Cusp conditions for eigenfunctions of n-electron systems

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Cusp conditions are derived for eigenfunctions of many-electron systems for the coalescence of more than two particles.

We consider an n-electron system described by the Hamiltonian in the infinite nuclear mass approximation:

$$H = -\tfrac{1}{2}\sum_{i=1}^{n}\Delta_i - Z\sum_{i=1}^{n} r_i^{-1} + \sum_{i<j}^{n} |x_i - x_j|^{-1}, \qquad (1)$$

$$x_i \in \mathbb{R}^3, \qquad r_i = |x_i| \;\forall i,$$

where Z denotes the nuclear charge. Let $\psi(x_1, \ldots, x_n)$ denote a (real) solution of the Schrödinger equation

$$(H - E)\psi = 0, \qquad (2)$$

with E its corresponding eigenvalue. Spin enters only via permutation symmetry.

It is well known that such an eigenfunction is a C^∞ function on $\mathbb{R}^{3n}\backslash M$, M denoting the set of points where the potential becomes singular.[1,2] At singularities $x_1 = 0$, $x_i \neq 0$ $\forall i > 1$ and $x_1 = x_2$, $x_i \neq x_j$, $x_i \neq x_1$, x_2 $\forall i$, $j > 2$ the eigenfunctions obey Kato's cusp conditions[1] and similar results hold for particle densities.[3-6] To our knowledge, there are almost no results on the behavior of eigenfunctions at coalescence points of more than two particles: For the simplest case, the two-electron atom, attempts have been made to expand the ground state $\psi(x_1, x_2)$ in the neighborhood of $R = (x_1^2 + x_2^2)^{1/2} = 0$ in powers of R and $\ln R$.[7,8]

In the following we shall derive cusp conditions for eigenfunctions at such points where more than two particles coalesce. The procedure is related to the derivation of the cusp condition for the one-electron density in Ref. 6.

We first fix the notation

$$V_k(x_1, \ldots, x_k) = -Z\sum_{i=1}^{k} r_i^{-1} + \sum_{i<j}^{k} |x_i - x_j|^{-1} \quad (1 \leq k \leq n). \qquad (3)$$

We shall use $3k$-dimensional spherical coordinates and write $(x_1, \ldots, x_k) = R\omega$, where $R^2 = \sum_{i=1}^{k} x_i^2$ and ω is the angular part (See, for instance, Ref. 7).

Further, we introduce $y = (x_{k+1}, \ldots, x_n)$. For notational simplicity, the index k in R, ω, and y is suppressed. By D_k we denote the set of all $y \in \mathbb{R}^{3(n-k)}$, for which $x_i \neq x_j$ for $k+1 \leq i, j \leq n$, and $x_i \neq 0$ for $k+1 \leq i \leq n$. Let S^{3k-1} denote the unit sphere in $\mathbb{R}^{3k}$ with the surface $\sigma_{3k-1} = 2\pi^{3k/2}/\Gamma(3k/2)$. ψ averaged over the angular part of $(x_1, \ldots, x_k)$ is defined by

$$\psi_{\mathrm{av}}(R, y) = \sigma_{3k-1}^{-1}\int_{S^{3k-1}} \psi(R\omega, y)\, d\omega. \qquad (4)$$

ψ obeys the following cusp condition.

Theorem 1.

For $y \in D_k$

$$\left.\frac{\partial \psi_{\mathrm{av}}(R, y)}{\partial R}\right|_{R=0} = C\left(-Zk + \frac{k(k-1)}{2\sqrt{2}}\right)\psi(0, y),$$

$$C = \frac{4}{(3k-1)\sqrt{\pi}}\,\frac{\Gamma(3k/2)}{\Gamma((3k-1)/2)}.$$

Proof. We rewrite (2) as

$$-\frac{\partial^2 \psi}{\partial R^2} - \frac{3k-1}{R}\frac{\partial \psi}{\partial R} + W\psi = 0, \qquad (6)$$

where

$$W = R^{-2}L_{3k}^2 - \sum_{i=k+1}^{n}\Delta_i + 2(V_n - E), \qquad (7)$$

with $R^{-2}L_{3k}^2$ denoting the angular part of $-\sum_{i=1}^{k}\Delta_i$. Multiplying (6) by R and introducing

$$u = R^{(3k-1)/2}\psi, \qquad (8)$$

we obtain

$$-R^{-(3k-1)/2+1}\frac{\partial^2 u}{\partial R^2} + \left(\frac{3k-1}{2} - 1\right)\frac{3k-1}{2}R^{-1}\psi + RW\psi = 0. \qquad (9)$$

Now we integrate (9) over $[\delta, R]$, $\delta > 0$. By partial integration of the first term we arrive, for $\delta \to 0$, at

$$-(3k-2)[\psi(R\omega,y)-\psi(0,y)]-R\frac{\partial\psi(R\omega,y)}{\partial R}+\int_0^R R'W\psi\,dR'=0. \tag{10}$$

Next we average (10) over the angular part, divide by R, and take the limit $R\to 0$. This leads to

$$\frac{\partial\psi_{av}(R,y)}{\partial R}\bigg|_{R=0}=[(3k-1)\sigma_{3k-1}]^{-1}\lim_{R\to 0}R^{-1}\int_0^R\int_{S^{3k-1}}R'W\psi\,d\omega\,dR'=[(3k-1)\sigma_{3k-1}]^{-1}\lim_{R\to 0}\int_{S^{3k-1}}RW\psi\,d\omega. \tag{11}$$

For $y\in D_k$ it is easily seen that

$$\lim_{R\to 0}R\int_{S^{3k-1}}\Big(-\sum_{i=k+1}^{n}\Delta_i+2(V_n-V_k-E)\Big)\psi\,d\omega=0. \tag{12}$$

Further, since L_{3k}^2 is an essentially self-adjoint operator on $C^\infty(S^{3k-1})$ (Ref. 9),

$$\int_{S^{3k-1}}1\cdot L_{3k}^2\psi\,d\omega=0\quad\text{for all } R. \tag{13}$$

Combining (11)–(13) and recognizing that $\psi(0,y)$ does not depend on ω, we obtain

$$\frac{\partial\psi_{av}(R,y)}{\partial R}\bigg|_{R=0}=[(3k-1)\sigma_{3k-1}]^{-1}\times\int_{S^{3k-1}}RV_k(R\omega)d\omega\,\psi(0,y)\quad(y\in D_k). \tag{14}$$

For the evaluation of the integral we need

$$\int_{S^{3k-1}}R\,|x_1|^{-1}d\omega=\frac{4\pi^{(3k-1)/2}}{\Gamma\left(\frac{3k-1}{2}\right)}\quad(1\le k\le n), \tag{15}$$

$$\int_{S^{3k-1}}R|x_1-x_2|^{-1}d\omega=\frac{2\sqrt{2}\,\pi^{(3k-1)/2}}{\Gamma\left(\frac{3k-1}{2}\right)}\quad(2\le k\le n). \tag{16}$$

We indicate the calculation of (15): Noting that

$$\int_{\mathbb{R}^{3k}}|x_1|^{-1}\delta\Big(\sum_{i=1}^{k}x_i^2-R^2\Big)dx_1\ldots dx_k=\tfrac{1}{2}R^{3k-2}\int_{S^{3k-1}}|R\omega|^{-1}d\omega, \tag{17}$$

we have

$$\int_{S^{3k-1}}R\,|x_1|^{-1}d\omega=R^{-3(k-1)}\sigma_{3k-4}\int_{|x_1|<R}(R^2-x_1^2)^{3(k-1)/2-1}|x_1|^{-1}dx_1$$

$$=2\pi\sigma_{3k-4}B(1,3(k-1)/2)=4\pi^{(3k-1)/2}/\Gamma((3k-1)/2), \tag{18}$$

where B denotes the beta function. Equation (16) is obtained analogously. Combining (14), (15), and (16), (5) follows.

Remarks:

(1) For convenience we considered $x_1=\cdots=x_k=0$; analogous results hold, of course, for $x_{i_1}=\cdots=x_{i_k}=0$ $(1\le i_j\le n)$.

(2) For $k=1$ we have $C=1$, and (5) is identical with Kato's result.[1]

(3) If $\psi(x_1,\ldots,x_n)$ is a mathematical ground state (i.e., no symmetry restrictions) of a Coulombic system, then $\psi>0$ for $r_i<\infty$ $(1\le i\le n)$.[10,11] Therefore, Theorem 1 implies

$$\frac{\partial\psi_{av}(R,y)}{\partial R}\bigg|_{R=0}<0\quad(y\in D_k) \tag{19}$$

for neutral systems, positive ions, and negative ions up to charge -2 (provided $Z\ge 1$). Particularly for the two-electronic case the physical and mathematical ground state coincide, so we have $\partial\psi_{av}(0)/\partial R<0$ for $k=1,2$.

(4) We note that the series expansion for the two-electron ground state in powers of R and $\ln R$,[7,8] which was mentioned before, has the correct cusp behavior [see (5)] for $R=0$. We now give the cusp condition for coalescence points $x_1=\cdots=x_k=x$ $(k\ge 2)$, $x\neq 0$. Let

$$\psi_{av}(R;X,y)=\sigma_{3k-1}^{-1}\int_{S^{3k-1}}\psi(R\omega+X,y)d\omega,\quad X\in\mathbb{R}^{3k} \tag{20}$$

the mean value of ψ taken over the surface of the ball $B_{3k}(X,R)$. For $X=(x,\ldots,x)$, $x\in\mathbb{R}^3$, $R^2=\sum_{i=1}^{k}(x_i-x)^2$ and we have the following theorem.

Theorem 1'.

For $y\in D_k$, $k\ge 2$, $x\neq 0$

$$\frac{\partial\psi_{av}(R;X,y)}{\partial R}\bigg|_{R=0}=C\frac{k(k-1)}{2\sqrt{2}}\psi(x,\ldots,x,y), \tag{21}$$

with C given in (5). The proof of (21) is essentially the same as for (5). This is easily seen by using

the transformation $\bar{x}_i = x_i - x$ $(1 \leq i \leq k)$ and reformulate the Schrödinger equation in the coordinates $\bar{x}_1, \ldots, \bar{x}_k, x_{k+1}, \ldots, x_n$.

Remarks:

(5) For $k=2$, the constant occurring on the right-hand side of (21) equals $32/(15\sqrt{2}\pi)$. This cusp condition differs from Kato's[1]

$$\left.\frac{\partial\tilde{\psi}(|x_1-x_2|, x_1+x_2)}{\partial|x_1-x_2|}\right|_{|x_1-x_2|=0} = \tfrac{1}{2}\psi\left(\frac{x_1+x_2}{2}, \frac{x_1+x_2}{2}\right), \tag{22}$$

due to the different way of averaging ψ: $\tilde{\psi}$ means the average of ψ taken over the sphere $|x_1 - x_2| = \text{const}$, with fixed $x_1 + x_2$.

(6) Due to the Pauli principle, a wave function ψ of an n-electron system vanishes at coalescence points of more than two electrons. Therefore by Theorem 1 and 1′

$$\left.\frac{\partial\psi_{av}(R,y)}{\partial R}\right|_{R=0} = \left.\frac{\partial\psi_{av}(R;X,y)}{\partial R}\right|_{R=0} = 0, \quad \text{for } y \in D_k, \quad (k>2).$$

Of course, it is straightforward to extend the results above to molecules with fixed nuclei. For instance, let us consider for simplicity a system with two nuclei and two electrons described by

$$H = -\tfrac{1}{2}\sum_{i=1}^{2}\Delta_i - \sum_{i=1}^{2}\left(\frac{Z_1}{|x_i - Y_1|} + \frac{Z_2}{|x_i - Y_2|}\right) + \frac{1}{|x_1 - x_2|}. \tag{23}$$

Then we obtain in an analogous manner

$$\left.\frac{\partial\psi_{av}(R;(Y_i,Y_i))}{\partial R}\right|_{R=0} = \frac{32}{15\pi}\left(-2Z_i + \frac{1}{\sqrt{2}}\right)\psi(Y_i, Y_i) \quad (i=1,2), \tag{24}$$

$$\left.\frac{\partial\psi_{av}(R;(Y_1,Y_2))}{\partial R}\right|_{R=0} = -\frac{32}{15\pi}(Z_1+Z_2)\psi(Y_1, Y_2), \tag{25}$$

and

$$\left.\frac{\partial\psi_{av}(R;(x,x))}{\partial R}\right|_{R=0} = \frac{32}{15\pi}\frac{1}{\sqrt{2}}\psi(x,x), \quad x \neq Y_1, Y_2 \tag{26}$$

with $\psi_{av}(R;X)$ always defined according to (20).

Furthermore, our procedure should also extend to general Coulombic many-particle systems; however, things become obscured by mass-weighted coordinates. Finally, it is straightforward to show that analogous results to (5) and (21), respectively, hold for the many-particle densities of bound states

$$\rho_k(x_1, \ldots, x_k) = \int_{\mathbb{R}^{3(n-k)}} |\psi(x_1, \ldots, x_n)|^2 \times dx_{k+1}, \cdots dx_n, \quad k \geq 1, \tag{27}$$

namely,

$$\left.\frac{d\tilde{\rho}_k(R;X)}{dR}\right|_{R=0} = 2C\left(-Zk\delta_{x,0} + \frac{k(k-1)}{2\sqrt{2}}\right)\rho_k(x, \ldots, x), \tag{28}$$

with C given in (5), $\delta_{x,0}$ denoting the Kronecker delta, and $\tilde{\rho}_k$ denoting the mean value of ρ_k analogously defined as in (20). For $k=1$, (28) reduces to the well known result for ρ_1.

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