A. SUPPLEMENTARY MATERIAL — PART A

A summary
of
collision time delay (life-time) matrix approach
to
determination
of
energies and widths of quasi-bound states

The notion of collision time-delay as an interpretation of the energy derivative of the scattering phase shift has been introduced to the literature by Wigner in 1955, Ref. 1. A generalization of this notion to inelastic collisions is the life-time matrix $\boldsymbol{Q}$ introduced by Smith, Ref. 2. The basic formula for this quantity is its relation to the scattering $\boldsymbol{S}$-matrix

$$\boldsymbol{Q}(E) = \imath\hbar \boldsymbol{S}^{\dagger}_{E}(E)\, \boldsymbol{S}(E)\,, \tag{A1}$$

the subscript 'E' denotes hereafter the derivative with respect to the energy. The relation was derived by Smith within the frame of stationary scattering states and was later proved and generalized to N>2-body scattering within the formal, time-dependent theory[3–5]. More recent formal considerations of this relation appeared in connection with the theory of sojourn time operators[7]. Applications of the life-time matrix concern various branches and aspects of scattering physics, such as thermodynamics of interacting gases[8,9], resonances in atom-diatom reactive scattering[10–13], tunneling through reaction barriers[14], quasi-bound states of diatomic molecules[15,16], atom-diatom van der Waals complexes[17–19], resonances in electron-molecule scattering[20–22]. In the majority of these applications the basic formula, Eq. (A1), was exploited for numerical evaluation of the life-time matrix. The energy derivative of the $\boldsymbol{S}$ matrix was determined via numerical differentiation[16,17,21] or directly[19,23–27]. Formulas explicitly involving scattering functions within the interaction region were exploited in Refs. 15 and 19 in the context of one channel and multichannel scattering, respectively. In this summary, the formula of Ref. 19, called 'a useful formula for the matrix $\boldsymbol{Q}$', plays the central role.

First, a derivation of the formula is presented. Next, it is used in an analysis of the energy dependence of the matrix $\boldsymbol{Q}$ near an isolated resonance. Of particular concern are some weak effects in this dependence which modify the basic Lorentzian profiles. The practical implications of the analysis are described. The final part concerns numerical implementation of the approach. A formula for Tr $\mathbf{Q}_E$ is derived. A smooth-variable-discretization (SVD) version of the log-derivative method is presented for evaluation of first- and second-order free-free transition amplitudes which appear in the formulas for $\boldsymbol{Q}$ and Tr $\mathbf{Q}_E$.

Introductory information. A nonreactive scattering system is considered and a set of orthogonal coordinates is used: x denotes the scattering coordinate, strictly, the distance between colliding subsystems, (ranging from 0 to ∞), and y is a collection of 'internal' coordinates, describing bounded modes of motion in the system. The other relevant characteristics of the chosen (x, y) coordinates are: the xx-th component of the metric tensor equals 1 and the Jacobian assumes a factorized form, $J(x, y)$=$c(x)j(y)$.

The Hamiltonian H for the scattering system consists, of course, of a 'free' part, H_0, and of interaction potential, V, which vanishes when $x\to\infty$. It is assumed that the subsystems move practically freely, i.e., $V(x, y)\approx 0$, when $x\geq x_\infty$. The part of $H_0(x, y)$, having the form K_x=$-\frac{\hbar^2}{2\mu}\frac{1}{c(x)}\frac{\partial}{\partial x}c(x)\frac{\partial}{\partial x}$, where μ is the reduced mass of the subsystems, can be identified as the kinetic energy operator of x-motion; the remaining part, $H^{\rm int}(x, y)$, can be thus termed the internal Hamiltonian.

In multichannel scattering at a given energy E, there are $N_{\rm o}$>1 states of $H^{\rm int}$ which are accessible, i.e., open, as initial and final states. If ϵ_i denotes the energy of i-th state then the relation $E-\epsilon_i=(\hbar k_i)^2/2\mu>0$ holds for $i=1,\ldots,N_{\rm o}$, meaning that there is some energy available to translational (x-) motion of noninteracting subsystems. k_i is the wavenumber associated with this motion. The functions of the scattering states of H (of outgoing-wave type) which evolve from the $N_{\rm o}$ states of H_0 are collected in the vector $\underset{1\times N_{\rm o}}{\boldsymbol{\Psi}^{(+)}}(E; x, y)$.

For application of Green's theorem, the configuration space of the scattering system is divided with a surface $x=\bar{x}$ in two regions, termed the 'internal' ($x\leq\bar{x}$) and the 'external' ($x\geq\bar{x}$) region, respectively. The division is formally arbitrary but the choice $\bar{x}=x_\infty$ is preferred as being the most convenient practically. With this choice, the internal and external regions become the 'interaction' and the 'asymptotic' regions, respectively.

In both the internal and the external regions a close-coupling representation of the scattering

functions is adopted,

$$\mathbf{\Psi}^{(+)}(E;x,y) = \underset{1\times N}{\widetilde{\mathbf{\Phi}}}(y;x)\ \underset{N\times N_{\rm o}}{\boldsymbol{F}^{(+)}}(E;x)\,, \tag{A2}$$

using an orthogonal basis in the y-coordinates, strictly, $\widetilde{\mathbf{\Phi}}(y;x){:=}c^{-1/2}(x)\,\mathbf{\Phi}(y;x)$ and $\big[\mathbf{\Phi}|\mathbf{\Phi}\big]{=}\boldsymbol{I}$ with $\big[X|Y\big]{:=}\int dy\, j(y)\, X^\dagger Y$. The basis $\mathbf{\Phi}(y;x)$ may be modified along the scattering coordinate but it becomes diabatic, i.e., $\frac{\partial}{\partial x}\mathbf{\Phi}(y;x){\approx}0$, in the asymptotic region, where it should be built of eigenfunctions of $H^{\rm int}$. Columns of $\boldsymbol{F}^{(+)}(E;x)$ are, of course, solutions of the coupled equations

$$\big[E\boldsymbol{I}-\boldsymbol{H}(x)\big]\boldsymbol{F}(E;x)=0\,, \tag{A3}$$

in which the $N{\times}N$ matrix operator $E\boldsymbol{I}{-}\boldsymbol{H}(x){:=}c(x)\big[\widetilde{\mathbf{\Phi}}|(E{-}H)\widetilde{\mathbf{\Phi}}\big]$ takes the form

$$E\boldsymbol{I}-\boldsymbol{H}(x)=\tfrac{1}{2\mu}[-\boldsymbol{p}_x^2+\hbar^2\boldsymbol{w}(E,x)]\,, \tag{A4}$$

where

$$\boldsymbol{p}_x{=}{-}\imath\hbar\big[\boldsymbol{I}\tfrac{d}{dx}+\boldsymbol{\alpha}(x)\big]\qquad\text{with}\quad \boldsymbol{\alpha}(x){:=}\big[\mathbf{\Phi}|\tfrac{\partial}{\partial x}\mathbf{\Phi}\big] \tag{A5}$$

and $\boldsymbol{w}(E;x)$ is a real symmetric matrix,

$$\boldsymbol{w}(E;x)=\tfrac{2\mu}{\hbar^2}[E\boldsymbol{I}{-}\boldsymbol{\epsilon}(x)]{+}\big[\tfrac{\partial}{\partial x}\mathbf{\Phi}|\mathbf{\Phi}\big]\big[\mathbf{\Phi}|\tfrac{\partial}{\partial x}\mathbf{\Phi}\big]{-}\big[\tfrac{\partial}{\partial x}\mathbf{\Phi}|\tfrac{\partial}{\partial x}\mathbf{\Phi}\big]:=\boldsymbol{b}(E;x)+\boldsymbol{\Delta}(x)\,, \tag{A6}$$

becoming diagonal in the asymptotic region, where $\boldsymbol{\Delta}(x){=}0$, and constant at infinity, i.e., $\big[\boldsymbol{b}(E;x)\big]_{i,j}{=}\delta_{i,j}[E{-}\epsilon_i(x)]\underset{x\to\infty}{\longrightarrow}\delta_{i,j}k_i^2$ for $i{=}1,\ldots,N$. ($k_i^2{=}{-}|k_i|^2$ for $i{>}N_{\rm o}$).

The matrix $\boldsymbol{F}^{(+)}(E;x)$ vanishes at point x_0 chosen close to 0, i.e. deeply inside classically forbidden region. In the external region, it is explicitly related to the scattering matrix $\boldsymbol{S}$

$$\boldsymbol{F}^{(+)}(E;x)=\boldsymbol{O}^{-}(E;x)-\boldsymbol{O}^{+}(E;x)\,\boldsymbol{S}(E)\,; \tag{A7}$$

$\underset{N\times N_{\rm o}}{\boldsymbol{O}^{\pm}}(E;x)$ are solutions of Eq. (A3) which satisfy the conditions

$$\big[\boldsymbol{O}^{\pm}(x)\big]_{i,j}\underset{x\to\infty}{\longrightarrow}\delta_{i,j}v_i^{-1/2}\exp[\pm\imath(k_ix+\ldots)]\,, \tag{A8}$$

where the dots stand for x-independent phase factors and the factor $v_i^{-1/2}$ with $v_i{:=}\hbar k_i/\mu$ serves to assure the normalization of the solutions to the unit flux. Using the flux operator[28] through the surface $x{=}\bar{x}$, $C(\bar{x};x,y){=}\frac{\imath}{\hbar}[H(x,y),\,\Theta(x{-}\bar{x})]$, where $\Theta(x){=}1\,(0)$ for $x{\geq}\,(<)\,0$, and its representation in the basis $\widetilde{\mathbf{\Phi}}$, $\boldsymbol{C}(\bar{x};x){:=}c(x)\big[\widetilde{\mathbf{\Phi}}|C(\bar{x})\,\widetilde{\mathbf{\Phi}}\big]$,

$$\boldsymbol{C}(\bar{x};x)=\tfrac{1}{2\mu}\left[\delta(x{-}\bar{x})\boldsymbol{p}_x+\boldsymbol{p}_x\delta(x{-}\bar{x})\right], \tag{A9}$$

one can state the normalization properties of the matrices $\boldsymbol{O}^{\pm}(E;x)$ as

$$\big(\boldsymbol{O}^{\varepsilon}|\boldsymbol{C}(\bar{x})\boldsymbol{O}^{\varepsilon'}\big)=\delta_{\varepsilon,\varepsilon'}(\delta_{\varepsilon,+}-\delta_{\varepsilon,-})\boldsymbol{I}_{\rm o}\qquad\text{for any }\bar{x}\,, \tag{A10}$$

where $\big(X|Y\big){:=}\int dx\, X^\dagger Y$ and $\boldsymbol{I}_{\rm o}$ denotes $N_{\rm o}{\times}N_{\rm o}$ unit matrix.

The scattering states of in-going wave type, $\mathbf{\Psi}^{(-)}(E;x,y)$, are represented in the basis $\widetilde{\mathbf{\Phi}}$ by functions $\boldsymbol{F}^{(-)}(E;x)$ The equality $\boldsymbol{F}^{(-)}(E;x){=}\boldsymbol{F}^{(+)\,*}(E;x)$ may be assumed in view of time-reversal invariance of H. Also, $\boldsymbol{S}{=}\boldsymbol{S}^T$. Thus, the relation takes place

$$\mathbf{\Psi}^{(+)}=-\mathbf{\Psi}^{(-)}\boldsymbol{S}\,. \tag{A11}$$

It is consistent with the well-known relation of scattering theory between 'in' and 'out' stationary scattering states, presented usually in the 'energy normalization' (cf. Ref. 29, chap. 7.2.3), since the conversion is: $\mathbf{\Psi}^{(\pm)}{=}{\pm}\frac{\sqrt{2\pi\hbar}}{\imath}\mathbf{\Psi}^{(\pm)}_{\rm energy}$.

When describing the energy dependence of the scattering states, it is convenient to use the following matrix Green function, cf. Ref. 30,

$$\boldsymbol{G}^{(+)}(E,\bar{x};x,x') := \langle x|\,\boldsymbol{G}^{(+)}(E,\bar{x})\,|x'\rangle := \langle x|\,\big[P_{\,[x_0,\bar{x}]}(E\boldsymbol{I}-\boldsymbol{H}) - \boldsymbol{L}^{+}(E,\bar{x})\big]^{-1}|x'\rangle \qquad \text{(A12)}$$

which involves the Bloch operator[31]

$$\boldsymbol{L}^{+}(E,\bar{x};x) := \tfrac{\imath\hbar}{2\mu}\delta(x-\bar{x})[\boldsymbol{p}_x + \imath\hbar\boldsymbol{l}^{+}(E,\bar{x})] \qquad \text{(A13)}$$

with the boundary condition matrix $\boldsymbol{l}^{+}(E,\bar{x})$ giving

$$\big(\boldsymbol{\phi}|\mathbf{L}^{+}(\bar{x})\widetilde{\boldsymbol{O}}^{+}\big) = 0$$

for the $N\times N$ solution matrix $\widetilde{\boldsymbol{O}}^{+}(E;x)$:

$$\widetilde{\boldsymbol{O}}^{+}_{i\,j}(E;x)=\boldsymbol{O}^{+}_{i\,j}(E;x) \qquad \text{for} \quad j\leq N_{\rm o},$$

$$\widetilde{\boldsymbol{O}}^{+}_{i\,j}(E;x) \underset{x\to\infty}{\longrightarrow} \delta_{i,j}v_j^{-1/2}\exp(-|k_j|x) \quad \text{for} \quad j>N_{\rm o}\,,$$

and for arbitrary $N\times 1$ matrix $\boldsymbol{\phi}(x)$. $P_{\,[x_0,\bar{x}]}$ denotes the projector on the internal part of the x-coordinate, $P_{\,[x_0,\bar{x}]}=\Theta(\bar{x}-x)\Theta(x-x_0)$.

Using the operator $\boldsymbol{G}^{(+)}(E,\bar{x})$, one can write

$$\boldsymbol{F}^{(+)}(E;x) = -\boldsymbol{G}^{(+)}(E,\bar{x})\boldsymbol{L}^{+}(E,\bar{x})\boldsymbol{F}^{(+)}(E)\,(x) \qquad \text{for} \quad x\in[x_0,\,\bar{x}]\,.$$

Thus, one gets the following formulas for the energy derivatives in the internal region (all arguments are omitted for clarity)

$$\boldsymbol{G}^{(+)}_{E} \;=\; -\boldsymbol{G}^{(+)}(P_{\,[x_0,\bar{x}]}\boldsymbol{I} - \boldsymbol{L}^{+}_{E})\,\boldsymbol{G}^{(+)}\,, \qquad \text{(A14)}$$

$$\boldsymbol{F}^{(+)}_{E} \;=\; -\boldsymbol{G}^{(+)}(P_{\,[x_0,\bar{x}]}\boldsymbol{F}^{(+)} + \boldsymbol{L}^{+}\boldsymbol{F}^{(+)}_{E})\,. \qquad \text{(A15)}$$

The second terms in these formulas can explicitly be written as

$$\boldsymbol{G}^{(+)}\boldsymbol{L}^{+}_{E}\boldsymbol{G}^{(+}\,(x,x') = -\tfrac{1}{\hbar^2}\boldsymbol{F}^{(+)}(x)\boldsymbol{C}^{-\,+}\boldsymbol{F}^{(-)\,\dagger}(x')\,, \qquad \text{(A16)}$$

$$\boldsymbol{G}^{(+)}\boldsymbol{L}^{+}\boldsymbol{F}^{(+)}_{E}\,(x) = \tfrac{\imath}{\hbar}\boldsymbol{F}^{(+)}(x)(\boldsymbol{C}^{-\,-} - \boldsymbol{C}^{-\,+}\boldsymbol{S})\,, \qquad \text{(A17)}$$

where the $\boldsymbol{C}$'s stand for the following matrix elements of the flux operator

$$\boldsymbol{C}^{\varepsilon\,\varepsilon'}(E,\bar{x}) := \imath\hbar\big(\boldsymbol{O}^{\varepsilon}_{E}\,|\,\boldsymbol{C}(\bar{x})\,\boldsymbol{O}^{\varepsilon'}\big) \qquad \text{for} \quad \varepsilon,\,\varepsilon'=+,-\,. \qquad \text{(A18)}$$

Finally, the formula expressing the Green theorem should written

$$\langle\Psi_2|\big[P_{\,[x_0,\bar{x}]}\,,E-H\big]\Psi_1\rangle = \big(\boldsymbol{F}_2|\big[P_{\,[x_0,\bar{x}]}\,,E\boldsymbol{I}-\boldsymbol{H}\big]\,\boldsymbol{F}_1\big) = \imath\hbar\big(\boldsymbol{F}_2|\boldsymbol{C}(\bar{x})\,\boldsymbol{F}_1\big)\,; \qquad \text{(A19)}$$

Ψ_i for $i=1,2$ denote here any functions of the (x,y) coordinates which vanish at x_0 and are representable in the basis $\widetilde{\boldsymbol{\Phi}}(y;x)$, i.e., $\Psi_i(x,y)=\widetilde{\boldsymbol{\Phi}}(y;x)\boldsymbol{F}_i(x)$ and $\boldsymbol{F}_i(x_0)=0$. After dividing the flux operator in the following way,

$$\boldsymbol{C}(\bar{x};x)=\tfrac{1}{\imath\hbar}\big[\boldsymbol{L}^{+}(\bar{x};x)-\boldsymbol{L}^{-\,\dagger}(\bar{x};x)\big]\,,$$

where $\boldsymbol{L}^{-}$ is defined by Eq. (A13) with $\boldsymbol{l}^{-}:=\boldsymbol{l}^{+\,\dagger}$ standing in place of $\boldsymbol{l}^{+}$, the formula (A19) can be rearranged to show that the space restricted Green operator $\boldsymbol{G}^{(+)}(E,\bar{x})$, defined in Eq.

(A12), and its analogue $\boldsymbol{G}^{(-)}(E,\bar{x})$, involving the operator $\boldsymbol{L}^{-}$, satisfy the usual 'hermicity' relation

$$\boldsymbol{G}^{(+)}(E,\bar{x})=\boldsymbol{G}^{(-)\,\dagger}(E,\bar{x})\,.$$

The **useful formula for the matrix $\boldsymbol{Q}$** is obtained by applying the Green theorem to functions $\Psi_1{:=}\boldsymbol{\Psi}^{(+)}$ and $\Psi_2{:=}\boldsymbol{\Psi}^{(+)}_E$ in the interaction region ($\bar{x}{=}x_\infty$) and consists of two terms,

$$\boldsymbol{Q}(E) = \boldsymbol{A}(E,x_\infty) - \boldsymbol{B}(E,x_\infty)\,. \tag{A20}$$

In accordance with their origin, the terms may be called, respectively, the 'volume term',

$$\boldsymbol{A}(E,x_\infty) = \langle\boldsymbol{\Psi}^{(+)}(E)|P_{\,[x_0,x_\infty]}\,\boldsymbol{\Psi}^{(+)}(E)\rangle = (\boldsymbol{F}^{(+)}(E)|P_{\,[x_0,x_\infty]}\,\boldsymbol{F}^{(+)}(E))\,, \tag{A21}$$

and the 'surface term',

$$\boldsymbol{B}(E,x_\infty) = \mathcal{S}^{\dagger}(E)\;\mathcal{C}(E,x_\infty)\;\mathcal{S}(E)\,, \tag{A22}$$

where $\mathcal{S}^{\dagger}{:=}(\boldsymbol{I}_{\rm o},\,-\boldsymbol{S}^{\dagger})$ and $\mathcal{C}{:=}\begin{pmatrix}\boldsymbol{C}^{--} & \boldsymbol{C}^{-+}\\ \boldsymbol{C}^{+-} & \boldsymbol{C}^{++}\end{pmatrix}$ is a hermitian matrix built of the matrices $\boldsymbol{C}^{\varepsilon\,\varepsilon'}(E,x_\infty)$, cf. Eq. (A18), which are diagonal and

$$\boldsymbol{C}^{--}{=}\boldsymbol{C}^{--\,*}{=}\boldsymbol{C}^{++}\,,$$

as it can be deduced from Eqs. (A8) and (A10). The two terms of the formula reflect Smith's definition of collision-time delay[2]. The matrix $\boldsymbol{A}$, strictly its trace, has the meaning of an average sojourn time of the scattering system within the interaction region[7] confined by the surface $x{=}x_\infty$. Therefore, the name 'soujourn-time matrix' is alternatively assigned to $\boldsymbol{A}$. The matrix $\boldsymbol{B}$ does not have such a strict interpretation. It acquires, however, the meaning of the time of free passage of the system through the confined region when the size of the region grows ad infinitum ($x_\infty{\longrightarrow}\infty$) and all oscillatory terms are removed (by an appropriate averaging, cf. Refs. 2,3).

Resonance decomposition of the matrix $\boldsymbol{Q}$. It what follows an analysis of energy dependence of the matrix $\boldsymbol{Q}$ in vicinity of an isolated resonance is presented. Use is made of the well-known results of the Feshbach resonance theory[32]. Two kinds of partitioning of the scattering states are essential in the theory. The first is the partitioning into mutually orthogonal open and closed channel parts,

$$|\boldsymbol{\Psi}^{(+)}\rangle{=}(P_{\rm o}{+}P_{\rm c})\,|\boldsymbol{\Psi}^{(+)}\rangle{=}|\boldsymbol{\Psi}^{(+)}_{\rm o}\rangle{+}|\boldsymbol{\Psi}^{(+)}_{\rm c}\rangle\,. \tag{A23}$$

Such partitioning is easily realized in the close-coupling approximation to the states using the asymptotic (diabatic) basis ${}_{\rm d}\boldsymbol{\Phi}{=}\boldsymbol{\Phi}(y)$. At a given energy E, each basis functions is easily ascribable to either open or closed scattering channel, i.e. $\underset{1\times N}{{}_{\rm d}\boldsymbol{\Phi}} = \big(\underset{1\times N_{\rm o}}{{}_{\rm d}\boldsymbol{\Phi}_{\rm o}}\;\underset{1\times N_{\rm c}}{{}_{\rm d}\boldsymbol{\Phi}_{\rm c}}\big)$. Thus, the projectors $P_{\rm o}$ and $P_{\rm c}$ are represented by the matrices

$${}_{\rm d}\boldsymbol{P}_{\rm o}{=}\begin{pmatrix}\boldsymbol{I}_{\rm o} & 0\\ 0 & 0\end{pmatrix}\;\text{ and }\;{}_{\rm d}\boldsymbol{P}_{\rm c}{=}\begin{pmatrix}0 & 0\\ 0 & \boldsymbol{I}_{\rm c}\end{pmatrix},\text{ respectively.}$$

The non-diabatic basis $\boldsymbol{\Phi}(y;x)$ is related at each x to the basis ${}_{\rm d}\boldsymbol{\Phi}$ through an orthogonal matrix $\boldsymbol{\Upsilon}(x)$ (see Sec. IIC). In this basis, the representation of the projectors P_a for $a{=}{\rm o},{\rm c}$ takes the form of the non-diagonal matrices $\boldsymbol{P}_a(x){=}\boldsymbol{\Upsilon}^T(x)\,{}_{\rm d}\boldsymbol{P}_a\,\boldsymbol{\Upsilon}(x)$. The respective parts of the functions $\boldsymbol{F}^{(+)}(x)$ are $\boldsymbol{F}^{(+)}_a(x){=}\boldsymbol{P}_a(x)\,\boldsymbol{F}^{(+)}(x)$.

The consequence of the partitioning (A23) for the matrix $\boldsymbol{A}$ is

$$\boldsymbol{A}(E,x_\infty) = \boldsymbol{A}_{\rm o}(E,x_\infty) + \boldsymbol{A}_{\rm c}(E)\,. \tag{A24}$$

The L^2 character of closed channel components of the scattering functions is reflected here by the fact that the matrix $\boldsymbol{A}_{\rm c}$ does not depend on x_∞. Thus, when exploiting the 'useful formula', Eq. (A20), one gets readily the matrix $\boldsymbol{Q}$ decomposed into open and closed channel parts

$$\boldsymbol{Q}(E) = \boldsymbol{Q}_{\rm o}(E) + \boldsymbol{A}_{\rm c}(E) \qquad \text{with} \qquad \boldsymbol{Q}_{\rm o}(E) := \boldsymbol{A}_{\rm o}(E, x_\infty) - \boldsymbol{B}(E, x_\infty)\,. \tag{A25}$$

The decomposition may be expected to be advantageous in the analysis of resonances which arise from bound states in the closed channel subspace, i.e., of the Feshbach-type resonances. At this point one may note that diagonal elements of the matrix $\boldsymbol{A}_{\rm c}$ are the quantities which are analyzed in the amplitude method for multichannel resonances proposed by Dalgarno and co-workers[33].

The second partitioning of the scattering states is into parts which vary rapidly ('r') and slowly ('d') with the energy in the vicinity of a bound state in the closed channel subspace,

$$|\boldsymbol{\Psi}_a^{(+)}\rangle = |\boldsymbol{\Psi}_a^{(+)}\rangle^{\rm d} + |\boldsymbol{\Psi}_a^{(+)}\rangle^{\rm r} \qquad \text{for } a{=}{\rm o}, {\rm c}\,. \tag{A26}$$

The arising four parts of the scattering states, $|\boldsymbol{\Psi}_a^{(+)}(E)\rangle^\alpha$ for a=o, c and α=r, d, are determined by the following equations:

$$|\boldsymbol{\Psi}_{\rm c}^{(+)}(E)\rangle^{\rm r} = |\Psi_s^{(B)}\rangle\, \mathbf{a}_s^{(+)}(E)\,, \qquad\qquad (E_s^{(B)} - H_{cc})\,|\Psi_s^{(B)}\rangle = 0\,,$$

$$|\boldsymbol{\Psi}_{\rm c}^{(+)}(E)\rangle^{\rm d} = \widetilde{G}_{\rm c}(E)\, H_{\rm co}\, |\boldsymbol{\Psi}_{\rm o}^{(+)}(E)\rangle \quad \text{with } \widetilde{G}_{\rm c}(E) := \sum_{n\neq s} \frac{|\Psi_n^{(B)}\rangle\langle\Psi_n^{(B)}|}{E - E_n^{(B)}}\,,$$

$$|\boldsymbol{\Psi}_{\rm o}^{(+)}(E)\rangle^{\rm r} = \widetilde{G}_{\rm o}^{(+)}(E)\, H_{\rm oc}\, |\boldsymbol{\Psi}_{\rm c}^{(+)}(E)\rangle^{\rm r} \text{ with } \widetilde{G}_{\rm o}^{(+)}(E) := \frac{1}{E^{(+)} - \widetilde{H}_{\rm o}(E)}\,,$$

$$\left(E^+ - \widetilde{H}_{\rm o}(E)\right) |\boldsymbol{\Psi}_{\rm o}^{(+)}\rangle^{\rm d} = 0\,,$$

where $\qquad H_{a\,a'} := P_a H P_{a'} \qquad$ for a, a'=o, c,

$$\widetilde{H}_{\rm o}(E) := H_{\rm oo} + V^{\rm opt}(E)\,,$$

$$V^{\rm opt}(E) := H_{\rm oc}\, \widetilde{G}_{\rm c}(E)\, H_{\rm co}\,.$$

and the vector of amplitudes of the largest, i.e., the closed channel resonance part is

$$\mathbf{a}_s^{(+)}(E) = -\imath \frac{\sqrt{\hbar}\boldsymbol{\gamma}(E)}{E - E^{\rm r}(E) + \frac{\imath}{2}\Gamma(E)}\,,$$

where $\quad E^{\rm r} = E_s^{(B)} + E^{\rm shft} \quad$ with $\quad E^{\rm shft} = {\rm Re}\langle\Psi_s^{(B)}|H_{\rm co}\, \widetilde{G}_{\rm o}^{(+)}(E)\, H_{\rm oc}|\,\Psi^{(B)}\rangle\,,$

$$\Gamma(E) = \boldsymbol{\gamma}(E)\,\boldsymbol{\gamma}^\dagger(E) \quad \text{and} \qquad \boldsymbol{\gamma}(E) = \tfrac{\imath}{\sqrt{\hbar}}\langle\Psi_s^{(B)}|\, H_{\rm co}\, |\boldsymbol{\Psi}_{\rm o}^{(+)}(E)\rangle^{\rm d}\,.$$

Obviously, this way of the 'r-d' partitioning is valid for energies E close to the bound state energy $E_s^{(B)}$ provided it is well separated from $E_{n\neq s}^{(B)}$. The well-known result of the theory is the decomposition of the matrix $\boldsymbol{S}$ into contributions of direct and resonance scattering

$$\boldsymbol{S}(E) = \boldsymbol{S}^{\rm d}(E) + \boldsymbol{S}^{\rm r}(E) \qquad \text{with} \qquad \boldsymbol{S}^{\rm r}(E) = -\imath \frac{\boldsymbol{\gamma}^{\rm T}(E)\,\boldsymbol{\gamma}(E)}{E - E^{\rm r}(E) + \frac{\imath}{2}\Gamma(E)} \tag{A27}$$

and $\boldsymbol{S}^{\rm d}$ being the $\boldsymbol{S}$-matrix which determines the asymptotic behavior of the functions $\langle x, y|\boldsymbol{\Psi}_{\rm o}^{(+)}(E)\rangle^{\rm d}$. The quantities $\boldsymbol{S}^{\rm d}$, $\boldsymbol{\gamma}$, and $E^{\rm r}$ are, of course, the components of the formula which vary slowly with the energy. When this variation is neglected, the approximate

formula for the matrix $\boldsymbol{S}$ is obtained on which several of the widely-used procedures[17,34] for detection and parametrization of resonances are based.

Advantages of exploiting the collision-time delay matrix for the determination of resonance characteristics have been noted by several authors, e.g. in Ref. 21. Approximate resonance formula for $\boldsymbol{Q}$, of Breit-Wigner type, has been derived in Ref. 17 from the approximate formula for $\boldsymbol{S}$ by resorting to so-called 'special orthogonality properties'.

In this text, formally exact isolated resonance decomposition of the collision-time delay matrix will be described. Providing an insight into the origin and structure of slowly varying components, it is instructive in devising some corrections to the Breit-Wigner type formula for $\boldsymbol{Q}$.

The *exact* decomposition of the collision-time delay matrix resulting from the Feshbach theory reads

$$\boldsymbol{Q}(E) = \boldsymbol{Q}^{\mathrm{d}}(E) + \boldsymbol{Q}^{\mathrm{r}}(E) + \boldsymbol{q}(E) \tag{A28}$$

where

$$\boldsymbol{Q}^{\mathrm{d}} \;=\; \imath\hbar\big(\boldsymbol{S}^{\mathrm{d}}_E\big)^{\dagger}\boldsymbol{S}^{\mathrm{d}}\,, \qquad \boldsymbol{Q}^{\mathrm{r}} = \big(\mathbf{a}_s^{(+)}\big)^{\dagger}\mathbf{a}_s^{(+)}\,, \tag{A29}$$

$$\boldsymbol{q} \;=\; \boldsymbol{q}^{\mathrm{r\,r}} + \boldsymbol{q}^{\mathrm{r\,d}} + \boldsymbol{q}^{\mathrm{d\,r}}\,, \tag{A30}$$

with

$$\boldsymbol{q}^{\mathrm{r\,r}} \;=\; -\boldsymbol{Q}^{\mathrm{r}}\big[E_E^{\mathrm{shft}} + \tfrac{\imath}{2}(\boldsymbol{\gamma}^*\boldsymbol{\gamma}_E^T - \boldsymbol{\gamma}_E^*\boldsymbol{\gamma}^T)\big]\,, \tag{A31}$$

$$\boldsymbol{q}^{\mathrm{r\,d}} \;=\; \big(\boldsymbol{q}^{\mathrm{d\,r}}\big)^{\dagger} = -\frac{\hbar\boldsymbol{\gamma}^{\dagger}\boldsymbol{\gamma}_E^*}{E - E^{\mathrm{r}} - \frac{\imath}{2}\Gamma}\,\boldsymbol{S}^{\mathrm{d}}\,. \tag{A32}$$

This decomposition can be derived starting either from Eq. (A1) or from Eq. (A20). In the former case, an expression for $\boldsymbol{S}_E$ is derived first, by differentiation of Eqs. (A27) and by making use of the relation

$$\boldsymbol{\gamma}^{\dagger}{=}\boldsymbol{S}^{\mathrm{d}\,\dagger}\boldsymbol{\gamma}^T \tag{A33}$$

which is the 'special orthogonality relation' of Ref. 17; actually it stems from Eq. (A11). In the latter case, the derivation refers directly to the equations defining the $|\boldsymbol{\Psi}_a^{(+)}\rangle^{\alpha}$-parts of the states, and to the equations satisfied by the energy derivatives of the open channel parts, $|\boldsymbol{\Psi}_{o,E}^{(+)}\rangle^{\alpha}$ for α=r, d. These equations are exploited together with the Green theorem, Eq. (A19), for converting the matrices $\boldsymbol{A}_{\mathrm{o}}^{\alpha\,\beta}{:=}{}^{\alpha}\langle\boldsymbol{\Psi}_o^{(+)}|P_{\,[x_0,x_\infty]}\,|\boldsymbol{\Psi}_o^{(+)}\rangle^{\beta}$ into expressions which involve $\boldsymbol{S}^{\alpha}$ and $\boldsymbol{S}^{\beta}$- parts of $\boldsymbol{S}$. In the course of the derivation, the following formula for the matrix $\boldsymbol{Q}^{\mathrm{d}}$ — analogue of Eq. (A20) for $\boldsymbol{Q}$ — is obtained

$$\boldsymbol{Q}^{\mathrm{d}} = \boldsymbol{A}_{\mathrm{o}}^{\mathrm{d\,d}} - \boldsymbol{B}^{\mathrm{d\,d}} - \boldsymbol{a}^{\mathrm{d\,d}}\,, \tag{A34}$$

where $\boldsymbol{a}^{\mathrm{d\,d}}{:=}{}^{\mathrm{d}}\langle\boldsymbol{\Psi}_{\mathrm{o}}^{(+)}|\,V_E^{\mathrm{opt}}\,|\boldsymbol{\Psi}_{\mathrm{o}}^{(+)}\rangle^{\mathrm{d}}$ and $\boldsymbol{B}^{\mathrm{d\,d}}{:=}\,\mathcal{S}^{\mathrm{d}\,\dagger}\,\mathcal{C}\,\mathcal{S}^{\mathrm{d}}$ with $\mathcal{S}^{\mathrm{d}\,\dagger}{:=}\big(\boldsymbol{I}_{\mathrm{o}}\,,\,-\boldsymbol{S}^{\mathrm{d}\,\dagger}\big)$.

The full outcome of the derivation, summarized in Schemes I and II, is the detailed resolution of the open and closed-channel parts of the matrix $\boldsymbol{Q}$ into resonance, direct, and direct-resonance interference terms.

Scheme 1.

Analysis of energy dependence of collision time delay matrix, $\boldsymbol{Q}=\boldsymbol{A}-\boldsymbol{B}$, near Feshbach resonance. Decomposition of **o**pen and **c**losed channel parts into **d**irect, **r**esonance, and **d**-**r** interference contributions.

$$
\begin{array}{lcccccccccc}
\boldsymbol{Q}^{\mathrm{d}} & := & \widetilde{\boldsymbol{A}}^{\mathrm{d}} & - & \boldsymbol{B}^{\mathrm{d\,d}\ a)} & = & \boldsymbol{Q}^{\mathrm{d}} & & + & \boldsymbol{a}^{\mathrm{d\,d}} & - & \boldsymbol{a}^{\mathrm{d\,d}} \\
\widetilde{\boldsymbol{Q}}^{\mathrm{r}} & := & \widetilde{\boldsymbol{A}}^{\mathrm{r}} & - & \boldsymbol{B}^{\mathrm{r\,r}} & = & & \boldsymbol{q}^{\mathrm{r\,r}} & + & \boldsymbol{a}^{\mathrm{r\,r}} + \boldsymbol{Q}^{\mathrm{r}} & - & \boldsymbol{a}^{\mathrm{r\,r}} \\
\widetilde{\boldsymbol{Q}}^{\mathrm{d-r}} & := & \widetilde{\boldsymbol{A}}^{\mathrm{d-r}} & - & (\boldsymbol{B}^{\mathrm{d\,r}}+\boldsymbol{B}^{\mathrm{r\,d}}) & = & & \boldsymbol{q}^{\mathrm{d\,r}}+\boldsymbol{q}^{\mathrm{r\,d}} & + & \boldsymbol{a}^{\mathrm{d\,r}}+\boldsymbol{a}^{\mathrm{r\,d}} & - & (\boldsymbol{a}^{\mathrm{d\,r}}+\boldsymbol{a}^{\mathrm{r\,d}}) \\
\hline
\boldsymbol{Q} & = & \boldsymbol{A} & - & \boldsymbol{B} & = & \boldsymbol{Q}^{\mathrm{d}} & + \boldsymbol{q} & + & \boldsymbol{a} + \boldsymbol{Q}^{\mathrm{r}} & - & \boldsymbol{a} \\
\hline
 & & & & \boldsymbol{Q} & = & & \boldsymbol{Q}_{\mathrm{o}} & & + & \boldsymbol{A}_{\mathrm{c}} &
\end{array}
$$

a) $\boldsymbol{B}^{\alpha\,\beta}:=\mathcal{S}^{\alpha\,\dagger}\,\mathcal{C}\,\mathcal{S}^{\beta}$ for $\alpha,\,\beta$=d, r; $\mathcal{S}^{\mathrm{d}\,\dagger}:=(\boldsymbol{I},\,-\boldsymbol{S}^{\mathrm{d}\,\dagger})$; $\mathcal{S}^{\mathrm{r}\,\dagger}:=(0\boldsymbol{I},\,-\boldsymbol{S}^{\mathrm{r}\,\dagger})$; see Eq. (A22)

Scheme 2.

Analysis of energy dependence of the sojourn time matrix $\boldsymbol{A}$ near Feshbach resonance. Decomposition of **o**pen and **c**losed channel parts into **d**irect, **r**esonance, and **d**-**r** interference contributions.

$$
\begin{array}{lcccccc}
\widetilde{\boldsymbol{A}}^{\mathrm{d}} & := & \boldsymbol{A}_{\mathrm{o}}^{\mathrm{d\,d}\ a)} & + & \boxed{}^{\,b)} & \longrightarrow & (-\boldsymbol{a}^{\mathrm{d\,d}}) \\
\widetilde{\boldsymbol{A}}^{\mathrm{r}} & := & \boldsymbol{A}_{\mathrm{o}}^{\mathrm{r\,r}} & + & \boldsymbol{A}_{\mathrm{c}}^{\mathrm{r\,r}\ c)} & + & (-\boldsymbol{a}^{\mathrm{r\,r}}) \\
\widetilde{\boldsymbol{A}}^{\mathrm{d-r}} & := & \boldsymbol{A}_{\mathrm{o}}^{\mathrm{d\,r}}+\boldsymbol{A}_{\mathrm{o}}^{\mathrm{r\,d}} & + & {}^{d)} & + & (-\boldsymbol{a}^{\mathrm{d\,r}}-\boldsymbol{a}^{\mathrm{r\,d}}) \\
\hline
\boldsymbol{A} & = & \boldsymbol{A}_{\mathrm{o}} & + & \boldsymbol{A}_{\mathrm{c}} & &
\end{array}
$$

a) $\boldsymbol{A}_{a}^{\alpha\,\beta}:={}^{\alpha}\langle\boldsymbol{\Psi}_{a}^{(+)}|P_{\,[0,R_\infty]}\,\boldsymbol{\Psi}_{a}^{(+)}\rangle^{\beta}$ for a=o, c and α,β=d, r

b) $\boldsymbol{A}_{\mathrm{c}}^{\mathrm{d\,d}}=-\sum_{\alpha,\beta}\boldsymbol{a}^{\alpha\,\beta}:=-\sum_{\alpha\,\beta}{}^{\alpha}\langle\boldsymbol{\Psi}_{\mathrm{o}}^{(+)}|V_{E}^{\mathrm{opt}}\boldsymbol{\Psi}_{\mathrm{o}}^{(+)}\rangle^{\beta}$ see Eq. (A35)

c) $\boldsymbol{A}_{\mathrm{c}}^{\mathrm{r\,r}}=\boldsymbol{Q}^{\mathrm{r}}$, see Scheme 1; *d)* $\boldsymbol{A}_{\mathrm{c}}^{\mathrm{d\,r}}=\boldsymbol{A}_{\mathrm{c}}^{\mathrm{r\,d}\,\dagger}=0\boldsymbol{I}$

The resolution of the closed-channel part of $\boldsymbol{Q}$ is

$$\boldsymbol{A}_{\rm c}(E) = \boldsymbol{Q}^{\rm r}(E) - \boldsymbol{a}(E)\,, \tag{A35}$$

where

$$\boldsymbol{a} := \langle \boldsymbol{\Psi}_{\rm o}^{(+)}|\, V_E^{\rm opt}\, |\boldsymbol{\Psi}_{\rm o}^{(+)}\rangle = -{}^{\rm d}\langle \boldsymbol{\Psi}_{\rm c}^{(+)}\, |\boldsymbol{\Psi}_{\rm c}^{(+)}\rangle^{\rm d}\,.$$

It is not surprising that the resonance term $\boldsymbol{Q}^{\rm r}$ appears in this part. Some comments are necessary, however, on the other terms that appear in $\boldsymbol{A}_{\rm c}$ and in $\boldsymbol{Q}$.

The term $\boldsymbol{a}$ is shown to arise solely from distant resonances, i.e., from $n{\neq}s$ bound states in the closed channel subspace. They contribute indirectly, via coupling to the open channel subspace, since there is no d-r interference within the closed channel subspace, ${}^{\rm d}\langle \boldsymbol{\Psi}_{\rm c}^{(+)}|\, \boldsymbol{\Psi}_{\rm c}^{(+)}\rangle^{\rm r}{=}0$. The counterpart of $\boldsymbol{a}$ in the entire matrix $\boldsymbol{Q}$, i.e. the sum $\boldsymbol{Q}^{\rm d}{+}\boldsymbol{q}$, encompasses a combination of effects. $\boldsymbol{Q}^{\rm d}$ is a contribution of direct scattering governed by the effective Hamiltonian within the open channel subspace which accounts for the presence of the distant resonances in the closed channel subspace. The term $\boldsymbol{q}$, arises due to d-r and r-r interference within the open channel subspace.

Relative strength of the corresponding terms in the matrices $\boldsymbol{Q}(E)$ and $\boldsymbol{A}_{\rm c}(E)$ can be estimated by inspection of the formulas for traces of these matrices. The formula for ${\rm Tr}\,\boldsymbol{Q}(E)$ reads

$${\rm Tr}\,\boldsymbol{Q}(E) := \mathcal{T}(E) = {\rm Tr}\,\boldsymbol{Q}^{\rm d} + \frac{\hbar\Gamma(1{+}g) + 2e(E{-}E^{\rm r})}{(E{-}E^{\rm r})^2 + (\Gamma/2)^2}\,, \tag{A36}$$

where

$$g = {\rm Re}\langle \Psi_s^{(B)}|\, H_{\rm c\,o}\, \widetilde{G}_{\rm o}^{(+)} P_{\,[x_0,x_\infty]}\, \widetilde{G}_{\rm o}^{(+)} H_{\rm o\,c}\, |\Psi_s^{(B)}\rangle + g_c \\ -\frac{1}{4\hbar}\boldsymbol{\gamma}\big(\widetilde{\boldsymbol{Q}}^{\rm d} + \widetilde{\mathcal{S}}^{\rm d\,\dagger}\,\mathcal{C}\,\widetilde{\mathcal{S}}^{\rm d}\big)\boldsymbol{\gamma}^\dagger\,,$$

$$e = {\rm Re}\langle \Psi_s^{(B)}|\, H_{\rm c\,o}\, \widetilde{G}_{\rm o}^{(+)} P_{\,[x_0,x_\infty]}\, |\boldsymbol{\Psi}_{\rm o}^{(+)}\rangle^{\rm d\,d}\langle \boldsymbol{\Psi}_{\rm o}^{(+)}\, |H_{\rm o\,c}\, |\Psi_s^{(B)}\rangle + e_c \\ -\tfrac{\imath}{2}\boldsymbol{\gamma}\big(\boldsymbol{C}^{-+}\boldsymbol{S}^{\rm d} - \boldsymbol{S}^{\rm d\,\dagger}\boldsymbol{C}^{+-}\big)\boldsymbol{\gamma}^\dagger\,,$$

where $\widetilde{\boldsymbol{Q}}^{\rm d}{:=}\boldsymbol{Q}^{\rm d}{+}\boldsymbol{a}^{\rm d\,d}$, $\widetilde{\mathcal{S}}^{\rm d\,\dagger}{:=}(\boldsymbol{I}_{\rm o},\, \boldsymbol{S}^{\rm d\,\dagger})$, and the symbols g_c and e_c denote the following expressions

$$g_{\rm c} \;=\; -{\rm Re}\langle \Psi_s^{(B)}|\, H_{\rm c\,o}\, \widetilde{G}_{\rm o}^{(+)} V_E^{\rm opt}\, \widetilde{G}_{\rm o}^{(+)} H_{\rm o\,c}\, |\Psi_s^{(B)}\rangle + \tfrac{1}{4\hbar}\boldsymbol{\gamma}\boldsymbol{a}^{\rm d\,d}\boldsymbol{\gamma}^\dagger\,, \tag{A37}$$

$$e_{\rm c} \;=\; -{\rm Re}\langle \Psi_s^{(B)}|\, H_{\rm c\,o}\, \widetilde{G}_{\rm o}^{(+)} V_E^{\rm opt}\, |\boldsymbol{\Psi}_{\rm o}^{(+)}\rangle^{\rm d\,d}\langle \boldsymbol{\Psi}_{\rm o}^{(+)}\, |H_{\rm o\,c}\, |\Psi_s^{(B)}\rangle\,. \tag{A38}$$

The formula for ${\rm Tr}\,\boldsymbol{A}_{\rm c}(E)$ has an analogous structure

$${\rm Tr}\,\boldsymbol{A}_{\rm c}(E) := \mathcal{T}_{\rm c}(E) = -{\rm Tr}\,\boldsymbol{a}^{\rm d\,d} + \frac{\hbar\Gamma(1{+}g_{\rm c}) + 2e_{\rm c}(E{-}E^{\rm r})}{(E{-}E^{\rm r})^2 + (\Gamma/2)^2}\,. \tag{A39}$$

[In the derivation of the above formulas, use has been made of Eqs. (A14)–(A17). Obviously, when referring to the Hamiltonian $\widetilde{H}_{\rm o}$, the equations (A14)-(A15) should involve the term $P_{\,[x_0,\bar{x}]}(\boldsymbol{I}{-}\boldsymbol{V}_E^{\rm opt})$ in place of the term $P_{\,[x_0,\bar{x}]}\boldsymbol{I}$].

In both formulas, (A36) and (A39), the quantities weakly dependent on the energy are written without the argument E. From now on they are called 'parameters'. Besides the basic resonance parameters, the energy $E^{\rm r}$ and the width Γ, there are the profile parameters: the resonance profile parameters, e and g (or $e_{\rm c}$ and $g_{\rm c}$), and the background profile parameter, ${\rm Tr}\,\boldsymbol{Q}^{\rm d}$ (or $-{\rm Tr}\,\boldsymbol{a}^{\rm d\,d}$).

Since none of the resonance profile parameters would appear in the approximation of narrow and isolated resonance [$\mathcal{T}_{\rm c}(E)$ is then a perfect Breit-Wigner profile, without any background]

the strength of these parameters, in particular, of the asymmetry parameters, e or $e_{\rm c}$, is an indication of departure from this approximation. The departure is definitely larger in the $\mathcal{T}(E)$ profile than in the $\mathcal{T}_{\rm c}(E)$ profile. This becomes evident when one compares the order of dependence of the parameters on the o-c coupling, $H_{\rm oc}{=}H_{\rm co}^{\dagger}$ [the coupling should be small, of course]. There are four o-c couplings involved in the formulas for $e_{\rm c}$ and $g_{\rm c}$ whereas only two $H_{\rm oc}$'s are involved in the additional terms of the formulas for e and g. On the basis of this observation one may conjuncture that more accurate values of the resonance energy and width can be extracted from the calculated $\mathcal{T}_{\rm c}(E)$ profile than from the $\mathcal{T}(E)$ profile. The conjuncture is further supported by the fact that the parameters g and $g_{\rm c}$ are rather hard to separate from Γ in practice.

The above analysis shows that the best way of exploitation of the collision-time delay matrix for the determination of energies and widths of isolated resonances of (predominantly) Feshbach-type is the following: to calculate the $\boldsymbol{A}_{\rm c}$-part of the matrix $\boldsymbol{Q}$ and to adopt the parametrization of the profile $\mathcal{T}_{\rm c}(E)$ indicated by Eq. (A39) (except the parameter $g_{\rm c}$ should better be omitted.)

Since $\Gamma{=}\sum_{i=1}^{N_{\rm o}}\Gamma_i$, where Γ_i denotes a partial width, the following formula applied to individual diagonal elements of $\boldsymbol{A}_c(E)$,

$$\big[\boldsymbol{A}_{\rm c}(E)\big]_{i,\,i} \approx c_i + \frac{\hbar\Gamma_i + e_i(E-E^{\rm r})}{(E-E^{\rm r})^2+(\Gamma/2)^2}\,. \tag{A40}$$

gives a way of determination of the partial widths.

Obviously, in cases of multichannel resonances resulting (exclusively or predominantly) from a tunneling mechanism, the decomposition into open and closed channel parts may not be useful and then the entire matrix $\boldsymbol{Q}$ should be analyzed. However, valid and recommendable remains the way of proceeding described above for $\boldsymbol{A}_{\rm c}$, i.e., the parametrization of the profile $\mathcal{T}(E)$ and of the diagonal elements of $\boldsymbol{Q}(E)$.

A comment on **numerical implementation of the collision time delay approach** to determination of resonances. It is certainly advantageous not to have to differentiate numerically the functions which vary rapidly. Such an advantage in evaluation of the matrix $\boldsymbol{Q}(E)$ at energies in resonance regions is offered by the 'useful formula', Eq. (A20). The energy derivatives appear explicitly only in the 'surface term' $\boldsymbol{B}$ of this formula. These derivatives can be done analytically, however, (by exploiting the properties of the Riccati-Hankel functions of which the matrices $\boldsymbol{O}^{\pm}(x_\infty)$ are built). While looking for resonance profiles in the function $\mathcal{T}_{\rm c}(E)$ or $\mathcal{T}(E)$, cf. Eqs. (A36) and (A39), it is advantageous when also derivatives of these functions can be determined in a way not requiring numerical differentiation. To this end the following formula, derived from Eqs. (A15) and (A17), can be used

$$\tfrac{d}{dE}\mathcal{T}_{\rm c}(E) = -2\,{\rm Re}\,{\rm Tr}\left(\boldsymbol{F}^{(+)}|\boldsymbol{P}_{\rm c}P_{\,[x_0,x_\infty]}\boldsymbol{G}^{(+)}P_{\,[x_0,x_\infty]}\boldsymbol{P}_{\rm c}\boldsymbol{F}^{(+)}\right) - \tfrac{2}{\hbar}\,{\rm Im}\,{\rm Tr}\,\boldsymbol{A}_{\rm c}\boldsymbol{C}^{-+}\boldsymbol{S}\,. \tag{A41}$$

When the projectors $\boldsymbol{P}_{\rm c}$ are removed and $\boldsymbol{A}_{\rm c}$ is replaced with $\boldsymbol{A}$, the formula gives ${\rm Tr}\,\boldsymbol{A}_E(E,x_\infty)$. For evaluation of $\mathcal{T}_E(E)$,

$$\mathcal{T}_E(E) = {\rm Tr}\,\boldsymbol{A}_E(E,x_\infty) - {\rm Tr}\,\boldsymbol{B}_E(E,x_\infty)\,, \tag{A42}$$

the respective expression for the surface term is also needed. It reads

$${\rm Tr}\,\boldsymbol{B}_E = -2\,{\rm Re}\,{\rm Tr}\,(\boldsymbol{C}_E^{++}-\boldsymbol{C}_E^{-+}\boldsymbol{S}) - \tfrac{2}{\hbar}\,{\rm Im}\,{\rm Tr}\,\boldsymbol{Q}\boldsymbol{C}^{-+}\boldsymbol{S}\,. \tag{A43}$$

Again, the energy derivatives involved in this expression can be done analytically.

The second-order free-free transition amplitudes

$$\left(\boldsymbol{F}^{(+)}|P_{\,[x_0,x_\infty]}\boldsymbol{\kappa}\,\boldsymbol{G}^{(+)}P_{\,[x_0,x_\infty]}\boldsymbol{\kappa}\boldsymbol{F}^{(+)}\right) := \boldsymbol{A}^{(2)}(x_\infty)\,, \tag{A44}$$

with $\boldsymbol{\kappa}$ standing here for $\boldsymbol{P}_{\rm c}$ or $\boldsymbol{I}$, can be evaluated with the help of the L- matrix (generalized log-derivative) propagation method.

The matrix Green function used in the L-matrix formulation of the transition amplitudes[35],

$$\boldsymbol{G}^0(E,\bar{x};x,x') := \langle x|\left[\tfrac{2\mu}{\hbar^2}\,P_{\,[x_0,\bar{x}]}(E\boldsymbol{I}-\boldsymbol{H}) - \boldsymbol{L}^0(\bar{x})\right]^{-1}|x'\rangle\,, \tag{A45}$$

involves a different Bloch operator than the function $\boldsymbol{G}^{(+)}(E,\bar{x};x,x')$, cf. Eq. (A13), namely,

$$\boldsymbol{L}^0(\bar{x},x) = -\left(\tfrac{\imath}{\hbar}\boldsymbol{p}_x\right)^\dagger\delta(x-\bar{x})\,.$$

The relation between the two Green functions is (cf. Ref. 36)

$$\boldsymbol{G}^{(+)}(E,\bar{x};x,x') = \tfrac{2\mu}{\hbar^2}\big\{\boldsymbol{G}^0(E,\bar{x};x,x') + \boldsymbol{\Psi}(E,\bar{x};x)\,[\boldsymbol{l}^+(E,\bar{x}) - \mathcal{L}_4(E;\bar{x})]^{-1}\,\boldsymbol{\Psi}(E,\bar{x};x')\big\}\,,$$

where $\boldsymbol{\Psi}(E,\bar{x};x)$ satisfies the equation

$$[E\boldsymbol{I}-\boldsymbol{H}(x)]\boldsymbol{\Psi}(E,\bar{x};x) = 0\boldsymbol{I} \tag{A46}$$

$$\text{and the conditions}\qquad \boldsymbol{\Psi}(E,\bar{x};x_0) = 0\boldsymbol{I}\,,\quad \boldsymbol{\Psi}(E,\bar{x};\bar{x}) = \boldsymbol{I}\,,$$

and $\mathcal{L}_4$ is the 4-th block of the symmetrized L-propagator for Eq. (A46), cf. Ref. 40,

$$\mathcal{L}_4(E;\bar{x}) = \tfrac{\imath}{\hbar}\boldsymbol{p}_x\boldsymbol{\Psi}(E,\bar{x};x{=}\bar{x})\,. \tag{A47}$$

Thus, the first-order free-free transition amplitudes ($\boldsymbol{A}$ and $\boldsymbol{A}_{\rm c}$) associated with the matrix $\boldsymbol{Q}$ and the second-order amplitudes associated with the energy derivative of $\boldsymbol{Q}$ can be expressed in terms of the quantities associated with the L-matrix formalism as

$$\boldsymbol{A} \;=\; [\boldsymbol{F}^{(+)}(x_\infty)]^\dagger\,\boldsymbol{J}\,\boldsymbol{F}^{(+)}(x_\infty)\,, \tag{A48}$$

$$\boldsymbol{A}^{(2)} = \tfrac{2\mu}{\hbar^2}\,[\boldsymbol{F}^{(+)}(x_\infty)]^\dagger\big\{\boldsymbol{J}^{(2)} + \boldsymbol{J}\,[\boldsymbol{l}^+(x_\infty) - \mathcal{L}_4(x_\infty)]^{-1}\,\boldsymbol{J}\big\}\,\boldsymbol{F}^{(+)}(x_\infty)\,, \tag{A49}$$

where $\boldsymbol{J}$ and $\boldsymbol{J}^{(2)}$ are the integrals $\boldsymbol{J}^{-,-}$ and $\boldsymbol{J}^{-,0(-)}$, respectively, in the notation of Ref. 36,

$$\boldsymbol{J} \;=\; \int_{x_0}^{x_\infty} dx\,[\boldsymbol{\Psi}(x_\infty;x)]^T\,\boldsymbol{\kappa}(x)\,\boldsymbol{\Psi}(x_\infty;x)\,, \tag{A50}$$

$$\boldsymbol{J}^{(2)} = \int_{x_0}^{x_\infty} dx\,[\boldsymbol{\Psi}(x_\infty;x)]^T\,\boldsymbol{\kappa}(x)\int_{x_0}^{x_\infty} dx'\,\boldsymbol{G}^0(x_\infty;x,x')\,\boldsymbol{\kappa}(x')\,\boldsymbol{\Psi}(x_\infty;x')\,, \tag{A51}$$

and $\boldsymbol{F}^{(+)}(x_\infty)$ has the form (A7). (For clarity, the dependence on E is not explicitly shown here).

Smooth-Variable-Discretization log-derivative method

for ....

... evaluation of free-free transition amplitudes

The integrals $\boldsymbol{J}$ and $\boldsymbol{J}^{(2)}$, Eqs. (A50)-(A51), are evaluated simultaneously with the matrix $\mathcal{L}_4(x_\infty)$, Eq. (A47). The formulas read:

$$\boldsymbol{z}_0^{-1} = 0\boldsymbol{I}\,, \quad \boldsymbol{u}_0 = \tfrac{h^2}{3}\boldsymbol{\kappa}_0\,, \quad \boldsymbol{u}_0^{(2)} = 0\boldsymbol{I}\,, \tag{A52}$$

$$\boldsymbol{u}_l^{(2)} = \mathcal{O}_{l-1,l}^T\,[\boldsymbol{u}_l^{(2)}]\;\mathcal{O}_{l-1,l} + \begin{cases} \boldsymbol{g}_l^{(2)} & \text{for } l=1,3,\ldots,2L-1, \\ 0\boldsymbol{I} & \text{for } l=2,4,\ldots,2L, \end{cases} \tag{A53}$$

$$\boldsymbol{u}_l = \mathcal{O}_{l-1,l}^T\,[\boldsymbol{u}_l^{(1)}]\;\mathcal{O}_{l-1,l} + \begin{cases} \boldsymbol{g}_l^{(1)} & \text{for } l \text{ odd}, \\ \frac{2h^2}{3}\boldsymbol{\kappa}_l & \text{for } l \text{ even}, \end{cases} \tag{A54}$$

$$\boldsymbol{z}_l = -\,\mathcal{O}_{l-1,l}^T\,\boldsymbol{z}_{l-1}^{-1}\;\mathcal{O}_{l-1,l} + \begin{cases} -6\boldsymbol{I} + \boldsymbol{g}_l & \text{for } l \text{ odd}, \\ 2\boldsymbol{I} - \frac{2h^2}{3}\boldsymbol{b}_l & \text{for } l \text{ even}, \end{cases} \tag{A55}$$

$$\boldsymbol{J}^{(2)} = \boldsymbol{u}_{2L}^{(2)}/h\,, \tag{A56}$$

$$\boldsymbol{J} = (\boldsymbol{u}_{2L} - \tfrac{h^2}{3}\boldsymbol{\kappa}_{2L})/h\,, \tag{A57}$$

$$\mathcal{L}_4 = (\boldsymbol{z}_{2L} - \boldsymbol{I} + \tfrac{h^2}{3}\boldsymbol{b}_{2L})/h\,, \tag{A58}$$

where

$$\boldsymbol{g}_l = [\tfrac{1}{8}\boldsymbol{I} + \tfrac{h^2}{48}\boldsymbol{b}_l]^{-1}\,, \tag{A59}$$

$$\boldsymbol{g}_l^{(1)} = \tfrac{h^2}{48}\,\boldsymbol{g}_l\,\boldsymbol{\kappa}_l\,\boldsymbol{g}_l\,, \tag{A60}$$

$$\boldsymbol{g}_l^{(2)} = \tfrac{h^2}{48}\,\boldsymbol{g}_l\,\boldsymbol{\kappa}_l\,\boldsymbol{g}_l^{(1)}\,, \tag{A61}$$

$$[\boldsymbol{u}_l^{(1)}] = \boldsymbol{z}_{l-1}^{-1}\,\boldsymbol{u}_{l-1}\,\boldsymbol{z}_{l-1}^{-1}\,, \tag{A62}$$

$$[\boldsymbol{u}_l^{(2)}] = \boldsymbol{z}_{l-1}^{-1}\,\{\boldsymbol{u}_{l-1}^{(2)}\,\boldsymbol{z}_{l-1}^{-1} - \boldsymbol{u}_{l-1}\,[\boldsymbol{u}_l^{(1)}]\}\,, \tag{A63}$$

$$\boldsymbol{b}_l{=}\boldsymbol{b}(x_l)\,, \quad \boldsymbol{\kappa}_l{=}\boldsymbol{\kappa}(x_l)\,, \quad x_l{=}x_0{+}lh\,, \qquad x_{2L}{=}x_\infty\,, \tag{A64}$$

and $\mathcal{O}_{l-1,l}$ is the overlap matrix between the bases $\boldsymbol{\Phi}(y;x)$ at the endpoints of the interval $[x_{l-1},x_l]$,

$$\mathcal{O}_{l-1,l}{=}\big[\boldsymbol{\Phi}(x_{l-1})\,|\boldsymbol{\Phi}(x_l)\big]\,. \tag{A65}$$

... evaluation of bound-free transition amplitudes

$$\boldsymbol{j}(E;x_\infty) = \int_{x_0}^{x_\infty} dx\,[\boldsymbol{\Psi}(E,x_\infty;x)]^T\;\underset{N\times 1}{\boldsymbol{\tau}(x)}\,, \tag{A66}$$

where $\boldsymbol{\tau}(x)$ is a vector of square-integrable functions, and $\boldsymbol{\Psi}(E,x_\infty;x)$ — the solution of the problem (A46). The integral $\boldsymbol{j}$ is also evaluated simultaneously with the matrix $\mathcal{L}_4(x_\infty)$. The algorithm is presented separately as it can be applied to a broader range of tasks than the one emerging from this work: the evaluation of the bound-resonance photo-transition amplitudes $\mathbf{T}(E_{\rm f}^{\rm res}J_{\rm f}p_{\rm f};E_{\rm i}^{B}J_{\rm i}p_{\rm i})$ defined in Eqs. (19)–(22) of the paper. Obviously, the $\mathbf{T}$ is obtained as $[\boldsymbol{F}^{(+)}(E;x_\infty)]^\dagger\,\boldsymbol{j}(E;x_\infty)$ for $E{=}E^{\rm res}$ and the vector $\boldsymbol{\tau}(x)$ is taken in the form $\boldsymbol{\Upsilon}^T(x)\mathbf{d}(x)\boldsymbol{F}(E^B;x)$.

The formulas of the algorithm are:

$$\boldsymbol{z}_0^{-1} = 0\boldsymbol{I}\,, \quad \boldsymbol{u}_0 = \tfrac{h^2}{3}\boldsymbol{\tau}_0\,, \tag{A67}$$

$$\boldsymbol{u}_l \;=\; \mathcal{O}_{l-1,l}^T\,\boldsymbol{z}_{l-1}^{-1}\,\boldsymbol{u}_{l-1} \,+\, \begin{cases} \frac{h^2}{6}\boldsymbol{g}_l\boldsymbol{\tau}_l & \text{for } l \text{ odd}, \\ \frac{2h^2}{3}\boldsymbol{\tau}_l & \text{for } l \text{ even}, \end{cases} \tag{A68}$$

$$\boldsymbol{z}_l \;=\; \text{Eq. (A55)}$$

$$\boldsymbol{j} \;=\; (\boldsymbol{u}_{2L} - \tfrac{h^2}{3}\boldsymbol{\tau}_{2L})/h\,, \tag{A69}$$

$$\mathcal{L}_4 \;=\; \text{Eq. (A58)}\,,$$

$$\text{where} \quad \boldsymbol{\tau}_l{=}\boldsymbol{\tau}(x_l)\,, \quad \boldsymbol{g}_l \text{ and } \mathcal{O}_{l-1,l} \quad \text{are as defined in Eqs. (A59) and (A65).} \tag{A70}$$

As mentioned in the paper, the present SVD version of the generalized log-derivative method has been obtained by a slight modification of the version which was proposed in Ref. 38 for equations in quasi-diabatic representations[39]. That quasi-diabatic version, in turn, is a simplified realization of the idea presented in Ref. 40: to exploit symmetry properties of coupled equations in non-diabatic representations within the generalized log-derivative propagation scheme[41]. The simplification was achieved by replacing the 'addition' of the L-propagators over the sectors $[x_{2p-2}, x_{2p}]$, given in Eqs. (64)–(67) of Ref. 40, with addition of the following effective L-propagators over halves of the sectors[42]

$$hL_{l-1,l} = \begin{pmatrix} -\boldsymbol{I}{+}h^2\boldsymbol{S}_{l-1} & \mathbf{t}_{l-1,l} \\ -\mathbf{t}_{l-1,l}^T & \boldsymbol{I}{-}h^2\boldsymbol{S}_l \end{pmatrix} \qquad \text{for} \quad l{=}2p{-}1, 2p \quad \text{and} \quad p{=}1,\ldots,L,$$

$$\text{where} \quad \boldsymbol{S}_l{=}\omega_l[\boldsymbol{I}{+}h^2\eta_l\boldsymbol{w}_l]^{-1}\boldsymbol{w}_l \qquad \text{with} \quad \omega_l{=}\tfrac{2}{3}\,(\tfrac{1}{3}) \quad \text{and} \quad \eta_l{=}\tfrac{1}{6}\,(0) \quad \text{for } l \text{ odd (even)}$$

and $\mathbf{t}_{l-1,l}$ is the transformation removing locally the first-derivative coupling term $2\boldsymbol{\alpha}(x)\frac{d}{dx}$ from Eq. (A3), determined as solution at $x{=}x_{l-1}$ of the initial-value problem

$$\boldsymbol{p}_x\mathbf{t}(x;\overline{x}){=}\mathbf{0} \quad \text{and} \quad \mathbf{t}(\overline{x};\overline{x}){=}\boldsymbol{I} \quad \text{with the initial condition posed at} \quad \overline{x}{=}x_l\,.$$

The conversion of the quasi-diabatic to the SVD algorithms consists in the following two operations:

(i) replacing the first-derivative-coupling-removing transformations $\mathbf{t}_{l-1,l}$ with the overlaps $\mathcal{O}_{l-1,l}$ for $l{=}1,\ldots,2L$ and

(ii) removing the term Δ_l from the matrices $\boldsymbol{w}_l{=}\boldsymbol{b}_l{+}\Delta_l$, cf. Eq. (A6).

Obviously, these operations are identities in the limit of completeness of the basis $\boldsymbol{\Phi}(y;x)$ because of the equalities $\mathbf{t}_{l-1,l}{=}\,\mathcal{O}_{l-1,l}$ and $\boldsymbol{\Delta}(x){=}0$ becoming then true. Correctness of the algorithms obtained by these operations when the basis is incomplete (truncated) requires actually proof. The proof[43] consists in showing that formulas (A52)–(A58) and (A67)–(A70) lead, in the $h{\to}0$ limit, to correct differential equations for the matrices $\mathcal{L}_4(\bar{x})$, $\boldsymbol{J}(\bar{x})$, $\boldsymbol{J}^{(2)}(\bar{x})$, and the vector $\boldsymbol{j}(\bar{x})$ as functions of $\bar{x}$ [the latter three come from replacing x_∞ with $\bar{x}$ in Eqs. (A50)–(A51) and (A66)],

$$\tfrac{d}{d\bar{x}}\,\mathcal{L}_4(\bar{x}) \;=\; -\mathbf{b}(\bar{x}) - \boldsymbol{\Delta}(\bar{x}) - \;\mathcal{L}_4^2(\bar{x}) + \boldsymbol{\alpha}^T(\bar{x})\;\mathcal{L}_4(\bar{x}) + \;\mathcal{L}_4(\bar{x})\,\boldsymbol{\alpha}(\bar{x})\,, \tag{A71}$$

$$\tfrac{d}{d\bar{x}}\boldsymbol{J}(\bar{x}) \;=\; \quad \boldsymbol{\kappa}(\bar{x}) + \big[\boldsymbol{\alpha}^T(\bar{x}) - \;\mathcal{L}_4(\bar{x})\big]\boldsymbol{J}(\bar{x}) + \boldsymbol{J}(\bar{x})\big[\boldsymbol{\alpha}(\bar{x}) - \;\mathcal{L}_4(\bar{x})\big]\,, \tag{A72}$$

$$\tfrac{d}{d\bar{x}}\boldsymbol{J}^{(2)}(\bar{x}) \;=\; -\boldsymbol{J}^2(\bar{x}) + \big[\boldsymbol{\alpha}^T(\bar{x}) - \;\mathcal{L}_4(\bar{x})\big]\boldsymbol{J}^{(2)}(\bar{x}) + \boldsymbol{J}^{(2)}(\bar{x})\big[\boldsymbol{\alpha}(\bar{x}) - \;\mathcal{L}_4(\bar{x})\big]\,, \tag{A73}$$

$$\tfrac{d}{d\bar{x}}\boldsymbol{j}(\bar{x}) \;=\; \quad \boldsymbol{\tau}(\bar{x}) + \big[\boldsymbol{\alpha}^T(\bar{x}) - \;\mathcal{L}_4(\bar{x})\big]\boldsymbol{j}(\bar{x})\,. \tag{A74}$$

Indeed, the term Δ appears, as it should, in the equation for the matrix $\mathcal{L}_4$. It becomes extracted in the derivation from the nonorthogonality relation of the overlap matrices,

$$\mathcal{O}^T(\bar{x};\bar{x}{+}h)\;\mathcal{O}(\bar{x};\bar{x}{+}h) = \boldsymbol{I} + h^2\boldsymbol{\Delta}(\bar{x}) + o(h^2)\,. \tag{A75}$$

Obviously, the SVD algorithms can easily be 'reduced' to the diabatic versions[36,48] [which were also exploited in this work, in the part of calculations using the BF-diabatic representation]. Namely, all the overlaps $\mathcal{O}_{l,l-1}$ should be set to $\boldsymbol{I}$ and all the $\boldsymbol{b}_l$'s should be replaced with $\frac{2\mu}{\hbar^2}[E\boldsymbol{I}-{}_{\rm BF}\mathbf{W}^{Jp}(R)]$ at the grid-points R_l.

Three digressions:

I. One may note that the three equations (A71)–(A73) can be written as

$$\tfrac{d}{d\bar{x}}\mathbb{L}(\bar{x}) = -\mathbb{B}(\bar{x}) - \mathbb{L}^2(\bar{x}) + \mathbb{A}^T(\bar{x})\mathbb{L}(\bar{x}) + \mathbb{L}(\bar{x})\mathbb{A}(\bar{x})\,, \tag{A76}$$

where the symbols $\mathbb{L}$, $\mathbb{B}$ and $\mathbb{A}$ denote the following 3×3 block-matrices

$$\mathbb{L} = \begin{pmatrix} \mathcal{L}_4 & \boldsymbol{J} & \boldsymbol{J}^{(2)} \\ \mathbf{0} & \mathcal{L}_4 & \boldsymbol{J} \\ \mathbf{0} & \mathbf{0} & \mathcal{L}_4 \end{pmatrix}, \qquad \mathbb{B} = \begin{pmatrix} \boldsymbol{b}{+}\boldsymbol{\Delta} & -\boldsymbol{\kappa} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{b}{+}\boldsymbol{\Delta} & -\boldsymbol{\kappa} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{b}{+}\boldsymbol{\Delta} \end{pmatrix}, \qquad \mathbb{A} = \begin{pmatrix} \boldsymbol{\alpha} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{\alpha} \end{pmatrix}.$$

$\mathbb{L}$ has the meaning of the (symmetrized) log-derivative matrix of solutions of the following equation

$$[E\mathbb{I}-\mathbb{H}(x)]\mathbb{F}(x){=}0 \qquad \text{with} \quad \mathbb{H} = \begin{pmatrix} \boldsymbol{H} & -\boldsymbol{\kappa} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{H} & -\boldsymbol{\kappa} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{H} \end{pmatrix} \quad \text{and} \quad \mathbb{I} = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{I} \end{pmatrix}. \tag{A77}$$

The block-structure of this equation resembles the arrangement-channel quantum mechanics[44]. Here, the arrangement channels are artificially created as copies of the single physical arrangement channel and the coupling between them

$$\mathbb{V}(x) = \begin{pmatrix} \mathbf{0} & -\boldsymbol{\kappa}(x) & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & -\boldsymbol{\kappa}(x) \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \end{pmatrix} \quad \text{has the feature:} \quad \mathbb{V}^3{=}0\,.$$

Exploitation of such nilpotent couplings is the essence of the artificial channel method of determination of transition amplitudes proposed by Shapiro, Ref. 45.

As Eq. (A76) suggests, formulas (A53)–(A68) of the present algorithm, concerning the evaluation of the integrals $\boldsymbol{J}$ and $\boldsymbol{J}^{(2)}$, can be derived from the basic formulas (A55) for the log-derivative $\mathcal{L}_4$ by applying them to the artificial coupled equations (A77) and by exploiting group-properties of triangular matrices.

Indeed, the respective working quantity $\mathbb{Z}_l := h\mathbb{L}(x_l){+}\mathbb{I}{-}h^2\mathbb{S}_l$ with $\mathbb{S}_l = \omega_l[\mathbb{I}{+}h^2\eta_l\widetilde{\mathbb{B}}_l]^{-1}\widetilde{\mathbb{B}}_l$ and $\widetilde{\mathbb{B}}_l = \begin{pmatrix} \mathbf{b}_l & -\boldsymbol{\kappa}_l & \mathbf{0} \\ \mathbf{0} & \mathbf{b}_l & -\boldsymbol{\kappa}_l \\ \mathbf{0} & \mathbf{0} & \mathbf{b}_l \end{pmatrix}$ contains the four working quantities of the algorithm (A52)–(A58),

$$\mathbb{Z}_l = \begin{pmatrix} \mathbf{z}_l & \mathbf{u}_l & \mathbf{u}_l^{(2)} \\ \mathbf{0} & \mathbf{z}_l & \mathbf{u}_l \\ \mathbf{0} & \mathbf{0} & \mathbf{z}_l \end{pmatrix}.$$

Defining the block-matrix $\mathbb{O}_{l-1,l} = \mathrm{diag}\big(\,\mathcal{O}_{l-1,l},\;\mathcal{O}_{l-1,l},\;\mathcal{O}_{l-1,l}\big)$, one gets the entire algorithm encoded in the following three lines

$$\mathbb{Z}_0^{-1} = 0\mathbb{I}\,, \tag{A78}$$

$$\mathbb{Z}_l = 2(\mathbb{I}{-}h^2\mathbb{S}_l) - \mathbb{O}_{l-1,l}^T\,\mathbb{Z}_{l-1}^{-1}\,\mathbb{O}_{l-1,l} \quad \text{for} \quad l{=}1,\ldots,2L, \tag{A79}$$

$$\mathbb{L}(x_{2L}) = (\mathbb{Z}_{2L}{-}\mathbb{I}{-}\tfrac{h^2}{3}\widetilde{\mathbb{B}}_{2L})/h\,. \tag{A80}$$

II. Eqs. (A76)–(A77) also suggest that the algorithm (A52)–(A58) is applicable to more general free-free transitions than considered here, namely, to transitions whose initial and final multichannel continuum states are not the same. Calculations on collision-induced absorption (CIA) in molecular gases[46] and state-to-state calculations on radiative-charge transfer in ionic atom + diatom systems[47] are examples of tasks which require evaluations of numerous transition amplitudes of this kind.
Obtaining the free-free transition amplitude

$$\boldsymbol{J}^{\rm if} := = \int_{x_0}^{x_\infty} dx\, [\boldsymbol{\Psi}^{\rm i}(E^{\rm i}, x_\infty; x)]^T\, \boldsymbol{\kappa}(x)\, \boldsymbol{\Psi}^{\rm f}(E^{\rm f}, x_\infty; x)$$

in which $\boldsymbol{\Psi}^{\rm i}$ and $\boldsymbol{\Psi}^{\rm f}$ are solutions of the boundary-value problem (A46) for operators $[E^{\rm i}\boldsymbol{I}-\boldsymbol{H}^{\rm i}]$ and $[E^{\rm f}\boldsymbol{I}-\boldsymbol{H}^{\rm f}]$, respectively, is equivalent to determining the log-derivative matrix $\mathbb{L}=\begin{pmatrix} \mathcal{L}_4^{\rm i} & \boldsymbol{J}^{\rm if} \\ \boldsymbol{0} & \mathcal{L}_4^{\rm f} \end{pmatrix}$ from the artificial equation

$$[\mathbb{E}-\mathbb{H}]\mathbb{F}=0 \quad \text{in which} \quad \mathbb{H}=\begin{pmatrix} \boldsymbol{H}^{\rm i}(x) & -\boldsymbol{\kappa}(x) \\ \boldsymbol{0} & \boldsymbol{H}^{\rm f}(x) \end{pmatrix} \quad \text{and} \quad \mathbb{E}=\begin{pmatrix} E^{\rm i}\boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & E^{\rm f}\boldsymbol{I} \end{pmatrix}.$$

Thus, application of the above algorithm to evaluation of the integral $\boldsymbol{J}^{\rm if}$ consists in:
(i) propagating simultaneously two independent quantities $\boldsymbol{z}_l^{\rm f}$ and $\boldsymbol{z}_l^{\rm f}$, related to $\mathcal{L}_4^{\rm i}$ and $\mathcal{L}_4^{\rm f}$, respectively, according to formula (A55) adjusted to the appropriate operator $[E^{\rm i}\boldsymbol{I}-\boldsymbol{H}^{\rm i}]$ or $[E^{\rm f}\boldsymbol{I}-\boldsymbol{H}^{\rm f}]$, cf. Eqs. (A4)–(A6), and
(ii) propagating the quantity $\boldsymbol{u}_l$, related now to $\boldsymbol{J}^{\rm if}$, according to the following modified version of formula (A68)

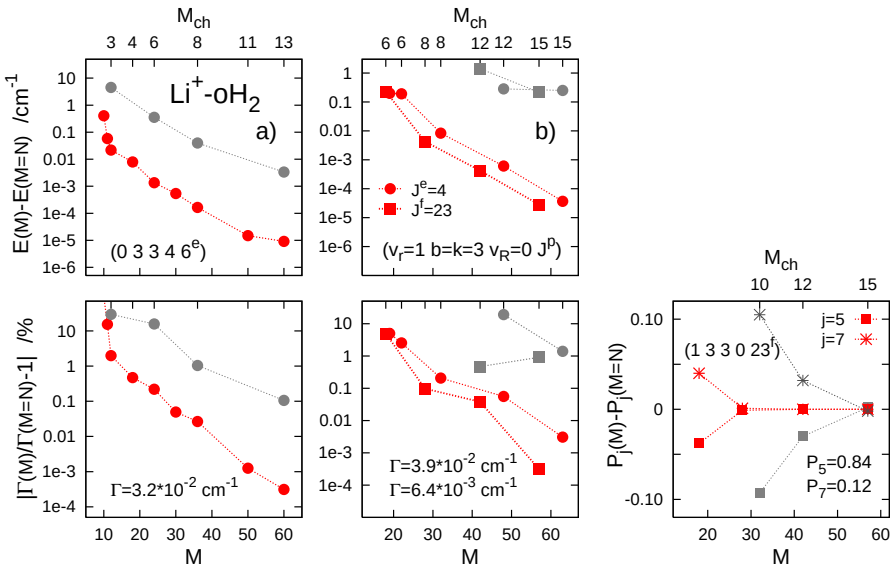
$$\boldsymbol{u}_l = \mathcal{O}_{l-1,l}^{{\rm i}\,T}\, \boldsymbol{z}_{l-1}^{{\rm i}\,-1}\, \boldsymbol{u}_{l-1}\, \boldsymbol{z}_{l-1}^{{\rm f}\,-1}\, \mathcal{O}_{l-1,l}^{\rm f} + \begin{cases} \frac{h^2}{48}\, \boldsymbol{g}_l^{\rm i}\, \boldsymbol{\kappa}_l\, \boldsymbol{g}_l^{\rm f} \\ \frac{2h^2}{3} \boldsymbol{\kappa}_l \end{cases}.$$

III. The algorithm for the integral $\boldsymbol{j}$, formulas (A67)–(A70), can be cast into the form (almost) identical with (A78)–(A80) if one redefines the blackboard bold symbols as follows:

$$\mathbb{L} = \begin{pmatrix} \mathcal{L}_4 & \boldsymbol{j} \\ \boldsymbol{0} & 0 \end{pmatrix}, \quad \widetilde{\mathbb{B}}_l = \begin{pmatrix} \mathbf{b}_l & -\boldsymbol{\tau}_l \\ \boldsymbol{0} & 0 \end{pmatrix}, \quad \mathbb{Z}_l = \begin{pmatrix} \mathbf{z}_l & \mathbf{u}_l \\ \boldsymbol{0} & 1 \end{pmatrix}, \quad \mathbb{O}_{l-1,l} = \begin{pmatrix} \mathcal{O}_{l-1,l} & \boldsymbol{0} \\ \boldsymbol{0} & 1 \end{pmatrix}.$$

The present definition of $\mathbb{L}$ requires that only formula (A78) be modified to: $\mathbb{Z}_0^{-1} = \begin{pmatrix} 0\mathbf{I} & \boldsymbol{0} \\ \boldsymbol{0} & 1 \end{pmatrix}$.

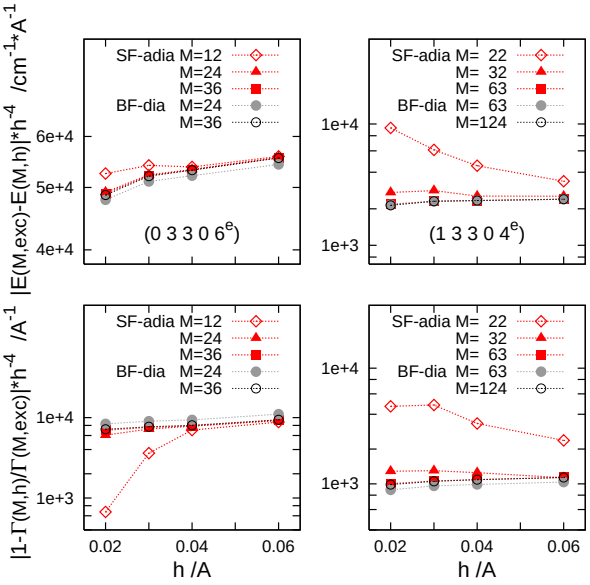
Fig. A1. Convergence tests of SVD log-derivative method in determination of predissociating states of Li^+–oH_2



Convergence with respect to the SF-adiabatic basis size $M\,(\leq N)$ in the determination of the energies $E^{\rm res}$ and the total widths Γ of exemplary states predissociating a) rotationally, and b) vibrationally, and in the determination of the populations $P_j{=}\Gamma_{0,j}/\Gamma$ of j levels of H_2 due to decay of a $v_r{=}1$ state. In each case shown, the 'complete' adiabatic basis ($M{=}N$) was constructed by including 28 vj channels, with $v{=}0{-}3$ and $j{\in}[0,13]$, into the original BF-diabatic basis. This set of channels together with the restriction $\lambda_{\rm max}{=}5$ gives $N{=}144$ basis functions $\Phi^{JMp}_{vj\lambda}$ or $\Phi^{JMp}_{vj\bar{l}}$ for states with $J^e{\geq}5$, $N{=}124$ functions for $J^e{=}4$ and $N{=}116$ — for $J^f{\geq}5$ states. Errors of the results due to truncation of the SF-adiabatic bases from N to M are shown with the red symbols. The grey symbols show errors of results obtained with the BF-diabatic bases that included $M_{\rm ch}$ lowest vj channels. The corresponding numbers of the included $v\,j\,\lambda$ states can be read on the axes with the label 'M'.

Convergence with the step size (h) in the SVD and in the diabatic log-derivative algorithms. 'exc' denotes result yielded by a given algorithm and a given size M of the respective basis when the step size $h{=}0.01\mathring{A}$ is used.

Generally, errors of results generated with the SVD algorithm behave the same as the accumulated discretization error of the diabatic version, i.e. they scale like $C{\times}h^4$ with nearly the same scaling factor C. A departure from this behavior may occur if the adiabatic basis is truncated too drastically, like from $N{=}144$ to $M{=}12$ in the case shown in the left panels or from $N{=}124$ to $M{=}22$ in the case of the right panels.



The conclusions of the tests:

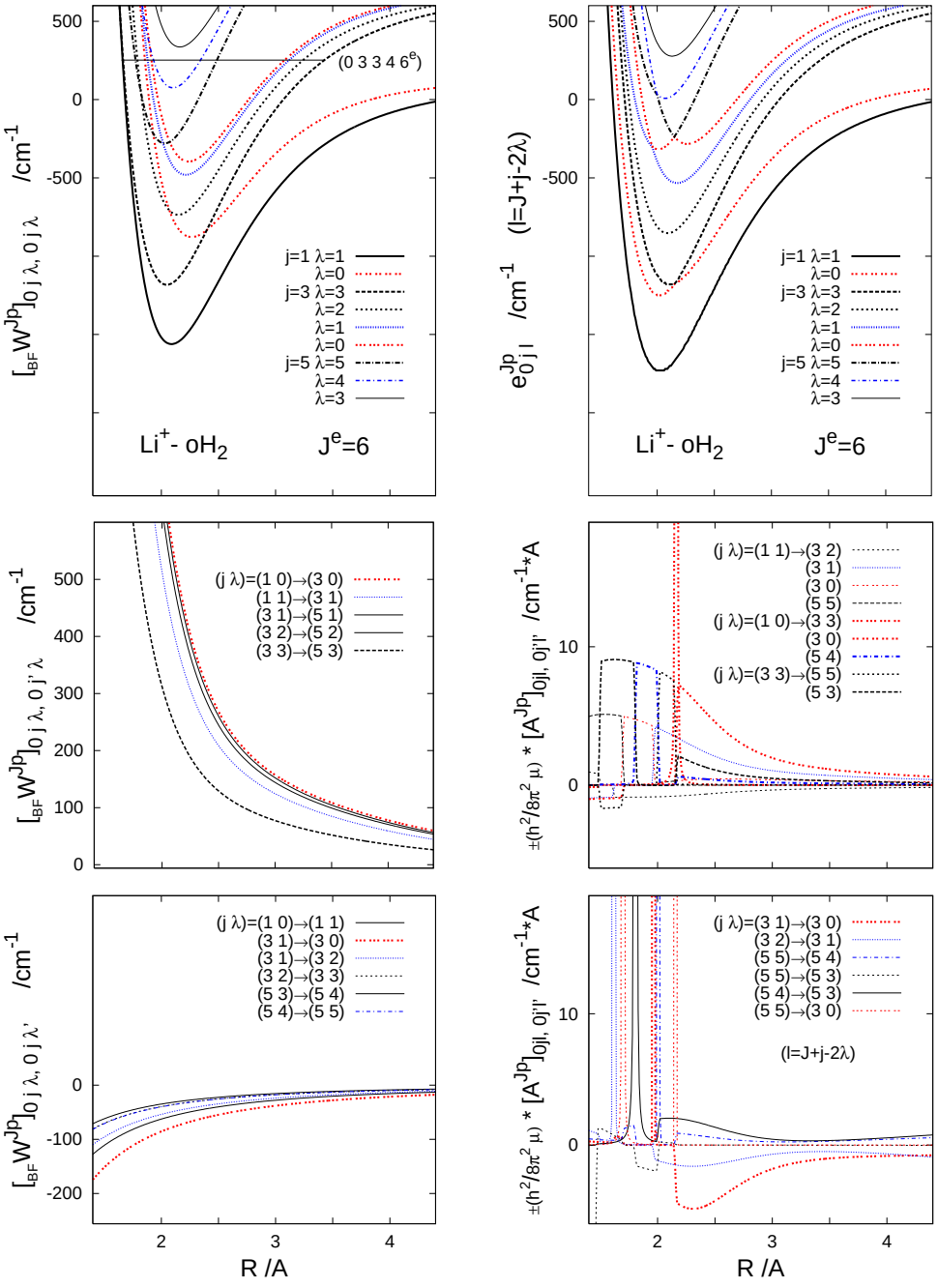
(i) In comparison with typical sizes of the BF-diabatic basis used in the determination of states of the complex with $v_r{=}0{-}1$, i.e. $N{\in}120{-}150$, the SF-adiabatic basis can be truncated by a factor of two, at least, without a risk of producing errors of the energies larger than $\sim$0.001 cm^{-1} and errors of the widths larger than $\sim$0.1 %.

(ii) Constant step sizes can be used in the SVD algorithm, practically the same as in the diabatic version.

Fig. A2. Li^++oH_2. Hamiltonian matrices in BF-diabatic and SF-adiabatic representations, cf. Eqs. (9)-(14) of the paper,

$$ {}_{\rm BF}\mathbf{H}^{Jp}(R) = -\frac{\hbar^2}{2\mu}\mathbf{I}\frac{d^2}{dR^2} + {}_{\rm BF}\mathbf{W}^{Jp}(R) $$

$$ \mathbf{H}^{Jp}(R) = -\frac{\hbar^2}{2\mu}\left[\mathbf{I}\frac{d^2}{dR^2} + 2\mathbf{A}^{Jp}(R)\frac{d}{dR} + \mathbf{B}^{Jp}(R)\right] + \mathbf{e}^{Jp}(R) $$



Left: the lowest elements of the matrix ${}_{\rm BF}\mathbf{W}^{Jp}(R)$ used in the tests on the $(0\,3\,3\,3\,6^e)$ quasi-bound state of the Li^+–oH_2 complex. The energy of the state is shown by the line within the diabatic potential (diagonal element of ${}_{\rm BF}\mathbf{W}^{Jp}(R)$) which supports the largest radial component to the function. The non-diagonal elements, describing rotational (middle panel) and Coriolis (bottom) couplings, are all smooth functions. Right: the corresponding adiabatic potentials and the non-adiabatic first-derivative couplings. The couplings exhibit several sharp peaks due to weakly avoided crossings of the adiabatic potentials. Treating these couplings directly, like in the quasi-diabatic method, would certainly require step sizes carefully adjusted and, on average, much smaller than needed for integration of the coupled equations in the diabatic representation. This underscores the profit of using the SVD approach described in conclusion (ii) of the tests reported in Fig. A1.

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