

Electron-electron cusp condition and asymptotic behavior for the Pauli potential in pair density functional theory

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In the ground state, the pair density n can be determined by solving a single auxiliary equation of a two-particle problem. Electron-electron cusp condition and asymptotic behavior for the Pauli potential of the effective potential of the two-particle equation are presented. © 2008 American Institute of Physics. [DOI: 10.1063/1.2838201]

I. INTRODUCTION

In the density matrix functional theory,¹⁻⁴ it was shown that the ground-state problem of an arbitrary system can be reduced to a two-particle problem, that is, only a single auxiliary equation of a two-particle system should be solved. The effective potential of the two-particle equation contains a term v_p of completely kinetic origin. The exact form of this Pauli potential is unknown. In this paper, the electron-electron cusp condition and asymptotic behavior for the Pauli potential are presented. The paper is organized as follows. In Sec. II, the asymptotic behavior for the Pauli potential is derived. Section III presents the electron-electron cusp condition for the Pauli potential. The last section is devoted to the discussion.

II. ASYMPTOTIC BEHAVIOR OF THE PAULI POTENTIAL OF THE PAIR FUNCTIONAL THEORY

First, the method of Levy *et al.*⁵ is generalized to derive the two-particle equation of the pair density functional theory and give an expression for the Pauli potential. (The derivation is essentially the same as the one given by Furche.⁶) The Schrödinger equation of the N -electron ground-state problem has the form

$$\hat{H}(\bar{N})\Psi(\bar{N}) = E_N\Psi(\bar{N}), \quad (1)$$

where \bar{M} signifies the coordinates of electrons $1, \dots, M$. Taking the following partition of the Hamiltonian of the N -electron system:

$$\hat{H}(\bar{N}) = \hat{H}(N, N-1) + \hat{H}(\bar{N}-2) + \sum_{j=1}^{N-2} \left(\frac{1}{r_{jN}} + \frac{1}{r_{jN-1}} \right), \quad (2)$$

where

$$\hat{H}(N, N-1) = -\frac{1}{2}\nabla_N^2 - \frac{1}{2}\nabla_{N-1}^2 + v(\mathbf{r}_N) + v(\mathbf{r}_{N-1}) + \frac{1}{r_{NN-1}} \quad (3)$$

and

$$\hat{H}(\bar{N}-2) = \sum_{j=1}^{N-2} \left(-\frac{1}{2}\nabla_j^2 + v(\mathbf{r}_j) \right) + \sum_{i<j}^{N-2} \frac{1}{r_{ij}}. \quad (4)$$

$v(\mathbf{r})$ is the external potential and the notation

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (5)$$

is applied. The pair density is defined as

$$n(\mathbf{r}_{N-1}, \mathbf{r}_N) = \frac{N(N-1)}{2} \int |\Psi(\bar{N})|^2 d(\bar{N}-2) d\sigma_{N-1} d\sigma_N. \quad (6)$$

Now, we define a function $\Phi(\bar{N})$ as

$$\Phi(\bar{N}) = \left(\frac{N(N-1)}{2} \right)^{1/2} \frac{\Psi(\bar{N})}{n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N)}. \quad (7)$$

From definitions (7) and (6), it follows that

$$\int |\Phi(\bar{N})|^2 d(\bar{N}-2) = 1, \quad (8)$$

for any \mathbf{r}_{N-1} and \mathbf{r}_N . Subtracting $E_{N-2,N}^0\Psi(\bar{N})$ from both sides of Eq. (1), multiplying by $\Phi(\bar{N})^*$, and integrating over all the coordinates of electrons $1, \dots, N-2$ and spin coordinates of electrons $N-1, N$,

$$\langle \Phi(\bar{N}) | \hat{H}(\bar{N}) - E_{N-2,N}^0 | \Psi(\bar{N}) \rangle = \mu \langle \Phi(\bar{N}) | \Psi(\bar{N}) \rangle, \quad (9)$$

where $E_{N-2,N}^0$ is the total energy of the $(N-2)$ -electron system (the one obtained after removing two electrons from the N -electron system) and

$$\mu = E(\bar{N}) - E_{N-2,N}^0. \quad (10)$$

After a simple manipulation, Eqs. (7)–(10) lead to

$$\begin{aligned} & [\hat{H}(N, N-1) + \tilde{v}_{\text{eff}}(\mathbf{r}_{N-1}, \mathbf{r}_N)] n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N) \\ & = \mu n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N), \end{aligned} \quad (11)$$

where the effective potential is given by

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$$\begin{aligned} \tilde{v}_{\text{eff}}(\mathbf{r}_{N-1}, \mathbf{r}_N) &= \langle \Phi(\bar{N}) | \hat{H}(\bar{N}-2) - E_{N-2,N}^0 | \Phi(\bar{N}) \rangle - n^{-1/2} [\nabla_N n^{1/2} \langle \Phi(\bar{N}) | \nabla_N \Phi(\bar{N}) \rangle + \nabla_{N-1} n^{1/2} \langle \Phi(\bar{N}) | \nabla_{N-1} \Phi(\bar{N}) \rangle] \\ &\quad - \frac{1}{2} \langle \Phi(\bar{N}) | \nabla_N^2 \Phi(\bar{N}) \rangle - \frac{1}{2} \langle \Phi(\bar{N}) | \nabla_{N-1}^2 \Phi(\bar{N}) \rangle \\ &\quad + \frac{6}{N(N-1)} \left(\int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N-1}} d\mathbf{r}_{N-2} + \int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N}} d\mathbf{r}_{N-2} \right), \end{aligned} \quad (12)$$

where $\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)$ is the density of $\Phi(\bar{N})$ associated with electron $N-1$ at point \mathbf{r}_{N-1} and electron N at point \mathbf{r}_N . Adding Eq. (12) to its complex conjugate, we obtain

$$\begin{aligned} \tilde{v}_{\text{eff}}(\mathbf{r}_{N-1}, \mathbf{r}_N) &= \langle \Phi(\bar{N}) | \hat{H}(\bar{N}-2) - E_{N-2,N}^0 | \Phi(\bar{N}) \rangle - \frac{1}{2n^{1/2}} [\nabla_N n^{1/2} \nabla_N \langle \Phi(\bar{N}) | \Phi(\bar{N}) \rangle + \nabla_{N-1} n^{1/2} \nabla_{N-1} \langle \Phi(\bar{N}) | \Phi(\bar{N}) \rangle] \\ &\quad - \frac{1}{4} \langle \Phi(\bar{N}) | \nabla_N^2 \Phi(\bar{N}) \rangle - \frac{1}{4} \langle \nabla_N^2 \Phi(\bar{N}) | \Phi(\bar{N}) \rangle - \frac{1}{4} \langle \Phi(\bar{N}) | \nabla_{N-1}^2 \Phi(\bar{N}) \rangle - \frac{1}{4} \langle \nabla_{N-1}^2 \Phi(\bar{N}) | \Phi(\bar{N}) \rangle \\ &\quad + \frac{6}{N(N-1)} \left(\int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N-1}} d\mathbf{r}_{N-2} + \int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N}} d\mathbf{r}_{N-2} \right). \end{aligned} \quad (13)$$

From Eq. (8), it follows that the second term disappears and the Laplacian terms can be expressed with the integral of the gradient of $\Phi(\bar{N})$, leading to the form

$$\begin{aligned} \tilde{v}_{\text{eff}}(\mathbf{r}_{N-1}, \mathbf{r}_N) &= \langle \Phi(\bar{N}) | \hat{H}(\bar{N}-2) - E_{N-2,N}^0 | \Phi(\bar{N}) \rangle \\ &\quad + \frac{1}{2} (\langle |\nabla_N \Phi(\bar{N})|^2 \rangle + \langle |\nabla_{N-1} \Phi(\bar{N})|^2 \rangle) \\ &\quad + \frac{6}{N(N-1)} \left(\int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N-1}} d\mathbf{r}_{N-2} \right. \\ &\quad \left. + \int \frac{\tilde{n}(\mathbf{r}_{N-2}, \mathbf{r}_{N-1}, \mathbf{r}_N)}{r_{N-2,N}} d\mathbf{r}_{N-2} \right). \end{aligned} \quad (14)$$

Inverting Eq. (11), \tilde{v}_{eff} can be written as

$$\begin{aligned} \tilde{v}_{\text{eff}} &= \frac{1}{2} \frac{\nabla_{N-1}^2 n^{1/2}}{n^{1/2}} + \frac{1}{2} \frac{\nabla_N^2 n^{1/2}}{n^{1/2}} - v(\mathbf{r}_{N-1}) - v(\mathbf{r}_N) - \frac{1}{r_{NN-1}} \\ &\quad + \mu. \end{aligned} \quad (15)$$

No term on the right hand side of Eq. (14) can ever be negative; consequently,

$$\tilde{v}_{\text{eff}} \geq 0. \quad (16)$$

Let us now turn to the asymptotic behavior of the pair density and the effective potential \tilde{v}_{eff} . From Eq. (11), it follows that

$$n(\mathbf{r}_{N-1}, \mathbf{r}_N) \rightarrow e^{-2\alpha r_{N-1}} e^{-2\alpha r_N}, \quad (17)$$

where

$$\alpha = [-\mu + \tilde{v}_{\text{eff}}(\infty, \infty)]^{1/2}. \quad (18)$$

From the inequality [Eq. (16)], we obtain

$$\alpha \geq \sqrt{-\mu}. \quad (19)$$

Multiplying Eq. (1) by an eigenstate $\Psi_l^*(\bar{N}-2)$ of the $(N-2)$ -electron system, integrating over the coordinates of $N-2$ electrons, and employing Eqs. (2)–(7), we obtain

$$\begin{aligned} &\left[-\frac{1}{2} \nabla_{N-1}^2 - \frac{1}{2} \nabla_N^2 + v(\mathbf{r}_{N-1}) + v(\mathbf{r}_N) \right. \\ &\quad \left. + \frac{1}{r_{N-1,N}} - \varepsilon_l \right] g_l(\mathbf{r}_{N-1}, \mathbf{r}_N) \\ &= -(N-2)n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N) \\ &\quad \times \left\langle \Psi_l(\bar{N}-2) \left(\frac{1}{r_{1,N-1}} + \frac{1}{r_{1,N}} \right) \Phi(\bar{N}) \right\rangle, \end{aligned} \quad (20)$$

where

$$\varepsilon_l = E_N - E_{N-2}^l, \quad (21)$$

E_{N-2}^l is the eigenvalue corresponding to the eigenfunction $\Psi_l(\bar{N}-2)$, and

$$g_l(\mathbf{r}_{N-1}, \mathbf{r}_N) = n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N) \int \Psi_l^*(\bar{N}-2) \Phi(\bar{N}) d(\bar{N}-2). \quad (22)$$

Considering now the case $l=0$,

$$g_0(\mathbf{r}_{N-1}, \mathbf{r}_N) = n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N) \int \Psi_0^*(\bar{N}-2) \Phi(\bar{N}) d(\bar{N}-2). \quad (23)$$

Equation (20) asymptotically gives $g_0(\mathbf{r}_{N-1}, \mathbf{r}_N) \rightarrow e^{-\sqrt{-\mu}r_{N-1}} e^{-\sqrt{-\mu}r_N}$ as $\varepsilon_0 = \mu$. Using the asymptotic form [Eq. (17)] of the pair density and the Schwartz inequality,

$$\left| \int \Psi_0^*(\bar{N}-2) \Phi(\bar{N}) d(\bar{N}-2) \right| \leq 1, \quad (24)$$

Eq. (23) leads to

$$\alpha \leq \sqrt{-\mu}. \quad (25)$$

From inequalities (19) and (25), it follows the equality

$$\alpha = \sqrt{-\mu}. \quad (26)$$

Then, Eq. (18) gives

$$\tilde{v}_{\text{eff}}(\infty, \infty) = 0. \quad (27)$$

It has the consequence that $\Phi(\bar{N})$ asymptotically collapses to the eigenfunction $\Psi_0(\bar{N}-2)$. It can be seen from Eqs. (7) and (14) that $\Phi(\bar{N})$ asymptotically cannot depend on the coordinates \mathbf{r}_{N-1} and \mathbf{r}_N . The last term on the right hand side of Eq. (14) gives the asymptotic form of the effective potential,

$$\tilde{v}_{\text{eff}} \rightarrow \frac{N-2}{r_{N-1}} + \frac{N-2}{r_N}. \quad (28)$$

In earlier papers, the two-particle equation [Eq. (9)] was written as

$$\left[-\frac{1}{2}\nabla_{N-1}^2 - \frac{1}{2}\nabla_N^2 + v(\mathbf{r}_{N-1}) + v(\mathbf{r}_N) + \frac{N-1}{r_{N-1,N}} + v_P(\mathbf{r}_{N-1}, \mathbf{r}_N) \right] n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N) = \mu n^{1/2}(\mathbf{r}_{N-1}, \mathbf{r}_N), \quad (29)$$

where v_P is the Pauli potential. Comparing Eqs. (3), (11), and (29), we are led to the relation

$$v_P = \tilde{v}_{\text{eff}} - \frac{N-2}{r_{N-1,N}}. \quad (30)$$

Equations (28) and (30) lead to the asymptotic form of the Pauli potential,

$$v_P \rightarrow (N-2) \left(\frac{1}{r_{N-1}} + \frac{1}{r_N} - \frac{1}{r_{N-1,N}} \right). \quad (31)$$

III. ELECTRON-ELECTRON CUSP CONDITION FOR THE PAULI POTENTIAL

To derive the electron-electron cusp condition for the Pauli potential, first, the two-particle equation [Eq. (29)] is written as

$$\left[-\frac{1}{2}\nabla_{N-1}^2 - \frac{1}{2}\nabla_N^2 + v(\mathbf{r}_{N-1}) + v(\mathbf{r}_N) + \frac{N-1}{r_{N-1,N}} + v_P(\mathbf{r}_{N-1}, \mathbf{r}_N) \right] \tilde{\chi}_0(\mathbf{r}_{N-1}, \mathbf{r}_N) = \mu \tilde{\chi}_0(\mathbf{r}_{N-1}, \mathbf{r}_N), \quad (32)$$

where the two-particle function $\tilde{\chi}_0$ is related to the pair density n as

$$n = N \frac{N-1}{2} |\tilde{\chi}_0|^2. \quad (33)$$

Now, we introduce relative and center of mass coordinates as

$$\mathbf{r} = \mathbf{r}_N - \mathbf{r}_{N-1} \quad (34)$$

and

$$\mathbf{R}_c = \frac{1}{2}(\mathbf{r}_N + \mathbf{r}_{N-1}). \quad (35)$$

The wave function $\tilde{\chi}_0$ can be written as

$$\tilde{\chi}_0(r, \Omega, \mathbf{R}_c) = \sum_{lm} R_{lm}(r, \mathbf{R}_c) Y_{lm}(\Omega), \quad (36)$$

where Y_{lm} are the spherical harmonics. The expansion of the Pauli potential v_P around $r=0$ leads to

$$v_P(r, \Omega, \mathbf{R}_c) = \frac{v_P^{-1}(\mathbf{R}_c)}{r} + \sum_{lm} v_{lm}^P(r, \mathbf{R}_c) Y_{lm}(\Omega), \quad (37)$$

where

$$v_{lm}^P(r, \mathbf{R}_c) = A_{lm}(\mathbf{R}_c) + B_{lm}(\mathbf{R}_c)r + C_{lm}(\mathbf{R}_c)r^2 + \dots \quad (38)$$

For the Coulomb external potential, the expansions

$$\begin{aligned} -Z \frac{1}{r_{N-1}} &= -Z \frac{1}{|\mathbf{R}_c + \mathbf{r}/2|} \\ &= -Z \sum_{l,m} \frac{4\pi}{2l+1} \frac{(r/2)^l}{R_c^{l+1}} Y_{lm}^*(\hat{\mathbf{R}}_c) Y_{lm}(\widehat{-\mathbf{r}/2}) \end{aligned} \quad (39)$$

and

$$\begin{aligned} -Z \frac{1}{r_N} &= -Z \frac{1}{|\mathbf{R}_c - \mathbf{r}/2|} \\ &= -Z \sum_{l,m} \frac{4\pi}{2l+1} \frac{(r/2)^l}{R_c^{l+1}} Y_{lm}^*(\hat{\mathbf{R}}_c) Y_{lm}(\widehat{\mathbf{r}/2}) \end{aligned} \quad (40)$$

can be applied for small r . Substituting the radial functions

$$R_{lm}(r, \mathbf{R}_c) = c_{lm}^{(0)}(\mathbf{R}_c) r^l + c_{lm}^{(1)}(\mathbf{R}_c) r^{l+1} + c_{lm}^{(2)}(\mathbf{R}_c) r^{l+2} + \dots \quad (41)$$

and expressions (36)–(41) into the two-particle equation [Eq. (32)] and equating the coefficients of r^{-1} to zero, we arrive at the equation

$$2c_{00}^{(1)} - (v_P^{-1} + N - 1)c_{00}^{(0)} = 0. \quad (42)$$

Now, the expansion [Eq. (36)] for the wave function $\tilde{\chi}_0$ is substituted into the pair density [Eq. (33)] and the spherical average of the pair density is taken around $r=0$,

$$\bar{n}|_{r=0} = \frac{N(N-1)}{2} \frac{1}{4\pi} |c_{00}^{(0)}|^2. \quad (43)$$

The derivative of the spherical average of n is

$$\left. \frac{\partial \bar{n}}{\partial r} \right|_{r=0} = \frac{N(N-1)}{2} \frac{1}{4\pi} 2c_{00}^{(0)} c_{00}^{(1)}. \quad (44)$$

Equations (43), (44), and (42) lead to the electron-electron cusp condition for the pair density,

$$\left. \frac{\partial \bar{n}}{\partial r} \right|_{r=0} \frac{1}{\bar{n}|_{r=0}} = v_P^{-1} + N - 1. \quad (45)$$

On the other hand, it is well known that the electron-electron cusp condition for the pair density has the form⁷

$$\left. \frac{\partial \bar{n}}{\partial r} \right|_{r=0} \frac{1}{\bar{n}|_{r=0}} = 1. \quad (46)$$

Equations (45) and (46) result to

$$v_p^{-1} = 2 - N. \quad (47)$$

Consequently, for small r , the Pauli potential should behave as

$$v_p = \frac{2 - N}{r}. \quad (48)$$

IV. DISCUSSION

The Pauli energy of the pair density functional theory was introduced by a density functional analogy: the difference of the kinetic energy and a Weizsäcker-type expression⁹ (constructed from the pair density instead of the density).¹ The Pauli potential is the functional derivative of the Pauli energy with respect to the pair density. For a two-electron system, the Pauli potential disappears. Both the asymptotic form [Eq. (31)] and electron-electron cusp condition [Eq. (48)] give this property correctly. It might be useful to write the asymptotic form [Eq. (31)] with relative and center of mass coordinates. Expanding the terms $1/r_{N-1}$ and $1/r_N$, we obtain the following forms:

$$v_p \rightarrow (N-2) \left(\frac{2}{R_c} - \frac{1}{r} \right), \quad (49)$$

if $R_c > r/2$, and

$$\tilde{v}_p \rightarrow (N-2) \frac{3}{r}, \quad (50)$$

if $R_c < r/2$.

As the exact form of the Pauli potential is not known, we have to find approximate expressions for numerical calculations. Exact relations that the Pauli potential should satisfy could be very useful in constructing approximate formulas. Earlier, we derived virial theorem and hierarchy of equations. These relations together with the presently derived asymptotic form [Eq. (31)] and electron-electron cusp condition [Eq. (48)] give possibility to obtain appropriate expression for the Pauli potential. This will be the subject of further future research. A fundamental problem in the density matrix

theory is the N -representability problem.^{7,8,10-22} An approximate functional does not generally satisfy N -representability. It is supposed that the fulfillment of the above mentioned exact relations is important from the point of view of N -representability, too.

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