E_{4,6}(\omega)$, $E_{4,7}(\omega)$, and $E_{4,8}(\omega)$, has been found equally accurate. Consequently, it has been adopted in the actual calculations, allowing for significant reduction of computational effort. For $1 \leq L \leq 3$, the extrapolated energies are lower than their counterparts computed with 8 primitives by at most 9.2 and 0.2 μHartree (for the ^{2}P and ^{4}P states, respectively). For $L = 4$, the extrapolation (4) results in the lowerings of 111.0 and 5.1 μHartree with respect to the $E_{4,5}(\omega)$ energies.

The estimates $E_L(\omega)$ (that comprise the energy contributions of partial waves with angular momenta up to L) have been extrapolated to the respective CBS limits $E(\omega)$ by fitting the values of $E_L(\omega)$ for $L = 2, 3$, and 4 to the expression:[21−23]

$$E_L(\omega) = E(\omega) + \frac{B(\omega)}{[L + C(\omega)]^\lambda} \tag{5}$$

where the exponent λ depends on the state in question ($\lambda = 3$ for ^{2}P and $\lambda = 5$ for ^{4}P). Extrapolations based upon the values of $E_L(\omega)$ for $L = 1, 2$, and 3 have turned out to be of significantly inferior accuracy and thus have not been used.

For each of the two states under study, the energies $E_L(\omega)$ computed for 12 values of ω have been fitted to the truncated power series:

$$E_L(\omega) = \sum_{k=0}^{6} E_L^{(k)} \omega^{(2-k)/2} \tag{6}$$

pertinent to the large ω asymptotics[24] with the energy coefficients $E_L^{(0)}$ and $E_L^{(1)}$ kept fixed at their exact L independent values (see below). The same fitting has been carried out for the

estimated CBS limits $E(\omega)$, producing the coefficients $E^{(k)}$ ($2 \leq k \leq 6$). Inspection of the resulting values of $E^{(2)}$ has revealed small but significant deviations from their recently available[24] exact counterparts. Consequently, the final energies $E(\omega)$ have been recomputed from the series (6) with corrected coefficients $E^{(k)}$ obtained as follows: For $0 \leq k \leq 2$, the exact values have been used, whereas for $3 \leq k \leq 6$, the values extrapolated from the coefficients $E_L^{(k)}$ ($2 \leq L \leq 4$) and $E^{(k)}$ have been employed, the pertinent extrapolations assuming the deviations of the higher-order coefficients from their exact values being given by quadratic polynomials of the respective deviations of the computed second-order coefficients. For the ^{2}P state, this final correction lowers the energies by as much as 66 μHartree (e.g., by 55 μHartree for $\omega = 10$ and 22 μHartree for $\omega = 1/2$). The corrections are much smaller for the ^{4}P state, amounting to less than 5 μHartree (e.g., 3.3 μHartree for $\omega = 10$ and 4.6 μHartree for $\omega = 1/2$).

3. RESULTS AND DISCUSSION

The ^{2}P doublet ground state arises from the $\bar{s}\bar{s}p_z$ configuration that is dominant at the small-correlation (large ω) limit with $E^{(0)} = 11/2$, $E^{(1)} = (5/2)(2/\pi)^{1/2}$, and the exact second-order energy coefficient that reads:[24]

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

$$\approx -0.176654 \tag{7}$$

The optimized basis-set parameters $\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ [eq 2] and the corresponding FCI energies $E_{L,N}(\omega)$ computed for $\omega = 1/2$ that are compiled in Table 1 exhibit smooth convergence to the $N \to \infty$ limits. Although this convergence is observed for all the aforementioned values of the confinement strength, linear dependencies among the basis functions limit the present calculations to $\omega \geq 0.1$ (compared with $\omega \geq 0.03$ in the case of the two-electron harmonium atom).[17]

The energy limits $E_L(\omega)$ for individual angular momenta are listed in Table 2 together with the extrapolated and corrected CBS limits $E(\omega)$. For the two values of ω, namely 10 and 1/2, for which the results of Monte Carlo calculations are available,[16] the corrected energies are found to be in excellent agreement with the previously published data. The computed energy coefficients (Table 3) are of potential use as benchmarks in checking and debugging of future analytical work. The differences between the extrapolated and the corrected values of these coefficients are quite significant, amounting to 68 μHartree for $E^{(2)}$ and 43 μHartree for $E^{(3)}$.

The interpolation of $E(\omega)$ between the large ω limit (eq 6) and the small ω limit of

$$E(\omega) = \tilde{E}^{(0)}\omega^{2/3} + \tilde{E}^{(1)}\omega \tag{8}$$

Table 2. Partial Wave and CBS Limits of the ^{2}P State Energies of the Three-Electron Harmonium Atom

ω	$E_1(\omega)$	$E_2(\omega)$	$E_3(\omega)$	$E_4(\omega)$	$E(\omega)^a$	$E(\omega)^b$
1000.	5562.944818	5562.910896	5562.905536	5562.903916	5562.902484	5562.902417
100.	569.814500	569.780963	569.775796	569.774252	569.772901	569.772838
10.	61.177964	61.145631	61.141032	61.139708	61.138588 ^{c}	61.138533^d
5.	31.832079	31.800462	31.796175	31.794970	31.793973	31.793923
2.	13.695898	13.665666	13.661932	13.660935	13.660149	13.660107
1.	7.373142	7.344405	7.341195	7.340394	7.339798	7.339766
0.5	4.043630	4.016874	4.014251	4.013669	4.013274 ^{c}	4.013253^d
0.4	3.346560	3.320557	3.318126	3.317615	3.317284	3.317266
0.3	2.630164	2.605217	2.603028	2.602608	2.602352	2.602340
0.2	1.883885	1.860586	1.858712	1.858413	1.858251	1.858246
0.15	1.492734	1.470709	1.469030	1.468807	1.468698	1.468699
0.1	1.081236	1.061133	1.059671	1.059538	1.059485	1.059493

^{a} From eq 5 with $\lambda = 3$. ^{b} After the final correction (see the text for explanation). ^{c} Compare with the energies of 61.138525, 61.138549, and 61.139485 obtained from the Monte Carlo calculations. [16] ^{d} Compare with the energies of 4.013240, 4.013224, and 4.013511 obtained from the Monte Carlo calculations. [16]

Table 3. Partial Wave and CBS Limits of the Energy Coefficients $E^{(k)}$ [eq 6] for the ^{2}P State of the Three-Electron Harmonium Atom

	$L = 1^a$	$L = 2^a$	$L = 3^a$	$L = 4^a$	extrapolated^b	corrected^c
$E^{(2)}$	-1.33904×10^{-1}	-1.68007×10^{-1}	-1.73460×10^{-1}	-1.75115×10^{-1}	-1.76586×10^{-1}	-1.76654×10^{-1}
$E^{(3)}$	1.29505×10^{-2}	1.86390×10^{-2}	2.15854×10^{-2}	2.27364×10^{-2}	2.39767×10^{-2}	2.40199×10^{-2}
$E^{(4)}$	-5.79129×10^{-4}	-8.26331×10^{-4}	-1.62200×10^{-3}	-1.96851×10^{-3}	-2.40436×10^{-3}	-2.41347×10^{-3}
$E^{(5)}$	-4.11410×10^{-5}	-1.32704×10^{-4}	-3.75221×10^{-5}	1.69114×10^{-5}	9.36887×10^{-5}	9.49301×10^{-5}
$E^{(6)}$	4.95919×10^{-6}	1.87513×10^{-5}	1.49576×10^{-5}	1.12262×10^{-5}	5.48519×10^{-6}	5.39176×10^{-6}

^{a} Obtained by fitting of the extrapolated energies $E_L(\omega)$ to eq 6. ^{b} Obtained by fitting of the extrapolated energies $E(\omega)$ to eq 6. ^{c} After the final correction (see the text for explanation). For $E^{(2)}$, the exact value (eq 7) is listed.

Table 4. Coefficients of the Padé Approximant (eq 9) for the Energies of the ^{2}P State of the Three-Electron Harmonium Atom

k	a_k	b_k	c_k	d_k
1	3.82211×10^{-4}	2.66583×10^{-4}	-1.03821	3.72579×10^{-1}
2	-8.22620×10^{-3}	1.17287×10^{-2}	-6.62884×10^{-1}	2.72429×10^{-1}
3	-2.65714×10^{-2}	1.90218×10^{-2}	-3.31207×10^{-1}	2.31675×10^{-1}
4	7.26721×10^{-3}	-7.89154×10^{-4}	2.20583×10^{-1}	1.44545×10^{-1}
5	-1.05700×10^{-2}	-3.50039×10^{-3}	6.26591×10^{-1}	1.62447×10^{-1}
6	3.77181×10^{-2}	1.82252×10^{-2}	9.57521×10^{-1}	2.34292×10^{-1}

where $\tilde{E}^{(0)} = (1/2) \, 3^{5/3}$ and $\tilde{E}^{(1)} = (1/2)(3 + 3^{1/2} + 6^{1/2})14$ can be readily accomplished with the help of the Padé approximants using $\omega^{1/6}$ as their arguments.[24] In particular, requesting the expression in which $\omega^{2/3}$ multiplies the [14/12] approximant to conform to both the limits (6) and (8) (and noting that the coefficients that multiply the $\omega^{-13/6}$ and $\omega^{-7/3}$ terms in the large ω power series vanish together with the small ω ones multiplying the $\omega^{7/6}$ and $\omega^{3/2}$ terms) uniquely determines all but one of the pertinent 27 coefficients. In turn, minimization of the maximum error with respect to the remaining coefficient yields the approximate expression:

$$E(\omega) = E^{(0)}\omega + E^{(1)}\omega^{1/2} + E^{(2)} + \sum_{k=1}^{6} \frac{a_k \, \omega^{1/6} + b_k}{\omega^{1/3} + c_k \, \omega^{1/6} + d_k} \tag{9}$$

(see Table 4 for the values of a_k, b_k, c_k, and d_k) that reproduces the corrected energies $E(\omega)$ within 5.6 μHartree. Interestingly, eq 9

affords the estimate $E(1/100) = 0.181677$ that compares quite well with the Monte Carlo result of $E(1/100) = 0.181936$.[16] In contrast, the power series (6) produces the poor estimate of $E(1/100) = 0.225517$.

The data computed for the ^{4}P quartet lowest-energy excited state that arises from the $\mathrm{s}p_x p_y$ configuration are presented in Tables 5−8. In this case, $E^{(0)} = 13/2$, $E^{(1)} = 2(2/\pi)^{1/2}$, and

$$E^{(2)} = \frac{23}{9} + \frac{8}{3\pi}[-4 + \sqrt{3} - 7\ln 2 + 4\ln(1 + \sqrt{3})]$$

$$\approx -0.0756103 \tag{10}$$

whereas the coefficients $E^{(0)}$ and $E^{(1)}$ are the same as those pertaining to the ^{2}P state.[14,24] The reduced electron−electron repulsion, reflected in the smaller absolute values of $E^{(1)}$ and $E^{(2)}$, results in higher convergence rates of the FCI energies. This enhanced convergence is apparent in both the dependences of

917

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Table 5. Optimized Basis Set Parameters $\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ [eq 2] and Corresponding FCI Energies $E_{L,N}(\omega)$ of the ^{4}P State of the Three-Electron Harmonium Atom with $\omega = 1/2$

N	$\alpha_{1,N}(1/2)$	$\beta_{1,N}(1/2)$	$E_{1,N}(1/2)$	$\alpha_{2,N}(1/2)$	$\beta_{2,N}(1/2)$	$E_{2,N}(1/2)$	$\alpha_{3,N}(1/2)$	$\beta_{3,N}(1/2)$	$E_{3,N}(1/2)$
4	0.942768	1.434508	4.3259606	0.943263	1.442992	4.3125639	0.941614	1.465746	4.3109809
5	0.947999	1.399152	4.3259583	0.948426	1.404443	4.3125593	0.947005	1.423446	4.3109748
6	0.951595	1.373620	4.3259577	0.952196	1.376518	4.3125582	0.950936	1.392373	4.3109732
7	0.954431	1.353081	4.3259576	0.955084	1.354419	4.3125579	0.953982	1.367908	4.3109728
8	0.956760	1.335578	4.3259575	0.957437	1.336069	4.3125578	0.956436	1.348491	4.3109726
∞			4.3259575			4.3125577			4.3109725

Table 6. Partial Wave and CBS Limits of the ^{4}P State Energies of the Three-Electron Harmonium Atom

ω	$E_1(\omega)$	$E_2(\omega)$	$E_3(\omega)$	$E_4(\omega)$	$E(\omega)^a$	$E(\omega)^b$
1000.	6550.405429	6550.389639	6550.387757	6550.387399	6550.387238	6550.387236
100.	665.900725	665.885057	665.883202	665.882854	665.882700	665.882697
10.	69.990094	69.974811	69.973031	69.972712	69.972576 ^{c}	69.972573 ^{c}
5.	36.012550	35.997498	35.995757	35.995455	35.995329	35.995325
2.	15.201977	15.187380	15.185701	15.185429	15.185322	15.185318
1.	8.041988	8.027896	8.026268	8.026027	8.025938	8.025933
0.5	4.325958	4.312558	4.310973	4.310770	4.310703 ^{d}	4.310698 ^{d}
0.4	3.557361	3.544232	3.542657	3.542469	3.542409	3.542404
0.3	2.772905	2.760165	2.758597	2.758428	2.758378	2.758374
0.2	1.963740	1.951627	1.950059	1.949919	1.949882	1.949879
0.15	1.544118	1.532508	1.530930	1.530812	1.530784	1.530782
0.1	1.107280	1.096459	1.094854	1.094768	1.094750	1.094751

^{a} From eq 5 with $\lambda = 5$. ^{b} After the final correction (see the text for explanation). ^{c} Compare with the energies of 69.972571, 69.972571, and 69.972624 obtained from the Monte Carlo calculations. [16] ^{d} Compare with the energies of 4.310690, 4.310690, and 4.310712 obtained from the Monte Carlo calculations. [16]

Table 7. Partial Wave and CBS Limits of the Energy Coefficients $E^{(k)}$ [eq 6] for the ^{4}P State Energies of the Three-Electron Harmonium Atom

	$L = 1^a$	$L = 2^a$	$L = 3^a$	$L = 4^a$	extrapolated^b	corrected^c
$E^{(2)}$	-5.73403×10^{-2}	-7.31870×10^{-2}	-7.50824×10^{-2}	-7.54447×10^{-2}	-7.56081×10^{-2}	-7.56103×10^{-2}
$E^{(3)}$	3.76541×10^{-3}	5.55339×10^{-3}	5.97127×10^{-3}	6.11889×10^{-3}	6.21146×10^{-3}	6.20753×10^{-3}
$E^{(4)}$	-2.12366×10^{-4}	-2.25364×10^{-4}	-4.04234×10^{-4}	-4.35596×10^{-4}	-4.55307×10^{-4}	-4.53956×10^{-4}
$E^{(5)}$	6.32038×10^{-6}	-1.66290×10^{-5}	1.32753×10^{-5}	1.89166×10^{-5}	2.05880×10^{-5}	2.08485×10^{-5}
$E^{(6)}$	1.02964×10^{-7}	2.37962×10^{-6}	4.94165×10^{-7}	-6.06493×10^{-8}	-8.38971×10^{-8}	-1.52385×10^{-7}

^{a} Obtained by fitting of the extrapolated energies $E_L(\omega)$ to eq 6. ^{b} Obtained by fitting of the extrapolated energies $E(\omega)$ to eq 6. ^{c} After the final correction (see the text for explanation). For $E^{(2)}$, the exact value (eq 10) is used.

Table 8. Coefficients of the Padé Approximant (eq 9) for the Energies of the ^{4}P State of the Three-Electron Harmonium Atom

k	a_k	b_k	c_k	d_k
1	1.43587×10^{-2}	-1.61112×10^{-3}	2.56382×10^{-1}	-4.13474×10^{-2}
2	-5.96215×10^{-5}	8.18610×10^{-4}	-7.25430×10^{-1}	2.42079×10^{-1}
3	-1.17585×10^{-2}	8.50060×10^{-3}	-3.78158×10^{-1}	1.77911×10^{-1}
4	-8.28147×10^{-6}	2.65891×10^{-5}	-2.32442×10^{-1}	4.67866×10^{-1}
5	1.25587×10^{-3}	-1.05411×10^{-4}	1.41377×10^{-1}	5.89617×10^{-2}
6	-3.78817×10^{-3}	-2.04825×10^{-3}	7.31118×10^{-1}	1.60196×10^{-1}

$E_{L,N}(\omega)$ on N (Table 5) and $E_L(\omega)$ on L (Table 6). Consequently, the agreement among the extrapolated and corrected energies and those published previously[16] is even closer than in the case of the ^{2}P state. The convergence of the energy coefficients to their CBS limits is also noticeably faster, the differences between the extrapolated and corrected values of

$E^{(2)}$ and $E^{(3)}$ amounting to 2.2 and 3.9 μHartree, respectively (Table 7).

The quality of the Padé approximation for the energies of the ^{4}P state is mixed. On one hand, the approximant with the coefficients listed in Table 8 reproduces these energies within 0.7 μHartree and yields the estimate of $E(1/100) = 0.182844$ that

918

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compares well with the Monte Carlo result of $E(1/100) = 0.182973$ [although the improvement over the power-series result of $E(1/100) = 0.184971$ is not as dramatic as for the analogous ^{2}P energy]. On the other hand, the approximant possesses a pole at $\omega \approx 2 \times 10^{-6}$ that precludes smooth interpolation between the small- and large-correlation limits.

4. EXAMPLE OF APPLICATION

When employed in conjunction with the Kohn−Sham formalism, the BLYP[25,26] and B3LYP[27] functionals allow for inclusion of electron correlation effects within the framework of one-electron theory, yielding reasonably accurate energies at relatively low computational cost. For this reason, these functionals remain one of the most popular choices among quantum chemists carrying out calculations on medium- and large-size systems.[28]

It is instructive to compare the performance of the BLYP and B3LYP functionals for the two lowest-energy electronic states of the three-electron harmonium atom. The accuracy of the approximate DFT energies is readily assessed by plotting $\Delta E(\omega) = E(\omega) - E^{(0)} \omega - E^{(1)} \omega^{1/2}$ (the energy contributions beyond the first order) vs $\omega^{-1/2}$. Inspection of Figure 1, in which the relevant HF energy contributions are also displayed, reveals relatively minor variations of the exact and the HF values of $\Delta E(\omega)$ with ω, their difference (which amounts to the correlation energy) depending weakly on ω. In contrast, the BLYP and B3LYP functionals fail spectacularly at the weak-correlation limit, the computed values of $\Delta E(\omega)$ exhibiting divergencies as ω tends to infinity. These divergencies are caused by the inaccurate exchange components of the approximate total energies.

For the ^{2}P doublet ground state of the three-electron harmonium atom, the performance of the B3LYP functional becomes quite satisfactory for $\omega \leq 2$ and does not worsen even at $\omega = 0.1$, which corresponds to the weakest confinement for which the present data are available. In contrast, the BLYP functional accounts for only a fraction of the electron correlation energy for smaller values of ω while sharing the large ω singular behavior with its B3LYP counterpart. The B3LYP energies of the ^{4}P quartet state are not as accurate as those of the doublet state but still follow the exact ones quite closely. Interestingly, the BLYP energies appear to converge to their HF rather than exact counterparts as ω decreases.

Overall, as expected, this test clearly favors the B3LYP functional over its BLYP congener. It also uncovers the need for improvement in the handling of the exchange part in these functionals.

It should be emphasized that the above picture of (dis)agreements among approximate energies computed at different levels of theory does not persist for smaller values of ω (and specially at the $\omega \rightarrow 0$ limit). Upon weakening of the confinement, localization of electrons (analogous to the Wigner crystallization of the homogeneous electron gas) occurs,[4,29] bringing about breakdown of the predominantly single-determinantal nature of the electronic wave function that manifests itself in the asymptotic vanishing of all natural orbital occupancies.[30]

5. CONCLUSIONS

Full configuration interaction calculations carried out in conjunction with careful optimization of basis sets and judicious extrapolation schemes provide benchmark energies for the ^{2}P ground state and the ^{4}P first excited state of the three-electron harmonium atom, allowing for numerical verification of the
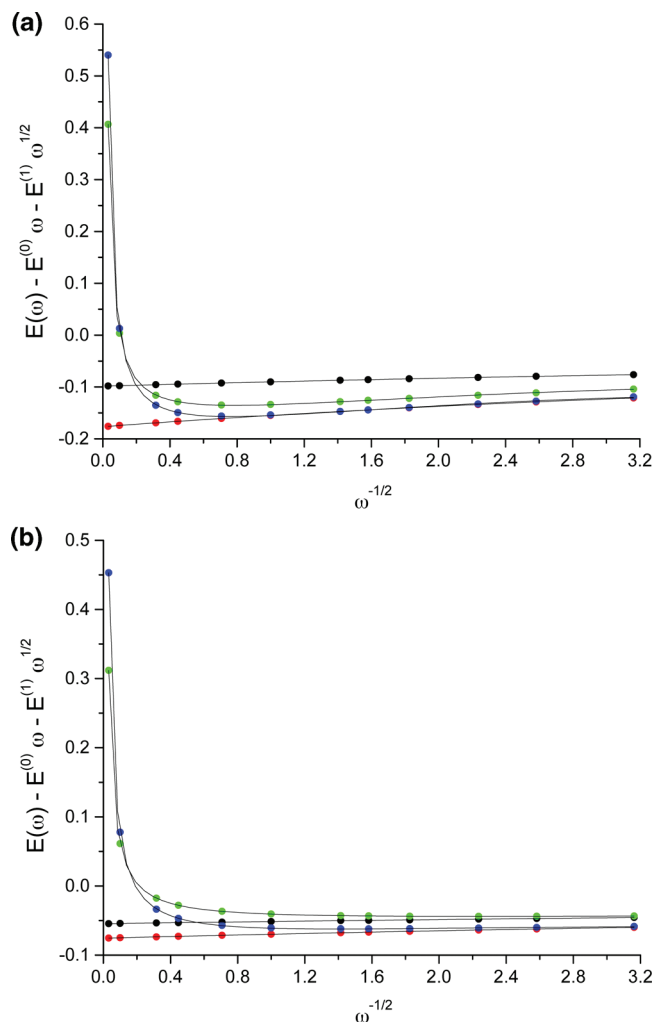
Figure 1. The energy contributions beyond the first order vs $\omega^{-1/2}$ for: (a) the ^{2}P state and (b) the ^{4}P state of the three-electron harmonium atom (red: exact; black: HF; green: BLYP; and blue: B3LYP).

recently obtained second-order energy coefficients[24] and confirming the few available results of Monte Carlo studies.[16] The final energy values, obtained by correcting the extrapolated data for residual errors in the low-order energy coefficients, appear to possess accuracy of ca. 20 μHartree for the doublet state and ca. 10 μHartree for the quartet one, making them suitable for calibration and testing of approximate electron correlation methods of quantum chemistry. The energy limits for individual angular momenta ranging from 1 to 4 are also available, facilitating comparisons with results of calculations involving finite basis sets.

For confinement strengths other than those studied in this paper, the energies can be readily computed with sufficient accuracy from the respective Padé approximants. If needed, the corresponding wave functions can also be obtained by following the present computational procedure while taking advantage of the aforedescribed dependence of the parameters $\alpha_{L,N}(\omega)$ and $\beta_{L,N}(\omega)$ on ω that provides a prescription for rapid construction of the optimal basis sets.

Extension of the present work to higher excited states of the three-electron harmonium atoms and to species with four and five electrons is conceptually straightforward and will be carried out in the near future.

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