Sum rules for generalized electron-pair moments of Hartree–Fock orbitals

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Sum rules for generalized electron-pair moments of Hartree–Fock orbitals

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For many-electron systems, the generalized electron-pair density function \( g(q;a,b) \) represents the probability density function for the magnitude \(|a\mathbf{r}_i + b\mathbf{r}_j|\) of two-electron vector \( a\mathbf{r}_i + b\mathbf{r}_j \), to be \( q \), where \( a \) and \( b \) are real-valued parameters. For Hartree–Fock wave functions, decomposition of \( g(q;a,b) \) into spin–orbital-pair components \( g^{ij}(q;a,b) \) shows that the second moments \( \langle q^2 \rangle_{(a,b)} \), associated with \( g^{ij}(q;a,b) \), satisfy several rigorous sum rules which connect one- and two-electron properties of spin–orbitals \( i \) and \( j \). The same is also true in momentum space. As an illustrative application, the orbital kinetic energies of the Rn atom are separated into the relative motion and center-of-mass motion contributions of electrons in two relevant orbitals. © 2001 American Institute of Physics. [DOI: 10.1063/1.1367371]

I. INTRODUCTION

In recent papers, we have studied\(^1\)\(^2\) a generalized electron-pair density function \( g(q;a,b) \) defined by

\[
g(q;a,b) = (4\pi q^2)^{-1} \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(q - |a\mathbf{r}_i + b\mathbf{r}_j|) \right\},
\]

(1)

where \( a \) and \( b \) are real-valued parameters, \( \delta(x) \) is the one-dimensional Dirac delta function, and the angular brackets \( \langle \rangle \) stand for the expectation value over the \( N \)-electron \( (N \geq 2) \) wave function \( \Psi(x_1, \ldots, x_N) \) with \( x_i = (\mathbf{r}_i, \sigma_i) \) being the combined position-spin coordinates of the electron \( i \). The generalized electron-pair density \( g(q;a,b) \) represents the probability density function for the magnitude \(|a\mathbf{r}_i + b\mathbf{r}_j|\) of two-electron vector \( a\mathbf{r}_i + b\mathbf{r}_j \) of any pair of electrons \( i \) and \( j \) to be \( q \), and is normalized to \( N(N-1)/2 \), the number of electron pairs. It has been shown\(^2\) that the function \( g(q;a,b) \) connects smoothly the single-electron density \( \rho(r) \), the electron-pair intracule (relative motion) density \( h(u) \), and the electron-pair extracule (center-of-mass motion) density \( d(R) \). Namely,

\[
g(q;1,1) = h(q), \quad g(q;1,0) = \frac{N-1}{2} \rho(q).
\]

(2)

If we define moments \( \langle q^k \rangle_{(a,b)} \) of the density \( g(q;a,b) \) by

\[
\langle q^k \rangle_{(a,b)} = 4\pi \int_0^\infty dq q^{k+2} g(q;a,b)
\]

\[
= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} |a\mathbf{r}_i + b\mathbf{r}_j|^k,
\]

(3)

we then find

\[
\langle q^k \rangle_{(1,1)} = \langle u^k \rangle, \quad \langle q^k \rangle_{(1,0)} = \frac{N-1}{2} \langle r^k \rangle,
\]

(4)

\[
\langle q^k \rangle_{(1,1)} = 2\langle R^k \rangle,
\]

corresponding to Eq. (2), and all the single-electron \( \langle r^k \rangle \), intracule \( \langle u^k \rangle \), and extracule \( \langle R^k \rangle \) moments are generated from the generalized electron-pair moments \( \langle q^k \rangle_{(a,b)} \). In addition, it has been found\(^9\) that there exists a rigorous sum rule for the second generalized electron-pair moments \( \langle q^2 \rangle_{(a,b)} \):

\[
\langle q^2 \rangle_{(a,b)} + \langle q^2 \rangle_{(a,-b)} = (a^2 + b^2)(N-1)\langle r^2 \rangle,
\]

(5)

which is valid for both exact and approximate wave functions of any atoms and molecules. It is interesting that the right-hand side of Eq. (5) is a single-electron property, while the left-hand side is a two-electron property if \( a \neq 0 \) and \( b \neq 0 \). For a special case of \( a = b = 1 \), Eq. (5) reads

\[
\langle u^2 \rangle + 4\langle R^2 \rangle = 2(N-1)\langle r^2 \rangle.
\]

(6)

Namely, the sum of the second intracule \( \langle u^2 \rangle \) and extracule \( \langle R^2 \rangle \) moments (the latter multiplied by 4) is exactly identical with the second single-electron moment \( \langle r^2 \rangle \) multiplied by 2\( (N-1) \).

When we introduce the corresponding electron-pair density \( \tilde{g}(t;a,b) \) and associated moments \( \langle t^n \rangle_{(a,b)} \) in momentum space, exactly the same discussion as in position space results\(^9\) in the momentum-space counterparts of Eqs. (5) and (6).

In the present paper, we discuss decomposition of the generalized electron-pair density \( g(q;a,b) \) and its second moment \( \langle q^2 \rangle_{(a,b)} \) into spin–orbital-pair contributions \( g^{ij}(q;a,b) \) and \( \langle q^2 \rangle_{(i,j)} \), respectively, within the Hartree–Fock framework. Several sum rules are derived which connect one- and two-electron properties associated with spin–orbitals \( i \) and \( j \). For atomic systems, sum rules for subshell contributions are also obtained. The isomorphism of determinant wave functions in position and momentum spaces leads that exactly the same sum rules hold in momentum space as well. An application of the present results is illus-
II. SUM RULES FOR HARTREE–FOCK ORBITALS

A. Position space

For an N-electron determinantal wave function composed of a set of orthonormal spin–orbitals \( \psi_i(\mathbf{r}) \ \eta_i(\sigma) \), the electron-pair density \( g(q;a,b) \), defined by Eq. (1), is rewritten as
\[
g(q;a,b) = \sum_{j=1}^{N-1} \sum_{i=1}^N g^{ij}(q;a,b),
\]
where the angular brackets abbreviate the integrations over \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), and the spin integral \( \delta(i,j) \) is unity if the spin–orbitals \( i \) and \( j \) have the same spin and is zero if they have the opposite spins. Corresponding to Eqs. (7a) and (7b), the generalized electron-pair moments \( \langle q^k \rangle_{(a,b)} \) are decomposed as
\[
\langle q^k \rangle_{(a,b)} = \sum_{i=1}^{N-1} \sum_{j=1}^N \langle q^{ij} \rangle_{(a,b)},
\]
where for a particular case of \( k = 2 \), the moment operator in Eq. (8b) satisfies an identity
\[
\frac{1}{2}[|\mathbf{r}_1 + \mathbf{r}_2|^2 + |\mathbf{r}_1 + \mathbf{ar}_1|^2] = \frac{1}{2}(a^2 + b^2)(r_1^2 + r_2^2) + 2a b r_1 \cdot r_2,
\]
which further yields
\[
\langle q^{ij} \rangle_{(a,b)} = \frac{1}{2}(a^2 + b^2)[(r_i^2) + (r_j^2)]
\]
\[
+ 2ab[(r_i \cdot r_j) - \delta_{ij}(|r_i|^2 + |r_j|^2)],
\]

B. Momentum space

The Hartree–Fock wave function in momentum space has exactly the same determinantal structure as in position space, provided the single-electron spatial function \( \psi_i(\mathbf{r}) \) is replaced with
\[ \phi_i(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp(-i\mathbf{p}\cdot\mathbf{r}) \phi_i(\mathbf{r}). \]  

Then the spin–orbital-pair components \( g^{ij}(r; a, b) \) and \( \langle \mathbf{r}^2 \rangle_{(a,b)}^{ij} \) of the generalized electron-pair density \( g(\mathbf{r}; a, b) \) and moments \( (\mathbf{r}^2)_{(a,b)} \) in momentum space satisfy various relations discussed above in position space, if the variables and functions are replaced appropriately. An exception is that the orbital density \( \Pi_i(\mathbf{p}) = |\phi_i(\mathbf{p})|^2 \) in momentum space has even inversion symmetry \( \Pi_i(-\mathbf{p}) = \Pi_i(\mathbf{p}) \) for any atoms and molecules. Therefore, the \( \langle \mathbf{p} \rangle_i \langle \mathbf{p} \rangle_{ij} \) term is absent in the momentum-space counterpart of Eq. (10a). 

Some explicit forms of the spin–orbital-pair sum rules in momentum space are 

\[ \langle \mathbf{r}^2 \rangle_{(a,b)}^{ij} + \langle \mathbf{r}^2 \rangle_{(a,-b)}^{ij} = (a^2 + b^2)\langle \mathbf{p}^2 \rangle_i \langle \mathbf{p}^2 \rangle_j \],   

(17a) 

\[ \langle \mathbf{v}^2 \rangle_i^{ij} + 4 \langle \mathbf{p}^2 \rangle_i^{ij} = 2 \langle \mathbf{v}^2 \rangle_i \langle \mathbf{p}^2 \rangle_j \],   

(17b) 

for any two spin–orbitals, and 

\[ \langle \mathbf{v}^2 \rangle_i^{ij} + 4 \langle \mathbf{p}^2 \rangle_i^{ij} = \langle \mathbf{v}^2 \rangle_i^{ij} + \langle \mathbf{p}^2 \rangle_j \],   

(18a) 

\[ \langle \mathbf{v}^2 \rangle_i^{ij} = 4 \langle \mathbf{p}^2 \rangle_i^{ij} = \langle \mathbf{v}^2 \rangle_i^{ij} + \langle \mathbf{p}^2 \rangle_j \],   

(18b) 

for two spin–orbitals with the same inversion symmetry, where \( p, v, \) and \( P \) are the momentum-space single-electron, intracule, and extracule radii, respectively. Even when two spin-orbitals have different inversion symmetries, Eqs. (18a) and (18b) are valid for Hartree wave functions where there are no exchange terms. Equation (17) is of our special interest, since the second single-electron moment \( \langle \mathbf{p}^2 \rangle \), appearing on the right-hand side is just twice the electronic kinetic energy \( T_i = \langle \mathbf{p}^2 \rangle_i /2 \) of the spin–orbital \( i \). When Eq. (17b) is applied, the sum \( T_i + T_j \) of the orbital kinetic energies is precisely decomposed into two contributions from the relative (intracule) and center-of-mass (extracule) motions of an electron pair. Some numerical results will be presented in the next section. 

We note that comparison of Eqs. (11) and (17a) gives an additional rigorous relation 

\[ \langle \mathbf{p}^2 \rangle_i + \langle \mathbf{p}^2 \rangle_j \langle \mathbf{q}^2 \rangle_{(a,b)}^{ij} + \langle \mathbf{q}^2 \rangle_{(a,-b)}^{ij} = \langle \mathbf{r}^2 \rangle_i + \langle \mathbf{r}^2 \rangle_j \langle \mathbf{r}^2 \rangle_{(a,b)}^{ij} + \langle \mathbf{r}^2 \rangle_{(a,-b)}^{ij}, \]   

(19a) 

which connects one- and two-electron moments in position and momentum spaces. If we consider all the spin–orbitals \( i \) and \( j \) belonging to the same subshell \( nl \) of an atom, Eq. (19a) is simplified to 

\[ \langle \mathbf{p}^2 \rangle_n \langle \mathbf{v}^2 \rangle_{(a,b)}^{nl} = \langle \mathbf{r}^2 \rangle_n \langle \mathbf{r}^2 \rangle_{(a,b)}^{nl}, \]   

(19b) 

for any values of \( a \) and \( b \). 

### III. AN ILLUSTRATIVE APPLICATION 

According to Eq. (17b), the sum of two orbital kinetic energies is exactly decomposed into the intracule and extracule contributions as 

\[ T_i + T_j = T_{\text{int}}^{ij} + T_{\text{ext}}^{ij}, \]   

(20a) 

where 

\[ T_{\text{int}}^{ij} = \langle \mathbf{v}^2 \rangle_i^{ij}, \quad T_{\text{ext}}^{ij} = \langle \mathbf{p}^2 \rangle_i^{ij}, \]   

(20b) 

If the Hartree orbitals are considered or if the Hartree–Fock orbitals \( i \) and \( j \) have the same inversion symmetry in momentum space, \( \phi_i(-\mathbf{p}) \phi_j(-\mathbf{p}) = \phi_i(\mathbf{p}) \phi_j(\mathbf{p}) \), then we have 

\[ T_{\text{int}}^{ij} - T_{\text{ext}}^{ij} = \frac{1}{2}(T_i + T_j), \]   

(20c) 

from Eq. (18b) and the intracule contribution is equal to the extracule one. In atomic systems, Eq. (20c) holds when the sum \( l_i + l_j \) of the azimuthal quantum numbers of two Hartree–Fock spin–orbitals is even. 

We have examined the intracule and extracule contributions in the orbital kinetic energies for the Rn atom (atomic number 86), in which 15 subshells, 1s to 6s, 2p to 6p, 3d to 5d, and 4f, are fully occupied. We have 3655 electron pairs in total, but the associated orbital kinetic energy pairs are classified into 120 different cases specified by two subshells \( nl \) and \( n'l' \). Among them, 66 subshell pairs with \( l + l' \) = even have \( T_{\text{int}}^{ij} / T_{\text{ext}}^{ij} = 1 \) due to Eq. (20c). The 1807 electron pairs in this category thus have exactly the same kinetic energy contributions from the relative and center-of-mass motions. For the remaining 54 subshell pairs with \( l + l' \) = odd (which include 1848 electron pairs), we have obtained the ratio \( T_{\text{int}}^{ij} / T_{\text{ext}}^{ij} \) from numerical Hartree–Fock calculations. The results are summarized in Table I in the descending order of the \( T_{\text{int}}^{ij} / T_{\text{ext}}^{ij} \) values. We find in the table that \( T_{\text{int}}^{ij} / T_{\text{ext}}^{ij} \geq 1 \) with no exceptions, which implies that the relative motion contribution is never smaller than the center-of-mass motion contribution in any pairs of the orbital kinetic energies. Though there are many exceptions, the ratio \( T_{\text{int}}^{ij} / T_{\text{ext}}^{ij} \) is generally larger when \( |l - l'| = 1 \) and \( |n - n'| \) is.
small. The largest value is 1.12029 for the 1s2p electron pairs, and the intracule contribution occupies 52.8% of the orbital kinetic energy sum $T_{1s} + T_{2p}$. The exchange effect, appeared in the orbital kinetic energies, is largest for these electron pairs. On the other hand, $T_{int}^{ij}/T_{ext}^{ij}$ is essentially unity for the sf electron pairs with $|i - j'| = 3$. When summed over all $1 \leq i < j \leq N$, the ratio $T_{int}/T_{ext}$ between the total intracule $T_{int}$ and extracule $T_{ext}$ contributions is 1.00891.

**IV. SUMMARY**

For Hartree–Fock wave functions, the generalized electron-pair density function $g(q;a,b)$ has been decomposed into spin–orbital-pair components $g^{ij}(q;a,b)$. Then the second moments $\langle q^{2}\rangle^{ij}_{(a,b)}$, associated with $g^{ij}(q;a,b)$, have been shown to satisfy several rigorous sum rules which connect one- and two-electron properties of spin–orbitals $i$ and $j$. The same is also true in momentum space. An application of the present results has been illustrated for the relative motion and center-of-mass motion decomposition of the orbital kinetic energies of the Rn atom.

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