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Nonperturbative Time-Independent Green Function of Matrix Schrödinger Equation. General Formalism and Quasiclassical Representation

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A Green function of time-independent multichannel Schrödinger equation is considered in matrix representation beyond a perturbation theory. Nonperturbative Green functions are obtained through the regular in zero and at infinity solutions of the multichannel Schrödinger equation for different cases of symmetry of the full Hamiltonian. The spectral expansions for the nonperturbative Green functions are obtained in simple form through multichannel wave functions. The developed approach is applied to obtain simple analytic equations for the Green functions and transition matrix elements for compound multipotential system within quasiclassical approximation. The limits of strong and weak interchannel interactions are studied.

KEY WORDS: Green function; Schrödinger equation; nonperturbative theory.

1. INTRODUCTION

The Green functions (GF) are applied often in physics because they make it possible to sum over all the virtual intermediate states of a quantum system in an analytic form without finding wave functions of the intermediate states participating in a quantum interaction (Economou, 1979). To find the GF one needs to obtain only two linearly independent solutions of the Schrödinger equation (SE), from which we can construct the GF in simple analytic form. Sometimes only the one solution may be enough to write out the GF (Ignat'ev and Polikanov, 1984).

If a quantum particle moves in a field of two or more than two potentials, one needs to consider the multichannel SE and GF. For each of the perturbed channels (potentials) the quantum particle has a set of unperturbed states. In a physics

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circumstance there are interactions of the channels with each other, which modify the unperturbed states and induce quantum transitions of the particle between the channels.

Ignat'ev and Polikanov (1984) applied a perturbative theory to obtain a multipotential (or multichannel) GF for the case where the interchannel couplings are weak. In the case of strong couplings, where the interchannel interaction is comparable with energy gap between the unperturbed quantum states, the perturbation theory is inapplicable and one has to study the total Hamiltonian beyond a perturbative approach. Aymar *et al*. (1996) and Pegarkov (2000) showed that in theoretical applications the GF of the nonperturbative Hamiltonian is needed in order to obtain a multichannel propagator and transition probability.

In the present paper the multichannel GF approach is developed for the nonperturbative regime of quantum interactions. A quasiclassical approximation is applied to construct the two- and three-channel GF and to obtain the transition probabilities in a simple analytic form.

2. FORMALISM OF NONPERTURBATIVE MULTICHANNEL GREEN FUNCTION

2.1. Multichannel Schrödinger Equation Beyond Perturbative Approximation

The SE in the case of few interacting channels may be written as

$$\{\mathbf{I}E - \mathbf{H}(R)\}\mathbf{\Phi}(R) = \mathbf{0},$$

$$\mathbf{I} = \|\delta_{ij}\|, \quad \mathbf{0} = \|0 \cdot \delta_{ij}\|, \quad i, j = 1, 2, \ldots, k, \tag{1}$$

where the Hamiltonian $\mathbf{H}(R)$ is presented in the following matrix form:

$$\mathbf{H}(R) = \mathbf{H}^0(R) + \mathbf{V}(R), \tag{2}$$

$$\mathbf{H}^0(R) = \left\| H_i^0(R)\delta_{ij} \right\| = -\mathbf{I}\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \mathbf{U}(R),$$

$$\mathbf{U}(R) = \mathrm{diag}\{U_1(R),\ U_2(R), \ldots,\ U_k(R)\}, \tag{3}$$

$\mathbf{U}(R)$ is the diagonal matrix containing the potentials of unperturbed channels $U_i(R)$ on its principal diagonal, $U_i(R)$ is the potential of the ith channel,

$$\mathbf{V}(R) = \|V_{ij}(R)\|, \tag{4}$$

is the nondiagonal matrix of the nonperturbative quantum couplings,

$$\left| \left(\int \mathbf{\Phi}_{m'}^*(R)\mathbf{V}(R)\mathbf{\Phi}_m(R)\, dR \right)_{ii} \right| \sim |E_m - E_{m'}|,$$

k is the number of all the quantum channels participating in the nonperturbative interaction.

A solution $\mathbf{\Phi}(R)$ of matrix SE (1) is presented here in form of a $(k \times k)$ matrix

$$\mathbf{\Phi}(R) = \|\phi_{ij}(R)\| \tag{5}$$

which contains all the partial solution vectors of the multichannel equation (1).

If the channel coupling vanishes, the nondiagonal matrix Hamiltonian equation (2) converges to the unperturbed diagonal Hamiltonian $\mathbf{H}^0(R)$ equation (3)

$$\lim_{\mathbf{V}(R)\to\mathbf{0}} \mathbf{H}(R) \to \mathbf{H}^0(R). \tag{6}$$

The nondiagonal matrix solution of the multichannel equation (1) should converge to the diagonal solution of the SE with unperturbed Hamiltonian equation (3):

$$\begin{gathered}\lim_{\mathbf{V}(R)\to\mathbf{0}} \mathbf{\Phi}(R) \to \mathbf{\Phi}^0(R),\\ \mathbf{\Phi}^0(R) \equiv \left\|\phi_i^0(R)\delta_{ij}\right\|,\\ \{\mathbf{I}E^0 - \mathbf{H}^0(R)\}\mathbf{\Phi}^0(R) = 0\end{gathered} \tag{7}$$

Equation (1) may be rewritten in the form of

$$\big(E - H_i^0(R)\big)\phi_{ij}(R) = \sum_{m=1}^{k} V_{im}(R)\phi_{mj}(R). \tag{8}$$

The wave function $\phi_{ij}(R)$ fits to the inhomogeneous SE for the ith channel. It is easy to obtain from Eqs. (5)–(8), that each of the functions $\phi_{ij}(R)$, $j = 1, 2, \ldots, k$ is a perturbed partial wave in the ith channel. Therefore, one may say, that the functional row $[\phi_{i1}(R), \phi_{i2}(R), \ldots, \phi_{ik}(R)]$ contains all the partial solutions for the ith channel and is the partial vector solution of the matrix SE (1). Then, the construction of the full multichannel solutions (MCS) $\mathbf{\Phi}(R)$ of matrix SE (1) is as follows:

(i) all the channel solutions of Eq. (1) are placed into MCS equation (5) by rows,
(ii) the function $\phi_{ij}(R)$ is a partial solution for the ith channel,
(iii) the partial wave $\phi_{ij}(R)$ is excited by another channel j interacted with the ith one.

For the case of pair interaction of the channels at fixed point X_{ij}:

$$V_{ij}(R) = V_{ij}(X_{ij})\delta_{jm},$$

$\phi_{ij}(R)$ is the wave transmitted from the jth channel to the ith one after a passage through channel interaction point X_{ij}.

One has to emphasize that only the MCS equation (5) may be used to construct the GF of the multichannel SE (1). It is simple to see below that the use of fundamental solutions in vector representation gives incorrect equation for the multichannel GF and its spectral expansion.

2.2. Green Function of Multichannel Schrödinger Equation

In consequence of Eqs. (6), (7) the limit of the nonperturbative multichannel GF is

$$\lim_{\mathbf{V}(R)\to\mathbf{0}} \mathbf{G}(R, R'; E) \to \mathbf{G}^0(R, R'; E),$$

$$\mathbf{G}^0(R, R'; E) = \left\| G_i^0(R, R'; E)\delta_{ij} \right\|, \tag{9}$$

where the diagonal matrix equation (9) fits the following inhomogeneous equation with the diagonal unperturbed Hamiltonian equation (3):

$$\{\mathbf{I}E - \mathbf{H}^0(R)\}\mathbf{G}^0(R, R'; E) = \mathbf{I}\delta(R - R')$$

and each of its components does the unperturbed one-channel SE as

$$\left\{E - H_i^0(R)\right\}G_i^0(R, R'; E) = \delta(R - R').$$

The time-independent GF of the multichannel nonperturbative Hamiltonian equation (2) fulfils the following second order differential inhomogeneous matrix equation:

$$\{\mathbf{I}E - \mathbf{H}(R)\}\mathbf{G}(R, R'; E) = \mathbf{I}\delta(R - R') \tag{10}$$

and is a nondiagonal matrix function of two variables R and R', which depends on energy E as on a parameter:

$$\mathbf{G}(R, R'; E) = \|G^{ij}(R, R'; E)\|. \tag{11}$$

The GF defined by Eqs. (10), (11) is continuous at $R = R'$:

$$\mathbf{G}(R + \epsilon, R; E) = \mathbf{G}(R - \epsilon, R; E), \quad \epsilon \to 0, \tag{12}$$

and has a first kind discontinuity there:

$$\frac{d}{dR}\mathbf{G}(R, R'; E)\bigg|_{R\to R'+\epsilon} - \frac{d}{dR}\mathbf{G}(R, R'; E)\bigg|_{R\to R'-\epsilon} = \frac{2\mu}{\hbar^2}\mathbf{I}. \tag{13}$$

Let me search a nonperturbative solution of the full inhomogeneous differential equation (10) in the form like the perturbative consideration of Ignat'ev and Polikanov (1984),

$$\mathbf{G}(R, R'; E) = \frac{2\mu}{\hbar^2}\begin{cases}\mathbf{\Phi}_2(R)\mathbf{A}(R'), & R > R',\\ \mathbf{\Phi}_1(R)\mathbf{B}(R'), & R < R',\end{cases} \tag{14}$$

where $\mathbf{\Phi}_1(R)$ and $\mathbf{\Phi}_2(R)$ are two linearly independent solutions of nonperturbative SE (1), fitted the standard boundary conditions in zero and at infinity, $\mathbf{A}(R)$ and $\mathbf{B}(R)$ are the matrices to be found. The multichannel functions $\mathbf{\Phi}_1(R)$ and $\mathbf{\Phi}_2(R)$ have the nondiagonal matrix form of Eq. (5).

Substituting Eq. (14) into Eq. (13) one gets

$$\mathbf{\Phi}_2'\mathbf{A} + \mathbf{\Phi}_1'\mathbf{B} = \mathbf{I}. \tag{15}$$

Premultiplying Eq. (15) by $[\mathbf{\Phi}_2']^{-1}$ on the left and allowing for Eq. (12) yield

$$\mathbf{A} = \left[\mathbf{\Phi}_2' - \mathbf{\Phi}_1'\mathbf{\Phi}_1^{-1}\mathbf{\Phi}_2\right]^{-1}, \tag{16}$$

if, of course,

$$\det\left[\mathbf{\Phi}_2' - \mathbf{\Phi}_1'\mathbf{\Phi}_1^{-1}\mathbf{\Phi}_2\right] \neq 0.$$

Like Eq. (16) one obtains, that

$$\mathbf{B} = -\left[\mathbf{\Phi}_1' - \mathbf{\Phi}_2'\mathbf{\Phi}_2^{-1}\mathbf{\Phi}_1\right]^{-1},$$
$$\det\left[\mathbf{\Phi}_1' - \mathbf{\Phi}_2'\mathbf{\Phi}_2^{-1}\mathbf{\Phi}_1\right] \neq 0. \tag{17}$$

Now let me show, that if both matrices of potentials $\mathbf{U}(R)$ and $\mathbf{V}(R)$ are either symmetric

$$\mathbf{V}(R) = \mathbf{V}^{\mathrm{T}}(R), \quad \mathbf{U}(R) = \mathbf{U}^{\mathrm{T}}(R) \tag{18}$$

or Hermitian (the superscript T means transpose, the superscript $+$ one does Hermitian conjugation, $\mathbf{A}^{-1}$ is the inverse matrix to $\mathbf{A}$. $\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$):

$$\mathbf{V}(R) = \mathbf{V}^{+}(R), \quad \mathbf{U}(R) = \mathbf{U}^{+}(R), \tag{19}$$

then Eqs. (16), (17) can be expressed through the regular MCS $\mathbf{\Phi}_1$ and $\mathbf{\Phi}_2$.

Substituted Eqs. (2), (3) into Eq. (1), premultiplied it by function $\mathbf{\Phi}_1'$ or $\mathbf{\Phi}_2'$ and used the fact, that

$$\mathbf{\Phi}\mathbf{\Phi}^{-1} = \mathbf{\Phi}^{-1}\mathbf{\Phi} = \mathbf{I},$$

one gets the equation

$$\left[\mathbf{\Phi}_{1,2}'(R)\mathbf{\Phi}_{1,2}^{-1}(R)\right]' - \mathbf{\Phi}_{1,2}'(R)\left[\mathbf{\Phi}_{1,2}^{-1}(R)\right]' = \frac{2\mu}{\hbar^2}[\mathbf{U}(R) + \mathbf{V}(R) - E\mathbf{I}]. \tag{20}$$

In order to find the functions $[\mathbf{\Phi}_{1,2}^{-1}]'$ the following property of the first derivative of a matrix function should be used (p is an integer, see Lancaster, 1969)

$$\frac{d}{dt}[\mathbf{A}(t)]^{-p} = -\mathbf{A}^{-p}(t)\frac{\mathbf{A}(t)}{dt}\mathbf{A}^{-p}(t),$$

then,

$$\left[\mathbf{\Phi}_{1,2}^{-1}(R)\right]' = -\mathbf{\Phi}_{1,2}^{-1}(R)\mathbf{\Phi}_{1,2}'(R)\mathbf{\Phi}_{1,2}^{-1}(R). \tag{21}$$

Substituting Eq. (21) into Eq. (20) yields the matrix nonperturbative Riccati equation in the form like the perturbative one obtained earlier by Ignat'ev and Polikanov (1984):

$$\mathbf{f}'_{1,2}(R) + [\mathbf{f}_{1,2}(R)]^2 = \frac{2\mu}{\hbar^2}[\mathbf{U}(R) + \mathbf{V}(R) - E\mathbf{I}], \tag{22}$$

where

$$\mathbf{f}_{1,2}(R) \equiv \mathbf{\Phi}'_{1,2}(R)\mathbf{\Phi}^{-1}_{1,2}(R).$$

Under the condition of Eq. (18) the functions $\mathbf{f}^{\mathrm{T}}_{1,2}(R)$ fit the Riccati equation (22) too. Therefore, if the equation

$$\mathbf{f}_{1,2}(R_0) = \mathbf{f}^{\mathrm{T}}_{1,2}(R_0)$$

is true in a fixed point R_0, then it is true for any R

$$\mathbf{f}_{1,2}(R) = \mathbf{f}^{\mathrm{T}}_{1,2}(R).$$

Making some transformations with Eqs. (16), (17) and substituting Eq. (21) to them permit to deduce finally the following equation for the nonperturbative GF (11) of the symmetric multichannel Schrödinger Hamiltonian

$$\mathbf{H}(R) = \mathbf{H}^{\mathrm{T}}(R), \tag{23}$$

$$\mathbf{G}(R, R'; E) = \frac{2\mu}{\hbar^2}\begin{cases}\mathbf{\Phi}_2(R)\mathbf{W}^{-1}\mathbf{\Phi}^{\mathrm{T}}_1(R'), & R > R',\\ \mathbf{\Phi}_1(R)[\mathbf{W}^{\mathrm{T}}]^{-1}\mathbf{\Phi}^{\mathrm{T}}_2(R'), & R < R',\end{cases} \tag{24}$$

where $\mathbf{W}$ is an invertible R-independent matrix

$$\mathbf{W} = \mathbf{\Phi}^{\mathrm{T}}_1(R)[\mathbf{\Phi}_2(R)]' - \left[\mathbf{\Phi}^{\mathrm{T}}_1(R)\right]'\mathbf{\Phi}_2(R) = \text{const} \neq \mathbf{0}. \tag{25}$$

The multichannel GF equation (24) obeys to the following symmetry properties

$$\mathbf{G}(R, R'; E) = \mathbf{G}^{\mathrm{T}}(R', R; E),$$

$$\mathbf{G}^{+}(R, R'; E) = \mathbf{G}^{*}(R', R; E).$$

If the GF (24) is a real one (of, in general, complex energy, $E \neq E^*$), then

$$\mathbf{G}^{+}(R, R'; E) = \mathbf{G}(R', R; E^*).$$

Starting from Eq. (22), assuming both potential matrices to be Hermitian, Eq. (19) and the energy to be real, one can deduce the following equations for the nonperturbative GF of the Hermitian Schrödinger Hamiltonian

$$\mathbf{H}(R) = \mathbf{H}^{+}(R), \tag{26}$$

$$\mathbf{G}(R,R';E)=\frac{2\mu}{\hbar^2}\begin{cases}\mathbf{\Phi}_2(R)\mathbf{W}^{-1}\mathbf{\Phi}_1^{+}(R'), & R>R',\\ \mathbf{\Phi}_1(R)[\mathbf{W}^{+}]^{-1}\mathbf{\Phi}_2^{+}(R'), & R<R',\end{cases}\tag{27}$$

$$\mathbf{W}=\mathbf{\Phi}_1^{+}(R)[\mathbf{\Phi}_2(R)]'-[\mathbf{\Phi}_1^{+}(R)]'\mathbf{\Phi}_2(R)=\text{const}\neq\mathbf{0},$$

$$\mathbf{G}(R,R';E)=\mathbf{G}^{+}(R',R;E).\tag{28}$$

If the Hamiltonian equation (2) has no symmetry

$$\mathbf{H}(R)\neq\begin{cases}\mathbf{H}^{\mathrm{T}}(R)\\ \mathbf{H}^{+}(R)\end{cases},\quad E\neq E^{*}\tag{29}$$

the nonperturbative GF equation (11) may be written only in its general form as

$$\mathbf{G}(R,R';E)=\frac{2\mu}{\hbar^2}\begin{cases}\mathbf{\Phi}_2'(R)\big[\mathbf{\Phi}_2(R')-\mathbf{\Phi}_1'(R')\mathbf{\Phi}_1^{-1}(R')\mathbf{\Phi}_2(R')\big]^{-1}, & R>R',\\ \mathbf{\Phi}_1(R)\big[\mathbf{\Phi}_2'(R')\mathbf{\Phi}_2^{-1}(R')\mathbf{\Phi}_1(R')-\mathbf{\Phi}_1'(R')\big]^{-1}, & R<R'.\end{cases}\tag{30}$$

without the simplifications made due to Eqs. (23), (26). The GF equations (24), (25), (27), (28), obtained here nonperturbatively, correspond with those applied by Wolken (1972), Aymar *et al*. (1996), Han and Yarkony (1996) to various problems in laser spectroscopy and chemical physics.

Let me consider now the multichannel Green function equation (24).

Using the determination of inverse matrix and properties of invertible matrices provided by Lancaster (1969) gives the multichannel Green function components as

$$\left.\begin{aligned}G^{ij}(R,R';E;R>R')&=\frac{2\mu}{\hbar^2}\frac{1}{|\mathbf{W}|}\textstyle\sum_{l,m=1}^{k}\phi_{il}^{2}(R)\phi_{jm}^{1}(R')A_{ml},\\ G^{ij}(R,R';E;R<R')&=\frac{2\mu}{\hbar^2}\frac{1}{|\mathbf{W}|}\textstyle\sum_{\tilde{l},\tilde{m}=1}^{k}\phi_{i\tilde{l}}^{2}(R)\phi_{j\tilde{m}}^{2}(R')A_{\tilde{l}\tilde{m}},\end{aligned}\right\}$$

$$|\mathbf{W}|\equiv\det\mathbf{W}=\sum_{l=1}^{k}\sum_{\alpha_l=1}^{k}W\big(\phi_{\alpha_l m}^{1},\phi_{\alpha_l l}^{2}\big)A_{ml},\tag{31}$$

$$A_{ml}=(-1)^{m+l}\sum_{P_l}(-1)^{t(P_l)}\prod_{r=1}^{l}\sum_{\alpha_r=1}^{l}W\big(\phi_{\alpha_r r}^{1},\phi_{\alpha_r r}^{2}\big),$$

$$P_l=\{\zeta_1,\zeta_2,\zeta_3,\ldots,\zeta_k\},\tag{32}$$

where P_l is a permutation $\{\zeta_1,\zeta_2,\zeta_3,\ldots,\zeta_k\}$ of $k-1$ following numbers 1, 2, 3, $\ldots$, $l-1$, $l+1$, $\ldots$, k written in any sequence, $t(P_l)$ is number of transpositions which bring the $\{\zeta_1,\zeta_2,\zeta_3,\ldots,\zeta_k\}$ permutation to the normally graduated one $\{1, 2, 3, \ldots, l-1, l+1, \ldots, k\}$ (the P_l permutation takes all the $(k-1)!$ possible permutations),

$$W(u, v) = uv' - vu'.$$

2.3. Spectral Expansion of Nonperturbative Multichannel Green Function

A spectral expansion of the nonperturbative GF can be obtained via eigenfunctions of multichannel Hamiltonian equation (2). So, the eigenfunctions $\mathbf{\Psi}_m(R)$ of the symmetric matrix Hamiltonian equation (23)

$$\mathbf{H}(R)\mathbf{\Psi}_m(R) = E_m\mathbf{\Psi}_m(R)$$

satisfy the following conditions of orthonormalization and completeness

$$\int dR\ \mathbf{\Psi}_m(R)\mathbf{\Psi}^{\mathrm{T}}_{m'}(R) = \mathbf{I}\delta_{mm'},$$

$$\sum_m \mathbf{\Psi}_m(R)\mathbf{\Psi}^{\mathrm{T}}_m(R') = \mathbf{I}\delta(R - R'). \qquad (33)$$

Substituting Eq. (33) into Eq. (10) and its simple transformations yield the following spectral expansion for the multichannel Green function equation (24)

$$\mathbf{G}(R, R'; E) = \sum_m \frac{\mathbf{\Psi}_m(R)\mathbf{\Psi}^{\mathrm{T}}_m(R')}{E - E_m + i0}.$$

The eigenfunctions of the Hermitian Hamiltonian equation (26) fit the equations

$$\int dR\mathbf{\Psi}_m(R)\mathbf{\Psi}^{+}_{m'}(R) = \mathbf{I}\delta_{mm'},$$

$$\sum_m \mathbf{\Psi}_m(R)\mathbf{\Psi}^{+}_m(R') = \mathbf{I}\delta(R - R').$$

and the spectral expansion for its Green function equation (27) is

$$\mathbf{G}(R, R'; E) = \sum_m \frac{\mathbf{\Psi}_m(R)\mathbf{\Psi}^{+}_m(R')}{E - E_m + i0}.$$

The spectral expansion for the multichannel Green function of the Hamiltonian without symmetry equations (29), (30) cannot be obtained because the set of its eigenfunctions does not form a basis.

2.4. Exact Expression of Nonperturbative Green Function Through the One Regular Multichannel Solution

The GF of the symmetric multichannel Hamiltonian, Eq. (24) can be simply expressed through only the regular in zero MCS $\mathbf{\Phi}_1(R)$. From Eqs. (24), (25) one gets

$$\mathbf{\Phi}_2(R) = \mathbf{\Phi}_1(R) \int_{|a>}^{R} \left[\mathbf{\Phi}_1^{\mathrm{T}}(X)\mathbf{\Phi}_2(X)\right]^{-1} \mathbf{W}\, dX, \tag{34}$$

where $|a>$ is the vector limit, that

$$\mathbf{\Phi}_1^{-1}(R)\mathbf{\Phi}_2(R)\Big|_{|R>=|a>} = \mathbf{0}.$$

Substituting Eq. (34) into Eq. (24) yields the expression of the nonperturbative GF equation (24) through only the regular in zero multichannel solution in the form of

$$\mathbf{G}(R, R'; E) = \frac{2\mu}{\hbar^2} \mathbf{\Phi}_1(R)\mathbf{J}(R_>)\mathbf{\Phi}_1^{\mathrm{T}}(R'),$$

$$\mathbf{J}(R) = \int_{|a>}^{R} \left[\mathbf{\Phi}_1^{\mathrm{T}}(X)\mathbf{\Phi}_2(X)\right]^{-1} \mathbf{W}\, dX, \quad R_> = \max\{R, R'\}.$$

The GF of the Hermitian multichannel Hamiltonian equation (27) may be written through Wronskian matrix equation (28) as

$$\mathbf{G}(R, R'; E) = \frac{2\mu}{\hbar^2} \mathbf{\Phi}_1(R)\mathbf{J}(R_>)\mathbf{\Phi}_1^{+}(R'),$$

where

$$\mathbf{J}(R) = \int_{|a>}^{R} \left[\mathbf{\Phi}_1^{+}(X)\mathbf{\Phi}_2(X)\right]^{-1} \mathbf{W}\, dX.$$

So, the nonperturbative multichannel GF may be expressed in simple analytic forms of Eqs. (24), (27), or (30). The form to write out the GF depends on symmetry of the full multichannel Hamiltonian equation (2) and can be various for different kinds of quantum interchannel interactions formed the nondiagonal coupling matrix equation (4).

The general expressions for GF, obtained in this section, are important for physics applications because, as it has been demonstrated by Wolken (1972), Aymar *et al.* (1996), Han and Yarkony (1996), Pegarkov (2000), they permit to calculate analytically the quantum transition probabilities without perturbative restrictions upon the interchannel interaction. Within a quasiclassical approximation one can obtain simple analytic equations for the nonperturbative multichannel solutions and Green's function.

3. QUASICLASSICAL APPROXIMATION FOR MULTICHANNEL SCHRÖDINGER EQUATION

3.1. Matrix Representation of Multichannel Wave Solutions

Within the quasiclassical approximation the matrix Schrödinger equation may be integrated in a nonperturbative matrix form where the multichannel solutions of the coupled equations (1) $\mathbf{\Phi}(R)$ are obtained in the following analytic form for all the points of R-variable excepted few singular points:

$$\mathbf{\Phi}(R) = \mathbf{E}^{+}(R_i, R)\mathbf{a}^{+} + \mathbf{E}^{-}(R_i, R)\mathbf{a}^{-}, \tag{35}$$

where $\mathbf{E}^{\pm}(R_1, R_2)$ are the diagonal matrices of quasiclassical waves, $\mathbf{a}^{\pm}$ are the nondiagonal R-independent matrices of wave amplitudes:

$$\mathbf{E}^{\pm}(R_1, R_2) = \left\| \lambda_m^{-1/2}(R_2) F_m^{\pm}(R_1, R_2)\delta_{ml} \right\|, \tag{36}$$

$$\mathbf{a}^{\pm} = \left\| a_{ml}^{\pm} \right\|, \quad m, l = 1, 2, \ldots, k. \tag{37}$$

In a classical permitted point R the wave in the mth channel $F_m^{\pm}(R_1, R_2)$ has the form of

$$F_m^{\pm}(R_1, R_2) = \exp\{\pm i L_m(R_1, R_2)\}, \tag{38}$$

and in a classical forbidden one

$$F_m^{\pm}(R_1, R_2) = \exp\{s|L_m(R_1, R_2)|\}, \tag{39}$$

where the sign s can be equal with 1 or -1 in dependence on the boundary condition for the mth channel, $\hbar\lambda_m(R)$ is the classical kinetic momentum in the mth channel, $L_m(R_1, R_2)$ is the reduced action along the channel potential $U_m(R)$

$$\lambda_m(R) = \hbar^{-1}[2\mu(E - U_m(R))]^{1/2}, \quad L_m(R_1, R_2) = \int_{R_1}^{R_2} \lambda_m(R)\, dR. \tag{40}$$

The quasiclassical representation for the multichannel solution equations (35)–(40) is true if the condition

$$\left| \frac{d\lambda_m^{-1}(R)}{dR} \right| \ll 1 \tag{41}$$

is fulfilled for all the channel potentials.

3.2. Quasiclassical Propagation of Multichannel Solutions Through Singular Points

The multichannel solution equation (35) propagates through the isolated turning point as follows:

if the $\phi_{ij}^{f}(R)$ component in a classical forbidden R-region has the following view

$$\phi_{ij}^{f}(R) = |\lambda_i(R)|^{-1/2} \frac{a_{ij}}{2} \exp\{-|L_i(R_i, R)|\}, \tag{42}$$

then its form in a classical permitted R-region is

$$\phi_{ij}^{p}(R) = \lambda_i(R)^{-1/2} a_{ij} \cos(|L_i(R_i, R)| - \pi/4); \tag{43}$$

if the wave component in the classical permitted region is

$$\phi_{ij}^{p}(R) = \lambda_i(R)^{-1/2}\{a_{ij}^{+}\exp\{i[|L_i(R_i, R)| + \pi/4]\} + a_{ij}^{-}\exp\{-i[|L_i(R_i, R)| + \pi/4]\}\}, \tag{44}$$

then in the classical forbidden region it is

$$\phi_{ij}^{f}(R) = |\lambda_i(R)|^{-1/2}(a_{ij}^{+} + a_{ij}^{-})\exp\{|L_i(R_i, R)|\}. \tag{45}$$

Equations (42)–(45) are a simple multichannel representation of the well-known one-channel formalism of Fröman and Fröman (1965).

The propagation through a branch point (the point of crossing of diabatic potentials and that of quasicrossing of adiabatic ones) changes the wave amplitudes equation (37). Here we consider the crossing picture, which the following conditions are true for

$$L_i \gg \mathbf{1}, \quad |\sigma_{ij}| \gg 1, \tag{46}$$

$$L_i \equiv L_i(R_i, R_i'), \quad \sigma_{ij} \equiv L_i(R_i, X_{ij}) - L_j(R_j, X_{ij}). \tag{47}$$

In a point R between two neighbouring branch points X_{ij-1}, X_{ij}, $X_{ij-1} < R < X_{ij}$ (Fig. 1) the multichannel solution, Eq. (35) may be written as a sum of incoming and outcoming matrix waves as

$$\mathbf{\Phi}^{<}(R) = \mathbf{E}^{+}(X_{ij}, R)\mathbf{a}^{+<} + \mathbf{E}^{-}(X_{ij}, R)\mathbf{a}^{-<}. \tag{48}$$

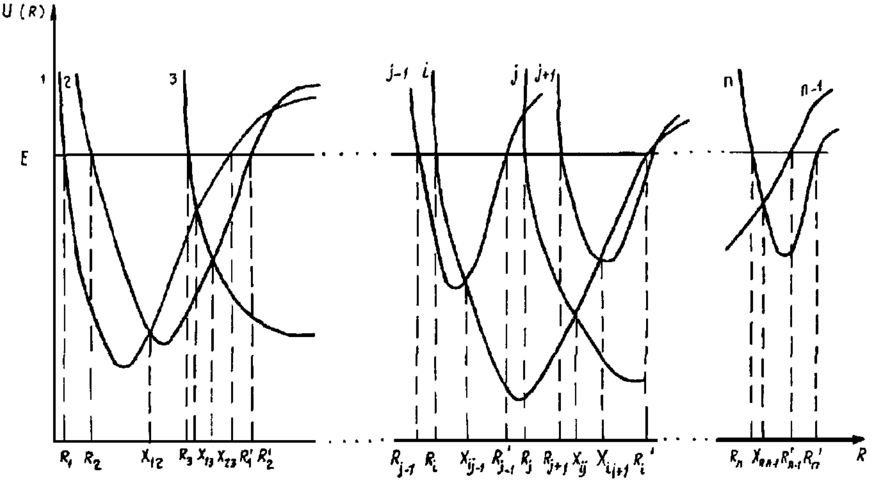

Fig. 1. Intersecting potentials in general multichannel case in dependence on variable R. $R_i(R_i')$ is the left (right) turning point in unperturbed potential $U_i(R)$, X_{ij} is the branch point (the point of crossing of the $U_i(R)$ and $U_j(R)$ potentials, $X_{ij} = X_{ji}$).

For the R-point between the next branch points X_{ij}, X_{ij+1}, $X_{ij} < R < X_{ij+1}$ the multichannel solution may be written as

$$\mathbf{\Phi}^{>}(R) = \mathbf{E}^{+}(X_{ij}, R)\mathbf{a}^{+>} + \mathbf{E}^{-}(X_{ij}, R)\mathbf{a}^{->}. \tag{49}$$

The amplitudes $\mathbf{a}^{\pm<}$ and $\mathbf{a}^{\pm>}$ in Eqs. (48), (49) are connected by the $k \times k$ matrix $\mathbf{N}_{ij}$:

$$\begin{cases} \mathbf{a}^{+>} = \mathbf{N}_{ij}\mathbf{a}^{+<} \\ \mathbf{a}^{->} = \mathbf{N}^{*}_{ij}\mathbf{a}^{-<} \end{cases}. \tag{50}$$

The $\mathbf{N}_{ij}$ matrix has the following structure:

$$\left[\begin{array}{l} \text{its components } N_{ml} = \delta_{ml} \text{ for all } m, l \neq i, j, \\ \text{its components } N_{ii}, N_{ij}, N_{ji}, N_{jj} \text{ form the } 2 \times 2 \text{ matrix } \aleph, \\ \aleph = \begin{Bmatrix} N_{ii} & N_{ij} \\ N_{ji} & N_{jj} \end{Bmatrix}. \end{array}\right. \tag{51}$$

The $\aleph$-matrix connects the wave amplitudes of the two interaction channels i and j on the left and right sides from the nonadiabatic point X_{ij} and is expressed in different analytic forms within either a *diabatic basis* or an *adiabatic basis* for the total energy E lying either above or under the crossing point energy $U_i(X_{ij})$ (case $E < U_i(X_{ij})$ is so-called *underbarrier nonadiabatic transition*, $E > U_i(X_{ij})$ is so-called *abovebarrier nonadiabatic transition*). Nikitin and Umanskii (1984), Eu (1984), and Nakamura (1987) studied in detail the 2×2 *matrix of nonadiabatic transitions* $\aleph$ in the problems of atomic collisions.

For the abovebarrier case the $\aleph$ matrix may be expressed as (the branch point lies into the classical permitted region, the diabatic and adiabatic curves are marked as those in Fig. 2)

– in the diabatic basis

$$\aleph^{\mathrm{d}} = \begin{Bmatrix} \sqrt{P_{ij}}\exp[i\psi_{ij}] & -\sqrt{1-P_{ij}}\exp[i\phi_{ij}] \\ \sqrt{1-P_{ij}}\exp[-i\phi_{ij}] & \sqrt{P_{ij}}\exp[-i\psi_{ij}] \end{Bmatrix}, \tag{52}$$

– in the adiabatic basis

$$\aleph^{\mathrm{a}} = \begin{Bmatrix} \sqrt{1-P_{ij}}\exp[i\phi_{ij}] & \sqrt{P_{ij}}\exp[i\psi_{ij}] \\ -\sqrt{P_{ij}}\exp[-i\psi_{ij}] & \sqrt{1-P_{ij}}\exp[-i\phi_{ij}] \end{Bmatrix}, \tag{53}$$

The nonadiabatic parameters P_{ij}, ψ_{ij}, ϕ_{ij} describe the interaction of the intersecting channel potentials $U_i(R)$ and $U_j(R)$. They depend on velocity of effective particle in the X_{ij} point, on the form of the potential curves and their reciprocal

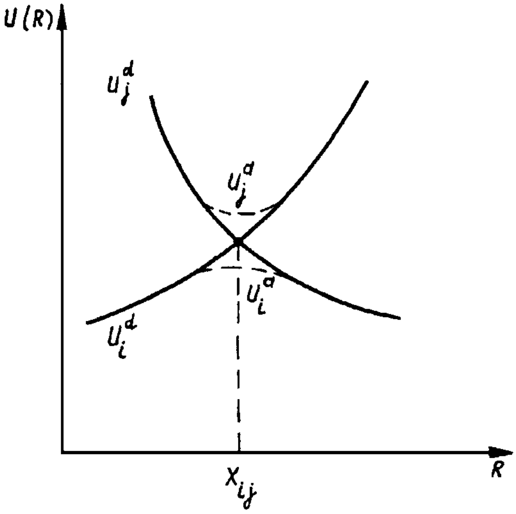

Fig. 2. Branches of diabatic (solid lines) and adiabatic (dashed lines) potentials $U^{\mathrm{d}}_{i,j}(R)$ and $U^{\mathrm{a}}_{i,j}(R)$ form diabatic and adiabatic bases. The subscripts of diabatic and adiabatic curves are the sames if $R < X_{ij}$.

position, on the interchannel coupling strength $|V_{ij}(R)|$. The functional form of the nonadiabatic parameters is determined by a model of interchannel nonadiabatic transitions. The choice of the model is subjected to the curves picture to be appropriate for the transition process. The model admitted gives only the analytic equations for the nonadiabatic parameters but the general form of the multichannel transition matrix **N** equations (51)–(53), connecting the quasiclassical wave amplitudes equation (50), is the same for all the models.

One can see from Eqs. (48)–(53) that the multichannel approach, developed here, may be applied with the same success either for the diabatic or adiabatic basis. A basis from the two ones is only a representation (a picture) to describe a two-curve crossing problem. So, one may use the diabatic basis, say about the *crossing diabatic potentials* $U_i^{\mathrm{d}}(R)$ and do the calculations with the diabatic 2×2 matrix $\aleph^{\mathrm{d}}$ equation (52). On the other side one may use the adiabatic basis, say about the *quasicrossing adiabatic potentials* $U_i^{\mathrm{a}}(R)$ and calculate with the adiabatic matrix $\aleph^{\mathrm{a}}$ equation (53). This choice of the basis brings no formal changes to the construction of the nonperturbative multichannel wave solutions equation (35).

Therefore, the nonperturbative multichannel approach elaborated in this paper is an universal one to solve the multichannel Schrödinger equation independently on the model of wave amplitude connection and type of basis used and may be applied to study *multipotential problems* in quantum mechanics.

3.3. Nonperturbative Propagation of Regular Solutions of Multichannel Schrödinger Equation

Using the rules formulated above permits to construct the regular in zero and regular at infinity nonperturbative solutions of the multichannel Schrödinger equation (1). In the R-point lying between two branch points X_{ij} and X_{ij+1}, $X_{ij} < R < X_{ij+1}$ both solutions are

$$\mathbf{\Phi}_1(R) = \mathbf{E}^+(X_{ij}, R)\mathbf{A}\mathbf{a}_L^+ + \mathbf{E}^-(X_{ij}, R)\mathbf{A}^*\mathbf{a}_L^-, \tag{54}$$

$$\mathbf{\Phi}_2(R) = \mathbf{E}^+(X_{ij}, R)\mathbf{B}\mathbf{a}_R^+ + \mathbf{E}^-(X_{ij}, R)\mathbf{B}^*\mathbf{a}_R^-, \tag{55}$$

where $\mathbf{A}$, $\mathbf{B}$, $\mathbf{a}_L^\pm$, $\mathbf{a}_R^\pm$ are the following R-independent matrices:

$$\mathbf{A} = \mathbf{N}_{ij}\mathbf{F}^+(X_{ij-1}, X_{ij})\mathbf{N}_{ij-1}\cdots\mathbf{N}_{13}\mathbf{F}^+(X_{12}, X_{13})\mathbf{N}_{12}, \tag{56}$$

$$\mathbf{B} = \mathbf{F}^+(X_{ij+1}, X_{ij})\mathbf{N}_{ij+1}^+\cdots\mathbf{N}_{nn-2}^+\mathbf{F}^+(X_{nn-1}, X_{nn-2})\mathbf{N}_{nn-1}^+, \tag{57}$$

$$\left.\begin{aligned} \mathbf{F}^\pm(X_1, X_2) &= \left\| F_m^\pm(X_1, X_2)\delta_{ml} \right\|, [\mathbf{F}^\pm]^{\mathrm{T}} = \mathbf{F}^\pm, \\ \mathbf{a}_{L,R}^\pm &= \left\| (a_{L,R}^\pm)_m \delta_{ml} \right\|, [\mathbf{a}_{L,R}^\pm]^{\mathrm{T}} = \mathbf{a}_{L,R}^\pm. \end{aligned}\right] \tag{58}$$

Here we consider the general case, where $E^* \neq E$ and, therefore, $L_m^* \neq L_m$. In opposite case, Eq. (58) are supplimented by the follows: $[\mathbf{F}^\pm]^+ = \mathbf{F}^\mp$, $[\mathbf{a}_{L,R}^\pm]^+ = \mathbf{a}_{L,R}^\mp$.

The channel left-side amplitudes are (both for open and closed m-channels)

in the classical permitted region

$$(a_L^\pm)_m = \frac{a_m}{2}\exp\left\{\pm i\left[L_m(R_m, X_{12}) - \frac{\pi}{4}\right]\right\},$$

in the classical forbidden region

$$(a_L^\pm)_m = \frac{a_m}{2}\exp\{-|L_m(R_m, X_{12})|\}.$$

The channel right-side amplitudes are

i) for the case of the closed m-channel:

in the classical permitted region

$$(a_R^\pm)_m = \frac{b_m}{2}\exp\left\{\pm i\left[L_m(R_m', X_{nn-1}) + \frac{\pi}{4}\right]\right\},$$

in the classical forbidden region

$$(a_R^\pm)_m = \frac{b_m}{2}\exp\{-|L_m(R_m', X_{nn-1})|\},$$

ii) for the case of the open m-channel:

$$(a_R^{\pm})_m = b_m^{\pm} \exp\left\{\pm i\left[L_m(R_m, X_{nn-1}) + \frac{\pi}{4}\right]\right\},$$

where a_m, b_m, $b_m^{\pm}$ are the constants.

The matrix amplitudes of regular solutions, equations (54), (55) are connected with each other by means of **T**-matrix as

$$\mathbf{A}\mathbf{a}_L^{+} = \mathbf{T}_1^{>}(ij)\mathbf{A}^{*}\mathbf{a}_L^{-}, \tag{59}$$

$$\mathbf{B}\mathbf{a}_R^{+} = \mathbf{T}_2^{>}(ij)\mathbf{B}^{*}\mathbf{a}_R^{-}. \tag{60}$$

Including Eqs. (54), (55) to the matrix Wronskian, Eqs. (25), (28) deduces its independence on the R-variable. In the quasiclassical approximation equations (25), (28) are formally equal with each other and have the form of

$$\begin{aligned}\mathbf{W} &= 2i\{\mathbf{a}_L^{-}\mathbf{S}\mathbf{a}_R^{+} - \mathbf{a}_L^{+}\mathbf{S}^{*}\mathbf{a}_R^{-}\},\\ \mathbf{S} &= \mathbf{A}^{+}\mathbf{B}\\ &= \mathbf{N}_{12}^{+}\mathbf{F}^{-}(X_{12}, X_{13})\mathbf{N}_{13}^{+}\cdots\mathbf{N}_{nn-2}^{+}\mathbf{F}^{-}(X_{nn-2}, X_{nn-1})\mathbf{N}_{nn-1}^{+}.\end{aligned} \tag{61}$$

The matrices **A** and **B**, Eqs. (56), (57) are the quasiclassical multichannel propagators evolving the regular channel waves along the multichannel passage from their origins to the R point: **A** propagates the multichannel wave from zero and **B** propagates it from infinity. Both propagators allow for only the interchannel interactions existed between the wave origin and the R point. So, the **A**-wave propagator involves the interactions lying between zero and R and no ones lying between infinity and R; the **B**-wave propagator involves the interactions lying between infinity and R and no ones lying between zero and R. For a quantum state in such multicurve potential the regular in zero solution, Eq. (54) must be equal to the regular at infinity one, Eq. (55) in an R-point as well as their first derivatives must be equal to each other in the same point too.

4. TWO- AND THREE-CHANNEL NONPERTURBATIVE GREEN FUNCTIONS IN QUASICLASSICAL APPROXIMATION

Within the method developed above one obtains the very simple analytic equations for the multichannel Green functions in the cases of two and three intersecting potentials.

The components $G^{ij}(R, R'; E; R < R')$ of the multichannel Green functions, Eqs. (24) and (27) may be received from $G^{ij}(R, R'; E; R > R')$ in accordance with symmetry of the functions as in order to get the $G^{ij}(R, R'; E; R < R')$-component of Eq. (24) it needs to replace the variables R and R' with each other in the $G^{ji}(R, R'; E; R > R')$-component

$$G^{ij}(R, R'; E; R < R') = G^{ji}(R, R'; E; R > R')|_{R \leftrightarrow R'}; \tag{62}$$

for the components of Eq. (27) the rule is

$$G^{ij}(R, R'; E; R < R') = [G^{ji}(R, R'; E; R > R')|_{R \leftrightarrow R'}]^{*}. \tag{63}$$

The $G^{ji \neq j}(R, R'; E; R > R')$-component is received from the $G^{ij \neq i}(R, R'; E; R > R')$ one as follows:

$$G^{ji \neq j}(R, R'; E; R > R') = G^{ij \neq i}(R, R'; E; R > R')|_{R \leftrightarrow R'}. \tag{64}$$

Therefore, one needs only to write out the diagonal components $G^{i=j}(R, R'; E; R > R')$ and nondiagonal ones like $G^{ji>j}(R, R'; E; R > R')$. The other components may be obtained from them by means of simple replace of indexes and/or variables as given by Eqs. (62)–(64).

4.1. Two-Channel Nonperturbative Green Functions

A two-channel Green function is written in the form of either Eq. (24) or Eq. (27), that depends on full energy E and types of the participated channel potentials.

4.1.1. Potentials "Attractive + Attractive"

The channel potentials are shown in Fig. 3(a). In this case the Wronskian is equal to

$$|\mathbf{W}| \equiv \det \mathbf{W} = P r_1 r_2 + (1 - P) r_{12} r_{21}, \tag{65}$$

where designations $r_{1,2}$, $r_{12,21}$ are given in Appendix.

In the classical permitted region on the left side from branch point X_{12} the Green function components are

$$R_{1,2} < R < X_{12},$$

$$\begin{aligned} G^{11(22)}(R, R'; E; R > R') = {}& -\frac{2\mu}{\hbar^2 |\mathbf{W}|} \left[\lambda_{1(2)}(R) \lambda_{1(2)}(R')\right]^{-1/2} \\ & \times \cos\left(L_{1(2)}(R_{1(2)}, R') - \pi/4\right) Q_{2(1)}(R), \end{aligned} \tag{66}$$

$$\begin{aligned} G^{12}(R, R'; E; R > R') = {}& \frac{2\mu}{\hbar^2 |\mathbf{W}|} [\lambda_1(R) \lambda_2(R')]^{-1/2} \sqrt{P(1 - P)} \\ & \times \sin(L_1 - L_2 - \sigma_{12} + \psi + \phi) \cos(L_1(R_1, R) - \pi/4) \\ & \times \cos(L_2(R_2, R') - \pi/4). \end{aligned} \tag{67}$$

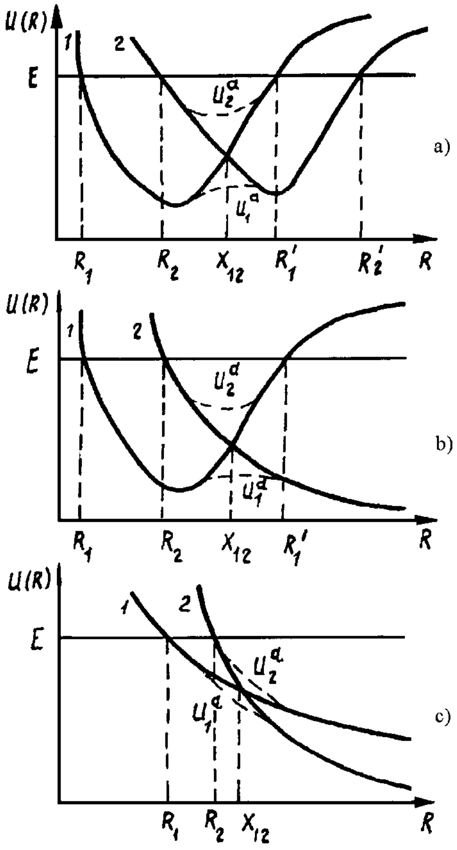

Fig. 3. System of two diabatic potentials marked as 1, 2. The dashed curves show adiabatic potentials designated as $U^{a}_{1,2}(R)$. (a) The "attractive + attractive" system, (b) the "attractive + repulsive" system, (c) the "repulsive + repulsive" system.

In the classical permitted region on the right side from the branch point one has

$$X_{12} < R < R'_{1,2},$$

$$G^{11(22)}(R, R'; E; R > R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}\left[\lambda_{1(2)}(R)\lambda_{1(2)}(R')\right]^{-1/2}$$

$$\times \cos\big(L_{1(2)}(R_{1(2)}, R\big) - L_{1(2)} + \pi/4)F_{2(1)}(R'),$$

$$G^{12}(R, R'; E; R > R') = \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_2(R')]^{-1/2}\sqrt{P(1-P)s}$$
$$\times \cos(L_1(R_1, R) - L_1 + \pi/4)$$
$$\times \cos(L_2(R_2, R') - L_2 + \pi/4),$$

where

$$s = \sin(\phi - \sigma_{12} - \psi),$$
$$F_{1,2}(R) = Pr_{1,2}\cos(L_{2,1}(R_{2,1}, R) \mp \psi - \pi/4)$$
$$+ (1-P)r_{21,12}\cos(L_{2,1}(R_{2,1}, R) \pm \sigma_{12} \mp \phi - \pi/4),$$
$$Q_{1,2}(R) = Pr_{1,2}\cos(L_{2,1}(R_{2,1}, R) - L_{2,1} \pm \psi + \pi/4)$$
$$+ (1-P)r_{12,21}\cos(L_{2,1}(R_{2,1}, R) \pm \sigma_{12} - L_{1,2} \mp \phi + \pi/4),$$
$$S_{1,2}(R) = Pd_1\cos(L_{2,1}(R_{2,1}, R) \mp \psi - \pi/4)$$
$$+ (1-P)d_2\cos(L_{2,1}(R_{2,1}, R) \pm \sigma_{12} \mp \phi - \pi/4)$$

and other designations are presented in Appendix.

4.1.2. Potentials "Attractive + Repulsive"

See Fig. 3(b); here

$$|\mathbf{W}| = Pr_1d_1 + (1-P)d_2r_{21}. \tag{68}$$

For the classical permitted region on the left side from the branch point X_{12} the component of nonperturbative Green function matrix are

$$R_{1,2} < R < X_{12},$$
$$G^{11}(R, R'; E; R > R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_1(R')]^{-1/2}\cos(L_1(R_1, R') - \pi/4)$$
$$\times [Pd_1\cos(L_1(R_1, R) - L_1 - \psi + \pi/4)$$
$$+ (1-P)d_2r_{21}\exp\{i[L_1(R_1, R) + \pi/4]\}],$$
$$G^{12}(R, R'; E; R > R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_2(R')]^{-1/2}\sqrt{P(1-P)}d_1d_2i\,e^{iL_1}$$
$$\times \cos(L_1(R_1, R) - \pi/4)\cos(L_2(R_2, R') - \pi/4),$$

$$G^{22}(R,R';E;R>R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_2(R)\lambda_2(R')]^{-1/2}\cos(L_2(R_2,R')-\pi/4)$$
$$\times[Pr_1d_1\exp\{i[L_2(R_2,R)+\pi/4]\}+(1-P)d_2$$
$$\times\cos(L_2(R_2,R)+\sigma_{12}-\phi-L_1+\pi/4)],$$

and for the classical permitted region on the right side from the branch point X_{12}:

$$X_{12} < R < R_1',$$

$$G^{11}(R,R';E;R>R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_1(R')]^{-1/2}$$
$$\times\cos(L_1(R_1,R)-L_1+\pi/4)S_2(R'),$$

$$G^{12}(R,R';E;R>R') = \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_2(R')]^{-1/2}\sqrt{P(1-P)s}\cos(L_1(R_1,R)$$
$$-L_1+\pi/4)\exp\{i[L_2(R_2,R')+\pi/4]\}.$$

$$G^{22}(R,R';E;R>R') = -\frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_2(R)\lambda_2(R')]^{-1/2}$$
$$\times F_1(R')\exp\{i[L_2(R_2,R)+\pi/4]\}.$$

4.1.3. Potentials "Repulsive + Repulsive"

See Fig. 3(c). The Wronskian matrix determinant is equal to unity

$$|\mathbf{W}| = \mathbf{1}.$$

For the classical permitted region on the left side from the branch point X_{12} the Green function matrix is

$$R_{1,2} < R < X_{12}, \quad m = 1,2,$$

$$G^{mm}(R,R';E;R>R') = -\frac{2\mu}{\hbar^2}[\lambda_m(R)\lambda_m(R')]^{-1/2}\ \cos(L_m(R_m,R')-\pi/4)$$
$$\times\exp\{i[L_m(R_m,R)+\pi/4]\},$$

$$G^{12}(R,R';E'R>R') = 0,$$

and for the classical permitted region on the right side from the branch point X_{12}:

$$X_{12} < R,$$

$$G^{11}(R, R'; E; R > R') = -\frac{2\mu}{\hbar^2}[\lambda_1(R)\lambda_1(R')]^{-1/2}$$

$$\times \exp\{i[L_1(R_1, R) + \pi/4]\}S_2(R'),$$

$$G^{12}(R, R'; E; R > R') = \frac{2\mu}{\hbar^2}[\lambda_1(R)\lambda_2(R')]^{-1/2}\sqrt{P(1-P)s}$$

$$\times \exp\{i[L_1(R_1, R) + \pi/4]\} \exp\{i[L_2(R_2, R') + \pi/4]\}.$$

$$G^{22}(R, R'; E; R > R') = -\frac{2\mu}{\hbar^2}[\lambda_2(R)\lambda_2(R')]^{-1/2}$$

$$\times \exp\{i[L_2(R_2, R) + \pi/4]\}S_1^*(R').$$

4.2. Three-Channel Nonperturbative Green's Functions of Potentials "Attractive + Attractive + Attractive"

The terms system is shown in Fig. 4. By the same way as above one obtains the three-channel Green matrix components as

G$(R, R'; E) = \|G^{ml}(R, R'; E)\|$, $m, l = 1, 2, 3$ for the classical permitted region lying between the branch points X_{13} and X_{23} are

$$X_{13} < R < R_{23},$$

$$G^{11}(R, R'; E; R > R') = \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_1(R')]^{-1/2}\cos(L_1(R_1, R) - L_1$$

$$+\pi/4)\,\{\mathcal{R}_2\cos(L_1(R_1, R') + \psi_{13} - \pi/4) + \mathcal{R}_1$$

$$\times \cos(L_1(R_1, R') - \sigma_{13} + \phi_{13} - \pi/4)\},$$

$$G^{12}(R, R'; E; R > R') = \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_2(R')]^{-1/2}\sqrt{P_{13}(1-P_{13})P_{23}(1-P_{23})}$$

$$\times s_1 s_2 \cos(L_1(R_1, R) - L_1 + \pi/4)$$

$$\times \cos(L_2(R_2, R') - \pi/4),$$

$$G^{13}(R, R'; E; R > R') = \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_1(R)\lambda_3(R')]^{-1/2}\sqrt{P_{13}(1-P_{13})}$$

$$\times s_1\mathcal{F}_2(R')\cos(L_1(R_1, R) - L_1 + \pi/4),$$

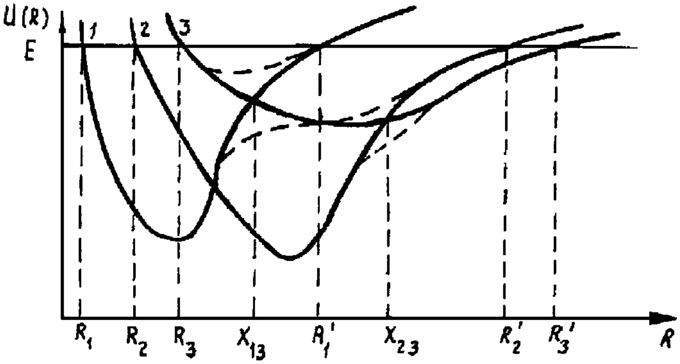

Fig. 4. System of three attractive diabatic potentials marked as 1, 2, 3. The dushed curves show adiabatic potentials.

$$
\begin{aligned}
G^{22}(R, R'; E; R > R') = {} & \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_2(R)\lambda_2(R')]^{-1/2}\cos(L_2(R_2, R') - \pi/4)\\
& \times\{P_{23}[P_{13}t_1t_3 + (1 - P_{13})t_{31}t_{13}]\cos(L_2(R_2, R)\\
& - L_2 - \psi_{23} + \pi/4) + (1 - P_{23})[P_{13}t_1t_{32}\\
& + (1 - P_{13})t_{31}t_{12}]\cos(L_2(R_2, R)\\
& - \sigma_{23} - L_3 + \phi_{23} + \pi/4)\},\\
G^{23}(R, R'; E; R > R') = {} & \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_2(R)\lambda_3(R')]^{-1/2}\sqrt{P_{23}(1 - P_{23})}\\
& \times s_2\mathcal{F}_1(R')\cos(L_2(R_2, R) - \pi/4),\\
G^{33}(R, R'; E; R > R') = {} & \frac{2\mu}{\hbar^2|\mathbf{W}|}[\lambda_3(R)\lambda_3(R')]^{-1/2}\mathcal{F}_1(R')\mathcal{F}_2(R),
\end{aligned}
$$

where

$$
\begin{aligned}
s_1 &= \sin(\sigma_{13} - \phi_{13} + \psi_{13}),\\
s_2 &= \sin(\sigma_{23} - L_2 + L_3 - \phi_{23} - \psi_{23}),\\
\mathcal{F}_1(R) &= P_{13}t_1\cos(L_3(R_3, R) - \psi_{13} - \pi/4)\\
&\quad + (1 - P_{13})t_{31}\cos(L_3(R_3, R) + \sigma_{13} - \phi_{13} - \pi/4),\\
\mathcal{F}_2(R) &= P_{23}t_2\cos(L_3(R_3, R) - L_3 + \psi_{23} + \pi/4)\\
&\quad + (1 - P_{23})t_{23}\cos(L_3(R_3, R) - L_2 + \sigma_{23} - \phi_{23} + \pi/4), \qquad (69)
\end{aligned}
$$

$$\begin{aligned}\mathcal{R}_1 &= (1-P_{13})\{P_{23}t_2t_{13} + 1(1-P_{23})t_{12}t_{23}\},\\ \mathcal{R}_2 &= P_{13}\{P_{23}t_2t_3 + (1-P_{23})t_{23}t_{32}\},\\ |\mathbf{W}| &= -t_1\mathcal{R}_2 - t_{31}\mathcal{R}_1,\end{aligned}$$

and other magnitudes are written in Appendix.

4.3. Quasiclassical Nonperturbative Green Functions in Limits of Weak and Strong Nonadiabatic Couplings

In this subsection the quasiclassical multichannel Green functions are calculated in the weak interchannel coupling and strong interchannel coupling limits analytically. An aim here is to obtain the limit expansions for the functions and to show, that the weak coupling expansion of the multichannel Green function corresponds with the perturbative expansion of full nonadiabatic resolvent.

4.3.1. Two Interacting Channels

The components of two-channel Green function can be written in a generalized form as follows:

$$G^{mm}(R, R'; E) = A\frac{a_1 + \alpha a_2}{b_1 + \alpha b_2}, \quad m, l = 1, 2, \tag{70}$$

$$G^{m\neq l}(R, R'; E) = \tilde{A}\frac{\sqrt{\alpha}}{b_1 + \alpha b_2}, \tag{71}$$

where α is

$$\alpha = \frac{1-P}{P}, \tag{72}$$

$A, \tilde{A}, a_1, a_2$ are the functions of R and R', but b_1, b_2 are independent on the R-variable.

The Green functions, Eqs. (70), (71) may be expanded over the α-parameter, Eq. (72)

$$\alpha < 1. \tag{73}$$

as the *Taylor–Maclaurins* series:

$$G^{mm}(R, R'; E) = \frac{A}{b_1}\left\{a_1 + \frac{a_2b_1 - a_1b_2}{b_1}R(b_2, \alpha)\right\}, \tag{74}$$

$$G^{m\neq l}(R, R'; E) = \frac{\tilde{A}}{b_1}\sqrt{\alpha}\left\{1 - \frac{b_2}{b_1}R(b_2, \alpha)\right\}, \tag{75}$$

where $R(b,\alpha)$ is the following series:

$$R(b,\alpha)=\sum_{n=1}^{\infty}\frac{(-2b)^{n-1}}{n!}\alpha^{n}. \tag{76}$$

The principal nonperturbative dependence of the two-channel Green functions, Eqs. (70), (71) concentrates into the $R(b,\alpha)$-term, Eq. (76). The other magnitudes A, $\tilde{A}$, a_1, a_2, b_1, b_2 depend on the interchannel interaction much weaker through only the phases ψ, ϕ.

For the opposite case, where

$$\alpha > 1, \tag{77}$$

the Green functions, Eqs. (70), (71) may be expanded over the α^{-1}-parameter and Eqs. (74), (75) transform to

$$G^{mm}(R,R';E)=\frac{A}{b_2}\left\{a_2+\frac{a_1b_2-a_2b_1}{b_2}R(b_1,\alpha^{-1})\right\}, \tag{78}$$

$$G^{m\neq l}(R,R';E)=\frac{\tilde{A}}{b_2}\sqrt{\alpha^{-1}}\left\{1-\frac{b_1}{b_2}R(b_1,\alpha^{-1})\right\}. \tag{79}$$

Therefore, in the case Eq. (73) the two-channel Green functions poles are due to the b_1-term (see Eqs. (74), (75)), while in the case Eq. (77) the poles are due to another term b_2 (see Eqs. (78), (79)). Thus, the poles in the weak interaction limit (so-called *diabatic limit*)

$$\alpha \ll 1, \quad \phi\to\phi_0, \quad \psi\to\psi_0 \tag{80}$$

are quite defferent from those in the strong interaction limit (so-called *adiabatic limit*)

$$\alpha \gg 1, \quad \phi\to\phi_\infty, \quad \psi\to\psi_\infty \tag{81}$$

Within the Landau–Zener model of the nonadiabatic interchannel transitions it can be calculated directly in an analytic form, that in the limit of weak interchannel interaction, Eq. (80) the two-channel Green function components $\|G^{ml}_{\text{two}}(R,R';E)\|$ are expressed through the diabatic one-channel Green functions $G^0_m(R,R';E)$ of unperturbed potentials $U_m(R)$. So, the G^{22} and G^{12} components have the form of

$$R, R' < X_{12}, \quad \alpha \ll 1, \quad \delta \ll 1, \tag{82}$$

$$\begin{aligned}G^{22}_{\text{two}}(R,R';E)=G^0_2(R,R';E)+\big\langle G^0_2(R<R_1)V_{21}(R_1)G^0_1(R_1,R_2)\\ \times V_{12}(R_2)G^0_2(R_2>R')\big\rangle_{R_1,R_2},\end{aligned} \tag{83}$$

$$G^{12}_{\text{two}}(R,R';E)=\big\langle G^0_1(R<R_1)V_{12}(R_1)G^0_2(R_1,R')\big\rangle_{R_1}. \tag{84}$$

The diagram representation for Eqs. (83), (84) is given in Fig. 5(a) and (c).

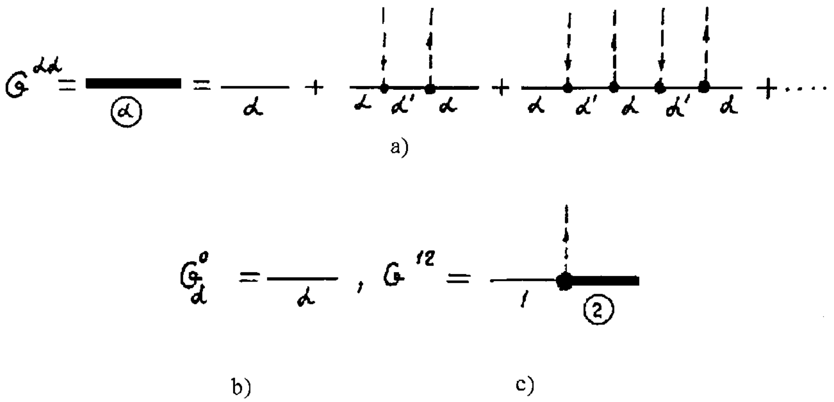

Fig. 5. Diagram representation of two-channel nonperturbative Green function. The diagonal component $G^{\alpha\alpha}(R, R'; E)$ is pictured as broad solid line (a), the unperturbed Green function $G^0_\alpha(R, R'; E)$ is drawn as the narrow one (b), the nondiagonal component $G^{\alpha\beta}(R, R'; E)$ is presented as diagram (c).

4.3.2. Three Interacting Channels

The same results can be obtained for the three-channel Green function $\|G^{ml}_{\text{three}}(R, R'; E)\|$, $m, l = 1, 2, 3$, where the weak interaction limit, Eqs. (80), (82) is putted firstly for the V_{13} coupling and then for both couplings V_{13}, V_{23}:

$$X_{13} < R, \quad R' < X_{23},$$

$$\delta_{13} \ll 1, \quad \delta_{23} \sim 1$$

$$G^{33}_{\text{three}}(R, R'; E; R > R') = G^{33}_{\text{two}}(R, R'; E; R > R') + \big\langle G^{33}_{\text{two}}(R > R_1)V_{31}(R_1) \times G^0_1(R_1, R_2)V_{13}(R_2)G^{33}_{\text{two}}(R_2 > R')\big\rangle_{R_1,R_2}, \tag{85}$$

$$G^{13}_{\text{three}}(R, R'; E; R > R') = \big\langle G^0_1(R > R_1)V_{13}(R_1)G^{33}_{\text{two}}(R_1 < R')\big\rangle_{R_1}, \tag{86}$$

$$G^{23}_{\text{three}}(R, R'; E; R < R') = G^{23}_{\text{two}}(R, R'; E; R < R') + \big\langle G^{23}_{\text{two}}(R < R_1)V_{31}(R_1) \times G^0_1(R_1 < R_2)V_{13}(R_2)G^{33}_{\text{two}}(R_2 < R')\big\rangle_{R_1,R_2}, \tag{87}$$

$$\delta_{13}, \delta_{23} \ll 1,$$

$$G^{33}_{\text{three}}(R, R'; E; R > R') = G^0_3(R, R'; E; R > R') + \big\langle G^0_3(R < R_1)V_{32}(R_1) \times G^0_2(R_1, R_2)V_{23}(R_2)G^0_3(R_2 > R')\big\rangle_{R_1,R_2} + \big\langle G^0_3(R > R_1)V_{31}(R_1)G^0_1(R_1, R_2)V_{13}(R_2) \times G^0_3(R_2 < R')\big\rangle_{R_1,R_2}, \tag{88}$$

$$G^{13}_{\text{three}}(R, R'; E; R > R') = \left\langle G^0_1(R > R_1)V_{13}(R_1)G^0_3(R_1 < R')\right\rangle_{R_1}, \tag{89}$$

$$G^{23}_{\text{three}}(R, R'; E; R < R') = \left\langle G^0_2(R < R_1)V_{23}(R_1)G^0_3(R_1 > R')\right\rangle_{R_1}. \tag{90}$$

In Eqs. (83)–(90) the $\langle\ \rangle_R$ symbol stands for the integration over the R variable, estimated by means of stationary phase method; $V_{12}(R)$ is the interaction of the $U_1(R)$ and $U_2(R)$ unperturbed diabatic potentials, $V_{23}(R)$ is that of the $U_2(R)$ and $U_3(R)$ unperturbed diabatic potentials. The diabatic one-channel Green functions $G^0_i(R, R'; E)$ in the quasiclassical approximation are presented in Appendix.

In the strong coupling limit, Eq. (81) the multichannel Green functions are expressed through the one-channel Green functions of the reconstructed adiabatic potentials $U^{\text{a}}_m(R)$ (see Figs. 3 and 4) in the forms like Eqs. (83)–(90).

5. NONPERTURBATIVE MATRIX ELEMENTS OF QUANTUM TRANSITIONS WITHIN QUASICLASSICAL APPROXIMATION

The time-independent multichannel Green functions obtained above may be applied to calculate the quantum transition probabilities beyond perturbation approximation.

The nonperturbative transition matrix element may be expressed via the T-transition operator as

$$T_{fi} = \langle\chi^0_f|T(E)|\chi^0_i\rangle,$$

where $\chi^0_{i,f}$ are the perturbation-free wave functions of the channels, $T(E)$ stands for the nonperturbative transition operator

$$T(E) = V + VG(E)V$$

and the $G(E)$-operator fits the following *exact* operator equation

$$G(E) = G_0 + VG(E)V \tag{91}$$

with perturbation-free resolvent G_0. The coordinate representation of resolvent $G(E)$ (91) is the nonperturbative matrix Green function.

A transition matrix element with the nonperturbative Green function can be written through the components of the Green matrix (11) as

$$M_{fi} = \sum_{l,m=1}^{k} \left\langle\chi^0_f(R)|V_{fl}(R)G^{lm}(R, R'; E)V_{mi}(R')|\chi^0_i(R')\right\rangle. \tag{92}$$

Within the quasiclassical approximation one can obtain simple analytic equations for the nonperturbative transition matrix element (92). As an example of them only the case of attractive channel is considered here, where two channels interact with each other nonperturbatively and the variables lie in the classical permitted region on the left side from the branch point X_{12}, $R > R'$ (see Subsection 4.1.1., Eqs. (66), (67)).

Using a stationary phase method to estimate the integrals in Eq. (92) gives

$$\begin{aligned} M_{fi} = \frac{A_f^* A_i\ \hbar^2}{\mu|\mathbf{W}|} \Big[\Big\{ & \sqrt{P(1-P)} \sin(L_1 - L_2 - \sigma_{12} + \psi + \phi) \\ & \times C_{f2}(X_{f2}) \cos(\sigma_{f2} - \tilde{q}_{f2}) - (Pr_2 \sin(\sigma_{f1} + L_1 + \psi - \tilde{q}_{f1}) \\ & + (1-P) r_{21} \sin(\sigma_{f1} + \sigma_{12} + L_2 - \phi - \tilde{q}_{f1})) C_{f1}(X_{f1}) \Big\} \\ & \times C_{1i}(X_{1i}) \cos(\sigma_{1i} - \tilde{q}_{1i}) + \Big\{ \sqrt{P(1-P)} \sin(L_1 - L_2 - \sigma_{12} + \psi + \phi) \\ & \times C_{f1}(X_{f1}) \cos(\sigma_{f1} - \tilde{q}_{f1}) - (Pr_1 \sin(\sigma_{f2} + L_2 - \psi - \tilde{q}_{f2}) \\ & + (1-P) r_{12} \sin(\sigma_{f2} - \sigma_{12} + L_1 + \phi - \tilde{q}_{f2})) C_{f2}(X_{f2}) \Big\} \\ & \times C_{2i}(X_{2i}) \cos(\sigma_{2i} - \tilde{q}_{2i}) \Big], \end{aligned} \tag{93}$$

where

$$C_{ij}(R) = V_{ij}(R) \left[\frac{\pi\mu}{\hbar^2 \lambda_i(R) |q_{ij}|} \right]^{1/2}$$

$$q_{ij}(X) = \left(\frac{dU_i(R)}{dR} - \frac{dU_j(R)}{dR} \right) \bigg|_{R=X}$$

$$\tilde{q}_{ij} = \frac{\pi}{4} \operatorname{sign}(q_{ij}),$$

A_i, A_j are the amplitudes of initial and final channel wave functions.

In the limit of the very weak interaction

$$P = 1; \quad 1 - P = 0;$$

$$\phi = \frac{\pi}{4}; \quad \psi = 0,$$

Eq. (93) takes the form

$$\begin{aligned} M_{fi}^{w} = -\frac{A_f^* A_i\ \hbar^2}{\mu} \Bigg[& \frac{\sin(\sigma_{f1} + L_1 - \tilde{q}_{f1}) \cos(\sigma_{1i} - \tilde{q}_{1i}) C_{f1}(X_{f1}) C_{1i}(X_{1i})}{\cos L_1} \\ & + \frac{\sin(\sigma_{f2} + L_2 - \tilde{q}_{f2}) \cos(\sigma_{2i} - \tilde{q}_{2i}) C_{f2}(X_{f2}) C_{2i}(X_{2i})}{\cos L_2} \Bigg], \end{aligned}$$

which corresponds to the well-known perturbative approximation over perturbation $|V_{12}|$.

In the limit of the very strong interaction

$$P = 0; \quad 1 - P = 1;$$

$$\phi = \phi^s; \quad \psi = \psi^s$$

Eq. (93) transforms to

$$M_{fi}^s = -\frac{A_f^* A_i \hbar^2}{\mu}\left[\frac{\sin\left(\sigma_{f1} + L_1^s - \tilde{q}_{f1}\right)\cos(\sigma_{1i} - \tilde{q}_{1i})C_{f1}(X_{f1})C_{1i}(X_{1i})}{\cos L_1^s}\right.$$
$$\left. + \frac{\sin\left(\sigma_{f2} + L_2^s - \tilde{q}_{f2}\right)\cos(\sigma_{2i} - \tilde{q}_{2i})C_{f2}(X_{f2})C_{2i}(X_{2i})}{\cos L_2^s}\right], \qquad (94)$$

where L_1^s and L_2^s are the reconstructed quasiclassical actions over the adiabatic potentials,

$$L_1^s = \sigma_{12} + L_2 - \psi^s,$$
$$L_2^s = -\sigma_{12} + L_1 + \psi^s.$$

Equation (94) corresponds to the perturbative approximation over $|V_{12}|^{-1}$ which is known as an *strong-field perturbative approximation.*

6. CONCLUSION

The time-independent nonperurbative approach presented in this paper has permited to obtain the multichannel wave functions and Green functions in the analytic form, which are useful to consider the principal picture of stationary quatum transitions and to receive simple equations for their cross sections beyond perturbation theory. The presented multichannel method permits to get the equations in the form to be appropriate for a simple physics analysis without routine numerical computations. The quasiclassical functions obtained above may be used, if the conditions, Eqs. (41), (46), are fulfilled.

APPENDIX

Let me introduce the following designations for the terms of two-channel functions used above:

$$r_1 = \cos(L_1 + \psi),$$
$$r_{21} = \cos(L_1 - \sigma_{12} + \phi),$$
$$r_2 = \cos(L_2 - \psi),$$
$$r_{12} = \cos(L_2 + \sigma_{12} - \phi),$$
$$d_1 = e^{i\psi},$$
$$d_2 = e^{i(\phi - \sigma_{12})},$$

and for the three-channel functions:

$$\begin{aligned}
t_1 &= \cos(L_1 + \psi_{13}),\\
t_{12} &= \cos(\sigma_{23} - \sigma_{13} - L_2 + \phi_{13} - \phi_{23}),\\
t_2 &= \cos(L_2 + \psi_{23}),\\
t_{13} &= \cos(L_3 + \sigma_{13} - \phi_{13} - \psi_{23}),\\
t_3 &= \cos(L_3 - \psi_{13} - \psi_{23}),\\
t_{23} &= \cos(L_3 + \sigma_{23} - \phi_{23}),\\
t_{31} &= \cos(\sigma_{13} - L_1 - \phi_{13}),\\
t_{32} &= \cos(\sigma_{23} - L_2 + \psi_{13} - \phi_{23}),
\end{aligned}$$

The diabatic one-channel Green function $G_m^0(R, R'; E)$ within the quasiclassical approximation is

for an attractive potential

$$\begin{aligned}
G_m^0(R, R'; E) = -\frac{2\mu}{\hbar^2}[\lambda_m(R)\lambda_m(R')]^{-1/2}\\
\times \frac{\cos(L_m(R_m, R_<) - \pi/4)\cos(L_m(R_m, R_>) - L_m + \pi/4)}{\cos L_m}
\end{aligned}$$

for a repulsive potential

$$\begin{aligned}
G_m^0(R, R'; E) = -\frac{2\mu}{\hbar^2}[\lambda_m(R)\lambda_m(R')]^{-1/2}\\
\times \cos(L_m(R_m, R_<) - \pi/4)\exp\{i[L_m(R_m, R_>) + \pi/4]\},
\end{aligned}$$

where

$$R_> = \max\{R, R'\}, \quad R_< = \min\{R, R'\}.$$

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