

Invariance of the Correlation Energy at High Density and Large Dimension in Two-Electron Systems

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We prove that, in the large-dimension limit, the high-density correlation energy E_c of two opposite-spin electrons confined in a D -dimensional space and interacting via a Coulomb potential is given by $E_c \sim -1/(8D^2)$ for any radial confining potential $V(r)$. This result explains the observed similarity of E_c in a variety of two-electron systems in three-dimensional space.

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Understanding and calculating the electronic correlation energy is one of the most important and difficult problems in molecular physics. In this pursuit, the study of high-density correlation energy using perturbation theory has been particularly profitable, shedding light on the physically relevant density regime and providing exact results for key systems, such as the uniform electron gas [1] and two-electron systems [2]. The former is the cornerstone of the most popular density functional paradigm (the local density approximation) in solid-state physics [3]; the latter provide important test cases in the development of new explicitly correlated methods [4,5] for electronic structure calculations [6]. Atomic units are used throughout.

The high-density correlation energy of the heliumlike ions is obtained by expanding both the exact [7] and Hartree-Fock (HF) [8] energies as a series in $1/Z$, yielding

$$E(Z, D, V) = E^{(0)}(D, V)Z^2 + E^{(1)}(D, V)Z + E^{(2)}(D, V) + \frac{E^{(3)}(D, V)}{Z} + \dots, \quad (1)$$

$$E_{\text{HF}}(Z, D, V) = E^{(0)}(D, V)Z^2 + E^{(1)}(D, V)Z + E_{\text{HF}}^{(2)}(D, V) + \frac{E_{\text{HF}}^{(3)}(D, V)}{Z} + \dots, \quad (2)$$

where Z is the nuclear charge, D is the dimension of the space, and V is the external Coulomb potential. Equations (1) and (2) share the same zeroth- and first-order energies because the exact and the HF treatment have the same zeroth-order Hamiltonian. Thus, in the high-density (large- Z) limit, the correlation energy is

$$\begin{aligned} E_c^{(2)}(D, V) &= \lim_{Z \rightarrow \infty} E_c(Z, D, V) \\ &= \lim_{Z \rightarrow \infty} [E(Z, D, V) - E_{\text{HF}}(Z, D, V)] \\ &= E^{(2)}(D, V) - E_{\text{HF}}^{(2)}(D, V). \end{aligned} \quad (3)$$

Despite intensive study [9,10], the coefficient $E^{(2)}(D, V)$ has not yet been reported in closed form. However, the accurate numerical estimate

$$E^{(2)} = -0.157\,666\,429\,469\,14 \quad (4)$$

has been determined for the important $D = 3$ case [10]. Combining (4) with the exact result [8]

$$E_{\text{HF}}^{(2)} = \frac{9}{32} \ln \frac{3}{4} - \frac{13}{432} \quad (5)$$

yields a value of

$$E_c^{(2)} = -0.046\,663\,253\,999\,48 \quad (6)$$

for the heliumlike ions in three-dimensional space.

In the large- D limit, the quantum world reduces to a simpler semiclassical one [11] 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 [12,13]. Indeed, just as one learns something about interacting systems by studying noninteracting ones and introducing the interaction perturbatively, one learns something about $D = 3$ by studying the large- D case and introducing dimension reduction perturbatively.

Singularity analysis [14] reveals that the energies of two-electron atoms possess first- and second-order poles at $D = 1$, and that the Kato cusp [15,16] is directly responsible for the second-order pole. In our previous work [17,18], we have expanded the correlation energy as a series in $1/(D - 1)$ but, although this is formally correct if summed to infinite order, such expansions falsely imply higher-order poles at $D = 1$. For this reason, we now follow Herschbach and Goodson [19,20], and expand both the exact and HF energies as a series in $1/D$. Although various possibilities exist for this dimensional expansion [14,21–23], it is convenient to write

$$E^{(2)}(D, V) = \frac{E^{(2,0)}(V)}{D^2} + \frac{E^{(2,1)}(V)}{D^3} + \dots, \quad (7)$$

$$E_{\text{HF}}^{(2)}(D, V) = \frac{E_{\text{HF}}^{(2,0)}(V)}{D^2} + \frac{E_{\text{HF}}^{(2,1)}(V)}{D^3} + \dots, \quad (8)$$

$$E_c^{(2)}(D, V) = \frac{E_c^{(2,0)}(V)}{D^2} + \frac{E_c^{(2,1)}(V)}{D^3} + \dots, \quad (9)$$

where

$$E_c^{(2,0)}(V) = E^{(2,0)}(V) - E_{\text{HF}}^{(2,0)}(V), \quad (10)$$

$$E_c^{(2,1)}(V) = E^{(2,1)}(V) - E_{\text{HF}}^{(2,1)}(V). \quad (11)$$

Such double expansions of the correlation energy were originally introduced for the heliumlike ions, and have led to accurate estimations of correlation [24,25] and atomic energies [26,27] via interpolation and renormalization techniques. Equations (7)–(9) apply equally to the 1S ground state of any two-electron system confined by a spherical potential $V(r)$.

For the heliumlike ions, it is known [19,20,28] that

$$E_c^{(2,0)}(V) = -\frac{1}{8}, \quad E_c^{(2,1)}(V) = -\frac{163}{384}, \quad (12)$$

and we have recently found [17] that $E_c^{(2,0)}(V)$ takes the same value in hookium (two electrons in a parabolic well [29–32]), spherium (two electrons on a sphere [33–36]), and ballium (two electrons in a ball [18,37,38]). In contrast, we found that $E_c^{(2,1)}(V)$ is V dependent. The fact that the term $E_c^{(2,0)}$ is invariant, while $E_c^{(2,1)}$ varies with the confinement potential allowed us to explain why the high-density correlation energy of the previous two-electron systems are similar, but not identical, for $D = 3$ [17,18]. On this basis, we conjectured [17] that

$$E_c^{(2)}(D, V) \sim -\frac{1}{8D^2} - \frac{C(V)}{D^3} \quad (13)$$

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

In this Letter, we prove that $E_c^{(2,0)}$ is indeed universal, and that, in the large- D limit, the high-density correlation energy of the 1S ground state of two electrons is given by (13) for any confining potential of the form

$$V(r) = \text{sgn}(m)r^m v(r), \quad (14)$$

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

$$v(r) = v_0 + v_1 r + v_2 r^2 + \dots \quad (15)$$

In order to prove the conjecture (13), we start with the conventional Schrödinger equation

$$\hat{H}\Psi_D = E_D\Psi_D, \quad (16)$$

and the general Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + Z^{m+2}[V(r_1) + V(r_2)] + \frac{1}{r_{12}}, \quad (17)$$

where Z is the confinement strength and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectronic distance. After the Jacobian-weighted transformation

$$\Phi_D = \mathcal{J}^{1/2}\Psi_D, \quad (18)$$

$$\mathcal{J} = r_1^{D-1} r_2^{D-1} \sin^{D-2}\theta, \quad (19)$$

where θ is the interelectronic angle, the Schrödinger equation (16) becomes

$$(\hat{\mathcal{T}} + \Lambda\hat{\mathcal{U}} + Z^{m+2}\hat{\mathcal{V}} + \hat{\mathcal{W}})\Phi_D = E_D\Phi_D, \quad (20)$$

in which, for states with zero total angular momentum, the kinetic, centrifugal, external, and Coulomb operators are, respectively

$$-2\hat{\mathcal{T}} = \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}\right) + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{4}\right), \quad (21)$$

$$\hat{\mathcal{U}} = \frac{1}{2\sin^2\theta}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right), \quad (22)$$

$$\hat{\mathcal{V}} = V(r_1) + V(r_2), \quad (23)$$

$$\hat{\mathcal{W}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}, \quad (24)$$

and

$$\Lambda = \frac{(D-2)(D-4)}{4}. \quad (25)$$

We now need to recast the Schrödinger equation so that perturbation theory can be applied. To achieve this, we successively introduce the scaled quantities

$$r \rightarrow \frac{\Lambda}{\kappa Z} r, \quad Z \rightarrow \frac{Z}{\kappa}, \quad (26)$$

where $\kappa = \Lambda^{m+1/m+2}$, and introduce the scaled energy

$$\mathcal{E}_D = \frac{\kappa^2 Z^2}{\Lambda} E_D. \quad (27)$$

The Schrödinger equation then takes the simple form

$$\left(\frac{1}{\Lambda}\hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} + \frac{1}{Z}\hat{\mathcal{W}}\right)\Phi_D = \mathcal{E}_D\Phi_D, \quad (28)$$

and it is clear that perturbation theory can now be used to expand the energy both in terms of Z and Λ .

In the $D = \infty$ limit, the kinetic term vanishes and classical electrostatics cause the electrons to settle into a fixed (“Lewis”) structure [19] that minimizes the effective potential

$$\hat{\mathcal{X}} = \hat{\mathcal{U}} + \hat{\mathcal{V}} + \frac{1}{Z}\hat{\mathcal{W}}. \quad (29)$$

The minimization conditions are

$$\frac{\partial \hat{\mathcal{X}}(r_1, r_2, \theta)}{\partial r_1} = \frac{\partial \hat{\mathcal{X}}(r_1, r_2, \theta)}{\partial r_2} = 0, \quad (30)$$

$$\frac{\partial \hat{\mathcal{X}}(r_1, r_2, \theta)}{\partial \theta} = 0, \quad (31)$$

and the stability condition implies $m > -2$. Assuming that the two electrons are equivalent [39], the resulting exact density and energy are

$$|\Phi_\infty|^2 = \delta(r_1 - r_\infty)\delta(r_2 - r_\infty)\delta(\theta - \theta_\infty), \quad (32)$$

$$\mathcal{E}_\infty = \hat{\mathcal{X}}(r_\infty, r_\infty, \theta_\infty), \quad (33)$$

where δ is the Dirac delta function. Substituting Taylor expansions of r_∞ and θ_∞ into (30) and (31) yields

$$r_\infty = \alpha + \frac{\alpha^2}{m+2} \left(\frac{1}{2\sqrt{2}} - \Lambda \frac{m+1}{m} \frac{v_1}{v_0} \right) \frac{1}{Z} + \dots, \quad (34)$$

$$\cos\theta_\infty = -\frac{\alpha}{4\sqrt{2}} \frac{1}{Z} + \dots, \quad (35)$$

where $\alpha^{-(m+2)} = \text{sgn}(m)mv_0$. The $m=0$ case requires special attention, and is found by taking the $m \rightarrow 0$ limit.

For the HF energy, things are simpler. The HF wave function is independent of θ , so the only angular dependence comes from the Jacobian (19). Moreover, because

$$\lim_{D \rightarrow \infty} \frac{\sin^{D-2}\theta}{\int_0^\pi \sin^{D-2}\theta d\theta} = \delta\left(\theta - \frac{\pi}{2}\right), \quad (36)$$

it follows [20] that $\theta_\infty^{\text{HF}} = \pi/2$. Solving (30), one finds that r_∞^{HF} and r_∞ are equal to second order in $1/Z$. Thus, in the large- D limit, the HF density and energy are

$$|\Phi_\infty^{\text{HF}}|^2 = \delta(r_1 - r_\infty^{\text{HF}})\delta(r_2 - r_\infty^{\text{HF}})\delta\left(\theta - \frac{\pi}{2}\right), \quad (37)$$

$$\mathcal{E}_\infty^{\text{HF}} = \hat{\mathcal{X}}\left(r_\infty^{\text{HF}}, r_\infty^{\text{HF}}, \frac{\pi}{2}\right), \quad (38)$$

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

Expanding (33) and (38) in terms of Z and D yields

$$E^{(2,0)}(V) = -\frac{1}{8} - \frac{1}{2(m+2)}, \quad (39)$$

$$E_{\text{HF}}^{(2,0)}(V) = -\frac{1}{2(m+2)}, \quad (40)$$

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

Subtracting these energies yields

$$E_c^{(2,0)}(V) = -\frac{1}{8}, \quad (41)$$

and 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 $V(r)$.

What is the origin of the constant in Eq. (41)? It comes directly from the leading coefficient ($1/4\sqrt{2}$) in the $1/Z$ expansion of θ_∞ [Eq. (35)] and, because that is determined via Eq. (31), it is independent of the external potential $V(r)$. This reveals that Eq. (41) applies to a pair of electrons in any radial external potential, but not to anisotropic external potentials.

Detailed analysis of $E_c^{(2,0)}$ shows that it results from contributions of $+1/8$ and $-1/4$ from the centrifugal potential \hat{U} and the Coulomb operator \hat{W} , respectively. The external potential \hat{V} , which contributes identically in the exact and HF treatments, does not contribute to the correlation energy. Kato has made a similar argument [15] to explain the behavior of the wave function as $r_{12} \rightarrow 0$. In a D -dimensional space, the Kato cusp condition is [16]

$$\frac{\partial \Psi_D}{\partial r_{12}} \Big|_{r_{12}=0} = \frac{1}{D-1} \Psi_D(r_{12}=0), \quad (42)$$

and arises from the cancellation of the singularities in the Coulomb operator and the D -dependent angular part of the kinetic operator [6]. These observations suggest a connection between the result (41) and the Kato cusp (42). For large but finite D , the discovery that the Kato cusp plays a key role in the large- Z limit would not be surprising for, in this limit, the only relevant information is the behavior (42) of the wave function near $r_{12} = 0$.

The $E^{(2,1)}$ and $E_{\text{HF}}^{(2,1)}$ coefficients can be found by considering the Langmuir vibrations of the electrons around their equilibrium positions [19,20]. 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

$$E_c^{(2,1)}(V) = -\frac{85}{128} - \frac{9/32}{(m+2)^{3/2}} + \frac{1/2}{(m+2)^{1/2}} + \frac{1/16}{(m+2)^{1/2} + 2}, \quad (43)$$

showing that $E_c^{(2,1)}$, unlike $E_c^{(2,0)}$, is potential dependent. It is singular at $m = -2$, tends to $-85/128$ as $m \rightarrow \infty$, and reaches a maximum of -0.388482 at $m \approx -0.344223$. The latter value of m corresponds to the minimum of the correlation energy in the large- D limit. Numerical values of $E_c^{(2,1)}$ are reported in Table I for various systems, and the

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

System	m	$-E^{(2,0)}$	$-E_{\text{HF}}^{(2,0)}$	$-E_c^{(2,0)}$	$-E_c^{(2,1)}$
Helium	-1	5/8	1/2	1/8	0.424 479
Airium	1	7/24	1/6	1/8	0.412 767
Hookium	2	1/4	1/8	1/8	0.433 594
Quartium	4	5/24	1/12	1/8	0.465 028
Sextium	6	3/16	1/16	1/8	0.486 771
Ballium	∞	1/8	0	1/8	0.664 063

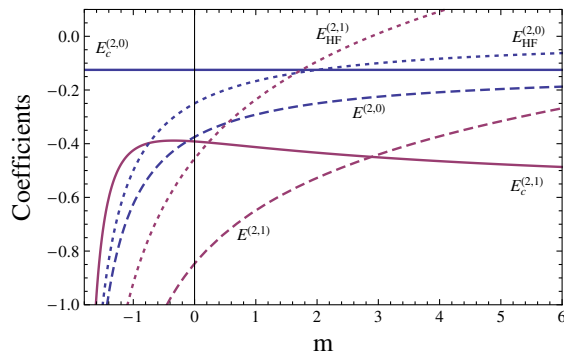


FIG. 1 (color online). Coefficients of the exact (dashed), HF (dotted), and correlation (solid) energies with respect to m , for $\nu(r) = 1$ [Eqs. (7)–(9)].

components of the correlation energy are shown graphically in Fig. 1.

In conclusion, we have proved that the leading term $E_c \sim -1/(8D^2)$ in the large- D expansion of the high-density correlation energy of an electron pair is invariant to the nature of the radial confining potential. Although formally divergent [40], truncated $1/D$ expansions have been found to be a powerful tool for the exploration of correlation effects and, in the present study, they help to explain the observation that, in finite-dimensional spaces such as $D = 3$, the correlation energy depends only weakly on the confining potential.

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