

Electron correlation in Hooke's law atom in the high-density limit

P. M. W. Gill and D. P. O'Neill^{a)}

Research School of Chemistry, Australian National University, Australian Capital Territory 0200, Australia

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Closed-form expressions for the first three terms in the perturbation expansion of the exact energy and Hartree–Fock energy of the lowest singlet and triplet states of the Hooke's law atom are found. These yield elementary formulas for the exact correlation energies (-49.7028 and $-5.807\,65$ mE_h) of the two states in the high-density limit and lead to a pair of necessary conditions on the exact correlation kernel $G(w)$ in Hartree–Fock–Wigner theory. © 2005 American Institute of Physics. [DOI: 10.1063/1.1862237]

I. INTRODUCTION

The correlation energy E_C of an electronic system is the difference between its exact energy E and its Hartree–Fock (HF) energy E_{HF} .^{1–3} Systems for which all three of these energies are known *exactly* are rare but they are valuable because they shed light on the mathematical description of electron correlation.

In the early days of quantum mechanics, Hylleraas⁴ undertook a pioneering study of the ground state of the helium-like ion (a system with a nucleus of charge Z and two electrons) and showed that it is possible to expand E as a power series in Z^{-1} . The first two terms can be found easily but the third has not yet been reported in closed form. The best numerical value to date

$$E = -Z^2 + \frac{5}{8}Z - 0.157\,666\,429\,469\,14 + O(Z^{-1}) \quad (1)$$

can be found in the work of Baker *et al.*⁵

However, Linderberg showed⁶ that one *can* find a closed-form expression for the corresponding term in the analogous expansion of E_{HF} . His result

$$E_{\text{HF}} = -Z^2 + \frac{5}{8}Z + \left(\frac{9}{32} \ln \frac{3}{4} - \frac{13}{432}\right) + O(Z^{-1}) \quad (2)$$

also implies that the correlation energy of the heliumlike ion is

$$E_C = -0.046\,663\,253\,999\,48 + O(Z^{-1}), \quad (3)$$

which tends to a constant as $Z \rightarrow \infty$. Such behavior is expected⁷ because, in this limit, the ground state of the ion remains nondegenerate.

Soon after Linderberg's work, Kestner and Sinanoglu introduced a hypothetical atom⁸ in which two electrons repel coulombically but are bound within a harmonic potential. The Schrödinger equation in atomic units for this atom, which we have called hookium,⁹ can be written as

$$\left[-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{Z^4}{2}(r_1^2 + r_2^2) + \frac{1}{r_{12}} \right] \Psi = E\Psi, \quad (4)$$

where Z^4 is the harmonic force constant. Its wave functions and energies take relatively simple forms^{10,11} for certain val-

ues of Z . If $Z = 1/\sqrt{2}$, the lowest singlet state has $E=2$ and

$$\Psi = \left(1 + \frac{r_{12}}{2}\right) \exp\left(-\frac{r_1^2 + r_2^2}{4}\right). \quad (5)$$

If $Z = 1/2$, the lowest triplet state has $E=5/4$ and

$$\Psi = (z_1 - z_2) \left(1 + \frac{r_{12}}{4}\right) \exp\left(-\frac{r_1^2 + r_2^2}{8}\right). \quad (6)$$

Our present interest, however, lies primarily in the high-density limit where $Z = \infty$.

In appropriately scaled lengths and energies,⁶ the Schrödinger equation for hookium becomes

$$\left[-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{r_1^2 + r_2^2}{2} + \frac{1}{Zr_{12}} \right] \Psi = E\Psi, \quad (7)$$

which can be treated by perturbation theory, expanding in the parameter Z^{-1} . In this paper, we show that the first three terms in the expansions of E , E_{HF} , and E_C for lowest singlet and triplet states of hookium can be found in closed form, thereby providing exact expressions for the associated correlation energies in the high-density limit. Some of the singlet results were obtained long ago by Byers Brown and co-workers^{12,13} but the present approach is more transparent and reveals a connection between the exact and HF energies that is not apparent in the earlier work.

Our approach also allows us easily to study the convergence behavior of E_C with respect to the excitation order n in a basis set of unperturbed (i.e., harmonic oscillator) wave functions. It is interesting to compare this with the convergence behavior with respect to angular momentum l which underpins the extrapolation schemes of Petersson *et al.*,¹⁴ Feller,¹⁵ and Helgaker *et al.*¹⁶

Finally, we note that the action intracule¹⁷ of any state of hookium in the high-density limit can also be found in closed form and we exploit this to determine *ab initio* values of the parameters in a correlation kernel for computing correlation energies from intracules.¹⁸ Atomic units are used throughout.

II. EXACT ENERGY OF SINGLET HOOKIUM

The perturbation expansion of the exact ground-state energy of singlet symmetry is

^{a)}Electronic mail: peter.gill@anu.edu.au

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

$$= 3Z^2 + \sqrt{\frac{2}{\pi}}Z + \sum_m \frac{\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle^2}{E_0 - E_m} + \dots, \quad (8)$$

where the sum includes all singly and doubly excited states, and the unperturbed wave functions and orbitals are

$$\Psi_0 = \psi_0(x_1)\psi_0(y_1)\psi_0(z_1)\psi_0(x_2)\psi_0(y_2)\psi_0(z_2), \quad (9)$$

$$\Psi_m = \psi_a(x_1)\psi_b(y_1)\psi_c(z_1)\psi_p(x_2)\psi_q(y_2)\psi_r(z_2), \quad (10)$$

$$\psi_k(x) = (2^k k! \sqrt{\pi})^{-1/2} H_k(x) \exp(-x^2/2). \quad (11)$$

Here H_k is the k th Hermite polynomial and $E_m - E_0 = a + b + c + p + q + r = 2n$ is the excitation level, i.e., the number of nodes in Ψ_m . It can be shown that

$$\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle = \sqrt{\frac{2}{\pi}} \frac{f(a,p)f(b,q)f(c,r)}{2n+1}, \quad (12)$$

$$f(a,p) = \begin{cases} \frac{i^{a-p}(a+p-1)!!}{\sqrt{2^{a+p}a!p!}} & a+p \text{ even} \\ 0 & a+p \text{ odd} \end{cases}, \quad (13)$$

and we therefore have

$$E^{(2)} = -\frac{2}{\pi} \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} \frac{f(a,p)^2 f(b,q)^2 f(c,r)^2}{2n(2n+1)^2}$$

$$= -\frac{2}{\pi} \sum_{x=0}^{\infty} \sum_{y=0}^{\infty} \sum_{z=0}^{\infty} \frac{1}{2n(2n+1)^2} \left[\sum_{a=0}^{2x} f(a, 2x-a)^2 \right]$$

$$\times \left[\sum_{b=0}^{2y} f(b, 2y-b)^2 \right] \left[\sum_{c=0}^{2z} f(c, 2z-c)^2 \right]$$

$$= -\frac{2}{\pi} \sum_{x=0}^{\infty} \sum_{y=0}^{\infty} \sum_{z=0}^{\infty} \frac{1}{2n(2n+1)^2} \frac{(2x)! (2y)! (2z)!}{2^{2x} x!^2 2^{2y} y!^2 2^{2z} z!^2}$$

$$= -\frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(1/2)_n}{2n(2n+1)n!}, \quad (14)$$

where $(1/2)_n$ is a Pochhammer symbol¹⁹ and the ground state is implicitly excluded in the first three lines. The last expression was also obtained by Benson and Byers Brown but it is convenient for our purposes to write it as

$$E^{(2)} = -\frac{2}{\pi} [F_0(1) - F_1(1)], \quad (15)$$

where we have introduced the functions

$$F_0(x) = \sum_{n=1}^{\infty} \frac{(1/2)_n x^{2n}}{2n n!} = -\ln \left(\frac{1 + \sqrt{1-x^2}}{2} \right), \quad (16)$$

$$F_1(x) = \sum_{n=1}^{\infty} \frac{(1/2)_n x^{2n}}{2n+1 n!} = \frac{\sin^{-1} x}{x} - 1, \quad (17)$$

$$F_3(x) = \sum_{n=1}^{\infty} \frac{(1/2)_n x^{2n}}{2n+3 n!} = \frac{\sin^{-1} x}{2x^3} - \frac{\sqrt{1-x^2}}{2x^2} - \frac{1}{3}. \quad (18)$$

Thus, the exact energy of singlet hookium is

$$E = 3Z^2 + \sqrt{\frac{2}{\pi}}Z + \left[1 - \frac{2}{\pi}(1 + \ln 2) \right] + O(Z^{-1}) \quad (19)$$

which is the analog of Eq. (1). White and Byers Brown¹² and Cioslowski and Pernal²⁰ also found Eq. (19) but employed a more complicated approach.

III. HF ENERGY OF SINGLET HOOKIUM

The perturbation expansion of the HF energy⁶ of the lowest singlet state is

$$E_{\text{HF}} = E_{\text{HF}}^{(0)} + E_{\text{HF}}^{(1)} + E_{\text{HF}}^{(2)} + \dots$$

$$= 3Z^2 + \sqrt{\frac{2}{\pi}}Z + 2 \sum_m \frac{\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle^2}{E_0 - E_m} + \dots, \quad (20)$$

where the sum now includes only the singly excited states

$$\Psi_m = \psi_a(x_1)\psi_b(y_1)\psi_c(z_1)\psi_0(x_2)\psi_0(y_2)\psi_0(z_2) \quad (21)$$

and $E_m - E_0 = a + b + c = 2n$ is the excitation level. Proceeding as for the exact energy, we obtain

$$E_{\text{HF}}^{(2)} = -\frac{4}{\pi} \sum_m \frac{f(a,0)^2 f(b,0)^2 f(c,0)^2}{2n(2n+1)^2}$$

$$= -\frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(1/2)_n}{2n(2n+1)} \frac{(1/2)^{2n}}{n!}. \quad (22)$$

This sum over n does not appear in the papers by Byers Brown but comparing it with Eq. (14) reveals a beautiful connection between the exact and HF energies of the singlet. We can write this as

$$E_{\text{HF}}^{(2)} = -\frac{4}{\pi} [F_0(1/2) - F_1(1/2)] \quad (23)$$

and the HF energy of the lowest singlet state of hookium is therefore

$$E_{\text{HF}} = 3Z^2 + \sqrt{\frac{2}{\pi}}Z + \frac{4}{3} - \frac{4}{\pi} [1 + \ln 2 + 2 \ln(\sqrt{3}-1)]$$

$$+ O(Z^{-1}), \quad (24)$$

which is the analog of Eq. (2). White and Byers Brown also obtained this but followed a complicated route¹² that does not involve Eq. (22).

It follows from the results above that the correlation energy of singlet hookium is

$$E_C = \frac{2}{\pi} [1 + \ln 2 + 4 \ln(\sqrt{3}-1)] - \frac{1}{3} + O(Z^{-1}) \quad (25)$$

and we note that its limiting value

$$E_S = -0.049\,702\,833\,165\,773\dots \quad (26)$$

which has been reported previously by Ivanov *et al.*²¹ is similar to that of the singlet heliumlike ion, Eq. (3).

IV. EXACT ENERGY OF TRIPLET HOOKIUM

The perturbation expansion of the exact energy of the lowest triplet state is

$$E = 4Z^2 + \frac{2}{3} \sqrt{\frac{2}{\pi}} Z + \sum_m \frac{\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle^2}{E_0 - E_m} + \dots, \quad (27)$$

where the sum includes all singly and doubly excited states, and the unperturbed wave functions and orbitals are

$$\Psi_0 = \hat{A}[\psi_0(x_1)\psi_0(y_1)\psi_1(z_1)\psi_0(x_2)\psi_0(y_2)\psi_0(z_2)], \quad (28)$$

$$\Psi_m = \hat{A}[\psi_a(x_1)\psi_b(y_1)\psi_c(z_1)\psi_p(x_2)\psi_q(y_2)\psi_r(z_2)]. \quad (29)$$

Here \hat{A} is the antisymmetrizer and $E_m - E_0 = a + b + c + p + q + r - 1 = 2n$ is the excitation level. One can show that

$$\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle = \sqrt{\frac{32 f(a,p) f(b,q) f(c,r+1) \sqrt{r+1}}{\pi (2n+1)(2n+3)}} \quad (30)$$

and combinatorial identities yield

$$\begin{aligned} E^{(2)} &= -\frac{16}{\pi} \sum_m \frac{f(a,p)^2 f(b,q)^2 f(c,r+1)^2 (r+1)}{2n(2n+1)^2 (2n+3)^2} \\ &= -\frac{8}{3\pi} \sum_{n=1}^{\infty} \frac{(1/2)_n}{2n(2n+1)(2n+3)} \frac{1}{n!}. \end{aligned} \quad (31)$$

As before, it is convenient to write this as

$$E^{(2)} = -\frac{8}{9\pi} \left[F_0(1) - \frac{3}{2} F_1(1) + \frac{1}{2} F_3(1) \right] \quad (32)$$

and it follows that the exact energy of the lowest triplet state of hookium is

$$E = 4Z^2 + \frac{2}{3} \sqrt{\frac{2}{\pi}} Z + \left[\frac{5}{9} - \frac{8}{27\pi} (4 + 3 \ln 2) \right] + O(Z^{-1}). \quad (33)$$

V. HF ENERGY OF TRIPLET HOOKIUM

The perturbation expansion of the HF energy of the lowest triplet state is

$$E_{\text{HF}} = 4Z^2 + \frac{2}{3} \sqrt{\frac{2}{\pi}} Z + 2 \sum_m \frac{\langle \Psi_0 | r_{12}^{-1} | \Psi_m \rangle^2}{E_0 - E_m} + \dots, \quad (34)$$

where the sum now includes only the singly excited states and $E_m - E_0 = a + b + c - 1 = 2n$ is the excitation level. Proceeding as for the exact energy, we obtain

$$\begin{aligned} E_{\text{HF}}^{(2)} &= -\frac{32}{\pi} \sum_m \frac{f(a,0)^2 f(b,0)^2 [f(c+1,1)^2 + 2f(c,2)^2]}{2n(2n+1)^2 (2n+3)^2} \\ &= -\frac{16}{15\pi} \sum_{n=1}^{\infty} \frac{(3n+5)(1/2)_n}{2n(2n+1)(2n+3)} \frac{(1/2)^{2n}}{n!}, \end{aligned} \quad (35)$$

which can be written as

$$E_{\text{HF}}^{(2)} = -\frac{16}{9\pi} \left[F_0(1/2) - \frac{21}{20} F_1(1/2) + \frac{1}{20} F_3(1/2) \right] \quad (36)$$

and the HF energy of the lowest triplet state of hookium is therefore

$$\begin{aligned} E_{\text{HF}} &= 4Z^2 + \frac{2}{3} \sqrt{\frac{2}{\pi}} Z + \frac{76}{135} - \frac{4}{135\pi} (62 - 3\sqrt{3}) \\ &\quad - \frac{16}{9\pi} [\ln 2 + 2 \ln(\sqrt{3} - 1)] + O(Z^{-1}). \end{aligned} \quad (37)$$

It follows from the results above that the correlation energy of the lowest triplet state of hookium is

$$\begin{aligned} E_{\text{C}} &= \frac{4}{135\pi} (22 - 3\sqrt{3}) + \frac{8}{9\pi} [\ln 2 + 4 \ln(\sqrt{3} - 1)] - \frac{1}{135} \\ &\quad + O(Z^{-1}) \end{aligned} \quad (38)$$

and we note that its limiting value

$$E_{\text{T}} = -0.005\,807\,652\,539\,920\dots \quad (39)$$

is an order of magnitude smaller than the value for the singlet state. This is physically reasonable for two reasons.

(1) The $2p_z$ orbital is larger than the $1s$ orbital and the electrons are therefore generally further apart in the triplet.

(2) The Fermi hole in the triplet prevents the electrons from approaching as closely as they do in the singlet.

VI. DISCUSSION

Although Eqs. (14), (22), (31), and (35) are superficially similar, their respective sums converge at significantly different rates. More precisely, the asymptotic expansion

$$\frac{(1/2)_n}{n!} \sim \frac{1}{\sqrt{\pi n}} \quad (40)$$

reveals that the n th term in the four sums is $O(n^{-5/2})$, $O(4^{-n})$, $O(n^{-7/2})$, and $O(4^{-n})$, respectively. We can make a number of observations from this. First, the HF energies of both states converge as 4^{-n} which is consistent with empirical studies^{15,16,22} that find that molecular HF energies converge exponentially with basis set size N . Second, the exact energies (and therefore the correlation energies) of the singlet and triplet converge only as $n^{-3/2}$ and $n^{-5/2}$, respectively, which is consistent with observations^{16,23,24} that the correlation energy converges only as an inverse power of N . Third, the exact energy of the triplet converges more rapidly than that of the singlet, which is consistent with the fact²⁵ that the leading terms in the partial-wave expansions of the triplet and singlet are $O[(l+1/2)^{-6}]$ and $O[(l+1/2)^{-4}]$, respectively.

In the high-density (i.e., $Z \rightarrow \infty$) limit, the exact wave functions of the scaled Schrödinger equation are symmetrized or antisymmetrized sums of products of uncoupled harmonic oscillator wave functions. In particular, the lowest singlet and triplet wave functions are

$$\Psi_{\text{S}} = \pi^{-3/2} \exp\left[-\frac{r_1^2 + r_2^2}{2}\right], \quad (41)$$

$$\Psi_T = \pi^{-3/2} \exp\left[-\frac{r_1^2 + r_2^2}{2}\right] (z_1 - z_2), \quad (42)$$

and the corresponding Wigner intracules

$$W_S(u, v) = \frac{2u^2 v^2}{\pi} \exp\left[-\frac{u^2 + v^2}{2}\right], \quad (43)$$

$$W_T(u, v) = \frac{2u^2 v^2}{\pi} \exp\left[-\frac{u^2 + v^2}{2}\right] \left(\frac{u^2 + v^2}{3} - 1\right), \quad (44)$$

and action intracules

$$A_S(w) = \frac{2w^2}{\pi} K_0(w), \quad (45)$$

$$A_T(w) = \frac{4w^3}{3\pi} K_1(w) - \frac{2w^2}{\pi} K_0(w) \quad (46)$$

(where K_n is a modified Bessel function of the second kind¹⁹) are simple functions.¹⁷

We have conjectured¹⁸ that the correlation energy and action intracule of an electronic system are related by

$$E_C = \int_0^\infty A(w)G(w)dw, \quad (47)$$

where $G(w)$ is a universal (but currently unknown) function that we have called the correlation kernel. If the conjecture is true for singlet and triplet hookium in the high-density limit, then it follows that the exact $G(w)$ must satisfy the two conditions

$$\int_0^\infty w^2 K_0(w)G(w)dw = \frac{\pi}{2} E_S, \quad (48)$$

$$\int_0^\infty w^3 K_1(w)G(w)dw = \frac{3\pi}{4} (E_S + E_T), \quad (49)$$

where E_S and E_T are the limiting singlet and triplet correlation energies derived above. While the exact $G(w)$ remains unknown, such conditions may be helpful as guides for constructing useful approximations.

To test their utility, we have determined the two parameters in the empirical correlation kernel¹⁸

$$G(w) = C j_0(\zeta w) \quad (50)$$

so that it satisfies the conditions. The required integrals

$$\int_0^\infty A_S(w)j_0(\zeta w)dw = \frac{1}{(1 + \zeta^2)^{3/2}}, \quad (51)$$

$$\int_0^\infty A_T(w)j_0(\zeta w)dw = \frac{1 - \zeta^2}{(1 + \zeta^2)^{5/2}} \quad (52)$$

are straightforward and yield the unique solution

$$C = \left(\frac{2E_S}{E_S + E_T}\right)^{3/2} E_S, \quad (53)$$

$$\zeta = \left(\frac{E_S - E_T}{E_S + E_T}\right)^{1/2}. \quad (54)$$

The discovery that the resulting values ($C = -0.119$ and $\zeta = 0.889$) are similar to those ($C = -0.099$ and $\zeta = 0.894$) obtained by fitting to the correlation energies of the helium and neon atoms¹⁸ is intriguing and suggests that the two necessary conditions above may indeed be of practical value.

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