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A tale of two electrons: Correlation at high density

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ABSTRACT

We review our recent progress in the determination of the high-density correlation energy E_c in two-electron systems. Several two-electron systems are considered, such as the well known helium-like ions (helium), and the Hooke's law atom (hookium). We also present results regarding two electrons on the surface of a sphere (spherium), and two electrons trapped in a spherical box (ballium). We also show that, in the large-dimension limit, the high-density correlation energy of two opposite-spin electrons interacting *via* a Coulomb potential is given by $E_c \sim -1/(8D^2)$ for any radial external potential $V(r)$, where D is the dimensionality of the space. This result explains the similarity of E_c in the previous two-electron systems for $D = 3$.

1. Introduction

The Hartree–Fock (HF) approximation ignores the correlation between electrons, but gives roughly 99% of the total electronic energy [1]. Moreover, it is often accurate for the prediction of molecular structure [2], computationally cheap and can be applied to large systems, especially within local (linear-scaling) strategies [3–10]. To reduce the computational cost still further, various numerical techniques have been developed including, for example, density fitting (or resolution of the identity) [11–16], pseudospectral and Cholesky decomposition [17–23], dual basis methods [24–29], and both attenuation [30,31] and resolution [32–35] of the Coulomb operator.

Unfortunately, the part of the energy which the HF approximation ignores can have important chemical effects and this is particularly true when bonds are formed and/or broken. Consequently, realistic model chemistries require a satisfactory treatment of electronic correlation.

The concept of electron correlation was introduced by Wigner [36] and defined as

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

by Löwdin [37], where E is the exact non-relativistic energy. Feynman referred to E_c as the 'stupidity energy' [38] because of the difficulties associated with its characterization in large systems.

Even though it is a formidable challenge to determine the correlation energy accurately, even in simple systems, recent heroic calculations on the helium atom [39–42] have demonstrated how near-exact results can be found. Indeed, this elementary chemical system has been compared to the number π by Schwartz [43]: *'For thousands of years mathematicians have enjoyed competing with one other to compute ever more digits of the number π. Among modern physicists, a close analogy is computation of the ground state energy of the helium atom, begun 75 years ago by E.A. Hylleraas.'*

Although E_c in the helium atom is now known very accurately, certain correlation effects remain incompletely understood and, for example, even the Coulomb hole [44] itself is more subtle than one might imagine. The primary effect of correlation is to decrease the likelihood of finding the two electrons close together and increase the probability of their being far apart. However, accurate calculations have revealed the existence of a secondary Coulomb hole, implying that correlation also brings distant electrons closer together [45]. The same observation has been made in the H_2 molecule by Per et al. [46] and it appears that secondary (or long-range) Coulomb holes may be ubiquitous in two-electron systems [47].

In order to get benchmark results for the development of intracule functional theory (IFT) [48–54], we have recently initiated an exhaustive study of two-electron systems [55]. In the present Frontiers Article, we review our recent progress in the determination of the correlation energy in various high-density two-electron systems: the helium-like ions (Section 2.1), two electrons on the surface of a sphere (Section 2.2), the Hooke's law atom (Section 2.3), and two electrons trapped in a spherical box (Section 2.4).

It is reasonable to ask whether an understanding of the high-density regime is relevant to normal chemical systems but it turns out that most of the high-density behaviour of electrons is surprisingly similar to that at typical atomic and molecular electron densities. Much can be learned about the languid waltz of a pair of electrons in a covalent bond from their frenetic jig

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in the high-density limit. Moreover, it has led to an understanding of key systems, such as the uniform electron gas [56,57], which form the cornerstone of the popular local density approximation in solid-state physics [58].

We also show (Section 3) that, in the large-dimension limit, the high-density correlation energy of two electrons is given by a simple universal rule which is independent of the external confining potential. Just as one learns about interacting systems by studying non-interacting ones and then introducing the interaction perturbatively, one can understand our three-dimensional world by studying high-dimensional analogues and introducing dimension-reduction perturbatively.

In this study, we confine our attention to the ^1S ground states of two-electron systems. This allows us to ignore the spin coordinates and focus on the spatial part of the wave function. Atomic units are used throughout.

2. High-density limit

For two electrons confined in a spherically-symmetric external potential $V(r)$, the Hamiltonian is

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

where the first two terms represent the kinetic energy of the electrons and $1/r_{12} = 1/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$ is the Coulomb operator (Figure 1). After a suitable scaling of the coordinates and energy [59,60], the Hamiltonian can be recast as

$$\widehat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + V(r_1) + V(r_2) + \frac{1}{Z}\frac{1}{r_{12}}, \tag{3}$$

where Z measures the confinement strength. Eq. (3) is well poised for a perturbation treatment in which the zeroth- and first-order Hamiltonians are

$$\widehat{H}^{(0)} = \hat{h}_1^{(0)} + \hat{h}_2^{(0)}, \quad \widehat{H}^{(1)} = \frac{1}{r_{12}}, \tag{4}$$

and the one-electron Hamiltonian is given by

$$\hat{h}_i^{(0)} = -\frac{1}{2}\nabla_i^2 + V(r_i). \tag{5}$$

The zeroth-order wave function satisfies the eigenequation

$$\widehat{H}^{(0)}\Psi_0(r_1, r_2) = E^{(0)}\Psi_0(r_1, r_2), \tag{6}$$

and the zeroth- and first-order energies are

$$E^{(0)} = \langle \Psi_0 | \widehat{H}^{(0)} | \Psi_0 \rangle, \tag{7}$$

$$E^{(1)} = \langle \Psi_0 | \widehat{H}^{(1)} | \Psi_0 \rangle. \tag{8}$$

Following Hylleraas [61], we can use perturbation theory to expand both the exact [61] and Hartree–Fock (HF) [62] energies as series in $1/Z$, yielding

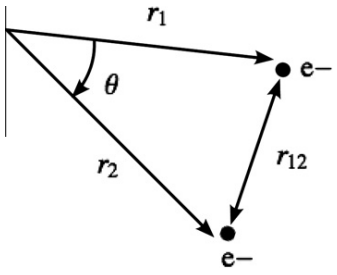

Figure 1. The basic coordinates of a two-electron system.

$$E(Z, D, V) = E^{(0)}(D, V)Z^2 + E^{(1)}(D, V)Z + E^{(2)}(D, V) + E^{(3)}(D, V)Z^{-1} + \cdots, \tag{9}$$

$$E_{\mathrm{HF}}(Z, D, V) = E_{\mathrm{HF}}^{(0)}(D, V)Z^2 + E_{\mathrm{HF}}^{(1)}(D, V)Z + E_{\mathrm{HF}}^{(2)}(D, V) + E_{\mathrm{HF}}^{(3)}(D, V)Z^{-1} + \cdots, \tag{10}$$

where D is the dimensionality of the space. It is straightforward to show that

$$E^{(0)}(D, V) = E_{\mathrm{HF}}^{(0)}(D, V), \tag{11}$$

$$E^{(1)}(D, V) = E_{\mathrm{HF}}^{(1)}(D, V) \tag{12}$$

and therefore, in the high-density (large-Z) limit, we find

$$\begin{aligned} E_{\mathrm{c}}^{(2)}(D, V) &= \lim_{Z\to\infty} E_{\mathrm{c}}(Z, D, V) \\ &= \lim_{Z\to\infty} [E(Z, D, V) - E_{\mathrm{HF}}(Z, D, V)] \\ &= E^{(2)}(D, V) - E_{\mathrm{HF}}^{(2)}(D, V). \end{aligned} \tag{13}$$

2.1. Helium

As a first example, we consider the D-dimensional helium-like ions (He) [61,63] where the electrons move in the Coulomb field of a nucleus with charge Z, *i.e.*,

$$V(r) = -\frac{Z}{r}. \tag{14}$$

From the foregoing section, we have

$$\hat{h}_0 = -\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{D-1}{r}\frac{d}{dr}\right] - \frac{1}{r}, \tag{15}$$

and the zeroth-order wave function is

$$\Psi_0(r_1, r_2) = \frac{4^D}{(D-1)^D \Gamma(D)} \exp\left[-\frac{2(r_1 + r_2)}{D-1}\right]. \tag{16}$$

The $E^{(0)}$ and $E^{(1)}$ values are given by

$$E^{(0)}(D, \mathrm{He}) = -\frac{4}{(D-1)^2}, \tag{17}$$

$$E^{(1)}(D, \mathrm{He}) = \frac{4}{(D-1)^2}\frac{\Gamma(D+\frac{1}{2})\Gamma(\frac{D+1}{2})}{\Gamma(D+1)\Gamma(\frac{D}{2})}, \tag{18}$$

where Γ is the Gamma function [64].

To compute the second-order energy $E^{(2)}$, we use the Hylleraas method [61], adopting the length and energy scaling of Herrick and Stillinger [65] and employing the conventional Hylleraas basis functions [61]

$$\psi_\omega \equiv \psi_{nlm} = s^n t^{2l} u^m \exp(-s/2), \tag{19}$$

where $\omega = (n, l, m)$ are non-negative integers and

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}, \tag{20}$$

are the conventional Hylleraas coordinates. The second-order energy, which minimizes the Hylleraas functional, is then given by

$$E^{(2)}(D, \mathrm{He}) = -\frac{1}{2}\mathbf{b}^{\mathrm{T}}\mathbf{A}^{-1}\mathbf{b}, \tag{21}$$

where

$$\mathbf{A}_{\omega_1\omega_2} = \mathbf{T}_{\omega_1\omega_2} - \frac{D-1}{2}\mathbf{L}_{\omega_1\omega_2} - 2E^{(0)}\mathbf{S}_{\omega_1\omega_2}, \tag{22}$$

$$\mathbf{b}_\omega = 2E^{(1)}\mathbf{S}_{0\omega} - \frac{D-1}{2}\mathbf{U}_{0\omega}, \tag{23}$$

In (22) and (23), **T**, **L**, **S** and **U** are the kinetic, electron-nucleus, overlap and repulsion matrices, respectively, and are defined by

$$T_{\omega_1\omega_2} = \frac{1}{2}\int [\partial_s\psi_{\omega_1}\partial_s\psi_{\omega_2} + \partial_t\psi_{\omega_1}\partial_t\psi_{\omega_2} + \partial_u\psi_{\omega_1}\partial_u\psi_{\omega_2} + s(u^2-t^2)(\partial_s\psi_{\omega_1}\partial_u\psi_{\omega_2} + \partial_u\psi_{\omega_1}\partial_s\psi_{\omega_2}) + t(s^2-t^2)(\partial_t\psi_{\omega_1}\partial_u\psi_{\omega_2} + \partial_u\psi_{\omega_1}\partial_t\psi_{\omega_2})]\,d\tau \quad (24)$$

and

$$L_{\omega_1\omega_2} = \int \psi_{\omega_1}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\psi_{\omega_2}\,d\tau, \quad (25)$$

$$S_{\omega_1\omega_2} = \int \psi_{\omega_1}\psi_{\omega_2}\,d\tau, \quad (26)$$

$$U_{\omega_1\omega_2} = \int \psi_{\omega_1}\frac{1}{r_{12}}\psi_{\omega_2}\,d\tau, \quad (27)$$

with the volume element and domain of integration [65]

$$d\tau = u(s^2-t^2)\mathscr{J}^{\frac{D-3}{2}}\,ds\,dt\,du, \quad (28)$$

$$\mathscr{J} = (s^2-u^2)(u^2-t^2), \quad (29)$$

$$\int d\tau = \int_0^\infty ds\int_0^s du\int_0^u dt. \quad (30)$$

All the matrix elements can be obtained in closed form using the general formula

$$\frac{4}{\Gamma(n+l+m+2D-3)}\int s^n t^l u^m e^{-s}\mathscr{J}^{\frac{D-3}{2}}\,ds\,dt\,du = B\left(\frac{m+1}{2},\frac{D-1}{2}\right)B\left(\frac{l+m+D-1}{2},\frac{D-1}{2}\right), \quad (31)$$

where

$$B(m,n) = \frac{\Gamma(m)\Gamma(n)}{\Gamma(m+n)} \quad (32)$$

is the beta function [64]. The E_2 value for $D = 3$ has been studied in great detail [66,67], but the only other helium whose E_2 value has been reported is 5-helium [65] and this value was obtained by exploiting interdimensional degeneracies [68]. Numerical values of $E^{(2)}$ for $2 \leqslant D \leqslant 7$ are given in Table 1.

$E^{(2)}_{\mathrm{HF}}$ values can be found by generalizing the Byers Brown–Hirschfelder equations [69] to obtain

$$E^{(2)}_{\mathrm{HF}} = -\int_0^\infty \frac{W(r)^2}{r^{D-1}\Psi_0(r,r)}\,dr, \quad (33)$$

$$W(r) = 2\int_0^r [J(x) - E^{(1)}]\Psi_0(x,x)x^{D-1}\,dx, \quad (34)$$

$$J(r) = \int_0^\infty \frac{\Psi_0(r,r)}{\max(r,x)}F\left[\frac{3-D}{2},\frac{1}{2},\frac{D}{2},\alpha^2\right]x^{D-1}\,dx, \quad (35)$$

where $\alpha = \frac{\min(x,r)}{\max(x,r)}$ and F is the Gauss hypergeometric function [64].

$E^{\mathrm{HF}}_2(D,\mathrm{He})$ has been reported for $D = 3$ by Linderberg [62] and Eq. (33) yields expressions such as

$$E^{(2)}_{\mathrm{HF}}(3,\mathrm{He}) = \frac{9}{32}\ln\frac{3}{4} - \frac{13}{432}, \quad (36)$$

$$E^{(2)}_{\mathrm{HF}}(5,\mathrm{He}) = -\frac{903}{1024}\ln\frac{3}{4} - \frac{35213}{124416}, \quad (37)$$

$$E^{(2)}_{\mathrm{HF}}(7,\mathrm{He}) = -\frac{5643101}{204800}\ln\frac{3}{4} - \frac{640149405049}{80621568000}. \quad (38)$$

Numerical values for $2 \leqslant D \leqslant 7$ are shown in Table 1.

2.2. Spherium

Spherium (Sp) consists of two electrons, interacting *via* a Coulomb potential but constrained to remain on the surface of a sphere of radius $R = 1/Z$ [70–73]. This model was introduced by Berry and co-workers [74–77] who used it to understand both weakly and strongly correlated systems, such as the ground and excited states of the helium atom, and also to suggest an alternating version of Hund's rule [78]. Seidl studied this system in the context of density functional theory [79] to test the ISI (interaction-strength interpolation) model [80]. More recently, we have performed a comprehensive study of the spherium ground state, using electronic structure methods ranging from HF theory to explicitly correlated treatments [70].

In this section, we consider D-spherium, the generalization in which the two electrons are trapped on a D-sphere of radius R. We adopt the convention that a D-sphere is the surface of a $(D+1)$-dimensional ball. (Thus, for example, the Berry system is 2-spherium.)

Quantum mechanical models for which it is possible to solve exactly for a finite portion of the energy spectrum are said to be quasi-exactly solvable [81] and we have recently discovered that D-spherium is a member of this small but distinguished family [71,73]. We have found that the Schrödinger equation for D-spherium can be solved exactly for a countably infinite set of R values and that the resulting wave functions are polynomials in the interelectronic distance $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$.

The zeroth-order Hamiltonian of D-spherium is

$$\widehat{H}_0 = -\frac{d^2}{d\theta^2} - (D-1)\cot\theta\frac{d}{d\theta}, \quad (39)$$

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

Table 1
Second-order energies and limiting correlation energies in two-electron systems.

System	$D = 2$	$D = 3$	$D = 4$	$D = 5$	$D = 6$	$D = 7$
Second-order exact energies, $-E^{(2)}(D,V)$, from (9)						
Helium	0.632740	0.157666	0.070044	0.039395	0.025208	0.017501
Spherium	0.227411	0.047637	0.019181	0.010139	0.006220	0.004189
Hookium	0.345655	0.077891	0.032763	0.017821	0.011153	0.007622
Ballium	0.057959	0.014442	0.006194	0.003333	0.002037	0.001352
Second-order HF energies, $-E^{(2)}_{\mathrm{HF}}(D,V)$, from (10)						
Helium	0.412607	0.111003	0.051111	0.029338	0.019020	0.013325
Spherium	0	0	0	0	0	0
Hookium	0.106014	0.028188	0.012904	0.007382	0.004776	0.003342
Ballium	0.324120	0.069618	0.028107	0.014770	0.008977	0.005983
Limiting correlation energies $-E^{(2)}_{\mathrm{c}}(D,V)$, from (13)						
Helium	0.220133	0.046663	0.018933	0.010057	0.006188	0.004176
Spherium	0.227411	0.047637	0.019181	0.010139	0.006220	0.004189
Hookium	0.239641	0.049703	0.019860	0.010439	0.006376	0.004280
Ballium	0.266161	0.055176	0.021913	0.011437	0.006940	0.004631

$$\Psi_n(\theta) = \mathscr{N} C_n^{\frac{D-1}{2}}(\cos\theta), \tag{40}$$

$$\varepsilon_n = n(n+D-1), \tag{41}$$

where $C_n^{\frac{D-1}{2}}$ is a Gegenbauer polynomial [64] and

$$\mathscr{N} = \sqrt{\frac{2^{D-3}(2n+D-1)\Gamma\left(\frac{D-1}{2}\right)^2\Gamma(n+1)}{\pi\Gamma(n+D-1)}}. \tag{42}$$

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

$$\left\langle C_0^{\frac{D-1}{2}} \middle| r_{12}^{-1} \middle| C_n^{\frac{D-1}{2}} \right\rangle = \frac{(n+1)_{D-2}}{\left(n+\frac{1}{2}\right)_{D-1}}, \tag{43}$$

where $(a)_n$ is the Pochhammer symbol [64]

$$(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)}. \tag{44}$$

From this, one can show that

$$E^{(0)}(D,\mathrm{Sp}) = 0, \tag{45}$$

$$E^{(1)}(D,\mathrm{Sp}) = \frac{\Gamma(D-1)\Gamma\left(\frac{D+1}{2}\right)}{\Gamma\left(D-\frac{1}{2}\right)\Gamma\left(\frac{D}{2}\right)} \tag{46}$$

and the second-order energy is given by

$$\begin{aligned} E^{(2)}(D,\mathrm{Sp}) &= \sum_{n=1}^{\infty} \frac{\langle\Psi_0|r_{12}^{-1}|\Psi_n\rangle^2}{\varepsilon_0-\varepsilon_n} \\ &= -\frac{\Gamma(D)}{4\pi}\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{(n+1)_{D-2}}{\left(n+\frac{1}{2}\right)_{D-1}^2}\left[\frac{1}{n}+\frac{1}{n+D-1}\right], \end{aligned} \tag{47}$$

which reduces to a generalized hypergeometric function. It is also easy to show [70] that $E^{(2)}_{\mathrm{HF}}(D,\mathrm{Sp}) = 0$.

The $E^{(2)}$ (and thus E_c) value for 2-spherium was first reported by Seidl [79] but elementary expressions for any D can be obtained from Eq. (47) and these are reported for $2 \leqslant D \leqslant 7$ in Table 2.

2.3. Hookium

Hookium (Ho) consists of two electrons that repel Coulombically but are bound to the origin by the harmonic potential

$$V(r) = \frac{Z^4}{2}r^2. \tag{48}$$

This system was introduced 50 years ago by Kestner and Sinanoglu [82] and solved analytically by Santos [83] and Kais et al. [84] for a particular value of the harmonic force constant. Later, Taut showed that it is quasi-exactly solvable in that its Schrödinger equation can be solved for a countably infinite set of force constants [85]. An interesting paper by Katriel et al. discusses similarities and differences between the hookium and helium atoms [86].

The one-electron Hamiltonian in D-hookium is

$$\hat{h}_0 = -\frac{1}{2}\left[\frac{d^2}{dr^2}+\frac{D-1}{r}\frac{d}{dr}\right]+\frac{r^2}{2}, \tag{49}$$

Table 2
$E^{(0)}$, $E^{(1)}$, $E^{(2)}$ and $E^{(2)}_{\mathrm{HF}}$ for D-spherium.

D	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$	$E^{(2)}_{\mathrm{HF}}$
2	0	1	$4\ln 2 - 3$	0
3	0	$\frac{8}{3\pi}$	$\frac{4}{3} - \frac{368}{27\pi^2}$	0
4	0	$\frac{4}{5}$	$\frac{64}{75}\ln 2 - \frac{229}{375}$	0
5	0	$\frac{256}{105\pi}$	$\frac{24}{35} - \frac{2\,650\,112}{385\,875\pi^2}$	0
6	0	$\frac{16}{21}$	$\frac{1024}{2205}\ln 2 - \frac{455\,803}{1\,389\,150}$	0
7	0	$\frac{8192}{3465\pi}$	$\frac{4924}{10\,395} - \frac{588\,637\,011\,968}{124\,804\,708\,875\pi^2}$	0

and the zeroth-order wave functions are

$$\Psi_\ell(r_1,r_2) = \prod_{k=1}^{D}\psi_{a_k}(x_{1,k})\psi_{b_k}(x_{2,k}), \tag{50}$$

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

$$\psi_a(x) = \sqrt{2^a a!\pi^{1/2}}H_a(x)\exp(-x^2/2), \tag{51}$$

where H_a is the ath Hermite polynomial [64]. The energy differences between the eigenstates are given by

$$\varepsilon_\ell - \varepsilon_0 = \sum_{k=1}^{D}(a_k+b_k) = 2n, \tag{52}$$

where $2n$ is the excitation level, *i.e.*, the number of nodes in Ψ_ℓ. It is not difficult to show that

$$E^{(0)}(D,\mathrm{Ho}) = D, \tag{53}$$

$$E^{(1)}(D,\mathrm{Ho}) = \frac{1}{\sqrt{2}}\frac{\Gamma\left(\frac{D-1}{2}\right)}{\Gamma\left(\frac{D}{2}\right)}. \tag{54}$$

Both $E^{(2)}$ and $E^{(2)}_{\mathrm{HF}}$ can be found by direct summation [87], as in Eq. (47). The sum includes all single and double excitations for $E^{(2)}$, but only singles for $E^{(2)}_{\mathrm{HF}}$. 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

$$\begin{aligned} \langle\Psi_0|r_{12}^{-1}|\Psi_\ell\rangle &= \frac{1}{\sqrt{2\pi}}\frac{\Gamma\left(\frac{D-1}{2}\right)\Gamma\left(n+\frac{1}{2}\right)}{\Gamma(n+2)} \\ &\quad\times\prod_{k=1}^{D}\frac{i^{a_k-b_k}}{\sqrt{\pi a_k! b_k!}}\Gamma\left(\frac{a_k+b_k+1}{2}\right). \end{aligned} \tag{55}$$

In this way, one eventually finds

$$E^{(2)}(D,\mathrm{Ho}) = -\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{4\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{\left(\frac{1}{2}\right)_n^2}{\left(\frac{D}{2}\right)_n}\frac{1}{n!n}, \tag{56}$$

$$E^{(2)}_{\mathrm{HF}}(D,\mathrm{Ho}) = -\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{2\Gamma\left(\frac{D}{2}\right)^2}\sum_{n=1}^{\infty}\frac{\left(\frac{1}{2}\right)_n^2}{\left(\frac{D}{2}\right)_n}\frac{(1/4)^n}{n!n}, \tag{57}$$

which reduce to generalized hypergeometric functions.

$E^{(2)}(3,\mathrm{Ho})$ has been derived by several groups [88,89,87], and the energies for other D have been reported in Ref. [59]. Closed-form expressions for $E^{(2)}$ and $E^{(2)}_{\mathrm{HF}}$, for $2 \leqslant D \leqslant 7$, are listed in Table 3.

2.4. Ballium

Ballium (Ba) was first studied by Alavi and co-workers [90–92] and consists of two electrons, repelling Coulombically, but confined within a ball of radius $R = 1/Z$. It has been used for the assessment of density-functional approximations [91,93,94] and the study of Wigner molecules [36] at low densities [95,96,92]. We recently obtained near-exact energies for various values of R [97].

The one-electron Hamiltonian for D-ballium is

$$\hat{h}_0 = -\frac{1}{2}\left[\frac{d^2}{dr^2}+\frac{D-1}{r}\frac{d}{dr}\right]+V(r), \tag{58}$$

and the external potential is defined by

$$V(r) = \begin{cases} 0, & \text{if } r < R, \\ \infty, & \text{otherwise}, \end{cases} \tag{59}$$

or equivalently

$$V(r) = (r/R)^m, \quad m \to \infty. \tag{60}$$

Table 3
$E^{(0)}$, $E^{(1)}$, $E^{(2)}$ and $E^{(2)}_{\mathrm{HF}}$ for D-hookium. (G is Catalan's constant [64]).

D	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$	$E^{(2)}_{\mathrm{HF}}$
2	2	$\sqrt{\frac{\pi}{2}}$	$2G-\pi\ln 2$	$-\frac{\pi}{32}\,{}_4F_3\left(1,1,\frac{3}{2},\frac{3}{2};2,2,2;\frac{1}{4}\right)$
3	3	$\sqrt{\frac{2}{\pi}}$	$1-\frac{2}{\pi}(1+\ln 2)$	$\frac{4}{3}-\frac{4}{\pi}\left[1+\ln\left(8-4\sqrt{3}\right)\right]$
4	4	$\frac{1}{2}\sqrt{\frac{\pi}{2}}$	$\frac{4-\pi}{16}+\frac{2G-\pi\ln 2}{4}$	$-\frac{\pi}{256}\,{}_4F_3\left(1,1,\frac{3}{2},\frac{3}{2};2,2,3;\frac{1}{4}\right)$
5	5	$\frac{2}{3}\sqrt{\frac{2}{\pi}}$	$\frac{5}{9}-\frac{8}{27\pi}(4+3\ln 2)$	$\frac{8}{27}-\frac{8}{27\pi}\left[8-3\sqrt{3}+6\ln\left(8-4\sqrt{3}\right)\right]$
6	6	$\frac{3}{8}\sqrt{\frac{\pi}{2}}$	$\frac{104-27\pi}{512}+\frac{9(2G-\pi\ln 2)}{64}$	$-\frac{3\pi}{2048}\,{}_4F_3\left(1,1,\frac{3}{2},\frac{3}{2};2,2,4;\frac{1}{4}\right)$
7	7	$\frac{8}{15}\sqrt{\frac{2}{\pi}}$	$\frac{89}{225}-\frac{128}{3375\pi}(23+15\ln 2)$	$\frac{416}{675}-\frac{16}{3375\pi}\left[368+15\sqrt{3}+240\ln\left(8-4\sqrt{3}\right)\right]$

Any physically acceptable eigenfunction of (2) must satisfy the Dirichlet boundary condition

$$\Psi(r_1=R)=\Psi(r_2=R)=0. \tag{61}$$

The associated zeroth-order wave function of the zeroth-order Hamiltonian (58) is

$$\Psi_0(r_1,r_2)=\frac{2}{J_{D/2}(\kappa)^2}\frac{J_{D/2-1}(\kappa r_1)}{r_1^{D/2-1}}\frac{J_{D/2-1}(\kappa r_2)}{r_2^{D/2-1}}. \tag{62}$$

In (62), $\kappa=j_{D/2-1,1}$ and $j_{\mu,k}$ is the kth zero of the Bessel function of the first kind $J_{D/2-1}$ [64]. The $E^{(0)}$ values are easily obtained from the relation

$$E^{(0)}(D,\mathrm{Ba})=\kappa^2. \tag{63}$$

For odd D, $E^{(1)}$ can be found in closed form *via* Eq. (8). For example, for $D=3$,

$$E^{(1)}(3,\mathrm{Ba})=2\left[1-\frac{\mathrm{Si}(2\pi)}{2\pi}+\frac{\mathrm{Si}(4\pi)}{4\pi}\right], \tag{64}$$

where Si is the sine integral function [64].

Using the basis functions

$$\psi_{nlm}=(1-x^2)(1-y^2)x^{2n}y^{2l}z^m, \tag{65}$$

where

$$x=r_1/R,\quad y=r_2/R,\quad z=r_{12}/R, \tag{66}$$

and n, l and m are non-negative integers, one finds that the second-order energy $E^{(2)}$ is given by (21) where

$$\mathbf{A}=\mathbf{T}-E^{(0)}\mathbf{S}, \tag{67}$$

$$\mathbf{b}=\mathbf{C}^{\mathrm{T}}[E^{(1)}\mathbf{S}-\mathbf{U}]. \tag{68}$$

The vector $\mathbf{C}$ contains the coefficients of the zeroth-order wave function (62) expanded in the basis set (65).

The integrals needed to compute the different matrix elements are of the form

$$\mathscr{I}_{nlm}=\int x^n y^l z^m\,d\tau, \tag{69}$$

with the volume element

$$d\tau=xyz\mathscr{J}^{\frac{D-3}{2}}dx\,dy\,dz, \tag{70}$$

$$\mathscr{J}=(x+y+z)(x-y+z)(x+y-z)(x-y-z), \tag{71}$$

and domain of integration

$$\int d\tau=\int_0^1 dx\int_0^1 dy\int_{|x-y|}^{x+y} dz. \tag{72}$$

One eventually finds

$$\mathscr{I}_{nlm}=\sqrt{\pi}\frac{\Gamma\left(\frac{D-1}{2}\right)}{\Gamma\left(\frac{D}{2}\right)}\frac{R^{n+l+m+2D}}{n+l+m+2D}(I_n^m+I_l^m), \tag{73}$$

and

$$I_a^b=\frac{{}_3F_2\left(\frac{a+D}{2},-\frac{b}{2},-\frac{b+D-2}{2};\frac{a+D+2}{2},\frac{D}{2};1\right)}{a+D}. \tag{74}$$

$E^{(2)}_{\mathrm{HF}}$ values can be found using the Byers Brown–Hirschfelder equations (see Section 2.1) and numerical values of $E^{(2)}$ and $E^{(2)}_{\mathrm{HF}}$ are listed in Table 1.

3. Large-dimension limit

3.1. The conjecture

In the large-D limit, the quantum world reduces to a simpler semi-classical one [98] and problems that defy solution in $D=3$ sometimes become exactly solvable. In favorable cases, such solutions provide useful insight into the $D=3$ case and this strategy has been successfully applied in many fields of physics [99,100].

Following Herschbach and Goodson [101,102], we expand both the exact and HF energies with respect to D. Although various asymptotic expansions exist [103] for this dimensional expansion, it is convenient [100] to write [103–106]

$$E^{(2)}(D,V)=\frac{E^{(2,0)}(V)}{D^2}+\frac{E^{(2,1)}(V)}{D^3}+\cdots, \tag{75}$$

$$E^{(2)}_{\mathrm{HF}}(D,V)=\frac{E^{(2,0)}_{\mathrm{HF}}(V)}{D^2}+\frac{E^{(2,1)}_{\mathrm{HF}}(V)}{D^3}+\cdots, \tag{76}$$

$$E^{(2)}_{\mathrm{c}}(D,V)=\frac{E^{(2,0)}_{\mathrm{c}}(V)}{D^2}+\frac{E^{(2,1)}_{\mathrm{c}}(V)}{D^3}+\cdots, \tag{77}$$

$$E^{(2,0)}_{\mathrm{c}}(V)=E^{(2,0)}(V)-E^{(2,0)}_{\mathrm{HF}}(V), \tag{78}$$

$$E^{(2,1)}_{\mathrm{c}}(V)=E^{(2,1)}(V)-E^{(2,1)}_{\mathrm{HF}}(V). \tag{79}$$

Such double expansions of the correlation energy were originally introduced for the helium-like ions, and have led to accurate estimations of correlation [107,108] and atomic energies [109,110] *via* interpolation and renormalization techniques. Eq. (77) applies equally to the ^1S ground state of any two-electron system confined by a spherical potential $V(r)$.

For helium, it is known [111,101,102] that

$$E^{(2,0)}_{\mathrm{c}}(\mathrm{He})=-\frac{1}{8},\quad E^{(2,1)}_{\mathrm{c}}(\mathrm{He})=-\frac{163}{384}, \tag{80}$$

and we have recently found [59] that

$$E^{(2,0)}_{\mathrm{c}}(\mathrm{Ho})=-\frac{1}{8},\quad E^{(2,1)}_{\mathrm{c}}(\mathrm{Ho})=-\frac{111}{256}, \tag{81}$$

$$E^{(2,0)}_{\mathrm{c}}(\mathrm{Sp})=-\frac{1}{8},\quad E^{(2,1)}_{\mathrm{c}}(\mathrm{Sp})=-\frac{53}{128}, \tag{82}$$

$$E^{(2,0)}_{\mathrm{c}}(\mathrm{Ba})=-\frac{1}{8},\quad E^{(2,1)}_{\mathrm{c}}(\mathrm{Ba})=-\frac{85}{128}. \tag{83}$$

The fact that $E_c^{(2,0)}$ is invariant to the external potential and $E_c^{(2,1)}$ depends only weakly on it explains why the high-density correlation energies (Table 1) of all the systems are similar, though not identical, for $D = 3$ [59,97].

On this basis, we conjectured [59] that

$$E_c^{(2)}(D,V) \sim -\frac{1}{8D^2} - \frac{C(V)}{D^3} \tag{84}$$

holds for *any* spherical confining potential, where the coefficient $C(V)$ varies slowly with $V(r)$.

3.2. The proof

In this section, we will summarize our proof of the conjecture (84). More details can be found in Ref. [60]. We prove that $E_c^{(2,0)}$ is universal, and that, for large D, the high-density correlation energy of the ^1S ground state of two electrons is given by (84) for any confining potential of the form

$$V(r) = \mathrm{sgn}(m) r^m v(r), \tag{85}$$

where $v(r)$ possesses a Maclaurin series expansion

$$v(r) = v_0 + v_1 r + v_2 \frac{r^2}{2} + \cdots. \tag{86}$$

After transforming both the dependent and independent variables [60], the Schrödinger equation can be brought to the simple form

$$\left(\frac{1}{\Lambda}\widehat{\mathscr{T}} + \widehat{\mathscr{U}} + \widehat{\mathscr{V}} + \frac{1}{Z}\widehat{\mathscr{W}}\right)\Phi_D = \mathscr{E}_D \Phi_D, \tag{87}$$

in which, for S states, the kinetic, centrifugal, external potential and Coulomb operators are, respectively,

$$-2\widehat{\mathscr{T}} = \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}\right) + \left(\frac{1}{r_1^2} + \frac{1}{r_1^2}\right)\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{4}\right), \tag{88}$$

$$\widehat{\mathscr{U}} = \frac{1}{2\sin^2\theta}\left(\frac{1}{r_1^2} + \frac{1}{r_1^2}\right), \tag{89}$$

$$\widehat{\mathscr{V}} = V(r_1) + V(r_2), \tag{90}$$

$$\widehat{\mathscr{W}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}, \tag{91}$$

and the dimensional perturbation parameter is

$$\Lambda = \frac{(D-2)(D-4)}{4}. \tag{92}$$

In this form, double perturbation theory can be used to expand the energy in terms of both $1/Z$ and $1/\Lambda$.

For $D = \infty$, the kinetic term vanishes and the electrons settle into a fixed ('Lewis') structure [101] that minimizes the effective potential

$$\widehat{\mathscr{X}} = \widehat{\mathscr{U}} + \widehat{\mathscr{V}} + \frac{1}{Z}\widehat{\mathscr{W}}. \tag{93}$$

The minimization conditions are

$$\frac{\partial \widehat{\mathscr{X}}(r_1, r_2, \theta)}{\partial r_1} = \frac{\partial \widehat{\mathscr{X}}(r_1, r_2, \theta)}{\partial r_2} = 0, \tag{94}$$

$$\frac{\partial \widehat{\mathscr{X}}(r_1, r_2, \theta)}{\partial \theta} = 0, \tag{95}$$

and the stability condition implies $m > -2$. Assuming that the two electrons are equivalent, the resulting exact energy is

$$\mathscr{E}_\infty = \widehat{\mathscr{X}}(r_\infty, r_\infty, \theta_\infty). \tag{96}$$

It is easy to show that

$$r_\infty = \alpha + \frac{\alpha^2}{m+2}\left(\frac{1}{2\sqrt{2}} - \Lambda\frac{m+1}{m}\frac{v_1}{v_0}\right)\frac{1}{Z} + \cdots, \tag{97}$$

$$\cos\theta_\infty = -\frac{\alpha}{4\sqrt{2}}\frac{1}{Z} + \cdots, \tag{98}$$

where $\alpha^{-(m+2)} = \mathrm{sgn}(m) m v_0$.

For the HF treatment, we have $\theta_\infty^{\mathrm{HF}} = \pi/2$. Indeed, the HF wave function itself is independent of θ, and the only θ dependence comes from the D-dimensional Jacobian, which becomes a Dirac delta function centered at $\pi/2$ as $D \to \infty$. Solving (94), one finds that r_∞^{HF} and r_∞ are equal to second-order in $1/Z$. Thus, in the large-D limit, the HF energy is

$$\mathscr{E}_\infty^{\mathrm{HF}} = \widehat{\mathscr{X}}\left(r_\infty^{\mathrm{HF}}, r_\infty^{\mathrm{HF}}, \frac{\pi}{2}\right), \tag{99}$$

and correlation effects originate entirely from the fact that θ_∞ is slightly greater than $\pi/2$ for finite Z.

Expanding (96) and (99) in terms of Z and D yields

$$E^{(2,0)}(V) = -\frac{1}{8} - \frac{1}{2(m+2)}, \tag{100}$$

$$E_{\mathrm{HF}}^{(2,0)}(V) = -\frac{1}{2(m+2)}, \tag{101}$$

thus showing that both $E^{(2,0)}$ and $E_{\mathrm{HF}}^{(2,0)}$ depend on the leading power m of the external potential but not on $v(r)$.

Subtracting these energies yields

$$E_c^{(2,0)}(V) = -\frac{1}{8}, \tag{102}$$

and this completes the proof that, in the high-density limit, the leading coefficient $E_c^{(2,0)}$ of the large-D expansion of the correlation energy is universal, *i.e.*, it does not depend on the external potential $V(r)$.

Table 4
$E^{(2,0)}$, $E_{\mathrm{HF}}^{(2,0)}$, $E_c^{(2,0)}$ and $E_c^{(2,1)}$ coefficients for various systems and $v(r) = 1$.

System	m	$-E^{(2,0)}$	$-E_{\mathrm{HF}}^{(2,0)}$	$-E_c^{(2,0)}$	$-E_c^{(2,1)}$
Helium	−1	5/8	1/2	1/8	0.424479
Airium	1	7/24	1/6	1/8	0.412767
Hookium	2	1/4	1/8	1/8	0.433594
Quartium	4	5/24	1/12	1/8	0.465028
Sextium	6	3/16	1/16	1/8	0.486771
Ballium	∞	1/8	0	1/8	0.664063

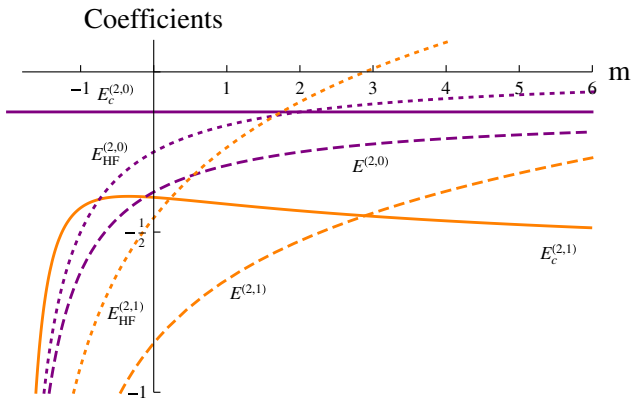

Figure 2. Coefficients of the exact (dashed), HF (dotted) and correlation (solid) energies with respect to m, for $v(r) = 1$ (Eqs. (75)–(77)).

The result (102) is related to the cusp condition [112–114]

$$\left.\frac{\partial \Psi_D}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{D-1}\,\Psi_D(r_{12}=0), \tag{103}$$

which arises from the cancellation of the Coulomb operator singularity by the D-dependent angular part of the kinetic operator [2].

The $E^{(2,1)}$ and $E_{\mathrm{HF}}^{(2,1)}$ coefficients can be found by considering the Langmuir vibrations of the electrons around their equilibrium positions [101,102]. The general expressions depend on v_0 and v_1, but are not reported here. However, for $v(r) = 1$, which includes many of the most common external potentials, we find

$$E_{\mathrm{c}}^{(2,1)}(V) = -\frac{85}{128} - \frac{9/32}{(m+2)^{3/2}} + \frac{1/2}{(m+2)^{1/2}} + \frac{1/16}{(m+2)^{1/2}+2}, \tag{104}$$

showing that $E_{\mathrm{c}}^{(2,1)}$, unlike $E_{\mathrm{c}}^{(2,0)}$, is potential-dependent. Numerical values of $E_{\mathrm{c}}^{(2,1)}$ are reported in Table 4 for various systems, and the components of the correlation energy are shown graphically in Figure 2.

4. Conclusion

In this Letter, we have reviewed our recent progress in the determination of the high-density correlation energy for four two-electron systems: the helium atom (He), the Hooke's law atom (Ho), two electrons confined on the surface of a sphere (Sp), and two electrons trapped in a ball (Ba). In the large-Z limit for $D = 3$, we have found

$$E_{\mathrm{c}}(\mathrm{He}) \approx E_{\mathrm{c}}(\mathrm{Sp}) \approx E_{\mathrm{c}}(\mathrm{Ho}) \approx E_{\mathrm{c}}(\mathrm{Ba}). \tag{105}$$

These striking similarities can be rationalized by treating the dimensionality D of space as a system parameter, and we have proved that, as D grows, all such correlation energies exhibit the same universal behaviour

$$E_{\mathrm{c}} \sim -1/(8D^2) \tag{106}$$

in a D-dimensional space. This is true *irrespective* of the nature of the external potential that confines the electrons.

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