

Analysis of individual resonance contributions to two-channel scattering

S.A. Rakityansky^{a*} and N. Elander^b

A quantum mechanical two-channel problem is considered within a method based on first-order differential equations that are equivalent to the corresponding Schrödinger equation but are more convenient for dealing with resonant phenomena. Using these equations, we can directly calculate the Jost matrix for practically any complex value of the energy. The spectral points (bound and resonant states) can therefore be located in a rigorous way, namely, as zeroes of the Jost matrix determinant. For each pole of the S-matrix, its residue can be calculated rather accurately, which makes it possible to obtain the Mittag-Leffler type expansion of the S-matrix as a sum of the singular terms (representing the resonances) and the background term (contour integral). As an example, the two-channel model by Noro and Taylor is considered. We demonstrate how the contributions of individual resonance poles to the scattering process can be analysed using the Mittag-Leffler expansion and the Argand plot technique.

Introduction

This work was motivated mainly by recent developments in quantum chemistry, more specifically, by studies of quantum resonances in chemical reactions. Initially, the theory of quantum resonances was developed by nuclear physicists, but nowadays it has become an interdisciplinary subject and an example of the unification of many branches of science.

The notion of a quantum resonance (which is also called a quasi-stationary or quasi-bound state) emerged at later stages of the development of quantum mechanics. Attention to such states was drawn by George Gamow in his pioneering works on the α -decay^{1,2} and then by Niels Bohr, who studied the energy dependence of nuclear scattering and introduced the idea of the compound nucleus,³ which is a relatively long-lived intermediate state of the colliding system. Over the years, nuclear physicists developed this idea into a rigorous theory and suggested various methods for locating resonances.

The role of resonances in solid-state and chemical physics was understood much later. Nowadays, it is clear that a full understanding of the properties of a quantum system and prediction of its behaviour cannot be achieved without knowing its spectrum, that is, the energies of its bound states and resonances. This applies even in technological applications. For example, modern semiconductor devices, such as solid-state lasers, based on nano-structures, cannot be properly designed without accurate treatment of various transitions among stationary and quasi-stationary states of the electrons and holes.

In quantum chemistry, the concept of short-lived transition states have been used since the 1970s,^{4,5} but it was not until the very end of the last century that combined experimental and theoretical research could confirm their existence.^{6,7} Nowadays, chemists actively discuss the so-called collision complexes. This

is precisely the concept of the compound nucleus introduced by Bohr about 70 years ago.

The concept of a collision complex has recently been successfully used even in modelling the damage to DNA molecules caused by radiation.⁸ The ability to analyse the resonance contribution to chemical reactions may therefore have a significant conceptual impact on chemistry, biology and even medicine. Identifying short-lived, resonant, intermediate states in a chemical reaction may make it possible to alter the outcome of a particular reaction by using fast laser pulses which excite or de-excite the intermediate states and thereby alter the reaction paths.

The objective of our work is to find a way of estimating quantitatively the contributions from each resonant state to the reaction probabilities. This is achieved by decomposing the scattering S-matrix in a sum of terms that represent individual resonances. Such a decomposition is possible on the basis of the Mittag-Leffler theorem of the complex analysis.⁹ As an example, we consider a two-channel model and demonstrate how the contributions of individual resonance poles can be analysed using the Argand plot technique.

Quantum resonances: overview

Resonance states are formed when quantum particles collide at certain (resonant) energies. Before moving apart, they stay together for a while. During the resonance lifetime, the particles move around each other and 'forget' the direction from which they came. Therefore, when the resonance eventually decays, the particles 'choose' the direction to move away at random.

In quantum mechanics, this physical concept is mathematically formulated as follows (see, for example, ref. 10). Resonant states are spectral points (the particular energies mentioned above), i.e. eigenstates of the Hamiltonian,

$$H\Psi = E\Psi, \quad (1)$$

with pure outgoing-wave asymptotics (which means no 'memory' of the incoming information). In the simple single-channel case, this means that the wave function describing a spectral state obeys the Schrödinger equation,

$$\left[\partial_r^2 + k^2 - \ell(\ell + 1)/r^2 \right] \psi_\ell(k, r) = V(r)\psi_\ell(k, r), \quad (2)$$

with $k^2 = 2mE$ (the units are such that $\hbar = c = 1$), and the amplitude of the incoming wave (i.e. the coefficient of the Riccati-Hankel function $h_\ell^{(-)}$ in its long-range asymptotics,

$$\psi_\ell(k, r) \xrightarrow{r \rightarrow \infty} f_\ell^{(in)}(k)h_\ell^{(-)}(kr) + f_\ell^{(out)}(k)h_\ell^{(+)}(kr), \quad (3)$$

is zero,

$$f_\ell^{(in)}(k) = 0. \quad (4)$$

This coefficient is called the Jost function. Spectral points, therefore, are such points on the complex energy surface, where the Jost function is zero. The probabilities of possible outcomes of the collision are determined by the S-matrix, which is the ratio

^aDepartment of Physics, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa.

^bDivision of Molecular Physics, Department of Physics, Stockholm University, Stockholm, SE-10691, Sweden.

*Author for correspondence. E-mail: rakitsa@science.unisa.ac.za

of the asymptotic coefficients,

$$S_\ell(k) = \frac{f_\ell^{(\text{out})}(k)}{f_\ell^{(\text{in})}(k)}, \quad (5)$$

and therefore has poles at all spectral points.

There are two types of spectral points: bound states and resonances. Bound states lie on the real negative axis (see Fig. 1), while a resonance energy,

$$E = E_r - \frac{i}{2}\Gamma, \quad (6)$$

has a negative imaginary part, which is called resonance width. The width Γ determines how long the resonance lives. Indeed, the probability of finding the system at any given place,

$$|\Psi(t_0)e^{-iE(t-t_0)}|^2 = |\Psi(t_0)|^2 e^{-\Gamma(t-t_0)},$$

exponentially diminishes with time due to the imaginary part of the energy. Another meaning of Γ is that it defines a window around the collision energy E_r , within which the resonance can be excited.

Two-channel problem

All real problems in physics and especially in quantum chemistry are multi-channel. This means that a collision of quantum systems (molecules, atoms, nuclei, etc.) may result in many different final products (channels),

$$A + B \longrightarrow \begin{cases} A + B, \\ C + D, \\ E + F, \\ \text{etc.} \end{cases}$$

Since our main objective is to study how the resonance poles of the S -matrix manifest themselves in experimentally observable collision data, we avoid unnecessary complications associated with spins of the particles and with long-range Coulomb forces. Furthermore, for the sake of clarity, we consider here a two-channel system, although all the equations can be easily generalized for an arbitrary number of channels.

In the two-channel case with the threshold energies ε_1 and ε_2 (below which the corresponding reactions are not allowed by the energy conservation law), the eigenstate equation (1) becomes a system of two coupled Schrödinger equations,

$$[\partial_r^2 + k_n^2 - \ell(\ell+1)/r^2] \psi_n = \sum_{n'} V_{nn'} \psi_{n'}, \quad n = 1, 2, \quad (7)$$

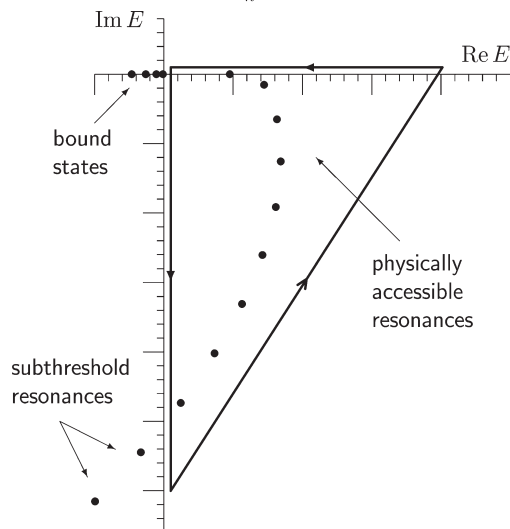


Fig. 1. Spectral points for the potential (19) and the integration contour (enclosing 9 resonance poles) for Equation (18).

where $k_n = \sqrt{2m_n(E - \varepsilon_n)}$ are the channel momenta. To simplify the notation, we dropped the angular-momentum subscript ℓ of the wave function.

This system has two linearly independent regular (i.e. nonsingular at $r = 0$) solutions, which can be combined in a square matrix

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}_1 \oplus \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}_2 = \begin{pmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{22} \end{pmatrix} = \psi. \quad (8)$$

Far away from the interaction region this matrix is a linear combination

$$\psi(E, r) \xrightarrow{r \rightarrow \infty} W^{(\text{in})}(E, r) f^{(\text{in})}(E) + W^{(\text{out})}(E, r) f^{(\text{out})}(E), \quad (9)$$

of the incoming and outgoing waves,

$$W^{(\text{in/out})} = \begin{pmatrix} h_\ell^{(\mp)}(k_1 r) & 0 \\ 0 & h_\ell^{(\mp)}(k_2 r) \end{pmatrix}. \quad (10)$$

The combination coefficients $f^{(\text{in/out})}(E)$ are called the Jost matrices. Similarly to Equation (5), the S -matrix is calculated as

$$S(E) = f^{(\text{out})}(E) [f^{(\text{in})}(E)]^{-1}. \quad (11)$$

It can be shown (see, for example, ref. 11) that pure outgoing-wave asymptotics is possible if and only if

$$\det f^{(\text{in})}(E) = 0, \quad (12)$$

which is a multi-channel version of the condition (4) that determines the spectral points.

In refs 11–16, we developed a method for calculating Jost matrices at any complex values of the energy E . Our method is based on the coupled system of first-order differential equations,

$$\partial_r F^{(\text{in})} = -\frac{1}{2i} K^{-1} W^{(\text{out})} V [W^{(\text{in})} F^{(\text{in})} + W^{(\text{out})} F^{(\text{out})}], \quad (13)$$

$$\partial_r F^{(\text{out})} = +\frac{1}{2i} K^{-1} W^{(\text{in})} V [W^{(\text{in})} F^{(\text{in})} + W^{(\text{out})} F^{(\text{out})}], \quad (14)$$

where

$$K = \begin{pmatrix} k_1 & 0 \\ 0 & k_2 \end{pmatrix}$$

and $F^{(\text{in/out})}(E, r) \xrightarrow{r \rightarrow 0} 1$. The system (13,14) is equivalent to the

corresponding Schrödinger equation (7), but is more convenient for dealing with resonant phenomena. This is because when solved along a complex path in the r -plane (see refs 11–16), Equations (13,14) give the Jost matrices, i.e.

$$F^{(\text{in/out})}(E, r) \xrightarrow{r \rightarrow \infty} f^{(\text{in/out})}(E). \quad (15)$$

This enables us to accurately locate the spectral points and calculate the S -matrix for complex energies.

Spectral decomposition

The S -matrix gives a complete description of the collision process. For example, the scattering cross section for the transition (with $\ell = 0$) from channel n to channel n' , is determined by the corresponding matrix element of S as follows

$$\sigma(n \rightarrow n') = \frac{\pi}{k_n} |\delta_{n'n} - S_{n'n}|^2. \quad (16)$$

When resonances are well isolated from each other and narrow, the cross section shows distinct peaks or other irregularities corresponding to each individual resonance. If, however, they are wide and overlap each other, the energy dependence of the cross section is rather complicated due to intricate interference of the resonances. Unfortunately, this is the case in

the majority of practical problems, which makes it extremely difficult to infer the contributions of individual resonances from the scattering cross section.

As a way of solving this problem, we suggest decomposing the S -matrix in a sum of terms representing individual resonances. The idea is based on the Mittag-Leffler theorem well known in complex analysis.⁹ The theorem itself is rather general. In plain words, it says that a meromorphic function can be expanded in a sum of an entire function and a series of its principal parts at all the poles. Practically, this can be done using the Cauchy integral formula. Indeed, for a contour enclosing N resonance poles the Cauchy formula reads

$$\oint \frac{S(\zeta)}{\zeta - E} d\zeta = 2\pi i S(E) + 2\pi i \sum_{j=1}^N \frac{\text{Res}[S(E_j)]}{E_j - E}, \quad (17)$$

where E is a point inside the contour and E_j are the resonance energies. Therefore, in the desired expansion,

$$S(E) = \sum_{j=1}^N \frac{\text{Res}[S(E_j)]}{E - E_j} + \frac{1}{2\pi i} \oint \frac{S(\zeta)}{\zeta - E} d\zeta, \quad (18)$$

the N selected poles are represented explicitly while the rest of them as well as the background are taken into account via the contour integral. Since we are able to calculate $S(E)$ numerically at complex E , the evaluation of its residues and the integral is straightforward. In order to understand what role a particular resonance plays in the scattering process, we can simply omit the corresponding term from the sum (18) and analyse the consequences.

Numerical example

As a testing ground, we chose the model proposed by Noro and Taylor.¹⁷ Their two-channel potential

$$V(r) = \begin{pmatrix} -1.0 & -7.5 \\ -7.5 & 7.5 \end{pmatrix} r^2 e^{-r}, \quad (19)$$

is of a short range and the threshold energies are $\mathcal{E}_1 = 0$ and $\mathcal{E}_2 = 0.1$ in the units such that $m_1 = m_2 = \hbar c = 1$. Despite its simplicity, this model has some features very common in quantum chemistry problems. In particular, the distribution of its resonance poles on the complex E -surface is typical for molecular collision complexes. In order to ‘upgrade’ this model to describe a realistic system, one would only need to adjust the parameters and add the Coulomb forces.

The spectral points we found (with $l = 0$) for this two-channel potential, and the integration contour for the expansion (18) are shown in Fig. 1. As can be seen, the system described by the potential (19) has four bound states and a string of overlapping resonances. Nine of the resonances, which lie at the physically accessible energies (i.e. above both thresholds), are enclosed by the integration contour and therefore are represented in the expansion (18) explicitly. Their parameters are given in Table 1.

As was expected, the cross sections have quite complicated energy dependence (see, for example, the elastic cross section for the first channel, shown in Fig. 2). Only the first extremely narrow resonance can be unmistakably associated with the irregularity shown on the second insert (for $4.765 \leq E \leq 4.775$). The influence of the other resonance poles cannot be derived from this curve. This is the problem where the spectral decomposition (18) may become a solution.

We obtain the S -matrix as a sum (18) of 10 terms, 9 poles and the background integral.

Excluding the terms, one at a time, we can estimate their

Table 1. Nine resonances enclosed by the integration contour shown in Fig. 1.

E_j	Γ
4.768197	0.001420
7.241200	1.511912
8.171217	6.508332
8.440526	12.562984
8.072643	19.145630
7.123813	26.025337
5.641023	33.070140
3.662702	40.194674
1.220763	47.339350

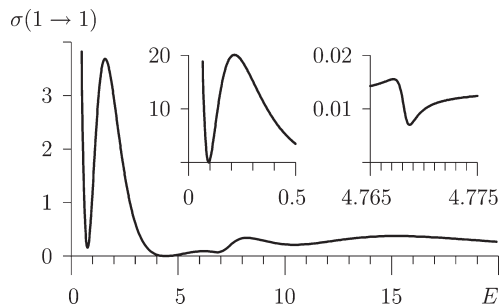


Fig. 2. Energy dependence of the elastic scattering cross section in channel 1 for the potential (19).

respective contributions. The cross section (16) is a quadratic function of the S -matrix, where the terms multiply each other and thus make things rather complicated. We can avoid this complication if we consider the S -matrix itself.

When the collision energy increases, the points representing the elements of the S -matrix in the complex plane, move along certain curves which are called the Argand plots. Figure 3 shows how the first-channel element of the S -matrix moves when the energy changes from 0.5 to 20.

It can be shown (see, for example, refs 18, 19) that, in the absence of resonances, Argand plots always move in circles in a clockwise direction. The resonances force them to change direction and make anti-clockwise loops or arcs when resonances are wide. An example of a closed anti-clockwise loop that corresponds to the first very narrow resonance, can be seen in Fig. 3.

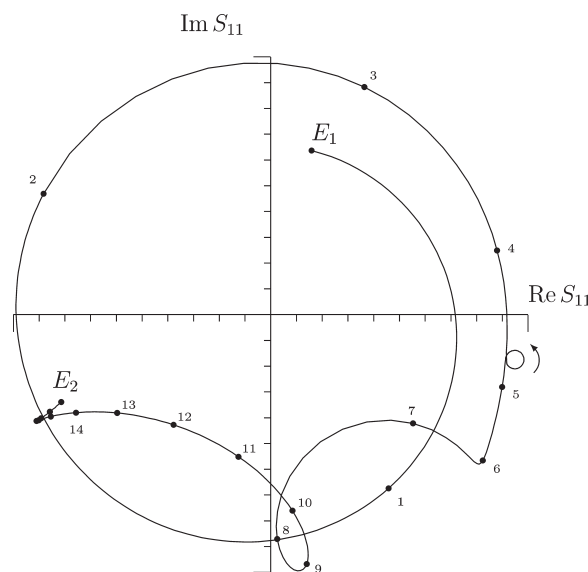


Fig. 3. Argand plot of $S_{11}(E)$ in the energy interval from $E_1 = 0.5$ to $E_2 = 20$. The dots on the curve indicate the points corresponding to $E = 1, 2, 3, \dots$

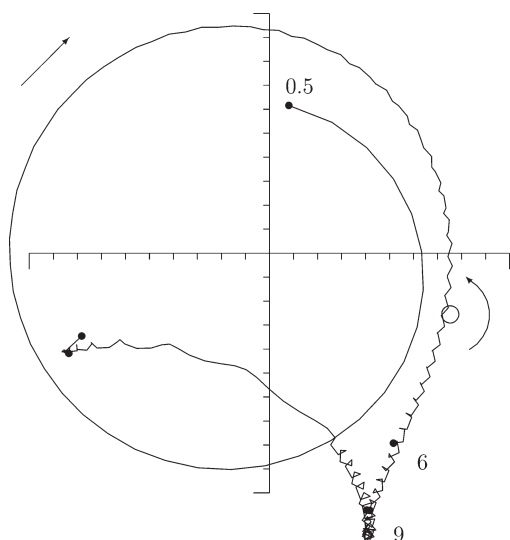


Fig. 4. Argand plot of $S_{11}(E)$ with the second pole excluded.

When we exclude the term corresponding to this resonance, nothing changes except that the loop disappears. When the second pole is excluded from the Mittag–Leffler expansion (18), the arc in the energy range between 6 and 9 disappears (see Fig. 4). We therefore can conclude that in this energy range the second resonance is dominant. Similarly (see Fig. 5), the third pole determines the energy dependence in the range from 9 to 15. The other resonance poles are too far from the real axis and have only collective influence. When all 9 poles are excluded, the Argand plot becomes purely non-resonant (Fig. 6).

Although this model might look artificial, the spectrum of resonances generated by the Noro and Taylor potential is similar to the spectra of some real atomic systems. For example, the existence of a string of overlapping resonances that starts with a narrow one, is a feature that characterizes the charge-transfer reaction $N^{3+} + H \rightarrow N^{2+} + H^+$ (refs 20–22).

Conclusion

The Jost function as well as Jost solutions of the Schrödinger equation are indispensable parts of any textbook on quantum scattering theory. However, after reading even a comprehensive text on this subject, one usually gets a feeling that the Jost function is a pure mathematical entity, very elegant, very useful in formal theory, but impractical for solving real physical problems. This is because none of the textbooks offers the reader any practical method for calculating the Jost function. The equations used in this paper fill the gap between mathematical theory of the Jost functions (which are matrices in the multi-channel case) and their practical applications.

Using these equations, we can directly calculate the Jost matrix for practically any complex value of the energy. The bound and resonant states can therefore be located as zeroes of the Jost matrix determinant. The possibility of calculating the residues of the S -matrix at its poles enables us to obtain the Mittag–Leffler type expansion of the S -matrix as a sum of the singular terms (representing the resonances) and the background term (contour integral). The contributions of individual resonances to the scattering process can be assessed by omitting the corresponding terms from the Mittag–Leffler expansion and examining the effect of the omission on the Argand plot of the S -matrix.

The analysis of the Noro and Taylor model, given in this paper, demonstrates the effectiveness and accuracy of the proposed method. With the inclusion of the Coulomb forces and some numerical modifications, this model can be applied to

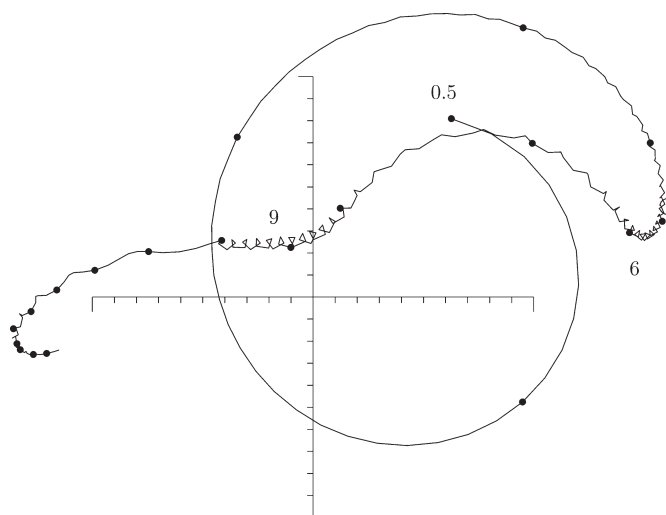


Fig. 5. Argand plot of $S_{11}(E)$ with the third pole excluded.

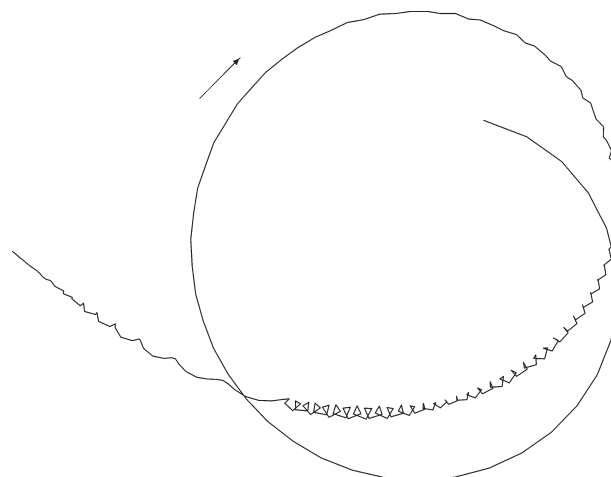


Fig. 6. Argand plot of $S_{11}(E)$ with all nine poles excluded.

charge-transfer reactions like $N^{3+} + H \rightarrow N^{2+} + H^+$ (refs 20–22) and others. Owing to an extremely high Coulomb barrier, the relative energy (\sim meV) at which these resonances appear could never be achieved in collision experiments. A new idea is to observe the collisions between particles moving in the same beam, so that their relative kinetic energy is very low. Electrostatic storage rings for this purpose are currently being built. For example, the ‘Desiree’ project in Stockholm is planned to have the possibility of merging a stored, multiply charged ion beam with a beam of neutral atoms. Similar experiments are also planned at other facilities.

Of course, the range of possible applications of the proposed method is much wider than the Noro and Taylor model. Our equations can easily be generalized for an arbitrary number of channels and thus used in various fields of quantum physics where the collisions are non-relativistic. For example, the same approach could be useful in analysing the resonant properties of semiconductor nano-structures as well as low-energy nuclear reactions. In all such problems the combination of the Jost-matrix method with the Argand plot technique would produce accurate and reliable results.

This article is based on a talk given at the 50th Annual Conference of the South African Institute of Physics, held in Pretoria, 5–7 July 2005.

Received 31 August 2005. Accepted 20 January 2006.

1. Gamow G.A. (1928). Zur Quantentheorie des Atomkernes. *Z. Phys.* **51**, 204–212.
 2. Gamow G.A. (1928). Zur Quantentheorie der Atomzertrümmerung. *Z. Phys.* **52**, 510–520.
 3. Bohr N. (1937). Neutron capture and nuclear constitution. *Nature* **137**, 344–348.
 4. Levine R.D. and Wu S-F. (1971). Resonances in reactive collisions: computational study of the H + H₂ collision. *Chem. Phys. Lett.* **11**, 557–561.
 5. Schatz G.C. and Kuppermann A. (1973). Role of direct and resonant (compound state) processes and of their interferences in the quantum dynamics of the collinear H + H₂ exchange reaction. *J. Chem. Phys.* **59**, 964–965.
 6. Schatz G.C. (2000). Detecting resonances. *Science* **288**, 1599–1600.
 7. Skodje R.T., Skouteris D., Manolopoulos D.E., Lee S-H., Dong F and Liu K. (2000). Observation of a transition state resonance in the integral cross section of the F + HD reaction. *J. Chem. Phys.* **112**, 4536–4552.
 8. Boudaïffa B., Cloutier P., Hunting D., Huels, M.A. and Sanche L. (2000). Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons. *Science* **287**, 1658–1660.
 9. Jeffreys H. and Jeffreys B.S. (1988). *Methods of Mathematical Physics*, 3rd edn, pp. 383–386. Cambridge University Press, Cambridge.
 10. Taylor J.R. (1972). *Scattering Theory*, p. 238. John Wiley, New York.
 11. Rakityansky S.A. (2004). Modified transfer matrix for nanostructures with arbitrary potential profile. *Phys. Rev. B* **70**, 205323, 1-16.
 12. Rakityansky S.A., Sofianos S.A. and Amos K. (1996). A method for calculating the Jost function for analytic potentials. *Nuovo Cim. B* **111**, 363–378.
 13. Sofianos S.A. and Rakityansky S.A. (1997). Exact method for locating potential resonances and Regge trajectories. *J. Phys. A: Math. Gen.* **30**, 3725–3737.
 14. Rakityansky S.A. and Sofianos S.A. (1998). Jost function for coupled partial waves. *J. Phys. A: Math. Gen.* **31**, 5149–5175.
 15. Sofianos S.A., Rakityansky S.A. and Massen S.E. (1999). Jost function for singular potentials. *Phys. Rev. A* **60**, 337–343.
 16. Rakityansky S.A. and Sofianos S.A. (1999). Jost function for coupled channels. *Few-Body Systems Suppl.* **10**, 93–96.
 17. Noro T and Taylor H.S. (1980). Resonance partial widths and partial photo-detachment rate using the rotated coordinate method. *J. Phys. B: Atom. Molec. Phys.* **13**, L377–L381.
 18. Kuppermann A. (1981). In *Potential Energy Surfaces and Dynamics Calculations for Chemical Reactions and Molecular Energy Transfer*, ed. D.G. Truhlar, pp. 375–420. Plenum Press, New York.
 19. Dalitz R.H. (1984). In *Resonances – Models and Phenomena. Lecture Notes in Physics*, vol. 211, pp. 1–26. Springer-Verlag, Berlin.
 20. McCarroll R. and Valrion P. (1980). *Proc. 11th Int. Conf. on Physics of Electronic and Atomic Collisions, Invited papers and progress reports*, p. 453. North-Holland, Amsterdam.
 21. Barany A., Brandas E., Elander N. and Rittby M. (1983). Resonances in low energy charge transfer between multiply charged ions and neutral atoms described with dilated Titchmarsh–Weyl theory — a progress report. *Physica Scripta* **T3**, 233–235.
 22. Rittby M., Elander N., Brandas E. and Barany A. (1984). Resonance structure in charge transfer cross sections: an application to the N³⁺ + H⁺ reaction. *J. Phys. B* **17**, L677–L681.
-