Note: The weak-correlation limit of the three-electron harmonium atom

Jerzy Cioslowski[a] and Eduard Matito[b]
Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland

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Harmonium atoms (HAs), i.e. systems described by the nonrelativistic Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{k=1}^{N}\hat{\nabla}_k^2 + \sum_{k>l=1}^{N} r_{kl}^{-1} + \frac{1}{2}\omega^2\sum_{k=1}^{N} r_k^2 , \tag{1}$$

are of much interest to both physicists and chemists.[1–3] The general forms of the energy asymptotics of these species at the $\omega \to 0$ and $\omega \to \infty$ limits are well known. At the weak-correlation limit that corresponds to $\omega \to \infty$, the energy E_D of the state D is given by the series[3–6]

$$E_D(\omega) = \sum_{j=0}^{\infty} E_D^{(j)} \omega^{(2-j)/2} . \tag{2}$$

The zeroth- and first-order energy coefficients, $E_D^{(0)}$ and $E_D^{(1)}$, that enter Eq. (2) are trivial to compute. In contrast, evaluation of $E_D^{(2)}$ and its high-order counterparts involves infinite summations. At the strong-correlation (or quasiclassical) limit of $\omega \to 0$, the energy asymptotics reads[1,3,7,8]

$$E_D(\omega) = E_D^{\mathrm{na}}(\omega) + \sum_{j=0}^{\infty} \tilde{E}_D^{(j)} \omega^{(2+j)/3}, \tag{3}$$

where the nonanalytical energy term $E_D^{\mathrm{na}}(\omega)$ that depends on the multiplicity of D vanishes at $\omega = 0$. In Eq. (3), $\tilde{E}_D^{(0)}$ equals the potential energy of the pertinent spherical Coulomb crystal at its equilibrium geometry.[1,3,7,8] The first- and second-order energy coefficients, $\tilde{E}_D^{(1)}$ and $\tilde{E}_D^{(2)}$, describe the zero-point energy of harmonic vibrations about this equilibrium and the lowest order anharmonic correction to it, respectively.[3]

The electronic states of HAs are conveniently labeled with the spinorbitals $\{a\}$ of the three-dimensional harmonic oscillator (with unit mass and force constant) from which the uncorrelated Slater determinant that arises within the zeroth-order perturbation theory of the $\omega \to \infty$ limit is built. In the widely studied case of the $s\bar{s}$ singlet ground state of the two-electron HA, closed-form expressions for $E_{s\bar{s}}^{(0)}$, $E_{s\bar{s}}^{(1)}$, $E_{s\bar{s}}^{(2)}$, $\tilde{E}_{s\bar{s}}^{(0)}$, $\tilde{E}_{s\bar{s}}^{(1)}$, and $\tilde{E}_{s\bar{s}}^{(2)}$ are presently known.[1,3,5,6,8] For the analogous sp_z triplet state, only the expressions for $E_{sp_z}^{(0)}$, $E_{sp_z}^{(1)}$, $\tilde{E}_{sp_z}^{(0)}$, and $\tilde{E}_{sp_z}^{(1)}$ have been published.[6]

The studies on the three-electron HAs have been quite scarce thus far. The energies of the $s\bar{s}p_z$ doublet ground state and the sp_xp_y quartet first excited state have been computed with Monte Carlo (MC)[9] and full configuration-interaction (FCI)[10] methods for 3 and 12 values of ω, respectively. Electronic structures of these states have been investigated within Hartree–Fock and pair-correlation approximations.[11–13] In addition, analysis of the strong correlation limit has yielded $\tilde{E}_{s\bar{s}p_z}^{(0)} = (1/2)\,3^{5/3}$ and $\tilde{E}_{s\bar{s}p_z}^{(1)} = (1/2)\,(3 + 6^{1/2} + 3^{1/2})$.[7] In this note, we present closed-form expressions for the zeroth-, first-, and second-order energy coefficients of the weak-correlation limits for the $s\bar{s}p_z$ and sp_xp_y states of the three-electron HA. The key equations that pertain to evaluation of these coefficients read

$$E_{abc}^{(0)} = \epsilon_a + \epsilon_b + \epsilon_c, \tag{4}$$

$$E_{abc}^{(1)} = \langle ab|\,|ab\rangle + \langle ac|\,|ac\rangle + \langle bc|\,|bc\rangle , \tag{5}$$

and

$$E_{abc}^{(2)} = E_{ab}^{(2)} + E_{ac}^{(2)} + E_{bc}^{(2)} + \Delta_{a,bc} + \Delta_{b,ac} + \Delta_{c,ab}, \tag{6}$$

where

$$E_{ab}^{(2)} = -\frac{1}{2}{\sum_{pq}}' \frac{\langle ab|\,|pq\rangle^2}{\epsilon_p + \epsilon_q - \epsilon_a - \epsilon_b}, \tag{7}$$

and

$$\Delta_{a,bc} = -2{\sum_{p}}' \frac{\langle ba|\,|bp\rangle\,\langle ca|\,|cp\rangle}{\epsilon_p - \epsilon_a} + {\sum_{p}}' \frac{\langle bc|\,|ap\rangle^2}{\epsilon_p + \epsilon_a - \epsilon_b - \epsilon_c} + \frac{\langle ac|\,|bc\rangle^2 - \langle ab|\,|cb\rangle^2}{\epsilon_b - \epsilon_c}, \tag{8}$$

the terms with vanishing denominators being excluded from the respective summations. In Eqs. (4), (7) and (8), ϵ_a denotes the orbital energy of the spinorbital a.

For the $s\bar{s}p_z$ state one obtains

$$E_{s\bar{s}p_z}^{(0)} = \tfrac{11}{2} \tag{9}$$

and

$$E_{s\bar{s}p_z}^{(1)} = E_{s\bar{s}}^{(1)} + E_{sp_y}^{(1)} + E_{\bar{s}p_z}^{(1)} = \frac{5}{2}\sqrt{\frac{2}{\pi}}. \tag{10}$$

The second-order energy coefficients for the $s\bar{s}$, sp_z, and $\bar{s}p_z$ states of the two-electron HA turn out to be given by the expressions:

$$E_{s\bar{s}}^{(2)} = -\frac{2}{\pi}\sum_{k=1}^{\infty}\frac{2^{-2k}(2k-1)!}{(2k+1)\,k!^2} = 1 - \frac{2}{\pi}(1 + \ln 2)$$

$$\approx -0.077891, \tag{11}$$

$$E^{(2)}_{sp_z} = -\frac{8}{3\pi}\sum_{k=1}^{\infty}\frac{2^{-2k}(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{5}{9} - \frac{8}{27\pi}(4+3\ln 2) \approx -0.017821, \quad (12)$$

and

$$E^{(2)}_{\bar{s}p_z} = -\frac{1}{3\pi}\sum_{k=1}^{\infty}\frac{2^{-2k}(6k+13)(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{7}{9} - \frac{1}{27\pi}(43+39\ln 2) \approx -0.047856, \quad (13)$$

the formulas for $E^{(2)}_{s\bar{s}}$ and $E^{(2)}_{sp_z}$ matching those obtained previously.[4–6] When combined with the nonadditivity terms,

$$\Delta_{s,\bar{s}p_z} = -\frac{1}{6\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(-4k^2+28k+47)(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{26}{27} - \frac{1}{54\pi}[146+6\sqrt{3}+282\ln 2 - 141\ln(2+\sqrt{3})] \approx -0.016540, \quad (14)$$

$$\Delta_{\bar{s},sp_z} = \frac{2}{3\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(2k-5)(2k-1)!}{(2k+1)\,k!^2} = \frac{4}{3} - \frac{2}{3\pi}[6+10\ln 2 - 5\ln(2+\sqrt{3})] \approx -0.013475, \quad (15)$$

and

$$\Delta_{p_z,s\bar{s}} = -\frac{4}{3\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(-2k^2-k+5)(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{22}{27} - \frac{2}{27\pi}[43-6\sqrt{3}+60\ln 2 - 30\ln(2+\sqrt{3})] \approx -0.003072 \quad (16)$$

these coefficients afford the final result

$$E^{(2)}_{s\bar{s},p_z} = -\frac{1}{2\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(2k-1)!}{(2k+1)(2k+3)\,k!^2} \times \left[(-12k^2+12k+49)+2^{2k}(12k+26)\right] = \frac{49}{9} + \frac{1}{6\pi}[-88+2\sqrt{3}-173\ln 2+98\ln(1+\sqrt{3})] \approx -0.176654. \quad (17)$$

Analogous calculations for the sp_xp_y state produce:

$$E^{(0)}_{sp_xp_y} = \tfrac{13}{2}, \quad (18)$$

$$E^{(1)}_{sp_xp_y} = E^{(1)}_{sp_x} + E^{(1)}_{sp_y} + E^{(1)}_{p_xp_y} = 2\sqrt{\frac{2}{\pi}}, \quad (19)$$

and

$$E^{(2)}_{sp_xp_y} = -\frac{8}{\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(2+2^{2k})(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{23}{9} + \frac{8}{3\pi}[-4+\sqrt{3}-7\ln 2+4\ln(1+\sqrt{3})] \approx -0.0756103, \quad (20)$$

where the pertinent intermediate quantities read:

$$E^{(2)}_{sp_x} = E^{(2)}_{sp_y} = E^{(2)}_{p_xp_y} = E^{(2)}_{sp_z} \quad (21)$$

[which follows from the identical intracular components of the states in question; compare Eq. (14)],

$$\Delta_{s,p_xp_y} = -\frac{16}{15\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(2k+5)(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{16}{135\pi}[-17+3\sqrt{3}+4\pi-30\ln 2 + 15\ln(2+\sqrt{3})] \approx -0.010470, \quad (22)$$

and

$$\Delta_{p_x,sp_y} = \Delta_{p_y,sp_x} = \frac{16}{15\pi}\sum_{k=1}^{\infty}\frac{2^{-4k}(k-5)(2k-1)!}{(2k+1)(2k+3)\,k!^2} = \frac{4}{135\pi}[-86+39\sqrt{3}+7\pi-120\ln 2 + 60\ln(2+\sqrt{3})] \approx -0.005839. \quad (23)$$

The newly obtained expressions for the second-order energy coefficients [Eqs. (17) and (20)] resemble those for the two-electron HA [Eqs. (11)–(13)] but are somewhat more involved. Interestingly, the zeroth-, first-, and second-order energy coefficients of the series (2) and (3) uniquely determine the 13 parameters of the [7/5] Padé approximant $F_{[7/5]}(x)$ that enters the approximate expression

$$E_D(\omega) \approx \omega^{2/3}\,F_{[7/5]}(\omega^{1/6}), \quad (24)$$

which conforms to both the small- and large-ω asymptotics.[14]

In summary, when combined with the previously known small-ω asymptotics, the closed-form second-order expressions for the energies of three-electron harmonium atoms at the weak-correlation limits allow for quite accurate predictions of energies of these species for all magnitudes of the confinement strength.

[a]Electronic mail: jerzy@wmf.univ.szczecin.pl.
[b]Electronic mail: ematito@gmail.com.

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[14]See supplementary material at http://dx.doi.org/10.1063/1.3553558 for the numerical coefficients that enter Eq. (24) and the accuracy of its energy predictions.