Correlation energy of two electrons in the high-density limit

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We consider the high-density-limit correlation energy E_c in $D \geq 2$ dimensions for the ^1S ground states of three two-electron systems: helium (in which the electrons move in a Coulombic field), spherium (in which they move on the surface of a sphere), and hookium (in which they move in a quadratic potential). We find that the E_c values are strikingly similar, depending strongly on D but only weakly on the external potential. We conjecture that for large D, the limiting correlation energy $E_c \sim -\delta^2/8$ in any confining external potential, where $\delta = 1/(D-1)$. © *2009 American Institute of Physics*. [doi:10.1063/1.3275519]

I. INTRODUCTION

The concept of electron correlation energy (E_c) is an old and important one, first introduced by Wigner[1] and later defined by Löwdin[2] as the error

$$E_c = E - E_{HF} \tag{1}$$

of the Hartree–Fock (HF) model. Understanding and calculating E_c is one of the most important and difficult problems in quantum chemistry and molecular physics.

The observation that HF theory is useful for the prediction of molecular structure[3] suggests that E_c often depends only weakly on the external potential. To explore this, we have studied the correlation energy $E_c(D,m,Z)$ of two opposite-spin electrons, confined to a D-dimensional space and moving in an external potential $Z^{m+2}V(r)$, where $V(r) \propto r^m$.

We consider three such systems. In D-helium, the electrons move in the Coulomb potential $V(r) = -1/r$. In D-spherium,[4] they move in a constant potential $V(r) = r^0$ on a D-sphere of radius $1/Z$. (In 2-spherium, for example, this is the surface of a three-dimensional ball.) In D-hookium (also known as Hooke's atom or harmonium),[5] they move in the harmonic potential $V(r) = r^2/2$.

After the length scaling $r \leftarrow Zr$, the Hamiltonians of the three systems reduce to the form[6,7]

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + V(r_1) + V(r_2) + \frac{1}{Zr_{12}}, \tag{2}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Following Hylleraas,[8] perturbation theory can then be used to expand both the exact and HF energies as series in $1/Z$, yielding

$$E = E_0(D,m)Z^2 + E_1(D,m)Z + E_2(D,m) + \mathcal{O}(Z^{-1}), \tag{3}$$

$$E_{HF} = E_0(D,m)Z^2 + E_1(D,m)Z + E_2^{HF}(D,m) + \mathcal{O}(Z^{-1}). \tag{4}$$

Many workers have investigated the energies

$$E_c(D,m) = \lim_{Z\to\infty} E_c = E_2(D,m) - E_2^{HF}(D,m) \tag{5}$$

that arise in the high-density limit. Studies of the heliumlike ions,[8,9] for example, showed that $E_c(3,-1) \approx 47$ mh (millihartrees) and several groups have noted that the limits for 3-spherium [$E_c(3,0) \approx 48$ mh] (Ref. 10) and 3-hookium [$E_c(3,2) \approx 50$ mh] (Refs. 11–13) are similar.

Two-dimensional systems have also been studied and, although the limiting energies for 2-helium [$E_c(2,-1) > 212$ mh],[14] 2-spherium [$E_c(2,0) \approx 227$ mh],[15,16] and 2-hookium [$E_c(2,2) > 162$ mh] (Ref. 17) are several times greater than their $D=3$ analogs, they appear similar to one another. Conversely, those for 4-helium [$E_c(4,-1) > 18$ mh] and higher heliums are much smaller.[14]

Such results suggest that the limiting correlation energies are similar, not only for $D=3$ as previously reported, but also for other D. It leads to the idea that the correlation energy of two electrons in the high-density limit depends strongly on the dimensionality of the space in which they move, but weakly on the external potential. To explore this, we have calculated the limiting correlation energies of the ^1S ground states of helium, spherium, and hookium for $D = 2,3,\ldots,8$. We use atomic units throughout.

II. HELIUM

The one-electron Hamiltonian in D-helium is

$$\hat{H}_0 = -\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{D-1}{r}\frac{d}{dr}\right] - \frac{1}{r} \tag{6}$$

and the zeroth-order wave function is

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = \frac{4^D}{(D-1)^D\Gamma(D)}\exp\left(-\frac{2r_1+2r_2}{D-1}\right). \tag{7}$$

The E_0 and E_1 values are

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$$E_0(D,-1) = -\frac{4}{(D-1)^2}, \tag{8}$$

$$E_1(D,-1) = \frac{4}{(D-1)^2}\frac{\Gamma\left(D+\frac{1}{2}\right)\Gamma\left(\frac{D+1}{2}\right)}{\Gamma(D+1)\Gamma\left(\frac{D}{2}\right)}, \tag{9}$$

where Γ is the Gamma function.[18]

E_2 values were computed using the Hylleraas method.[8] We adopted the length and energy scaling of Herrick and Stillinger[19] and used the Hylleraas basis functions[8]

$$\psi_{n,l,m} = s^n t^l u^m \exp(-s/2), \tag{10}$$

where $s=r_1+r_2$, $t=r_1-r_2$, and $u=r_{12}$. The second-order energy, which minimizes the Hylleraas functional, is then given by

$$E_2(D,-1) = -\tfrac{1}{2}\mathbf{b}^{\mathrm{T}}\mathbf{A}^{-1}\mathbf{b}, \tag{11}$$

where

$$\mathbf{A}_{\omega_1\omega_2} = \mathbf{M}_{\omega_1\omega_2} - \frac{D-1}{2}\mathbf{L}_{\omega_1\omega_2} - 2E_0\mathbf{S}_{\omega_1\omega_2}, \tag{12}$$

$$\mathbf{b}_{\omega} = 2E_1\mathbf{S}_{0\omega} - \frac{D-1}{2}\mathbf{V}_{0\omega} \tag{13}$$

with $\omega=(n,2l,m)$. In Eqs. (12) and (13), **M**, **L**, **S**, and **V** are the kinetic, electron-nucleus, overlap, and repulsion matrices, respectively. Details can be found elsewhere.[19,20] The Hylleraas basis was progressively enlarged by increasing the maximum values of n, l, and m until the most difficult case ($D=2$) converged to six digits.

Although the E_2 value for 3-helium has been studied in great detail (as in, for example, the work of Morgan and co-workers[9,21]), the only other helium whose E_2 value has been reported[19] (by exploiting interdimensional degeneracies[22,23]) is 5-helium.

Although Loeser and Herschbach have investigated the dimensional dependence of the HF energy of helium,[24,7] $E_2^{\mathrm{HF}}(D,-1)$ has been reported[25] only for $D=3$. All values can be found using the generalization

$$E_2^{\mathrm{HF}}(D,-1) = -\int_0^\infty \frac{W(r)^2}{r^{D-1}\Psi_0(\mathbf{r},\mathbf{r})}dr, \tag{14}$$

$$W(r) = 2\int_0^r [J(x)-E_1]\Psi_0(\mathbf{x},\mathbf{x})x^{D-1}dx \tag{15}$$

of the Byers-Brown–Hirschfelder equations,[26] where

$$J(r) = \int_0^\infty \frac{\Psi_0(\mathbf{r},\mathbf{r})}{\max(r,x)}F\left[\frac{3-D}{2},\frac{1}{2},\frac{D}{2},\alpha^2\right]x^{D-1}dx, \tag{16}$$

$\alpha=\min(x,r)/\max(x,r)$, and F is the hypergeometric function.[18] For odd D, this yields simple expressions such as

$$E_2^{\mathrm{HF}}(3,-1) = +\frac{9}{32}\ln\frac{3}{4} - \frac{13}{432}, \tag{17}$$

$$E_2^{\mathrm{HF}}(5,-1) = -\frac{903}{1024}\ln\frac{3}{4} - \frac{35\,213}{124\,416}. \tag{18}$$

Equations (11) and (14) yield the large-D expansions[27]

$$E_2(D,-1) \sim -\frac{5}{8}\delta^2 - \frac{31}{384}\delta^3 + \ldots, \tag{19}$$

$$E_2^{\mathrm{HF}}(D,-1) \sim -\frac{1}{2}\delta^2 + \frac{3}{32}\delta^3 + \ldots, \tag{20}$$

$$E_c(D,-1) \sim -\frac{1}{8}\delta^2 - \frac{67}{384}\delta^3 + \ldots, \tag{21}$$

where, following previous work,[28,29] we use $\delta=1/(D-1)$.

III. SPHERIUM

The zeroth-order Hamiltonian of D-spherium is

$$\hat{H}_0 = -\frac{d^2}{d\theta^2} - (D-1)\cot\theta\frac{d}{d\theta}, \tag{22}$$

where θ is the interelectronic angle and the associated eigenfunctions and eigenvalues are, respectively,

$$\Psi_n(\theta) = \mathcal{N}C_n^{D-1/2}(\cos\theta), \tag{23}$$

$$\varepsilon_n = n(n+D-1), \tag{24}$$

where $C_n^{D-1/2}$ is a Gegenbauer polynomial[18] and

$$\mathcal{N} = \sqrt{\frac{2^{D-3}(2n+D-1)\Gamma\left(\frac{D-1}{2}\right)^2\Gamma(n+1)}{\pi\Gamma(n+D-1)}}. \tag{25}$$

Using the partial-wave expansion of r_{12}^{-1}, one finds

$$\langle C_0^{D-1/2}|r_{12}^{-1}|C_n^{D-1/2}\rangle = \frac{(n+1)_{D-2}}{\left(n+\frac{1}{2}\right)_{D-1}}, \tag{26}$$

where $(a)_n$ is a Pochhammer symbol[18] and, therefore,

$$E_1(D,0) = \frac{\Gamma(D-1)\Gamma\left(\frac{D+1}{2}\right)}{\Gamma\left(D-\frac{1}{2}\right)\Gamma\left(\frac{D}{2}\right)}. \tag{27}$$

The second-order energy is given by

$$E_2(D,0) = \sum_{n=1}^{\infty}\frac{\langle\Psi_0|r_{12}^{-1}|\Psi_n\rangle^2}{\varepsilon_0-\varepsilon_n} = -\frac{\Gamma(D)}{4\pi}\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{(n+1)_{D-2}}{\left(n+\frac{1}{2}\right)_{D-1}^2} \times\left[\frac{1}{n}+\frac{1}{n+D-1}\right], \tag{28}$$

which reduces to generalized hypergeometric functions. It is easy to show[16] that $E_0(D,0)=0$ and

$$E_2^{\mathrm{HF}}(D,0) = 0. \tag{29}$$

The E_2 (and thus E_c) value for 2-spherium was recently reported by Seidl.[15] However, simple expressions for any D can be obtained from Eq. (28). For example,

$$E_c(2,0) = 4\ln 2 - 3, \tag{30a}$$

$$E_c(3,0) = \frac{4}{3} - \frac{368}{27\pi^2}, \tag{30b}$$

$$E_c(4,0) = \frac{64}{75}\ln 2 - \frac{229}{375}, \tag{30c}$$

$$E_c(5,0) = \frac{24}{35} - \frac{2\,650\,112}{385\,875\pi^2}. \tag{30d}$$

Equation (28) also yields the large-D expansion

$$E_c(D,0) \sim -\frac{1}{8}\delta^2 - \frac{21}{128}\delta^3 + \frac{21}{512}\delta^4 + \ldots. \tag{31}$$

IV. HOOKIUM

The one-electron Hamiltonian in D-hookium is

$$\hat{H}_0 = -\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{D-1}{r}\frac{d}{dr}\right] + \frac{r^2}{2} \tag{32}$$

and the zeroth-order wave functions are

$$\Psi_\ell(\mathbf{r}_1,\mathbf{r}_2) = \prod_{k=1}^{D} \psi_{a_k}(x_{1,k})\psi_{b_k}(x_{2,k}) \tag{33}$$

where $x_{i,k}$ is the kth Cartesian coordinate of electron i, and a_k and b_k are non-negative integers. The orbitals are the one-dimensional harmonic oscillator wave functions

$$\psi_a(x) = \sqrt{2^a a!\,\pi^{1/2}}H_a(x)\exp(-x^2/2), \tag{34}$$

where H_a is the ath Hermite polynomial.[18] The energy difference between the eigenstates are given by

$$\varepsilon_\ell - \varepsilon_0 = \sum_{k=1}^{D}(a_k + b_k) = 2n, \tag{35}$$

where $2n$ is the excitation level, i.e., the number of nodes in Ψ_ℓ. It is not difficult to show that $E_0(D,2)=D$ and

$$E_1(D,2) = \frac{1}{\sqrt{2}}\frac{\Gamma\left(\frac{D-1}{2}\right)}{\Gamma\left(\frac{D}{2}\right)}. \tag{36}$$

Both E_2 and E_2^{HF} can be found by direct summation,[13] as in Eq. (28). The sum includes all single and double excitations for E_2, but only singles for E_2^{HF}. The integral $\langle\Psi_0|r_{12}^{-1}|\Psi_\ell\rangle$ vanishes unless all of the a_k+b_k are even and, in that case, it is given by

$$\langle\Psi_0|r_{12}^{-1}|\Psi_\ell\rangle = \frac{1}{\sqrt{2\pi}}\frac{\Gamma\left(\frac{D-1}{2}\right)\Gamma\left(n+\frac{1}{2}\right)}{\Gamma(n+2)} \times\prod_{k=1}^{D}\frac{i^{a_k-b_k}}{\sqrt{\pi a_k!\,b_k!}}\Gamma\left(\frac{a_k+b_k+1}{2}\right). \tag{37}$$

In this way, one eventually finds

$$E_2(D,2) = -\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{4\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{\left(\frac{1}{2}\right)_n^2}{\left(\frac{D}{2}\right)_n}\frac{1}{n!\,n}, \tag{38}$$

$$E_2^{\mathrm{HF}}(D,2) = -\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{2\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{\left(\frac{1}{2}\right)_n^2}{\left(\frac{D}{2}\right)_n}\frac{(1/4)^n}{n!\,n}, \tag{39}$$

which reduce to generalized hypergeometric functions.

$E_2(3,2)$ has been derived by several groups[11,13,30] but the energies for other D have not been reported before. All can be found in closed form and the first few are

$$E_2(2,2) = 2G - \pi\ln 2, \tag{40a}$$

$$E_2(3,2) = 1 - \frac{2}{\pi}(1+\ln 2), \tag{40b}$$

$$E_2(4,2) = \frac{1}{4}\left[2G - \pi\ln 2 + 1 - \frac{\pi}{4}\right], \tag{40c}$$

$$E_2(5,2) = \frac{5}{9} - \frac{8}{27\pi}(4+3\ln 2), \tag{40d}$$

where G is Catalan's constant.[18] Similar remarks pertain to the HF energies with odd D, such as

$$E_2^{\mathrm{HF}}(3,2) = \frac{4}{3} - \frac{4}{\pi}[1+\ln(8-4\sqrt{3})], \tag{41a}$$

$$E_2^{\mathrm{HF}}(5,2) = \frac{8}{27} - \frac{8}{27\pi}[8-3\sqrt{3}+6\ln(8-4\sqrt{3})]. \tag{41b}$$

Equations (38) and (39) also yield the large-D expansions

$$E_2(D,2) \sim -\frac{1}{4}\delta^2 - \frac{5}{32}\delta^3 + \frac{3}{64}\delta^4 + \ldots, \tag{42}$$

$$E_2^{\mathrm{HF}}(D,2) \sim -\frac{1}{8}\delta^2 + \frac{7}{256}\delta^3 + \frac{21}{1024}\delta^4 + \ldots, \tag{43}$$

$$E_c(D,2) \sim -\frac{1}{8}\delta^2 - \frac{47}{256}\delta^3 + \frac{27}{1024}\delta^4 + \ldots. \tag{44}$$

V. RESULTS AND DISCUSSION

Numerical values of E_2, E_2^{HF}, and E_c, for $D=2,\ldots,8$ and $m=-1$, 0, and 2 are reported in Table I. The E_2 values for

TABLE I. Second-order energies and limiting correlation energies in two-electron systems.

System	m	$D=2$	$D=3$	$D=4$	$D=5$	$D=6$	$D=7$	$D=8$
				Second-order exact energies, $-E_2(D,m)$, from Equation (3)				
Helium	−1	0.632 740	0.157 666	0.070 044	0.039 395	0.025 208	0.017 501	0.012 854
Spherium	0	0.227 411	0.047 637	0.019 181	0.010 139	0.006 220	0.004 189	0.003 007
Hookium	+2	0.345 655	0.077 891	0.032 763	0.017 821	0.011 153	0.007 622	0.005 533
				Second-order HF energies, $-E_2^{\mathrm{HF}}(D,m)$, from Equation (4)				
Helium	−1	0.412 607	0.111 003	0.051 111	0.029 338	0.019 020	0.013 325	0.009 852
Spherium	0	0	0	0	0	0	0	0
Hookium	+2	0.106 014	0.028 188	0.012 904	0.007 382	0.004 776	0.003 342	0.002 469
				Limiting correlation energies $-E_c(D,m)$, from Equation (5)				
Helium	−1	0.220 133	0.046 663	0.018 933	0.010 057	0.006 188	0.004 176	0.003 002
Spherium	0	0.227 411	0.047 637	0.019 181	0.010 139	0.006 220	0.004 189	0.003 007
Hookium	+2	0.239 641	0.049 703	0.019 860	0.010 439	0.006 376	0.004 280	0.003 065

helium were found by the Hylleraas technique described in Sec. II. Other results were obtained from Eqs. (14), (28), (29), (38), and (39).

As m increases (for constant D), although the exact and HF energies decrease in magnitude from helium to spherium and then increase from spherium to hookium, the correlation energies always increase. However, the smallness of that increase is striking; E_c is almost independent of m, especially for large D. The correlation energies of helium and hookium differ by only 8% for $D=2$, and this drops to just 2% for $D=8$.

As D increases (for constant m), all of the energies decrease dramatically and the correlation energies fall by almost two orders of magnitude between $D=2$ and $D=8$. Herrick and Stillinger have explained this in D-helium[19] by observing that the Jacobian $(r_1 r_2)^{D-1}$ creates a "dimensionality barrier" that keeps both electrons far from the nucleus and therefore allows them to avoid each other more easily when D is large. Similar arguments apply to D-spherium and D-hookium and, presumably, in general.

The observed dependence of the correlation energy on D and m is consistent with the large-D expansions (21), (31), and (44), all of which take the form

$$E_c(D,m) \sim -\delta^2/8 - C\delta^3, \tag{45}$$

where the coefficient $C \approx 1/6$ varies slowly with m. Such an expression implies that E_c depends primarily on the dimensionality of space, in which the electrons move but with a small correction from the shape of the confining external potential.

We conjecture that Eq. (45) is true for all confining external potentials $V(r)$. To explore this, it would be useful to extend Table I to include "airium" $[V(r)=r]$, "ballium"[31] $[V(r)=r^{\infty}]$, and other such systems. These studies will be reported elsewhere.

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