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LETTER

Note on the electron–electron counterbalance hole

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Abstract The electron–electron counterbalance hole implies that two *parallel* spin electrons cannot be at opposite positions with respect to the spatial inversion center, if it exists. The hole is known to appear for any approximate and exact wave functions with an *even* inversion parity. We point out that for particular cases, the counterbalance hole also appears when wave functions have an *odd* inversion parity and two electrons with *anti-parallel* spins are involved.

Keywords Counterbalance holes · Coalescence holes · Inversion symmetry · Permutation symmetry

The presence of electron–electron coalescence holes (or Fermi holes) is a fundamental property of many-electron wave functions and implies that two parallel spin electrons have zero probability of being found at the same point in three-dimensional space (see, e.g., [1]). A partner hole recently found is the electron–electron counterbalance hole [2, 3], which means that if the spatial inversion parity is even, two parallel spin electrons cannot be at opposite positions with respect to the inversion center. In the present short paper, we report that the counterbalance hole additionally appears for some odd inversion parity and anti-parallel spin cases. We also find the possibility of coalescence holes for anti-parallel spin electrons.

When an N-electron system ($N \geq 2$) has a spatial inversion symmetry, an associated anti-symmetric electron wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is an eigenfunction of the spatial inversion operator $\hat{\Lambda}$,

$$\begin{aligned}\hat{\Lambda}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) &= \Psi(-\mathbf{x}_1, -\mathbf{x}_2, \ldots, -\mathbf{x}_N) \\ &= \lambda\, \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N),\end{aligned} \tag{1}$$

where $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ is the combined position–spin coordinate of the electron i, $-\mathbf{x}_i = (-\mathbf{r}_i, s_i)$, and $\lambda = +1$ (even) or -1 (odd) is the inversion parity of $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$. If we replace $\mathbf{x}_1$ with $-\mathbf{x}_1$ and put $\mathbf{x}_i = \mathbf{O}_i = (\mathbf{0}_i, s_i)$ for $i \geq 3$ in Eq. 1, we obtain

$$\Psi(\mathbf{x}_1, -\mathbf{x}_2, \mathbf{O}_3, \ldots, \mathbf{O}_N) = \lambda\, \Psi(-\mathbf{x}_1, \mathbf{x}_2, \mathbf{O}_3, \ldots, \mathbf{O}_N), \tag{2}$$

where $\mathbf{0}$ is the zero vector and $\mathbf{O}_i$ indicates that the electron i with spin s_i is located at the inversion center (i.e., the spatial coordinate origin).

On the other hand, the anti-symmetric property of the wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ means

$$\hat{P}_k\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = p_k\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{3}$$

where $\hat{P}_k$ is one of the $N!$ permutations of N electron labels (both the position and spin coordinates) and $p_k = +1$ (even) or -1 (odd) is the permutation parity. If $\hat{P}_k$ is chosen to be the transposition of the electron labels 1 and 2, a particular case of Eq. 3 reads

$$\Psi(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_3, \ldots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N), \tag{4}$$

which immediately gives the electron–electron coalescence hole [1],

$$\Psi(\mathbf{x}, \mathbf{x}, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0, \tag{5}$$

for $\mathbf{x}_1 = \mathbf{x}_2 = \mathbf{x}$, i.e., the zero probability of finding electrons 1 and 2 for the same position and spin.

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If we combine Eqs. 2 and 4 and put $\mathbf{x}_1 = \mathbf{x}_2 = \mathbf{x}$, then we have

$$(1+\lambda)\Psi(\mathbf{x}, -\mathbf{x}, \mathbf{O}_3, \ldots, \mathbf{O}_N) = 0, \tag{6}$$

which gives a generalized form of the counterbalance hole [3],

$$\Psi(\mathbf{x}, -\mathbf{x}, \mathbf{O}_3, \ldots, \mathbf{O}_N) = 0, \tag{7}$$

for *even* inversion parity ($\lambda = +1$) wave functions, i.e., two electrons with *parallel* spins cannot be at opposite positions $\mathbf{r}$ and $-\mathbf{r}$, when the remaining electrons are at the inversion center. Due to Eq. 5, however, note that Eq. 7 and analogous relations to appear are automatically satisfied for $N \geq 5$, because wave functions vanish if we place three or more electrons at the inversion center simultaneously.

We now focus on the fact that the permutation operator $\hat{P}_k$ can be rewritten [4–6] as

$$\hat{P}_k = \hat{P}_k^r \hat{P}_k^s, \tag{8}$$

where $\hat{P}_k^r$ and $\hat{P}_k^s$ permute *only* the labels of the position coordinates and spin coordinates, respectively. Our concern below is two particular types of wave functions: (a) spatially anti-symmetric and spin symmetric wave functions $\Psi^r(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, which satisfy

$$\hat{P}_k^r \Psi^r(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = p_k \Psi^r(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{9a}$$

$$\hat{P}_k^s \Psi^r(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \Psi^r(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{9b}$$

for any k, and (b) spatially symmetric and spin anti-symmetric wave functions $\Psi^s(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, which satisfy

$$\hat{P}_k^r \Psi^s(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \Psi^s(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{10a}$$

$$\hat{P}_k^s \Psi^s(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = p_k \Psi^s(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{10b}$$

for any k. All two-electron wave functions belong to these types. Wave functions for systems with more than two electrons are also Ψ^r type for states of maximum spin multiplicity (i.e., maximum spin angular momentum S and its z component M_S quantum numbers).

We first examine the $\Psi^r(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ wave function. When the transposition of the electron position labels 1 and 2 is considered in Eq. 9a, we have

$$\Psi^r(\mathbf{r}_2, s_1, \mathbf{r}_1, s_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = -\Psi^r(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \mathbf{x}_3, \ldots, \mathbf{x}_N). \tag{11}$$

When $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$, Eq. 11 gives the electron–electron coalescence hole,

$$\Psi^r(\mathbf{r}, s_1, \mathbf{r}, s_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0, \tag{12}$$

in which the equality of the spin coordinates s_1 and s_2 is not required, unlike the case of Eq. 5. For Ψ^r type wave functions, the coalescence hole appears for any electron pairs irrespective of their spins. Similarly, a combination of Eqs. 2 and 11 leads to

$$(1+\lambda)\Psi^r(\mathbf{r}, s_1, -\mathbf{r}, s_2, \mathbf{O}_3, \ldots, \mathbf{O}_N) = 0, \tag{13}$$

which is analogous to Eq. 6, but there is no spin equality requirement, as is the case of Eq. 12. A counterbalance hole appears for even inversion parity wave functions again.

Next, we consider the $\Psi^s(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ wave function. For the transposition of the position labels 1 and 2, Eq. 10a gives

$$\Psi^s(\mathbf{r}_2, s_1, \mathbf{r}_1, s_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = \Psi^s(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \mathbf{x}_3, \ldots, \mathbf{x}_N). \tag{14}$$

In this case, the coalescence hole is not found in three-dimensional spatial sense. Instead, Eq. 10b yields a new coalescence hole in spin sense: choosing the transposition of the spin labels 1 and 2 for $\hat{P}_k^s$ in Eq. 10b, we obtain

$$\Psi^s(\mathbf{r}_1, s, \mathbf{r}_2, s, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0, \tag{15}$$

which means that the same spin function is not allowed for Ψ^s type wave functions. The spin coalescence hole implicitly means that the Ψ^s type wave functions are realistic only for two-electron systems (cf. [7]). On the other hand, a combination of Eqs. 2 and 14 yields another new relation

$$(1-\lambda)\Psi^s(\mathbf{r}, s_1, -\mathbf{r}, s_2, \mathbf{O}_3, \ldots, \mathbf{O}_N) = 0. \tag{16}$$

We immediately find that the counterbalance hole,

$$\Psi^s(\mathbf{r}, s_1, -\mathbf{r}, s_2, \mathbf{O}_3, \ldots, \mathbf{O}_N) = 0, \tag{17}$$

appears for *odd* inversion parity ($\lambda = -1$) wave functions. Two spins may be different in Eq. 17. The above relation concludes that the counterbalance hole emerges for anti-parallel spin electrons as well, when wave functions have odd inversion parity.

The appearance of the electron–electron counterbalance hole for odd inversion parity wave functions is most simply illustrated for the helium atom and its isoelectronic ions. The singlet wave functions are Ψ^s type with $S = M_S = 0$. In this case, two spins are anti-parallel in the sense of the spin quantum numbers. According to Eq. 17, the counterbalance hole appears for odd inversion parity functions. Typical examples are singly excited 1s*nl* states with odd *l* such as the 1s2p and 1s4f states. A general form of the singlet P spatial function given by Hylleraas [8] confirms the statement. The Hartree–Fock [9] and correlated [10] numerical results of the electron-pair extracule densities have also shown the hole for the 1s2p singlet P state. The two-electron triplet wave functions are Ψ^r type, and the presence of the counterbalance hole is already known [3, 6, 11]. For the function with $S = 1$ and $M_S = 0$, the two spins are apparently anti-parallel. However, Eqs. 12 and 13 show the presence of the coalescence and counterbalance holes, respectively.

In summary, we have pointed out that the electron–electron counterbalance holes appear for some odd inversion parity and anti-parallel spin cases of $N < 5$ systems, in addition to the even inversion parity and parallel spin cases reported in the literature. The momentum-space wave function has [3] the same inversion and permutation symmetries as the corresponding position-space wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, and hence, the present discussion holds as well in momentum space (see, e.g., [12]). Since the presence of the counterbalance hole directly affects the electron–electron counterbalance and extracule densities, the present results would be useful in the study of these densities (see, e.g., [9, 10, 13–23]).

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