The Behaviour of the First-Order Density Matrix at the Coulomb Singularities of the Schrödinger Equation

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The cusp conditions of Kato for a spinless n-electron wave function at the Coulomb Singularities of the Schrödinger Equation are used to derive corresponding conditions for the first-order density matrix. These results are applied to the united-atom expansion of the electronic energy of polyatomic molecules resulting in an exact relation between the coefficients of the quadratic and cubic terms in this expansion. Finally it is shown how the cusp condition for the first-order density matrix is modified if the wave function includes electron spin in a proper way.

The last years have seen an increased interest in using density matrices for the quantum mechanical description of atomic and molecular systems. This made it necessary to investigate the *general* properties of these quantities i. e. those which are common to all density matrices, which can be derived from exact or approximate n-electron wave functions.

The most important one is the question of *n-representability*. It turns out, that not all p-th order density matrices $\Gamma^{(p)}$ one can construct and which fulfill the relations (13 a, b) can be derived from an *antisymmetric* n-electron wave function Φ in the manner described by the definition of $\Gamma^{(p)}$ given by Eq. (12). The necessary and sufficient conditions for this representation to be true for a *given* $\Gamma^{(p)}$ are still not quite known, but extensive advances have been made on this important question, mainly through the work of Coleman [1].

Another general property is the explicit dependance of $\Gamma^{(p)}$ on the spin variables for the case of a wave function for which S and M_S are good quantum numbers. This dependance has been derived in detail for the first and second order density matrices as well as for the corresponding transition densities between two different wave functions [2–4].

The behaviour of first-order density matrices under *spatial* symmetry operations was investigated by the author [2]. In this paper we are concerned with the behaviour of the first-order density matrix at the Coulomb singularities of the wave equation. This question will be treated in Chapter II using the results of Kato [5] on the same problem for a *spinless* n-electron wave function which are reviewed in Chapter I. In Chapter III we give an application of the results of Chapter II for the first-order density matrix to the united-atom expansion of the electronic energy of polyatomic molecules. The extension of the results of Chapter II to wave functions containing the electron spin in a proper way is given in Chapter IV.

I. Kato's Boundary conditions for a spinless wave function

The Schrödinger equation for an n-electron atom neglecting nuclear motion and spin-orbit as well as other higher interactions has the form

$$(H-E)\,\Psi = \left\{\sum_{i=1}^{n}\left(-\tfrac{1}{2}\Delta_i - \frac{Z}{r_i}\right) + \sum_{i>j}\sum\frac{1}{r_{ij}} - E\right\}\Psi = 0\,, \qquad (1)$$

where r_i is the distance of the i-th electron from the nucleus of charge Z and r_{ij} the distance of electrons i and j. We see, that some of the coefficients

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[2] W. A. Bingel, J. Chem. Phys. **32**, 1522 [1960].

[3] R. McWeeny, Proc. Roy. Soc., Lond. A **259**, 554 [1961].

[4] W. A. Bingel, J. Chem. Phys. **34**, 1066 [1961].

[5] T. Kato, Commun. Pure Appl. Math. **10**, 151 [1957].

of this differential equation become infinite for each of the manifolds

$$M_i: \quad r_i = 0, \quad i = 1, 2 \ldots n \tag{2 a}$$

$$M_{ij}: \quad r_{ij} = 0, \quad 1 \leqq i < j \leqq n \tag{2 b}$$

of the $3n$-dimensional configuration space. The singular points of the wave equation (1) are therefore contained in the manifold

$$M_1 \cup M_2 \cup \ldots \cup M_n \cup M_{12} \cup \ldots \cup M_{n-1n}. \tag{2 c}$$

It is of some interest to investigate the behaviour of the wave function Ψ at these singularities of the wave equation (1). An indication of the general behaviour to be expected is given by the special case $n = 1$. The one-electron wave functions are known, in particular the lowest state 1s has the form

$$\psi_{1s} = N_{1s}\, e^{-Z r_1} = N_{1s} \exp\{-Z \cdot \sqrt{x_1^2 + y_1^2 + z_1^2}\}. \tag{3}$$

While this wave function is continuous even at $r_1 = 0$, the first partial derivatives of ψ with respect to x_1, y_1 or z_1 do not exist at $r_1 = 0$. Rather, ψ has a *cusp* at $r_1 = 0$ characterized by the cusp-condition

$$(\mathrm{d}\psi/\mathrm{d}r_1)_{r_1=0} = -Z\,\psi(0). \tag{4}$$

This condition holds true for all discrete states $(n\,l\,m)$ – even for the continuous ones – but is trivial for the states with $l > 0$, since then both sides of (4) are equal to zero. KATO [5] has shown, how Eq. (4) can be generalized to the case of n-electron spinless wave functions $\Psi(\boldsymbol{R}) \equiv \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n)$ which are solutions of Eq. (1). This generalized cusp-condition for the case where the point $\boldsymbol{R}$ of configuration space is contained in one and only one of the manifolds (2 a) has the form

$$\left(\frac{\partial \overline{\Psi}}{\partial r_1}\right)_{r_1=0} = -Z \cdot \Psi(0, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) \tag{5}$$

for M_1; the cusp-condition for M_i alone follows from Eq. (5) by interchanging electrons 1 and i. The bar over Ψ on the left side of Eq. (5) implies averaging Ψ over a small sphere $r_1 = \text{const.}$, holding the positions of electrons 2 to n fixed on both sides of Eq. (5).

For the singularity described by one and only one of the manifolds M_{ij} the generalized cusp-condition derived by KATO is

$$\left(\frac{\partial \overline{\Psi}}{\partial r_{12}}\right)_{r_{12}=0} = +\tfrac{1}{2}\Psi(\boldsymbol{r}, \boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n) \tag{6}$$

for M_{12}; the one for M_{ij} can again be got from Eq. (6) by a suitable permutation. The bar over Ψ now denotes the following angular average of Ψ: the vector $\boldsymbol{r} = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$ as well as $\boldsymbol{r}_3 \ldots \boldsymbol{r}_n$ are held fixed and the difference vector $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ is rotated over the surface of a small sphere $r_{12} = \text{constant}$.

As has been mentioned already, the cusp conditions (5) and (6) are derived under the assumption, that only one of the singular manifolds (2) is involved. How the wave function behaves at points in configuration space which lie in more than one of these manifolds simultaneously is not known at present. FOCK has given reasons why a logarithmic term of the form $\ln(r_1^2 + r_2^2)$ should be present in the wave function for the 2-electron case, if both r_1 and r_2 are small. This however is contradicted by theorem I contained in KATO's paper, which states that the wave function should be bounded everywhere, even at these higher singularities of the wave equation.

The cusp conditions (5) and (6) are given in a differential form as derived by KATO. For later use it is more convenient to rewrite them in an integrated form, namely

$$M_1: \quad \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) = \Psi(0, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n)(1 - Z\,r_1) + \boldsymbol{r}_1 \cdot \boldsymbol{a}_1(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n) + O(r_1^2) \tag{5'}$$

and for

$$M_{12}: \quad \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) = \Psi(\boldsymbol{r}, \boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)(1 + \tfrac{1}{2} r_{12}) + \boldsymbol{r}_{12} \cdot \boldsymbol{c}_{12}(\boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n) + O(r_{12}^2), \tag{6'}$$

where $\boldsymbol{r} = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$. Upon performing the angular averages asked for in Eqs. (5) and (6) on the integrated expressions for Ψ in Eqs. (5′) and (6′) the scalar product terms containing the vectors $\boldsymbol{a}_1$ and $\boldsymbol{c}_{12}$ drop out and the subsequent differentiation then immediately leads back to Eqs. (5) and (6) respectively.

In order to better understand these cusp conditions it is well to consider a special case, namely the S-states of the 2-electron atoms. Here the wave function has the special form

$$\Psi = \psi(r_1, r_2, r_{12}) \tag{7}$$

i. e. it depends only on the three radial coordinates out of a total of six. Starting from Eq. (5′) we can assume r_1 to be small compared to r_2, then

$r_{12} \approx r_2 - r_1 \cos \Theta_{12}$ and

$$\Psi = \psi(r_1, r_2, r_2 - r_1 \cos \Theta_{12})$$
$$= \psi(0, r_2, r_2) + r_1 \left(\frac{\partial \psi}{\partial r_1}\right)_{r_1=0} - r_1 \cos \Theta_{12} \left(\frac{\partial \psi}{\partial r_{12}}\right)_{r_1=0} + \dots$$
$$= \psi(0, r_2, r_2)\,(1 - Z r_1) + \boldsymbol{r}_1 \cdot \boldsymbol{a}_1(\boldsymbol{r}_2) + \dots .$$

Comparison of the last two expressions gives

$$\left(\frac{\partial \psi}{\partial r_1}\right)_{r_1=0} = -Z\,\psi(0, r_2, r_2) \qquad (8\,a)$$

and

$$|\boldsymbol{a}_1| = \left|\left(\frac{\partial \psi}{\partial r_{12}}\right)_{r_1=0}\right| \qquad (8\,b)$$

with the vector $\boldsymbol{a}_1$ directed towards electron 2. Starting from Eq. (6′) and small r_{12}, we have

$$r_1 \approx r + \tfrac{1}{2} r_{12} \cos \alpha\,, \qquad r_2 \approx r - \tfrac{1}{2} r_{12} \cos \alpha$$

where α is the angle between the mean vector

$$\boldsymbol{r} = \tfrac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$$

and the difference vector $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$, Then

$$\Psi = \psi(r + \tfrac{1}{2} r_{12} \cos \alpha, r - \tfrac{1}{2} r_{12} \cos \alpha, r_{12})$$
$$= \psi(r, r, 0) + r_{12} \left(\frac{\partial \psi}{\partial r_{12}}\right)_{r_{12}=0} + r_{12} \cos \alpha \cdot \tfrac{1}{2} \left(\frac{\partial \psi}{\partial r_1} - \frac{\partial \psi}{\partial r_2}\right)_{r_{12}=0} + \dots$$
$$= \psi(r, r, 0)\,(1 + \tfrac{1}{2} r_{12}) + \boldsymbol{r}_{12} \cdot \boldsymbol{c}_{12}(\boldsymbol{r}) + \dots .$$

Comparison of the last two lines gives

$$\left(\frac{\partial \psi}{\partial r_{12}}\right)_{r_{12}=0} = +\tfrac{1}{2} \psi(r, r, 0) \qquad (9\,a)$$

and

$$|\boldsymbol{c}_{12}| = \tfrac{1}{2} \left|\left(\frac{\partial \psi}{\partial r_1} - \frac{\partial \psi}{\partial r_2}\right)_{r_{12}=0}\right| \qquad (9\,b)$$

with the vector $\boldsymbol{c}_{12}$ directed towards the common position $\boldsymbol{r}$ of electrons 1 and 2. Eqs. (8 a) and (9 a) are identical with the special cusp conditions given previously by ROOTHAAN [6], Eqs. (8 b) and (9 b) give the absolute values of the vectors $\boldsymbol{a}_1$ and $\boldsymbol{c}_{12}$ for this special case. The direction of these vectors as described in the text is also of some interest.

Finally it should be mentioned, that the generalized cusp conditions, both in their differential [Eqs. (5) and (6)] and their integrated form [Eqs. (5′) and (6′)] also hold for molecular wave functions around each nucleus, if the origin of coordinates coincides with that nucleus and the nuclear charge Z in Eqs. (5), (6), (5′) and (6′) is taken to be the nuclear charge Z_α of that nucleus α. This can be seen as follows: If the above conditions are fulfilled, the HAMILTONian for the molecular wave function differs from Eq. (1) by the terms

$$-\sum_{\substack{\beta \\ (\beta \neq \alpha)}} Z_\beta \sum_{i=1}^{n} \frac{1}{r_{i\beta}}\,, \qquad (10)$$

which express the COULOMB attraction of all n electrons by the nuclei β *different* from the choosen one of index α. If now electron 1 coincides with nucleus α no additional singularities are introduced into the molecular wave equation by the terms in Eq. (10) corresponding to electron 1 and the derivation of Eq. (5) proceeds in the previous way as given by KATO. Since Eq. (10) does not contain any electron repulsion terms at all, Eq. (6) is at once seen to hold for the molecular case also.

As an example we treat an 1-electron diatomic molecule AB in a σ-state. By expanding the wave function around center a, we must have

$$\psi(r_a, \vartheta_a, \varphi_a) = \sum_{l=0}^{\infty} r_a{}^l f_l(r_a) \cdot P_l(\cos \vartheta_a)$$
$$= f_0(0) + r_a (f_0'(0) + f_1(0) \cos \vartheta_a) + O(r_a{}^2)$$
$$= \psi(0) \cdot (1 - Z_a r_a) + \boldsymbol{r}_a \cdot \boldsymbol{a}_1 + \dots .$$

Comparison of the last two lines shows that

$$\left(\frac{\mathrm{d} f_0}{\mathrm{d} r_a}\right)_{r_a=0} = -Z_a f_0(0), \quad |a_1| = f_1(0) \qquad (11\,a, b)$$

with the vector $\boldsymbol{a}_1$ directed towards the other nucleus b. Eq. (11 a) shows that only the spherically symmetric part of the molecular wave function *as seen from nucleus a* is involved in the cusp condition.

II. Boundary condition for the first order density matrix

The p-th order density matrix $\Gamma^{(p)}$ constructed from an n-electron wave function Φ is defined by

$$\Gamma^{(p)}(x, x') = \int \Phi^*(x, y)\, \Phi(x', y)\, \mathrm{d}y\,. \qquad (12)$$

Here x and y stand for all the coordinates (spatial and spin) of electrons 1 to p and $p+1$ to N respectively. From Eq. (12) and the assumed normalisation of Φ it follows that

$$\Gamma^{(p)}(x', x) = \Gamma^{(p)}(x, x')^* \qquad (13\,a)$$

and

$$\mathrm{tr}\, \Gamma^{(p)} = \int \Gamma^{(p)}(x, x)\, \mathrm{d}x = 1\,, \qquad (13\,b)$$

i. e. all density matrices derivable from a wave function must be hermitian and of finite trace.

[6] C. C. J. ROOTHAAN, Rev. Mod. Phys. **32**, 194 [1960].

We now consider the first order density matrix ($p=1$) for a spinfree wave function. Eq. (12) then specializes to

$$\Gamma^{(1)}(\boldsymbol{r},\boldsymbol{r}') \equiv \gamma(\boldsymbol{r},\boldsymbol{r}') = \int \Psi^*(\boldsymbol{r},\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi(\boldsymbol{r}',\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n . \quad (14)$$

Substituting for Ψ the expression (5′) valid for small r_1, we get – assuming Ψ to be real –

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = (1-Z\,r)\,(1-Z\,r') \int |\Psi(0,\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)|^2\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n + (\boldsymbol{r}+\boldsymbol{r}') \cdot \int \boldsymbol{a}(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi(0,\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n$$

or

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \gamma(0,0) \cdot (1 - Z(r+r')) + (\boldsymbol{r}+\boldsymbol{r}') \cdot \boldsymbol{b} + \ldots \quad (15\,\mathrm{a})$$

where

$$\boldsymbol{b} = \int \boldsymbol{a}(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi(0,\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n . \quad (15\,\mathrm{b})$$

Eq. (15 a) is the desired cusp condition for the first-order density matrix in integrated form. For the diagonal element, that is the total charge density of the state described by the wave function Ψ this becomes

$$\gamma(\boldsymbol{r}) \equiv \gamma(\boldsymbol{r},\boldsymbol{r}) = \gamma(0) \cdot (1 - 2\,Z\,r) + 2\,\boldsymbol{r} \cdot \boldsymbol{b} + O(r^2). \quad (15\,\mathrm{c})$$

Averaging this over the angular coordinates and taking the derivative with respect to r at $r=0$ then gives the differential form of the cusp condition

$$\left(\frac{\mathrm{d}\bar{\gamma}}{\mathrm{d}r}\right)_{r=0} = -2\,Z\,\bar{\gamma}(0) \quad (16)$$

which involves only the spherically symmetric part of the charge density around the nucleus. The cusp condition for the first order *transition* density

$$\gamma_{1,2}(\boldsymbol{r},\boldsymbol{r}') = \int \Psi_1^*(\boldsymbol{r},\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi_2(\boldsymbol{r}',\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n$$

between two different states 1 and 2 in its differential form is again given by Eq. (16); the integrated form is now

$$\gamma_{1,2}(\boldsymbol{r},\boldsymbol{r}') = \gamma_{1,2}(0,0)\,(1 - Z(r+r')) + \boldsymbol{r} \cdot \boldsymbol{b}_1 + \boldsymbol{r}' \cdot \boldsymbol{b}_2 + O(r^2) \quad (17\,\mathrm{a})$$

with

$$\boldsymbol{b}_1 = \int \boldsymbol{a}_1^*\, \Psi_2\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n , \qquad \boldsymbol{b}_2 = \int \boldsymbol{a}_2\, \Psi_1^*\, \mathrm{d}\boldsymbol{r}_2 \ldots \mathrm{d}\boldsymbol{r}_n . \quad (17\,\mathrm{b})$$

For an atom, the inversion of all electrons is one of the symmetry operations. If now Ψ_1 and Ψ_2 have the *same* parity, the first order transition density matrix is even under inversion of both $\boldsymbol{r}$ and $\boldsymbol{r}'$ and the vectors $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ must be zero from reasons of symmetry. This is naturally always the case if $\Psi_1 \equiv \Psi_2$, then $\boldsymbol{b}_1 = \boldsymbol{b}_2 = \boldsymbol{b}$ of Eq. (15 b) must vanish.

If Ψ_1 and Ψ_2 have *opposite* parity, the first order transition density matrix is odd under inversion of both $\boldsymbol{r}$ and $\boldsymbol{r}'$ and $\gamma_{1,2}(0,0)$ must vanish, as can be seen from Eq. (17 a).

III. Application to united-atom expansions

The electronic energy of a polyatomic molecule can be expanded in powers of the distances R_α of the nuclei α from the united atom. The first coefficients of this expansion

$$E = W_\mathrm{u} + \sum_\alpha (E_{2,\alpha} R_\alpha^2 + E_{3,\alpha} R_\alpha^3) + \ldots \quad (18)$$

are given by [7, 8]

$$E_{1,\alpha} = 0 , \quad (19\,\mathrm{a})$$

$$E_{2,\alpha} = Z_\alpha \left(\tfrac{1}{6}\varrho_{0,0}(0) - \mathcal{R}_2 \cdot P_2(\cos\Theta_\alpha)\right), \quad (19\,\mathrm{b})$$

$$E_{3,\alpha} = Z_\alpha \cdot \tfrac{1}{12}\left(\frac{\mathrm{d}\varrho_{00}}{\mathrm{d}r}\right)_{r=0} . \quad (19\,\mathrm{c})$$

Here Θ_α, φ_α are the polar angles of the α-th nucleus of charge Z_α referred to a coordinate system with origin at the united-atom position, $\frac{1}{4\pi}\varrho_{00}(r)$ is the spherically symmetric part of the electron density of the united atom in the state u with total energy W_u and $\mathcal{R}_2$ is the electric field gradient at the nucleus of the united atom.

In many cases the united-atom state u corresponding to the molecular state in question is an S-state, then $\mathcal{R}_2 = 0$ and the coefficients $E_{2,\alpha}$ in Eq. (19 b) depend only on the charge density at the nucleus. Then Eq. (16) can be used to determine the coefficients $E_{3,\alpha}$ of the cubic terms in the expansion (18) from the coefficients $E_{2,\alpha}$ of the quadratic terms from the relation

$$E_{3,\alpha} = -\sum_\beta Z_\beta \cdot E_{2,\alpha} . \quad (20)$$

[7] W. A. Bingel, J. Chem. Phys. **30**, 1250, 1254 [1959].
[8] W. A. Bingel, Z. Naturforschg. **16 a**, 668 [1961].

For diatomic molecules AB the expansion (18) can be expressed in terms of the internuclear distance $R = R_a + R_b$ alone. For this special case we have [7]

$$E(R) = W_u + E_2 R^2 + E_3 R^3 + \ldots , \qquad (21\,a)$$

$$E_2 = \frac{Z_a Z_b}{Z_a + Z_b} \left(\tfrac{1}{6} \varrho_{00}(0) - \mathcal{R}_2\right), \qquad (21\,b)$$

$$E_3 = \frac{Z_a Z_b (Z_a^2 + Z_b^2)}{(Z_a + Z_b)^3} \cdot \tfrac{1}{12} \left(\frac{d\varrho_{00}}{dr}\right)_{r=0} . \qquad (21\,c)$$

If $\mathcal{R}_2 = 0$ then Eq. (16) with $Z = Z_a + Z_b$ gives the relation

$$E_3 = -\frac{Z_a^2 + Z_b^2}{Z_a + Z_b} \cdot E_2 . \qquad (22)$$

This result (for $Z_a = Z_b$) was quoted without proof in an earlier communication [9] and used by BUCKINGHAM and DUPARC [10] in estimating the accuracy of *calculated* values of E_2 and E_3 for very short range interactions of the systems H + H, H + He and He + He. This can be done, since Eq. (22) holds strictly for the exact values of E_2 and E_3 only, calculated from Eqs. (21 b, c) with the exact united atom wave functions. If one uses *approximate* wave functions, as BUCKINGHAM and DUPARC did, the ratio E_3/E_2 will deviate from the exact one given by Eq. (22) and this deviation will in general become smaller as the approximate united atom wave function becomes better energy-wise, see the table in [10].

IV. Boundary conditions for the first-order density matrix including spin

The cusp conditions Eqs. (5) and (6) refer to a *spinfree* n-electron wave function, and the same limitation also applies to Eqs. (15) and (16) for the corresponding first-order density matrix. We will now derive the cusp condition for the first-order density matrix, when the wave function includes electron spin in a proper way.

We start out with a spinfree wave function Ψ_1 which is a solution of the SCHRÖDINGER equation (1). From this Ψ_1 we can form a wave function Φ including spin which is also a solution of Eq. (1), namely [11, 12]

$$\Phi_{S,M} = (f_s^n)^{-1/2} \sum_k \Psi_k \, \Theta_{S,M;k} \qquad (23\,a)$$

where

$$\Psi_k = \left(\frac{f_s^n}{n!}\right)^{1/2} \sum_P U^*_{k,1}(P) \, P \, \Psi_1 . \qquad (23\,b)$$

Here the Θ_k's are spin eigenfunctions for the total spin S and its z-component M constructed according to the branching rule. They span the irreducible representation $\mathfrak{D}_s$ and the spatial functions Ψ_k constructed from Ψ_1 according to (23 b) form a basis for the dual representation $\tilde{\mathfrak{D}}_s$ of the permutation group for the n electrons, for which the $U(P)$ are the representation matrices.

Since all P commute with the HAMILTONian (1), all Ψ_k are solutions of (1) for the same energy E and therefore the cusp conditions (5), (6), (5′) and (6′) hold for all of them. For the wave function (23 a), the first-order density matrix including spin is [12]

$$\gamma(\boldsymbol{x}, \boldsymbol{x}') = \gamma_+(\boldsymbol{r}, \boldsymbol{r}') \cdot \alpha(s)\, \alpha(s') + \gamma_-(\boldsymbol{r}, \boldsymbol{r}') \cdot \beta(s)\, \beta(s'), \qquad (24)$$

where the *partial* density matrices γ_+ and γ_- expressed in terms of the spatial functions Ψ_k are given by Eq. (A 7) of [2]. Using these expressions and the fact, that all Ψ_k fulfill the cusp conditions (5′), it can easily be shown that the cusp conditions (15 a) hold for the partial densities γ_+ and γ_- also, each with an appropriate $\boldsymbol{b}_+$ or $\boldsymbol{b}_-$ in the scalar product. Then the spinless first-order density matrix

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = \gamma_+(\boldsymbol{r}, \boldsymbol{r}') + \gamma_-(\boldsymbol{r}, \boldsymbol{r}')$$

derived from the wave function (23 a) containing the spin as well as the *spin*-density matrix

$$\gamma_{\text{spin}}(\boldsymbol{r}, \boldsymbol{r}') = \tfrac{1}{2}[\gamma_+(\boldsymbol{r}, \boldsymbol{r}') - \gamma_-(\boldsymbol{r}, \boldsymbol{r}')]$$

fulfill this relation, with appropriate vectors

$$\boldsymbol{b} = \boldsymbol{b}_+ + \boldsymbol{b}_- \quad \text{and} \quad \boldsymbol{b}_{\text{spin}} = \tfrac{1}{2}(\boldsymbol{b}_+ - \boldsymbol{b}_-).$$

Finally, it can be shown, that the same form of the cusp condition also obtains for the corresponding *transition* quantities.

[9] W. A. BINGEL, J. Chem. Phys. **38**, 274 [1963].
[10] R. A. BUCKINGHAM and D. M. DUPARC, J. Chem. Phys. **38**, 275 [1963].
[11] M. KOTANI et al., Table of Molecular Integrals, Tokyo 1955, Chapter I.
[12] See Appendix of [2].