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Original Investigations

Semiclassical Bound-Continuum Franck–Condon Factors Uniformly Valid at 4 Coinciding Critical Points: 2 Crossings and 2 Turning Points

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A uniform semiclassical approximation to bound-continuum Franck–Condon factors is derived by applying differential topological mapping techniques on a suitable three dimensional integralrepresentation. This approach even holds uniformly if two potentialcurve intersections (real or complex conjugate) and two turning points come close or coincide. The resulting Franck–Condon matrix element is expressed in terms of two generic swallowtail (A_4) integrals whose unfolding parameters are obtained from a single algebraic equation amenable to fast standard routines. Transitional approximations to this result are shown to cover all previously known approaches and to lead to a generalization of a formula of K. Sando and F. H. Mies [*1*]. A simple and fast trapezoidal method to evaluate the generic swallowtail integrals and other generic integrals of odd determinacy is presented, which even permits the derivation of numerical error bounds.

Key words: Bound-continuum Franck–Condon factors – Semiclassical matrix elements – Excimer spectra

1. Introduction

On page 152 of Ref. [3] a sequel was promised which would offer a completely uniform treatment of bound-continuum Franck–Condon (FC) integrals with two real or complex conjugate crossings which may come close or coincide with two of the three turning points. The underlying publication presents the solution of this problem. It is presented in terms of swallowtail (SWT) integrals whose need has been foreboded in Ref. [3].

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SWT integrals are generalized Airy-type integrals with a quintic integration variable polynom in the exponent. This solution however would only be a formal one of little practical value, if we had not found a method for calulating SWT integrals by an as fast and simple numerical routine as nowadays Airy functions can be evaluated. There is another improvement over Ref. [3] which deserves being mentioned. In Ref. [3] the bound state functions have been approached by matching two Airy uniform Langer functions at the midphase point. Here we employ integral representations for harmonic oscillator states which allow making use of the two turning point uniform vibrational functions of Ref. [2] in the FC integral (25) of Ref. [3]. If one thinks of applying multidimensional saddlepoint methods this improvement is the crucial point since it is not obvious how to continue the matching procedure into the complex plane.

The plan of this paper is as follows:
In Sect. 2 we derive the above mentioned integral represention for the vibrational functions.

In Sect. 3 the FC integral composed of Miller–Good vibrational functions and Airy uniform continuum functions is converted to a three dimensional one and after exploiting its differential topological structure it is asymptotically mapped on generic or canonical SWT integrals. The mapping equations which determine the unfolding parameters of the SWT integrals are decoupled and brought into a form suitable for a fast numerical solution.

In Sect. 4 two transitional approximations for the SWT integrals are derived. One leads back to the partially uniform treatment in Ref. [3] and the other provides a generalization of formula (A-25) of K. Sando and F. H. Mies in Ref. [1].

Sect. 5 offers a simple and fast numerical method for calculating SWT integrals and other generic integrals of an odd determinacy like wigwam A_6, hyperbolic umbilics D_4^-, D_4^+ etc. Error formulae are given which allow to predict the size of the integration meshs necessary to obtain any desired accuracy.

Finally, in Sect. 6 we collect transitional approximation formulae for the intensities of the various caustics that may occur in bound-continuum FC factors through the coincidence of two or more critical points. We also show plots of the corresponding intensity patterns or spectra.

2. Integral Representations for Harmonic Oscillator States

In this section we derive for the harmonic oscillator functions

$$\chi_n(q) = e^{-q^2/2} H_n(q) \pi^{-1/4} 2^{-n/2} (n!)^{-1/2}, \qquad n = 0, 1, 2, \ldots \tag{1}$$

normalized according to

$$\int_{-\infty}^{+\infty} dq\, \chi_n^2(q) = 1 \tag{2}$$

integral representations which form the basis of stationary phase or saddlepoint mapping techniques applied in Sect. 3. A representation of this kind valid for positive values of q has been published by M. S. Child and P. M. Hunt in the appendix of Ref. [4]. Here we need representations which are valid on the whole real q-axis and not only on its positive part. We shall see, that this requirement necessitates to distinguish between even and odd vibrational quantum numbers according to the parity of the functions (1).

We start from Eqs.

$$H_{2k}(q)=(-1)^k 2^{2k} k! L_k^{(-1/2)}(q^2), \tag{3}$$

$$H_{2k+1}(q)=(-1)^k 2^{2k+1} k! q L_k^{(1/2)}(q^2), \qquad k=0,1,2,\ldots \tag{4}$$

and

$$L_k^{(\alpha)}(y)=\frac{y^{-\alpha}}{k!}e^{y}\frac{d^k}{dy^k}(y^{k+\alpha}e^{-y}) \tag{5}$$

on pp. 240–241 of Ref. [5]. Cauchy's formula for the k-th derivative

$$\frac{d^k}{dy^k}f(y)=\frac{k!}{2\pi i}\int_{\gamma(y)}\frac{dz\, f(z)}{(z-y)^{k+1}},$$

where the integration path $\gamma(y)$ is a zero-homologous, positively oriented cycle enclosing the point $z=y$, and the linear map $z\to t=i(2z/y-1)$ then yield

$$L_k^{(\alpha)}(y)=\frac{(-1)^k e^{y/2}}{2^\alpha 2\pi}\int_{\gamma(i)}\frac{dt\, e^{(i/2)yt}(1-it)^{k+\alpha}}{(1+it)^{k+1}}. \tag{6}$$

The contour deformation $\gamma(i)\to -\infty\le t\le +\infty$ and $1+it=e^{i\delta}\sqrt{1+t^2}$ with

$$\operatorname{tg}\delta=t \tag{7}$$

then leads to the integral representation

$$L_k^{(\alpha)}(y)=\frac{(-1)^k e^{y/2}}{2^\alpha 2\pi}\int_{-\infty}^{+\infty}dt\frac{e^{i[(y/2)t-(2k+1+\alpha)\delta(t)]}}{(1+t^2)^{\frac{1}{2}(1-\alpha)}}, \tag{8}$$

which is ideally suited for deriving various uniform asymptotic approximations via stationary phase mappings.

Inserting (8) into (3), (4) and (1), we find the desired integral representations valid on the whole real q-axis

$$\chi_n(q)=\begin{cases}\dfrac{(2n+1)^{1/4}\alpha_n}{2\pi}\displaystyle\int_{-\infty}^{+\infty}dt\frac{e^{(i/2)[q^2t-(2n+1)\delta(t)]}}{(1+t^2)^{3/4}}, & \text{for } n=2k \\ & k=0,1,2,\ldots \\ \dfrac{(2n+1)^{-1/4}}{2\pi\alpha_n}\displaystyle\int_{-\infty}^{+\infty}dt\frac{q\, e^{(i/2)[q^2t-(2n+1)\delta(t)]}}{(1+t^2)^{1/4}}, & \text{for } n=2k+1,\end{cases} \tag{9}$$

where

$$\alpha_n=2^{(n+1)/2}\Gamma\left(1+\frac{n}{2}\right)(n!)^{-1/2}(2n+1)^{-1/4}\pi^{-1/4} \tag{10}$$

Table 1. The coefficients α_n in Eq. (10)

n	0	1	2	3	4	∞
α_n	1.0623	1.0116	1.0046	1.0024	1.0015	1.0000

and $\delta(t)$ is defined by (7). A simple calculation with a pocket computer yields Table 1 for the coefficients α_n in Eq. (10).

We note, that we safely may replace Eq. (10) by the approximation

$$\alpha_n \simeq 1. \tag{11}$$

Now it is straightforward to write down integral representations for the continuum functions (23) and the normalized Miller–Good vibrational functions (1)–(6) of Ref. [2]. Since these expressions are basic to all further approximations, we enlist them here for convenience.

The energy normalized continuum functions are

$$\psi_{E_2}(x) = \left(\frac{2m}{\hbar^2}\right)^{1/2} z'(x)^{-1/2}(2\pi)^{-1} \int_{-\infty}^{+\infty} dt\, e^{i[(t^3/3) - z(x)t]} \tag{12}$$

$$z'(x)^2 z(x) = \frac{2m}{\hbar^2}[E_2 - V_2(x)], \qquad z(x_3) = 0, \qquad V_2(x_3) = E_2. \tag{13}$$

The normalized Miller–Good vibrational functions are

$$\psi_n(x) = \left(\frac{m}{\hbar^2} E_1'(n)\right)^{1/2} q'(x)^{-1/2} \chi_n(q(x)), \qquad n = 0, 1, 2, \ldots \tag{14}$$

$$\left.\begin{aligned} &q'(x)^2[2n+1-q^2(x)] = \frac{2m}{\hbar^2}[E_1(n) - V_1(x)], \qquad q(x_{1,2}) = \mp(2n+1)^{1/2}, \\ &V_1(x_{1,2}) = E_1(n), \qquad x_1 < x_2. \end{aligned}\right\} \tag{15}$$

We define

$$k_i(x) = \sqrt{\frac{2m}{\hbar^2}[E_i - V_i(x)]}, \qquad i = 1, 2 \tag{16}$$

and

$$u_i(x) = -k_i(x)^2 \tag{17}$$

such that Eq. (4) of Ref. [2] which supplements (15) now is

$$\int_{x_1}^{x_2} dx\, k_1(x) = \pi(n + \tfrac{1}{2}), \qquad k_1(x_{1,2}) = 0, \qquad x_1 < x_2. \tag{18}$$

It is interesting to note that if the χ_n in (14) are replaced by their Airy uniform approximation to (9), and (11) is used, one just obtains the simplified version φ_s of Miller's boundstate functions at the end of Sect. 2 in Ref. [3]. Thus, the use of (9) in FC integrals avoids the matching problem mentionned in the introduction.

3. Asymptotical Reduction of the FC Integral to SWT Form

From (14), (12) and (9) we note that the FC integral for a bound continuum transition with a transition moment $\mu(t_3)$ (electronic moment, r-centroid etc.)

$$M=\int_{-\infty}^{+\infty} dt_3\, \psi_n(t_3)\mu(t_3)\psi_{E_2}(t_3) \tag{19}$$

can be approximated within percent accuracy by the three dimensional integral

$$M\simeq\int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2 \int_{-\infty}^{+\infty} dt_3\, \rho(t_1, t_2, t_3)\, e^{i\Phi(t_1,t_2,t_3)} \tag{20}$$

with the phase function

$$\Phi=\Phi_1+\Phi_2, \tag{21}$$

$$\Phi_1=\tfrac{1}{2}[t_1 q(t_3)^2-(2n+1)\delta(t_1)]=\Phi_1(t_1, t_3) \tag{22}$$

$$\Phi_2=\frac{t_2^3}{3}-z(t_3)t_2=\Phi_2(t_2, t_3). \tag{23}$$

The stationary points of Φ follow from the three Eqs.

$$\frac{\partial\Phi_1}{\partial t_1}=0, \tag{24}$$

$$\frac{\partial\Phi_2}{\partial t_2}=0, \tag{25}$$

$$\frac{\partial\Phi}{\partial t_3}=\frac{\partial\Phi_1}{\partial t_3}+\frac{\partial\Phi_2}{\partial t_3}=0. \tag{26}$$

With (7), (13), (15) and (17) we obtain

$$\begin{aligned} &q(t_3)^2(1+t_1^2)=2n+1\\ &t_2^2=z(t_3)\\ &t_1 q(t_3)q'(t_3)=t_2 z'(t_3) \end{aligned} \tag{27}$$

and hence

$$u_1(t_3)=u_2(t_3), \tag{28}$$

i.e. the Mulliken condition (see also Eq. (33) in Ref. [3])

$$V_1(t_3)-E_1(n)=V_2(t_3)-E_2. \tag{29}$$

From (27) we infer that *the number of stationary points is twice the number of solutions of (29), i.e. twice the number of crossings. Henceforth we assume that there are two real or complex conjugate crossings at* $t_3=x_a$ *and* $t_3=x_b$.

Next we determine the values of the phase Φ at such a stationary point t_3. From (27), (22) and (7) we find for any solution t_3 of Eq. (29)

$$\left.\begin{aligned} &S_1(t_3)=\Phi_1(t_1(t_3),t_3)=\pm\left[\frac{9^2}{2}\sqrt{\frac{2n+1}{q^2}-1}-(n+\tfrac{1}{2})\delta\right],\\ &\cos\delta=\sqrt{\frac{q^2}{2n+1}},\qquad q=q(t_3). \end{aligned}\right\} \tag{30}$$

Note that S_1 is an even function of q

$$S_1(-q)=S_1(q). \tag{31}$$

It is evident, that $S_1(q)$ can be written as an action integral. In order to do so, we form the derivative

$$\frac{dS_1}{dq}=\frac{1}{q'(t_3)}\frac{dS_1}{dt_3}=\frac{1}{q'(t_3)}\left(\frac{\partial\Phi_1}{\partial t_1}\frac{dt_1}{dt_3}+\frac{\partial\Phi_1}{\partial t_3}\right)=qt_1$$

and with the help of Eq. (30), $S_1(q=0)=\mp\pi/2(n+\frac{1}{2})$, and (27) we find

$$S_1(q)=\mp\frac{\pi}{2}(n+\tfrac{1}{2})\pm\int_0^q dp\,p\sqrt{\frac{2n+1}{p^2}-1}. \tag{32}$$

Defining the midphase point x_0 as in Ref. [3], Eq. (7) by

$$\int_{x_1}^{x_0}dx\,k_1(x)=\int_{x_0}^{x_2}dx\,k_1(x)=\frac{\pi}{2}(n+\tfrac{1}{2}) \tag{33}$$

and changing to the integration variable x in Eqs. (15) and (18), the integral in Eq. (32) becomes

$$S_1(t_3)=\begin{cases}\pm\displaystyle\int_{t_3}^{x_1}dx\,k_1(x) & \text{for } t_3\leq x_0\\[2ex] \pm\displaystyle\int_{x_2}^{t_3}dx\,k_1(x) & \text{for } x_0\leq t_3.\end{cases} \tag{34}$$

This means, that the integration path always goes to (or comes from) that turning point x_1, x_2 which is situated at the same side of x_0 as t_3 is.

Repeating this discussion once more with Eqs. (27), (23) and (13), we find

$$S_2(t_3)=\Phi_2(t_2(t_3),t_3)=-\tfrac{2}{3}z(t_3)t_2(t_3)=\mp\int_{x_3}^{t_3}dx\,k_2(x). \tag{35}$$

The relative sign of S_1 and S_2 in the phase Φ at any stationary point with a crossing value t_3

$$S(t_3)=\Phi(t_1(t_3),t_2(t_3),t_3)=S_1(t_3)+S_2(t_3), \tag{36}$$

is fixed by Eqs. (24)–(26) according to $dS/dt_3=0$, such that we finally obtain

$$S(t_3)=\int_{x_{12}}^{t_3}dx\,k_1(x)-\int_{x_3}^{t_3}dx\,k_2(x). \tag{37}$$

The absolute sign in Eq. (37) is unimportant since, as we shall see, the unfolding parameters of the SWT integrals depend on $S(t_3)^2$ only. The symbol x_{12} in Eq. (37) expresses in shorthand notation the choice of the integration path in Eq. (34) and its obvious continuation through x_0 into the complex x-plane.

There are additional differential topological properties of the phase function (21) which are of importance if one wishes to derive uniform asymptotic approximations for the integral (20). These properties can be gathered from the matrix of the second derivatives, i.e. the Hessian matrix,

$$H_{ik} = \frac{\partial^2 \Phi}{\partial t_i \, \partial t_k}, \qquad i, k = 1, 2, 3, \tag{38}$$

at the stationary or critical points of Φ and from higher derivative forms, see Ref. [6] Chapts. 4 and 8. From Eqs. (21)–(28) we obtain at a stationary point with the crossing value t_3 the Hessian matrix

$$H_{ik} = \begin{pmatrix} t_1 q^4/(2n+1) & 0 & qq' \\ 0 & 2t_1 qq'/z' & -z' \\ qq' & -z' & t_1 z'(qq'/z')' \end{pmatrix} = \mathcal{H}, \tag{39}$$

where $q' = dq/dt_3$, $z' = dz/dt_3$. Recallings Eqs. (13), (15) and the first Eq. in (27) we note that t_1 vanishes at the bound state turning points $t_3 = x_1$ or $t_3 = x_2$. Thus, the rank of (39) drops there from its maximal value 3 to the value 2. It cannot decrease below the value 2, because z' in Eq. (12) is always positive. This means: the corank = 3-rank is always less or equal 1, viz.

$$\text{cor}\,(\mathcal{H}) \leq 1. \tag{40}$$

Therefore, according to the splitting lemma (see Ref. [6], pp. 61) the phase function (21) can always be unfolded, modulo a Morse function, within the cuspoid family (see Ref. [6], p. 154, Table 8.1 and pp. 166). Now, all what remains is to find the determinacy of Φ, $\sigma(\Phi)$. The codimension of Φ then is anyway fixed in the cuspoid family. Again, since cor $(\mathcal{H}) \leq 1$, the determinacy $\sigma(\Phi)$ is uniquely related to the number of stationary points. If there are k crossings and hence $2k$ stationary points we have

$$\sigma(\Phi) = 2k + 1. \tag{41}$$

We henceforth consider 2 crossings only. Then Φ in Eqs. (21)–(23) is strongly equivalent via a complex diffeomorphism (holomorphic map), see Ref. [7], to the universal unfolding

$$\Phi = \Phi(t_1, t_2, t_3) = \bar{\Phi}(\bar{t}_1, \bar{t}_2, \bar{t}_3) = i(\bar{t}_1^2 + \bar{t}_2^2) + f(t) \tag{42}$$

$$f(t) = \frac{t^5}{5} + \frac{f_3}{3} t^3 + \frac{f_2}{2} t^2 + f_1 t + f_0. \tag{43}$$

From (43) we note the codimension 3 (without f_0) and for k crossings cod $(\Phi) = 2k - 1$ in general.

A further reduction of the number of unfolding parameters f_i, $i = 0, \ldots, 3$ follows if we recall Eqs. (21)–(23). The phase function Φ has the symmetry

$$\Phi(-t_1, -t_2, t_3) = -\Phi(t_1, t_2, t_3). \tag{44}$$

That is why the stationary points (27) occur in pairs which give rise to the $\pm$ signs in Eqs. (31)–(35). The mapping (42) deforms the symmetry (44) into

$$f(-t) = -f(t) \tag{45}$$

which implies

$$f_2 = f_0 = 0 \tag{46}$$

in Eq. (43). A similar case of codimension reduction by symmetry has been discussed in Chap. 14, Sect. 15 of Ref. [6].

If we reparametrize f_3 and f_1 according to

$$-f_3 = t_a^2 + t_b^2, \qquad f_1 = t_a^2 t_b^2, \tag{47}$$

the stationary point of $\bar{\Phi}$ in (42) are determined by

$$\bar{t}_1 = \bar{t}_2 = 0, \qquad f'(t) = 0, \tag{48}$$

which yields

$$t^2 = t_{a,b}^2. \tag{49}$$

Conditions which fix the unfolding parameters t_a, t_b in (47) are found by writing down Eq. (42) at the corresponding stationary values of the variables t_i and the transformed variables $\bar{t}_i$, t. With Eqs. (49), (48), (43), (42), (37) and (36) we obtain

$$\left.\begin{aligned} S(x_a) &\equiv S_a = f(t_a) = \tfrac{2}{15} t_a^3 (5 t_b^2 - t_a^2) \\ S(x_b) &\equiv S_b = f(t_b) = \tfrac{2}{15} t_b^3 (5 t_a^2 - t_b^2), \end{aligned}\right\} \tag{50}$$

or

$$\tfrac{15}{2}(S_b \mp S_a) = (t_a \mp t_b)^3 [3 t_a t_b \pm (t_a^2 + t_b^2)]. \tag{51}$$

The smooth parameter change

$$t_b^2 + t_a^2 = 2\sigma\sqrt{\tau(1+\omega)}, \qquad \sigma = \pm 1, \qquad t_b^2 - t_a^2 = 2\sqrt{\tau} \tag{52}$$

and several straightforward algebraic manipulations then lead to the "solution"

$$\sigma = \operatorname{sign}\,(S_a^2 + S_b^2), \tag{53}$$

$$\begin{aligned} h_+(\omega) &\equiv \omega^3 \left(\frac{3 + 2\sqrt{1+\omega}}{3\sqrt{\omega} + 2\sqrt{1+\omega}}\right)^2 \left(\frac{\sqrt{\omega} + \sqrt{1+\omega}}{1 + \sqrt{1+\omega}}\right)^3 = \frac{2 S_a^2}{(S_b - S_a)^2} \\ &\equiv Q_1, \qquad S_a \leq S_b \end{aligned} \tag{54}$$

or

$$h_-(\omega) \equiv \frac{\omega^3 (4\omega - 5)^2}{(4 - 5\omega)^2} = \frac{4 S_a^2 S_b^2}{(S_b^2 - S_a^2)^2} \equiv Q \tag{55}$$

and

$$\tau = \left|\frac{225(S_b^2 - S_a^2)}{32(4-5\omega)}\right|^{2/5} \operatorname{sign}(S_b^2 - S_a^2). \tag{56}$$

The *real* mapping $\omega \to h_-(\omega)$, Eq. (55), is bijective (smooth) for $-\infty \leq \omega \leq 0$. Hence, Eq. (55) has for $-\infty \leq Q \leq 0$ a unique real solution which is bounded by

$$-|Q|^{1/3}(\tfrac{25}{16})^{1/3} \leq \omega \leq -|Q|^{1/3}(\tfrac{16}{25})^{1/3}, \quad \text{for } Q \leq 0. \tag{57}$$

Therefore it is easy to calculate ω for $Q \leq 0$ from (55) with the help of any standard routine just starting with the bounds (57). E.g. inverse quadratic interpolation may be applied. This procedure converges very fast since the bounds (57) are rather narrow. If however Q in Eq. (55) is positive, ω is uniquely defined by Eq. (54). In this case the inhomogeneity Q_1 in (54) is positive and we find the bounds

$$(\tfrac{25}{32})^{1/3} Q_1^{1/3} \leq \omega \leq (\tfrac{32}{25})^{1/3} Q_1^{1/3}, \quad \text{for } 0 \leq Q. \tag{58}$$

Again, Eq. (54) is easily solved by the above mentioned standard routines. We may assume henceforth, that the unfolding parameters $t_{a,b}^2$ are known from Eqs. (56), (53) and (52).

In order to write the integral (20) in the new variables $\bar{t}_1$, $\bar{t}_2$, t in Eq. (42), we need the Jacobian $\mathcal{J}$ of this transform. At the stationary points $\mathcal{J}$ is simply related to the Hessian determinant of Φ in the variables t_i, $i = 1, 2, 3$, $H = \det(\mathcal{H})$, Eq. (39), and the Hessian determinant $\bar{H}$ of Φ in the variables $\bar{t}_1$, $\bar{t}_2$, t, viz.

$$\bar{H} = \mathcal{J}^2 H \tag{59}$$

(see p. 16 in Ref. [8]). From Eqs. (42)–(49) and from (39), (28), (27) we find

$$\left.\begin{aligned} \mathcal{J}^4 &= \left[\frac{\partial(t_1, t_2, t_3)}{\partial(\bar{t}_1, \bar{t}_2, t)}\right]^4 = \frac{64 t^2 (t_b^2 - t_a^2)^2 z'^2 (2n+1)^2}{\bar{t}_1^2 q^8 (u_2' - u_1')^2}, \\ t^2 &= t_{a,b}^2, \qquad t_3 = x_a, x_b. \end{aligned}\right\} \tag{60}$$

Note that at a coincidence of a turning point and a crossing point, $t_{a,b}^2 \to 0$, the vanishing of t^2 in the numerator is compensated by the vanishing of $\bar{t}_1^2$ in the denominator. Similary, if the two crossings x_a, x_b coincide, then $t_a^2 = t_b^2$, and the vanishing of $(t_b^2 - t_a^2)^2$ is compensated by $(u_2' - u_1')^2$. The same regularity of $\mathcal{J}$ holds of course if both coincidences occur simultaneously.

Now we are prepared to derive the *leading* uniform asymptotic contribution to the integral M, Eq. (20). Following theorem 9.1. on p. 457 in Ref. [9] we expand the transformed integrand Eq. (20), $\mathcal{J}\rho\, e^{i\bar{\Phi}}$, at the stationary values $t^2 = t_{a,b}^2$ according to

$$\mathcal{J}\rho\, e^{i\bar{\Phi}} \simeq (c_0 + c_2 t^2)\, e^{i\bar{\Phi}} \tag{61}$$

and the leading asymptotic contribution to M is

$$M \simeq \int_{-\infty}^{+\infty} d\bar{t}_1 \int_{-\infty}^{+\infty} d\bar{t}_2 \int_{-\infty}^{+\infty} dt\, (c_0 + c_2 t^2)\, e^{i\bar{\Phi}}. \tag{62}$$

A term $c_1 t$ has been omitted in Eq. (61) because $\mathscr{J}\rho$ turns out to be *even* in t. At $t^2 = t_a^2$ we obtain

$$c_0 + c_2 t_a^2 = \mathscr{J}_a \rho_a \tag{63}$$

and $t^2 = t_b^2$ yields

$$c_0 + c_2 t_b^2 = \mathscr{J}_b \rho_b, \tag{64}$$

with the solution

$$c_0 = \frac{\rho_a \mathscr{J}_a t_b^2 - \rho_b \mathscr{J}_b t_a^2}{t_b^2 - t_a^2}, \qquad c_2 = \frac{\rho_b \mathscr{J}_b - \rho_a \mathscr{J}_a}{t_b^2 - t_a^2}. \tag{65}$$

Besides our anticipation that ρ is an even function of t, the explicit form of ρ in Eq. (20) was not necessary up to now. Inspection of (65) shows that for the leading asymptotic contribution (62) it is sufficient to calculate ρ at the stationary points as it is indicated by the subscripts a and b.

Going from Eq. (19) back to Eqs. (14), (12), (11), and (9) we find that at a stationary point with the crossing values $t_3 = x_a, x_b$, the function ρ is given by

$$\rho = \frac{m}{\hbar^2} (2E_1'(n))^{1/2} (2\pi)^{-2} q'^{-1/2} z'^{-1/2} (2n+1)^{-1/2} \mu \begin{cases} (q^2)^{3/4} & \text{for } n = \text{even} \\ q(q^2)^{1/4} & \text{for } n = \text{odd} \end{cases}. \tag{66}$$

Eq. (62) is the uniform asymptotic approximation to the FC integral (19) which we intended to derive. Its detailed form follows from (66), (65), (60), (15) and (13). We obtain

$$M \simeq (t_b^2 - t_a^2)^{-1} [(\gamma_a t_b^2 - \gamma_b t_a^2) F_0 + (\gamma_b - \gamma_a) F_2], \tag{67}$$

where

$$\gamma_{a,b} = \frac{2m}{\hbar^2} (E_1'(n))^{1/2} \sigma_q^n \mu(t_3) \left\{ \frac{t_{a,b}^2 (t_b^2 - t_a^2)}{k_{1,2}^2(t_3) [u_2'(t_3) - u_1'(t_3)]^2} \right\}^{1/4}, \qquad t_3 = x_a, x_b, \tag{68}$$

$$\sigma_q = \frac{q(t_3)}{\sqrt{q^2(t_3)}}, \tag{69}$$

and F_0, F_2 are the SWT integrals

$$F_{2k} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, t^{2k} e^{if(t)}, \qquad k = 0, 1 \tag{70}$$

$$f(t) = \frac{t^5}{5} - \frac{t^3}{3} (t_a^2 + t_b^2) + t t_a^2 t_b^2. \tag{71}$$

We conclude this section with the remark that by construction the approximation (67) holds uniformly if one or two turning points coincide with one or two crossings. This can explicitly be seen in Eq. (68). A zero of $k_{1,2}^2$ is compensated by a zero of $t_{a,b}^2$, the coincidence of the two crossings x_a, x_b leads to a zero of $u_2' - u_1'$, which is compensated by $t_b^2 - t_a^2$. A further important property of Eq. (67) is, that it is symmetric with respect to the exchange of the subscripts a and b.

4. Transitional Approximations

One type of transitional approximation to (70) is obtained if the integration domain is split into two components $\mathscr{D}_a$ and $\mathscr{D}_b$. In each of the subdomains $\mathscr{D}_a$ and $\mathscr{D}_b$ we apply to (71) one of the two mappings

$$f(t) = g_{a,b}(s) = \frac{s^3}{3} - \beta_{a,b} s. \tag{72}$$

The unfolding parameter β_a is determined by putting in $\mathscr{D}_a$

$$f(\pm t_a) = g_a(\pm\sqrt{\beta_a}) \tag{73}$$

and β_b is determined by putting

$$f(\pm t_b) = g_b(\pm\sqrt{\beta_b}) \tag{74}$$

in $\mathscr{D}_b$. With (50) we obtain from (73) and (74)

$$\beta_a^3 = t_a^6(t_b^2 - \tfrac{1}{5}t_a^2)^2 = \tfrac{9}{4}S_a^2 \tag{75}$$

$$\beta_b^3 = t_b^6(t_a^2 - \tfrac{1}{5}t_b^2)^2 = \tfrac{9}{4}S_b^2. \tag{76}$$

Expressing the Jacobians in $\mathscr{D}_{a,b}$ with the help of the analog of Eq. (59) in terms of the second derivatives of $f(t)$ and $g_{a,b}(s)$, we find for (70) the leading asymptotic approximation

$$F_{2k} \simeq t_a^{2k}\left[\frac{\beta_a}{t_a^2(t_a^2 - t_b^2)^2}\right]^{1/4} \mathscr{A}i\,(-\beta_a) + t_b^{2k}\left[\frac{\beta_b}{t_b^2(t_b^2 - t_a^2)}\right]^{1/4} \mathscr{A}i\,(-\beta_b). \tag{77}$$

If this transitional approximation, which is uniform for $t_a \to 0$ and $t_b \neq 0$ or $t_b \to 0$ and $t_a \neq 0$, is applied in Eqs. (67) and (68), we rediscover Eq. (50) in Ref. [3], viz.

$$M \simeq \sum_{s=a,b} \frac{2m}{\hbar^2}(E_1'(n))^{1/2}\mu(x_s)\sigma_{q_s}^n\left[\frac{\beta_s}{k_{1,2}^2(x_s)(u_2'(x_s) - u_1'(x_s))^2}\right]^{1/4} \mathscr{A}i(-\beta_s) \tag{78}$$

$$\beta_s^3 = \tfrac{9}{4}S_s^2, \qquad \sigma_{q_s} = q(x_s)(q^2(x_s))^{-1/2}. \tag{79}$$

As mentioned already, this transitional approximation to M uniformizes the mutual coincidence of a crossing and a turning point. But this uniformization is only partial since the second crossing must stay well separated from the first one.

There is a second type of transitional approximation to (70), which uniformizes the coincidence of the two crossings $t_a^2 = t_b^2$ but for t_a^2 away from turning points, i.e. $t_a^2 \neq 0$. To derive it, we decompose the integration domain of (70) into the subdomains $\mathscr{D}_\pm$, put

$$f(t)=g_\pm(s)=\frac{s^3}{3}-\beta_\pm s+\alpha_\pm \tag{80}$$

and determine the unfolding parameters $\beta_\pm$, $\alpha_\pm$ according to

$$f(t_{b,a})=g_+(\pm\sqrt{\beta_\pm})=S_{b,a} \tag{81}$$

$$f(-t_{b,a})=g_-(\pm\sqrt{\beta_-})=-S_{b,a}. \tag{82}$$

Expanding the transformed integrand of (70) linearly in s (as this has been done in t in Eq. (61)), the leading approximation results

$$F_{2k}\simeq d_1\cos\alpha\mathscr{A}i(-\beta)-d_2\sin\alpha\mathscr{A}i'(-\beta) \tag{83}$$

$$d_1=t_b^{2k}\left[\frac{\beta}{t_b^2(t_b^2-t_a^2)^2}\right]^{1/4}+t_a^{2k}\left[\frac{\beta}{t_a^2(t_b^2-t_a^2)^2}\right]^{1/4} \tag{84}$$

$$d_2=\frac{4\beta}{3(f_a-f_b)}\left\{t_a^{2k}\left[\frac{\beta}{t_a^2(t_b^2-t_a^2)^2}\right]^{1/4}-t_b^{2k}\left[\frac{\beta}{t_b^2(t_b^2-t_a^2)^2}\right]^{1/4}\right\} \tag{85}$$

$$\beta^3=\tfrac{9}{16}(f_a-f_b)^2,\qquad \alpha=\tfrac{1}{2}(f_a+f_b),\qquad f_{a,b}=f(t_{a,b})=S_{a,b}, \tag{86}$$

which obviously is symmetric if a and b are exchanged. With Eqs. (67) and (68), Eqs. (83)–(86) lead to

$$M\simeq(\lambda_a+\lambda_b)\cos\alpha\,\mathscr{A}i\,(-\beta)-\frac{4\beta(\lambda_a-\lambda_b)}{3(S_a-S_b)}\sin\alpha\,\mathscr{A}i'(-\beta) \tag{87}$$

$$\lambda_{a,b}=\frac{2m}{\hbar^2}(E_1'(n))^{1/2}\mu(x_{a,b})\sigma_{qa,b}^n\left[\frac{\beta}{k_{1,2}^2(x_{a,b})(u_2'(x_{a,b})-u_1'(x_{a,b}))^2}\right]^{1/4} \tag{88}$$

$$\beta^3=\tfrac{9}{16}(S_a-S_b)^2,\qquad \alpha=\tfrac{1}{2}(S_a+S_b),\qquad \sigma_{q_{a,b}}=q(x_{a,b})(q^2(x_{a,b}))^{-1/2}, \tag{89}$$

where according to (37)

$$S_{a,b}=\int_{x_{12}}^{x_{a,b}}dx\,k_1(x)-\int_{x_3}^{x_{a,b}}dx\,k_2(x). \tag{90}$$

The approximation (87) is a uniform generalization of formula (A-25) in Ref. [1], which does not contain the $\mathscr{A}i'\,(-\beta)$ term of (87). As indicated above, Eq. (87) uniformizes the merging of the two crossings x_a and x_b. But this must happen well separated from all other turning points. If this is not guaranteed, recourse must be made to Eqs. (67)–(71) which cover all the transitional cases and the SWT caustic.

5. Numerical Calculation of Generic Integrals with Odd Determinacy

The idea of the method can be explained most distinctly at the simplest case, Airy's integral,

$$\mathscr{A}i\,(z)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{i((t^3/3)+zt)}. \tag{91}$$

The shift into the complex t-plane $t \to t + i\alpha$, $\alpha \geq 0$ gives

$$\mathscr{A}i\,(z) = e^{(\alpha^3/3) - \alpha z} \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, e^{-\alpha t^2 + i[(t^3/3) + (z - \alpha^2)t]}, \qquad \alpha \geq 0. \tag{92}$$

In contrast to Eq. (91), the integrand of Eq. (92) is ideally suited to apply the summation formula of Poisson, see Ref. [10]

$$\int_{-\infty}^{+\infty} dt\, \varphi(t) = h \sum_{n=-\infty}^{+\infty} \varphi(h[n + \tfrac{1}{2}]) - \sum_{m=-\infty}^{+\infty} (1 - \delta_{m0})(-1)^m \int_{-\infty}^{+\infty} dt\, \varphi(t)\, e^{(i/h)2\pi m t}. \tag{93}$$

After decomposing (93) into even and odd parts we thus obtain

$$\mathscr{A}i\,(z) = h \sum_{k=0}^{\infty} \psi(h[k + \tfrac{1}{2}]) - \Delta(p), \qquad p = \frac{2\pi}{h}, \qquad h > 0, \tag{94}$$

$$\psi(t) = \pi^{-1}\, e^{(\alpha^3/3) - \alpha z - \alpha t^2} \cos\left[\frac{t^3}{3} + t(z - \alpha^2)\right], \qquad \alpha \geqslant 0 \tag{95}$$

$$\Delta(p) = \sum_{r=1}^{\infty} (-1)^r R(rp), \tag{96}$$

$$R(p) = e^{\alpha p}\, \mathscr{A}i\,(z + p) + e^{-\alpha p}\, \mathscr{A}i\,(z - p) = R(-p). \tag{97}$$

Eq. (94) is an *exact* trapezoid summation formula for $\mathscr{A}i\,(z)$. How accurate is it to neglect Δ on the right hand side? This question may be answered by an asymptotic estimate of (96) for large positive values of $p = 2\pi/h > 0$. If z in (97) is real, then $|\mathscr{A}i\,(z)| < 1$ and

$$R(p) < e^{-\alpha p} + e^{\alpha p}\, \mathscr{A}i\,(z + p).$$

Assuming further that $p + z > 10$, the asymptotics of $\mathscr{A}i\,(z + p)$ yields

$$R(p) < e^{-\alpha p} + (z + p)^{-1/4}\, e^{\alpha p - \frac{2}{3}(z + p)^{3/2}}, \tag{98}$$

and we note that for any given z, and $\alpha > 0$, there is always a steplength h with $0 < h < 1$ such that to any desired accuracy, Eq. (94) may be replaced by the asymptotic trapezoid formula

$$\mathscr{A}i\,(z) \simeq h \sum_{k=0}^{N} \psi(h[k + \tfrac{1}{2}]). \tag{99}$$

The cutoff value N is determined by the rate of decreasing of ψ, i.e. by the value of α in Eq. (95). For instance, if one choses $\alpha = 1$, $h = 2\pi/26 \simeq 0.242$, $N = 24$, Eqs. (95) and (99) may be used to calculate $\mathscr{A}i(z)$ in the range $-10 \leqslant z \leqslant 0$ with an error $\Delta < 3 \cdot 10^{-8}$, and for $z \geqslant 0$ this error even decreases to $\Delta < 5 \cdot 10^{-12}$.

As a further application of this summation method, we discuss the particular SWT integral

$$F(z) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, e^{i((t^5/5) + zt)}, \qquad z = z^*, \tag{100}$$

which is needed in the next Section for calculating the spectrum of a SWT caustic. With $t_a^2 = i\sqrt{z} = -t_b^2$ in (70), we obtain from (77) and (83) the transitional approximations

$$F(z) \simeq \begin{cases} \left(\frac{-3}{20z}\right)^{1/6} [\mathscr{A}i\,(\zeta_1) + \mathscr{A}i\,(-\zeta_1)], \qquad \zeta_1 = (\tfrac{36}{25})^{1/3}(-z)^{5/6}, \quad \text{for } z<0 \\ 2^{1/2}(\tfrac{18}{25})^{1/12} z^{-1/6}\left[\cos\left(\frac{\pi}{8}\right)\cos a\,\mathscr{A}i\,(\zeta_2) - \frac{\sin(\pi/8)}{(\frac{18}{25})^{1/6} z^{5/12}} \sin \alpha\,\mathscr{A}i'\,(\zeta_2)\right], \\ \alpha = \frac{2^{3/2}}{5} z^{5/4}, \qquad \zeta_2 = (\tfrac{18}{25})^{1/3} z^{5/6} \quad \text{for } z>0 \end{cases} \tag{101}$$

and hence the primitive asymptotic limits

$$F(z) \underset{z\to-\infty}{\longrightarrow} (2\pi)^{-1/2}|z|^{-3/8} \sin\left(\tfrac{4}{5}|z|^{5/4} + \frac{\pi}{4}\right) \tag{102}$$

$$F(z) \underset{z\to+\infty}{\longrightarrow} (2\pi)^{-1/2} z^{-3/8}\, e^{-(2^{3/2}/5)z^{5/4}} \cos\left(\frac{2^{3/2}}{5} z^{5/4} - \frac{\pi}{8}\right) \tag{103}$$

which could have been derived also directly from Eq. (70) by application of the ordinary stationary phase or saddle point method. Eqs. (102) and (103) are now used to write down the error estimates of the trapezoid formula for Eq. (100). The shift $t \to t + i\alpha$, $\alpha > 0$ in (100) leads to the definition

$$\varphi(t) = \pi^{-1}\, e^{-(\alpha^5/5) - z\alpha - \alpha t^4 + 2\alpha^3 t^2} \cos\left[\frac{t^5}{5} - 2\alpha^2 t^3 + (\alpha^4 + z)t\right] \tag{104}$$

and the Poisson sum

$$F(z) = h \sum_{k=0}^{\infty} \varphi(h[k + \tfrac{1}{2}]) - \delta(p), \qquad p = \frac{2\pi}{h}, \qquad h>0, \tag{105}$$

where

$$\delta(p) = \sum_{r=1}^{\infty} (-1)^r T(rp) \tag{106}$$

$$T(p) = e^{\alpha p} F(z+p) + e^{-\alpha p} F(z-p) = T(-p), \alpha > 0. \tag{107}$$

Since z is real in Eq. (100) we obviously have $|F(z)| < 1$ and with (103) we get

$$T(p) < e^{-\alpha p} + \frac{\exp(\alpha p - (2^{3/2}/5)(z+p)^{5/4})}{(2\pi)^{1/2}(z+p)^{3/8}}, \qquad \alpha > 0 \tag{108}$$

as an error estimate in the asymptotic trapezoid formula

$$F(z) \simeq h \sum_{k=0}^{N} \varphi(h[k + \tfrac{1}{2}]), \tag{109}$$

where φ is defined by (104). As an application of (109) let us discuss the value $F(0) = \pi^{-1/5} 5^{-4/5} \sin(2\pi/5)$. We put $\alpha = 1$ and the cutoff in the sum (109) is at

$|\varphi| \leq 2{,}66 \cdot 10^{-10}$. For $h = 0{,}2$ we obtain from (109) $F_a(0) = 0,\ 383508423$, $N_a = 13$ and $T_a(p) < 2{,}575 \cdot 10^{-6}$ is the estimate (108). For $h = 0{,}1$ we find from (109) $N_b = 25$, $F_b(0) = 0{,}383506701$, which is the exact value above up to and including the ninth digit. $T(p)$ satisfies in this case $T_b(p) < 5{,}684 \cdot 10^{-18}$. The difference $|F_a(0) - F_b(0)|$ is bounded by $T_a(p)$ as it must.

These few examples demonstrate both the simplicity and the general applicability of the method developped in this Section.

6. Caustics in Bound–Continuum FC-Transitions

A caustic is normally attributed to a striking optical phenomenon: sharp, bright curves to which the light rays are tangential. Caustic means the burning due to the large intensity in these regions. All types of wavefields may give rise to caustics if in the corresponding oscillatory integral representing the field amplitude two or more critical points come close or coincide, see Ref. [11]. The same behaviour of the stationary points in Eq. (20) also leads to more or less pronounced peaks or to oscillatory structures in the corresponding FC spectra. We have four critical points which may come close or coincide: two of three turning points and two crossing points. Consequently three types of caustics may occur:

i) a turning point-crossing point caustic, well separated from the other crossing point, see Fig. 1,

ii) a SWT caustic, due to the confluence of two turning points with two crossing points to a fourfold critical point, see Fig. 2,

iii) a crossing point – crossing point caustic, well separated from all turning points, see Fig. 3.

In the immediate vicinity of the confluence points of caustics i) and ii), the action integrals (37), (50) may be expanded according to (see Figs. 1 and 2)

$$S_{a,b} = \frac{2}{3}\left(\frac{1}{u'_{2b,a}} - \frac{1}{u'_{1b,a}}\right) k_{b,a}^3 - \frac{4}{15}\left[\frac{u''_{2b,a}}{(u'_{2b,a})^3} - \frac{u''_{1b,a}}{(u'_{1b,a})^3}\right] k_{b,a}^5 + O(k_{b,a}^7) \tag{110}$$

where

$$k_{b,a} = k_1(x_{b,a}) = k_2(x_{b,a}), \tag{111}$$

and (see Eqs. (16)–(17))

$$u_{ib,a} = u_i(x_{b,a}), \qquad u'_{ib,a} = u'_i(x_{b,a}), \qquad V_{ik} = V_i(x_k), \qquad V'_{ik} = V'_i(x_k), \quad \text{etc.} \tag{112}$$

Keeping in case i) only linear contributions to the expansion of x_b at the turning point x_2, see Fig. 1, we find

$$k_b^2 \simeq \frac{2mV'_{12}(E_2 - V_{22})}{\hbar^2(V'_{12} - V'_{22})}, \qquad u'_{ib} \simeq u'_{i2}, \tag{113}$$

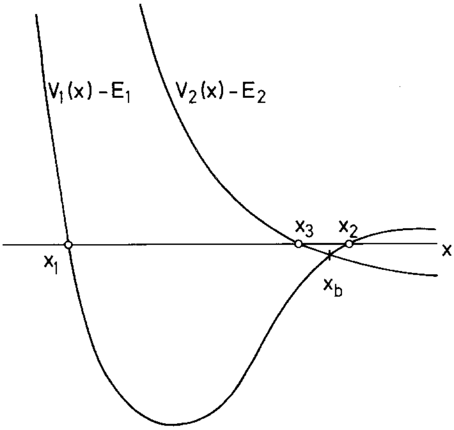

Fig. 1.

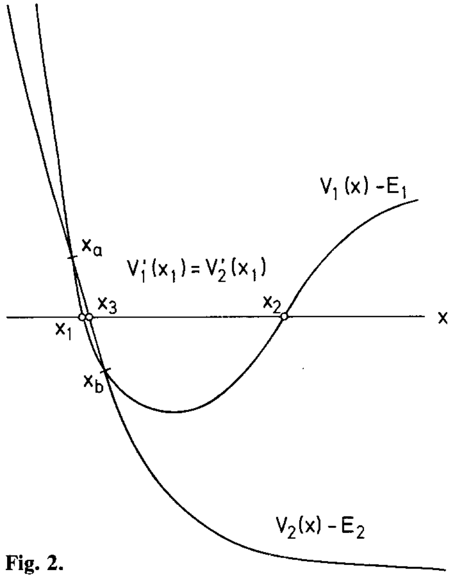

Fig. 2.

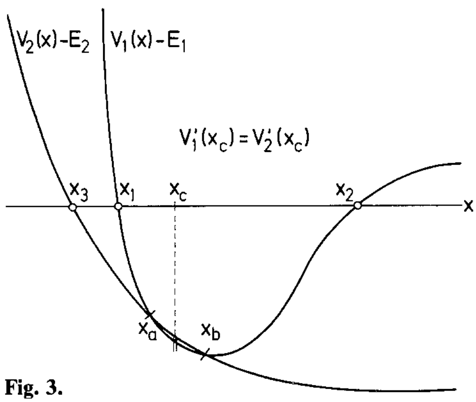

Fig. 3.

Fig. 1. The turning point-crossing point caustic i)

Fig. 2. The swallowtail caustic ii)

Fig. 3. The crossing point-crossing point caustic iii)

and in case ii) by quadratic approximation at x_1, since $u'_{11}(x)=u'_2(x_1)$, see Fig. 2,

$$k^2_{b,a} \simeq \mp\delta u'_{11}, \qquad \delta=\sqrt{\frac{2u_{21}}{u''_{11}-u''_{21}}}, \qquad u'_{2b,a}-u'_{1b,a}\simeq \pm\delta u''_{11}. \tag{114}$$

If the crossing point x_a is far in the forbidden region on the left hand side of x_3 as in Fig. 1, we obtain from Eqs. (78), (79), (110) and (113) for the FC transition amplitude *in the immediate vicinity of the caustic i)* the expression

$$\left.\begin{aligned} M &\simeq M_0\,\mathscr{A}i\left(\frac{V_{22}-E_2}{\varepsilon_0}\right)\\ \varepsilon_0^3 &= \frac{\hbar^2(V'_{12}-V'_{22})V'^2_{22}}{2mV'_{12}},\\ M_0 &= \left(\frac{2m}{\hbar^2}\right)^{1/3}(E'_1(n))^{1/2}\mu(x_2)\sigma''_2|V'_{12}V'_{22}|^{-1/6}|V'_{12}-V'_{22}|^{-1/3}. \end{aligned}\right\} \tag{115}$$

As a typical FC-spectrum to (115), the function $I_0(z) = 60|\mathcal{A}i\,(-z)|^2$ is plotted versus z in Fig. 4. Since Eq. (115) is only valid in the vicinity of $E_2 = V_{22}$, this expression should only be used to determine say V_{22} and ε_0 from the position and width of the dominant peak in Fig. 4.

Now we discuss the FC spectrum of the SWT caustic, case ii) see Fig. 2. We assume that the confluence point in Fig. 2 is the turning point x_1, $u_1(x_1) = 0$, which only can happen for some particular vibrational energy $E_1 = E_1(n)$ if $V_1'(x_1) = V_2'(x_1)$. These two conditions are simultaneously satisfied only for rather particular shapes of the two potentials $V_1(x)$ and $V_2(x)$. In general however one may approach this exact coincidence situation very closely. If x_1 is an exact coincidence point, Eqs. (114), (110) and $u''_{ib,a} \simeq u''_{i1}$ yield $Q = -1$ in Eq. (55), which implies $\omega = -1$. From (56) and (52) we find

$$\left.\begin{aligned} -\tau &= t_a^2 t_b^2 = (V_{21} - E_2)\varepsilon_1^{-1}, \qquad t_a^2 + t_b^2 = 0 \\ \varepsilon_1^5 &= \frac{\hbar^4}{8m^2} V_{11}'^2 (V_{11}'' - V_{21}'')\,\mathrm{sign}\,(V_{11}') \end{aligned}\right\} \tag{116}$$

and from Eqs. (67)–(71)

$$\left.\begin{aligned} M &\simeq M_1 F\left(\frac{V_{21} - E_2}{\varepsilon_1}\right) \\ M_1 &= (E_1'(n))^{1/2} \sigma_1^n \mu(x_1) 2^{3/5} \left(\frac{m}{\hbar^2}\right)^{2/5} |V_{11}'|^{-2/5} |V_{11}'' - V_{21}''|^{-1/5} \end{aligned}\right\} \tag{117}$$

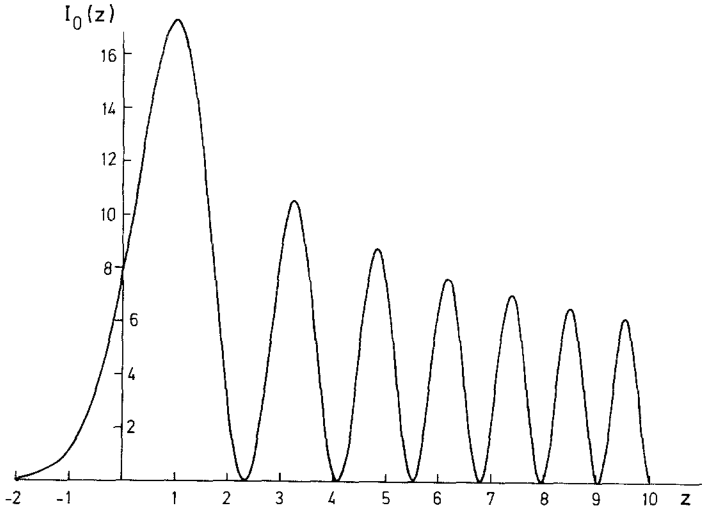

Fig. 4. The spectrum of a turning point-crossing point caustic i) $I_0(z) = 60|\mathcal{A}i\,(-z)|^2$

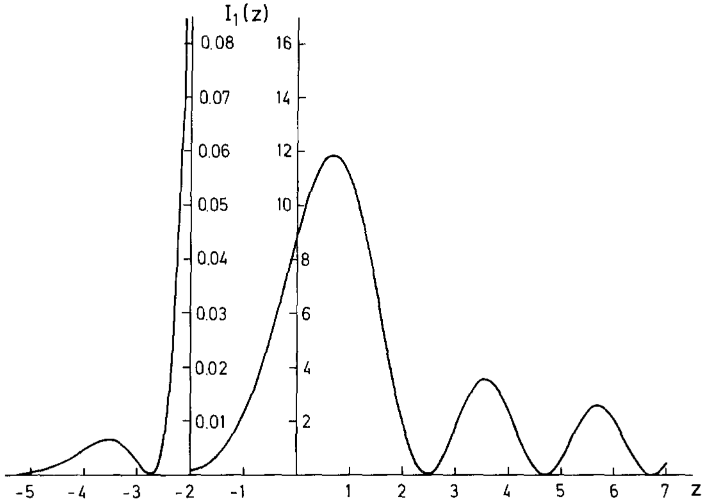

Fig. 5. The spectrum of a swallowtail caustic ii) $I_1(z) = 60|F(-z)|^2$, $F(z)$ is defined by Eq. (100)

where the function $F(z)$ is defined by Eq. (100). In Fig. 5 the function $I_1(z) = 60|F(-z)|^2$ is plotted versus z as a FC-spectrum, typical for a SWT caustic. We note, that in contrast to Fig. 4, the spectrum corresponding to Eq. (117), Fig. 5, shows oscillations even on the left hand side of main peak. From the asymptotic expression (103) we conclude that the number of these oscillations is infinite in principle, but they are exponentially damped.

As the last case we study the caustic iii). If the two crossing points x_b and x_a are situated close enough at the coincidence point x_c, see Fig. 3, a quadratic approximation similar to Eq. (114) holds. The convergence of (110) however is too slow since the turning points are too far away from x_c. We therefore expand the action integrals $S_{b,a}$, Eq. (37), for fixed E_1 with respect to E_2 at

$$E_{2c} = V_{2c} + E_1 - V_{1c}, \qquad V_{ic} = V_i(x_c), \tag{118}$$

where x_c is defined by

$$V'_{1c} \equiv V'_1(x_c) = V'_2(x_c) \equiv V'_{2c}. \tag{119}$$

From Eqs. (87)–(90) we finally obtain just formula (A-25) of Ref. [1], viz.

$$\left.\begin{aligned} &M \simeq M_2 \cos \alpha_c \mathcal{A}i\,(-\beta_c) \\ &M_2 = \left(\frac{4m}{\hbar^2 k_{1c}}\right)^{2/3} |V''_{2c} - V''_{1c}|^{-1/3} (E'_1(n))^{1/2} \sigma^n_c \mu(x_c), \end{aligned}\right\} \tag{120}$$

$$\alpha_c = \int_{x_1}^{x_c} dx\, k_1(x) - \int_{x_3}^{x_c} dx\, k_2(x) \tag{121}$$

$$\beta_c^3 = \frac{k_{1c}(k_{1c} - k_{2c})^3}{u''_{1c} - u''_{2c}}, \qquad k_{ic} = k_i(x_c), \qquad u''_{ic} = u''_i(x_c). \tag{122}$$

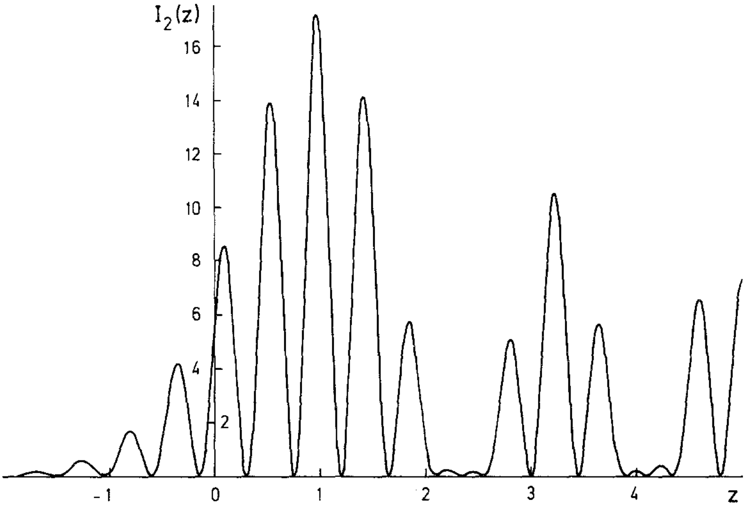

Fig. 6. The spectrum of a crossing point-crossing point caustic iii) $I_2(z) = 60 \cos^2 (10-7z)|\mathscr{A}i\ (-z)|^2$

In the immediate vicinity of $E_2 = E_{2c}$ we find, keeping linear terms in $E_2 - E_{2c}$ only,

$$\alpha_c = \alpha_c(E_2) \simeq \alpha_c(E_{2c}) + \frac{m}{\hbar^2}(E_{2c} - E_2) \int_{x_3}^{x_c} \frac{dx}{k_2(x)}\bigg|_{E_2 = E_{2c}} \tag{123}$$

$$\beta_c \simeq \frac{E_{2c} - E_2}{\varepsilon_2}, \qquad \varepsilon_2^3 = \frac{\hbar^2}{m}(E_1 - V_{1c})(V''_{1c} - V''_{2c}). \tag{124}$$

A typical spectrum corresponding to Eq. (120) is shown in Fig. 6. The intensity choosen in Fig. 6 is $I_2(z) = 60 \cos^2(10 - 7z)|\mathscr{A}i\ (-z)|^2$. Again we note oscillations on the long wavelength side of the main peak. Now these oscillations are even more rapid as in the case of the SWT caustic, Fig. 5. Passing from the caustic i) to the caustic iii), we may say that the SWT caustic ii) is a transitional case, which just shows the birth of the rapid oscillations on the way from the Condon reflection spectrum Fig. 4 to the modulated continuum spectrum Fig. 6.

Here we end our more qualitative studies of bound-continuum FC factors. The practical usefulness of this formalism is obvious and will be demonstrated by application to the analysis of experimental data.

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