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LETTER

Curvilinear and surficial electron holes in atoms and molecules

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Abstract The antisymmetric property of many-electron wave functions results in the well-known Fermi hole, which implies that any two electrons with the same spin cannot be at the same point in space. We here point out that for certain types of antisymmetric wave functions, there exist curvilinear and surficial electron holes which imply that two electrons cannot be on particular curves and surfaces in space.

Keywords Curvilinear electron hole · Surficial electron hole · Fermi hole · Permutation symmetry

1 Introduction

A general form of the Pauli principle states (see, e.g., Ref. [1]) that the wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ of an N-electron system ($N \geq 2$) must be totally antisymmetric with respect to permutation of electron labels,

$$\hat{P}_k \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = p_k \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N), \quad (1)$$

where $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ is the combined position-spin coordinate of the electron i, $\hat{P}_k$ is one of the $N!$ permutations of N electron labels, and $p_k = +1$ (even) or -1 (odd) is the associated parity. If $\hat{P}_k$ is chosen to be the transposition of the electron labels 1 and 2, Eq. (1) reads $\Psi(\mathrm{x}_2, \mathrm{x}_1, \mathrm{x}_3, \ldots, \mathrm{x}_N) = -\Psi(\mathrm{x}_1, \mathrm{x}_2, \mathrm{x}_3, \ldots, \mathrm{x}_N)$ which results in

$$\Psi(\mathrm{x}, \mathrm{x}, \mathrm{x}_3, \ldots, \mathrm{x}_N) = 0, \quad (2)$$

for any coordinate $\mathbf{x}$. Since relations analogous to Eq. (2) are obtained for any pairs of electrons i and j, Eq. (2) is a naive expression of the Fermi hole (see, e.g., Ref. [2]) that any two electrons with parallel spins cannot occupy the same position $\mathbf{r}$ in space.

The Fermi hole prohibits two parallel-spin electrons from being at the same *point* in space. In the present study, we focus on the fact that the permutation $\hat{P}_k$ is a product of four component permutation operators corresponding to four different kinds (three spatial and one spin) of electron coordinates. We then find that for certain types of antisymmetric wave functions, there exist curvilinear and surficial electron holes which imply that two electrons cannot be on particular *curves* and *surfaces* in space. In many-electron atoms, an example of the curvilinear electron hole is a circular hole which means that two electrons are not allowed on the same circle specified by a set of radial and zenith angular values. A simple example of surficial electron holes is a radial hole which means that two electrons cannot be on the same sphere irrespective of its radial value.

2 Component permutation operators

The position coordinate $\mathbf{r}_i$ of the electron i consists of three components; for example, (r_i, θ_i, ϕ_i) in the spherical coordinates, (x_i, y_i, z_i) in the Cartesian coordinates, and (ξ_i, η_i, ϕ_i) in the elliptic coordinates. Together with the spin coordinate s_i, we express the vector $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ as (a_i, b_i, c_i, d_i), where the four coordinate components can be arranged in an arbitrary order. We now introduce permutation operators $\hat{P}_k^w$ ($w = a, b, c, d$; $k = 1, 2, \ldots, N!$), which permute *only* the indices of the variables w_i.

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Then the usual permutation $\hat{P}_k$ appearing in Eq. (1) is written as

$$\hat{P}_k = \hat{P}_k^a \hat{P}_k^b \hat{P}_k^c \hat{P}_k^d. \tag{3}$$

Partially combined permutation operators $\hat{P}_k^{ab}$ and $\hat{P}_k^{abc}$ defined by

$$\hat{P}_k^{ab} = \hat{P}_k^a \hat{P}_k^b, \quad \hat{P}_k^{abc} = \hat{P}_k^a \hat{P}_k^b \hat{P}_k^c, \tag{4}$$

are also introduced for convenience. The component permutation operators $\hat{P}_k^s$ and $\hat{P}_k^{xyz}$ were used in the literature [3, 4].

We now consider three particular types of N-electron wave functions $\Psi^a(\mathrm{x}_1, \ldots, \mathrm{x}_N)$, $\Psi^{ab}(\mathrm{x}_1, \ldots, \mathrm{x}_N)$, and $\Psi^{abc}(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, which satisfy

$$\hat{P}_k^a \Psi^a = p_k \Psi^a \quad \text{and} \quad \hat{P}_k^{bcd} \Psi^a = \Psi^a, \tag{5a}$$

$$\hat{P}_k^{ab} \Psi^{ab} = p_k \Psi^{ab} \quad \text{and} \quad \hat{P}_k^{cd} \Psi^{ab} = \Psi^{ab}, \tag{5b}$$

$$\hat{P}_k^{abc} \Psi^{abc} = p_k \Psi^{abc} \quad \text{and} \quad \hat{P}_k^{d} \Psi^{abc} = \Psi^{abc}, \tag{5c}$$

respectively. The wave function Ψ^a is antisymmetric with respect to the variable a_i and symmetric with respect to the variables b_i, c_i, and d_i. The functions Ψ^{ab} and Ψ^{abc} have analogous meanings, and in general the superscripts to Ψ specify the antisymmetric coordinate components. Because of the relations (3)–(5), the wave functions Ψ^a, Ψ^{ab}, and Ψ^{abc} have properties

$$\hat{P}_k \Psi^a(\mathrm{x}_1, \ldots, \mathrm{x}_N) = p_k \Psi^a(\mathrm{x}_1, \ldots, \mathrm{x}_N), \tag{6a}$$

$$\hat{P}_k \Psi^{ab}(\mathrm{x}_1, \ldots, \mathrm{x}_N) = p_k \Psi^{ab}(\mathrm{x}_1, \ldots, \mathrm{x}_N), \tag{6b}$$

$$\hat{P}_k \Psi^{abc}(\mathrm{x}_1, \ldots, \mathrm{x}_N) = p_k \Psi^{abc}(\mathrm{x}_1, \ldots, \mathrm{x}_N), \tag{6c}$$

and all of them fulfill the antisymmetry requirement, Eq. (1), of the Pauli principle. These antisymmetric wave functions are subjects of our discussion below.

3 Curvilinear and surficial electron holes

When the permutation operator $\hat{P}_k$ is chosen to be the transposition of the electron labels 1 and 2, Eqs. (6a)–(6c) combined with Eqs. (5a)–(5c) read

$$\begin{aligned}&\Psi^a(a_2, b_1, c_1, d_1, a_1, b_2, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)\\ &\quad = -\Psi^a(a_1, b_1, c_1, d_1, a_2, b_2, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N),\end{aligned} \tag{7a}$$

$$\begin{aligned}&\Psi^{ab}(a_2, b_2, c_1, d_1, a_1, b_1, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)\\ &\quad = -\Psi^{ab}(a_1, b_1, c_1, d_1, a_2, b_2, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N),\end{aligned} \tag{7b}$$

$$\begin{aligned}&\Psi^{abc}(a_2, b_2, c_2, d_1, a_1, b_1, c_1, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)\\ &\quad = -\Psi^{abc}(a_1, b_1, c_1, d_1, a_2, b_2, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N),\end{aligned} \tag{7c}$$

respectively.

If $a_1 = a_2 = a$, Eq. (7a) gives

$$\Psi^a(a, b_1, c_1, d_1, a, b_2, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0. \tag{8a}$$

Since analogous results follow for any pairs of electrons, Eq. (8a) implies that any two electrons cannot have the same value for the coordinate component a_i, provided that the wave function is antisymmetric with respect to a_i and symmetric with respect to b_i, c_i, and d_i. If a_i is one of the three spatial coordinate components, any two electrons are prohibited to be on a plane or surface specified by a. This is a surficial electron hole. If the spin coordinate s_i is assigned to a_i, the same spin function is not allowed.

For a particular case of $a_1 = a_2 = a$ and $b_1 = b_2 = b$, Eq. (7b) results in

$$\Psi^{ab}(a, b, c_1, d_1, a, b, c_2, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0. \tag{8b}$$

Thus any two electrons cannot have the same value for the coordinate components a_i and b_i, with respect to which the wave function is antisymmetric. If a_i and b_i are chosen to be two spatial coordinates, we obtain a curvilinear electron hole that two electrons are not allowed to be on a line or curve defined by a and b. If the spin coordinate s_i is assigned to a_i, we meet a surficial electron hole that two parallel-spin electrons cannot be on a plane or surface specified by b.

When $a_1 = a_2 = a$, $b_1 = b_2 = b$, and $c_1 = c_2 = c$, Eq. (7c) yields

$$\Psi^{abc}(a, b, c, d_1, a, b, c, d_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) = 0, \tag{8c}$$

which generally means that any two electrons cannot have the same values for the three coordinate components except d_i, provided that the wave function is antisymmetric with respect to a_i, b_i, c_i and symmetric with respect to d_i. If we choose d_i as the spin coordinate s_i and a_i, b_i, c_i as the spatial coordinates, two electrons cannot be at the same spatial point. In this case, however, there are no restrictions for the electron spins, different from the case of the traditional Fermi hole. If we can choose d_i as one of the spatial coordinates and a_i as s_i, we then have a curvilinear electron hole that two electrons with parallel spins cannot be on a line or curve specified by b and c.

4 Illustrations

For two-electron systems where the wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ is the product of a spatial function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ and a spin function $\Theta(s_1, s_2)$, the appearance of curvilinear and surficial electron holes is most simply illustrated.

We first consider two-electron singlet states. In this case, $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric and $\Theta(s_1, s_2)$ is antisymmetric. The wave function belongs to the Ψ^a-type with $a = s$, and a trivial result follows that two electrons cannot have the same spin in singlets.

Next we consider the He atom in triplet states, where $\Theta(s_1, s_2)$ is symmetric. For ^{3}S states, the spatial function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is generally given [5] by

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=f(r_1,r_2,\cos\theta_{12})-f(r_2,r_1,\cos\theta_{12}), \tag{9}$$

where $\cos\theta_{12}=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)$ and (r_i, θ_i, ϕ_i) is the spherical coordinates of $\mathbf{r}_i$. The spatial function (9) is antisymmetric with respect to r and symmetric with respect to θ and ϕ. Thus the ^{3}S wave functions are Ψ^a-type with $a = r$, which implies the presence of a radial hole that two electrons cannot be on the same sphere simultaneously. For ^{3}P states, the general form of $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is [5]

$$\begin{aligned}\psi(\mathbf{r}_1,\mathbf{r}_2) &= g(r_1,r_2,\cos\theta_{12})\cos\theta_2\\ &\quad - g(r_2,r_1,\cos\theta_{12})\cos\theta_1.\end{aligned} \tag{10}$$

We find the ^{3}P wave function is antisymmetric with respect to r and θ, and symmetric with respect to ϕ and s. We now encounter a Ψ^{ab}-type wave function with (a, b) = (r, θ), which means the presence of a circular hole that the two electrons in ^{3}P states cannot be on the same circle, specified by r and θ, simultaneously. For ^{3}D states, an examination of the general form of $\psi(\mathbf{r}_1, \mathbf{r}_2)$, given in Ref. [5], leads to an analogous result of circular holes.

Kolos and coworkers performed highly accurate calculations of the H_2 molecule in various electronic states (see, e.g., Ref. [6] for a review). For triplets states with gerade symmetry, they expanded [7, 8] the spatial function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ by two-electron basis functions $\chi_{\Lambda,j}(\mathbf{r}_1, \mathbf{r}_2)$:

$$\begin{aligned}\chi_{\Lambda,j}(\mathbf{r}_1,\mathbf{r}_2) &= (x_1+iy_1)^{\Lambda} f_{\Lambda,j}(\mathbf{r}_1,\mathbf{r}_2)\\ &\quad -(x_2+iy_2)^{\Lambda} f_{\Lambda,j}(\mathbf{r}_2,\mathbf{r}_1),\end{aligned} \tag{10}$$

where Λ is the total angular momentum quantum number around the molecular axis and Λ = 0, 1, 2 correspond to Σ, Π, Δ states, respectively. The symbols (x_k, y_k) denote the Cartesian coordinates of $\mathbf{r}_k$ perpendicular to the molecular axis. In the usual elliptic coordinates (ξ_k, η_k, ϕ_k), the function $f_{\Lambda,j}(\mathbf{r}_1, \mathbf{r}_2)$ is given [8] by

$$\begin{aligned}f_{\Lambda,j}(\mathbf{r}_1,\mathbf{r}_2) &= \exp(-\alpha\xi_1-\alpha'\xi_2)\xi_1^{l_j}\eta_1^{m_j}\xi_2^{l'_j}\eta_2^{m'_j}(2r_{12}/R)^{n_j}\\ &\quad\times[\exp(\beta\eta_1+\beta'\eta_2)+(-1)^{m_j+m'_j+\Lambda}\\ &\quad\times\exp(-\beta\eta_1-\beta'\eta_2)],\end{aligned} \tag{12}$$

where r_{12} and R are the interelectronic and internuclear distances, respectively. The other symbols represent parameters. Note that in the elliptic coordinates,

$$x_k+iy_k=(R/2)[(\xi_k^2-1)(1-\eta_k^2)]^{1/2}\exp(i\phi_k), \tag{13a}$$

$$\begin{aligned}r_{12}^2 &= (R/2)^2\{(\xi_1^2-1)(1-\eta_1^2)-2[(\xi_1^2-1)(1-\eta_1^2)\\ &\quad\times(\xi_2^2-1)(1-\eta_2^2)]^{1/2}\cos(\phi_1-\phi_2)\\ &\quad+(\xi_2^2-1)(1-\eta_2^2)+(\xi_1\eta_1-\xi_2\eta_2)^2\}.\end{aligned} \tag{13b}$$

We find the variable r_{12} is symmetric with respect to the permutation of any of ξ, η, and ϕ. For Σ states (i.e., $\Lambda = 0$), an analysis of the spatial function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ shows that the function is antisymmetric with respect to the variables ξ and η, while symmetric with respect to ϕ. Thus the wave function is Ψ^{ab}-type with (a, b) = (ξ, η). The two electrons in $^3\Sigma$ states are not allowed to be on the same circle, specified by ξ and η, around the molecular axis. When $\Lambda \geq 1$, however, the spatial function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is antisymmetric with respect to the simultaneous permutation of the three spatial variables ξ, η, and ϕ due to the presence of the $(x_k + iy_k)^{\Lambda}$ term, i.e., the wave function is Ψ^{abc}-type with (a, b, c) = (ξ, η, ϕ), and hence only the usual Fermi hole appears. Exactly the same results follow for triplet states with ungerade symmetry, if the factor $(-1)^{m_j+m'_j+\Lambda}$ in Eq. (12) is replaced with $(-1)^{m_j+m'_j+\Lambda+1}$.

As examples of systems with more than two electrons, we consider the ground ^{2}S state of the Li atom and the ground ^{1}S state of the Be atom in the Hartree-Fock approximation. In the standard notation, the Li Hartree-Fock wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ is

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=6^{-1/2}|\,1s\alpha(\mathbf{x}_1)\quad 1s\beta(\mathbf{x}_2)\quad 2s\alpha(\mathbf{x}_3)\,|. \tag{14}$$

The wave function is free from the variables θ and ϕ. Then $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ is symmetric with respect to θ and ϕ, while antisymmetric with respect to r and s. We thus have a radial hole that two electrons with the same spin cannot be on the same sphere simultaneously. An analogous examination finds that a radial hole also appears for the Be atom described by

$$\begin{aligned}&\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)=24^{-1/2}\\ &\quad|\,1s\alpha(\mathbf{x}_1)\quad 1s\beta(\mathbf{x}_2)\quad 2s\alpha(\mathbf{x}_3)\quad 2s\beta(\mathbf{x}_4)\,|.\end{aligned} \tag{15}$$

The radial holes in the Hartree-Fock approximation were also reported in the literature [9].

5 Summary and remarks

We have shown that for certain types of antisymmetric wave functions, there exist curvilinear and surficial electron holes which imply that two electrons are not allowed to be simultaneously on particular curves and surfaces in space. For simple atoms and H_2 molecule, the presence of circular holes and radial holes has been illustrated.

We hope the present results are useful for deeper understanding of the electronic structure of atoms and molecules. For example, a new property may be added to the theory of reduced density matrices [2], since the vanishing N-electron wave function $\Psi = 0$ implies that all the pth order matrices $\Gamma^{(p)}$ vanish for $2 \leq p \leq N$. In the literature [10–13], electron holes were discussed in relation to Hund's rules (see also Refs. [14, 15]). The vanishing points of wave functions are also a nontrivial concern in Monte Carlo studies as nodal problems (see, e.g., Ref. [16]).

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