

A Physical Interpretation of the Cusp Conditions for Molecular Wave Functions

W. A. BINGEL

Lehrstuhl für Theoretische Chemie der Universität Göttingen

Received May 2, 1967

The cusp conditions for the Coulomb- and Correlation-cusp of molecular wave functions are derived directly in integrated form from the Schrödinger equation. For the Coulomb-cusp the slope of the wave function at nucleus α is given by the *directional* derivative

$$-\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{1\alpha}}\right)_{r_{1\alpha}=0} = Z_{\alpha} + d \cdot \cos \vartheta_1.$$

The magnitude of d remains undetermined, the direction of steepest slope ($\vartheta_1 = 0$) coincides with that of the vector of the intramolecular electric field \mathbf{E} produced by the other electrons and nuclei at the position of nucleus α .

For the correlation cusp the corresponding directional derivative is shown to be

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}}\right)_{r_{12}=0} = \frac{1}{2} + c \cdot \cos \alpha.$$

Here both the magnitude of c and the direction of the polar axis for the angle α remain undetermined. The special cases of an 1-electron molecule and a 2-electron atom are considered.

Die Bedingungen für den Coulomb- und Korrelations-cusp molekularer Wellenfunktionen werden in integrierter Form direkt aus der Schrödingergleichung abgeleitet. Für den Coulomb-cusp ist die Ableitung der Wellenfunktion am Kern α durch die Richtungsableitung

$$-\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{1\alpha}}\right)_{r_{1\alpha}=0} = Z_{\alpha} + d \cdot \cos \vartheta_1$$

gegeben. Der Betrag von d bleibt unbestimmt, die Richtung der stärksten Abnahme von $\Psi(\vartheta_1 = 0)$ stimmt mit der des Vektors des innermolekularen elektrischen Feldes \mathbf{E} überein, das von den anderen Elektronen und Kernen am Ort des Kerns α erzeugt wird.

Für den Korrelations-cusp ergibt sich die entsprechende Richtungsableitung zu

$$+\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}}\right)_{r_{12}=0} = \frac{1}{2} + c \cdot \cos \alpha.$$

Hier bleiben der Betrag von c und die Polarachse für den Winkel α unbestimmt. Die Sonderfälle eines Eielektronenmoleküls und eines Zweielektronenatoms werden diskutiert.

Les conditions de rebroussement pour le rebroussement coulombien et de corrélation des fonctions d'ondes moléculaires sont déduites directement sous forme intégrée à partir de l'équation de Schrödinger. Pour le rebroussement coulombien la pente de la fonction d'onde au noyau α est donnée par la dérivée directionnelle,

$$-\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{1\alpha}}\right)_{r_{1\alpha}=0} = Z_{\alpha} + d \cdot \cos \vartheta_1.$$

La valeur de d demeure indéterminée, la direction de plus grande pente ($\vartheta_1 = 0$) coïncide avec celle du vecteur champ électrique intramoléculaire \mathbf{E} produit par les autres électrons et les noyaux à l'endroit du noyau α .

Pour le rebroussement de corrélation on montre que la dérivée directionnelle correspondante est:

$$\left(\frac{1}{\bar{\Psi}} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} + c \cdot \cos \alpha .$$

Dans ce cas la valeur de c aussi bien que la direction de l'axe polaire pour l'angle α demeurent indéterminés. On considère les cas particuliers d'une molécule à 1 électron et d'un atome à 2 électrons.

1. Introduction

In recent years there has been an increasing interest in the behaviour of molecular wave functions Ψ at those points of configuration space, where two or more particle positions coincide. For the coalescence of one electron with a nucleus Ψ has a cusp which is due to that singularity of the wave equation where the corresponding Coulomb attraction term becomes infinite. A similar cusp also occurs if the positions of two electrons coincide. There is a very simple relation between the *average* slope and the value of the wave function at such a singular point which was first proved rigorously by T. KATO [1]. Later it was conjectured by the author [2], that these *differential* cusp conditions are equivalent to the following *integrated* expressions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \Psi(0, \mathbf{r}_2, \dots, \mathbf{r}_n) \cdot (1 - Z_\alpha r_1) + \mathbf{r}_1 \cdot \mathbf{a}(\mathbf{r}_2, \dots, \mathbf{r}_n) + O(r_1^2) \quad (1)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \Psi(\mathbf{r}_0, \mathbf{r}_0, \mathbf{r}_3, \dots, \mathbf{r}_n) \cdot (1 + \frac{1}{2} r_{12}) + \mathbf{r}_{12} \cdot \mathbf{c}(\mathbf{r}_0, \mathbf{r}_3, \dots, \mathbf{r}_n) + O(r_{12}^2) . \quad (2)$$

Eq. (1) gives the behaviour of Ψ near the Coulomb-cusp at nucleus α , the vectors \mathbf{r}_i giving the electron positions measured from that nucleus. For the correlation cusp of Eq. (2) the \mathbf{r}_i can be measured from any common origin, and $\mathbf{r}_0 = \frac{1}{2} \cdot (\mathbf{r}_1 + \mathbf{r}_2)$ is the point of coalescence of electrons 1 and 2.

If in Eq. (1) one averages Ψ over the angle variables ϑ_1, φ_1 and then takes the derivative with respect to r_1 for $r_1 = 0$, the differential form for the Coulomb-cusp results. Starting from Eq. (2), a similar procedure yields the differential form of the correlation cusp.

The earlier work by the author [2] is open to improvement on two counts: firstly, Eqs. (1) and (2) were not proved from first principles and secondly, the vectors \mathbf{a} and \mathbf{c} were left undetermined. They occur in the angle-dependant part of Eqs. (1) and (2), which drop out in going over to the differential form because of the angular averages involved there. They therefore add to our previous knowledge of the behaviour of Ψ in the vicinity of a singularity.

Work on this problem was therefore started by the author with the aim of deriving Eqs. (1) and (2) directly from the wave equation. The same problem was considered in a recent paper by PACK and BYERS-BROWN [3], who derived Eqs. (1) and (2) without however determining the value of the vector coefficients \mathbf{a} and \mathbf{c} , which according to them "are not determined by the Coulomb singularity". This statement is quite correct, since the Coulomb singularity does in fact determine only the spherically symmetric part of the cusp. However, the *direction* of the vector \mathbf{a} , which gives the direction of smallest (or steepest) slope of the wave function is shown to be parallel to the electric field produced by the other electrons and nuclei at the nucleus in question. This angle-dependant part of the Coulomb-cusp therefore results from what one may call an *intramolecular* Stark-effect.

In the approximation used here, the angle-dependant part of the correlation cusp remains undetermined. It probably can be obtained only in a higher approximation.

2. Derivation of the Coulomb-cusp

The Schrödinger equation for a molecule neglecting nuclear motion and spin-orbit as well as other higher interactions is

$$(H - W) \Psi = \left\{ - \left(\frac{1}{2} \Delta_1 + \frac{Z_\alpha}{r_{1\alpha}} \right) + \left(- \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{Z_\beta}{r_{1\beta}} + \sum_{j=2}^n \frac{1}{r_{1j}} \right) + \left[\sum_{j=2}^n - \left(\frac{1}{2} \Delta_j + \sum_{\beta'} \frac{Z_{\beta'}}{r_{j\beta'}} \right) + \sum_{\substack{i>j \geq 2}} \sum \frac{1}{r_{ij}} \right] - W \right\} \Psi = 0. \quad (3)$$

Here the Hamiltonian H has already been partitioned in a way which reflects the assumed arrangement of electron positions: electron 1 is close to nucleus α , i.e. $r_{1\alpha}$ is supposed to be small compared to all other distances such as $r_{1\beta}$, r_{1j} etc. We can then expand the second term in Eq. (3):

$$\left(- \sum_{\substack{\beta \\ (\beta \neq \alpha)}} \frac{Z_\beta}{r_{1\beta}} + \sum_{j=2}^n \frac{1}{r_{1j}} \right) = \left(- \sum_{\substack{\beta \\ (\beta \neq \alpha)}} \frac{Z_\beta}{R_{\alpha\beta}} + \sum_{j=2}^n \frac{1}{r_{j\alpha}} \right) + \mathbf{r}_{1\alpha} \cdot (\mathbf{E}_n + \mathbf{E}_e) + O(r_{1\alpha}^2) \quad (4)$$

where

$$\mathbf{E}_n = \sum_{\substack{\beta \\ (\beta \neq \alpha)}} Z_\beta \frac{\mathbf{R}_{\alpha\beta}}{R_{\alpha\beta}^3} \quad (5)$$

is the vector of the electric field produced by the other nuclei $\beta \neq \alpha$ at the position of nucleus α and

$$\mathbf{E}_e = \sum_{j=2}^n \frac{\mathbf{r}_{j\alpha}}{r_{j\alpha}^3} \quad (6)$$

is the electric field at nucleus α produced by the other electrons $j = 2 \dots n$. Let $\mathbf{E} = \mathbf{E}_n + \mathbf{E}_e$, we can then rewrite Eq. (3) to give

$$\left\{ - \left(\frac{1}{2} \Delta_1 + \frac{Z_\alpha}{r_{1\alpha}} \right) + \mathbf{r}_{1\alpha} \cdot \mathbf{E} + O(r_{1\alpha}^2) + \left(- \sum_{j=2}^n \frac{1}{2} \Delta_j + \frac{Z_\alpha - 1}{r_{j\alpha}} + \sum_{\substack{\beta \\ (\beta \neq \alpha)}} \frac{Z_\beta}{r_{j\beta}} + \sum_{i>j \geq 2} \sum \frac{1}{r_{ij}} \right) - \left(W + \sum_{\substack{\beta \\ (\beta \neq \alpha)}} \frac{Z_\beta}{R_{\alpha\beta}} \right) \right\} \Psi \equiv \{h(1) + \mathbf{r}_{1\alpha} \cdot \mathbf{E} + O(r_{1\alpha}^2) + H'(2 \dots n) - W'\} \Psi = 0. \quad (7)$$

In this form the physical interpretation is clear: the n electrons are decomposed into two parts, electron 1 in the field of nucleus α and the remaining electrons in the field of all nuclei, but with the nuclear charge of nucleus α reduced by one. These two parts are coupled by the second term in Eq. (7), which — to first order in $r_{1\alpha}$ — represents the effect on electron 1 of the electric field produced by the other electrons and nuclei. Therefore it gives rise to an intramolecular Stark-effect of electron 1.

One might be tempted to treat Eq. (7) by conventional perturbation theory in a similar way as it is done for the Stark-effect in an external electric field. In 0-th order one then gets

$$[h(1) + H'(2 \dots n) - W'_0] \Psi_0 = 0 \quad (8)$$

which separates into the two noninteracting parts ($\Psi_0 = \varphi_0 \cdot \Phi_0$)

$$[h(1) - \varepsilon] \varphi_0(1) = 0 \quad \text{and} \quad [H' - (W'_0 - \varepsilon)] \Phi_0(2 \dots N) = 0. \quad (9a, b)$$

Since (9a) is just the Schrödinger-equation for a H-like atom, its lowest $1s$ solution would give

$$\Psi_0 = (Z_\alpha^3/\pi)^{1/2} e^{-Z_\alpha r_{1\alpha}} \Phi_0(2 \dots N) = \Psi_0(0, \mathbf{r}_2 \dots \mathbf{r}_n) (1 - Z_\alpha r_{1\alpha} + \dots) \quad (9c)$$

i.e. the spherically symmetric part of the Coulomb-cusp of Eq. (4). Proceeding in this way, the 1-st order correction to the unperturbed wave function would then be determined from

$$[h(1) + H'(2 \dots N) - W'_0] \Psi^{(1)} + \mathbf{r}_{1\alpha} \cdot \mathbf{E} \Psi_0 = 0 \quad (10)$$

since the 1-st order correction to the energy vanishes. This equation, which contains the Stark-effect term, would then be expected to give the angle-dependant term in the cusp condition (1).

Unfortunately, this perturbation treatment does not work. Firstly, the solutions of Eq. (10) cannot be written in the form $\varphi^{(1)}(1) \cdot \Phi^{(1)}(2 \dots N)$, since the electric field \mathbf{E} depends on the coordinates of electrons $2 \dots n$ [see Eq. (6)].

Secondly, even the 0-th order solution (9c) is incorrect. The explicit expression for the φ_0 -part used there obtains only, if the usual boundary conditions for $r_{1\alpha} = 0$ and $r_{1\alpha} = \infty$ hold for Eq. (9a). But Eqs. (7) to (9) were derived by an expansion, assuming $r_{1\alpha}$ to be small. Therefore, only the boundary condition at $r_{1\alpha} = 0$ remains and the correct φ_0 is different from the $1s$ solution.

We therefore use an expansion method which is equivalent to that used by PACK et al. [3], but take terms up to $r_{1\alpha}$ into account (two orders more than PACK et al. uses), in the hope of determining the angle-dependant term of the cusp condition (1).

We now introduce polar coordinates $r_1, \vartheta_1, \varphi_1$ for electron 1 with the origin at nucleus α , and choose the direction of the polar axis parallel to the total electric field \mathbf{E} . The perturbation term in Eq. (7) then is $+r_1 \cdot \mathbf{E} \cdot \cos \vartheta_1$, which has $C_{\infty v}$ -symmetry. This is also true of the total Hamiltonian in (7). Therefore, if the total wave function Ψ is to be different from zero for $r_1 = 0$, it must be of symmetry species Σ as far as the angles ϑ_1, φ_1 of electron 1 are concerned. The expansion of Ψ must then be of the form:

$$\Psi = \sum_{l=0}^{\infty} \Psi_l(r_1, \mathbf{r}_2 \dots \mathbf{r}_n) \cdot P_l(\cos \vartheta_1). \quad (11)$$

Introducing this expansion into Eq. (7), we get:

$$(H - W) \Psi = 0 = \sum_l P_l(\cos \vartheta_1) \left\{ -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} - \frac{l(l+1)}{r_1^2} \right) - \frac{Z_\alpha}{r_1} + (H' - W') + r_1 \mathbf{E} \cos \vartheta_1 + O(r_1^2) \right\} \Psi_l = 0. \quad (12)$$

Since $\Psi_l \sim r_1^l$ for small r_1 if Ψ is to be well behaved at $r_1 = 0$, the first two terms ($l = 0$ and $l = 1$) of (11) are sufficient to derive the cusp condition (1). We therefore integrate (12) over the angles ϑ_1, φ_1 to get an equation for Ψ_0 :

$$(H' - W') \Psi_0 = \frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) \Psi_0 + \frac{Z_\alpha}{r_1} \Psi_0 - \frac{1}{3} E r_1 \Psi_1 + O(r_1^2). \quad (13a)$$

If we first multiply (12) by $\cos \vartheta_1$ and then integrate, we get the equation

$$(H' - W') \Psi_1 = \frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} - \frac{2}{r_1^2} \right) \Psi_1 + \frac{Z_\alpha}{r_1} \Psi_1 - E r_1 \Psi_0 + O(r_1^2) \quad (13b)$$

for Ψ_1 . Originally, there was also a term with Ψ_2 in (13b), which is proportional to r_1^2 however and can therefore be dropped. The "ansatz"

$$\Psi_0 = \Psi(0, \mathbf{r}_2 \dots \mathbf{r}_n) + ar_1 + br_1^2 + \dots, \Psi_1 = -\Psi(0, \mathbf{r}_2 \dots \mathbf{r}_n) \cdot r_1(d + er_1 + \dots) \quad (14)$$

already incorporates our knowledge about the behaviour of Ψ_l for small r_1 (see above). Introducing it into (13a, b), collecting equal powers of r_1 and setting their coefficients equal to zero, we get from (13a) for the terms with

$$\begin{aligned} (r_1)^{-1}: a &= -Z_\alpha \Psi(0, \mathbf{r}_2 \dots \mathbf{r}_n) \\ (r_1)^0: b &= \frac{1}{3}[Z_\alpha^2 + (H' - W')] \Psi(0, \mathbf{r}_2 \dots \mathbf{r}_n) \end{aligned}$$

and an expression for the coefficient c from the $(r_1)^1$ -term. Eq. (13b) gives in the same way from

$$\begin{aligned} (r_1)^{-1}: d - d &= 0 \\ (r_1)^0: e &= -\frac{1}{2} Z_\alpha d \\ (r_1)^1: 5f &= \left\{ \frac{1}{\Psi(0)} (H' - W') \Psi(0) + \frac{1}{2} Z_\alpha^2 \right\} d - E. \end{aligned}$$

With these values of the coefficients we finally get from (11) and (14)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = \Psi(0, \mathbf{r}_2 \dots \mathbf{r}_n) (1 - Z_\alpha r_1 - d \cdot r_1 \cos \vartheta_1) + O(r_1^2) \quad (15)$$

i.e. the cusp condition (1).

Our hope of determining the angle-dependant term of the Coulomb-cusp has only been partially fulfilled: its *magnitude* — as given by the coefficient d — remains undetermined, but its *direction* is indeed shown to lie parallel to the intramolecular electric field vector \mathbf{E} . Together with the magnitude the *sign* of the coefficient d is not known. It is physically reasonable however to assume that the direction of *steepest* descent of the wave function is the same as the direction of \mathbf{E} , rather than the opposite. With this in mind the signs in Eqs. (14) and (15) have been chosen in such a way that the coefficient d itself is positive.

Eq. (15) shows, that the slope of Ψ at nucleus α depends on the direction in which we take it. This is shown in Fig. 1, where the directional derivative

$$-\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_1} \right)_{\substack{r_1=0 \\ \vartheta_1=\text{const.}}} = Z_\alpha + d \cos \vartheta_1 \quad (16)$$

is plotted as a polar diagram. As a consequence the level lines $\Psi = \text{const.}$ near nucleus α are not small concentric circles (unless $d = 0$) but rather small confocal ellipses with the major axis parallel to the electric field vector \mathbf{E} .

This situation can be visualized most easily in the special case of a molecule with only one electron such as H_3^+ . Here the electronic contribution (6) to \mathbf{E} vanishes and the electric field vector $\mathbf{E} = \mathbf{E}_n$ can easily be obtained from (5) for all nuclei. Fig. 2 shows the resulting level lines $\Psi = \text{const.}$ for the linear, bent and equilateral geometry of H_3^+ . In the linear case the contributions to E_b from the end-protons cancel each other. Therefore E_b — and presumably also the coefficient d — vanishes, which leads to a spherically symmetric cusp. On the other hand the cusps of the end-protons are angle-dependent in the manner indicated in Fig. 2. It should be noted, that in the bent form the direction of steepest slope at the end-protons does not coincide with the bond directions. This results from the vector addition of the contributions to \mathbf{E} from the other two nuclei. For the equi-

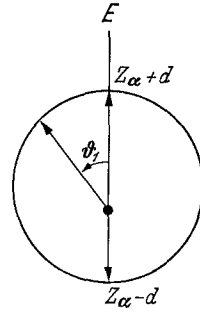
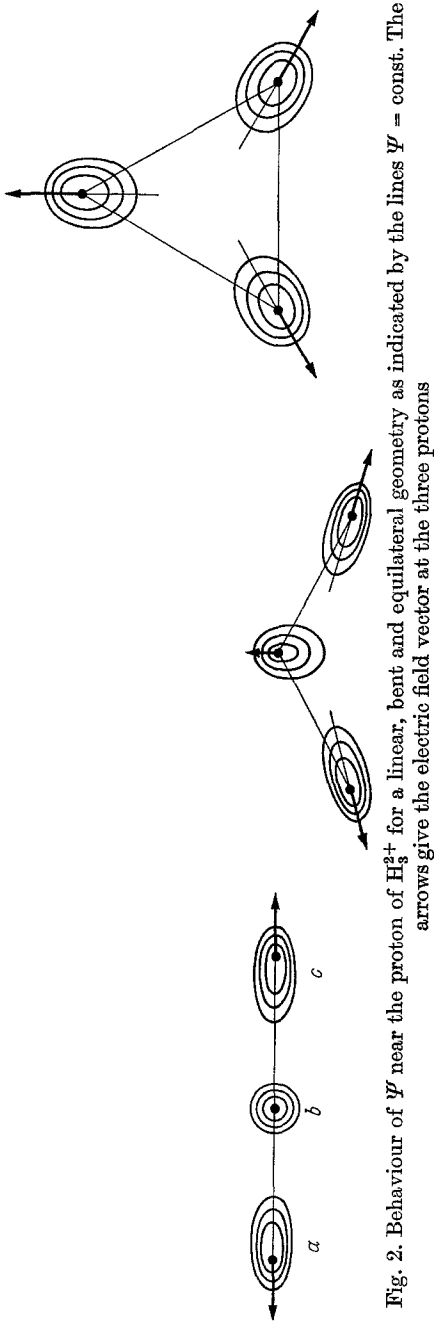


Fig. 1. Polar plot of the directional derivative (16), giving the slope of the wave function in different directions at a Coulomb cusp

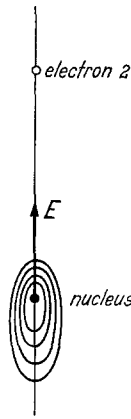


Fig. 3

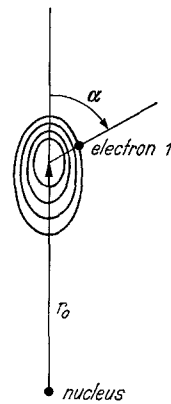


Fig. 4

Fig. 3. Behaviour of Ψ near the nucleus in 2-electron atoms as a function of the position of electron 1 for a fixed position of electron 2

Fig. 4. Behaviour of Ψ near a correlation cusp as a function of the position of electron 1. The position of electron 2 is always diametrically opposite to that of electron 1

lateral geometry each electric vector points outwards radially. This was to be expected from reasons of symmetry.

Another case which can be discussed very easily are the atoms with two electrons. Here E_n vanishes, the electronic contribution to the electric field at the

nucleus is

$$\mathbf{E}_e = \mathbf{r}_2/r_2^3 \quad (17)$$

and Eq. (15) takes the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(0, \mathbf{r}_2) [1 - Zr_1 - d(r_2) r_1 \cos \vartheta_{12}]. \quad (18)$$

For a fixed position of electron 2, this expression for Ψ is plotted in Fig. 3 as a function of the position of electron 1. It shows the polarisation of Ψ near the nucleus, which in another context is also called angular correlation.

For S -states of 2-electron atoms this relation was derived already by the author [2]. It was also shown there, that in this special case the value of the coefficient $d(r_2)$ is given by

$$\Psi(0, r_2) \cdot d(r_2) = \left| \left(\frac{\partial \Psi}{\partial r_{12}} \right)_{r_1=0} \right|. \quad (19)$$

3. The Correlation Cusp

We now consider the situation, where two electrons — say electrons 1 and 2 — are close to each other. The wave equation can then be partitioned as follows

$$\begin{aligned} (H - W) \Psi = & \left\{ -\frac{1}{2}(\Delta_1 + \Delta_2) - \sum_{\alpha} Z_{\alpha} \left(\frac{1}{r_{1\alpha}} + \frac{1}{r_{2\alpha}} \right) + \frac{1}{r_{12}} + \sum_{j=3}^n \left(\frac{1}{r_{1j}} + \frac{1}{r_{2j}} \right) + \right. \\ & \left. + \sum_{j=3}^n \left(\frac{1}{2} \Delta_j + \sum_{\alpha} \frac{Z_{\alpha}}{r_{j\alpha}} \right) + \sum_{i>j \geq 3} \frac{1}{r_{ij}} - W \right\} \Psi = 0. \end{aligned} \quad (20)$$

Instead of \mathbf{r}_1 and \mathbf{r}_2 we now introduce $\mathbf{r}_0 = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and expand the terms coupling electrons 1 and 2 to all nuclei and the other electrons, assuming r_{12} to be small. We then get

$$\begin{aligned} \left\{ \left(-\Delta_{12} + \frac{1}{r_{12}} \right) + O(r_{12}^2) + \left(-\frac{1}{2} \Delta_0 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{0\alpha}} \right) + \sum_{j=3}^n \left(-\frac{1}{2} \Delta_j - \sum_{\alpha} \frac{Z_{\alpha}}{r_{j\alpha}} + \frac{2}{r_{0j}} \right) + \right. \\ \left. + \sum_{i>j \geq 3} \frac{1}{r_{ij}} - W \right\} \Psi = \{h_{12} + O(r_{12}^2) + h_0 + H'(3 \dots n) - W\} \Psi = 0. \end{aligned} \quad (21)$$

The physical interpretation of this decomposition is as follows: the first term describes the relative motion of electrons 1 and 2 around their center of gravity under the influence of their mutual repulsion; the third term describes the motion of a "dielectron" of mass 2 and charge -2 in the field of all nuclei and the last term determines the motion of the remaining electrons $3 \dots n$ in the field of all nuclei, a charge -2 at the point of coalescence of electrons 1 and 2 and their mutual repulsion. It should be noted, that — up to linear terms in r_{12} — there is no coupling between the first term and the others in Eq. (21). This has the consequence, that introducing the expansion

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \dots \mathbf{r}_n) = \Psi(\mathbf{r}_0, \mathbf{r}_0, \mathbf{r}_3 \dots \mathbf{r}_n) \cdot (1 + b r_{12} + \dots) + r_{12} \cos \alpha \cdot (c + \dots) \quad (22)$$

into (21) we do get the expected result $b = +\frac{1}{2}$, but neither the coefficient c nor the direction of the polar axis z for the angle $\alpha = \sphericalangle(z, \mathbf{r}_{12})$ are determined. We have shown however that the integral form of the correlation cusp condition (2) follows indeed directly from the wave equation.

For the special case of 2-electron atoms we can get more detailed information. Here (21) simplifies to

$$[h_{12} + O(r_{12}^2) + h_0 - W] \Psi(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (23)$$

and $\Psi = \varphi(\mathbf{r}_0) \cdot \chi(\mathbf{r}_{12})$ to the same order, where the two factors are solutions of

$$(\hbar_{12} - \varepsilon) \chi = 0, \quad [\hbar_0 - (W - \varepsilon)] \varphi = 0 \quad (24a, b)$$

respectively. It can be shown, that the relation

$$\hat{\mathbf{L}} = \hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2 = \hat{\mathbf{l}}_{12} + \hat{\mathbf{l}}_0 \quad (25)$$

holds for the vector operators of angular momentum in this case. If Ψ is to be an eigenfunction of $\hat{\mathbf{L}}^2$, φ and χ must be eigenfunctions of $\hat{\mathbf{l}}_0^2$ and $\hat{\mathbf{l}}_{12}^2$ respectively. For an S -state the solution must have the form

$$\Psi = \varphi_s(r_0) \chi_s(r_{12}) + \varphi_p(\mathbf{r}_0) \chi_p(\mathbf{r}_{12}) + \dots \quad (26)$$

Using the explicit form of Eq. (24a), and its solutions for small r_{12} , it is then easy to show, that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_s(r_0) \chi_s(0) \cdot (1 + \frac{1}{2} r_{12} + \dots) + \varphi_p(\mathbf{r}_0) \cdot \text{const.} \cdot r_{12} \cos \alpha + \dots \quad (27)$$

This has the form of Eq. (2). Furthermore, it was shown earlier [2] that the polar axis of the angle α coincides in this case with the position vector \mathbf{r}_0 of the point of coalescence of the two electrons and (27) takes the final form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_s(r_0) \chi_s(0) \cdot (1 + \frac{1}{2} r_{12}) + \mathbf{r}_{12} \cdot \mathbf{r}_0 f(r_0) + O(r_{12}^2). \quad (28)$$

The lines $\Psi = \text{const.}$ in the vicinity of the correlation cusp (see Fig. 4) are again confocal ellipses with the major axis parallel to the vector \mathbf{r}_0 .

This work was supported in part by the "Deutsche Forschungsgemeinschaft" within the "Schwerpunktprogramm Theoretische Chemie". Part of this work was done during the authors visits - sponsored by a NATO research grant - of Dr. BERTHIER's group in Paris and Prof. McWEENY's group at the University of Sheffield.

References

1. KATO, T.: Commun. pure appl. Math. **10**, 151 (1957).
2. BINGEL, W. A.: Z. Naturforsch. **18a**, 1249 (1963).
3. PACK, R. T., and W. BYERS BROWN: J. chem. Physics **45**, 556 (1966).

Prof. Dr. W. A. BINGEL
Lehrstuhl für Theoretische Chemie
der Universität
3400 Göttingen