Sum rules for generalized electron-pair moments

LETTERS TO THE EDITOR

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NOTES

Sum rules for generalized electron-pair moments

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In a recent paper[1] published in this journal, we have studied a generalized electron-pair density function $g(q;a,b)$ defined by

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

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 ($N \geqslant 2$) wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ with $\mathbf{x}_i\equiv(\mathbf{r}_i,\sigma_i)$ 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[1] that the function $g(q;a,b)$ smoothly connects the single-electron density[2] $\rho(r)$, the electron-pair intracule (relative motion) density[3–5] $h(u)$, and the electron-pair extracule (center-of-mass motion) density[3–5] $d(R)$:

$$g(q;1,-1)=h(q),$$
$$g(q;1,0)=\frac{N-1}{2}\rho(q),\quad g(q;1,+1)=\frac{1}{8}d\left(\frac{q}{2}\right). \tag{2}$$

Moreover, $\rho(r)$ has been found[1] to be a local extremum function of $g(q;1,b)$ with respect to the parameter b.

If we define moments $\langle q^n\rangle_{(a,b)}$ of the electron-pair density $g(q;a,b)$ by

$$\langle q^n\rangle_{(a,b)}\equiv 4\pi\int_0^\infty dq\,q^{n+2}g(q;a,b) = \left\langle\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}|a\mathbf{r}_i+b\mathbf{r}_j|^n\right\rangle, \tag{3}$$

we then find

$$\langle q^n\rangle_{(1,-1)}=\langle u^n\rangle,\quad \langle q^n\rangle_{(1,0)}=\frac{N-1}{2}\langle r^n\rangle,$$
$$\langle q^n\rangle_{(1,+1)}=2^n\langle R^n\rangle, \tag{4}$$

corresponding to Eq. (2), and all the single-electron $\langle r^n\rangle$, intracule $\langle u^n\rangle$, and extracule $\langle R^n\rangle$ moments are generated from the generalized electron-pair moments $\langle q^n\rangle_{(a,b)}$.

In the present note, we point out that there exists a rigorous equality for the second generalized electron-pair moments $\langle q^2\rangle_{(a,b)}$, which connects one- and two-electron properties of atoms and molecules described by any exact or approximate wave function. The same is true in momentum space. An illustrative example is given for the decomposition of the electronic kinetic energy into the electron-pair relative and center-of-mass motion contributions. Hartree atomic units are used throughout.

For a particular case of $n=2$, a term in the summation of Eq. (3) satisfies an identity

$$|a\mathbf{r}_i+b\mathbf{r}_j|^2=2a^2r_i^2+2b^2r_j^2-|a\mathbf{r}_i-b\mathbf{r}_j|^2, \tag{5}$$

where $r_i=|\mathbf{r}_i|$. We therefore obtain a rigorous sum rule

$$\langle q^2\rangle_{(a,b)}+\langle q^2\rangle_{(a,-b)}=2(a^2+b^2)\langle q^2\rangle_{(1,0)}, \tag{6}$$

for the second generalized electron-pair moments $\langle q^2\rangle_{(a,b)}$. Equation (6) implies that for any values of the parameters a and b, the sum of two second moments $\langle q^2\rangle_{(a,b)}$ and $\langle q^2\rangle_{(a,-b)}$, symmetric with respect to the parameter b, is equal to a constant $\langle q^2\rangle_{(1,0)}$ multiplied by $2(a^2+b^2)$. Furthermore, $\langle q^2\rangle_{(1,0)}$ is nothing but a single-electron property $[(N-1)/2]\langle r^2\rangle$ as shown by Eq. (4), while $\langle q^2\rangle_{(a,b)}+\langle q^2\rangle_{(a,-b)}$ is a two-electron property if $a\neq 0$ and $b\neq 0$. It is also important that Eq. (6) is valid for both exact and approximate wave functions of any atoms and molecules. Such a rigorous relation has not been reported in the literature.

For a special case of $a=b=1$, Eq. (6) reads

$$\langle u^2\rangle+4\langle R^2\rangle=2(N-1)\langle r^2\rangle. \tag{7}$$

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 $2(N-1)$. Using the tabulations of the numerical values of the Hartree–Fock intracule and extracule moments[6–8] together with Hartree–Fock single-electron moment values,[9] we have numerically confirmed the validity of Eq. (7) for the 102 atoms He through Lr in their ground states. Since $\langle r^2 \rangle$ is known[10] to be proportional to the Langevin–Pauli diamagnetic susceptibility, Eq. (7) enables us to separate the property into the relative and center-of-mass motion contributions of electron pairs.

If we introduce the corresponding electron-pair density $\overline{g}(t;a,b)$ and associated moments $\langle t^n \rangle_{(a,b)}$ in momentum space

$$\overline{g}(t;a,b) \equiv (4\pi t^2)^{-1} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(t - |a\mathbf{p}_i + b\mathbf{p}_j|) \right\rangle, \tag{8}$$

$$\langle t^n \rangle_{(a,b)} \equiv 4\pi \int_0^\infty dt\, t^{n+2} \overline{g}(t;a,b) = \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} |a\mathbf{p}_i + b\mathbf{p}_j|^n \right\rangle, \tag{9}$$

exactly the same discussion as in position space results in

$$\langle t^2 \rangle_{(a,b)} + \langle t^2 \rangle_{(a,-b)} = 2(a^2+b^2)\langle t^2 \rangle_{(1,0)}, \tag{10}$$

for the second moments $\langle t^2 \rangle_{(a,b)}$ in momentum space. When $a=b=1$, Eq. (10) becomes

$$\langle \nu^2 \rangle + 4\langle P^2 \rangle = 2(N-1)\langle p^2 \rangle, \tag{11}$$

where ν and P are the intracule and extracule radii,[6–8] respectively, while p is the single-electron radius in momentum space. For the 102 atoms from He to Lr, numerical validity of Eq. (11) has been checked based on the momentum-space intracule $\langle \nu^n \rangle$ and extracule $\langle P^n \rangle$ moments reported in Refs. 6, 7, and 11 and the single-electron momentum moments $\langle p^n \rangle$ reported in Ref. 12. Equation (11) is of our special interest, since the second single-electron moment $\langle p^2 \rangle$ appearing on the right-hand side is just twice the electronic kinetic energy T, which is the negative of the total energy E of atoms due to the virial theorem. When Eq. (11) is applied, the kinetic energy T is precisely decomposed into two contributions from the relative (intracule) and center-of-mass (extracule) motions: For $N \geqslant 2$:

$$T = T_{\text{int}} + T_{\text{ext}}, \tag{12}$$

where

$$T_{\text{int}} = \frac{\langle \nu^2 \rangle}{4(N-1)}, \quad T_{\text{ext}} = \frac{\langle P^2 \rangle}{N-1}. \tag{13}$$

Examination of the intracule and extracule moments given in Refs. 6, 7, and 11 for the 102 atoms He through Lr shows that within the Hartree–Fock framework, $T_{\text{int}}/T_{\text{ext}}=1$ for the first three atoms He, Li, and Be, where only s orbitals are occupied. For the remaining 99 atoms, $T_{\text{int}}/T_{\text{ext}}>1$ with no exceptions: As the atomic number increases, the ratio increases from unity, takes the maximum value 1.026 at the Ne atom, and then decreases towards the Lr atom where $T_{\text{int}}/T_{\text{ext}}=1.008$. The situation is changed when the electron correlation is taken into account. The correlated intracule $\langle \nu^2 \rangle$ and extracule $\langle P^2 \rangle$ moments reported for the nine atoms He–Ne in Refs. 13 and 14 show that the ratio $T_{\text{int}}/T_{\text{ext}}$ again increases from He (0.897) to Ne (1.020), though the value is smaller than the corresponding Hartree–Fock one. However, $T_{\text{int}}/T_{\text{ext}}<1$ for the first four atoms He–B, and the extracule contribution is larger than the intracule one in these atoms. The electron correlation modifies the relative significance of the intracule and extracule contributions to the kinetic energy.

In summary, we have discussed that there exists an exceptional rigorous sum rule between the second one- and two-electron moments, which are apparently independent of each other. We finally note that a two-electron ''symmetric'' sum rule

$$(a'^2+b'^2)[\langle q^2 \rangle_{(a,b)} + \langle q^2 \rangle_{(a,-b)}] = (a^2+b^2)[\langle q^2 \rangle_{(a',b')} + \langle q^2 \rangle_{(a',-b')}], \tag{14}$$

also follows from Eq. (6).

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