

# Properties of harmonium atoms from FCI calculations: Calibration and benchmarks for the ground state of the two-electron species

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When used in conjunction with appropriate extrapolation schemes, full configuration interaction (FCI) calculations employing systematic sequences of spherical Gaussian primitives with even-tempered exponents shared by functions of different angular momenta are capable of affording ground-state energies of the two-electron harmonium atoms with a few- $\mu$ Hartree accuracy that is sufficient for calibration and benchmarking of approximate electron correlation theories of quantum chemistry. The present approach, which is slated for use in future computations of electronic properties of harmonium atoms with between three and five electrons, calls for a series of 15 FCI runs involving basis sets with between four and eight Gaussian primitives of the sp, spd and spdf type. Its applicability is limited by linear dependencies among basis functions that become significant for small (*i.e.* less than 0.03) values of the force constant.

## 1 Introduction

Exactly (quasi-)solvable models of quantum mechanics that pertain to real physical systems are few and far between. Among nontrivial instances of such models, the two-electron nonrelativistic harmonium atom,<sup>1–3</sup> defined by the Hamiltonian

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

with  $N = 2$  (here and in the following the atomic units are used), has attracted much attention from both chemists and physicists. Since harmonium atoms differ from their ordinary (Coulombic) counterparts only in the external potential, they are ideally suited for testing, calibration, and benchmarking of approximate electronic structure methods of quantum chemistry. Indeed, the two-electron harmonium (especially with the force constant  $\omega$  set to 1/2) has been widely employed in studies of various quantities associated with the density functional theory (DFT).<sup>4–13</sup> The ground-state energies and wavefunctions of this species are available in closed analytical forms for certain (infinitely many) values of  $\omega^2$  and as very accurate results of numerical calculations and interpolating approximates otherwise.<sup>3</sup>

Despite being of even greater interest, harmonium atoms with  $N > 2$  have been studied far less than their two-electron counterparts. With analytical solutions of the respective Schrödinger equations unknown, the investigations published so far have either relied on approximate methods or concerned asymptotic limits. Thus, the ground-state properties of the three-electron harmonium have been estimated with the help of an approximate pair model and computed for several values of  $\omega$  with moderate-quality electron correlation methods.<sup>14</sup>

The ground-state energies and wavefunctions of the three- and four-electron species have been analytically determined at the strong-correlation limit of  $\omega \rightarrow 0$ .<sup>15,16</sup> In addition, energies of several states of harmonium atoms have been approximately computed with Monte-Carlo approaches for  $2 \leq N \leq 8$  and a few values of  $\omega$ .<sup>17</sup>

The availability of highly accurate electronic structure data for many-electron harmonium atoms would not only provide the means for testing approximate electron-correlation methods on more complicated systems (note that many of these methods become exact in the case of only two electrons being present) but also aid in the reliable theoretical description of three-dimensional quantum dots.<sup>18</sup> These species, which result from confinement of electrons in parabolic potentials and thus are identical with harmonium atoms, undergo Wigner crystallization at the strong-correlation limit, forming the so-called spherical Coulomb crystals.<sup>19–22</sup> Such crystals emerge in diverse branches of physics including, to name a few, studies of dusty plasmas<sup>23</sup> and ultra-cold ions in electro-magnetic traps.<sup>24,25</sup>

In light of these facts, it would be desirable to develop a robust numerical approach to the computation of electronic properties of harmonium atoms. Such an approach should produce data of benchmark quality for species with diverse (though small) numbers of electrons and magnitudes of the force constant spanning a broad range. Preferably, it should employ only the widely available quantum-chemical software. The full configuration interaction (FCI) method<sup>26</sup> used in conjunction with Gaussian basis sets readily satisfies these criteria. In fact, FCI calculations on two-dimensional quantum dots have been already reported to produce data of useful accuracy.<sup>27</sup>

The research reported in this paper aims at answering several questions. First of all, it determines the magnitudes of  $\omega$  for which sufficient accuracy can be attained with reasonable computational effort. Second, it addresses the issue of the optimal choices of the basis-set size, the maximum value of the

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angular momentum, and the exponents of the primitives involved. Third, it tests the viability of extrapolation schemes to the complete-basis-set (CBS) limit.

The present benchmarks open an avenue to calculations on harmonium atoms with between three and five electrons, the results of which will be presented elsewhere.

## 2 Numerical procedures

All the calculations described in this paper have employed uncontracted basis sets which, for each value of the angular momentum between 0 and  $L$  ( $0 \leq L \leq 3$ ), involve equal numbers  $N$  ( $2 \leq N \leq 8$ ) of spherical Gaussian primitives with exponents  $\zeta_{L,N}^k(\omega)$  that are even-tempered<sup>28</sup> according to the formula

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

The parameters  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$ , which depend on  $N$  and the maximum angular momentum  $L$  but not on the angular momenta of individual primitives, have been optimized (to within the relative accuracy of  $10^{-6}$ ) by minimizing the FCI energies  $E_{L,N}(\omega)$  with a combination of simplex and Newton-Raphson methods.

The computed energies  $E_{L,N}(\omega)$  have been extrapolated to the respective  $N \rightarrow \infty$  limits  $E_L(\omega)$  by fitting the actual energy values for  $N = 4, 5, 6, 7$  and  $8$  with the double-exponential expression

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

which generalizes the Dunning extrapolation.<sup>29</sup> The resulting system of five non-linear equations has been solved analytically with the help of the Ramanujan algorithm.<sup>30</sup>

In turn, the estimates  $E_L(\omega)$  have been extrapolated to the respective CBS limits  $E(\omega)$  by fitting the values of  $E_L(\omega)$  for  $L = 1, 2$  and  $3$  with the expression<sup>31–33</sup>

$$E_L(\omega) = E(\omega) + \frac{B(\omega)}{[L + C(\omega)]^3} \quad (4)$$

It should be noted that, although being significantly closer to the exact energies than their unextrapolated counterparts, the estimates  $E_L(\omega)$  and  $E(\omega)$  are not variational.

All the calculations have been carried out by computing the respective one- and two-electron integrals with the Gaussian03 suite of programs<sup>34</sup> and inputting them into the FCI program of Knowles and Handy.<sup>35</sup>

## 3 Results

The force constant  $\omega$  measures the magnitude of electron correlation effects in harmonium atoms. In the two-electron species, the critical force constant  $\omega_{\text{crit}} \approx 0.04012$  constitutes the boundary between the weak- and strong-correlation regimes.<sup>3</sup> For  $\omega > \omega_{\text{crit}}$ , the system is essentially a set of two three-dimensional harmonic oscillators perturbed by Coulombic coupling. Consequently, it is amenable to description within the perturbation theory, which yields<sup>3</sup>

$$E(\omega) = 3\omega + (2/\pi)^{1/2}\omega^{1/2} + \Delta + O(\omega^{-1/2}) \quad (5)$$

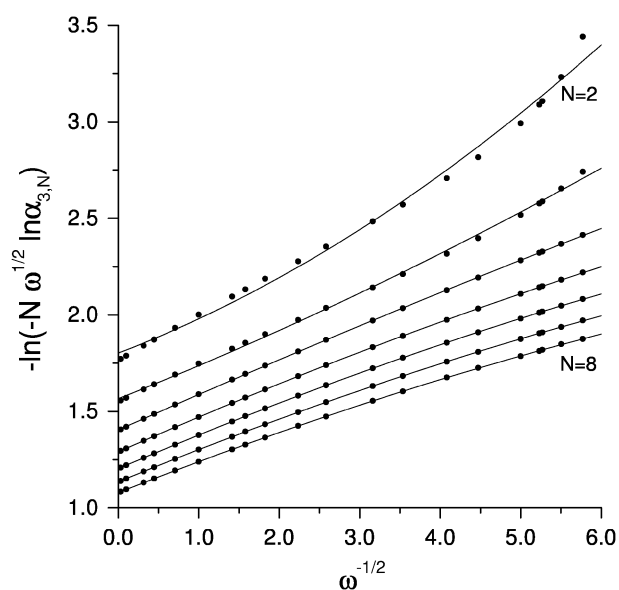
where

$$\Delta = -(2/\pi) [1 - (\pi/2) + \ln 2] \approx -0.0779 \quad (6)$$

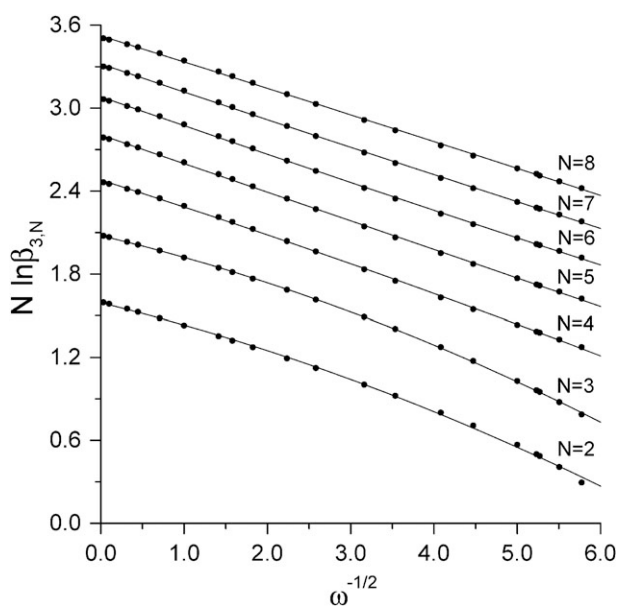
for the ground-state energy. For  $\omega < \omega_{\text{crit}}$ , the system has the characteristics of the respective Coulomb crystal perturbed by quantum effects due to kinetic energy. The different natures of the two regimes are reflected in the ground-state electron densities  $\rho(r)$ , which at  $r = 0$  possess maxima for  $\omega > \omega_{\text{crit}}$  and minima for  $\omega < \omega_{\text{crit}}$ , the transition being accompanied by changes in the patterns of the natural orbital occupancies.<sup>3</sup>

Although the optimized basis-set parameters  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$  vary smoothly with  $\omega$  (Fig. 1 and 2), the calculations become progressively more difficult as  $\omega$  becomes smaller than  $\omega_{\text{crit}}$ . This is due to the extent of linear dependences among the primitives with even-tempered exponents increasing rapidly as  $\beta_{L,N}(\omega) \rightarrow 1$ , which is exactly the behavior observed within the strong-correlation regime. Apparently, reproduction of electron densities that exhibit both minima (for  $r = 0$ ) and maxima (for some  $r > 0$ ) requires combinations of exponential functions with almost degenerate exponents. In practice, FCI calculations with the presently employed Gaussian basis sets are found to be limited to magnitudes of force constant greater than *ca.* 0.03. This conclusion is likely to remain valid for harmonium atoms with more than two electrons.

The dependences of  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$  on  $\omega$  follow simple empirical equations. In particular, both the values of  $-\ln(-N\omega^{1/2}\ln\alpha_{L,N})$  (Fig. 1) and  $M\ln\beta_{L,N}$  (Fig. 2) are accurately approximated for  $N \geq 4$  by second-order polynomials in  $\omega^{-1/2}$ , the quadratic contributions diminishing with increasing  $N$ . For basis sets composed of two and three primitives, the dependences are less regular, making the corresponding FCI energies  $E_{L,2}(\omega)$  and  $E_{L,3}(\omega)$  unsuitable for extrapolation to their  $N \rightarrow \infty$  limits. Thanks to careful optimization of  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$  for each  $\omega$ , these limits are approached quite rapidly (Table 1). For example, the present calculations



**Fig. 1** The dependence of  $-\ln(-N\omega^{1/2}\ln\alpha_{3,N})$  on  $\omega^{-1/2}$  for  $L = 3$ . The respective results for  $L = 0, 1$ , and  $2$  are qualitatively identical. The solid lines are fitted second-order polynomials in  $\omega^{-1/2}$ .



**Fig. 2** The dependence of  $N \ln \beta_{3,N}$  on  $\omega^{-1/2}$  for  $L = 3$ . The respective results for  $L = 0, 1$ , and  $2$  are qualitatively identical. The solid lines are fitted second-order polynomials in  $\omega^{-1/2}$ .

yield  $E_{0,8}(1/2) = 2.0343349$ , which is only  $10^{-7}$  higher than that previously obtained with 16 Gaussian functions.<sup>36</sup>

Further improvements in the accuracy of the FCI energies are afforded by extrapolations, first to the limit of  $N \rightarrow \infty$  [eqn (3)] and then to the CBS limit [eqn (4)]. The first extrapolation produces energies  $E_L(\omega)$  that comprise partial-wave contributions with angular momenta not greater than  $L$  to electron correlation (Table 2). Of particular interest are values of  $E_0(\omega)$ , which account for the radial correlation only. These data, computed for 20 different values of  $\omega$ , agree to all digits with the previously published unextrapolated values<sup>36</sup> for  $\omega = \frac{5-\sqrt{17}}{24}$ , whereas in four cases (for  $\omega = 1/10, 1/2, 10$ , and  $100$ ) they are slightly lower. At the weak correlation limit of  $\omega \rightarrow \infty$ , the computed  $E_L(\omega)$  conform to eqn (5) with  $\Delta = -0.0322, -0.0683, -0.0728$ , and  $-0.0740$  for  $L = 0, 1, 2$ , and  $3$ , respectively.

The additional energy lowerings due to the  $N \rightarrow \infty$  extrapolation are quite significant, reaching  $6 \times 10^{-6}$  for large force constants (Fig. 3). It should be noted that attempts to include the values of  $E_{L,2}(\omega)$  and  $E_{L,3}(\omega)$  (by augmenting the r.h.s. of eqn (3) with one additional exponential function) produce complex fitting parameters, which in turn yield  $E_L(\omega)$  with erratic dependences on  $\omega$ . This behavior can be traced

**Table 2** The extrapolated FCI energies  $E_L(\omega)$

$\omega$	$E_0(\omega)$	$E_1(\omega)$	$E_2(\omega)$	$E_3(\omega)$
0.03	0.2048423	0.1872390	0.1872166	0.1872131
0.033	0.2202746	0.2020557	0.2020386	0.2020337
0.036	0.2354390	0.2166582	0.2166424	0.2166358
0.0365373 <sup>a,b</sup>	0.2381290	0.2192527	0.2192367	0.2192297
0.04	0.2552949	0.2358356	0.2358161	0.2358069
0.05	0.3034506	0.2825685	0.2825213	0.2825038
0.06	0.3499504	0.3279304	0.3278382	0.3278107
0.08	0.4394013	0.4156531	0.4154468	0.4153963
0.1 <sup>b</sup>	0.5254738	0.5004581	0.5001264	0.5000511
0.15	0.7312496	0.7041286	0.7034928	0.7033557
0.2	0.9284684	0.9000238	0.8991221	0.8989284
0.3	1.3079338	1.2778695	1.2765446	1.2762559
0.4	1.6750883	1.6440424	1.6423981	1.6420337
0.5 <sup>b</sup>	2.0343345	2.0026161	2.0007208	2.0002946
1.0	3.7672141	3.7338360	3.7311874	3.7305644
2.0	7.0971063	7.0625814	7.0592759	7.0584674
5.0	16.752298	16.716790	16.712809	16.711796
10.0	32.491021	32.455033	32.450678	32.449546
100.0	307.94625	307.90950	307.90448	307.90313
1000.0	3025.1986	3025.1616	3025.1563	3025.1549

<sup>a</sup>  $\frac{5-\sqrt{17}}{24}$ . <sup>b</sup> Values of  $\omega$  for which closed-form expressions for ground-state wavefunctions are known.<sup>2</sup>

back to the less regular variation of these quantities with  $\omega$  (see above).

Extrapolation to the CBS limit concludes the present approach to the calculation of highly accurate energies of harmonium atoms. The assumed dependence of  $E_L(\omega)$  on  $L$  [eqn (4)] follows from the well-known expression for the partial-wave contributions to the total energies of atoms.<sup>31–33</sup> The computed values of the parameter  $C(\omega)$  (Table 3) are of the order of unity, confirming the validity of the extrapolation formula. Inspection of the data compiled in Table 4 reveals that the final estimates  $E(\omega)$  are indeed very close to their exact counterparts  $E_{\text{exact}}(\omega)$  obtained from highly accurate numerical calculations.<sup>3</sup> In general, the relative error in the ground-state energy is found to increase (although not monotonically) with decreasing  $\omega$ . For the three exactly solvable cases (*i.e.* for  $\omega = 1/2, 1/10$ , and  $\frac{5-\sqrt{17}}{24}$ ), the absolute errors amount to  $2.7 \times 10^{-6}, 0.9 \times 10^{-6}$ , and  $3.2 \times 10^{-6}$ , respectively.

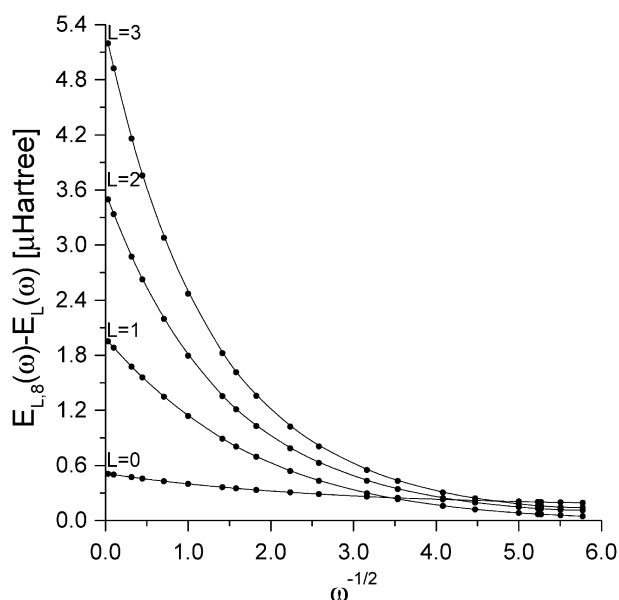
## 4 Discussion and conclusions

When used in conjunction with appropriate extrapolation schemes, full configuration interaction (FCI) calculations employing systematic sequences of spherical Gaussian primitives with even-tempered exponents shared by functions of different

**Table 1** The optimized basis-set parameters  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$  [eqn (2)], and the corresponding FCI energies  $E_{L,N}(\omega)$  for  $\omega = 1/2$

$N$	$\alpha_{0,N}(1/2)$	$\beta_{0,N}(1/2)$	$E_{0,N}(1/2)$	$\alpha_{1,N}(1/2)$	$\beta_{1,N}(1/2)$	$E_{1,N}(1/2)$	$\alpha_{2,N}(1/2)$	$\beta_{2,N}(1/2)$	$E_{2,N}(1/2)$	$\alpha_{3,N}(1/2)$	$\beta_{3,N}(1/2)$	$E_{3,N}(1/2)$
2	0.898029	2.009527	2.0346069	0.921854	1.843789	2.0031763	0.918244	1.928701	2.0014523	0.916622	1.965956	2.0011404
3	0.916926	1.869962	2.0343778	0.931256	1.750024	2.0027231	0.928348	1.813974	2.0008693	0.926757	1.849451	2.0004754
4	0.926391	1.760091	2.0343470	0.939376	1.658507	2.0026460	0.936816	1.708176	2.0007632	0.935242	1.738049	2.0003479
5	0.934293	1.667381	2.0343388	0.944925	1.591401	2.0026266	0.942742	1.631419	2.0007360	0.941332	1.656181	2.0003141
6	0.940191	1.597030	2.0343363	0.949216	1.540707	2.0026203	0.947326	1.573196	2.0007271	0.946075	1.593691	2.0003028
7	0.944974	1.541756	2.0343353	0.952572	1.500670	2.0026180	0.950968	1.527403	2.0007237	0.949892	1.544341	2.0002984
8	0.948858	1.497469	2.0343349	0.955411	1.467665	2.0026170	0.953994	1.490021	2.0007222	0.953091	1.503934	2.0002965
$\infty^a$			2.0343345			2.0026161			2.0007208			2.0002946

<sup>a</sup> The extrapolated energies  $E_0(1/2), E_1(1/2), E_2(1/2), E_3(1/2)$  (see Table 2).



**Fig. 3** Energy lowerings  $E_{L,s}(\omega) - E_L(\omega)$  due to the  $N \rightarrow \infty$  extrapolation [eqn (3)] vs.  $\omega^{-1/2}$  for  $L = 0, 1, 2$ , and  $3$ .

**Table 3** The extrapolated CBS FCI energies  $E(\omega)$ , and the fitting parameters  $B(\omega)$  and  $C(\omega)$  [eqn (4)]<sup>a</sup>

$\omega$	$E(\omega)$	$B(\omega)$	$C(\omega)$
0.03	0.1872113	0.0000702	0.3629550
0.033	0.2020296	0.0003433	1.3604246
0.036	0.2166274	0.0015440	2.6855343
0.0365373	0.2192205	0.0019025	2.8938786
0.04	0.2357927	0.0038838	3.4905798
0.05	0.2824845	0.0026278	2.1512992
0.06	0.3277867	0.0021208	1.4530776
0.08	0.4153593	0.0023872	1.0102549
0.1	0.4999991	0.0030226	0.8743757
0.15	0.7032647	0.0049495	0.7893690
0.2	0.8988003	0.0069403	0.7834242
0.3	1.2760627	0.0106568	0.8067809
0.4	1.6417868	0.0139182	0.8341648
0.5	2.0000027	0.0167701	0.8582649
1.0	3.7301221	0.0269870	0.9368954
2.0	7.0578750	0.0381769	1.0092729
5.0	16.711030	0.0522846	1.0860066
10.0	32.448674	0.0614006	1.1294380
100.0	307.90205	0.0802971	1.2085527
1000.0	3025.1538	0.0874696	1.2355678

<sup>a</sup> See footnotes on Table 2.

angular momenta are capable of affording ground-state energies of the two-electron harmonium atoms with a few- $\mu$  Hartree accuracy that is sufficient for calibration and benchmarking of approximate electron correlation theories of quantum chemistry. Although the present prescription, which calls for 15 FCI runs, each involving optimization of the basis-set parameters, is not competitive in terms of computational efficiency for the two-electron species, it opens an avenue to systematic, fully automated computations of electronic properties of harmonium atoms with greater numbers of particles. Since in those cases the errors in the energy estimates are expected to be comparable to those presently encountered, this approach is slated to constitute a superior alternative to

**Table 4** Comparison of the extrapolated CBS FCI energies  $E(\omega)$  with their exact counterparts  $E_{\text{exact}}(\omega)$ <sup>a</sup>

$\omega$	$E(\omega)/\omega$	$E_{\text{exact}}(\omega)/\omega$	Rel. err.
0.03	6.240375	6.240321	$8.71 \times 10^{-6}$
0.033	6.122109	6.122094	$2.38 \times 10^{-6}$
0.036	6.017428	6.017497	$-1.15 \times 10^{-5}$
0.0365373	5.999914	6.000000	$-1.43 \times 10^{-5}$
0.04	5.894817	5.894977	$-2.71 \times 10^{-5}$
0.05	5.649691	5.649806	$-2.04 \times 10^{-5}$
0.06	5.463112	5.463177	$-1.20 \times 10^{-5}$
0.08	5.191991	5.192016	$-4.78 \times 10^{-6}$
0.1	4.999991	5.000000	$-1.71 \times 10^{-6}$
0.15	4.688432	4.688426	$1.12 \times 10^{-6}$
0.2	4.494001	4.493993	$1.88 \times 10^{-6}$
0.3	4.253542	4.253534	$1.97 \times 10^{-6}$
0.4	4.104467	4.104460	$1.66 \times 10^{-6}$
0.5	4.000005	4.000000	$1.33 \times 10^{-6}$
1.0	3.730122	3.730121	$3.01 \times 10^{-7}$
2.0	3.528938	3.528939	$-2.82 \times 10^{-7}$
5.0	3.342206	3.342207	$-4.31 \times 10^{-7}$
10.0	3.244867	3.244869	$-3.41 \times 10^{-7}$
100.0	3.079020	3.079021	$-6.47 \times 10^{-8}$
1000.0	3.025154	3.025154	$-7.75 \times 10^{-9}$

<sup>a</sup> See footnotes on Table 2.

Monte-Carlo calculations, accuracy of which rapidly degrades with the increasing number of particles.<sup>17</sup>

Further research is necessary to understand the observed dependences of the optimal basis-set parameters  $\alpha_{L,N}(\omega)$  and  $\beta_{L,N}(\omega)$  on the force constant  $\omega$ . Being able to predict values of these quantities would significantly decrease numerical effort and thus extend the usefulness of the present approach to even larger harmonium atoms.

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## References

- 1 E. Santos, *Anal. R. Soc. Esp. Fis. Quim.*, 1968, **64**, 177.
- 2 M. Taut, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1993, **48**, 3561.
- 3 J. Cioslowski and K. Pernal, *J. Chem. Phys.*, 2000, **113**, 8434 and the references cited therein.
- 4 P. M. Laufer and J. B. Krieger, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1986, **33**, 1480.
- 5 S. Kais, D. R. Hersbach, N. C. Handy, C. W. Murray and G. J. Laming, *J. Chem. Phys.*, 1993, **99**, 417.
- 6 C. Filippi, C. J. Umrigar and M. Taut, *J. Chem. Phys.*, 1994, **100**, 1290.
- 7 C.-J. Huang and C. J. Umrigar, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1997, **56**, 290.
- 8 Z. Qian and V. Sahni, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1998, **57**, 2527.
- 9 M. Taut, A. Ernst and H. Eschrig, *J. Phys. B: At., Mol. Opt. Phys.*, 1998, **31**, 2689.
- 10 S. Ivanov, K. Burke and M. Levy, *J. Chem. Phys.*, 1999, **110**, 10262.
- 11 P. Hessler, J. Park and K. Burke, *Phys. Rev. Lett.*, 1999, **82**, 378.

- 12 W. M. Zhu and S. B. Trickey, *J. Chem. Phys.*, 2006, **125**, 094317.
- 13 E. V. Ludeña, V. Karasiev, A. Artemiev and D. Gómez, in *Functional N-representability in density Matrix and Density Functional Theory: An illustration for Hooke's Atom*, ed. J. Cioslowski, Kluwer Academic/Plenum Publishers, New York, 2000, ch. 10.
- 14 M. Taut, K. Pernal, J. Cioslowski and V. Staemmler, *J. Chem. Phys.*, 2003, **118**, 4861.
- 15 J. Cioslowski and K. Pernal, *J. Chem. Phys.*, 2006, **125**, 064106.
- 16 J. Cioslowski and E. Grzebielucha, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2008, **77**, 032508.
- 17 K. Varga, P. Navratil, J. Usukura and Y. Suzuki, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 205308.
- 18 L. Jacak, P. Hawrylak and A. Wojs, *Quantum Dots*, Springer-Verlag, Berlin, 1998.
- 19 J. Cioslowski and E. Grzebielucha, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2008, **78**, 026416 and references cited therein.
- 20 P. Ludwig, S. Koose and M. Bonitz, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **71**, 046403 and references cited therein.
- 21 S. W. Apolinario, B. Partoens and F. M. Peeters, *New J. Phys.*, 2007, **9**, 283 and references cited therein.
- 22 O. Arp, D. Block, M. Bonitz, H. Fehske, V. Golubnychiy, S. Koose, P. Ludwig, A. Melzer and A. Piel, *J. Phys. Conf. Ser.*, 2005, **11**, 234.
- 23 M. Bonitz, D. Block, O. Arp, V. Golubnychiy, H. Baumgartner, P. Ludwig, A. Piel and A. Filinov, *Phys. Rev. Lett.*, 2006, **96**, 075001.
- 24 M. Drewsen, C. Brodersen, L. Hornekaer, J. S. Hangst and J. P. Schiffer, *Phys. Rev. Lett.*, 1998, **81**, 2878.
- 25 D. J. Wineland, J. C. Bergquist, W. M. Itano, J. J. Bollinger and C. H. Manney, *Phys. Rev. Lett.*, 1987, **59**, 2935.
- 26 A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill Printing Company, New York, First edn, Revised edn, 1982.
- 27 M. Rontani, C. Cavazzoni, D. Bellucci and G. Goldoni, *J. Chem. Phys.*, 2006, **124**, 124102.
- 28 K. Ruedenberg, R. C. Raffanetti and R. D. Bardo, *Energy, Structure, and Reactivity. Proceedings of the 1972 Boulder Seminar Research Conference on Theoretical Chemistry*, ed. D. W. Smith, Wiley, New York, 1973, p. 164.
- 29 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **99**, 1914.
- 30 S. Ramanujan, *J. Ind. Math. Soc.*, 1912, 94.
- 31 R. N. Hill, *J. Chem. Phys.*, 1985, **83**, 1173.
- 32 W. Kutzelnigg and J. D. Morgan, *J. Chem. Phys.*, 1992, **96**, 4484.
- 33 W. Kutzelnigg and J. D. Morgan, *J. Chem. Phys.*, 1992, **97**, 8821 (Erratum).
- 34 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision E.01)*, Gaussian, Inc., Wallingford, CT, 2004.
- 35 P. Knowles and N. Handy, *Comput. Phys. Commun.*, 1989, **54**, 75.
- 36 J. Katriel, S. Roy and M. Springborg, *J. Chem. Phys.*, 2005, **123**, 104104.