Theory of Unidimensional Molecular Collisions. Broken Path Model

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A harmonic oscillator model for reactive chemical collisions is proposed. The model is solved rigorously for the reaction $H_2 + H = H + H_2$. The results show the appearance of quite narrow resonance peaks for the reaction cross sections.

I. Introduction

The theoretical study of chemical reactions from the standpoint of the general collision theory[1] requires the knowledge of the cross sections involved in the reaction. Recently, a number of experiments have been conducted on this subject.[2] From the theoretical point of view, the problem of the reaction cross sections is a very difficult one, and not as much has been done. However, classical approaches have been explored recently.[3] Also, a quantum mechanical solution for a reasonable potential surface has been attempted.[4]

Even in the simplest case, the solution of the problem is very difficult. For this reason, it seems worthwhile to study a model with an interaction potential which only roughly approximates the real one, but which is exactly solvable. The model will be described in section II. It is similar to the model discussed by Eyring.[5]

Section III is devoted to the discussion of some features of the cross section of the reaction

$$H_2 + H = H + H_2 \qquad \text{(I-1)}$$

in the case of a head on collision.

II. The Broken Path Model

Let us take the simple case of reaction I-1 in one dimension. Using Born–Oppenheimer's approximation,[3,4] we write the Schroedinger equation of the system as (see Figure 1)

$$-\frac{\hbar^2}{2M_H}\left[\frac{\partial^2}{\partial r_{12}^2}+\frac{\partial^2}{\partial r_{23}^2}-\frac{\partial^2}{\partial r_{12}\partial r_{23}}\right]\Psi + V\Psi = E\Psi \qquad \text{(II-1)}$$

The solutions for $r_{23} > q_\alpha$ (reactants or entrance channel) are of the form

$$\phi_\alpha = [A_\alpha' e^{ik_\alpha r_\alpha} + B_\alpha' e^{-ik_\alpha r_\alpha}]\varphi_\alpha \qquad \text{(II-2)}$$

and for $r_{12} > q_\beta$ (products or exit channel)

$$\phi_\beta = A_\beta' e^{ik_\beta r_\beta}\varphi_\beta \qquad \text{(II-3)}$$

where $r_\alpha = r_{23} + {}^1/_2\, r_{12}$ and $r_\beta = r_{12} + {}^1/_2\, r_{23}$. B_α is the amplitude of the ingoing wave. A_α and A_β are the amplitudes of the outgoing waves for channels α and β. B_β is zero because there are no ingoing waves in channel β. q_α and q_β are the smallest distances of no interaction.

In the region where all three atoms interact, the function V (eq II-1) has a complicated form.[6] The solution of eq II-1 in this region is extremely difficult; in principle, one could either search for approximate solutions of the exact equation, using variation or perturbation methods, or look for an approximate potential which is exactly solvable. In this paper we choose the latter approach.

The exact potential V is thus replaced by two (or eventually more) "cut parabolic saddles" (Figures 2 and 3). The approximation also replaces the usually curved reaction path by a broken line.

Analytically, in region I, we have

$$V_1 = -k'x^2 + ky^2 + V^0 \qquad \text{(II-4)}$$

with x and y defined in eq II-5.

(1) M. A. Eliason and J. Hirschfelder, *J. Chem. Phys.*, **30**, 1426 (1959).

(2) See, for example, D. Beck, E. F. Greene, and J. Ross, *ibid.*, **37**, 2895 (1962); S. Datz, D. R. Herschbach, and E. H. Taylor, *ibid.*, **35**, 1549 (1961).

(3) M. Karplus, R. N. Porter, and R. D. Sharma, *ibid.*, **43**, 3259 (1965).

(4) K. Pitzer and E. M. Mortensen, Special Publication No. 16, The Chemical Society, London, 1962.

(5) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1954.

(6) S. Sato, *J. Chem. Phys.*, **23**, 592 (1955).

$$x = r_{12}\cos\theta_1 - r_{23}\sin\theta_1$$
$$y = r_{12}\sin\theta_1 + r_{23}\cos\theta_1 \qquad \text{(II-5)}$$

where x is the distance along the reaction path, with y the distance perpendicular to the reaction path. That is

$$V_1 = V^0 + r_{12}^2(k\cos^2\theta_1 - k'\sin^2\theta_1) + r_{23}^2(k\sin^2\theta_1 - k'\cos^2\theta_1) + 2r_{12}r_{23}(k + k')\cos\theta_1\sin\theta_1 \qquad \text{(II-6)}$$

Similarly, in region II

$$V_2 = V^0 + r_{12}^2(k\cos^2\theta_2 - k'\sin^2\theta_2) + r_{23}^2(k\sin^2\theta_2 - k'\cos^2\theta_2) + 2r_{12}r_{23}(k + k')\cos\theta_2\sin\theta_2 \qquad \text{(II-7)}$$

Equation II-1 is now solvable in each of the regions of configuration space (Figure 3). Let us then find the solutions for region I. Using normal coordinates[7]

$$Q_{11} = h_1 r_{12} + h_2 r_{23}$$
$$Q_{21} = h_3 r_{12} + h_4 r_{23} \qquad \text{(II-8)}$$

eq II-1 splits into two equations

$$\frac{d^2\phi_{11}}{dQ_{11}^2} + \frac{2}{\hbar^2}\left[E_{11} - \frac{\lambda_{11}}{2}Q_{11}^2\right]\phi_{11} = 0 \qquad \text{(II-9)}$$

and

$$\frac{d^2\phi_{21}}{dQ_{21}^2} + \frac{2}{\hbar^2}\left[E_{21} + \frac{\lambda_{21}}{2}Q_{21}^2\right]\phi_{21} = 0 \qquad \text{(II-10)}$$

Equation II-9 is the usual Hermite equation for harmonic oscillators. Equation II-10 is a confluent hypergeometric equation, which has two linearly independent solutions known as the parabolic cylinder or Weber functions[8]

$$D_{-(1/2)-(i\epsilon/2)}(Q_{21}\sqrt{2i\gamma_{21}});\quad D_{-(1/2)+(i\epsilon/2)}(Q_{21}\sqrt{-2i\gamma_{21}}) \qquad \text{(II-11)}$$

where $\epsilon = 2E_{21}/\hbar\sqrt{\lambda_{21}}$ and $\gamma_i = \sqrt{\lambda_i}/\hbar$. The complete solution for region I is then

$$\Psi_1 = \exp\left\{-\frac{\gamma_{11}}{2}Q_{11}^2\right\}H_n(Q_{11}\sqrt{\gamma_{11}}) \times [A_1 D_{-(1/2)-(i\epsilon/2)}(Q_{21}\sqrt{2i\gamma_{21}}) + B_1 D_{-(1/2)+(i\epsilon/2)}(Q_{21}\sqrt{-2i\gamma_{21}}) \qquad \text{(II-12)}$$

For region II, we have, similarly

$$\Psi_2 = \exp\left\{-\frac{\gamma_{12}}{2}Q_{12}^2\right\}H_n(Q_{12}\sqrt{\gamma_{12}}) \times [A_2 D_{-(1/2)-(i\epsilon/2)}(Q_{22}\sqrt{2i\gamma_{22}}) + B_2 D_{-(1/2)+(i\epsilon/2)}(Q_{22}\sqrt{-2i\gamma_{22}})] \qquad \text{(II-13)}$$

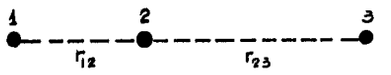

Figure 1. Activated complex.

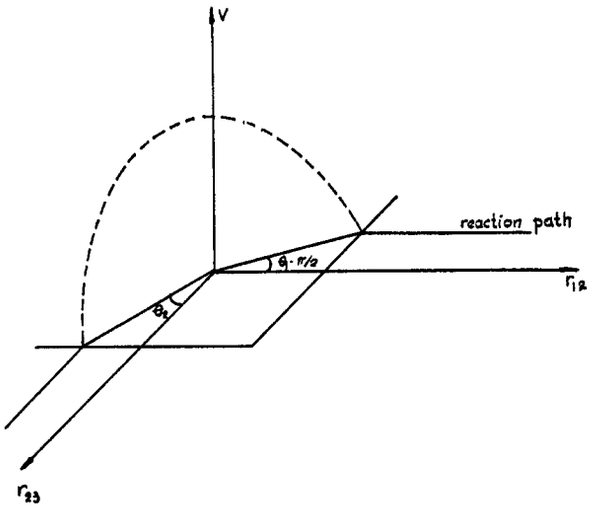

Figure 2. Potential energy.

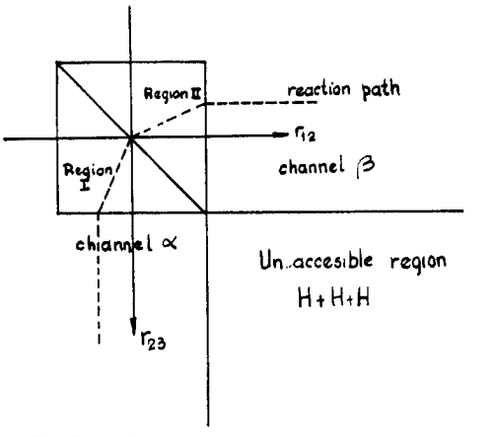

Figure 3. Configuration space.

Let us now specialize in cases in which all oscillators are in their fundamental levels. For reaction I-1 this is not a bad assumption since the activation energy is about 7 kcal/mole, whereas the energy needed to excite the first vibrational level is *ca.* 12 kcal/mole.

Now the problem is reduced to that of finding the values of the different A's and B's. This is done using the conditions of continuity of the functions and the first derivatives at the boundaries of the regions.

(7) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(8) P. M. Morse and H. Feshbach, "Methods of Theoretical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

Four boundary channel α–region I

$$\varphi_\alpha(A'e^{ik_\alpha r_\alpha} + B_\alpha'e^{-ik_\alpha r_\alpha})|_\alpha = \Psi_1|_\alpha \quad \text{(II-14)}$$

$$ik_\alpha\varphi_\alpha(A_\alpha'e^{ik_\alpha r_\alpha} - B_\alpha'e^{-ik_\alpha r_\alpha})|_\alpha = \Psi_1'|_\alpha \quad \text{(II-15)}$$

For boundary region I–region II

$$\Psi_1|_0 = \Psi_2|_0 \quad \text{(II-16)}$$

$$\Psi'|_0 = \Psi_2'|_0 \quad \text{(II-17)}$$

For boundary region II–channel β

$$\Psi_2|_\beta = A_\beta'e^{ik_\beta r_\beta}\varphi_\beta|_\beta \quad \text{(II-18)}$$

$$\Psi_2'|_\beta = ik_\beta A_\beta'e^{ik_\beta r_\beta}\varphi_\beta|_\beta \quad \text{(II-19)}$$

Using conditions of orthogonality of the wave functions of the stable oscillators, we get simpler relations.

For boundary channel α–region I

$$A_\alpha e^{ik_\alpha r_\alpha} + B_\alpha e^{-ik_\alpha r_\alpha} = A_1\chi_\alpha + B_1\chi_\alpha^* \quad \text{(II-20)}$$

$$ik_\alpha(A_\alpha e^{ik_\alpha r_\alpha} - B_\alpha e^{-ik_\alpha r_\alpha}) = A_1\chi_\alpha' + B_1\chi_\alpha^{*\prime} \quad \text{(II-21)}$$

For boundary region I–region II

$$A_1\kappa_1 + B_1\kappa_1^* = A_2\kappa_2 + B_2\kappa_2^* \quad \text{(II-22)}$$

$$A_1\kappa_1' + B_1\kappa_1^{*\prime} = A_2\kappa_2' + B_2\kappa_2^{*\prime} \quad \text{(II-23)}$$

For boundary region II–channel β

$$A_\beta e^{ik_\beta r_\beta} = A_2\chi_\beta + B_2\chi_\beta^* \quad \text{(II-24)}$$

$$ik_\beta A_\beta e^{ik_\beta r_\beta} = A_2\chi_\beta' + B_2\chi_\beta^{*\prime} \quad \text{(II-25)}$$

Here, we used the definitions

$$\chi_\alpha = \left(\frac{\nu_\alpha}{\pi}\right)^{1/4}\int_{-\infty}^{\infty} dr_{12}\exp\{-\tfrac{1}{2}[\nu_\alpha(r_{12} + q_\alpha tg\theta_1)^2 + \gamma_{11}Q_{11}^2]\}D_{-(1/2)-(i\epsilon/2)}(Q_{21}\sqrt{2i\gamma_{21}}) \quad \text{(II-26)}$$

$$A_\alpha = A_\alpha'\exp\left(-\frac{k_\alpha^2}{8\nu_\alpha}\right)$$

$$B_\alpha = B_\alpha'\exp\left(-\frac{k_\alpha^2}{8\nu_\alpha}\right)$$

and similar expressions for χ_β and A_β'.

Also

$$\kappa_1 = \int_{-\infty}^{\infty} dx\exp\{-\tfrac{1}{2}(\gamma_{12}Q_{12}^2 + \gamma_{11}Q_{11}^2)\} \times D_{-(1/2)-(i\epsilon/2)}(Q_{21}\sqrt{2i\gamma_{21}}) \quad \text{(II-27)}$$

$$\kappa_2 = \int_{-\infty}^{\infty} dx\exp\{-\gamma_{12}Q_{12}^2\}D_{-(1/2)-(i\epsilon/2)}(Q_{22}\sqrt{2i\gamma_{22}}) \quad \text{(II-28)}$$

with $\nu_\alpha = \sqrt{0.5M_HF_{HH}}$ and $x = (1/\sqrt{2})(r_{12} + r_{23})$.

Integration of these expressions gives (see Appendix)

$$\chi_\alpha = (1/h_3)\left(\frac{\nu_\alpha}{\gamma_{21}}\right)^{1/4}\exp(-q_\alpha^2c_\alpha)\frac{1}{(4a_\alpha^2 + 1)} \times \left(\frac{2a_\alpha + i}{2a_\alpha - i}\right)^{i\epsilon/4}D_{-(1/2)-(i\epsilon/2)}(-b_\alpha q_\alpha\sqrt{2i}) \quad \text{(II-29)}$$

and a similar expression for χ_β

$$\kappa_1 = \frac{\sqrt{2\pi}}{(h_3 + h_4)\sqrt{\gamma_{21}}}\frac{1}{(4a_1^2 + 1)^{1/4}} \times \left(\frac{2a_1 + i}{2a_1 - i}\right)^{i\epsilon/4}D_{-(1/2)-(i\epsilon/2)}(0) \quad \text{(II-30)}$$

and a similar expression for κ_2. a_α, b_α, c_α, etc., are numerical constants which depend on the parameters of the potential energy, and are defined in the Appendix.

Upon solving eq II-20–25, we obtain

$$A_\alpha/B_\alpha = (\Omega_1/\Omega_2)e^{-2ik_\alpha r_\alpha} \quad \text{(II-31)}$$

$$A_\beta/B_\alpha = \frac{2ik_\alpha\Delta_1\Delta_\beta}{\Omega_2}e^{-ik_\alpha r_\alpha - ik_\beta r_\beta} \quad \text{(II-32)}$$

where

$$\Omega_1 = -C_1(D_1C_3 - D_2C_4) + C_2(D^{2*}C_3 - D_1^*C_4) \quad \text{(II-33)}$$

$$\Omega_2 = -C_1(D_1C_5 - D_2C_6) + C_2(D_2^*C_5 - D_4^*C_6) \quad \text{(II-34)}$$

and

$$\Delta_\beta = \chi_\beta\chi_\beta^{*\prime} - \chi_\beta'\chi_\beta^*; \quad \Delta_1 = \kappa_1\kappa_1^{*\prime} - \kappa_1'\kappa_1^*$$
$$D_1 = \kappa_2\kappa_1^{*\prime} - \kappa_2'\kappa_2^*; \quad D_2 = \kappa_2\kappa_1 - \kappa_2'\kappa_2^*$$
$$C_1 = \chi_\beta^{*\prime} - ik_\beta\chi_\beta^*; \quad C_2 = \chi_\beta' - ik_\beta\chi_\beta \quad \text{(II-35)}$$
$$C_3 = ik_\alpha\chi_\alpha + \chi_\alpha'; \quad C_4 = ik_\alpha\chi_\alpha^* + \chi_\alpha^{*\prime}$$
$$C_5 = ik_\alpha\chi_\alpha - \chi_\alpha'; \quad C_6 = ik_\alpha\chi_\alpha^* - \chi_\alpha^{*\prime}$$

If some of the oscillators are in excited states, then the matching procedure described here is not sufficient. In that case a more general theory, the R-matrix theory[9], may be used. The use of this theory will be discussed in separate papers.

III. Discussion of Results

In this section we discuss the coefficients

$$T = |A_\beta|^2/|B_\alpha|^2 \quad \text{(III-1)}$$

$$R = |A_\alpha|^2/|B_\alpha|^2 \quad \text{(III-2)}$$

where T is the probability of reactive scattering and R is the probability of elastic scattering.

(9) A. M. Lane and R. G. Thomas, *Rev. Mod. Phys.*, **30**, 257 (1958).

The parameters of the interaction potential V varied with the range of physically reasonable values. The results of some calculations for different values of the parameters are shown in Table I. In all the cases we observed the presence of resonances (see Figure 4). Just at the top of the resonance peaks, II-31 and -32 are not very accurate (estimated error at the top, <15).

Table I: Position and Width of First Resonances[a]

k	k'	θ_1, deg	θ_2, deg	Reduced width	First resonance, ϵ
5	−0.20	50	40	10^{-8}	0.8
5	−0.20	60	30	5×10^{-3}	0.27
5	−0.20	70	20	2×10^{-3}	1.1
3	−0.20	60	30	10^{-3}	0.6
7	−0.20	60	30	10^{-2}	0.9

[a] Force constants are given in mdynes/A; $q_c = 0.1$ A $- \epsilon$ is defined by eq II-11.

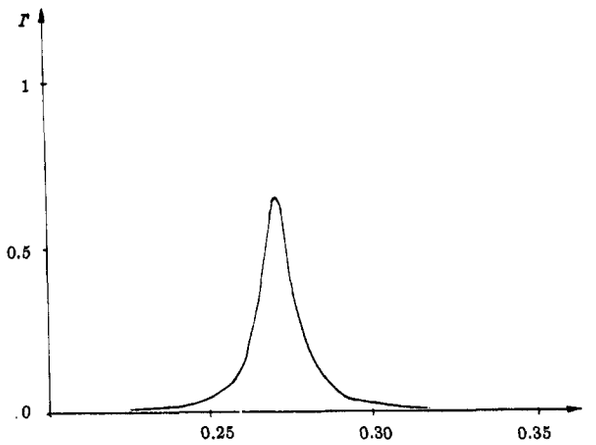

Figure 4. First resonance: $k = 5.0$, $k' = -0.2$; $\theta_1 = 60°$, $\theta_2 = 30°$; $q\sigma = q\beta = 0.1$ A; *cf.* eq II-11 for ϵ.

Though all the cases of Table I were computed using eq II-31 and -32, Breit and Wigner's resonance formula[10] gives a more accurate estimate at the top of the peak. Also, the functional dependence on the parameters c_α (which is a function of the interaction potential parameters) and q_α (the range of the potential) is better seen in that formula.

$$T\alpha\frac{\Gamma\Gamma_\beta}{(E - E_r)^2 + {}^1/_4\Gamma^2} \qquad \text{(III-3)}$$

where

$$\Gamma_\alpha\alpha k_\alpha|\chi_\alpha|^2; \quad \Gamma_\beta\alpha k_\beta|\chi_\beta|^2; \quad \Gamma = \Gamma_\alpha + \Gamma_\beta \qquad \text{(III-4)}$$

is the total width of the level. In our case

$$\Gamma \approx \exp(-2c_\alpha q_\alpha^2) \qquad \text{(III-5)}$$

as may be seen from (II-29). The estimated widths of Table I are given using this formula. It is clear that the dependence on the parameters of the potential, particularly q_α, is very strong. For this reason, more accurate calculations are needed to prove the existence of such a behavior.

In particular, we are studying the unidimensional reaction with a Eyring–Sato[6] potential, using a variational method. Our preliminary results indicate that for $q_\alpha = 0.35$, c_α is of the order of 7; that is, the levels are relatively broad.

Resonances in molecular collisions have been discussed in several cases.[11-13] The influence of these resonances in chemical reactions is to reduce the steric factor.[14] The precise nature of these resonances will be discussed in forthcoming papers. They may be due to some kind of dynamical matching between the motion of the atoms, but they may also be due to a poor overlap of the internal wave function with the channel wave functions. This overlap would be greater in a "curved reaction path."

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Appendix

After some elementary transformations we may write (II-26) in the form

$$\chi_\alpha = \left(\frac{\nu_\alpha}{\pi}\right)^{1/2}\frac{e^{-c\alpha' r_{21}^2}}{h_3\sqrt{\gamma_{21}}}\int_{-\infty}^{\infty} dx \times e^{-a\alpha x^2 - b\alpha' x r_{21}} D_{-(1/2)-(i\epsilon/2)}(x\sqrt{2i}) \qquad \text{(A-1)}$$

where

$$a_\alpha = \frac{1}{2h_3^2\gamma_{21}}(\nu_\alpha + \gamma_{11}h_2^2) \qquad \text{(A-2)}$$

$$b_\alpha' = \frac{1}{h_3\sqrt{\gamma_{21}}}[\gamma_{11}h_1(h_2 - h_1h_4/h_3) - \nu_\alpha(h_4/h_3 - tg\theta_1)] \qquad \text{(A-3)}$$

$$c_\alpha' = {}^1/_2[\nu_\alpha(h_4/h_3 - tg\theta_1)^2 + \gamma_{11}(h_2 - h_1h_4/h_3)^2] \qquad \text{(A-4)}$$

(10) See, for example, T. Y. Wu and T. Ohmura, "Quantum Theory of Scattering," Prentice-Hall Inc., Englewood Cliffs, N. J., 1962.

(11) S. Matthiess and V. G. Neudachin, *Soviet Phys. JETP*, **18**, 95 (1964).

(12) A. M. Brodskii and A. Y. Temkin, *Dokl. Akad. Nauk SSSR*, **152**, 127 (1963).

(13) L. Blum, *Bull. Am. Phys. Soc.*, **9**, 42 (1964).

(14) L. Blum, *Nuovo Cimento*, **35**, 1164 (1964).

Using the integral representation of the Weber function[15]

$$D_{-(1/2)-(i\epsilon/2)}(x\sqrt{2i}) = \frac{e^{-ix^2/2}}{\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \times \int_0^\infty dt\, e^{-(t^2/2)-(xt\sqrt{2i})}t^{-(1/2)+(i\epsilon/2)} \quad \text{(A-5)}$$

we get

$$\chi_\alpha = \left(\frac{\nu_\alpha}{\pi\gamma_{21}}\right)^{1/2} \frac{e^{-c\alpha' r_{23}^2}}{h_3\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \int_{-\infty}^\infty dx\, e^{-a\alpha x^2 - b\alpha' x r_{23}} \times \int_0^\infty dt\, e^{-t^2/2 - xt\sqrt{2i}}t^{-(1/2)+(i\epsilon/2)} \quad \text{(A-6)}$$

Changing the order of integration

$$\chi_\alpha = \left(\frac{\nu_\alpha}{\pi\gamma_{21}}\right)^{1/2} \frac{e^{-c\alpha' r_{23}^2}}{h_3\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \int_0^\infty dt\, e^{-t^2/2}t^{-(1/2)+(i\epsilon/2)} \times \int_{-\infty}^\infty dx\, e^{-x^2(a\alpha + i/2) - x(b\alpha' r_{23} + t\sqrt{2i})} \quad \text{(A-7)}$$

$$\chi_\alpha = (1/h_3)\left(\frac{\nu_\alpha}{\pi\gamma_{21}}\right)^{1/2} \frac{e^{-c\alpha' r_{23}^2}}{\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \frac{\sqrt{\pi}}{(a_\alpha + i/2)^{1/2}} \times \int_0^\infty dt\, e^{-t^2/2}t^{-(1/2)+(i\epsilon/2)} \exp\left[\frac{(b_\alpha' r_{23} + t\sqrt{2i})^2}{2(2a_\alpha + i)}\right] \quad \text{(A-8)}$$

$$= (1/h_3)\left(\frac{\nu_\alpha}{\pi\gamma_{21}}\right)^{1/2} \frac{e^{-c\alpha' r_{23}^2}}{\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \frac{e^{-b\alpha' r_{23}^2/2(2a+i)}}{(a_\alpha + i/2)^{1/2}} \times \int_0^\infty dt\, e^{-t^2/2[(2a\alpha - i)/2a\alpha + i)] + [(b\alpha' r_{23} t\sqrt{i})/(2a\alpha + i)]} \times t^{-(1/2)+(i\epsilon/2)} \quad \text{(A-9)}$$

and changing variables to

$$t' = t\left(\frac{2a_\alpha - i}{2a_\alpha + i}\right)^{1/2} \quad \text{(A-10)}$$

we get

$$\chi_\alpha = 1/h_3\left(\frac{\nu_\alpha}{\gamma_{21}}\right) \frac{e^{-c\alpha' r_{23}^2}}{\Gamma\left(\frac{1}{2}+\frac{i\epsilon}{2}\right)} \frac{e^{-b\alpha' r_{23}^2/2(2a\alpha+i)}}{(a_\alpha + i/2)^{1/2}} \times \left(\frac{2a_\alpha + i}{2a_\alpha - i}\right)^{1/4(i+i\epsilon)} \int_0^\infty dt'\, e^{-t'^2/2 + t'\sqrt{2i}b\alpha r_{23}} t'^{-(1/2)+(i\epsilon/2)} \quad \text{(A-11)}$$

where

$$b_\alpha = \frac{b_\alpha'}{4a_\alpha^2 + 1} \quad \text{(A-12)}$$

Recalling the definition of the Weber function A-5, we get, after some simplifications

$$\chi_\alpha = 1/h_3\left(\frac{\nu_\alpha}{\gamma_{21}}\right)^{1/2} e^{-c\alpha' q\alpha^2} \frac{1}{(4a_\alpha^2 + 1)^{1/4}} \left(\frac{2a_\alpha + i}{2a_\alpha - i}\right)^{i\epsilon/4} \times D_{-(1/2)-(i\epsilon/2)}(-b_\alpha q_\alpha \sqrt{2i}) \quad \text{(A-13)}$$

with $c_\alpha = c_\alpha' - a_\alpha b_\alpha^2$.

To find κ_1 and κ_2 we note that (II-27) and (II-28) can be written as

$$\frac{1}{\sqrt{2\gamma_{2j}}(h_3 + h_4)} \int_{-\infty}^\infty dx\, e^{-a_j x^2} D_{-(1/2)-(i\epsilon/2)}(x\sqrt{2i}) \quad \text{(A-14)}$$

with $j = 1, 2$ and

$$a_1 = \frac{1}{2(h_3 + h_4)^2\gamma_{21}}[\gamma_{12}(h_5 + h_6)^2 + \gamma_{11}(h_1 + h_2)^2] \quad \text{(A-15)}$$

$$a_2 = \frac{\gamma_{12}(h_5 + h_6)^2}{\gamma_{22}(h_7 + h_8)^2} \quad \text{(A-16)}$$

Using (A-13) we get

$$\kappa_j = \frac{\sqrt{\pi}}{\sqrt{2\gamma_{2j}}(h_3 + h_4)} \frac{1}{(4a_j^2 + 1)^{1/4}} \times \left(\frac{2a_j + i}{2a_j - i}\right)^{i\epsilon/4} D_{-(1/2)-(i\epsilon/2)}(0) \quad \text{(A-17)}$$

(15) I. S. Gradshtein and I. M. Ryzhik, "Tablitsii Integralov Summi Riadov i Proizvedenii," Moscow, 1962.