Two-electron atomic wave functions which satisfy proportionality relations between one- and two-electron moments

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Based on momentum- and position-space analyses of the moment operators for two-electron atoms, it is shown that there exists a family of two-electron wave functions which satisfy a proportionality relation,

$$\langle r_1^\nu \rangle / \langle r_{12}^\nu \rangle = \langle p_1^\nu \rangle / \langle p_{12}^\nu \rangle = 2^{-\nu/2},$$

between the one- and two-electron moments in position and momentum spaces, where ν is an arbitrary number for which the moments are well-defined.

Key words: Two-electron atomic wave function — One- and two-electron moments — Momentum space

1. Introduction

The position and momentum representations are alternative ways to investigate the electronic structure of atoms and molecules. However, the momentum-space treatment has received little attention, partly because the potential energy operator is usually given in terms of positions and partly because the solution of integral Schrödinger equations in momentum space is not well-established. Nevertheless, there are continuous efforts to solve directly the momentum-space Schrödinger equation (see [1, 2] and references therein). They have brought definite developments to the electronic structure theory of atoms and molecules and also to the theory of Compton profile [3, 4], in which the momentum wave function constitutes a natural basis of discussion.

Previously, we have successfully applied the momentum-space method to the van der Waals interaction among ground-state hydrogen atoms, and several two- and

three-body interaction constants have been determined almost exactly together with the first order perturbation wave function of the system (see [5] and references therein). The momentum-space technique has also been applied to the one-electron multi-center Coulomb problem and the accuracy comparable to the position-space method has been numerically verified for the hydrogen molecular ion (see [6] and references therein). The Fock expansion [7, 8] of the kernel of the integral Schrödinger equation has been fully utilized (see [9, 10] for review). These studies have given a clue to derive various sum rules and interrelations among different types of integrals over hydrogenic orbitals [11, 12]. However, the above applications have been essentially limited to problems of one-electron nature.

In the present paper, we point out an interesting aspect of the one- and two-electron operators r_1^ν, r_{12}^ν, p_1^ν, p_{12}^ν, and their expectation values, which has been found in the momentum-space study of the two-electron atomic Schrödinger equation: If the wave function for the state under consideration can be described by a single product of a symmetric spatial function and an antisymmetric spin function, there exists a family of spatial functions which satisfy certain proportionality relations between the one- and two-electron moments $\langle r_1^\nu \rangle$ and $\langle r_{12}^\nu \rangle$ in position space and $\langle p_1^\nu \rangle$ and $\langle p_{12}^\nu \rangle$ in momentum space, where ν is any number for which these moments are defined. For a special case of $\nu = -1$, we have a relation $\langle 1/r_{12} \rangle = \langle 1/r_1 \rangle/\sqrt{2}$. When these functions are employed as trial functions, we can then perform the variational procedure without evaluating the electron repulsion integral. In the next section, we clarify the existence of this special class of spatial functions and discuss their properties. In Sect. 3, numerical illustrations are given. Atomic units are used throughout this paper.

2. Special family of two-electron atomic wave functions

2.1. Momentum-space consideration and functions $\phi(p_1, p_2) = f(p_1^2 + p_2^2)$

For a two-electron atom, we consider a case where an approximate total wave function is expressible by a single product of spatial and spin functions. We denote the normalized spatial function as $\phi(p_1, p_2)$ in momentum space.

The roles of the one- and two-electron operators r_1^ν and r_{12}^ν are represented in momentum space by the functions

$$F_\nu(p_1, p_2) = \int V_\nu(p_1 - p_1', p_2 - p_2') \phi(p_1', p_2') \, dp_1' \, dp_2', \tag{1a}$$

$$G_\nu(p_1, p_2) = \int W_\nu(p_1 - p_1', p_2 - p_2') \phi(p_1', p_2') \, dp_1' \, dp_2', \tag{1b}$$

where

$$V_\nu(p_1, p_2) \equiv (2\pi)^{-6} \int r_1^\nu \exp(-i[p_1 \cdot r_1 + p_2 \cdot r_2]) \, dr_1 \, dr_2, \tag{2a}$$

$$W_\nu(p_1, p_2) \equiv (2\pi)^{-6} \int r_{12}^\nu \exp(-i[p_1 \cdot r_1 + p_2 \cdot r_2]) \, dr_1 \, dr_2. \tag{2b}$$

The functions F_ν and G_ν correspond, respectively, to $r_1^\nu \psi(\mathbf{r}_1, \mathbf{r}_2)$ and $r_{12}^\nu \psi(\mathbf{r}_1, \mathbf{r}_2)$ in position space, where $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is the Fourier transform of $\phi(\mathbf{p}_1, \mathbf{p}_2)$. The multiplicativity of the operators r_1^ν and r_{12}^ν is lost in momentum space. The expression for V_ν is easily rearranged as

$$V_\nu(\mathbf{p}_1, \mathbf{p}_2) = I_\nu(\mathbf{p}_1)\delta(\mathbf{p}_2), \tag{3a}$$

where

$$I_\nu(\mathbf{p}) \equiv (2\pi)^{-3} \int r^\nu \exp(-i\mathbf{p} \cdot \mathbf{r}) \, d\mathbf{r}$$

$$= (2\pi^2)^{-1} \int_0^\infty r^{\nu+2} j_0(pr) \, dr \tag{3b}$$

with $j_n(x)$ being the spherical Bessel function of the first kind, and

$$\delta(\mathbf{p}) = (2\pi)^{-3} \int \exp(-i\mathbf{p} \cdot \mathbf{r}) \, d\mathbf{r} \tag{3c}$$

is the three-dimensional Dirac delta function. Then the one-electron contribution F_ν is reduced to

$$F_\nu(\mathbf{p}_1, \mathbf{p}_2) = \int I_\nu(\mathbf{p}_1 - \mathbf{p})\phi(\mathbf{p}, \mathbf{p}_2) \, d\mathbf{p}. \tag{4}$$

To obtain an expression for G_ν which compares with Eq. (4), we introduce the orthogonal transformations of the variables $(\mathbf{p}_1, \mathbf{p}_2)$ and $(\mathbf{r}_1, \mathbf{r}_2)$:

$$\begin{aligned}
&\mathbf{q} \equiv (\mathbf{p}_1 - \mathbf{p}_2)/\sqrt{2}, &&\mathbf{Q} \equiv (\mathbf{p}_1 + \mathbf{p}_2)/\sqrt{2}, \\
&\mathbf{s} \equiv (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2}, &&\mathbf{S} \equiv (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}, \\
&q^2 + Q^2 = p_1^2 + p_2^2, &&d\mathbf{q}\, d\mathbf{Q} = d\mathbf{p}_1\, d\mathbf{p}_2, \\
&s^2 + S^2 = r_1^2 + r_2^2, &&d\mathbf{s}\, d\mathbf{S} = d\mathbf{r}_1\, d\mathbf{r}_2.
\end{aligned} \tag{5a}$$

So long as the original pairs $(\mathbf{r}_1, \mathbf{p}_1)$ and $(\mathbf{r}_2, \mathbf{p}_2)$ are conjugate, the transformed pairs $(\mathbf{s}, \mathbf{q})$ and $(\mathbf{S}, \mathbf{Q})$ are also conjugate and the relation,

$$\mathbf{p}_1 \cdot \mathbf{r}_1 + \mathbf{p}_2 \cdot \mathbf{r}_2 = \mathbf{q} \cdot \mathbf{s} + \mathbf{Q} \cdot \mathbf{S}, \tag{5b}$$

holds. Then we can rewrite Eq. (2b) as

$$W_\nu(\mathbf{p}_1, \mathbf{p}_2) = (2\pi)^{-6} \int (\sqrt{2}\, s)^\nu \exp(-i[\mathbf{q} \cdot \mathbf{s} + \mathbf{Q} \cdot \mathbf{S}]) \, d\mathbf{s}\, d\mathbf{S}$$

$$= 2^{\nu/2} I_\nu(\mathbf{q})\delta(\mathbf{Q}). \tag{6}$$

We also introduce a momentum wave function $\phi'(\mathbf{q}, \mathbf{Q})$ defined by

$$\phi'(\mathbf{q}, \mathbf{Q}) \equiv \phi([\mathbf{Q} + \mathbf{q}]/\sqrt{2}, [\mathbf{Q} - \mathbf{q}]/\sqrt{2}) = \phi(\mathbf{p}_1, \mathbf{p}_2). \tag{7}$$

We thus have an expression

$$G_\nu(\mathbf{p}_1, \mathbf{p}_2) = 2^{\nu/2} \int I_\nu(\mathbf{q} - \mathbf{p})\phi'(\mathbf{p}, \mathbf{Q}) \, d\mathbf{p}, \tag{8}$$

which is analogous to Eq. (4) apart from the constant prefactor.

Comparison of Eqs. (4) and (8) shows that if the equality $\phi = \phi'$ holds, the function G_ν resulting from the two-electron operator reduces to the form of the function F_ν resulting from the one-electron operator. To see such a possibility, we return to the relation of the two sets of variables (p_1, p_2) and (q, Q). Since the definition (5) expresses a rotation of coordinate axes, we immediately find that if the spatial function $\phi(p_1, p_2)$ takes a form

$$\phi(p_1, p_2) = f(p_1^2 + p_2^2), \tag{9a}$$

then the modified function $\phi'(q, Q)$ has exactly the same form

$$\phi'(q, Q) = f(q^2 + Q^2), \tag{9b}$$

where $f(x)$ is an arbitrary well-behaved function which satisfies proper boundary conditions in momentum space. For this type of spatial functions, we obtain from Eqs. (4) and (8) the following interesting relation

$$G_\nu(p_1, p_2) = 2^{\nu/2} F_\nu(q, Q)$$
$$= 2^{\nu/2} F_\nu([p_1 - p_2]/\sqrt{2}, [p_1 + p_2]/\sqrt{2}). \tag{10}$$

For a particular case of $\nu = -1$, which has motivated the present study, the contributions of the nuclear attraction operator $1/r_1$ and the electron repulsion operator $1/r_{12}$ are embodied, after the angular integrations, by the function

$$F_{-1}(p_1, p_2) = (\pi p_1)^{-1} \int_0^\infty Q_0([p^2 + p_1^2]/2pp_1) \, pf(p^2 + p_2^2) \, dp, \tag{11}$$

where $Q_n(x)$ is the Legendre function of the second kind.

Now using Eqs. (4) and (8), we obtain the momentum-space representations of $\langle r_1^\nu \rangle$ and $\langle r_{12}^\nu \rangle$ as

$$\langle r_1^\nu \rangle = \int \phi*(p_1, p_2) \left[\int I_\nu(p_1 - p)\phi(p, p_2) \, dp \right] dp_1 \, dp_2, \tag{12a}$$

$$\langle r_{12}^\nu \rangle = 2^{\nu/2} \int \phi'*(q, Q) \left[\int I_\nu(q - p)\phi'(p, Q) \, dp \right] dq \, dQ, \tag{12b}$$

which finally lead to the desired result

$$\langle r_1^\nu \rangle = 2^{-\nu/2}\langle r_{12}^\nu \rangle, \tag{13a}$$

for the spatial wave functions $\phi(p_1, p_2) = f(p_1^2 + p_2^2)$. Since the moment operators p_1^ν and p_{12}^ν are multiplicative in momentum space, it immediately follows that this family of functions also satisfies

$$\langle p_1^\nu \rangle = 2^{-\nu/2}\langle p_{12}^\nu \rangle, \tag{13b}$$

and hence

$$\langle r_1^\nu \rangle / \langle r_{12}^\nu \rangle = \langle p_1^\nu \rangle / \langle p_{12}^\nu \rangle = 2^{-\nu/2}. \tag{13c}$$

Namely, a proportionality relation always holds between the one- and two-electron moments in both position and momentum spaces with the same proportionality constant.

2.2. Position-space consideration and functions $\psi(\underline{r}_1, \underline{r}_2) = g(r_1^2 + r_2^2)$

Discussion in position space proceeds in an exactly analogous way to the momentum-space discussion given in the preceding subsection.

Based on the orthogonal transformations [Eq. (5a)], we use the relation $r_{12}^\nu = 2^{\nu/2} s^\nu$ and introduce a modified position wave function

$$\psi'(\underline{s}, \underline{S}) \equiv \psi([\underline{S} + \underline{s}]/\sqrt{2}, [\underline{S} - \underline{s}]/\sqrt{2}) = \psi(\underline{r}_1, \underline{r}_2). \tag{14}$$

We then find that Eq. (13) again holds for *another* family of wave functions $\psi(\underline{r}_1, \underline{r}_2) = g(r_1^2 + r_2^2)$, where $g(x)$ is an arbitrary well-behaved function satisfying appropriate boundary conditions in position space.

For $\nu = -1$, Eq. (13) yields a relation

$$\langle 1/r_1 \rangle = \sqrt{2} \langle 1/r_{12} \rangle, \tag{15}$$

between the nuclear attraction and electron repulsion integrals. When a function from the families $\phi(\underline{p}_1, \underline{p}_2) = f(p_1^2 + p_2^2)$ and $\psi(\underline{r}_1, \underline{r}_2) = g(r_1^2 + r_2^2)$ is used as a trial function in the variational calculation, we can avoid the evaluation of the electron repulsion integral, which is the most tedious part of the calculation. Note that the functions $f(p_1^2 + p_2^2)$ and $g(r_1^2 + r_2^2)$ are symmetric with respect to the exchange of the electron labels and therefore the accompanied spin function must be antisymmetric to obtain an acceptable wave function.

2.3. Equivalence of two families of functions

Apparently, there seem to exist two families of functions $\phi(\underline{p}_1, \underline{p}_2) = f(p_1^2 + p_2^2)$ and $\psi(\underline{r}_1, \underline{r}_2) = g(r_1^2 + r_2^2)$ which always fulfill the proportionality relation, Eq. (13). However, this is not true. It can be proved that the two families are a pair of Fourier transforms and they constitute a single family.

Let us consider the Fourier transform $g(\underline{r}_1, \underline{r}_2)$ of a function $f(p_1^2 + p_2^2)$:

$$g(\underline{r}_1, \underline{r}_2) = (2\pi)^{-3} \int f(p_1^2 + p_2^2) \exp(+i[\underline{p}_1 \cdot \underline{r}_1 + \underline{p}_2 \cdot \underline{r}_2]) \, d\underline{p}_1 \, d\underline{p}_2. \tag{16a}$$

Using the expansion [13]

$$\exp(i\underline{p} \cdot \underline{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(pr) Y_{lm}^*(\Omega_p) Y_{lm}(\Omega_r) \tag{17}$$

and integrating over the angular variables, we find

$$g(\underline{r}_1, \underline{r}_2) = (2/\pi) \int\int_0^\infty f(p_1^2 + p_2^2) j_0(p_1 r_1) j_0(p_2 r_2) p_1^2 p_2^2 \, dp_1 \, dp_2. \tag{16b}$$

Introducing the polar coordinates for the two-dimensional quadrant space defined by the moduli p_1 and p_2, we can rewrite Eq. (16b) as

$$g(\underline{r}_1, \underline{r}_2) = (2/\pi)(r_1 r_2)^{-1} \int_0^\infty p^3 f(p^2)$$
$$\times \left[\int_0^{\pi/2} \sin(pr_1 \cos\theta) \sin(pr_2 \sin\theta) \sin\theta \cos\theta \, d\theta \right] dp, \tag{16c}$$

where $p = (p_1^2 + p_2^2)^{1/2}$ and $\theta = \arctan(p_2/p_1)$. The angular integration in Eq. (16c) can be carried out using the differentiated form of the formula (3.711) of [14], and we finally obtain

$$g(\underline{r}_1, \underline{r}_2) = r^{-2} \int_0^\infty p^3 f(p^2) J_2(pr) \, dp, \tag{16d}$$

where $J_n(x)$ is the Bessel function of the first kind and $r = (r_1^2 + r_2^2)^{1/2}$. Equation (16d) implies that the Fourier transform of $f(p_1^2 + p_2^2)$ is a function of $r = (r_1^2 + r_2^2)^{1/2}$. Conversely, the Fourier transform of $g(r_1^2 + r_2^2)$ is shown to be a function of $p = (p_1^2 + p_2^2)^{1/2}$. In this sense, the functions $f(p_1^2 + p_2^2)$ and $g(r_1^2 + r_2^2)$ constitute a single family.

3. Numerical illustrations

In order to see the property of the functions $\phi(\underline{p}_1, \underline{p}_2) = f(p_1^2 + p_2^2)$ and $\psi(\underline{r}_1, \underline{r}_2) = g(r_1^2 + r_2^2)$ as approximations to the two-electron atomic wave function, we have examined the moment ratio $\langle r_1^n \rangle / [2^{-n/2} \langle r_{12}^n \rangle]$ $(-2 \leq n \leq 4)$. For the ground states of several helium-like atoms, nearly exact values of these moments have been reported [15]. The results are summarized in Table 1. Except for a few cases, the ratios are found to be around unity as Eq. (13) implies, and the deviation from unity decreases as the nuclear charge increases. For $1 \leq n \leq 3$, the deviation is small (within 10%) except for H^-, while for $n = -2$ it is large in all cases. For $n = -1$, the deviation is about 20%, and this means that the energy expectation value obtained from the functions $f(p_1^2 + p_2^2)$ and $g(r_1^2 + r_2^2)$ will not be good. These features suggest that the functions $f(p_1^2 + p_2^2)$ and $g(r_1^2 + r_2^2)$ are relatively reasonable for the description of intermediate region, but do not suit for accurate description of the near-nucleus region in position space and the high-momentum region in momentum space.

As a simple example of the variational application, we have studied a class of two-electron functions with two parameters,

$$g_\mu(r) = N_\mu r^\mu K_\mu(\alpha r), \qquad (\alpha, \mu > 0)$$
$$r = (r_1^2 + r_2^2)^{1/2}, \tag{18a}$$

Table 1. Proportionality between $\langle r_1^n \rangle$ and $\langle r_{12}^n \rangle$ for the ground states of the helium-like atoms from H^- through N^{5+}. The values for the moments are taken from [15]

Atom	$\langle r_1^n \rangle / [2^{-n/2} \langle r_{12}^n \rangle]$					
	$n = -2$	-1	1	2	3	4
H^-	3.5996	1.5534	0.8686	0.9455	1.1906	1.6229
He	2.0540	1.2622	0.9243	0.9485	1.0486	1.2244
Li^+	1.8284	1.2124	0.9394	0.9628	1.0501	1.1996
Be^{2+}	1.7336	1.1902	0.9469	0.9711	1.0544	1.1945
B^{3+}	1.6815	1.1776	0.9514	0.9764	1.0578	1.1934
C^{4+}	1.6484	1.1695	0.9544	0.9801	1.0605	1.1933
N^{5+}	1.6255	1.1638	0.9566	0.9828	1.0626	1.1935

where $K_\mu(x)$ is the modified Bessel function and N_μ is the normalization constant,

$$N_\mu^2 = \alpha^{2\mu+6}\Gamma(2\mu+6)/\{\pi^3 2^{2\mu+4}\Gamma(2\mu+3)[\Gamma(\mu+3)]^2\}, \tag{18b}$$

in which $\Gamma(x)$ is the gamma function. The Fourier transformation of Eq. (18a) yields the corresponding momentum wave function,

$$f_\mu(p) = N_\mu[2^{2+\mu}\Gamma(\mu+3)\alpha^\mu](p^2+\alpha^2)^{3+\mu},$$
$$p = (p_1^2+p_2^2)^{1/2}. \tag{19}$$

For a helium-like atom with nuclear charge Z, the variation with respect to the parameters ν and α has given the optimum values,

$$\mu_{\text{opt}} = 1/2, \qquad \alpha_{\text{opt}} = (32/15\pi)(2Z-1/\sqrt{2}), \qquad E_{\text{opt}} = -\alpha_{\text{opt}}^2/2, \tag{20a}$$

and

$$g_{1/2}(r) = (8\alpha^6/15\pi^3)^{1/2}\exp(-\alpha r), \tag{20b}$$

$$f_{1/2}(p) = (2\sqrt{15}\,\alpha^{7/2}/\pi)(p^2+\alpha^2)^{7/2}. \tag{20c}$$

For $Z = 2$ (helium atom), E_{opt} is obtained to be -2.500017, which is 87.4% of the Hartree–Fock limit value [16, 17] and 86.1% of the nearly exact value [15, 18]. The energy expectation value is poor as expected. The associated position moments $\langle r_1^n \rangle$ and $\langle r_{12}^n \rangle$ are given in Table 2 and compared with the nearly exact values [15]. The moment $\langle r_1 \rangle$ is satisfactory and the moment $\langle r_{12} \rangle$ may be within an acceptable range of deviation. For the other moments, the error is large again.

These numerical experiences suggest that the functions $\phi(p_1, p_2) = f(p_1^2+p_2^2)$ and $\psi(r_1, r_2) = g(r_1^2+r_2^2)$ are not useful for the accurate description of the two-electron electronic state, so long as we stand on the variational criterion. Rather, the theoretical structure of the one- and two-electron moments clarified in this study should be stressed. The existence of this special family of two-electron wave function may be helpful to understand the property of the one- and two-electron operators. The present results can be also used for semi-quantitative or pedagogical discussion and for the construction of simple models of the electron correlation

Table 2. Comparison of the position moments for He obtained from Eq. (20) with the nearly exact values reported in [15]

n	$\langle r_1^n \rangle$			$\langle r_{12}^n \rangle$		
	Eq. (20)	Exact	Error[a]	Eq. (20)	Exact	Error[a]
-2	4.0000	6.0174	-33.5	2.0000	1.4648	36.5
-1	1.5184	1.6883	-10.1	1.0737	0.9458	13.5
1	0.9111	0.9295	-2.0	1.2884	1.4221	-9.4
2	1.0500	1.1635	-12.0	2.1000	2.5164	-16.5
3	1.4577	1.9679	-25.9	4.1229	5.3080	-22.3
4	2.3625	3.9735	-40.5	9.4499	12.9812	-27.2

[a] Relative errors in %

problem. Finally we note that the generalization of the present study to many-electron atoms is possible. However, the resultant spatial function is symmetric, and the difficulty will be that the accompanied spin function must be antisymmetric for all permutations to obtain an acceptable approximation to the total electronic wave function.

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