Integral Coalescence Conditions In $D \geq 2$ Dimension Space

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Abstract

We have derived the integral form of the cusp and node coalescence conditions satisfied by the wavefunction at the coalescence of two charged particles in $D \geq 2$ dimension space. From it we have obtained the differential form of the coalescence conditions. These expressions reduce to the well-known integral and differential coalescence conditions in $D = 3$ space. It follows from the results derived that the approximate Laughlin wavefunction for the fractional Quantum Hall Effect satisfies the node coalescence condition. It is further noted that the integral form makes evident that unlike the electron-nucleus coalescence condition, the differential form of the electron-electron coalescence condition cannot be expressed in terms of the electron density at the point of coalescence. From the integral form, the integral and differential coalescence conditions for the pair-correlation function in $D \geq 2$ dimension space are also derived. The known differential form of the pair function cusp condition for the uniform electron gas in dimensions $D = 2, 3$ constitute a special case of the result derived.
I. INTRODUCTION

The non relativistic wavefunction exhibits a cusp or a node at the coalescence of any two charged particles because of the singularity associated with the Coulomb interaction between them. The differential form of the cusp coalescence condition satisfied by the wavefunction for both electron-electron and electron-nucleus coalescence was derived for dimensions $D = 3$ by Kato [1]. This form of the cusp condition is in terms of the spherical average of the wavefunction taken about the singularity. It is this differential form that is most extensively employed in the literature. The integral form of the electron-electron and electron-nucleus cusp and node coalescence condition for $D = 3$ was originally conjectured by Bingel [2]. They have been derived rigorously from the Schrodinger equation by Pack and Byers Brown [3]. The integral form of the coalescence conditions, however, is more general, and therefore more significant, because it retains the angular dependence of the wavefunction at coalescence. The differential form is then readily obtained from the integral form by spherically averaging and differentiating. An example of the usefulness of the integral form is the following. Over the past two and a half decades, there has been uncertainty [4] about whether the local effective potential energy of Kohn-Sham density functional theory [5] was finite or singular at the nucleus of atoms. Employing the differential form of the cusp condition, it was initially proved [4] that the potential energy is finite at the nucleus of spherically symmetric atoms. However, using the integral form, the conclusion of finiteness can be generalized [6] to atoms of arbitrary symmetry, to molecules, and to periodic and aperiodic solids. As another example, it is well known that the differential form of the electron-nucleus cusp condition may be expressed [7] in terms of the spherical average of the electron density about the nucleus. It has consequently been assumed [8] that the differential form of the electron-electron cusp condition can similarly be expressed in terms of the density at the point of electron coalescence. The integral form of the electron-electron cusp condition makes clear that no such expression in terms of the density can exist.

At present, there is considerable interest in both lower dimensional systems such as the two-dimensional ($D = 2$) electron gas [9], the two-dimensional gas in the presence of a magnetic field (the Quantum Hall Effect) [10], and in their higher-dimensional $D \geq 4$ generalizations [11]. Motivated by this interest, we have derived the integral form of the
The cusp and node coalescence condition for dimensions $D \geq 2$. It becomes evident that the approximate Laughlin\[10\] wavefunction for the fractional Quantum Hall effect satisfies the $D = 2$ node coalescence condition. The $D \geq 2$ differential form of the cusp condition is then obtained by spherically averaging about the singularity over $D$-dimensional space and differentiating. Employing the integral cusp condition, we have also derived the integral and differential forms of the pair correlation function at the coalescence of two identical particles in $D \geq 2$ dimensions. The differential form of the cusp condition for the pair correlation function for the uniform electron gas for $D = 3 \[12\]$ and $D = 2 \[13\]$ constitute a special case of our result. The use of cusp conditions for the pair-correlation function in $D = 3$ spin-density functional theory is expounded in Ref. 14. More recent work on nuclear cusp conditions relevant to density functional theory is described in Ref.15.

II. DERIVATION

Consider a nonrelativistic system of $N$ charged particles in $D \geq 2$ dimension space with the Hamiltonian ($\hbar = e = 1$)

$$
\hat{H} = -\sum_{i=1}^{N} \frac{1}{2m_i} \nabla_{i}^2 + \sum_{j>i=1}^{N} \frac{Z_i Z_j}{r_{ij}},
$$

where $m_i$ and $Z_i$ are the mass and charge of the $i$th particle, and $r_{ij} = |r_i - r_j|$. In $D$ dimension space, $r = (x_1, x_2, ..., x_D)$, $r = \sqrt{\sum_{k=1}^{D} x_k x_k}$ and $\nabla^2 = \sum_{k=1}^{D} \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_k}$. Due to the Coulomb potential energy term, the Hamiltonian is singular when any two particle $i$ and $j$ coalesce ($r_{ij} \to 0$). For the wavefunction $\Psi(r_1, r_2, ..., r_N)$ which satisfies the Schrödinger equation

$$
\hat{H}\Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N),
$$

to be bounded and remain finite at the singularities, it must satisfy a cusp coalescence condition. If the wavefunction vanishes at the singularity, it must satisfy a node coalescence condition.

We are interested in the form of the wavefunction when two particles approach each other, i.e. when $r_{ij}$ is very small. Following Pack and Byers Brown\[3\] we focus our attention on
two particles 1 and 2, and transform their coordinates $r_1$ and $r_2$ to the center of mass $R_{12}$ and relative coordinates $r_{12}$ as
\[
R_{12} = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2},
\]
\[
r_{12} = r_1 - r_2.
\]

The Hamiltonian of Eq. (1) may then be rewritten as
\[
\hat{H} = -\frac{1}{2\mu_{12}} \nabla^2_{r_{12}} + \frac{Z_1 Z_2}{r_{12}} - \frac{1}{2(m_1 + m_2)} \nabla^2_{R_{12}} + \sum_{i=3}^{N} N_i \left( \frac{Z_1}{r_{1i}} + \frac{Z_2}{r_{2i}} \right) \]
\[
+ \sum_{i=3}^{N} \frac{1}{2m_i} \nabla^2_{r_i} + \sum_{j>i=3}^{N} \frac{Z_i Z_j}{r_{ij}},
\]

where $\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of particles 1 and 2. When particle 1 and 2 are within a small distance of each other ($0 < r_{12} < \varepsilon$), and all other particles are well separated, there is only one singularity in the Hamiltonian. Retaining only terms of lower order in $r_{12}$, Eq. (3) reduces to
\[
[-\frac{1}{2\mu_{12}} \nabla^2_{r_{12}} + \frac{Z_1 Z_2}{r_{12}} + O(\varepsilon^0)]\Psi(r_1, r_2, \ldots, r_N) = 0,
\]

where $O(\varepsilon^0)$ refers to terms of order zero (constant) and higher order in $r_{12}$ and the vector components $(r_{12})_k, k = 1, 2, \ldots D$).

Eq. (4) is a one-electron-atom equation in D dimension space. Furthermore, it is not an eigenvalue equation. We are interested in the solution of the equation that are finite and continuous at the singularities. Thus, in the limit as $r_1 \to r_2$, we could write the wavefunction in two parts as
\[
\Psi(r_1, r_2, \ldots, r_N) = \Psi(r_2, r_2, \ldots, r_N) + \delta\Psi(r_1, r_2, \ldots, r_N),
\]

where the term $\delta\Psi(r_1, r_2, \ldots, r_N)$ must vanish at the singularity $r_1 = r_2$. From the above it follows that we need consider only terms of first-order in $r_{12}$ in $\delta\Psi$ when $r_1$ is near $r_2$. Dropping the subscript 12, and writing $r_{12}$ as $r$, we see that $\delta\Psi$ could have terms of the form $r_D B(r_2, r_3, \ldots, r_N)$, or $\sum_l n_l B_l(r_2, \ldots, r_N)$ where $l$ denotes the 2 to $(D - 1)$-dimensional subspace and $n_l$ the distance in the subspace, or $r \cdot C(r_2, \ldots, r_N)$. Here, $r_D = r$ is just the conventional distance in D dimensional space. As an example of the second kind of
terms, consider the case of D= 4. There are four 3-dimensional subspaces, and six 2-
dimensional subspaces. The distances in the 3-dimensional subspaces constitute the terms
\[ \sqrt{x_1^2 + x_2^2 + x_3^2}, \sqrt{x_1^2 + x_2^2 + x_4^2}, \sqrt{x_2^2 + x_3^2 + x_4^2}, \text{ and } \sqrt{x_1^2 + x_4^2 + x_3^2}. \]
The distances in the 2-dimensional subspaces are \( \sqrt{x_i^2 + x_j^2} \), where \( i \neq j \), and \( i, j = 1, 2, 3, 4 \). In the limit \( r \to 0 \), such terms do not affect the \( O(D) \) symmetry of the first two terms on the left side of Eq.(5). However, the Laplacian of these terms is singular since \( \nabla^2 r = \frac{d-1}{r} \), where \( r_d \) is the distance in the \( d \)-dimensional subspace. These singularities cannot be cancelled by the Coulomb potential energy singularity term of Eq.(5). Thus, their coefficients must vanish. Therefore, (recovering the subscript 12), Eq.(6) must be written as
\[ \Psi(r_1, r_2, \ldots, r_N) = \Psi(r_2, r_3, \ldots, r_N) + r_{12} B(r_2, r_3, \ldots, r_N) + r_{12} \cdot C(r_2, r_3, \ldots, r_N) + O(\epsilon^2) \] (7)
Next substitute Eq. (6) for \( \Psi(r_1, r_2, \ldots, r_N) \) into Eq.(4) and employ \( \nabla^2 r = 0 \). For the Coulomb potential energy singularity to be cancelled we have
\[ - \frac{1}{2 \mu_{12}} \frac{D-1}{r_{12}} B(r_2, r_3, \ldots, r_N) + \frac{Z_1 Z_2}{r_{12}} \Psi(r_2, r_3, \ldots, r_N) = 0. \] (8)
At the point of coalescence, the wavefunction is \( \Psi(r_2, r_3, \ldots, r_N) \). Since we require the wavefunction to be finite at this point we have
\[ B(r_2, r_3, \ldots, r_N) = \frac{2 Z_1 Z_2 \mu_{12}}{D-1} \Psi(r_2, r_3, \ldots, r_N). \] (9)
Thus, in the limit as \( r_{12} \to 0 \), we may write the wavefunction as
\[ \Psi(r_1, r_2, \ldots, r_N) = \Psi(r_2, r_3, \ldots, r_N) (1 + \frac{2 Z_1 Z_2 \mu_{12}}{D-1} r_{12}) + r_{12} \cdot C(r_2, r_3, \ldots, r_N). \] (10)
This is the general form of the integral cusp coalescence condition in D-dimension space. Note
that this expression is equally valid even if the wavefunction vanishes at the point of coalescence, i.e. if \( \Psi(r_2, r_3, \ldots, r_N) = 0 \). This latter is referred to as a node coalescence condition.
By taking the spherical average of Eq.(10) about the point of coalescence in D-dimension
space, we obtain the differential form of the cusp condition:
\[ \left( \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12} \to 0} = \frac{2 Z_1 Z_2 \mu_{12}}{D-1} \Psi(r_{12} = 0), \] (11)
where \( \bar{\Psi} \) is the spherically averaged wavefunction. For the electron-nucleus coalescence,
\( Z_1 = -1, Z_2 = Z \) the nuclear charge , and \( \mu_{12} \approx m_e \) the mass of the electron. For the
electron-electron coalescence, \( Z_1 = -1, Z_2 = -1, \mu_{12} = \frac{1}{2} m_e \). In \( D = 3 \) dimensions, the
traditional integral and differential cusp conditions are recovered.

It follows from the definition of the density $\rho(r_1)$ which is

$$\rho(r_1) = N \int \Psi^\ast(r_1, r_2, \ldots r_N)\Psi(r_1, r_2, \ldots r_N) dr_2 \ldots dr_N,$$

that the differential form of the electron-nucleus cusp condition may be expressed in terms of the density at and about the nucleus. In this case with the nuclear positions fixed, the wavefunction does not depend upon the nuclear coordinates. Then when the electron at $r_1$ approaches a nucleus, say fixed at the origin, the integral for the density which is over all the remaining $N - 1$ electrons can be performed. It is evident from the integral cusp coalescence condition Eq.(10) and the above definition of the density, that there can be no such differential form of the cusp condition for electron-electron coalescence. Such expressions in the literature [8] are therefore invalid.

It is however, possible to derive the integral and differential forms of the cusp condition in D-dimensions for the two-particle correlation function $p(r_1 r_2)$ defined as

$$p(r_1 r_2) = \frac{N(N - 1)}{2} \int \Psi^\ast(r_1, r_2, \ldots r_N)\Psi(r_1, r_2, \ldots r_N) dr_3 \ldots dr_N.$$  

(13)

In the limit as $r_1 \rightarrow r_2$ and employing the integral cusp expression of Eq.(10) we have that to first-order in $r_{12}$

$$p(r_1 r_2) = p(r_2 r_2)(1 + \frac{2Z_1Z_2\mu_{12}}{D - 1}r_{12})^2 + \frac{N(N - 1)}{2} \int (r_{12} \cdot C(r_2, \ldots r_N))^2 dr_3 \ldots dr_N + N(N - 1)(1 + \frac{2Z_1Z_2\mu_{12}}{D - 1}r_{12}) \int (r_{12} \cdot C(r_2, \ldots r_N))\Psi(r_2, r_2, \ldots r_N) dr_3 \ldots dr_N + O(\epsilon^3).$$  

(14)

This is the integral form of the cusp coalescence condition for the pair-correlation function. The differential form of the cusp condition for the correlation function is

$$\left( \frac{\partial \bar{p}(r_1 r_2)}{\partial r_{12}} \right)_{r_{12} \rightarrow 0} = \frac{4Z_1Z_2\mu_{12}}{D - 1} p(r_2 r_2).$$  

(15)

where $\bar{p}$ is the spherical average of the correlation function. The differential cusp condition derived for the uniform electron gas in dimensions $D = 3$ and 2 constitute a special case of this general form of the differential cusp condition.
III. CONCLUDING REMARKS

In this paper we have derived the integral and differential forms of the coalescence condition satisfied by the wavefunction at the coalescence of two charged particles in $D \geq 2$ dimensions. The corresponding integral and differential cusp conditions for the pair correlation function in $D \geq 2$ dimensional space are thereby derived. These results are also valid for the case of a more generalized Hamiltonian which includes a term of the form $\sum_i v(r_i)$, where $v(r_i)$ is a local external potential. This is because such terms do not contribute any singularities at the coalescence of the two charged particles. Such an external potential could effectively arise for example in the presence of an electric or magnetic field. The coalescence conditions constitute rigorous constraints on the construction and evaluation of approximate wavefunctions. Thus, having derived the integral coalescence condition for $D = 2$, we now understand that the approximate Laughlin wavefunction \cite{10} does in fact satisfy the node coalescence condition. The Laughlin wavefunction is

$$\Psi_m(z_1, ..., z_N) = \prod_{j<k} (z_j - z_k)^m \exp\left[-\frac{1}{4} \sum_{l} |z_l|^2 \right],$$

(16)

where $m$ is an odd integer, and $z_j = x_j + iy_j$ is the location of the $j$th particle expressed as a complex number. It is evident that this wavefunction satisfies the node coalescence condition for $m \geq 3$. The cusp conditions also impose constraints on the construction of approximate energy functionals within density functional theory \cite{14, 16}, and on the wavefunction functionals of the density employed in quantal density functional theory \cite{17}. The integral cusp condition in one dimension, (which is different in form from the result derived for dimension $D \geq 2$), and from which emanates some very interesting physics, is to be published elsewhere \cite{18}.

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