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journal or publication title	The journal of chemical physics
volume	108
number	6
page range	2515-2518
year	1998-02-08
URL	http://hdl.handle.net/10258/743

doi: info:doi/10.1063/1.475635

Electron-electron counterbalance hole in Hartree–Fock theory

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(Received 3 October 1997; accepted 4 November 1997)

The electronic extracule density $E(\mathbf{R})$ and its spherical average $d(R)$ are probability densities of finding the center-of-mass vector $(\mathbf{r}_j + \mathbf{r}_k)/2$ and its magnitude $|\mathbf{r}_j + \mathbf{r}_k|/2$ of any two electrons j and k to be $\mathbf{R}$ and R , respectively. Theoretical analysis of spin–orbital-pair contributions $E_{jk}(\mathbf{R})$ and $d_{jk}(R)$ to the extracule densities shows that within the Hartree–Fock framework, there exists an “electron-electron counterbalance hole” $E_{jk}(\mathbf{0}) = d_{jk}(0) = 0$ between two electrons in spin–orbitals j and k with the same spin and the same spatial inversion symmetry, which implies that the center-of-mass vector (or distance) of these electrons cannot be zero or these electrons cannot be exactly at the opposite positions in space with respect to the inversion center. The same is also true in momentum space. The electron-electron counterbalance hole may be considered as a complement to the familiar electron-electron coalescence or Fermi hole for two electrons with the same spin. We also point out that the electron-electron counterbalance and coalescence densities are rigorously proportional for a pair of spin–orbitals with different spins. © 1998 American Institute of Physics. [S0021-9606(98)02506-9]

I. INTRODUCTION

The intracule $I(\mathbf{u})$ and extracule $E(\mathbf{R})$ densities, as well as their spherical averages $h(u)$ and $d(R)$, are a couple of electron-pair densities useful to analyze and characterize the motion of a pair of electrons in atoms and molecules (see, e.g., Ref. 1 for a review). For an N -electron system ($N \geq 2$), the intracule densities $I(\mathbf{u})$ and $h(u)$ are defined by

$$I(\mathbf{u}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^N \delta[\mathbf{u} - (\mathbf{r}_j - \mathbf{r}_k)] \right\rangle,$$

$$h(u) \equiv \frac{1}{4\pi} \int d\Omega_u I(\mathbf{u}), \quad (1)$$

where $\mathbf{u} \equiv (u, \Omega_u)$ with $\Omega_u \equiv (\theta_u, \phi_u)$, $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function, and the angular brackets $\langle \rangle$ stand for the expectation value. The intracule densities $I(\mathbf{u})$ and $h(u)$ are the probability density functions for the relative vector $\mathbf{r}_j - \mathbf{r}_k$ and its magnitude $|\mathbf{r}_j - \mathbf{r}_k|$ of any pair of electrons j and k to be $\mathbf{u}$ and u , respectively. On the other hand, the extracule densities $E(\mathbf{R})$ and $d(R)$ are defined by

$$E(\mathbf{R}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^N \delta[\mathbf{R} - (\mathbf{r}_j + \mathbf{r}_k)/2] \right\rangle,$$

$$d(R) \equiv \frac{1}{4\pi} \int d\Omega_R E(\mathbf{R}), \quad (2)$$

and represent the probability density functions for the center-of-mass vector $(\mathbf{r}_j + \mathbf{r}_k)/2$ and its magnitude $|\mathbf{r}_j + \mathbf{r}_k|/2$ of any pair of electrons j and k to be $\mathbf{R}$ and R , respectively, where $\mathbf{R} \equiv (R, \Omega_R)$ with $\Omega_R \equiv (\theta_R, \phi_R)$. For various applications of the intracule and extracule densities, see Ref. 1, for example.

A special case of $I(\mathbf{u})$ at $\mathbf{u} = \mathbf{0}$ or $h(u)$ at $u = 0$ defines the electron-electron coalescence density $I(\mathbf{0}) = h(0)$, which is the probability density of finding any two electrons at the same position. Analogously, a special case of $E(\mathbf{R})$ at $\mathbf{R}$

$= \mathbf{0}$ or $d(R)$ at $R = 0$ yields the electron-electron counterbalance density $E(\mathbf{0}) = d(0)$, which is the probability density of finding any two electrons at the opposite positions with respect to the origin (i.e., the nucleus in atoms). The electron-electron coalescence density $h(0)$ appears in the evaluation of the relativistic² and radiative³ corrections for atoms and molecules, and its properties have been reported in several studies.^{4–8} In particular, the presence of the electron-electron coalescence or Fermi hole $I_{jk}(\mathbf{0}) = h_{jk}(0) = 0$ in the Hartree–Fock theory is well-known between two electrons in spin–orbitals j and k with the same spin.

On the other hand, little is known about the properties of the electron-electron counterbalance density $E(\mathbf{0}) = d(0)$. In the present paper, we point out that in the Hartree–Fock approximation, there exists an electron-electron counterbalance hole $E_{jk}(\mathbf{0}) = d_{jk}(0) = 0$ between two electrons in spin–orbitals j and k , if their spin functions are the same and their spatial functions have the same inversion symmetry with respect to the coordinate origin. The electron-electron counterbalance hole can be regarded as a partner of the familiar electron-electron coalescence or Fermi hole. The next section describes a proof of the counterbalance hole in position space. We also point out that a relation $d_{jk}(0) = 8h_{jk}(0) = 8(\rho_j, \rho_k)$ is exactly valid for spin–orbitals j and k with different spins, where (ρ_j, ρ_k) is the overlap between spin-reduced one-electron orbital densities. In Section III, the momentum-space correspondence is explained, and in Section IV, an illustrative example is presented. Hartree atomic units are used throughout this paper.

II. ELECTRON-ELECTRON COUNTERBALANCE HOLE IN POSITION SPACE

Using the kernel of Fourier transformations, the three-dimensional Dirac delta function $\delta(\mathbf{r})$ can be expressed as

$$\delta(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{s} \exp(i\mathbf{s} \cdot \mathbf{r}). \quad (3)$$

Then the three-dimensional extracule density $E(\mathbf{R})$ defined by Eq. (2) is rewritten as

$$E(\mathbf{R}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^N E_{jk}(\mathbf{R}), \quad (4a)$$

where

$$E_{jk}(\mathbf{R}) = \pi^{-3} \int d\mathbf{s} \exp(+2i\mathbf{s} \cdot \mathbf{R}) G_{jk}(\mathbf{s}), \quad (4b)$$

$$G_{jk}(\mathbf{s}) = \langle \exp(-i\mathbf{s} \cdot \mathbf{r}_j) \exp(-i\mathbf{s} \cdot \mathbf{r}_k) \rangle. \quad (4c)$$

Similarly, the spherically averaged extracule density $d(R)$ is rewritten as

$$d(R) = \sum_{j=1}^{N-1} \sum_{k=j+1}^N d_{jk}(R), \quad (5a)$$

where

$$\begin{aligned} d_{jk}(R) &= (4\pi)^{-1} \int d\Omega_R E_{jk}(\mathbf{R}) \\ &= \pi^{-3} \int d\mathbf{s} j_0(2Rs) G_{jk}(\mathbf{s}), \end{aligned} \quad (5b)$$

in which $j_l(x)$ is the l th order spherical Bessel function of the first kind.

For a single Slater determinant wave function composed of N spin-orbitals $\psi_j(\mathbf{r})\eta_j(\sigma)$, the Condon-Slater rules (see, e.g., Ref. 9) rearrange the function $G_{jk}(\mathbf{s})$ [Eq. (4c)] as

$$G_{jk}(\mathbf{s}) = f_{jj}^*(\mathbf{s})f_{kk}^*(\mathbf{s}) - \delta_{m_{sj}m_{sk}} f_{jk}^*(\mathbf{s})f_{kj}^*(\mathbf{s}), \quad (6a)$$

where m_{sj} denotes the spin quantum number of the spin-orbital j , δ_{jk} is the Kronecker delta, and

$$f_{jk}(\mathbf{s}) \equiv \int d\mathbf{r} \exp(+i\mathbf{s} \cdot \mathbf{r}) \psi_j^*(\mathbf{r}) \psi_k(\mathbf{r}) = f_{kj}^*(-\mathbf{s}). \quad (6b)$$

If we recall the relation

$$\int d\mathbf{s} \exp[-i\mathbf{s} \cdot (\mathbf{r} + \mathbf{r}')] = (2\pi)^3 \delta(\mathbf{r} + \mathbf{r}'), \quad (7)$$

together with $j_0(0) = 1$, the contribution $E_{jk}(\mathbf{0}) = d_{jk}(0)$ from spin-orbitals j and k to the electron-electron counterbalance density $E(\mathbf{0}) = d(0)$ is obtained from Eqs. (4b) and (5b) as

$$\begin{aligned} E_{jk}(\mathbf{0}) = d_{jk}(0) &= \pi^{-3} \int d\mathbf{s} G_{jk}(\mathbf{s}) \\ &= 8[g_{jj,kk} - \delta_{m_{sj}m_{sk}} g_{jk,kj}], \end{aligned} \quad (8a)$$

where

$$g_{jj,kk} = \int d\mathbf{r} |\psi_j(\mathbf{r})|^2 |\psi_k(\mathbf{r})|^2, \quad (8b)$$

$$g_{jk,kj} = \int d\mathbf{r} [\psi_j^*(-\mathbf{r}) \psi_k(-\mathbf{r})] [\psi_k^*(\mathbf{r}) \psi_j(\mathbf{r})]. \quad (8c)$$

From Eqs. (8a) to (8c), we immediately find that

$$E_{jk}(\mathbf{0}) = d_{jk}(0) = 0, \quad (9)$$

provided that $m_{sj} = m_{sk}$ and

$$\psi_j(-\mathbf{r}) = \psi_j(\mathbf{r}), \quad \psi_k(-\mathbf{r}) = \psi_k(\mathbf{r}),$$

or

$$\psi_j(-\mathbf{r}) = -\psi_j(\mathbf{r}), \quad \psi_k(-\mathbf{r}) = -\psi_k(\mathbf{r}).$$

Namely, there exists an electron-electron counterbalance hole between a pair of electrons, if they have the same spin and their spatial functions have the same inversion symmetry with respect to the origin. In atomic systems, the electron-electron counterbalance hole appears for two electrons with like spin when the sum $l_j + l_k$ of their orbital azimuthal quantum numbers is even. An analogous discussion holds also for molecules with inversion symmetry. In linear molecules with $D_{\infty h}$ point group symmetry, for example, similar combinations of molecular orbitals with spatial *gerade* and *ungerade* symmetries generate the counterbalance hole for two electrons with the same spin. The physical picture of the counterbalance hole is that the center-of-mass vector (or distance) of these electrons cannot be zero, or these electrons cannot be exactly at the opposite positions with respect to the coordinate origin (i.e., the nucleus in atoms or the inversion center of molecules).

In the Hartree approximation, the second terms (with the subscript jk, kj) in Eqs. (6a) and (8a) do not appear and hence $E_{jk}(\mathbf{0})$ and $d_{jk}(0)$ cannot be zero for any spin-orbitals j and k . Therefore the counterbalance hole is a result of the quantum-mechanical requirement that electronic wave functions must be antisymmetric, as is the coalescence hole. The electron-electron coalescence and counterbalance holes are considered to be complementary in the sense that they appear for the relative and center-of-mass motions of a pair of electrons with the same spin. However, there is an essential difference between the two holes: the counterbalance hole is subject to the additional condition of spatial symmetries of relevant spin-orbitals as mentioned above, but the coalescence hole is not.

A similar analysis of spin-orbital-pair contributions to the electron-electron coalescence density $I(\mathbf{0}) = h(0)$ results in

$$I_{jk}(\mathbf{0}) = h_{jk}(0) = (1 - \delta_{m_{sj}m_{sk}}) g_{jj,kk}. \quad (10)$$

Equation (10) straightforwardly proves the Fermi hole $h_{jk}(0) = 0$ for a pair of spin-orbitals j and k with the same spin. At the same time, Eq. (10) combined with Eqs. (8a) and (8b) shows that if $m_{sj} \neq m_{sk}$,

$$d_{jk}(0) = 8h_{jk}(0) = 8(\rho_j, \rho_k), \quad (11)$$

where

$$(\rho_j, \rho_k) \equiv \int d\mathbf{r} \rho_j(\mathbf{r}) \rho_k(\mathbf{r}), \quad (12a)$$

$$\rho_j(\mathbf{r}) \equiv |\psi_j(\mathbf{r})|^2. \quad (12b)$$

Namely, the electron-electron counterbalance and coalescence densities are exactly proportional for a pair of spin-orbitals with different spins. The proportionality constant is $8 = 2^3$, where the factor 2 comes from the denominator in the

TABLE I. The electron-electron counterbalance and coalescence densities in position space for the ground-state nitrogen atom.

Spin-orbital pair	Counterbalance density	Coalescence density
1s α 1s β	93.649373	11.706172
1s α 2s α	0	0
1s α 2s β	3.751679	0.468960
1s α 2p $_{+1}\alpha$	1.288967	0
1s α 2p $_{0}\alpha$		
1s α 2p $_{-1}\alpha$		
1s β 2s α	3.751679	0.468960
1s β 2s β	0	0
1s β 2p $_{+1}\alpha$	0.644483	0.080560
1s β 2p $_{0}\alpha$		
1s β 2p $_{-1}\alpha$		
2s α 2s β	0.474500	0.059313
2s α 2p $_{+1}\alpha$	0.616902	0
2s α 2p $_{0}\alpha$		
2s α 2p $_{-1}\alpha$		
2s β 2p $_{+1}\alpha$	0.308451	0.038556
2s β 2p $_{0}\alpha$		
2s β 2p $_{-1}\alpha$		
2p $_{+1}\alpha$ 2p $_{0}\alpha$	0	0
2p $_{+1}\alpha$ 2p $_{-1}\alpha$	0	0
2p $_{0}\alpha$ 2p $_{-1}\alpha$	0	0
Total	110.203638	13.060754

Dirac delta function in Eq. (2) and the factor 3 originates from the three dimensionality of space. Moreover, these two-electron properties can be rigorously obtained from the overlap of the one-electron orbital densities in this particular case. See also Refs. 7 and 10.

III. ELECTRON-ELECTRON COUNTERBALANCE HOLE IN MOMENTUM SPACE

Definitions exactly analogous to Eq. (2) apply to the momentum-space extracule density $\bar{E}(\mathbf{P})$ and its spherical average $\bar{d}(P)$:

$$\bar{E}(\mathbf{P}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^N \delta[\mathbf{P} - (\mathbf{p}_j + \mathbf{p}_k)/2] \right\rangle,$$

$$\bar{d}(P) \equiv \frac{1}{4\pi} \int d\Omega_P \bar{E}(\mathbf{P}), \quad (13)$$

where $\mathbf{P} \equiv (P, \Omega_P)$ with $\Omega_P \equiv (\theta_P, \phi_P)$. The functions $\bar{E}(\mathbf{P})$ and $\bar{d}(P)$ are probability densities for the center-of-mass momentum vector $(\mathbf{p}_j + \mathbf{p}_k)/2$ and its magnitude $|\mathbf{p}_j + \mathbf{p}_k|/2$ of any pair of electrons j and k to be $\mathbf{P}$ and P , respectively. Setting $\mathbf{P} = \mathbf{0}$ and $P = 0$ in Eq. (13), we obtain the electron-electron counterbalance density $\bar{E}(\mathbf{0}) = \bar{d}(0)$ and its components $\bar{E}_{jk}(\mathbf{0}) = \bar{d}_{jk}(0)$ arising from spin-orbitals j and k .

A momentum-space N -electron wave function is given by the $3N$ -dimensional Fourier transformation of the corresponding position-space wave function. Then the Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, provided that the one-electron spatial function $\psi_k(\mathbf{r})$ is replaced with its momentum-space counterpart,

$$\phi_k(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp(-i\mathbf{p} \cdot \mathbf{r}) \psi_k(\mathbf{r}). \quad (14)$$

Then the analysis parallel to that in position space leads us to the electron-electron counterbalance hole in momentum space $\bar{E}_{jk}(\mathbf{0}) = \bar{d}_{jk}(0) = 0$ for two electrons in momentum spin-orbitals j and k , when they have the same spin and the same inversion symmetry in momentum space. We also find an exact relation $\bar{d}_{jk}(0) = 8\bar{h}_{jk}(0) = 8(\gamma_j, \gamma_k)$ for momentum-space spin-orbitals j and k with different spins, where $\bar{h}_{jk}(0)$ is the momentum-space coalescence density and (γ_j, γ_k) is the overlap between spin-reduced one-electron momentum orbital densities $\gamma_j(\mathbf{p}) \equiv |\phi_j(\mathbf{p})|^2$ and $\gamma_k(\mathbf{p}) \equiv |\phi_k(\mathbf{p})|^2$.

IV. AN ILLUSTRATIVE EXAMPLE

The nitrogen atom has 7 electrons and hence 21 different pairs of spin-orbitals. For its ground 4S state with $1s^2 2s^2 2p^3$ electronic configuration, we have calculated the electron-electron counterbalance density $d_{jk}(0)$ for a spin-orbital-pair j and k , by using the numerical Hartree-Fock method. The results are summarized in Table I. Also shown there for comparison are the corresponding values of coalescence densities $h_{jk}(0)$. The brace appearing in the first column of the table means that each of the grouped spin-orbital-pairs has the given value, *not* that the sum of these pairs takes the given value. It is clear in Table I that the electron-electron counterbalance hole exists for 5 pairs of spin-orbitals with $m_{sj} = m_{sk}$ and $l_j + l_k = \text{even}$. On the other hand, the electron-electron coalescence hole is found for 11 pairs of spin-orbitals with $m_{sj} = m_{sk}$, including those pairs which possess the counterbalance hole. Table I also clarifies that the major part of the total counterbalance or coalescence

TABLE II. The electron-electron counterbalance and coalescence densities in momentum space for the ground-state nitrogen atom.

Spin-orbital pair	Counterbalance density	Coalescence density
1s α 1s β	0.006019	0.000752
1s α 2s α	0	0
1s α 2s β	0.020797	0.002600
1s α 2p $_{+1}\alpha$	0.036763	0
1s α 2p $_{0}\alpha$		
1s α 2p $_{-1}\alpha$		
1s β 2s α	0.020797	0.002600
1s β 2s β	0	0
1s β 2p $_{+1}\alpha$	0.018381	0.002298
1s β 2p $_{0}\alpha$		
1s β 2p $_{-1}\alpha$		
2s α 2s β	0.887994	0.110999
2s α 2p $_{+1}\alpha$	0.660669	0
2s α 2p $_{0}\alpha$		
2s α 2p $_{-1}\alpha$		
2s β 2p $_{+1}\alpha$	0.330335	0.041292
2s β 2p $_{0}\alpha$		
2s β 2p $_{-1}\alpha$		
2p $_{+1}\alpha$ 2p $_{0}\alpha$	0	0
2p $_{+1}\alpha$ 2p $_{-1}\alpha$	0	0
2p $_{0}\alpha$ 2p $_{-1}\alpha$	0	0
Total	4.074051	0.247719

density is due to the electrons in the innermost $1s$ orbital, which are confined in a small region in the vicinity of the nucleus. We can also verify the relation $d_{jk}(0)=8h_{jk}(0)$ numerically for spin-orbital-pairs with unlike spins.

Table II summarizes spin-orbital-pair contributions to the electron-electron counterbalance and coalescence densities in momentum space. Since the spin functions and the inversion symmetries of orbital functions are the same in position and momentum spaces, the counterbalance and coalescence holes in momentum space appear for the same spin-orbital-pairs as in position space. In contrast to position space, however, the electrons in the valence $2s$ and/or $2p$ orbitals give the largest contributions to the total counterbalance and coalescence densities, because the position-momentum reciprocity implies that diffuse orbitals in position space correspond to tight orbitals around $\mathbf{p}=0$ in momentum space. The relation $\bar{d}_{jk}(0)=8\bar{h}_{jk}(0)$ is seen in Table II, when the two spin functions are different.

ACKNOWLEDGMENT

This work has been supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

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