Partial-wave decomposition of the ground-state wavefunction of the two-electron harmonium atom

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Abstract An exact formula for the collective occupancy of natural orbitals with an angular momentum l is derived for the ground state of the two-electron harmonium atom. For confinement strengths ω that correspond to polynomial correlation factors as well as at the weak ($\omega \rightarrow \infty$) and strong ($\omega \rightarrow 0$) correlations limits, it reduces to closed-form expressions. At the former limit, a similar result obtains for the partial-wave contributions to the ground-state energy. Slow convergence of the collective occupancies to their leading large- l asymptotics provided by Hill's formula is uncovered. As the rate of convergence decreases strongly with ω , a complete breakdown of Hill's formula ensues upon the confinement strength becoming infinitesimally small. The relevance of these findings to the performance of the extrapolation schemes for the estimation of the complete-basis-set limits of quantum-mechanical observables is discussed.

Keywords Partial-wave decomposition · Two-electron harmonium atom · Electron correlation

1 Introduction

The vast majority of modern quantum-chemical calculations rely on approximating electronic wavefunctions (or their equivalents) with linear combinations of basis

functions. The choice of these functions is dictated by computational expedience and usually does not reflect singularities present in the potential energy. Thus, at the one-electron level, the commonly employed Gaussian-type basis functions do not possess cusps at nuclei, and at the many-electron level, the Slater determinants do not reproduce the electron–electron coalescence cusps.

The failure to properly reproduce the particle–particle coalescence asymptotics bears upon the rates of convergence of the computed energies and other observables to their complete-basis-set (CBS) limits [1]. Whereas in practice this convergence is sufficiently rapid for the solutions of the Hartree–Fock equations [2, 3], obtaining accurate approximations to correlated electronic wavefunctions is much more difficult [4, 5]. In order to alleviate this problem, two distinct strategies have been developed, namely inclusion of a correlation factor in the trial function [6–8] and extrapolation to the CBS limit [9, 10]. Successful implementations of the latter approach hinge upon understanding how the approximate wavefunction approaches its exact counterpart as the size of the basis set increases.

In a seminal paper [4], Hill carefully analyzed this asymptotic behavior for singlet ground states of two-electron systems. Results of that investigation, subsequently rederived [11] and generalized to excited states [5] and explicitly correlated basis functions [12], have opened an avenue to a plethora of extrapolation formulae that furnish approximate CBS limits for the total energy in terms of the energies computed with sequences of basis sets truncated at particular values of angular momenta [9, 10].

Among Hill's results, the large- l asymptotics [4]

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^6 v_l = \frac{5\pi}{4} \int |\Psi(\vec{r}, \vec{r})|^2 r^5 d\vec{r}, \quad (1)$$

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which relates the rate of decay of the collective occupancy (per spin) ν_l of the natural orbitals (NOs) with the angular momentum l to the spatial part $\Psi(\vec{r}_1, \vec{r}_2)$ of the underlying electronic wavefunction, is of particular interest. Unfortunately, rigorous analysis of deviations of the collective occupancies from their asymptotic estimates given by Eq. (1), which would certainly aid in the development in more accurate extrapolation formulae, has not been carried out thus far. As demonstrated in the present paper, such an analysis, which is quite difficult (if not outright impossible) for fully Coulombic systems (i.e., the helium-like species) due to the unavailability of an explicit expression for ν_l , becomes facile upon replacing the external Coulombic potential with the harmonic one.

2 Theory

The two-electron harmonium atom, described by the non-relativistic Hamiltonian [13, 14]

$$\hat{H} = -\frac{1}{2}(\hat{\nabla}_1^2 + \hat{\nabla}_2^2) + \frac{1}{2}\omega^2(r_1^2 + r_2^2) + \frac{1}{r_{12}}, \quad (2)$$

is an archetype of quasi-solvable systems of relevance to electronic structure theory. As such, it has been repeatedly employed in calibration and benchmarking of approximate electron correlation methods, especially in the context of the density functional theory [15–20]. Its three- and four-electron counterparts have also been extensively studied [21–25].

The spatial part of the $^1S_+$ ground-state wavefunction $\Psi(\omega; \vec{r}_1, \vec{r}_2)$ of the two-electron harmonium atom is given by the expression [13, 14]

$$|\vec{r}_1 - \vec{r}_2|^{2j-1} = (r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12})^{(j-1/2)} \\ = \sum_{l=0}^{\infty} \sum_{p=0}^{\min(j,l)} \sum_{q=p}^j \sum_{k=0}^{j-q} B_{jlpqk} r_{<}^{l+2k-2p+2q} r_{>}^{-l+2k+2p-1} (r_1^2 + r_2^2)^{j-q-2k} P_l(\cos\theta_{12}), \quad (8)$$

$$\Psi(\omega; \vec{r}_1, \vec{r}_2) = \exp\left[-\frac{\omega}{2}(r_1^2 + r_2^2)\right] g(\omega; |\vec{r}_1 - \vec{r}_2|), \quad (3)$$

where the correlation factor $g(\omega; r)$ (inclusive of the normalization constant) has the power series representation

$$B_{jlpqk} = (-1)^q (2l+1) \frac{2^{k+q} (2q+1)}{2l-2p+2q+1} \frac{j!}{k!(j-2k-q)!(2k+2q+1)!!} \binom{2p}{p} \binom{2l-2p}{l-p} \binom{2q-2p}{q-p} \binom{2l-2p+2q}{l-p+q}^{-1}. \quad (10)$$

$$g(\omega; r) = \sum_{j=0}^{\infty} C_j(\omega) r^j. \quad (4)$$

It is worth noting that, since the ratio $C_1(\omega)/C_0(\omega)$ is fixed at $\frac{1}{2}$ by the electron–electron coalescence cusp condition, setting $\vec{r}_1 = \vec{r}_2 = 0$ in Eq. (3) yields $C_0(\omega) = \Psi(\omega; \vec{0}, \vec{0})$ and $C_1(\omega) = \frac{1}{2}\Psi(\omega; \vec{0}, \vec{0})$. For certain values of $\omega \in \{\omega_K\}$, the series (4) terminates at the K th power of r ($K \geq 1$). The first four elements of the set $\{\omega_K\}$ are $\omega_1 = \frac{1}{2}$, $\omega_2 = \frac{1}{10}$, $\omega_3 = \frac{5-\sqrt{17}}{24}$, and $\omega_4 = \frac{35-3\sqrt{57}}{712}$ [13, 14].

Because to its spherical symmetry, $\Psi(\omega; \vec{r}_1, \vec{r}_2)$ can be partitioned into contributions $\Psi_l(\omega; r_1, r_2)$ due to individual angular momenta l ,

$$\Psi(\omega; \vec{r}_1, \vec{r}_2) = \sum_{l=0}^{\infty} \Psi_l(\omega; r_1, r_2) P_l(\cos\theta_{12}), \quad (5)$$

where $P_l(t)$ is the l th Legendre polynomial and θ_{12} is the angle between the vectors $\vec{r}_1$ and $\vec{r}_2$. The norm $(2l+1)^{-1} \langle \Psi_l(\omega; r_1, r_2) | \Psi_l(\omega; r_1, r_2) \rangle$ equals $\nu_l(\omega)$ that according to Eq. (1) has the large- l asymptotics of

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2}\right)^6 \nu_l(\omega) = \frac{5\pi}{4} |g(\omega; 0)|^2 \int \exp(-2\omega r^2) r^5 d\vec{r} \\ = \frac{15\pi^2}{16} \omega^{-4} |\Psi(\omega; \vec{0}, \vec{0})|^2. \quad (6)$$

Computations of the partial-wave contributions commence with application of the identities [26]

$$|\vec{r}_1 - \vec{r}_2|^{2j} = (r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12})^j \\ = \sum_{l=0}^j \sum_{k=0}^{j-l} A_{jlk} (r_1r_2)^{l+2k} (r_1^2 + r_2^2)^{j-l-2k} P_l(\cos\theta_{12}) \quad (7)$$

and

$$\text{where } r_{<} = \min(r_1, r_2), r_{>} = \max(r_1, r_2), \\ A_{jlk} = (-1)^l (2l+1) \frac{2^{l+k} j!}{(j-l-2k)!(2l+2k+1)!! k!}, \quad (9)$$

and

Combining Eqs. (3), (4), and (5) with Eqs. (7)–(10) produces

$$\Psi_l(\omega; r_1, r_2) = \Psi_l^+(\omega; r_1, r_2) + \Psi_l^-(\omega; r_1, r_2), \quad (11)$$

where the contributions due to the terms with even and odd powers of r in the expansion (4) read

$$\begin{aligned} \Psi_l^+(\omega; r_1, r_2) = & \exp\left[-\frac{\omega}{2}(r_1^2 + r_2^2)\right] \sum_{j=l}^{\infty} C_{2j}(\omega) \\ & \times \left[\sum_{k=0}^{j-l} A_{jlk} (r_1 r_2)^{l+2k} (r_1^2 + r_2^2)^{j-l-2k} \right] \end{aligned} \quad (12)$$

and

$$\begin{aligned} \Psi_l^-(\omega; r_1, r_2) = & \exp\left[-\frac{\omega}{2}(r_1^2 + r_2^2)\right] \sum_{j=1}^{\infty} C_{2j-1}(\omega) \\ & \times \left[\sum_{p=0}^{\min(j,l)} \sum_{q=p}^j \sum_{k=0}^{j-q} B_{jlpqk} r_{<}^{l+2k-2p+2q} \right. \\ & \left. \times r_{>}^{-l+2k+2p-1} (r_1^2 + r_2^2)^{j-q-2k} \right], \end{aligned} \quad (13)$$

respectively.

When employed in conjunction with the identity

$$\begin{aligned} & \int_0^{\infty} \int_0^{\infty} r_{<}^{\alpha} r_{>}^{\alpha'} (r_1^2 + r_2^2)^{\beta} \exp\left[-\omega(r_1^2 + r_2^2)\right] r_1^2 r_2^2 dr_1 dr_2 \\ & = \frac{2^{-(\alpha+\alpha'+4)/2} \omega^{-(\alpha+\alpha'+2\beta+6)/2}}{\alpha+3} \\ & \times \Gamma\left(\frac{\alpha+\alpha'+2\beta+6}{2}\right) {}_2F_1\left(1, -\frac{\alpha'+1}{2} \middle| -1\right) \end{aligned} \quad (14)$$

where $\Gamma(t)$ and ${}_2F_1\left(\frac{a_1, a_2}{b_1} \middle| t\right)$ are the pertinent gamma and hypergeometric functions, respectively, Eqs. (12) and (13) yield

$$\begin{aligned} v_l(\omega) = & \sum_{j=l}^{\infty} \sum_{j'=l}^{\infty} \frac{C_{2j}(\omega) C_{2j'}(\omega)}{\omega^{j+j'+3}} D_{ljj'}^{++} \\ & + 2 \sum_{j=1}^{\infty} \sum_{j'=l}^{\infty} \frac{C_{2j-1}(\omega) C_{2j'}(\omega)}{\omega^{j+j'+5/2}} D_{ljj'}^{-+} \\ & + \sum_{j=1}^{\infty} \sum_{j'=1}^{\infty} \frac{C_{2j-1}(\omega) C_{2j'-1}(\omega)}{\omega^{j+j'+2}} D_{ljj'}^{--}, \end{aligned} \quad (15)$$

where

$$D_{ljj'}^{++} = \frac{\pi^3}{2l+1} (j+j'+2)! \sum_{k=0}^{j-l} \sum_{k'=0}^{j'-l} 2^{-4(l+k+k'+1/2)} \binom{2l+2k+2k'+2}{l+k+k'+1} A_{jlk} A_{j'lk'}, \quad (16)$$

$$\begin{aligned} D_{ljj'}^{-+} = & \frac{\pi^2}{2l+1} \Gamma\left(j+j'+\frac{5}{2}\right) \sum_{p=0}^{\min(j,l)} \sum_{q=p}^j \sum_{k=0}^{j-q} \sum_{k'=0}^{j'-l} \frac{2^{-(l+2k+2k'+q-5/2)}}{2l+2k+2k'-2p+2q+3} \\ & \times {}_2F_1\left(1, -(k+k'+p) \middle| l+k+k'-p+q+\frac{5}{2} \middle| -1\right) A_{j'lk'} B_{jlpqk}, \end{aligned} \quad (17)$$

and

$$\begin{aligned} D_{ljj'}^{--} = & \frac{\pi^2}{2l+1} (j+j'+1)! \sum_{p=0}^{\min(j,l)} \sum_{q=p}^j \sum_{k=0}^{j-q} \sum_{p'=0}^{\min(j',l)} \sum_{q'=p'}^{j'} \sum_{k'=0}^{j'-q'} \frac{2^{-(2k+2k'+q+q'-3)}}{2(l+k+k'-p-p'+q+q')+3} \\ & \times {}_2F_1\left(1, l-(k+k'+p+p')+\frac{1}{2} \middle| l+k+k'-p-p'+q+q'+\frac{5}{2} \middle| -1\right) B_{jlpqk} B_{j'lp'q'k'}. \end{aligned} \quad (18)$$

Although it is unlikely that in general the sums that enter Eqs. (16)–(18) are reducible to simple analytical expressions, they permit rapid computations of the collective occupancies for arbitrary angular momenta.

2.1 The case of a polynomial correlation factor

When $\omega = \omega_K$, the wavefunction (3) can be written in a closed form as the correlation factor $g(\omega; r)$ is a polynomial of degree K in the interelectron distance r . Accordingly, the even/even and odd/even terms in the rhs of Eq. (15) contribute only to the collective occupancies of NOs with $l \leq 2 \left\lfloor \frac{K-1}{2} \right\rfloor$. In contrast, the odd/odd terms do not vanish for any value of the angular momentum, giving rise to the large- l asymptotics of $v_l(\omega)$. For individual (j, j') combinations, the summations in Eq. (18) can be carried out explicitly, producing expressions involving the digamma function $\gamma(t)$, e.g.,

$$D_{111}^{--} = 2\pi^2 (2l+1) \frac{(2l-3)!!}{(2l+3)!!} \left(4(-16l^5 - 48l^4 - 32l^3 - 4l^2 - 23l + 36) \frac{(2l-5)!!}{(2l+3)!!} + (-4l^2 - 4l + 5) \left[\gamma\left(\frac{2l-3}{4}\right) - \gamma\left(\frac{2l-1}{4}\right) \right] \right), \quad (19)$$

$$D_{112}^{--} = 6\pi^2 (2l+1) \frac{(2l-3)!!}{(2l+3)!!} \left(4(64l^7 + 256l^6 + 80l^5 - 432l^4 + 380l^3 + 1424l^2 + 667l - 1485) \frac{(2l-7)!!}{(2l+5)!!} + (4l^2 + 4l - 7) \left[\gamma\left(\frac{2l-5}{4}\right) - \gamma\left(\frac{2l-3}{4}\right) \right] \right), \quad (20)$$

$$D_{122}^{--} = 18\pi^2 (2l+1) \frac{(2l-5)!!}{(2l+5)!!} \left(4(-512l^{10} - 1280l^9 + 5888l^8 + 11136l^7 - 35712l^6 - 49344l^5 + 76112l^4 + 50312l^3 - 54758l^2 + 183873l - 225540) \frac{(2l-9)!!}{(2l+5)!!} + (-16l^4 - 32l^3 + 88l^2 + 104l - 189) \times \left[\gamma\left(\frac{2l-7}{4}\right) - \gamma\left(\frac{2l-5}{4}\right) \right] \right), \quad (21)$$

etc. These expressions have the large- l asymptotics of

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^{2(j+j'+1)} D_{ljj'}^{--} = \mathcal{D}_{jj'}^{--}, \quad (22)$$

where $\mathcal{D}_{11}^{--} = \frac{15}{4}\pi^2$, $\mathcal{D}_{12}^{--} = -\frac{315}{4}\pi^2$, $\mathcal{D}_{22}^{--} = \frac{8505}{4}\pi^2$, etc. Consequently, the leading large- l asymptotics of $v_l(\omega)$ reads [compare Eqs. (15) and (22)]

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^6 v_l(\omega) = \frac{15\pi^2}{4} \omega^{-4} [C_1(\omega)]^2 = \frac{15\pi^2}{16} \omega^{-4} |\Psi(\omega; \vec{0}, \vec{0})|^2, \quad (23)$$

in agreement with the corollary (6) of Hill's formula. Equation (19) reproduces the collective occupancies produced

by the previously published expressions valid for $K = 1$ [27, 28] and $K = 2$ [28].

2.2 The weak-correlation limit

At the weak-correlation limit of $\omega \rightarrow \infty$, closed-form expressions for the collective occupancies are readily obtainable. The wavefunctions $\{\Phi_{nlm}(\omega; \vec{r})\}$ of a three-dimensional harmonic oscillator with the circular frequency ω ,

$$\Phi_{nlm}(\omega; \vec{r}) = 2 \left(\frac{\omega^3}{\pi} \right)^{1/4} \left[\frac{(2n)!!}{(2n+2l+1)!!} \right]^{1/2} \times L_n^{l+1/2}(\omega r^2) (2\omega r^2)^{l/2} \exp\left(-\frac{\omega}{2} r^2\right) Y_l^m(\theta, \varphi), \quad (24)$$

provide a suitable basis set for such calculations thanks to the simple form of the respective two-electron integral

$$V_{l'n'}(\omega) = \left\langle \Phi_{nlm}(\omega; \vec{r}_1) \Phi_{000}(\omega; \vec{r}_2) \left| \frac{1}{r_{12}} \right| \Phi_{000}(\omega; \vec{r}_1) \Phi_{n'l'm'}(\omega; \vec{r}_2) \right\rangle = \left(\frac{8\omega}{\pi} \right)^{1/2} 2^{-(2n+2n'+l)} \frac{(2n+2n'+2l-1)!}{(n+n'+l-1)!} \times \left[\frac{(n+l)! (n'+l)!}{n! (2n+2l+1)! n'! (2n'+2l+1)!} \right]^{1/2}, \quad (25)$$

which facilitates explicit evaluation of the sums that enter the expressions

$$\tilde{v}_l(\omega) = (2l+1) \sum_{n,n'=0}^{\infty} \left[\frac{V_{l'n'}}{2\omega(n+n'+l)} \right]^2 \quad (26)$$

and

$$E_l^{(2)} = -(2l+1) \sum_{n,n'=0}^{\infty} \frac{V_{l'n'}^2}{2\omega(n+n'+l)}, \quad (27)$$

Table 1 The collective occupancies of NOs at the four largest values of ω that correspond to polynomial correlation factors

l	$\nu_l(\omega_K)$			
	$K = 1$	$K = 2$	$K = 3$	$K = 4$
0	9.755557×10^{-1}	9.146744×10^{-1}	8.392861×10^{-1}	7.637280×10^{-1}
1	2.375865×10^{-2}	8.478905×10^{-2}	1.606437×10^{-1}	2.344602×10^{-1}
2	5.910989×10^{-4}	4.626236×10^{-4}	5.577958×10^{-5}	1.809789×10^{-3}
3	7.141400×10^{-5}	5.589217×10^{-5}	9.702106×10^{-6}	1.412707×10^{-6}
4	1.539745×10^{-5}	1.205081×10^{-5}	2.993862×10^{-6}	2.857688×10^{-7}
5	4.574478×10^{-6}	3.580215×10^{-6}	1.016854×10^{-6}	1.383782×10^{-7}
6	1.671905×10^{-6}	1.308516×10^{-6}	3.973200×10^{-7}	6.519386×10^{-8}
7	7.070209×10^{-7}	5.533500×10^{-7}	1.746623×10^{-7}	3.183796×10^{-8}
8	3.332811×10^{-7}	2.608425×10^{-7}	8.439335×10^{-8}	1.641902×10^{-8}
9	1.708878×10^{-7}	1.337453×10^{-7}	4.400492×10^{-8}	8.940612×10^{-9}
10	9.370289×10^{-8}	7.333657×10^{-8}	2.441966×10^{-8}	5.114637×10^{-9}
20	1.690606×10^{-9}	1.323153×10^{-9}	4.578093×10^{-10}	1.054168×10^{-10}
50	7.564718×10^{-12}	5.920527×10^{-12}	2.071120×10^{-12}	4.896421×10^{-13}
100	1.217710×10^{-13}	9.530410×10^{-14}	3.339285×10^{-14}	7.924784×10^{-15}

where $E_l^{(2)}$ is the incremental contribution to the second-order energy $E^{(2)}$ [and also to its correlation component $E_{corr}^{(2)}$ for $l \neq 0$] arising from $\Psi_l(\omega; r_1, r_2)$. Application of well-known algebraic techniques [29] to these expressions, which follow for $l \neq 0$ from straightforward arguments based upon perturbation theory [30], produces

$$E_l^{(2)} = -\frac{4^{-l}}{\pi(2l+1)l} {}_3F_2\left(\begin{matrix} l, l+\frac{1}{2}, l+\frac{1}{2} \\ l+\frac{3}{2}, 2l+2 \end{matrix} \middle| 1 \right) \quad (28)$$

and

$$\tilde{\nu}_l(\omega) = \left[\frac{4^{-l}}{2\pi l^2} {}_3F_2\left(\begin{matrix} l, l, l+\frac{1}{2} \\ l+1, 2l+2 \end{matrix} \middle| 1 \right) + E_l^{(2)} \right] \omega^{-1}. \quad (29)$$

In Eqs. (24), (28), and (29), $L_n^{l+1/2}(t)$, $Y_l^m(\theta, \varphi)$, and ${}_3F_2\left(\begin{matrix} a_1, a_2, a_3 \\ b_1, b_2 \end{matrix} \middle| t \right)$ are the pertinent generalized Laguerre polynomial, spherical harmonic, and generalized hypergeometric function, respectively. Equation (29) yields the leading asymptotics $\{\tilde{\nu}_l(\omega)\}$ of the collective

occupancies at the limit of $\omega \rightarrow \infty$ that, in excellent agreement with the previously published results of numerical calculations [14], equal $\frac{127-48\pi+36\ln 2}{24\pi} \omega^{-1} \approx 1.534321462 \cdot 10^{-2} \omega^{-1}$ for $l = 1$ and $\frac{-2053+720\pi-300\ln 2}{360\pi} \omega^{-1} \approx 8.864544969 \cdot 10^{-4} \omega^{-1}$ for $l = 2$.

2.3 The strong-correlation limit

At the strong-correlation limit of $\omega \rightarrow 0$, the wavefunction (3) is given by its asymptotic expression [13, 14]

$$\begin{aligned} \Psi(\omega; \vec{r}_1, \vec{r}_2) &\approx \tilde{\Psi}(\omega; \vec{r}_1, \vec{r}_2) \\ &= \frac{3^{1/8}}{2^{5/6} \pi^{3/2}} \omega^{5/3} \exp\left[-\frac{\omega}{4} (\vec{r}_1 + \vec{r}_2)^2\right] \\ &\quad \times \exp\left[-\frac{\sqrt{3}}{4} \omega (|\vec{r}_1 - \vec{r}_2| - r_0)^2\right], \end{aligned} \quad (30)$$

where $r_0 = (\frac{2}{\omega^2})^{1/3}$. The corresponding leading asymptotics $\{\tilde{\nu}_l(\omega)\}$ of the collective occupancies is given by

$$\begin{aligned} \tilde{\nu}_l(\omega) &= \frac{16\pi^2}{2l+1} \frac{3^{1/4}}{2^{5/3} \pi^3} \omega^{10/3} \int_0^\infty \int_0^\infty \left(\frac{2l+1}{2} \int_0^\pi \exp\left[-\frac{\omega}{4} (r_1^2 + r_2^2 + 2r_1 r_2 \cos \theta_{12})\right] \right. \\ &\quad \times \exp\left[-\frac{\sqrt{3}}{4} \omega \left(\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}} - r_0\right)^2\right] P_l(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} \Big)^2 r_1^2 r_2^2 dr_1 dr_2. \end{aligned} \quad (31)$$

Table 2 Ratios of the collective occupancies of NOs to the respective asymptotic estimates [Eq. (23)] at the four largest values of ω that correspond to polynomial correlation factors

l	$\frac{16}{15} \pi^{-2} \omega_K^4 \Psi(\omega_K; \vec{0}, \vec{0}) ^{-2} \left(l + \frac{1}{2}\right)^6 v_l(\omega_K)$			
	$K = 1$	$K = 2$	$K = 3$	$K = 4$
0	0.121488	0.145539	0.380930	1.458749
1	2.156895	9.835114	53.152806	326.466459
2	1.150164	1.150164	0.395576	54.011954
3	1.046288	1.046288	0.518071	0.317455
4	1.019022	1.019022	0.722141	0.290076
5	1.009200	1.009200	0.817617	0.468237
6	1.004966	1.004966	0.870434	0.601047
7	1.002904	1.002904	0.902988	0.692683
8	1.001807	1.001807	0.924564	0.756977
9	1.001180	1.001180	0.939632	0.803398
10	1.000803	1.000803	0.950584	0.837862
20	1.000058	1.000058	0.987013	0.956434
50	1.000002	1.000002	0.997857	0.992771
100	1.000000	1.000000	0.999459	0.998173

The integrals that enter Eq. (31) can be evaluated (in the asymptotic sense) with Laplace's method, yielding [22]

$$\tilde{v}_l(\omega) = 2^{7/3} (2l+1) \omega^{1/3} \exp \left[-(2\omega)^{1/3} (2l+1)^2 \right]. \quad (32)$$

These collective occupancies properly sum to the number of electrons,

$$\lim_{\omega \rightarrow 0} \sum_{l=0}^{\infty} \tilde{v}_l(\omega) = \lim_{\omega \rightarrow 0} \int_0^{\infty} \tilde{v}_l(\omega) dl = 1 \quad (33)$$

but obviously do not conform to Hill's asymptotic formula

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^6 \tilde{v}_l(\omega) = \frac{5 \cdot 3^{5/4}}{2^{17/3} \pi} \omega^{-2/3} \exp \left(-\frac{3^{1/2}}{2^{1/3} \omega^{1/3}} \right). \quad (34)$$

3 Discussion and conclusions

The collective occupancies of natural orbitals pertaining to ground states of two-electron harmonium atoms with the four largest confinement strengths that give rise to polynomial correlation factors are listed in Table 1. As expected, the values of $v_0(\omega_K)$ gradually decrease with K as weakening of the confinement (note that $\forall_K \omega_{K+1} < \omega_K$) gives rise to stronger electron correlation. Interestingly, this depopulation of the s -type orbitals does not translate into uniform increases in the collective occupancies of NOs with nonzero angular momenta l . The key to understanding of this phenomenon lies in the behavior of the even/even, odd/even, and odd/odd terms in Eq. (15), namely the vanishing

of the first two types of contributions for $l > 2 \left\lceil \frac{K-1}{2} \right\rceil$. Thus, at least for $\omega \in \{\omega_K\}$, decreasing ω results in predominant enhancement of the collective occupancies of NOs with low values of l . The range of the angular momenta at which this mechanism is operative steadily increases with the extent of electron correlation.

In light of this observation, one anticipates large deviations of the collective occupancies from their asymptotic counterparts given by Hill's formula. Indeed, inspection of Table 2, in which the ratios of the computed data from Table 1 to those obtained from Eq. (23) are compiled, reveals dramatic failures of the asymptotic predictions for small angular momenta, attainment of the asymptotic convergence requiring larger and larger values of l as the electrons become more correlated. Consequently, the complete breakdown of Hill's asymptotics at the strong-correlation limit of $\omega \rightarrow 0$ comes as no surprise.

It is instructive to compare the exact expressions (28) and (29) with the asymptotic ones, i.e.,

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^6 \tilde{v}_l(\omega) = \frac{15}{16\pi} \omega^{-1} \quad (35)$$

and

$$\lim_{l \rightarrow \infty} \left(l + \frac{1}{2} \right)^4 E_l^{(2)} = -\frac{3}{4\pi}. \quad (36)$$

The convergence of the exact collective occupancies and energy increments to their asymptotic counterparts is found to be rather slow, the differences at $l = 5$ amounting to 9.3 and 3.6 %, respectively, and decreasing to 3.0 and 1.1 % at $l = 10$. Thus, even at the weak-correlation limit of $\omega \rightarrow \infty$, significant deviations from the leading asymptotic terms of Hill's formulae are observed.

The results of the present study have direct relevance to construction of approximate extrapolation schemes that aim at estimation of the CBS limits. Relying on the dominance of the leading large- l asymptotic terms in the partial-wave expansions, these schemes are commonly employed in electronic structure calculations on systems with small to moderate electron correlation. As clearly demonstrated by the aforesaid data, such extrapolations are bound to fail for strongly correlated species, especially when the nondynamical correlation effects are significant.

In addition to providing benchmarks for extrapolation schemes, Eqs. (28) and (29) give rise to some new identities of mathematical interest. First, combining Eq. (28) with the known asymptotic expansions for the total energy and its $l = 0$ component at the limit of $\omega \rightarrow \infty$ [31] yields the identity

$$\sum_{l=1}^{\infty} \frac{4^{-l}}{(2l+1)l} {}_3F_2 \left(\begin{matrix} l, l + \frac{1}{2}, l + \frac{1}{2} \\ l + \frac{3}{2}, 2l + 2 \end{matrix} \middle| 1 \right) = \pi - 3. \quad (37)$$

In turn, employing this result in conjunction with Eqs. (29) and the known expression for $\tilde{v}_0(\omega)$ [31], one arrives at

$$\sum_{l=1}^{\infty} \frac{4^{-l}}{l^2} {}_3F_2 \left(\begin{matrix} l, l, l + \frac{1}{2} \\ l + 1, 2l + 2 \end{matrix} \middle| 1 \right) = 2 \ln 2 - 1. \quad (38)$$

To author's best knowledge, the identities (37) and (38), which can also be derived from the integral representation of the generalized hypergeometric function, have not been previously published.

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