Electronic Wave Functions near Coalescence Points

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The behavior of many-electron wave functions near points where the positions of some of the electrons coincide or where they coincide with positions of nuclei is investigated. A representation theorem for many-electron functions near such points is given extending previous results of Kato (cusp conditions) and Hoffmann-Ostenhof and Seiler. Furthermore, the influence of the Pauli principle on the local behavior of fermionic wave functions near many-particle coalescence points is studied.

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We present here mathematically rigorous results on the behavior of many-electron wave functions at many-particle coalescence points; details of our proofs will appear elsewhere.

Let H be the nonrelativistic Hamiltonian of an N-electron atom or molecule with fixed nuclei in suitable units,

$$H=-\sum_{i=1}^{N}\Delta_i+V(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)\,, \tag{1}$$

where in the case of K nuclei with positions $\mathbf{X}_a$, $a=1,\dots,K$, and charges Z_a,

$$V=-\sum_{a=1}^{K}\sum_{i=1}^{N}\frac{Z_a}{|\mathbf{r}_i-\mathbf{X}_a|}+\sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\,. \tag{2}$$

We consider real-valued solutions ψ [1] to the corresponding Schrödinger equation $H\psi=E\psi$ (E is the energy) in the neighborhood of a many-particle coalescence point (CP). Let $G=\prod_{i<j}|\mathbf{r}_i-\mathbf{r}_j|\prod_{i,a}|\mathbf{r}_i-\mathbf{X}_a|$. A point $x_{\mathrm{CP}}=(\mathbf{r}_1^0,\dots,\mathbf{r}_N^0)\in\mathbf{R}^{3N}$ is called a coalescence point if $G(x_{\mathrm{CP}})=0$, that is to say, if some of the interelectronic or the electron-nuclear distances are zero. Here the $\mathbf{r}_i$ are the positions of the electrons; spin will only enter via permutation symmetry of $\psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$.

How does a many-electron wave function behave near such CP's? Since the potential is not defined at CP's, ψ will be nonanalytic there. The nature of this nonanalyticity is determined to a certain extent by the singularity of the potential. For two-particle CP's there are well-known results by Kato [2] which have found numerical applications [3], and for many-particle CP's see [4,5]. In [2] and [4] the local behavior of the suitable averaged wave function near a CP is described. These results are only nontrivial for the case where the considered wave function does not vanish at this CP. Without this restriction we give here a representation result for the wave function itself near a many-particle CP. (For a formal discussion in the case of two-particle CP's, see [6].)

Also the fermionic nature of many-electron systems influences the behavior of many-electron wave functions near CP's. At m-electron CP's ($m\geq 3$) an electronic wave function must vanish, but, and this will be made precise in Theorem 2, we will state how fast at least it must vanish.

Before we can state our results we have to introduce some notation. Let $d=3N$ and $x=(x_1,\dots,x_d)=(\mathbf{r}_1,\dots,\mathbf{r}_N)\in\mathbf{R}^d$ and $\Delta=\sum_{i=1}^{N}\Delta_i$, so that the Schrödinger equation reads

$$[-\Delta+V(x)]\psi=E\psi\,. \tag{3}$$

We introduce harmonic homogeneous polynomials $P_M(x_1,x_2,\dots,x_d)$ of degree M. This means that $\Delta P_M=0$ and $P_M(\lambda x)=\lambda^M P_M(x)$ for $\lambda\in\mathbf{R}^1$. We introduce d-dimensional polar coordinates $x=r\omega$, where $r=|x|$ and $\omega=x/|x|\in S^{d-1}$, with S^{d-1} the unit sphere in $\mathbf{R}^d$. In these coordinates P_M can be written as

$$P_M(r\omega)=r^M Y_M(\omega)\,, \tag{4}$$

where $Y_M(\omega)$ is a surface harmonic or "hyperspherical harmonic" [7,8], the d-dimensional generalization of the usual spherical harmonics. The Laplace operator in polar coordinates reads

$$\Delta=\frac{\partial}{\partial r^2}+\frac{d-1}{r}\frac{\partial}{\partial r}-\frac{L^2}{r^2}\,, \tag{5}$$

where $-L^2$ is the Laplace Beltrami operator on S^{d-1} (in three dimensions it would be angular momentum). A surface harmonic Y_M satisfies

$$L^2Y_M=M(M+d-2)Y_M\,. \tag{6}$$

Now suppose that $\psi(x_1,\dots,x_d)$ satisfies (3) with V given by (2) in the neighborhood of a CP. We translate x_{CP} into the origin, that is to say, $\mathbf{r}_i\to\mathbf{r}_i-\mathbf{r}_i^0$. Obviously we can split V given by (2) in these new coordinates [still denoted by $(x_1,\dots,x_d)$] in a unique way so that

$$V-E\to W/r+U\,, \tag{7}$$

where U is bounded in a sufficiently small d-dimensional ball centered at the origin. W is homogeneous of degree zero so that $W=W(\omega)$.

We can now formulate our representation result for real-valued solutions ψ_{CP} of

$$(-\Delta+W/r+U)\psi_{\mathrm{CP}}=0 \tag{8}$$

in the neighborhood of the origin.

Theorem 1.—Let $\psi_{\mathrm{CP}}\not\equiv 0$ be a real-valued solution to (8) in the neighborhood of the origin. Then there exists a harmonic homogeneous polynomial $P_M=r^M Y_M\not\equiv 0$ of degree M such that the behavior of ψ_{CP} for $r\rightarrow 0$ is determined by this P_M in the following way: Writing ψ_{CP} as

$$\psi_{\mathrm{CP}}(r\omega)=Y_M(\omega)\int_{S^{d-1}}\psi_{\mathrm{CP}}(r\omega)Y_M(\omega)d\omega+\eta(r\omega)$$

(so obviously, $\int\psi_{\mathrm{CP}}\eta\, d\omega=0$), then, for $r\rightarrow 0$,

$$\psi_{\mathrm{CP}}=P_M\{1+a_M r+O(r^2)\}+\eta(r\omega), \tag{9}$$

with

$$a_M=\frac{1}{2M+d-1}\frac{\int Y_M^2 W d\omega}{\int Y_M^2 d\omega} \tag{10}$$

and

$$|\eta|=O(r^{M+1}). \tag{11}$$

Here $d\omega$ means surface measure on S^{d-1}, and O denotes the usual order relation.

There is an immediate consequence of (9)–(11) which relates to the "cusp conditions" in Refs. [2,4,5] (which are nontrivial only if $M=0$).

Corollary.—Let $\psi_{\mathrm{av}}^{(M)}(r)=r^{-M}(\int\psi_{\mathrm{CP}}^2 d\omega)^{1/2}$. Then

$$\left[\frac{d}{dr}\psi_{\mathrm{av}}^{(M)}\right](0)=a_M\psi_{\mathrm{av}}^{(M)}(0). \tag{12}$$

To see this we first note that by Theorem 1,

$$\int\psi_{\mathrm{CP}}^2 d\omega=r^{2M}\int Y_M^2 d\omega[1+2a_M r+O(r^2)]+O(r^{2M+2}).$$

This implies $\psi_{\mathrm{av}}^{(M)}(r)=(\int Y_M^2 d\omega)^{1/2}[1+a_M r+O(r^2)]$ from which (12) follows immediately.

Some remarks and explications might be appropriate. (i) Theorem 1 holds true in an appropriate formulation for general Coulombic systems, hence with moving nuclei. (ii) We also want to emphasize that the splitting of ψ_{CP} into $Y_M\int\psi_{\mathrm{CP}}Y_M d\omega$ and η is natural since a_M is uniquely determined by P_M whereas η is not. (iii) In general P_M in Theorem 1 is not known and, as the hydrogen atom shows, M can be any non-negative integer. If P_M is known then a_M can be calculated in principle; e.g., for the ground state of orthohelium it is known that ψ behaves near the nucleus like $P_2=|\mathbf{r}_1|^2-|\mathbf{r}_2|^2$ [9]. (iv) Let us consider the relation of our results on the local behavior of a wave function to those using Fock expansions. We mention here only a few important more recent results [9–12]. There one tries to expand the wave function near a CP in terms of powers of r and $\ln r$ (where the coefficients are functions of ω), and according to these investigations the first nonvanishing term where logarithms show up is of order $r^{M+2}|\ln r|$. Clearly such a series has to satisfy (9)–(11) of Theorem 1 [in particular it must have the property (12)], and the first logarithmic term is contained in η. (v) The potential in (2) depends only on interparticle distances implying that $W(\omega)=W(-\omega)$ in (8). Without this symmetry property Theorem 1 would not be true. For example, take $d=3$ and $V=x_1(x_1^2+x_2^2+x_3^2)^{-1}$. Then we can show that a local solution ψ of $\Delta\psi=V\psi$ behaves in general like $\psi=P_M+O(r^{M+1}|\ln r|)$ for some $P_M\not\equiv 0$ in the neighborhood of the origin. (vi) If x_{CP} is not a CP then in (8) $W\equiv 0$ and hence $a_M=0$ in Theorem 1. But (9) and (11) remain valid. In fact two of us [13] recently proved a representation result like Theorem 1 for rather general potentials. The present result is a considerable strengthening of these findings for the Coulombic case.

Sketch of proof.—The proof of Theorem 1 is based on results derived in Ref. [13]. The relevant result for our purposes reads as follows for the Coulombic case: If ψ_{CP} does not vanish faster than polynomially, then for some $P_M=r^M Y_M\not\equiv 0$,

$$\begin{gathered}\psi_{\mathrm{CP}}=P_M+\phi\,,\\ \phi=O(r^{M+\delta})\ \text{for}\ r\rightarrow 0\ \text{for any}\ 0<\delta<1\,.\end{gathered} \tag{13}$$

That ψ does not vanish faster than polynomially at CP's is a consequence of the strong unique continuation property [14] of the Schrödinger operator given in (3) [15].

Now let $\{Y_{l,m}\}$ denote the set of orthonormal real-valued hyperspherical harmonics on S^{d-1}, where $l=0,1,2,\ldots$ and $0\le m\le h(l)-1$, with

$$h(l)=\frac{(2l+d-2)(l+d-3)!}{(d-2)!l!}$$

and [compare (6)]

$$L^2 Y_{l,m}=l(l+d-2)Y_{l,m}. \tag{14}$$

Without loss of generality we assume $Y_M=Y_{M,0}$. Further, we represent ψ_{CP} by

$$\psi_{\mathrm{CP}}(r\omega)=\sum_{l=0}^{M+1}\sum_{m=0}^{h(l)-1}\psi_{l,m}(r)Y_{l,m}(\omega)+\mu(r\omega), \tag{15}$$

with

$$\psi_{l,m}(r)=\int_{S^{d-1}}\psi_{\mathrm{CP}}Y_{l,m}d\omega \tag{16}$$

and

$$\int\mu Y_{l,m}d\omega=0\ \text{for}\ 0\le l\le M+1. \tag{17}$$

We investigate the terms in (15) separately: Multiplication of Eq. (8) from the left by $Y_{l,m}$ and integration over S^{d-1} leads, taking (13) into account, to

$$-\psi''_{l,m}-\frac{d-1}{r}\psi'_{l,m}+\frac{l(l+d-2)}{r^2}\psi_{l,m}$$

$$=-\int_{S^{d-1}}Y_{l,m}\left(\frac{W}{r}+U\right)(P_M+\phi)d\omega\,. \quad (18)$$

Using ordinary differential equation techniques it can be easily shown that for $r\rightarrow 0$

$$\psi_{M,0}=r^M[1+a_Mr+O(r^{1+\delta})]\ \ [a_M \text{ given by (10)}]\,, \quad (19)$$

whereas for the other cases with $l\leq M+1$,

$$\psi_{l,m}=O(r^{M+1})\,. \quad (20)$$

To obtain (20) for $l=M+1$, $W(\omega)=W(-\omega)$ is essential.

Now assume for the moment that

$$\mu(r\omega)=O(r^{M+1})\,, \quad (21)$$

then we obtain, by inserting (20) and (21) into (15),

$$\psi_{\mathrm{CP}}=\psi_{M,0}Y_M+\eta(r\omega)\,, \quad (22)$$

with η satisfying (11). Further by (19) we get

$$\psi_{\mathrm{CP}}=r^MY_M[1+a_Mr+O(r^{1+\delta})]+\eta\,. \quad (23)$$

But as a result of (18), by variation of constants,

$$\psi_{M,0}=r^M\left[1+\int_0^r t^{-2M-d+1}\int_0^t s^{M+d-1}\int_{S^{d-1}}Y_M\left(\frac{W(\omega)}{s}+U(s\omega)\right)\psi_{\mathrm{CP}}(s\omega)d\omega\,ds\,dt\right]\,, \quad (24)$$

so that (23) and (24) finally lead to

$$\psi_{M,0}=r^M[1+a_Mr+O(r^2)]\,,$$

which together with (22) verifies (9).

Hence it remains to show the validity of (21): Let Q_{M+1} denote the orthogonal projection of $L^2(S^{d-1})$ onto the linear span of $\{Y_{l,m}: l>M+1,\ 0\leq m\leq h(l)-1\}$, then clearly $Q_{M+1}\psi_{\mathrm{CP}}=\mu$ and $\Delta\mu=Q_{M+1}(V\psi_{\mathrm{CP}})$. Since in the quadratic form sense $Q_{M+1}L^2Q_{M+1}\geq M(M+d)Q_{M+1}$ it can be shown that $f(r)=\{\int[\mu(r\omega)]^2d\omega\}^{1/2}$ satisfies for small r the differential inequality

$$-f''-\frac{d-1}{r}f'+\frac{M(M+d)}{r^2}f\leq \mathrm{const}\times r^{M-1}\,.$$

This implies (via standard comparison techniques) that $f(r)=O(r^{M+1})$. But μ satisfies an inhomogeneous equation so we can use a mean value inequality due to Hinz and Kalf [16] suitably adopted for our purposes (see Ref. [13]) to obtain from the L^2 estimate for μ (namely, the estimate for f), a pointwise estimate for μ proving (21). Thereby the actual Coulombic nature of the potential plays an essential role.

We now discuss the influence of the Pauli principle on the behavior of many-electron wave functions near many-electron CP's. In nonrelativistic quantum mechanics spin can be accounted for entirely by requiring that an N-electron wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ transforms according to specific irreducible representations of the symmetric group $\mathcal{S}^N$. From Theorem 1 we have near an N-electron CP, x_{CP}, which we take without loss to be the origin, that

$$\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)=P_M(\mathbf{r}_1,\ldots,\mathbf{r}_N)+O(|x|^{M+1})\,. \quad (25)$$

Now if ψ transforms according to some irreducible representation of $\mathcal{S}^N$, P_M must show the same transformation properties [17].

Let us first discuss the case where the total spin $s=N/2$, so that both ψ and P_M in (25) must be antisymmetric with respect to interchange of any pair $(\mathbf{r}_i,\mathbf{r}_j)$. We want to determine the smallest possible M such that a harmonic homogeneous polynomial $P_M(\mathbf{r}_1,\ldots,\mathbf{r}_N)\not\equiv 0$ exists, satisfying this requirement. This can be done fairly easily using Cartesian coordinates; with hyperspherical coordinates this might turn out to be tedious [8,18].

We indicate the construction of such a minimal P_M. Let for given $\varphi_i(\mathbf{r}_i)$, $i=1,\ldots,N$, ϕ_N be the corresponding Slater determinant; hence

$$\phi_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\mathcal{A}\prod_{i=1}^N\varphi_i(\mathbf{r}_i)\,, \quad (26)$$

where $\mathcal{A}$ is the usual antisymmetrizer [19].

Let $\mathbf{r}_i=(x_i,y_i,z_i)$. We pick for the $\varphi_i(x_i,y_i,z_i)$ monomials in increasing order, so that $\varphi_i(\mathbf{r}_i)$ for $i=1,2,\ldots,N$ becomes 1, $x_2,y_3,z_4,x_5^2,y_6^2,z_7^2,x_8y_8,\ldots,x_{11}^3,y_{12}^3,\ldots$. So we have one monomial of degree 0, three of degree 1, six of degree 2, etc., or $n_m=\frac{1}{2}(m+1)(m+2)$ of degree m. We claim that with this choice (important is that no monomial is missing) ϕ_M is indeed harmonic and has minimal degree. To see this we note that

$$\Delta\mathcal{A}\prod_{i=1}^N\varphi_i(\mathbf{r}_i)=\mathcal{A}\sum_{j=1}^N\Delta_j\varphi_j(\mathbf{r}_j)\prod_{i\neq j}^N\varphi_i(\mathbf{r}_i)\,. \quad (27)$$

Here we used the fact that Δ (symmetric in the particle coordinates) commutes with $\mathcal{A}$ as well as the linearity of $\mathcal{A}$. But $\Delta_j\varphi_j$ is a linear combination of monomials which already occur among the other φ_j by our construction, so $\Delta\phi_N\equiv 0$.

Using (28) it is not difficult to determine the degree $g(N)$ of the polynomial ϕ_N and some of its properties. We summarize our findings.

Proposition 1.—

$$g(N)=\tfrac{1}{8}k(k+1)(k+2)(k+3)+\beta(N)(k+1)\,, \quad (28)$$

where $k=[\alpha]$, the largest integer $\leq\alpha$, and where α is the unique positive root of the cubic equation

$$(a+1)(a+2)(a+3)=6N \tag{29}$$

and

$$\beta(N)=N-\tfrac{1}{6}(k+1)(k+2)(k+3)\,. \tag{30}$$

Further, for any two integers N_1 and N_2,

$$g(N_1+N_2)\geq g(N_1)+g(N_2)\geq 2g([(N_1+N_2)/2])\,. \tag{31}$$

For large N, $g(N)$ satisfies

$$g(N)=\tfrac{1}{8}(6N)^{4/3}-\tfrac{3}{2}N+\tfrac{1}{24}(6N)^{2/3}+O(N^{1/3})\,. \tag{32}$$

The functions $\varphi_1,\ldots,\varphi_N$ are ordered in "blocks" of different monomials with the same degree m. A block is complete if it has length n_m. Further, k in (28) is the degree of the polynomials in the highest closed block. $\beta(N)$ is the number of monomials of degree $k+1$ which do not form a complete block. Obviously, $0\leq\beta(N)<\frac{1}{2}(k+2)(k+3)$. If $\beta\neq 0$, there are $\binom{n_k+1}{\beta}$ equivalent P_M's. (31) follows easily from the construction and the asymptotics of $g(N)$ follow from (28)-(30).

Let us now consider the general case; hence we consider an N-electron function $\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ that satisfies (25) with given spin s. Let N_1 and N_2 be integers such that

$$s=(N_2-N_1)/2,\quad N_1+N_2=N,\quad N_2\geq N_1\geq 0\,. \tag{33}$$

From the representation theory of the symmetric group $\mathcal{S}^N$ [19] it is straightforward to show the following generalization of proposition 1.

Theorem 2.—Suppose we have an N-electron wave function satisfying (25) with total spin s. Then $\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ must vanish at an N-electron CP at least like

$$M(N,s)=g(N/2+s)+g(N/2-s)\,. \tag{34}$$

Furthermore, denoting $M_0(N):=\min_s M(N,s)$,

$$M_0(N)=\begin{cases}2g(N/2), & N \text{ even},\\ g(N/2+\frac{1}{2})+g(N/2-\frac{1}{2}), & N \text{ odd},\end{cases} \tag{35}$$

and for $N\to\infty$,

$$M_0(N)=\tfrac{1}{4}(3N)^{4/3}-\tfrac{3}{2}N+\tfrac{1}{12}(3N)^{2/3}+O(N^{1/3})\,. \tag{36}$$

Some remarks might be appropriate. (i) At m-electron CP's, $m<N$, $\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ must vanish at least of order $M_0(m)$. (ii) $M(N,s)$ is minimal for $s=0$ or $\frac{1}{2}$, a consequence of (32). So for ground states of atoms where s can be larger than $\frac{1}{2}$, $M_0(N)$ will be a lower bound to the order of vanishing at N-electron CP's. But for other systems $M(N,s)$ is indeed achieved (e.g., harmonic oscillator). (iii) The $N^{4/3}$ behavior looks a bit like Thomas-Fermi theory though no energy considerations were made. For ν-dimensional particles, $g_\nu(N)\sim N^{(\nu+1)/\nu}$.

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[1] Strictly speaking, ψ is a distributional solution (see any modern book on elliptic partial differential equations). Since V is real valued, the requirement that ψ be real valued is no restriction.

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[14] There is a rich literature on unique continuation. For a recent survey, see C. Kenig, in *Harmonic Analysis and Partial Differential Equations*, edited by J. Garcia-Cuerva, Lecture Notes in Mathematics Vol. 1384 (Springer, Berlin, 1989), pp. 69-89.

[15] Surprisingly the strong unique continuation property as we need it for Theorem 1 has not been established earlier. We shall give a rather simple proof in our detailed version of this paper combining an ansatz due to Leray [10] with a result presented in L. Hörmander, Commun. Partial Diff. Eq. **8**, 21 (1983).

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[17] Obviously if ψ has other specific transformation properties, e.g., a definite angular momentum or some other spatial symmetry, this must show up in the symmetry properties of the corresponding P_M.

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