Exact separation of radial and angular correlation energies in two-electron atoms

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Partitioning of helium atom’s correlation energy into radial and angular contributions, although of fundamental interest, has eluded critical scrutiny. Conventionally, radial and angular correlation energies of helium atom are defined for its ground state as deviations, from Hartree–Fock and exact values, of the energy obtained using a purely radial wavefunction devoid of any explicit dependence on the interelectronic distance. Here, we show this rationale to spuriously associate the contribution from radial-angular coupling entirely to the angular part underestimating the radial one, thereby also incorrectly predict non-vanishing residual radial probability densities. We derive analytic matrix elements for the high precision Hylleraas basis set framework to seamlessly uncouple the angular correlation energy from its radial counterpart. The resulting formula agrees with numerical cubature yielding precise purely angular correlation energies for the ground as well as excited states. Our calculations indicate 60.2% of helium’s correlation energy to arise from strictly radial interactions; when excluding the contribution from the radial-angular coupling, this value drops to 41.3%.

High precision variational calculations of two-electron atoms have rigorously enabled quantitative agreement of first-principles predictions with such subtle physical measurements as relativistic and Lamb shift contributions to atomic transition frequencies [1]. Arguably, the most critical prerequisite for reaching such accuracies is an explicit dependence of variational trial functions on the interelectronic separation, \( u = |\mathbf{r}_1 - \mathbf{r}_2| \). Historically, it was the inclusion of this variable along with \( s = r_1 + r_2 \) and \( t = r_2 - r_1 \), in the wavefunction that enabled Hylleraas to predict the ground and first excited states of helium very accurately [2].

Correlation energy of helium is the difference between its non-relativistic exact ground state energy, \( E_0^{\text{exact}} = -2.903724377034119598311 \text{ au} \) [3], and its Hartree–Fock (HF) limit, \( E_0^{\text{HF}} = -2.861679995612 \text{ au} \) [4], i.e., \( E_c = E_0^{\text{exact}} - E_0^{\text{HF}} = -0.0420443814221194 \text{ au} \). Taylor and Parr [5] conjectured that a complete wavefunction in tates (translation energy arising from the motion of the electrons, \( c = \mathbf{r}_1 - \mathbf{r}_2 \)) enters the third independent coordinate \( \theta \), the angle subtended between the two position vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \). To date, insufficient efforts have gone into critically inspecting the validity of such an additive interpretation of \( E_c \). In the 50s, Green and others [11, 12] have employed few-parameters Hylleraas [2] and Chandrasekhar [13] wavefunctions in configuration interaction calculations to partition \( E_0 \) into \( E_0^{\text{HF}} \) and three correlation terms of radial, angular and mixed characters. This approach, however, resulted in \( E_c = -0.0688 \text{ au} \) for helium, largely overestimating the actual value. Later, the calculations of Moiseyev revealed the coupling between radial and angular components of \( E_c \) to emerge in high order terms of \( 1/Z \)-perturbation theory [8].

The purposes of this letter are to, firstly, expose the residual radial correlation that is present in an exact wavefunction and is not captured by a fully radial wavefunction devoid of \( u \)-dependence. Then, we present a new strategy based on analytic matrix elements to compute precise pure angular correlation energies, \( E_0^{\text{ang}} \), for helium and its isoelectronic ions. We formulate the problem using the explicitly correlated wavefunction Ansatz

\[
\Psi (\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha s/2} \sum_{l,m,n=0} C_{lmmn} s^{l'} t^{m'} u^{n'} \tag{1}
\]

where \( l, m, n \in \mathbb{Z} \). The convergence of the trial function is studied by progressively increasing the number of basis functions, which varies as \( N = (\Omega + 1)(\Omega + 2)(\Omega + 3)/6 \) [14]. We have optimized the exponent \( \alpha \) in all our calculations performed with quadruple precision. For the choice of \( l' = l - n \), \( m' = 2m \) and \( n' = n - 2m \), we obtain a Kinoshita wavefunction [15], which for \( \Omega = 11 \) (\( N = 364 \)) results in the exact ground state energy \(-2.90372438 \text{ au} \). Alas, the Kinoshita wavefunction converges rather poorly for the excites states.
wavefunction was computed using six Slater-type functions related (i.e. HF) radial probability densities of helium. HF

FIG. 1. Differences between exact, fully radial, and uncorrelated (i.e. HF) radial probability densities of helium. HF wavefunction was computed using six Slater-type functions with optimal exponents.

Purely radial Hylleraas wavefunctions are obtained by setting \( n' = 0 \), satisfying \( N = (\Omega + 1)(\Omega + 2)/2 \).

\[
\Psi_{\text{rad}}(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha s/2} \sum_{l=0}^{\infty} C_l s^l t^{m'}
\]

With \( \Omega = 40 \), along with variationally optimized \( \alpha \), we obtain the energies of \( 1s^2 \), \( 1s^12s^1 \), and \( 1s^13s^1 \) states of Helium as \(-2.87902846 \), \(-2.14419704 \), and \(-2.06079381 \) au, respectively, the ground state energy deviating from Goldman’s precise value \([6]\) by merely \( 3 \times 10^{-7} \) au. Koga had earlier noted superior convergence of the ground state energy using a radial Kinoshita wavefunction with \( l' = l - m \), and \( m' = 2m \) \([17]\). With these constraints we obtain the improved values, \(-2.87902875 \), \(-2.14419727 \), and \(-2.06079404 \) au, for the lowest three singlet states of helium. By modifying the radial Kinoshita framework as an optimal \( N \)–term wavefunction, as proposed by Koga \([17]\),

\[
\Psi_{\text{rad}}(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha s/2} \sum_{i=0}^{N} C_i s^l t^{m'}
\]

we find a more precise radial limit of helium’s ground state energy converging to \(-2.8790287673153 \) au for \( N = 43 \). In this case, we have varied \( m' = m \) as a positive integer, and ensured one of the \( N \) terms to be the singlet \( l = 0, m = 0 \) term.

With such a precise energy estimation, the corresponding radial wavefunction is expected to capture all the radial dependence beyond that of HF. To further elucidate the point, let us consider the reduced radial density function

\[
\rho(\vec{r}_1) = 8\pi^2 \int_0^\infty r_2^2 dr_2 \int_0^\pi \sin \theta d\theta |\Phi_1(\mathbf{r}_1, \mathbf{r}_2)|^2
\]

where \( \Phi \) can be \( \Psi(\mathbf{r}_1, \mathbf{r}_2) \), \( \Psi_{\text{rad}}(\mathbf{r}_1, \mathbf{r}_2) \) or \( \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \). For all three wavefunctions, the reduced density function follows \( \int_0^\infty \rho(\vec{r}_1) r_2^2 dr_2 = 1 \).

In Fig. 1 we find the change in \( \rho \) while going from the HF to an exact wavefunction to be different than while going from an HF wavefunction to an exclusively radial one. Such a trend implies the exact wavefunction to capture radial correlation that is coupled to the angular degree of freedom and is inaccessible to \( \Psi_{\text{rad}} \) that lacks \( u \)-dependence. While purely radial correlation has the effect of larger divergence in density from that of HF, the radial correlation coupled with the angular counterpart has the opposing effect of bringing the electron density closer to the HF one. Subtracting \( \rho_{\text{rad}} \) from the exact \( \rho \) indeed reveals such a trend (Fig. 1).

![FIG. 1](image1.png)

FIG. 1. Differences between exact, fully radial, and uncorrelated (i.e. HF) radial probability densities of helium. HF wavefunction was computed using six Slater-type functions with optimal exponents.

The situation is similar also in the case of \( 1s^12s^1 \) and \( 1s^13s^1 \) states. For both, we find the probability density from a purely radial wavefunction to deviate from that of an exact wavefunction (see Fig. 2). However, for the excited states, the residual radial correlation seems to decrease with increase in energy. At this point, it is worth noting that, as pointed out in Ref. \([8]\) the total correlation in excited states is essentially angular. Later we will quantify \( E_{\text{c}} \) for these states precisely.

We now divert our attention to the exact separation of radial and angular correlation energies based on analytic expressions for the matrix elements. Our derivation is grounded on the fact that \( \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \) is the varia-
Direct substitutions of \( \Delta \) can now be written as
we arrive at
\[
E \text{ionically best radial wavefunction separable in } \rho, \text{lacking any dependence on } u. \text{ Hence, separating the kinetic energy terms that are dependent on the } u \text{ variable should provide angular correlation energy via the virial theorem } E_c = -T. \text{ We begin our derivation with the kinetic energy operator in the } s, t \text{ and } u \text{ variables}
\]
\[
\begin{align*}
\hat{T}_{stu} &= \left( \partial_s^2 + \partial_t^2 + \partial_u^2 \right) - \frac{4s}{(s^2 - t^2)} \partial_s + \frac{4t}{(s^2 - u^2)} \partial_t \\
&\quad - \frac{2}{u} \partial_u - \frac{2s(u^2 - t^2)}{u(s^2 - t^2)} \partial_s^2 - 2t \left( \frac{s^2 - u^2}{u(s^2 - t^2)} \right) \partial_t \partial_u
\end{align*}
\]
For our purpose, it is vital to decouple the kinetic energy operator as \( \hat{T}_{stu} = \hat{T}_{rad} + \hat{T}_{ang} \), individual terms defined as
\[
\hat{T}_{rad} = -\frac{1}{2} \sum_{i=1}^{2} r_i^{-2} \partial_r r_i^{-2} \partial_r; \quad \hat{T}_{ang} = -\frac{1}{2} \nabla_\theta^2
\]
but retain the Hylleraas’ coordinates representation that facilitates analytic computation of the matrix elements. To this end, we invoke the substitutions \( r_1 = (s-t)/2 \), \( r_2 = (s+t)/2 \), and \( u = r_{12} \). With the latter quantity defined as
\[
u = r_{12} = r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_{12}
\]
we arrive at \( u. du = r_1r_2 \sin \theta_{12} d\theta_{12} \). A purely angular Laplacian can now be written as
\[
\nabla_\theta^2 = \left[ r_1^{-2}(\sin \theta)^{-1} + r_2^{-2}(\sin \theta)^{-1} \right] \partial_\theta (\sin \theta \partial_\theta)
\]
Direct substitutions of \( r_1, r_2, \theta \) along with \( \sin^2 \theta = 1 - \cos^2 \theta \) results in a more useful expression which is directly expressed in the Hylleraas coordinates as
\[
\nabla_\theta^2 = \left[ \frac{1}{u(s^2 - t^2)^2} + \frac{1}{u(s^2 + t^2)^2} \right] \partial_u \left\{ -u^2 - 2 \right\} \partial_u \partial_u
\]
This Laplacian when operating on a primitive basis function \( |l', m', n'\rangle = e^{-as/s^2} t^{m'} u^{n'} \)
yields
\[
\nabla_\theta^2 |l', m', n\rangle = |l', m', n\rangle \left[ \frac{n'(s^2 + t^2)}{(s + t)^2} + \frac{n'(s + t)}{(s + t)^2} \right] - \frac{n'(s^2 - t^2)}{(s + t)^2} \langle u \rangle - \frac{(n' - 2) s^2 t^2 u^{-3}}{(s + t)^2}
\]
where we have multiplied the resulting expression with the volume element \( u(s^2 - t^2) \).

Deriving the angular kinetic energy matrix elements is now readily accomplished with the use of Maclaurin series for \( 1/(s-t) \) and \( 1/(s+t) \) yielding
\[
\langle l' m' n' \rangle - \frac{1}{2} \nabla_\theta^2 |l' m' n'\rangle = -\frac{1}{2} e^{-as/s^2} t^{m'} u^{n'} s^{-1}
\]
\[
\left[ n' \left( s^2 + t^2 \right) u^{-1} - \left( n' + 2 \right) u - \left( n' - 2 \right) s^2 t^2 u^{-3} \right]
\]
\[
\left[ (s + t) \sum_{k=0}^{\infty} \left( t/s \right)^k + (s - t) \sum_{k=0}^{\infty} (-1)^k \left( t/s \right)^k \right]
\]

where \( L = l' + l' \), \( M = m' + m' \) and \( N = n' + n' \).

Closed form expression for the angular kinetic energy matrix elements can then be written as a sum of two series: one over odd indices and the other over even indices.

\[
\langle l' m' n' |T_{ang}| l m n\rangle = -n' \sum_{k=0,2,4,6,\ldots}^{N_t} \left[ n' \mathcal{I}(L + 2 - k, M + k, N - 1) + n' \mathcal{I}(L - k, M + 2 + k, N - 1) - (n' + 2) \mathcal{I}(L - k, M + k, N + 1) - (n' - 2) \mathcal{I}(L + 2 - k, M + 2 + k, N - 3) \right]
\]
\[
- n' \sum_{k=1,3,5,\ldots}^{N_t} \left[ n' \mathcal{I}(L + 1 - k, M + 1 + k, N - 1) + n' \mathcal{I}(L - 1 - k, M + 3 + k, N - 1) - (n' + 2) \mathcal{I}(L - 1 - k, M + 1 + k, N + 1) - (n' - 2) \mathcal{I}(L + 1 - k, M + 3 + k, N - 3) \right]
\]
In the above equation, the primitive integral takes the usual form \[19\]
\[\mathcal{I}(a, b, c) = \int_0^\infty ds \int_0^s du \int_0^u dt e^{-s^2 t^2 u^2} = \frac{\Gamma(a + b + c + 3)}{(b + 1) (b + c + 2)} \]
\[(12)\]

We note in passing that the dependence on the exponent can be incorporated by the scaling relation \(T^{\text{ang}} = \alpha^2 \langle \Psi | T^{\text{ang}} | \Psi \rangle / \langle \Psi | \Psi \rangle\), where the factor 1/8 in the volume element cancels out. To evaluate the accuracy of Eq. \(11\) we have performed calculations with Hamiltonian matrix elements computed using numerical cubature [18] instead of analytic formulae. For a given \(\alpha\), the results of these calculations agree perfectly with those computed using analytic matrix elements. In Table II we compare selectively the matrix elements of the angular kinetic energy from both procedures. For various values of \(\Omega\), we report the expectation value of \(T^{\text{ang}}\) in the ground state. For \(N_z = 625\), we reach convergence in the series agreeing with cubature. The resulting value of \(E_c^{\text{ang}} = -T^{\text{ang}} = -0.01675049\) au accounts for 39.8% of total \(E_c\). In contrast, difference between the ground state energies of \(\Psi^{\text{exact}}\) and \(\Psi^{\text{rad}}\), thus far defined [9] as the angular correlation energy, is as high as 58.7%. The exact value of radial correlation energy can now be deduced as \(E_c^{\text{rad}} = E_c - E_c^{\text{ang}} = -0.02529389\) au, and can be correctly identified as the dominant contributor to the total correlation energy of He. Hence we feel that the previous limit of \(E_c^{\text{rad}}\), defined as the difference between the energy obtained using a purely radial wavefunction and the HF energy, can at best be denoted as \(E_c - E_c^{\text{ang}} - E_c^{\text{ang-rad}}\).

**TABLE II.** Total and correlation energies of helium for the lowest three \(S\)-states. Also given are average values of \(s\), \(t\) and \(u\) along with their standard deviations. All values are in au.

| Property   | 1s\(^2\) | 1s\(^2\)2s\(^1\) | 1s\(^1\)3s\(^1\) |
|------------|----------|-----------------|-----------------|
| \(E\)      | -2.90372438 | -2.14597405 | -2.06127200 |
| \(E_c^{\text{ang}}\) | -0.01675049 | -0.00113042 | -0.00030431 |
| \(E_c^{\text{rad}}\) | -0.02529389 | | |
| \(\langle s\rangle\) | 1.85894459 | 5.94612193 | 13.02334671 |
| \(\langle t\rangle\) | 0.65422575 | 4.44779651 | 11.52344922 |
| \(\langle u\rangle\) | 1.42207026 | 5.26906586 | 12.30451548 |
| \(\sigma_s\) | 0.76518757 | 2.15794814 | 4.53801299 |
| \(\sigma_t\) | 0.55202685 | 2.13562968 | 4.53528083 |
| \(\sigma_u\) | 0.70296195 | 2.12900831 | 4.52075484 |

Our approach also enables the calculation of \(E_c^{\text{ang}}\) for excited states as expectation values. However, to achieve precise results, the exponent \(\alpha\) needs to be optimized for each state separately. The resulting values are collected along with the expectation values and standard deviations of \(s\), \(t\) and \(u\) in Table II. The latter values are in close agreement with results from previous multi-configuration HF calculations [20, 21]. The magnitudes of the standard deviations of these variables are of the same order as their respective average values indicating a broad spread of the wavefunctions in these variables. Also, it is not possible to determine \(E_c^{\text{rad}}\) for \(1s^12s^1\), and \(1s^13s^1\) states because excited states in the HF theory are ambiguous. For instance, a previous study [22] has shown the excited states within this model to be non-orthogonal to the ground state rendering a linear superposition wavefunction impossible. In Table II overall one notes \(E_c^{\text{ang}}\) to gradually vanish with increasing energy and average inter-electronic distance.

![FIG. 3. Variation of correlation energies across two-electron atoms. Solid red line corresponds to \(E_c^{\text{ang}}\) estimated using the virial theorem as \(-T^{\text{ang}}\) while the dotted red line corresponds to the deviation of the energy computed using \(\Psi^{\text{rad}}\) from the exact energy. Solid blue line points to \(E_c^{\text{rad}}\) computed as \(E_c - E_c^{\text{ang}}\), while the blue dotted line is the deviation of the energy computed using \(\Psi^{\text{rad}}\) from the HF energy.](image-url)

Scanning through the two-electron atoms \(\text{H}^-\) until \(\text{Ne}^+\), we have computed \(E_c^{\text{rad}}\) and \(E_c^{\text{ang}}\), using both: the conventional approach wherein the contribution from the radial-angular coupling is associated with the angular term, and using an exact formalism that is free of such coupling. The results are displayed in Fig. 3. As the most striking feature of this figure, one notes the conventional estimation of \(E_c^{\text{ang}}\) to be more negative than the exact result, while, to the same extent, conventional estimation of \(E_c^{\text{rad}}\) less negative than the exact one. This trend can be understood as follows: Briefly, for helium, exact separation of the kinetic energy operator results in \(E_c^{\text{rad}} = 0.602 E_c\) and \(E_c^{\text{ang}} = 0.398 E_c\). In contrary, previous conventions suggest \(E_c^{\text{rad}} = 0.413 E_c\) and \(E_c^{\text{ang}} = 0.587 E_c\), wrongly undermining the importance of radial interactions over the angular one. Our analysis reveals the conventional \(E_c^{\text{ang}}\) to include 0.378\(E_c\) arising from radial-angular coupling, and half of this value must be added to the conventional \(E_c^{\text{rad}}\) to predict the exact value correctly.
Furthermore, we find the total correlation energy to increase with $Z$ for lighter atoms, but converging already near $Z = 10$ (see Fig. 3). The same plot also reveals the individual radial and angular components to also converge, with deviations of less than 0.0001 au between $\text{F}^7^+$ and $\text{Ne}^{8^+}$. Owing to a somewhat unbounded nature, we find the radial correlation to be dominant for the lightest system, $\text{H}^-$, with $E^\text{rad}_c$ accounting for 78.9% of $E_c$.

In conclusion, we present a strategy to correctly partition the correlation energy of two-electron atoms into radial and angular contributions. We have shown previous estimations of radial correlation energy of helium, based on a limiting radial wavefunction, to underestimate the exact value due to the neglect of radial-angular coupling thereby suggesting wrongly $E^\text{ang}_c$ to be larger than $E^\text{rad}_c$. Since an HF wavefunction is entirely devoid of the angular interaction, the corresponding kinetic energy of two-electron atoms arises exclusively from many-body correlation. In fact, this term is one of the essential ingredients of the hitherto unknown exact exchange-correlation (XC) functional in the density functional theory [23]. It will be of interest to see if the presented results aid in the design of modern XC functionals predicting correct angular kinetic energy, at least for the limiting case of two-electron atoms.

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