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Multichannel Siegert quantization with complex rotated coordinates: Application to molecular resonances

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A coupled-channel approach with complex rotated coordinates and boundary conditions identical to those used for bound states is shown to lead to an accurate determination of the widths of resonances in the heavy particle motion of molecular systems.

We describe in this paper how the merging of two currently developing techniques makes it possible to study both the bound states and the resonances of a molecular system on the same footing. These techniques are as follows:

(i) The determination of bound levels in a multichannel situation[1,2] from the propagation of the components of the wave function with the correct boundary behavior in the interior and exterior nonclassical regions, and matching of these components and of their derivatives at some intermediate point.

(ii) The introduction of a complex rotated cordinate $re^{i\theta}$ for the interfragment distance, which transforms the otherwise divergent Siegert components of the wave function of a resonance into localized functions.[3,4]

I. DESCRIPTION OF THE METHOD

Our own approach[5] to the calculation of bound-state energies in a coupled-channel situation proceeds from the Fox-Goodwin propagator, as presented by Norcross and Seaton.[6] If a matrix of N-independent solutions $\underline{U}$ is considered, instead of actually propagating $\underline{U}$, one may consider the matrix $\underline{\mathcal{R}}$ such that

$$\underline{\mathcal{R}}_{m+1}\underline{U}_{m+1}=\underline{U}_m\,, \tag{1}$$

where m and $m+1$ are the indices of two adjacent points on a grid. The matrix $\underline{\mathcal{R}}$ may be propagated with the equation

$$\underline{\mathcal{R}}_{m+1}=(2\underline{\beta}_m-\underline{\alpha}_{m-1}\underline{\mathcal{R}}_m)^{-1}\underline{\gamma}_{m+1}\,, \tag{2}$$

where $\underline{\alpha}$, $\underline{\beta}$, and $\underline{\gamma}$ are three matrices characteristic of the multichannel Numerov procedure.[2,6] The matching condition can be shown to be

$$\det|\underline{\alpha}_{m-1}\underline{\mathcal{R}}_m-2\underline{\beta}_m+\underline{\gamma}_{m+1}\underline{\mathcal{R}}_m|=0\,, \tag{3}$$

a relation which is reminiscent of that met in Cooley's method[7] for the one-channel problem, or equivalently

$$\det|\underline{\mathcal{R}}^{-1}_{m+1}-\underline{\mathcal{R}}_m|=0\,, \tag{4}$$

a relation which is reminiscent of that met in Johnson's renormalized Numerov approach to the bound-state coupled-channel problem.[2] In (3) and (4), $\underline{\mathcal{R}}$ and $\hat{\underline{\mathcal{R}}}$ result, respectively, from the outward and inward propagations. A noteworthy feature of such calculations is that the initial values of $\underline{\mathcal{R}}$ in the interior and exterior regions can be chosen somewhat arbitrarily: The memory of these initial values is rapidly lost as one progresses toward the classical region. It is in fact possible to choose simply $\underline{\mathcal{R}}\equiv 0$ as the boundary condition.

The next stage in order to deal with resonances instead of bound states is the introduction of both closed and open channels, with an initialization of $\underline{\mathcal{R}}$ for the open channels in the exterior region suggested by the Siegert form of the components. We take the open part of $\underline{\mathcal{R}}$ to be diagonal with

$$\underline{\mathcal{R}}_{ii}\propto\exp(ik_ih)\,, \tag{5}$$

where h is the propagation step and k_i the wave number in the ith open channel. The iterative matching procedure based on (3) and (4) converges now to a complex energy of the form $E=E_r-i\Gamma$, this being due to the fact that such boundary conditions can only be fulfilled with complex wave numbers. The initial values given to the matrix elements of $\hat{\underline{\mathcal{R}}}$ for the inward propagation [Eq. (5)] are modified iteratively through the relation linking each k_i to E.

The final stage is to transform r into $re^{i\theta}$ into the coupled equations. We have observed that one may either maintain the Siegert initialization in the open channels, or even start, for θ large enough, from *a zero initialization*. Just as for the bound-state case, the correct $\underline{\mathcal{R}}$ matrix is progressively built in as a result of the inward calculation. With a program following the latter prescription, bound states and resonances are treated exactly on the same footing, the matching procedure converging either to a real energy (within the accuracy of the calculation) in the former case or to a complex energy in the latter case.

II. ILLUSTRATIVE CALCULATIONS

As a first example, we consider the Fesbach resonances of a two-channel situation with an harmonic potential (the closed channel) intersected by a linear potential (the open channel). Analytic expressions for the widths and shifts of the resonances are available[8] in the limit of small interchannel coupling. In order to give some meaning to a Siegert initialization in the open channel, the linear potential is smoothly joined onto a decreasing exponential outside the interaction range. Table I gives the results for the three lowest resonances with the present technique, with the following variants:

(a) real coordinate, Siegert initialization,
(b) complex coordinate ($\theta = 0.5$ rad), Siegert initialization,
(c) complex coordinate ($\theta = 0.5$ rad), zero initialization.

A very satisfactory agreement with the analytical results (d) is observed in all cases, with, however, a somewhat better performance for the calculations with a complex rotation. We interpret this as meaning that with a real coordinate the initial $\underline{\mathcal{R}}$ matrix reduced to its open part given by Eq. (5) is only an approximate guess, while with rotation the initial $\underline{\mathcal{R}}$ matrix does not matter anymore. The inward $\underline{\mathcal{R}}$ matrices at the matching point in cases (b) and (c) are practically identical so that results of (b) and (c) are the same within the number of figures shown in the table. As another alternative, we let the potential of the open channel be linear for arbitrary r. With $\theta = 0.5$ rad and zero initialization the same results are obtained. It is also possible to perform a calculation (e) with no interchannel coupling, a complex coordinate, and zero initialization. This calculation performed under the same conditions as (c) leads to the bound energies of the harmonic potential, with spurious widths and shifts which are six orders of magnitude smaller than the widths and shifts of (c).

As a second example which is closer to the dynamics of a real molecular system, we have reconsidered the calculation of the photodissociation rate for a model linear triatomic molecule.[9,10] The initial state is represented by two coupled oscillators, while the various channels for dissociation correspond to the various eigenstates of one of these oscillators and the atom-diatom motion. These eigenstates can serve as a basis for expanding the wave functions of both the initial and the final states. With parameters appropriate for the ICN molecule it is observed[11] that an accurate value for the zero-point energy of the initial state can be obtained with four closed channels. The main channel for dissociation corresponds to the final-state oscillator in its zero-point level. The associated rates can be obtained from the phase shift in the open channel.[11]

Since this is a problem with two coordinates, say x and y, with the coupled equations determining a set of functions of x, the atom-diatom distance, we are faced in fact with two alternatives: (a) changing x *and* y into $\tilde{x} = xe^{i\theta}$ and $\tilde{y} = ye^{i\varphi}$ in the starting Hamiltonian $\mathcal{H}(x,y)$ and deriving from this transformed Hamiltonian a set of coupled equations in the variable $\tilde{x}$ and (b) changing x into $\tilde{x}$ in the set of coupled equations obtained from $\mathcal{H}(x,y)$. In alternative (a) the energy of the bound initial state can only be real after convergence has been attained. For instance the calculation restricted to one closed channel is necessarily yielding a $\tilde{y}$-dependent complex energy, this being due to the presence of some matrix elements depending on operators built from $\tilde{y}$. Results in Table II are to be read as follows: The column labeled $(\tilde{x}, \tilde{y})$ corresponds to alternative (a), with $\varphi = \theta = 0.01$ rad that labeled $(\tilde{x}, y)$ to (b), with $\theta = 0.01$ rad. The column (x, y) gives results obtained from the phase shift. The initial bound

TABLE I. Shifts (Δ) and widths (Γ) in cm^{-1} of the three lowest resonances ($v = 0, 1, 2$) of a harmonic potential intersected at the equilibrium distance by a linear potential of slope 65 000 cm^{-1}/A. The zero-point energy is 1000 cm^{-1}, the reduced mass 7.5 astons, and the interchannel coupling 10 cm^{-1}: (a) Coupled-channel approach with a real coordinate; (b) and (c) with a complex rotated coordinate; (d) analytical results; and (e) with no interchannel coupling. The numbers in parentheses are powers of ten.

	(a)		(b) or (c)		(d)		(e)	
v	Δ	Γ	Δ	Γ	Δ	Γ	Δ	Γ
0	0.470 97(−2)	5.405 26(−2)	0.468 30(−2)	5.456 89(−2)	0.468 35(−2)	5.456 77(−2)	0.4226(−8)	0.8408(−8)
1	−2.585 12(−2)	3.570 86(−2)	−2.601 53(−2)	3.596 17(−2)	−2.601 34(−2)	3.596 27(−2)	0.1590(−7)	0.2657(−7)
2	−3.304 82(−2)	2.616 45(−2)	−3.318 45(−2)	2.629 10(−2)	−3.318 32(−2)	2.629 33(−2)	0.3813(−7)	0.7265(−7)

TABLE II. Calculations for a model for the linear ICN molecule, with parameters given in Ref. 11, except for the interstate coupling which is ten times larger. All energies are in units of the zero-point energy of the final oscillator. n is the number of channels: $n \leqslant 4$, closed channels only; $n = 5$: four closed channels and one open channel. $(\tilde{x},\tilde{y})$ and $(\tilde{x},y)$: two variants of the complex coordinate method with zero initialization in the open channel. θ is 0.01 rad. (x,y): conventional phase shift analysis, the bound-state energies being obtained by extrapolation to zero coupling with an artificial open channel. The numbers in parentheses are powers of ten.

n	$(\tilde{x},\tilde{y})$	$(\tilde{x},y)$	(x,y)
1	$5.8734-i0.7258(-4)$	$5.8735-i0.1638(-9)$	5.8735
2	$5.8060-i0.1392(-2)$	$5.8061-i0.1193(-7)$	5.8061
3	$5.8003-i0.1950(-3)$	$5.8003-i0.1859(-7)$	5.8003
4	$5.8000-i0.1368(-4)$	$5.8000-i0.1922(-7)$	5.8000
5	$5.8012-i0.1723(-2)$	$5.8012-i0.1716(-2)$	$5.8011-i0.1687(-2)$
5	$5.4009-i0.2142(-2)$	$5.4009-i0.2139(-2)$	$5.4008-i0.2118(-2)$
5	$5.0003-i0.2441(-2)$	$5.0003-i0.2442(-2)$	$5.0003-i0.2440(-2)$
5	$4.5996-i0.2513(-2)$	$4.5996-i0.2516(-2)$	$4.5995-i0.2520(-2)$

state is studied with up to four channels, the two potential surfaces being placed in such a way that its energy should be 5.8 in units of the zero-point energy of the final oscillator. With $n = 4$, the spurious widths of methods $(\tilde{x},\tilde{y})$ and $(\tilde{x},y)$ are of the same order as the error on the real part of the energy. The fifth channels is the main dissociation channel. The resonance energies obtained with the three methods and $n = 5$ are in very close agreement. The widths are now several orders of magnitude larger than the spurious widths. The lowest three lines give the resonance energies for three other excitation energies, the unshifted initial energy being now 5.4, 5.0, or 4.6. The same close agreement is observed. A full account of this two-coordinate problem, with a description of the coupled equations solved in the various alternatives, will be published elsewhere.

As a word of conclusion we may say that the promise of the complex rotated coordinate method, which is to transform the wave function of resonances into localizable ones, opens not only the route to the use of linear expansions in bases of integrable functions[12] but also the route to a coupled-channel approach with bound-state boundary conditions. In such a procedure, the dependence of the energy versus the rotation angle is for a wide variation of this angle only due to possible inaccuracies in the computer code used to integrate the coupled equations. There is, therefore, no counterpart to the "trajectory study" of the linear expansion procedure.[12] Furthermore, the initialization problem in the exterior region is completely solved, while with a real coordinate there is only approximate knowledge of the initial form to be given to the matrix to be propagated.

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[12] See, for instance, for various illustrations of this technique, the special issue of Int. J. Quantum Chem. 14, 343ff (1978).