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The Behaviour of the Second-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 are used to derive corresponding conditions for the second-order density matrix $\Gamma^{(2)}(r_1 r_2, r_1' r_2')$.

Die cusp-Bedingungen von Kato für das Verhalten einer spinfreien n-Elektronenfunktion an den Coulomb-Singularitäten der Schrödingergleichung werden zur Ableitung entsprechender Bedingungen für die reduzierte Dichtematrix zweiter Ordnung $\Gamma^{(2)}(r_1 r_2, r_1' r_2')$ benutzt.

Les conditions de rebroussement de Kato pour une fonction d'onde, sans spin, à n électrons, sont utilisées pour déduire des conditions correspondantes pour la matrice de densité du second ordre $\Gamma^{(2)}(r_1 r_2, r_1' r_2')$.

1. Introduction

The renewed interest in the use of reduced density matrices for a quantum mechanical description of atomic and molecular systems is evident by the many papers published in the last years on this special subject [*1*].

This interest was partly stimulated by the hope that it might be possible to determine the energies by a *direct* calculation of the 2nd-order *density matrices* $\Gamma^{(2)}$ of such systems without using its *wave-functions* at all. It was felt that this density matrix approach might be a way around the difficulties encountered in conventional calculations using approximate wave functions, namely the very sharp increase in computational time with increasing number of electrons for a fixed absolute accuracy of the calculated energies.

While an expression for the total energy in terms of $\Gamma^{(2)}$ exists [*2*] which can be used in an variational approach for the approximate calculation of the energy, the main stumbling block has been what is called the *n-representability problem.* This means that not all p-th order density matrices $\Gamma^{(p)}$ one can construct and which fulfill the symmetry relations (6 a—c) can be derived from an antisymmetric n-electron wave function according to the definition of $\Gamma^{(p)}$ given by (5). The n.a.s. conditions for this to be true for a *given* $\Gamma^{(2)}$ have now been derived [*3*] although they are not yet in a form suitable for numerical applications. One can hope though that the near future will bring numerical calculations using $\Gamma^{(2)}$ only and then one will see whether the hope expressed above will be realised in practise.

In this paper we are concerned with *general* properties of density matrices such as the explicit spin-dependence of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ for the important case of a wave function with S and M_S being good quantum numbers, which has been obtained previously [*4, 5, 6*]. The symmetry properties of $\Gamma^{(1)}$ under the spatial symmetry

operations of the Hamiltonian have also been treated in some detail [*4*, *7*]. The behaviour of $\Gamma^{(1)}$ at the Coulomb-singularities of the Schrödinger equation has been considered in a previous paper of the author [*8*] as well as by STEINER [*9*].

The present paper deals with the same problem for the 2nd-order density matrix $\Gamma^{(2)}$.

Finally it should be mentioned that besides the interest in $\Gamma^{(2)}$ for the direct calculation of the energy, the quantities $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are also very useful for the interpretation of previously calculated approximate wave functions and for the comparison of different such wave functions for the same system.

2. KATO's cusp conditions for a spinless wave function

We shall follow the presentation and nomenclature of a previous paper by the author [*8*] and just review shortly the results obtained there.

The SCHRÖDINGER equation for an n-electron molecule is

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

where $r_{i\alpha}$ is the distance of the i-th electron from the α-th nucleus of charge Z_α and r_{ij} the interelectronic distance for electrons i and j. This differential equation becomes singular whenever one of the conditions

$$r_{i\alpha} = 0, \qquad i = 1, 2 \ldots n,\ \alpha = a, b \ldots \tag{2a}$$

$$r_{ij} = 0, \qquad 1 \le i < j \le n \tag{2b}$$

holds. At these singular points of the differential Eq. (1) its solutions Ψ also have a certain type of singularity whereas otherwise they are regular functions [*10*]. Up to now the case where one and only one of the conditions (2a) *or* (2b) occurs has been investigated rigorously by T. KATO [*10*]. His results are that in this case Ψ has a *cusp*, and that the *average* slope of Ψ at such a point is given by

$$\left(\frac{\partial\,\overline{\Psi}}{\partial r_1}\right)_{r_1=0} = -\,Z_\alpha\Psi\,(0, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) \qquad \text{for } \boldsymbol{r}_{1a} = 0 \qquad \text{(Coulomb-cusp)} \tag{3a}$$

$$\left(\frac{\partial\,\overline{\Psi}}{\partial r_{12}}\right)_{r_{12}=0} = +\,\tfrac{1}{2}\Psi\,(\boldsymbol{r}, \boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n) \quad \text{for } \boldsymbol{r}_{12} = 0 \qquad \text{(Correlation cusp)}\,. \tag{3b}$$

For (3a) the coordinate system is centered on nucleus a and the bar over Ψ indicates an angular average over ϑ_1, φ_1. For (3b) the origin of the coordinate system is irrelevant, the bar now indicates averaging Ψ over a small sphere centered at $\boldsymbol{r} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$ by rotating the vector $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$.

As shown in the previous paper [*8*], the differential form (3a, b) of the cusp conditions given by KATO [*10*] is equivalent to the integral form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) = \Psi(0, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\,(1 - Z_a \cdot r_1) + \boldsymbol{r}_1 \cdot \boldsymbol{a}_1(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n) + O(r_1^2) \tag{4a}$$

and

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_n) = \Psi(\boldsymbol{r}, \boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\,(1 + \tfrac{1}{2}\,r_{12}) + \boldsymbol{r}_{12} \cdot \boldsymbol{c}_{12}(\boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n) + O(r_{12}^2) \tag{4b}$$

where

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

3. Cusp conditions for the second order density matrix

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

$$\Gamma^{(p)}(x, x') = \int \Phi^*(x, y)\, \Phi(x', y)\, dy \tag{5}$$

where x and y are abbreviations for all space and spin coordinates of electrons 1 to p and $p+1$ to n respectively. It follows then that

$$\Gamma^{(p)}(x', x) = \Gamma^{(p)}(x, x')^* \tag{6a}$$

$$\Gamma^{(p)}(Px, x') = \Gamma^{(p)}(x, Px') = \varepsilon_p\, \Gamma^{(p)}(x, x') \tag{6b}$$

$$tr\, \Gamma^{(p)} = \int \Gamma^{(p)}(x, x)\, dx = 1\,. \tag{6c}$$

In other words, all density matrices derivable from a wave function must be hermitian, antisymmetric in both sets of variables and of finite trace**.

For the 2nd-order density matrix of a spinless wave function, Eq. (5) takes the form

$$\Gamma^{(2)}(\boldsymbol{r}_1\, \boldsymbol{r}_2;\, \boldsymbol{r}_1'\, \boldsymbol{r}_2') = \int \Psi^*(\boldsymbol{r}_1\, \boldsymbol{r}_2\, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, \Psi(\boldsymbol{r}_1'\, \boldsymbol{r}_2'\, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n\,. \tag{7}$$

Introducing the expression (4a) for the Coulomb-cusp for both Ψ^* and Ψ we get:

$$\Gamma^{(2)}(\boldsymbol{r}_1\, \boldsymbol{r}_2,\, \boldsymbol{r}_1'\, \boldsymbol{r}_2') = \Gamma^{(2)}(0\boldsymbol{r}_2,\, 0\boldsymbol{r}_2')\cdot[1 - Z(r_1 + r_1')] + \boldsymbol{r}_1\cdot\boldsymbol{b}^*(\boldsymbol{r}_2\boldsymbol{r}_2') + \boldsymbol{r}_1'\cdot\boldsymbol{b}(\boldsymbol{r}_2'\boldsymbol{r}_2) + \ldots \tag{8a}$$

with

$$\boldsymbol{b}(\boldsymbol{r}_2'\boldsymbol{r}_2) = \int \boldsymbol{a}(\boldsymbol{r}_2'\boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, \Psi^*(0, \boldsymbol{r}_2\boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \tag{8b}$$

for the case, where *both* r_1 and r_1' are small. Obviously, Eq. (6a) is fulfilled, application of Eq. (6b) to (8a, b) gives the other combinations (r_2, r_2' small etc.) for this case.

If Eq. (4a) is used only once, we get instead

$$\Gamma^{(2)}(\boldsymbol{r}_1\boldsymbol{r}_2,\, \boldsymbol{r}_1'\boldsymbol{r}_2') = \Gamma^{(2)}(0\boldsymbol{r}_2,\, \boldsymbol{r}_1'\boldsymbol{r}_2')\,(1 - Zr_1) + \boldsymbol{r}_1\cdot\boldsymbol{b}^*(\boldsymbol{r}_2\boldsymbol{r}_1'\boldsymbol{r}_2')\,, \tag{9a}$$

with

$$\boldsymbol{b}^*(\boldsymbol{r}_2\boldsymbol{r}_1'\boldsymbol{r}_2') = \int \boldsymbol{a}^*(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi(\boldsymbol{r}_1'\boldsymbol{r}_2'\boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \tag{9b}$$

for the case where r_1 only is small. The other combinations follow by the use of (6a, b).

If one puts $\boldsymbol{r}_2' = \boldsymbol{r}_2$ in (8), integrates over $\boldsymbol{r}_2$ and uses the relation [see Eq. (5)]

$$\gamma(\boldsymbol{r}_1, \boldsymbol{r}_1') \equiv \Gamma^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_1') = \int \Gamma^{(2)}(\boldsymbol{r}_1\boldsymbol{r}_2, \boldsymbol{r}_1'\boldsymbol{r}_2)\, d\boldsymbol{r}_2 \tag{10a}$$

one gets

$$\gamma(\boldsymbol{r}_1, \boldsymbol{r}_1') = \gamma(0,0)\,[1 - Z(r_1 + r_1')] + \boldsymbol{r}_1\cdot\boldsymbol{b}^* + \boldsymbol{r}_1'\cdot\boldsymbol{b} + \ldots \tag{11a}$$

with

$$\boldsymbol{b} = \int \boldsymbol{b}(\boldsymbol{r}_2\boldsymbol{r}_2)\, d\boldsymbol{r}_2 = \int \boldsymbol{a}(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi^*(0\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_n\,, \tag{11b}$$

which agrees with Eq. (15a, b) of [8], if Ψ is real.

* With the normalisation used by P. O. Löwdin [2], a factor $\binom{N}{p}$ occurs on the r.h.s. of Eq. (5) and (6c).

** This however is only a necessary but not sufficient condition for $\Gamma^{(p)}$ being n-representable, see chapter 1.

The same procedure, but starting from Eq. (9) instead, gives another cusp-condition for γ which we give here only for the sake of completeness:

$$\gamma(\boldsymbol{r}_1, \boldsymbol{r}_1') = \gamma(0, \boldsymbol{r}_1') \cdot (1 - Zr_1) + \boldsymbol{r}_1 \cdot \boldsymbol{b}^*(\boldsymbol{r}_1') \,, \tag{12a}$$

where

$$\boldsymbol{b}^*(\boldsymbol{r}_1') = \int \boldsymbol{b}^*(\boldsymbol{r}_2 \boldsymbol{r}_1' \boldsymbol{r}_2)\, d\boldsymbol{r}_2 = \int \boldsymbol{a}^*(\boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, \Psi(\boldsymbol{r}_1' \boldsymbol{r}_2 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_n \,. \tag{12b}$$

We next derive the conditions on $\Gamma^{(2)}$ resulting from the *correlation-cusp* in Ψ. Proceeding as above but with (4b) instead of (4a) we get

$$\Gamma^{(2)}(\boldsymbol{r}_1 \boldsymbol{r}_2, \boldsymbol{r}_1' \boldsymbol{r}_2') = \Gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}, \boldsymbol{r}'\boldsymbol{r}')\, (1 + \tfrac{1}{2}\, r_{12} + \tfrac{1}{2}\, r_{1'2'}) + \boldsymbol{r}_{12} \cdot \boldsymbol{d}^*(\boldsymbol{r}\boldsymbol{r}') + \boldsymbol{r}_{1'2'} \cdot \boldsymbol{d}(\boldsymbol{r}'\boldsymbol{r}) + \ldots \tag{13a}$$

where

$$\boldsymbol{d}(\boldsymbol{r}'\boldsymbol{r}) = \int \boldsymbol{c}(\boldsymbol{r}'\boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, \Psi^*(\boldsymbol{r}\boldsymbol{r}\boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \tag{13b}$$

for the case where *both* $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{1'2'}$ are small. Eq. (6a) is fulfilled by (13a).

If Eq. (4b) is used just once, we get finally

$$\Gamma^{(2)}(\boldsymbol{r}_1 \boldsymbol{r}_2, \boldsymbol{r}_1' \boldsymbol{r}_2') = \Gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}, \boldsymbol{r}_1' \boldsymbol{r}_2') \cdot (1 + \tfrac{1}{2}\, \boldsymbol{r}_{12}) + \boldsymbol{r}_{12} \cdot \boldsymbol{d}^*(\boldsymbol{r}\boldsymbol{r}_1' \boldsymbol{r}_2') + \ldots \tag{14a}$$

where

$$\boldsymbol{d}^*(\boldsymbol{r}\boldsymbol{r}_1' \boldsymbol{r}_2') = \int \boldsymbol{c}^*(\boldsymbol{r}, \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, \Psi(\boldsymbol{r}_1' \boldsymbol{r}_2' \boldsymbol{r}_3 \ldots \boldsymbol{r}_n)\, d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_n \tag{14b}$$

for the case where only r_{12} is small.

4. Discussion

In conclusion, a few remarks about the derived cusp-conditions for $\Gamma^{(2)}$ may be in order.

First of all, Eq. (3a, 4a) were derived under the assumption that all of $\boldsymbol{r}_2 \ldots \boldsymbol{r}_n$ are different from each other and from the zero vector. However, the integration in (8b) goes over all space and therefore contains a part, where this assumption is violated. It seems reasonable to assume however, that the infinitesimal extent of this part ensures that it makes no change in the result (8a, b). The same remark obtains for Eq. (9—14) also.

Secondly, Eq. (8—14) do not contain *all* of the possible combinations. For example, Eq. (8) together with the use of Eq. (6b) take care of only four out of a total of six possible combinations of two vectors going to zero out of a total of four. For the remaining two combinations (r_1 *and* $r_2 \to 0$ or r_1' *and* $r_2' \to 0$) one needs the behaviour of the wave function when two electrons approach a nucleus *simultaneously* (3-body collision-type of singularity). As mentioned before, this behaviour of Ψ when two — or even more — of Eq. (2a, b) hold, is still unknown.

In this connection, the statement in [8] concerning the logarithmic terms introduced by FOCK [11] in an expansion of Ψ for the 2-electron case needs to be clarified. Theorem II of KATO's paper [10] ensures the boundedness of Ψ even at these higher singularities. This theorem by itself does not exclude a term of the form $(r_1^2 + r_2^2) \cdot ln(r_1^2 + r_2^2)$ as introduced by FOCK. Whether such a term actually occurs however is still open to doubt due to the formal nature of FOCK's expansion.

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References

[*1*] Since a list of all papers published would be rather long, reference should be made to the following review articles: COLEMAN, A. J.: Rev. Mod. Phys. **35**, 668 (1963). — TER HAAR, D.: Rep. Progr. Phys. **24**, 304 (1961). — MCWEENY, R.: Rev. Mod. Phys. **32**, 355 (1960).

[*2*] LÖWDIN, P. O.: Phys. Rev. **97**, 1474 (1955).

[*3*] GARROD, C., and J. K. PERCUS: J. Math. Phys. **5**, 1756 (1964).

[*4*] BINGEL, W. A.: J. Chem. Phys. **32**, 1522 (1960).

[*5*] MCWEENY, R., and Y. MIZUNO: Proc. Roy. Soc. (London) **A 259**, 554 (1961).

[*6*] BINGEL, W. A.: J. Chem. Phys. **34**, 1066 (1961).

[*7*] — J. Chem. Phys. **36**, 2842 (1962).

[*8*] — Z. Naturforschg. **18a**, 1249 (1963).

[*9*] STEINER, E.: J. Chem. Phys. **39**, 2365 (1963).

[*10*] KATO, T.: Commun. Pure Appl. Math. **10**, 151 (1957).

[*11*] FOCK, V.: D.K.N.V.S. Forh. **31**, 138 and 145 (1958).

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