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A closed-form relation for dimension-dependent two-electron matrix elements of the interelectronic distance

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The evaluation of matrix elements of two electron atoms is fundamental for the study of the electronic properties of those systems. We add to this knowledge by presenting an explicit expression for the matrix elements of the inverse of the interelectronic distance of two-electron atoms in any spatial dimension D. The basis functions used are the D-dependent hydrogenic wavefunctions $\{1s^2, 2p^2, 3d^2, 4f^2, 5g^2, \ldots, 21y^2, \ldots\}$, extending and including, in this way, the results of the previous basis set $\{1s^2, 2p^2, 3d^2, 4f^2\}$. The methodology used does not employ Fourier integral transforms as in previous works but hypergeometric transformation formulas.

KEY WORDS: matrix elements, high-dimensional systems, two-electron atoms

AMS subject classification: 81Q05, 81V45, 33C20

1. Introduction

Two-electron atoms are the simplest ones to show electron–electron interactions. Matrix elements of the electron–electron distance are necessary for calculating ground state properties of helium-like atoms. Because of the recent theoretical interest in the properties of atoms in high dimensions [1], those evaluations have been extended to two-electron atoms in D dimensions [2–4]. At the present time, there are formulas for matrix elements involving the D-dependent hydrogenic wavefunctions $\{1s^2, 2p^2, 3d^2, 4f^2\}$ as a basis set. While the electron–nucleus distances are given in terms of hydrogen-type radial wave functions, the angular dependence is given by Gegenbauer polynomials in the cosine of the angle between the electron–nucleus distance vectors. The basis functions are products of the preceeding two types of functions. In this note, the evaluation of the matrix elements was restricted to spherical symmetry where orbital angular momentum

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quantum numbers for both electrons are equal; thus, the results apply to D-dependent S-states.

In [2–4] the corresponding integrals were evaluated by Fourier integral methods. In the present work, we present a general formula for the D-dependent matrix elements formed from the general basis set $\{1s^2, 2p^2, 3d^2, 4f^2, 5g^2, \ldots, 21y^2, \ldots\}$. In this way, we have extended the evaluation to include any matrix element of the D-dependent S-state. The corresponding integrals are evaluated by hypergeometric function relations, so use of Fourier transforms is not necessary.

Herrick and Stillinger calculated the binding energies of the D-dimensional helium-like ions [3], and Herrick calculated excited states for the D-dimensional helium atom [2]. In both cases, a two-parameter Hylleras–Eckart–Chandrasehkar function and the Chandrasehkar modification of it with a Fourier transform scheme and a change of coordinate system was used. Herrick found that as the dimension increases, the binding energy decreases [2]. The approach of Summerfield and Loeser is similar to that of Herrick but extends the basis set matrix elements [4].

In the present work we obtain a general analytical expression for any basis set, using hypergeometric expressions, extending, in this way, previous results.

2. The matrix elements

To derive the close-form relation for the D-dependent matrix element $\langle n\mu_D| 1/r_{12}|n'\mu'_D\rangle$, where r_{12} is the interelectronic distance, we start by writing our generalized D-dependent two-electron wave function as

$$\Psi = R(r_1, r_2)\Theta(\theta_D)s(\sigma), \tag{1}$$

where θ_D is the angle between the electron–nucleus radii r_1 and r_2, D is the dimension, $R(r_1, r_2)$ is the D-dependent two-electron radial wave function, $\Theta(\theta_D)$ is the D-dependent angular wave functions and $s(\sigma)$ is the spin function. The D-dependent two-electron radial wave function $R(r_1, r_2)$ will be given by a product of two D-dependent one-electron radial wave functions, each one constructed from the three-dimensional one-electron radial wave function [5]

$$R_{\eta,l}(r) = \mathrm{e}^{-(\beta r/2)} \sum_{p=0}^{\eta-l-1} (-1)^p \binom{\eta+l}{p} \frac{(\beta r)^{\eta-p-1}}{(\eta-l-p-1)!}, \tag{2}$$

and making the transformations $l \to \mu_D = l + (1/2)(D-3)$ and $\eta \to n = \eta + (1/2)(D-3)$. Thus, the D-dependent two-electron radial wave function will be given by

$$R(r_1, r_2) = \mathrm{e}^{-\beta(r_1+r_2)/2} \sum_{p=0}^{n-\mu_D-1} \sum_{p'=0}^{n-\mu_D-1} (-1)^{p+p'} \binom{n+\mu_D+D-3}{p} \binom{n+\mu_D+D-3}{p'} \times \frac{(\beta r_1)^{n-p-1}(\beta r_2)^{n-p'-1}}{(n-\mu_D-p-1)!(n-\mu_D-p'-1)!}. \tag{3}$$

The angular part of the wave function will be given by Gegenbauer polynomials

$$C^{\alpha}_{\mu_D} = \sum_{t=0}^{[\mu_D/2]} \frac{(-1)^t (\alpha)_{\mu_D - t} (\cos(\theta_D))^{\mu_D - 2t}}{t!(\mu_D - 2t)!}. \tag{4}$$

Substitution of equations (3) and (4) in equation (1) gives the unnormalized D-dependent two-electron wave function as

$$\begin{aligned}\Psi(r_1, r_2, \theta_D) = \mathrm{e}^{-\beta(r_1+r_2)/2} \sum_{p=0}^{n-\mu_D-1} \sum_{p'=0}^{n-\mu_D-1} \sum_{t=0}^{[\mu_D/2]} \Bigg[(-1)^{p+p'+t} \binom{n+\mu_D+D-3}{p} \\ \times \binom{n+\mu_D+D-3}{p'} \\ \times \frac{(\beta r_1)^{n-p-1} (\beta r_2)^{n-p'-1} (\alpha)_{\mu_D-t} (2\cos\theta_D)^{\mu_D-2t}}{(n-\mu_D-p-1)!(n-\mu_D-p'-1)!t!(\mu_D-2t)!} \Bigg] s(\sigma),\end{aligned} \tag{5}$$

where n is the principal quantum number, μ_D is the secondary quantum number, $\alpha = D/2 - 1$, $\beta = 2\kappa^2 z/(n - 1 + \kappa)$, $\kappa = (D - 1)/2$ and z is the nuclear charge. Let us note that this two-electron wave function includes electron correlation by means of the terms in θ_D.

The matrix elements will be given by

$$\left\langle n\mu_D \left| \frac{1}{r_{12}} \right| n'\mu'_D \right\rangle = \frac{\int_0^\infty \int_0^\infty \int \Psi(r_1, r_2, \theta_D)(1/r_{12})\Psi(r_1, r_2, \theta_D)\, \mathrm{d}^D r_1\, \mathrm{d}^D r_2\, \mathrm{d}\Omega_D}{\int_0^\infty \int_0^\infty \int \Psi(r_1, r_2, \theta_D)\Psi(r_1, r_2, \theta_D)\, \mathrm{d}^D r_1\, \mathrm{d}^D r_2\, \mathrm{d}\Omega_D}. \tag{6}$$

On interchanging sums and integrations and performing the necessary integrations we obtain

$$\left\langle n\mu_D \left| \frac{1}{r_{12}} \right| n'\mu'_D \right\rangle = \frac{\sum_{p=0}^{n-\mu_D-1} \sum_{p'=0}^{n-\mu_D-1} \sum_{p''=0}^{n'-\mu'_D-1} \sum_{p'''=0}^{n'-\mu'_D-1} \sum_{t=0}^{[\mu_D/2]} \sum_{t'=0}^{[\mu'_D/2]} CEI_1}{\sum_{p=0}^{n-\mu_D-1} \sum_{p'=0}^{n-\mu_D-1} \sum_{p''=0}^{n'-\mu'_D-1} \sum_{p'''=0}^{n'-\mu'_D-1} \sum_{t=0}^{[\mu_D/2]} \sum_{t'=0}^{[\mu'_D/2]} CEI_2}, \tag{7}$$

where

$$\begin{aligned}C = \frac{(-1)^{p+p'+p''+p'''} \binom{n+\mu_D+D-3}{p} \binom{n+\mu_D+D-3}{p'} \binom{n'+\mu'_D+D-3}{p''}}{(n-\mu_D-p-1)!(n-\mu_D-p'-1)!(n'-\mu'_D-p''-1)!} \\ \times \frac{\binom{n'+\mu'_D+D-3}{p'''} (\beta)^{2n-p-p'-2} (\beta')^{2n'-p''-p'''-2}}{(n'-\mu'_D-p'''-1)!},\end{aligned} \tag{8}$$

$$E = \frac{(-1)^{t+t'}(\alpha)_{\mu_D - t}(\alpha)_{\mu'_D - t'}(2)^{\mu_D + \mu'_D - 2t - 2t'}}{t!t'!(\mu_D - 2t)!(\mu'_D - 2t')!}, \tag{9}$$

$$I_1 = \int_0^\infty \int_0^\infty \int r_1^{D-1} r_2^{D-1}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}\Omega_D \biggl[\mathrm{e}^{-\xi(r_1+r_2)} r_1^{n+n'-p-p''-2} r_2^{n+n'-p'-p'''-2} \times \frac{1}{r_{12}} (\cos\theta_D)^{\mu_D + \mu'_D - 2t - 2t'} \biggr], \tag{10}$$

$$I_2 = \int_0^\infty \int_0^\infty \int r_1^{D-1} r_2^{D-1}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}\Omega_D \biggl[\mathrm{e}^{-\xi(r_1+r_2)} r_1^{n+n'-p-p''-2} r_2^{n+n'-p'-p'''-2} \times (\cos\theta_D)^{\mu_D + \mu'_D - 2t - 2t'} \biggr], \tag{11}$$

$$\xi = \left(\frac{\beta}{2} + \frac{\beta'}{2} \right). \tag{12}$$

The integration over the spin coordinates does not appear in the above equations because the one performed in the numerator cancels out the one performed in the denominator.

We now describe the different steps to perform the integrations. Let us then begin the evaluation of I_1 with the integration over the angles

$${}_\Omega I_1 = \frac{1}{r_>} \int_0^\pi \frac{(\cos\theta_D)^{\mu+\mu'-2t-2t'} \sin^{D-2}\theta_D}{(1+\varepsilon^2 - 2\varepsilon\cos\theta_D)^{1/2}} \int \mathrm{d}\Omega_{D-1}, \tag{13}$$

here the inverse of the interelectronic distance has been substituted by its expression in terms of the interelectronic angle as $1/r_{12} = 1/(1+\varepsilon^2 - 2\varepsilon\cos\theta_D)^{1/2}$, $\mathrm{d}\Omega_D = \sin^{D-2}\theta_D\, \mathrm{d}\theta_D\, \mathrm{d}\Omega_{D-1}$, ε is equal to $r_</r_>$ where $r_<$ and $r_>$ are the smaller and larger of r_1 and r_2, respectively [6]. Using the trigonometric relation $\cos^2 x + \sin^2 x = 1$, the hypergeometric function for the binomial $(1-x)^{-a} = {}_1F_0(a; \_; x)$ and $S_n = \int \mathrm{d}\Omega_{D-1} = 2\pi^{(D-1)/2}/\Gamma((D-1)/2)$, we can write equation (13) as follows:

$${}_\Omega I_1 = \frac{1}{r_>} S_n \sum_{k=0}^\infty \int_0^\pi \frac{(a)_k \sin^{D-2+2k}\theta_D}{k!(1+\varepsilon^2 - 2\varepsilon\cos\theta_D)^{1/2}}\, \mathrm{d}\theta_D, \tag{14}$$

where $a = t + t' - \mu/2 - \mu'/2$ and $(a)_k$ is Pochhammer's symbol. The integral of the above equation can be evaluated using the formula 3.665.2 in [7] giving

$${}_\Omega I_1 = S_n \frac{1}{r_>} \sum_{k=0}^\infty \frac{(a)_k}{k!} B\left(\frac{D+2k-1}{2}, \frac{1}{2} \right) {}_2F_1\left(\frac{1}{2}, \frac{3-D-2k}{2}; \frac{D+2k}{2}; \left(\frac{r_<}{r_>} \right)^2 \right), \tag{15}$$

where $B(a,b)$ is the beta function defined by $B(a,b) = \Gamma(a)\Gamma(b)/\Gamma(a+b)$ and ${}_2F_1(a,b;c;z)$ is Gauss's hypergeometric function. Substitution of the above result in equation (10) gives

$$I_1 = S_n \int_0^\infty \int_0^\infty \sum_{k=0}^\infty \left[\frac{(a)_k}{k!} \mathrm{e}^{-\xi(r_1+r_2)} r_1^{D+n+n'-p-p''-3} r_2^{D+n+n'-p'-p'''-3} \right.$$
$$\times \frac{1}{r_>} B\left(\frac{D+2k-1}{2}, \frac{1}{2}\right)$$
$$\left. \times\, {}_2F_1\left(\frac{1}{2}, \frac{3-D-2k}{2}; \frac{D+2k}{2}; \left(\frac{r_<}{r_>}\right)^2\right)\right] \mathrm{d}r_1\, \mathrm{d}r_2. \quad (16)$$

The integration over r_1 is

$${}_{r_1}I_1 = \int_0^\infty \mathrm{e}^{-\xi r_1} \frac{1}{r_>} {}_2F_1\left(\frac{1}{2}, \frac{3-D-2k}{2}; \frac{D+2k}{2}; \left(\frac{r_<}{r_>}\right)^2\right) r_1^{D+n+n'-p-p''-3}\, \mathrm{d}r_1. \quad (17)$$

The above integral separates into two integrals which upon evaluation gives

$${}_{r_1}I_{1_1} = \int_0^{r_2} \mathrm{e}^{-\xi r_1} \frac{1}{r_2} {}_2F_1\left(\frac{1}{2}, \frac{3-D-2k}{2}; \frac{D+2k}{2}; \left(\frac{r_1}{r_2}\right)^2\right) r_1^{D+n+n'-p-p''-3}\, \mathrm{d}r_1$$
$$= \sum_{i=0}^\infty \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} r_2^{-(2i+1)} \xi^{-(D+n+n'-p-p''+2i-2)}$$
$$\times \gamma\big(D+n+n'-p-p''+2i-2, \xi r_2\big), \quad (18)$$

and

$${}_{r_1}I_{1_2} = \int_{r_2}^\infty \mathrm{e}^{-\xi r_1} \frac{1}{r_1} {}_2F_1\left(\frac{1}{2}, \frac{3-D-2k}{2}; \frac{D+2k}{2}; \left(\frac{r_2}{r_1}\right)^2\right) r_1^{D+n+n'-p-p''-3}\, \mathrm{d}r_1$$
$$= \sum_{i=0}^\infty \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} r_2^{2i} \xi^{-(D+n+n'-p-p''-2i-3)}$$
$$\times \Gamma\big(D+n+n'-p-p''-2i-3, \xi r_2\big). \quad (19)$$

Now substitution of equations (18) and (19) in equation (10) and integration of the result over r_2 gives

$${}_{r_2}I_{1_1} = \sum_{i=0}^\infty \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} \xi^{-(D+n+n'-p-p''+2i-2)}$$
$$\times \int_0^\infty \mathrm{e}^{-\xi r_2} r_2^{D+n+n'-p'-p'''-2i-4} \gamma\big(D+n+n'-p-p''+2i-2, \xi r_2\big)\, \mathrm{d}r_2$$

$$= G \sum_{i=0}^{\infty} \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} \cdot (D+n+n'-p-p''+2i-2)^{-1} \times {}_2F_1\Big(1, 2D+2n+2n'-p-p'-p''-p'''-5; D+n+n'-p-p''+2i-1; \frac{1}{2}\Big), \tag{20}$$

$$ {}_{r_2}I_{1_2} = \sum_{i=0}^{\infty} \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} \xi^{-(D+n+n'-p-p''-2i-3)} \times \int_0^{\infty} \mathrm{e}^{-\xi r_2} r_2^{D+n+n'-p'-p'''+2i-3} \Gamma\big(D+n+n'-p-p''-2i-3, \xi r_2\big)\, \mathrm{d}r_2 $$
$$= G \sum_{i=0}^{\infty} \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} \cdot \big(D+n+n'-p'-p'''+2i-2\big)^{-1} \times {}_2F_1\Big(1, 2D+2n+2n'-p-p'-p''-p'''-5; D+n+n'-p'-p'''+2i-1; \frac{1}{2}\Big), \tag{21}$$

where

$$G = \frac{\Gamma(2D+2n+2n'-p-p'-p''-p'''-5)}{(2\xi)^{(2D+2n+2n'-p-p'-p''-p'''-5)}}. \tag{22}$$

Then,

$$I_1 = S_n \sum_{k=0}^{\infty} G' \sum_{i=0}^{\infty} \frac{(1/2)_i((3-D-2k)/2)_i}{i!((D+2k)/2)_i} \times \Big[\big(D+n+n'-p'-p'''+2i-2\big)^{-1} \times {}_2F_1\Big(1, 2D+2n+2n'-p-p'-p''-p'''-5; D+n+n'-p'-p'''+2i-1; \frac{1}{2}\Big) + \big(D+n+n'-p-p''+2i-2\big)^{-1} \times {}_2F_1\Big(1, 2D+2n+2n'-p-p'-p''-p'''-5; D+n+n'-p-p''+2i-1; \frac{1}{2}\Big)\Big], \tag{23}$$

which upon several transformations in the hypergeometric functions, it becomes

$$
\begin{aligned}
I_1 = S_n \sum_{k=0}^{\infty} G' \sum_{j=0}^{\infty} & \frac{(1)_j (2D + 2n + 2n' - p - p' - p'' - p''' - 5)_j}{j!} \left(\frac{1}{2}\right)^j \\
\times \Bigg[& \big(D + n + n' - p - p'' - 2\big)^{-1} \big(D + n + n' - p - p'' - 1\big)_j^{-1} \\
& \times {}_4F_3\Bigg(\frac{1}{2}, \frac{3 - D - 2k}{2}, \frac{D + n + n' - p - p'' - 2}{2}, \\
& \qquad \frac{D + n + n' - p - p'' - 1}{2}; \\
& \qquad \frac{D + 2k}{2}, \frac{D + n + n' - p - p'' + j - 1}{2}, \\
& \qquad \frac{D + n + n' - p - p'' + j}{2}; 1\Bigg) \\
& + \big(D + n + n' - p' - p''' - 2\big)^{-1} \big(D + n + n' - p' - p''' - 1\big)_j^{-1} \\
& \times {}_4F_3\Bigg(\frac{1}{2}, \frac{3 - D - 2k}{2}, \frac{D + n + n' - p' - p''' - 2}{2}, \\
& \qquad \frac{D + n + n' - p' - p''' - 1}{2}; \frac{D + 2k}{2}, \\
& \qquad \frac{D + n + n' - p' - p''' + j - 1}{2}, \\
& \qquad \frac{D + n + n' - p' - p''' + j}{2}; 1\Bigg)\Bigg], \qquad (24)
\end{aligned}
$$

where

$$
G' = G \frac{(a)_k}{k!} B\left(\frac{D + 2k - 1}{2}, \frac{1}{2}\right). \qquad (25)
$$

The evaluation of I_2 is straightforward if we recall that $\mathrm{d}\Omega_D = \sin^{D-2}\theta_D \, \mathrm{d}\theta_D \, \mathrm{d}\Omega_{D-1}$ in the angular integration, giving

$$
\begin{aligned}
I_2 = S_n \sum_{k=0}^{\infty} & \frac{(a)_k \pi^{1/2} \Gamma((D - 1 + 2k)/2)(D + n + n' - p - p'' - 3)!}{k! \Gamma((D + 2k)/2)} \\
& \times \frac{(D + n + n' - p' - p''' - 3)!}{\xi^{2D+2n+2n'-p-p'-p''-p'''-4}}. \qquad (26)
\end{aligned}
$$

Table 1 presents some values of different matrix elements for several dimensions and several different nuclear charges. In these particular cases, our results agree with all previous results of [2–4]. On the other hand, the correspondence between the results obtained with Fourier methods [2–4] and those obtained with hypergeometric relations, as discussed here, allows us to establish interesting relations for sums of hypergeomet-

Table 1
Some values for different matrix elements using equation (7) for several dimensions and nuclear charges.

Matrix element	Dimension	$z=1$	$z=2$	$z=3.5$	$z=7.81543$
$\left\langle 1s^2 \middle\vert \frac{1}{r_{12}} \middle\vert 1s^2 \right\rangle$	$D=3$	5/8	1.25	2.1875	4.88464275
	$D=5$	21/32	1.3125	2.296875	5.128875937
	$D=7$	0.6703125	1.340625	2.34609375	5.238780422
	$D=9$	0.678292	1.356584821	2.374023438	5.301146855
	$D=21$	0.694595	1.389190908	2.43108409	5.428562151
$\left\langle 2p^2 \middle\vert \frac{1}{r_{12}} \middle\vert 2p^2 \right\rangle$	$D=3$	111/512	0.43359375	0.7587890625	1.694360801
	$D=5$	1001/2880	0.6951388889	1.216493056	2.716404663
	$D=7$	0.42489624	0.8497924805	1.487136841	3.320746823
	$D=9$	0.475247396	0.9504947917	1.663365885	3.714262755
	$D=21$	0.595634946	1.191269891	2.08472231	4.655143223
$\left\langle 3d^2 \middle\vert \frac{1}{r_{12}} \middle\vert 3d^2 \right\rangle$	$D=3$	0.1074869797	0.214974	0.3762044427	0.8400569616
	$D=5$	0.2159685407	0.4319370815	0.7558898920	1.687887012
	$D=7$	0.2949549212	0.5899098424	1.032342224	2.30519954
	$D=9$	0.3531169442	0.7062338884	1.235909305	2.759760759
	$D=21$	0.5171795147	1.034359029	1.810128301	4.041980294

ric functions, as the one obtained through the evaluation of the $\langle 1s^2|1/r_{12}|1s^2\rangle$ matrix element

$$\sum_{k=0}^{\infty} \frac{(1/2)_k((3-D)/2)_k}{(1+D/2)_k k!} {}_2F_1(1, 2D-1;\, D+2k+1;\, 1/2)$$
$$= \frac{\Gamma((D+1)/2)\Gamma(D+1/2)\Gamma(D)}{\Gamma(D/2)(D-1)\Gamma(2D-1)} 4^{D-1}.$$

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