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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 \( |ar_i + br_j| \) of two-electron vector \( ar_i + br_j \), 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
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I. INTRODUCTION

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

\[
g(q;a,b) = (4\pi q^2)^{-1} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(q - |ar_i + br_j|),
\]

where \( a \) and \( b \) are real-valued parameters, \( \delta(x) \) is the one-dimensional Dirac delta function, and the angular brackets \( \langle \cdot \rangle \)
stand for the expectation value over the \( N \)-electron \((N \geq 2)\) wave function \( \Psi(x_1, \ldots, x_N) \) with \( x_i = (r_i, \sigma_i) \) 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 \( |ar_i + br_j| \) of two-electron vector \( ar_i + br_j \) 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\(^4-8\) \( h(u) \), and the
electron-pair extracule (center-of-mass motion) density\(^9\) \( d(R) \).
Namely,

\[
\begin{align*}
g(q;1, -1) &= h(q), \\
g(q;1, 0) &= \frac{N-1}{2} \rho(q), \\
g(q;1, +1) &= \frac{1}{8} \left[ \frac{q}{2} \right]^2.
\end{align*}
\]

(2)

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

\[
\langle q^k \rangle_{(a,b)} = 4\pi \int_0^\infty dq \, q^{k+1} g(q;a,b)
= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} |ar_i + br_j|^k,
\]

we then find

\[
\begin{align*}
\langle q^k \rangle_{(1,-1)} &= \langle u^k \rangle, \\
\langle q^k \rangle_{(1,0)} &= \frac{N-1}{2} \langle r^k \rangle,
\end{align*}
\]

(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
\( \tilde{g}(r;a,b) \) and associated moments \( \langle r^2 \rangle_{(a,b)} \) 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
determinantal 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-

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trated for the separation of the orbital kinetic energies of the Rn atom into the relative motion and center-of-mass motion contributions of electrons in two relevant orbitals. Hartree atomic units are used throughout.

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 $\psi_i(r)\eta_i(\sigma)$, the electron-pair density $g(q;a,b)$, defined by Eq. (1), is rewritten as

$$g(q;a,b) = \sum^{N-1}_{i=1} \sum^N_{j=i+1} g_{ij}(q;a,b), \quad (7a)$$

$$g_{ij}(q;a,b) = (4\pi q^2)^{-1}\{\psi_i(r_i)\psi_j(r_j)\} \left[ \delta(q - |a r_i + b r_j|) + \delta(q - |b r_i + a r_j|) \right]$$

$$\times \left| \psi_i(r_i)\psi_j(r_j) - \delta(i,j)\psi_j(r_i)\psi_j(r_j) \right|, \quad (7b)$$

where the angular brackets abbreviate the integrations over $r_i$ and $r_j$, 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

$$\langle q^k \rangle_{(a,b)} = \sum^{N-1}_{i=1} \sum^N_{j=i+1} \langle q^k \rangle_{ij}(a,b), \quad (8a)$$

$$\langle q^k \rangle_{ij}(a,b) = 4\pi \int_0^{\infty} dq q^{k+2} g_{ij}(q;a,b)$$

$$= \langle \psi_i(r_i)\psi_j(r_j) \rangle \left[ \delta(q - |a r_i + b r_j|) + \delta(q - |b r_i + a r_j|) \right]$$

$$\times \left| \psi_i(r_i)\psi_j(r_j) - \delta(i,j)\psi_j(r_i)\psi_j(r_j) \right|, \quad (8b)$$

For a particular case of $k=2$, the moment operator in Eq. (8b) satisfies an identity

$$\frac{1}{2}[|a r_i + b r_j|^2 + |b r_i + a r_j|^2]$$

$$= \frac{1}{2}(a^2 + b^2)(r_i^2 + r_j^2) + 2ab r_i \cdot r_j, \quad (9)$$

where $r_i=|r_i|$. We then find from Eq. (8b) that

$$\langle q^2 \rangle_{(a,b)} = \frac{1}{2}(a^2 + b^2)(r_i^2 + r_j^2)$$

$$+ 2ab(\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle - \delta(i,j)\langle r_i^2 \rangle - \langle r_i \rangle^2), \quad (10a)$$

where

$$\langle \mathbf{r}_i \rangle = \int d\mathbf{r} \psi^*_i(\mathbf{r})\mathbf{r}\psi_i(\mathbf{r}). \quad (10b)$$

Therefore, Eqs. (10) for $\langle q^2 \rangle_{(a,b)}$ and $\langle q^2 \rangle_{(a,-b)}$ generate a rigorous sum rule

$$\langle q^2 \rangle_{(a,b)} + \langle q^2 \rangle_{(a,-b)} = (a^2 + b^2)(\langle r_i^2 \rangle + \langle r_j^2 \rangle), \quad (11)$$

for the second generalized electron-pair moments associated with the spin–orbitals $i$ and $j$. Summation of Eq. (11) over $1 \leq i < j < N$ results in Eq. (5). For any values of the parameters $a$ and $b$ and any pairs of spin–orbitals $i$ and $j$, Eq. (11) shows that the sum of two symmetric electron-pair moments $\langle q^2 \rangle_{(a,b)}$ and $\langle q^2 \rangle_{(a,-b)}$ is equal to a single-electron property $\langle r_i^2 \rangle + \langle r_j^2 \rangle$, multiplied by $a^2 + b^2$. For any two sets of parameters $(a,b)$ and $(a',b')$, Eq. (11) also gives

$$\frac{\langle q^2 \rangle_{(a,b)} + \langle q^2 \rangle_{(a,-b)}}{a^2 + b^2} = \frac{\langle q^2 \rangle_{(a',b')} + \langle q^2 \rangle_{(a',-b')}}{a'^2 + b'^2}. \quad (12)$$

Note that Eqs. (11) and (12) are valid for both exact and approximate Hartree–Fock wave functions, since they originate from the operator identity, Eq. (9), not from a particular property of spin–orbitals.

For a special case of $a=b=1$, Eq. (11) reads

$$\langle u^2 \rangle_{ij} + 4\langle R^2 \rangle_{ij} = 2[\langle r_i^2 \rangle + \langle r_j^2 \rangle], \quad (13)$$

Namely, the sum of the second intracule $\langle u^2 \rangle_{ij}$ and extracule $\langle R^2 \rangle_{ij}$ moments (the latter multiplied by 4), associated with the spin–orbitals $i$ and $j$, is exactly twice the sum of the second single-electron moments $\langle r_i^2 \rangle$ and $\langle r_j^2 \rangle$ of the relevant two spin–orbitals. Equation (13) enables us to separate the sum of orbital single-electron moments into the relative motion and center-of-mass motion contributions in a precise manner.

When the system under consideration has spatial inversion symmetry, we can also derive a direct relation between $\langle q^2 \rangle_{(a,b)}$, instead of the symmetric sum, and single-electron orbital moments. If the spatial function $\psi_i(r)$ has inversion symmetry $\psi_i(-r) = (-1)^\lambda_i\psi_i(r)$ specified by an index $\lambda_i$, the first term $\langle\mathbf{r}_i \cdot \mathbf{r}_j \rangle$ in the brackets after the coefficient $2ab$ in Eq. (10a) vanishes. The second term $\delta(i,j)\langle r_i \rangle^2$ is also zero, if the spin–orbitals $i$ and $j$ have different spins or their spatial inversion symmetries are the same, $\psi_i(-r) = \psi_i(r)\psi_i(r)$. In this particular case, Eq. (10a) is simplified to

$$\langle q^2 \rangle_{ij} = \frac{1}{2}(a^2 + b^2)[\langle r_i^2 \rangle + \langle r_j^2 \rangle], \quad (14a)$$

which further yields

$$\langle u^2 \rangle_{ij} + 4\langle R^2 \rangle_{ij} = \langle r_i^2 \rangle + \langle r_j^2 \rangle, \quad (14b)$$

for the spin–orbital-pair intracule and extracule moments when $a=1$ and $b = \pm 1$. The relative motion and center-of-mass motion contributions in Eq. (13) are the same in this case. When the spin–orbitals $i$ and $j$ belong to the same subshell $nl$ of an atom, where $n$ and $l$ are the principal and azimuthal quantum numbers, Eqs. (14a) and (14b) always hold as well as an equality $\langle r_i^2 \rangle = \langle r_j^2 \rangle$. We then have

$$\langle q^2 \rangle_{(a,b)} = \frac{1}{2}(a^2 + b^2)(N_{nl} - 1)\langle r_i^2 \rangle, \quad (15a)$$

$$\langle u^2 \rangle_{(a,b)} = 4\langle R^2 \rangle_{(a,b)} = N_{nl} - 1 \langle r_i^2 \rangle, \quad (15b)$$

where our subshell normalization is $\langle q^0 \rangle_{(a,b)} = N_{nl}(N_{nl} - 1)/2$ and $\langle r^0 \rangle_{(a,b)} = N_{nl}$, in which $N_{nl}(\geq 2)$ is the number of electrons in the subshell $nl$. Equation (15b) was also reported in Ref. 10.

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 $\psi_i(r)$ is replaced with
\[ \phi_i(p) = (2\pi)^{-3/2} \int dr \exp(-i p \cdot r) \phi_i(r). \]  

Then the spin–orbital-pair components \( \tilde{g}^{ij}(r;a,b) \) and \( \langle r^2 \rangle^{ij}_{(a,b)} \) of the generalized electron-pair density \( \tilde{g}(r;a,b) \) and moments \( \langle r^2 \rangle^{ij}_{(a,b)} \) 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 \( \Pi_i(p) = |\phi_i(p)|^2 \) in momentum space has even inversion symmetry \( \Pi_i(-p) = \Pi_i(p) \) for any atoms and molecules. Therefore, the \( \langle p \rangle_{ij} \) term is absent in the momentum-space counterpart of Eq. (10a) if there is a special interatomic interaction. Some explicit forms of the spin–orbital-pair sum rules in momentum space are

\[
\begin{align*}
\langle r^2 \rangle^{ij}_{(a,b)} + \langle r^2 \rangle^{ij}_{(-a,-b)} &= (a^2 + b^2)[\langle p^2 \rangle_i + \langle p^2 \rangle_j], \quad (17a) \\
\langle v^2 \rangle^{ij}_{(a,b)} + 4\langle p^2 \rangle^{ij} &= 2(\langle p^2 \rangle_i + \langle p^2 \rangle_j), \quad (17b)
\end{align*}
\]

for any two spin–orbitals, and

\[
\begin{align*}

\langle r^2 \rangle^{ij}_{(a,b)} &= \frac{1}{2} (a^2 + b^2) [\langle p^2 \rangle_i + \langle p^2 \rangle_j], \quad (18a) \\
\langle v^2 \rangle^{ij} &= 4\langle p^2 \rangle^{ij} = \langle p^2 \rangle_i + \langle p^2 \rangle_j, \quad (18b)
\end{align*}
\]

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 one of our special interest, since the second-electron moment \( \langle p^2 \rangle \), appearing on the right-hand side is just twice the electronic kinetic energy \( T_i = \langle p^2 \rangle_i / 2 \) 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

\[
\begin{align*}
\langle p^2 \rangle_i + \langle p^2 \rangle_j &= \langle r^2 \rangle^{ij}_{(a,b)} + \langle r^2 \rangle^{ij}_{(-a,-b)} \\
&= \langle r^2 \rangle_i + \langle r^2 \rangle_j + \langle r^2 \rangle^{ij}_{(a,b)} + \langle r^2 \rangle^{ij}_{(-a,-b)}, \quad (19a)
\end{align*}
\]

which connects one- and two-electron motions 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

\[
\langle p^2 \rangle^2 n^4 \delta_{(a,b)}^{(a,b)} = \langle r^2 \rangle^2 n^4 \delta_{(a,b)}, \quad (19b)
\]

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

\[
T_i + T_j = T^\text{int}_{ij} + T^\text{ext}_{ij}, \quad (20a)
\]

where

\[
T^\text{int}_{ij} = \frac{1}{2} (v^2)^{ij}, \quad T^\text{ext}_{ij} = \langle p^2 \rangle^{ij}. \quad (20b)
\]

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

\[
T^\text{int}_{ij} - T^\text{ext}_{ij} = \frac{1}{2} (T_i + T_j), \quad (20c)
\]

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 \( l + l' = 1 \) and \( n + n' = 1 \) are included. 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 \( l + l' = 1 \) and \( n + n' = 0 \), the sums are given by the following expressions:

\[
\begin{align*}
T^\text{int}_{nl} &= 0, \\
T^\text{ext}_{nl} &= \frac{1}{2} (T_i + T_j).
\end{align*}
\]

The results are summarized in Table I in the descending order of the \( T^\text{int}_{nl} / T^\text{ext}_{nl} \) values. We find in the table that \( T^\text{int}_{nl} / T^\text{ext}_{nl} \) is generally larger when \( l + l' = 1 \) and \( n + n' = 0 \) is
small. The largest value is 1.120 29 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, $T_{\text{int}}^{ij} / T_{\text{ext}}^{ij}$ is essentially unity for the sf electron pairs with $|l-l'|=3$. When summed over all $1 \leq i < j \leq N$, the ratio $T_{\text{int}} / T_{\text{ext}}$ between the total intracule $T_{\text{int}}$ and extracule $T_{\text{ext}}$ contributions is 1.008 91.

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 $\langle q^2 \rangle_{(a,b)}^{ij}$, 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.