THE CUSP CONDITIONS FOR MOLECULAR WAVE FUNCTIONS*

by

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Abstract

The cusp conditions are derived which describe the behavior of the wave function at the singularities of the Coulomb potential corresponding to the coalescence of two or more particles. In this derivation, the wave function is not spherically averaged; the fixed-nuclei approximation is not required; and the wave function may have nodes at the singular points. In addition to the general treatment, the cusp conditions for diatomic molecules are discussed in three different coordinate systems.

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I. Introduction

Let us consider a spatial* wave function, $\Phi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, which is an exact solution of the N-particle, non-relativistic Schrödinger equation,

$$(H - E)\Phi = 0. \tag{1}$$

Here, the Hamiltonian, $H = T + V$, is the sum of the kinetic energy operator, T, and the potential energy, V. The potential energy is the sum of Coulombic terms and is thus singular where any two particles coalesce. Now, Kato[1] has proved that Φ is everywhere bounded. Hence, $E\Phi$ and $H\Phi$ are everywhere bounded, and the singularities of V must be exactly cancelled in $H\Phi = (T+V)\Phi$. This cancellation will occur only if Φ has cusps (or nodes) at the singular points of V. We thus define the <u>cusp conditions</u> as descriptions of the proper behavior of Φ at those singular points.

For an N-electron atom in the heavy-nucleus approximation, Kato[1] proved the following cusp conditions:

$$\left(\frac{\partial \hat{\Phi}}{\partial r_{12}}\right)_{r_{12}=0} = \gamma (\Phi)_{r_{12}=0}. \tag{2}$$

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* All spin dependence is omitted until Section VI.

Here, r_{12} is the distance between the coalescing particles 1 and 2; $\hat{\Phi}$ is Φ averaged over a small sphere about the singularity; and γ is a constant. At an electron-electron singularity, $\gamma = \frac{1}{2}$, while at a nucleus-electron singularity, γ = -Z. Here Z is the nuclear charge.

Bingel[2] has integrated Kato's result and removed the spherical average restriction by adding an angular dependent term to obtain

$$\Phi = (\Phi)_{r_{12}=0}\left[1 + \gamma r_{12} + \underline{u}_{12} \cdot \underline{r}_{12} + O(r_{12}^2)\right], \tag{3}$$

where

$$\underline{u}_{12} = (\underline{\nabla}_{12}\Phi)_{r_{12}=0} \Big/ (\Phi)_{r_{12}=0} - \gamma\, \underline{r}_{12}/r_{12} \,.$$

$\underline{u}_{12}$ depends on the other particles and is not fully specified by the behavior of Φ at $r_{12}=0$. Eq. (3) is valid for molecules as well as atoms, but it is valid only in the fixed-nuclei approximation, and it does not apply if Φ has a node at $r_{12}=0$. From Eq. (3) Bingel derived the cusp conditions on the first order density matrix and the probability density. Steiner[3] has also derived the cusp conditions on the probability density of an N-electron atom. Hirschfelder[4] has presented a method for removing electron-electron singularities from the Hamiltonian, but it has limited applicability since the resulting Hamiltonian is not Hermitian.

In our study, the cusp conditions are derived directly by solving the Schrödinger equation where two particles are very close together. The fixed-nuclei approximation and angular averaging are not required, and nodes in Φ are allowed. As a special case we discuss the cusp conditions in confocal elliptic coordinates for fixed-nuclei diatomic molecules. Then, we consider the coalescence of three or more particles and generalize our two-particle results to find many-particle cusp conditions which are sufficient to insure removal of all singularities involved. No difficulty results from the inclusion of spin in the wave function.

The satisfaction of the cusp conditions should improve an approximate wave function. Indeed, an approximate wave function must satisfy the cusp conditions to give good values for either the charge density near the Coulomb singularities or the field gradient ($\propto r_{12}^{-3}$). In addition, the removal of the singularities is probably particularly important in perturbation theory[5]. But the satisfaction of the cusp conditions does not seem to greatly affect the energy calculated by variational treatments. Roothaan and Weiss[6] carried out Hartree-Fock and Rayleigh-Ritz energy optimization calculations on Helium using correlated orbitals of several forms. The values of γ which they obtained from their wave functions converged very slowly toward the correct values as more general orbital forms were chosen. Similar slow convergence of the value of γ was observed by Kolos and Roothaan[7] in their calculations of correlated orbitals for the H_2 molecule. In fact, the convergence is so slow that, as Pekeris[8] noted, his extremely accurate, 1078-term Helium wave function still has a 5 per cent error in its electron-electron value of γ. However, Kim, Chang, and Hirschfelder[9] found that imposing the cusp conditions on a Guillemin-Zener wave function for H_2^+ did not raise the calculated energy significantly. And Conroy[10] used the cusp conditions to restrict his choice of wave functions in his variational calculations of the energy of a number of small diatomic molecules.

II. Derivation of the Cusp Conditions

We derive the cusp conditions by expanding the Schrödinger equation about a singular point of the potential, V. Let us begin by putting the equation into a form which simplifies the expansion. In a space-fixed coordinate system the N-particle Schrödinger equation is

$$\left[-\sum_{i=1}^{N}\frac{1}{2m_i}\nabla_i^2+\sum_{1=i<j}^{N}\frac{Z_iZ_j}{r_{ij}}-E\right]\Phi=0. \tag{4}$$

Eq. (4) is in atomic units: the distances, r_{ij} , are in units of the Bohr radius, the masses, m_i , are in units of the electron mass, and the charges, Z_i , are in units of the proton charge. Let us focus attention on particles 1 and 2 (which could be any two of the N particles) by transforming to their center of mass, $\underline{\sigma}_{12}=(m_1\underline{r}_1+m_2\underline{r}_2)/(m_1+m_2)$, and relative, $\underline{r}_{12}=\underline{r}_1-\underline{r}_2$, coordinates.* We leave the coordinates of particles 3,..., N unchanged. Then,

$$-\frac{1}{2m_1}\nabla_1^2-\frac{1}{2m_2}\nabla_2^2=\frac{-1}{2(m_1+m_2)}\nabla_\sigma^2-\frac{1}{2\mu_{12}}\nabla_r^2, \tag{5}$$

where $\mu_{12}=m_1m_2/(m_1+m_2)$, $\underline{\nabla}_r=\hat{i}\,\frac{\partial}{\partial(x_1-x_2)}+\cdots$, and $\underline{\nabla}_\sigma=\hat{i}\,\frac{\partial}{\partial(\sigma_{12})_x}+\cdots$. And with all dependence on particles 1 and 2 written explicitly, the Schrödinger equation becomes

$$\left[\begin{array}{l}\frac{-1}{2(m_1+m_2)}\nabla_\sigma^2-\frac{1}{2\mu_{12}}\nabla_r^2-\sum\limits_{i=3}^{N}\frac{1}{2m_i}\nabla_i^2+\frac{Z_1Z_2}{r_{12}}\\ +\sum\limits_{j=3}^{N}Z_j\left(\frac{Z_1}{r_{1j}}+\frac{Z_2}{r_{2j}}\right)+\sum\limits_{3=i<j}^{N}\frac{Z_iZ_j}{r_{ij}}\quad-E\end{array}\right]\Phi=0. \tag{6}$$

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*If Eq. (4) were the electronic Schrödinger equation of an atom or molecule in the fixed-nuclei approximation, the coordinates would already be the relative coordinates for nucleus-electron singularities.

To consider Eq. (6) near the singular point, $r_{12}=0$, let particles 1 and 2 be within an arbitrarily small distance of each other $(0 \le r_{12} \le \epsilon)$, but let all other particles be separated $(\epsilon << r_{ij}$ for all $1 \le i < j$ with $3 \le j \le N)$. On this interval, $r_{12}=0$ is the only singular point of V. If we now examine Eq. (6) and retain explicitly only those parts which will be of lower order in r_{12} than Φ, it is clear that

$$\left[-\frac{1}{2\mu_{12}}\nabla_r^2 + \frac{Z_1 Z_2}{r_{12}} + O(\epsilon^0)\right]\Phi = 0\,, \qquad (7)$$

where $O(\epsilon^n)$ implies terms of order n and higher in r_{12}.

To conveniently expand Φ, let $\mathbf{r}_{12}$ be expressed in spherical polar coordinates $(r_{12}, \theta_{12}$ and $\varphi_{12})$. Then,

$$\left[\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{\mathcal{L}^2}{r_{12}^2} - \frac{2K}{r_{12}} + O(\epsilon^0)\right]\Phi = 0\,, \qquad (8)$$

where $K = Z_1 Z_2 \mu_{12}$ and

$$\mathcal{L}^2 = -\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left\{\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right\} - \frac{1}{\sin^2\theta_{12}}\frac{\partial^2}{\partial\varphi_{12}^2}\,.$$

The spherical harmonics, $Y_{lm}(\theta_{12},\varphi_{12})$, are the only bounded eigenfunctions of $\mathcal{L}^2$. They satisfy the condition,

$\mathcal{L}^2 Y_{\ell m} = \ell(\ell+1) Y_{\ell m}$. The $Y_{\ell m}$ span the angular space of Eq. (8). Hence, Φ can be written as the sum

$$\Phi = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} f_{\ell m}(r_{12})\, Y_{\ell m}(\theta_{12}, \varphi_{12}) \,. \tag{9}$$

When this sum is substituted into Eq. (8), the linear independence of the $Y_{\ell m}$ requires that the coefficient of each $Y_{\ell m}$ in the resulting sum is zero:

$$\left[\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{\ell(\ell+1)}{r_{12}^2} - \frac{2K}{r_{12}} + O(\epsilon^0)\right] f_{\ell m}(r_{12}) = 0 \,. \tag{10}$$

The point $r_{12} = 0$ is a regular singular point of this second order differential equation (10). Therefore, Eq. (10) must have at least one solution of the form,[11,12]

$$f_{\ell m}(r_{12}) = \sum_{k=0}^{\infty} \omega_{k;\ell m}\, r_{12}^{k+\alpha_{\ell m}} \,, \tag{11}$$

where $\omega_{0;\ell m} \neq 0$, in general. It should be remembered that $\Phi = \Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)$. Hence, the $\omega_{k;\ell m} = \omega_{k;\ell m}(\mathbf{r}_{12}, \mathbf{r}_3, \cdots, \mathbf{r}_N)$ are bounded, continuous functions of the positions of the other particles. Now if we substitute this sum into Eq. (10) and collect powers of r_{12} ,

$$\sum_{k=0}^{\infty} \left[\left\{(\alpha_{\ell m}+k)(\alpha_{\ell m}+k+1) - \ell(\ell+1)\right\} \omega_{k;\ell m} - 2K\omega_{k-1;\ell m} + O(\omega_{k-2;\ell m})\right] r_{12}^{k+\alpha_{\ell m}-2} = 0 \,.$$

Due to the linear independence of the powers of r_{12} on the interval $0 \leq r_{12} \leq \epsilon$, the coefficient of each power must be zero, and we get explicit expressions for two recursion relations,

$$\left\{ \alpha_{\ell m}(\alpha_{\ell m}+1) - \ell(\ell+1) \right\} w_{0;\ell m} = 0 , \tag{12}$$

$$\left\{ (\alpha_{\ell m}+1)(\alpha_{\ell m}+2) - \ell(\ell+1) \right\} w_{1;\ell m} - 2K\, w_{0;\ell m} = 0. \tag{13}$$

The satisfaction of these two relations insures that both the r_{12}^{-2} and the r_{12}^{-1} singularities are removed from the equation. From Eq. (12), either $\alpha_{\ell m} = \ell$ or $\alpha_{\ell m} = -(\ell+1)$. But $\alpha_{\ell m} = -(\ell+1)$ must be rejected as it produces a solution which is unbounded at $r_{12} = 0$. Setting $\alpha_{\ell m} = \ell$ in Eq. (12) and Eq. (13), we obtain a solution for $f_{\ell m}$,

$$f_{\ell m}(r_{12}) = w_{0;\ell m}\, r_{12}^{\ell} \left[1 + \frac{K}{(\ell+1)} r_{12} + O(\epsilon^2) \right]. \tag{14}$$

In fact, for any allowable ℓ, the function $f_{\ell m}$ is the only bounded solution of Eq. (10). This can be easily demonstrated by using the Wronskian method[13] to construct the other solution.

Now, let n be the smallest value of ℓ for which $w_{0;\ell m} \neq 0$. Then, as $r_{12} \to 0$, $\Phi \to r_{12}^{n}$. Thus, if $n > 0$, the function Φ has a node at $r_{12} = 0$; and if n = 0, the function Φ has a cusp at $r_{12} = 0$. In either case the <u>cusp conditions</u>, the behavior of Φ near $r_{12} = 0$, are specified by Φ itself, which is

$$\Phi = r_{12}^{n} \left[\begin{array}{l} \displaystyle\sum_{m=-n}^{n} w_{0;nm} Y_{nm}(\theta_{12},\varphi_{12}) \left\{ 1 + \frac{Z_1 Z_2 \mu_{12}}{(n+1)} r_{12} \right\} + \\ \displaystyle + r_{12} \sum_{m=-(n+1)}^{n+1} w_{0;n+1,m} Y_{n+1,m}(\theta_{12},\varphi_{12}) + O(\epsilon^2) \end{array} \right] . \tag{15}$$

These cusp conditions can also be written in a differentiated form analogous to Kato's result (Eq. (2)),

$$\left[\frac{\partial (r_{12}^{-n} \Phi)}{\partial r_{12}} \right]_{r_{12}=0} =$$

$$= \left[\frac{Z_1 Z_2 \mu_{12}}{(n+1)} + \frac{\displaystyle\sum_{m=-(n+1)}^{(n+1)} w_{0;n+1,m} Y_{n+1,m}(\theta_{12},\varphi_{12})}{\displaystyle\sum_{m=-n}^{n} w_{0;n,m} Y_{nm}(\theta_{12},\varphi_{12})} \right] \left(r_{12}^{-n} \Phi \right)_{r_{12}=0} . \tag{16}$$

Here $\displaystyle (r_{12}^{-n} \Phi)_{r_{12}=0} = \sum_{m=-n}^{n} w_{0;n,m} Y_{nm}(\theta_{12},\varphi_{12})$.

For the special case of $n = 0$, the cusp conditions can be written more simply. Setting $n = 0$ in Eq. (15), we see that

$$\frac{W_{0;00}}{(4\pi)^{1/2}} = (\Phi)_{r_{12}=0} .$$

If we also write the spherical harmonics in their real forms, we have

$$\Phi = (\Phi)_{r_{12}=0} \left[\begin{array}{l} 1 + Z_1 Z_2 \mu_{12} r_{12} + r_{12} (U_{12})_x \sin\theta_{12} \cos\varphi_{12} + \\ + r_{12} (U_{12})_y \sin\theta_{12} \sin\varphi_{12} + r_{12} (U_{12})_z \cos\theta_{12} + O(\epsilon^2) \end{array} \right], \tag{17}$$

where the functions $(U_{12})_i(\underline{\sigma}_{12}, \underline{r}_3, \cdots, \underline{r}_N)$ are given by

$$(U_{12})_x = \left(\frac{3}{2}\right)^{1/2} \frac{(W_{0;1,-1} - W_{0;1,1})}{W_{0;00}} ,$$

etc.. The differentiated form of the cusp conditions is thus

$$\left(\frac{\partial \Phi}{\partial r_{12}}\right)_{r_{12}=0} = \left[\begin{array}{l} Z_1 Z_2 \mu_{12} + (U_{12})_x \sin\theta_{12} \cos\varphi_{12} + \\ + (U_{12})_y \sin\theta_{12} \sin\varphi_{12} + (U_{12})_z \cos\theta_{12} \end{array} \right] (\Phi)_{r_{12}=0} . \tag{18}$$

(We note that $Z_1Z_2\mu_{12}$ reduces to the γ of Eq. (2) in the fixed nuclei approximation.) Since $r_{12}\sin\theta_{12}\cos\phi_{12} = x_{12}$, etc., we can also write Eq. (17) in terms of vectors. This gives

$$\Phi = (\Phi)_{r_{12}=0}\left[1+Z_1Z_2\mu_{12}r_{12} + \underline{u}_{12}\cdot\underline{r}_{12} + O(\epsilon^2)\right], \qquad (19)$$

which is Bingel's result (Eq. (3)).

III. Diatomic Molecule Cusp Conditions

In treating diatomic molecules, it is convenient to know the cusp conditions in additional coordinate systems. In this section we present the nucleus-electron cusp conditions in confocal elliptic coordinates, inter-particle coordinates, and spherical polar coordinates for the special case of the N-electron, fixed-nuclei diatomic molecule.

A. Confocal Elliptic (Prolate Spheroidal) Coordinates[14]

The cusp conditions can be obtained in different coordinate systems by making a change of variables in Eq. (15). However, in the case of confocal elliptic coordinates, it is simpler to derive the cusp conditions directly. Because the derivation is similar to that given in the previous section, we present only a summary of the results.

We first write the electronic Schrödinger equation in confocal elliptic coordinates and then expand it about a nucleus-electron singularity of the potential, V. The confocal elliptic coordinates of the ith electron are $\xi_i = (r_{i\alpha} + r_{i\beta})/R$, $\eta_i = (r_{i\alpha} - r_{i\beta})/R$, and φ_i. Here α and β are the two nuclei, R is the internuclear distance, and φ is the azimuthal angle. The ranges of the variables are: $1 \leq \xi_i < \infty$, $-1 \leq \eta_i \leq 1$, and $0 \leq \varphi_i \leq 2\pi$. In these coordinates, the electronic Schrödinger equation is

$$\left[\begin{array}{l} \sum_{i=1}^{N} \left\{ -\frac{1}{2}\nabla_i^2 - \frac{2}{R}(Z_\alpha + Z_\beta)\frac{\xi_i}{(\xi_i^2 - \eta_i^2)} + \frac{2}{R}(Z_\alpha - Z_\beta)\frac{\eta_i}{(\xi_i^2 - \eta_i^2)} \right\} \\ + \sum_{1=i<j}^{N} \frac{1}{r_{ij}} - E \end{array} \right] \Phi = 0, \tag{20}$$

where

$$\nabla_i^2 = \frac{4}{R^2(\xi_i^2 - \eta_i^2)} \left\{ \frac{\partial}{\partial \xi_i}(\xi_i^2 - 1)\frac{\partial}{\partial \xi_i} + \frac{\partial}{\partial \eta_i}(1 - \eta_i^2)\frac{\partial}{\partial \eta_i} + \frac{(\xi_i^2 - \eta_i^2)}{(\xi_i^2 - 1)(1 - \eta_i^2)}\frac{\partial^2}{\partial \varphi_i^2} \right\}. \tag{21}$$

Now, let electron i be very close to nucleus α $(1 \leq \xi_1 \leq 1 + \epsilon$ and $-1 \leq \eta_1 \leq -1 + \epsilon)$, but let the other electrons be separated from all other particles $(\epsilon \ll \xi_i^2 - \eta_i^2$, for all $i > 1$, and $\epsilon \ll r_{ij}$ for all i and j; but any R). Then, in this region, $\xi_1 = 1, \eta_1 = -1$ is the only singular point of V. If we write explicitly only those parts of Eq. (20) which will be of lower order in ϵ than Φ, we find that

$$\frac{-2}{R^2(\xi_1^2-\eta_1^2)}\left[\begin{matrix}\frac{\partial}{\partial\xi_1}(\xi_1^2-1)\frac{\partial}{\partial\xi_1}+\frac{\partial}{\partial\eta_1}(1-\eta_1^2)\frac{\partial}{\partial\eta_1}+\left\{\frac{1}{(\xi_1^2-1)}+\frac{1}{(1-\eta_1^2)}\right\}\frac{\partial^2}{\partial\varphi_1^2}\\ +R(Z_\alpha+Z_\beta)\xi_1-R(Z_\alpha-Z_\beta)\eta_1+O(\epsilon^1)\end{matrix}\right]\Phi=0. \tag{22}$$

Eq. (22) is separable on our region. We let $\Phi=\chi(\xi_1)N(\eta_1)\Psi(\varphi_1)$ and obtain the following three equations:

$$\left[\frac{\partial^2}{\partial\varphi_1^2}+m^2\right]\Psi_m=0, \tag{23}$$

$$\left[\frac{\partial}{\partial\xi_1}(\xi_1^2-1)\frac{\partial}{\partial\xi_1}-\frac{m^2}{(\xi_1^2-1)}+R(Z_\alpha+Z_\beta)\xi_1+\lambda+O(\epsilon)\right]\chi_{m,\lambda}=0, \tag{24}$$

and

$$\left[\frac{\partial}{\partial\eta_1}(1-\eta_1^2)\frac{\partial}{\partial\eta_1}-\frac{m^2}{(1-\eta_1^2)}-R(Z_\alpha-Z_\beta)\eta_1-\lambda+O(\epsilon)\right]N_{m,\lambda}=0. \tag{25}$$

Here m^2 and λ are separation constants. The solutions of the φ_1 equation are

$$\Psi_m(\varphi_1)=A_m\cos m\varphi_1+B_m\sin m\varphi_1, \tag{26}$$

where m = 0,1,2,...,∞ . The only bounded solutions of the ξ_1 and η_1 equations are obtained by expressing $X_{m\lambda}$ as a series in $(\xi_1 - 1)$ and $N_{m\lambda}$ as a series in $(1+\eta_1)$. These solutions are:

$$X_{m\lambda} = (\xi_1 - 1)^{\frac{m}{2}}\left[1 - \frac{\{\frac{m}{2}(m+1) + R(Z_\alpha + Z_\beta) + \lambda\}}{2(m+1)}(\xi_1 - 1) + O(\epsilon^2)\right] \tag{27}$$

and

$$N_{m\lambda} = (1+\eta_1)^{\frac{m}{2}}\left[1 + \frac{\{\frac{m}{2}(m+1) - R(Z_\alpha - Z_\beta) + \lambda\}}{2(m+1)}(1+\eta_1) + O(\epsilon^2)\right] . \tag{28}$$

In general, Φ will be a linear superposition of such solutions. If n is the smallest m for which A_m and B_m are not zero, the solution and the cusp conditions are given by*

$$\Phi = (\xi_1 - 1)^{\frac{n}{2}}(1+\eta_1)^{\frac{n}{2}}\begin{bmatrix} 1 - \{\frac{n}{2}(n+1) + R(Z_\alpha + Z_\beta) + \lambda\}\frac{(\xi_1 - 1)}{2(n+1)} \\ + \{\frac{n}{2}(n+1) - R(Z_\alpha - Z_\beta) + \lambda\}\frac{(1+\eta_1)}{2(n+1)} \end{bmatrix}\begin{bmatrix} A_n \cos n\varphi_1 + \\ + B_n \sin n\varphi_1 \end{bmatrix} +$$

$$+ (\xi_1 - 1)^{\frac{n+1}{2}}(1+\eta_1)^{\frac{n+1}{2}}\left[A_{n+1}\cos(n+1)\varphi_1 + B_{n+1}\sin(n+1)\varphi_1\right] + O(\epsilon^{n+2}) . \tag{29}$$

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* The solution for electron 1 near nucleus β is obtained by simply changing η_1 to $-\eta_1$ and $R(Z_\alpha - Z_\beta)$ to $-R(Z_\alpha - Z_\beta)$ in this equation. The ξ_1 terms are unchanged.

Here $A_m(r_2,\cdots,r_N)$ and $B_m(r_2,\cdots,r_N)$ are bounded, continuous functions not specified by the behavior of Φ at the singularity.

If $n>0$ in Eq. (29), Φ has a node at $\xi_1=1, \eta_1=-1$. But if n = 0, then Φ has a cusp which is described by

$$\Phi = (\Phi)_{\substack{\xi_1=1\\ \eta_1=-1}}\left[1-\{R(Z_\alpha+Z_\beta)+\lambda\}\frac{(\xi_1-1)}{2}+\{-R(Z_\alpha-Z_\beta)+\lambda\}\frac{(1+\eta_1)}{2}\right]+$$

$$+(\xi_1-1)^{1/2}(1+\eta_1)^{1/2}\left[A_1\cos\varphi_1+B_1\sin\varphi_1\right]+O(\epsilon^2). \tag{30}$$

Here $(\Phi)_{\substack{\xi_1=1\\ \eta_1=-1}}=A_0$. If n = 0, and also $\Phi\neq\Phi(\varphi_1)$, then the cusp conditions in confocal elliptic coordinates can be written in the simple differentiated forms,

$$\left(\frac{\partial\Phi}{\partial\xi_1}\right)_{\substack{\xi_1=1\\ \eta_1=-1}}=-\frac{1}{2}\{\lambda+R(Z_\alpha+Z_\beta)\}(\Phi)_{\substack{\xi_1=1\\ \eta_1=-1}}, \tag{31}$$

and

$$\left(\frac{\partial\Phi}{\partial\eta_1}\right)_{\substack{\xi_1=1\\ \eta_1=-1}}=-\frac{1}{2}\{-\lambda+R(Z_\alpha-Z_\beta)\}(\Phi)_{\substack{\xi_1=1\\ \eta_1=-1}}. \tag{32}$$

Eq. (31) and Eq. (32) can be obtained from Eq. (20) by simply setting

$$\frac{\partial^2\Phi}{\partial\varphi_1^2}=0,$$

assuming all derivatives are bounded, and then picking out the terms with singular coefficients. In such a way, Kolos and Roothaan[7] obtained, for the case $Z_\alpha = Z_\beta = 1$, cusp conditions which are equivalent to Eq. (31) and Eq. (32).

B. Inter-particle Coordinates

The cusp conditions in inter-particle coordinates are readily obtained from the confocal elliptic results by a change of variables. For example, consider an N-electron, fixed-nuclei diatomic molecule, and let

$$(\Phi)_{r_{1\alpha}=0} \neq 0 \qquad \text{and} \qquad \Phi \neq \Phi(\varphi_1) .$$

The (nonorthogonal) inter-particle distances, $r_{1\alpha}$ and $r_{1\beta}$, are given by $r_{1\alpha} = R(\xi_1+\eta_1)/2$ and $r_{1\beta} = R(\xi_1-\eta_1)/2$. Changing to these coordinates in Eq. (31) and Eq. (32), we obtain the cusp conditions in the very simple form,*

$$\left(\frac{\partial \Phi}{\partial r_{1\alpha}}\right)_{\substack{r_{1\alpha}=0 \\ r_{1\beta}\ \text{Constant}}} = -Z_\alpha (\Phi)_{r_{1\alpha}=0} . \qquad (33)$$

C. Spherical Polar Coordinates

We can easily give the diatomic molecule cusp conditions in spherical polar coordinates. Consider the example used in

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* A corresponding equation at $r_{1\beta}=0$ is obtained by interchanging α and β in Eq. (33).

part B above. Since the nuclei are fixed, we take the internuclear axis to be the z axis in Eq. (17) and find that

$$\left(\frac{\partial \Phi}{\partial r_{1\alpha}}\right)_{\substack{r_{1\alpha}=0 \\ \theta_1 \text{ Constant}}} = \left[-Z_\alpha + (u_{1\alpha})_z \cos\theta_{1\alpha}\right](\Phi)_{r_{1\alpha}=0} \quad . \tag{34}$$

We note that Φ must be spherically symmetric in the coordinates of electron 1 in order for Eq. (34) to become as simple as Eq. (33).

IV. Probability Density Cusp Conditions

The cusp conditions can be applied to the electron probability density. The spinless electron probability density, ρ_1, of an N-electron atom or molecule in the fixed-nuclei approximation, is defined by

$$\rho_1(\underline{r}_1) = \int_{sp.} \Phi^* \Phi \, d\underline{r}_2 \cdots d\underline{r}_N \quad . \tag{35}$$

Here $d\underline{r}_i = dx_i dy_i dz_i$, with the coordinate system centered on the nucleus (α) of interest. To obtain the cusp conditions on ρ_1, we begin with Eq. (15), the cusp conditions on Φ . We note that in these coordinates $r_{12} = r_1$, and in this approximation, $Z_1 Z_2 \mu_{12} = -Z_\alpha$, where Z_α is the charge of nucleus α . We now substitute Eq. (15) into the definition of ρ_1 and use that fact that $z + z^* = 2\,\mathrm{Re}\,z$, for any complex number, z . Then, the cusp conditions are specified by ρ_1 itself,

$$\rho_1(\underline{r}_1) = r_1^{2n} \begin{bmatrix} W_{nn}(\theta_1,\varphi_1)\left\{1 - \frac{2Z_\alpha}{(n+1)} r_1\right\} + \\ +2\,\mathrm{Re}\, W_{n,n+1}(\theta_1,\varphi_1) r_1 + O(\epsilon^2) \end{bmatrix}, \tag{36}$$

where

$$W_{nm}(\theta_1,\varphi_1) = \sum_{j=-n}^{n} \sum_{k=-m}^{m} Y_{nj}^*(\theta_1,\varphi_1) Y_{mk}(\theta_1,\varphi_1) \int_{SP_1} w_{0;nj}^* w_{0;mk}\, d\underline{r}_2 \cdots dr_N .$$

If n = 0,

$$\rho_1(\underline{r}_1) = W_{00}\left\{1 - 2Z_\alpha r_1\right\} + 2\,\mathrm{Re}\, W_{01} r_1 + O(\epsilon^2). \tag{37}$$

Thus, at $r_1 = 0$, the function

$$W_{00} = (\rho_1)_{r_1=0}.$$

We now put Eq. (37) into the differentiated form of the cusp conditions,

$$\left(\frac{\partial\rho_1}{\partial r_1}\right)_{r_1=0} = (\rho_1)_{r_1=0}\left[-2Z_\alpha + 2\frac{\mathrm{Re}\, W_{01}}{W_{00}}\right]. \tag{38}$$

Here $\mathrm{Re}\, W_{01}$ contains angular terms from the Y_{1m}, similar to those of Eq. (17), which will not generally be zero for molecules.

However, for a fixed-nucleus atom, ρ_1 can always be chosen invariant to inversion of the coordinates (even parity). Then, since the parity of $Y_{\ell m}$ is $(-1)^{\ell}$, ρ_1 will contain only $Y_{\ell m}$ with even ℓ. Thus, W_{01} is zero for this case, and we have Steiner's[3] result,

$$\left(\frac{\partial \rho_1}{\partial r_1}\right)_{r_1=0} = -2 Z_\alpha (\rho_1)_{r_1=0} . \tag{39}$$

For molecules, we can either use Eq. (38) or take the spherical average of Eq. (37),

$$\hat{\rho}_1(r_1) = \frac{1}{4\pi} \int_{4\pi} \rho_1(\underline{r}_1)\, d\Omega_1 ,$$

and obtain, as Bingel[2] did,

$$\hat{\rho}_1(r_1) = W_{00}[1 - 2Z_\alpha r_1] + O(\epsilon^2) .$$

Or,

$$\left(\frac{\partial \hat{\rho}_1}{\partial r_1}\right)_{r_1=0} = -2 Z_\alpha (\hat{\rho}_1)_{r_1=0} = -2 Z_\alpha (\rho_1)_{r_1=0} .$$

V. Cusp Conditions at the Coalescence of M Particles

Since the Coulomb potential is a two-particle potential, it is clear that if an N-particle wave function Φ satisfies the cusp conditions (Eq. (15)) at the point of coalescence of each pair of its particles, it removes all singularities from the Schrödinger equation. Hence, if any set of the particles coalesce, $(H-E)\Phi$ will remain bounded.

However, we are not able to determine directly the form which the exact solution will have near the point of coalescence of three or more particles. Consider M particles $(3 \leq M \leq N)$ close together $(0 \leq r_{ij} \leq \epsilon$ for $1 \leq i < j \leq M)$ and the other N-M particles separated. Then, Eq. (4) becomes

$$\left[-\sum_{k=1}^{M} \frac{1}{2m_k} \nabla_k^2 + \sum_{1=i<j}^{M} \frac{Z_i Z_j}{r_{ij}} + O(\epsilon^0) \right] \Phi = 0. \tag{40}$$

Since there is no coordinate system in which this equation is separable, we are not able to solve it directly. However, there are various forms for Φ which will satisfy the cusp conditions (Eq. (15)) for each pair of the M particles. Hence, we are led to define the M-particle cusp conditions (for $M \geq 3$) as any conditions which insure that when M particles coalesce, the two-particle cusp conditions are satisfied for each pair of the M particles.

One of the simplest forms for $\underline{\Phi}$ which satisfies this requirement can be expressed as a product with each factor satisfying a two-particle cusp condition. For example, a possible form, for a $\underline{\Phi}$ which does not have a node where the M particles coalesce, would be[4]

$$\underline{\Phi}(\underline{r}_1, \cdots, \underline{r}_N) =$$

$$= \underline{\Phi}_0 \prod_{1 \le i < j}^{M} \left\{ 1 + Z_i Z_j \mu_{ij} r_{ij} + \underline{r}_{ij} \cdot \underline{u}_{ij} + O(r_{ij}^2) \right\}, \qquad (41)$$

where

$$\underline{\Phi}_0 = \left(\underline{\Phi}\right)_{\substack{r_{ij}=0, \\ 1 \le i < j \le M}} = \underline{\Phi}(\underline{\sigma}, \underline{r}_{M+1}, \cdots \underline{r}_N),$$

and

$$\underline{u}_{ij} = \underline{u}_{ij}(\underline{\sigma}, \underline{r}_{M+1}, \cdots \underline{r}_N).$$

Here $\underline{\sigma}$ is the center of mass of the M particles. Direct substitution of Eq. (41) into Eq. (40) shows that the singularities are removed.

Generalizations of cusp conditions of the form of Eq. (41) are possible. For example, we can choose $\underline{\Phi}_0$ and $\underline{u}_{ij}$ to be any bounded, continuous functions of all the variables, $\underline{r}_1, \ldots, \underline{r}_N$, such that

$$\left(\Phi_0\right)_{\substack{r_{ij}=0 \\ 1\le i<j\le M}} = \left(\Phi\right)_{\substack{r_{ij}=0 \\ 1\le i<j\le M}},$$

and such that

$$\underline{\nabla}_k \Phi_0, \quad \nabla_k^2 \Phi_0, \quad \underline{\nabla}_k \underline{u}_{ij}, \qquad \text{and} \quad \nabla_k^2 \underline{u}_{ij}$$

exist and are bounded for all k when the M particles coalesce.

Thus we are able to construct wave functions which suffice to remove the singularities but do not necessarily have the same form as the exact solution.

VI. Inclusion of Spin

The N-particle wave function Φ discussed in the previous sections is a spatial wave function with no spin dependence. In addition, no consideration was given to the Pauli Principle. In order to be physically acceptable, wave functions must be eigenfunctions of spin, properly symmetrized with respect to interchange of particles. However, it has been shown[2,15] that the exact, properly symmetrized, spin eigensolutions, Ψ, of the Schrödinger equation can always be constructed by taking proper linear combinations of N-particle spatial wave functions times spin functions. Hence, if all the Φ's used to construct Ψ satisfy the cusp conditions, Ψ will satisfy the cusp conditions.*

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* The integrated forms, such as Eq. (15), apply directly if the $w_{0;nm}$ contain the spin functions. But differentiated forms, such as Eq. (16), do not directly apply since division by spin functions is not defined.

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$$\Phi = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\xi_1^2 - 1)^{\frac{|m|}{2}} \Phi_{\ell m}(\xi_1) P_\ell^m(\eta_1) e^{im\varphi_1},$$

and showed that

$$\left(\frac{\partial \Phi_{00}}{\partial \xi_1}\right)_{\xi_1=1} = -\frac{R}{2}(Z_\alpha + Z_\beta)(\Phi_{00})_{\xi_1=1} + O(R^2).$$

15. M. Kotani et al., Table of Molecular Integrals (Tokyo, 1955) Chap. I.