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Effective resolvent applied to interacting resonances

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Abstract. The wave operator theory of quantum dynamics is applied to characterize coupled metastable states. The theory extends to quasi bound states methods which are standard for dealing with bound levels. It is shown that interacting resonances can be investigated by means of small-dimensional effective Hamiltonians containing all the significant information of intrinsic properties which drive the various dynamical processes taking place. The study of the vibrational predissociation of I_2Ne, mediated by intramolecular energy redistribution, illustrates the power of the method. In addition to its accuracy to determine spectroscopic profiles and survival probabilities, it results more efficient than usual energy or time-domain numerical calculations.

PACS. 33.40.+f Multiple resonances (including double and higher-order resonance processes, such as double nuclear magnetic resonance, electron double resonance, and microwave optical double resonance) – 33.80.Gj Diffuse spectra; predissociation, photodissociation – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules

Introduction

In many areas of physics, transitory excited species are created and decay through one or several continua. The excitation can result from collisions, for example, with highly charged ions yielding a large variety of phenomena. More specific excitations can be produced by photons. These excited states are associated with resonances which have been extensively studied since many years. Powerful approaches have been developed which deal essentially with continuum functions, the close-coupling method being among the most widely used. Isolated resonances are usually associated with Lorentzian shapes characterized by their energy and width while much more intriguing shapes can be found for interacting resonances. This complexity reflects a dynamical evolution imprinted by the competition between reversible and irreversible processes corresponding to interactions between resonances and continua. Thus a rich variety of situations can be found as illustrated, in the simplest cases, by the various Fano profiles. The exciting interplay between reversibility and irreversibility is of paramount importance for the theory and challenges the various approaches.

Interacting resonance states will be investigated in the framework of the theory of wave operators [1] and effective Hamiltonians. For bound states, one arrives to effective Hamiltonians whose diagonalization leads to exact energies [2,3]. The theory was recently extended to dynamics and applied to isolated resonances [4]. The aim of this letter is to demonstrate how powerful is this approach for interacting resonances. It is not only efficient as compared with usual methods (close coupling, wave packet propagation...) to get accurate results for spectroscopy (absorption spectra) and dynamics (survival probabilities), but also provides, from the effective Hamiltonian, the intrinsic properties of the resonances. In our method, the wave operator establishes a one-to-one correspondence between n states of a model space and n solutions which are similar to the Gamow-Siegert states. In turn, Møller wave operators of scattering theory establish a one-to-one correspondence between plane waves and exact solutions [5].

The basic theory is briefly described in the following two sections, where the definition of the dynamical quantities of interest is also included. A numerical application to coupled resonances in the fragmentation of a van der Waals two-dimensional model system is given in the last section, the corresponding results being analyzed and discussed.

The effective resolvent

The wave operator theory of quantum dynamics focuses on projections of the resolvent onto a small-dimensional

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model space which contains the states which play an important role in the physical processes [1,4]. The model space is spanned by zero–order orthonormal quasi bound states $\{|\phi_i\rangle\}$, $i = 1, 2, ...n$ corresponding to the resonances. The projected resolvent, or effective resolvent, is written in the form

$$P_0 \frac{1}{z-H} P_0 = \frac{P_0}{z - H^{\mathrm{eff}}(z)} \cdot \qquad (1)$$

P_0 is the projector onto the model space:

$$P_0 = \sum_i^n |\phi_i\rangle\langle\phi_i|; \quad \langle\phi_i|\phi_j\rangle = \delta_{ij}; \quad i, j = 1, 2, ...n. \qquad (2)$$

z is the variable energy extended in the complex plane. H is the Hamiltonian of the system and $H^{\mathrm{eff}}(z)$ is the effective Hamiltonian defined in the model space. In the right-hand side of equation (1), the shorthand notation $P_0/(z - H^{\mathrm{eff}}(z))$ means the inversion of the operator $(z-H^{\mathrm{eff}}(z))$ in the model space. Projected resolvents were previously investigated by many authors most often by using partitioning techniques [6–10]. However, many developments remained rather formal, using simple models, without producing efficient computational schemes.

The effective Hamiltonian defined through equation (1) is energy-dependent and non-Hermitian. However it becomes meaningful when it depends as less as possible on the energy. For example, in the case of sharp resonances, the main structure of the projected resolvent is numerically dominated by a few poles in the second Riemann sheet ($\mathrm{Im}(z) < 0$) and the z-dependence can be neglected. This hypothesis corresponds, for isolated resonances, to Breit-Wigner profiles and exponential decays. This assumption concerning the energy dependence will be further considered for the case of two interacting resonances investigated in this letter. Under this assumption, the effective Hamiltonian may formally be expressed as

$$H^{\mathrm{eff}} = \sum_{i=1}^n E_i\, |\psi_i)(\psi_i|; \qquad (3)$$

$$(\psi_i|\psi_j) = \delta_{ij}; \quad i, j = 1, 2, ..., n. \qquad (4)$$

n is the dimension of the model space. The n eigenvalues E_i are complex energies corresponding to exact poles, and the representation of H^{eff} becomes a n-dimensional complex symmetric matrix. We have denoted by $(\,|\,)$ the symmetric inner product [11]. The spectroscopic and dynamical observables proceed immediately from equation (3). We define the relevant (projected) density of states corresponding to an initial state $|\phi\rangle$ and belonging to the model space by

$$\rho(E) = -\frac{1}{\pi}\mathrm{Im}\left\langle \phi \left| \frac{P_0}{E - H^{\mathrm{eff}}} \right| \phi \right\rangle \qquad (5)$$

$$= -\frac{1}{\pi}\mathrm{Im}\sum_{i=1}^n \frac{c_i^2}{E - E_i}; \qquad c_i = (\psi_i|\phi). \qquad (6)$$

$E = \mathrm{Re}(z)$ is the energy on the real energy axis. Hereafter we will use the term density of states for $\rho(E)$ instead of relevant (projected) density of states. The probability amplitude of remaining in the initial state, at time t, is given by the autocorrelation function

$$c(t) = \frac{1}{2\pi \mathrm{i}} \int_C \left\langle \phi \left| \frac{P_0}{z - H^{\mathrm{eff}}} \right| \phi \right\rangle \mathrm{e}^{\frac{-\mathrm{i}z}{\hbar}t}\, \mathrm{d}z \qquad (7)$$

$$= \sum_{j=1}^n c_j\, \mathrm{e}^{\frac{-\mathrm{i}E_j}{\hbar}t}, \qquad (8)$$

whose modulus squared provides the survival probability of the $|\phi\rangle$ state along time. The contour C runs from $+\infty$ to $-\infty$ on the real-energy axis.

Computation of the effective Hamiltonian

The key point of the method is the computational determination of the effective Hamiltonian which may be written in the form

$$H^{\mathrm{eff}}(z) = P_0 H \Omega(z). \qquad (9)$$

The wave operator is given by

$$\Omega(z) = P_0 + \frac{Q_0}{z-H} H P_0\ , \qquad (10)$$

where Q_0 is the projector onto the space which is orthogonal to the model space, *i.e.*, $Q_0 + P_0 = 1$ and $Q_0 P_0 = 0$. Again, $Q_0/(z - H)$ is a shorthand notation of $Q_0(z - H)^{-1}Q_0$. Expression (9) shows that, as for bound states, the calculation of an effective Hamiltonian requires the preliminary determination of the wave operator. To this end, we have used in this work a perturbation-iteration method which includes analytical continuation by means of an optical potential, leading to a complex-symmetric Hamiltonian matrix [12]. The procedure requires a computational effort proportional to nN^2, where n is the dimension of the model space and N is the dimension of the large matrix representing the Hamiltonian. The numerical efficiency of the method is strengthened by the performance of an iterative code which enables to determine several inner eigensolutions of large complex-symmetric matrices [13].

Numerical application in a two-dimensional realistic case

Interacting resonances can be found in van der Waals complexes, for example, when Intramolecular Vibrational Relaxation (IVR) interplays with fragmentation. These complexes are representative of molecular systems bound by heterogeneous interactions, *e.g.*, those formed by a conventional chromophore such as I_2, Br_2 or Cl_2 (at a vibrational level labelled by v) which is surrounded by one (or several) rare gas atom(s) loosely bound by van der Waals forces. Such systems are extensively experimentally studied: typically, after an optical excitation preparing the diatomic in

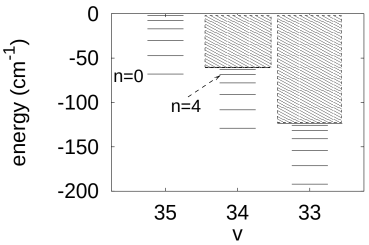

Fig. 1. Quasi bound states and continua in I_2Ne (T shape). v labels the vibrational levels related to the I–I coordinate and n those of the Ne–I_2 coordinate. $|35,0\rangle$ and $|34,4\rangle$ are the two resonance states investigated in this paper.

a precise electronic and vibrational state, there is a transfer of one or several vibrational quanta to the weak bond and the rare gas atom eventually evaporates [14]. For the lowest vibrational diatomic levels, the resonances are well isolated; they become coupled (IVR) typically near the closing threshold, that is, when at least two vibrational quanta must be released for the evaporation. We have considered here the high vibrational levels $v = 34$, 35 of the I_2Ne system in T shape and excited to the B electronic state of I_2. The resonance states are labeled $|v,n\rangle$, n being the quantum number associated with the Ne–I_2 stretching motion. As illustrated in Figure 1, we have a quite generic example of two interacting resonances. The $|\phi_1\rangle = |35,0\rangle$ and $|\phi_2\rangle = |34,4\rangle$ states are nearly degenerate and coupled to various quasi bound states and continua. Such a picture is frequently found in molecular physics (diexcited Rydberg states, collision with highly charged ions, nonadiabatic transitions...). The two resonance states $|\phi_1\rangle$ and $|\phi_2\rangle$, spanning the model space of dimension $n = 2$, will be investigated by using wave operators and effective Hamiltonians.

In the numerical application, the bidimensional Hamiltonian is written down in Jacobi coordinates. Regarding the potential, it is described as an addition of pairwise analytic interactions [15]. We used a basis set of 10 vibrational states for I_2 ($v = 28{-}37$) and a discrete variable representation (DVR) grid with 300 points for the coordinate describing the vibrational motion of Ne in the field of I_2, leading to $N = 3\,000$, the size of the large matrix representing the Hamiltonian. The computational scheme avoids the diagonalization of the full Hamiltonian matrix which would require a computational time proportional to N^3. Analytical continuation was done by adding a Complex Absorbing Potential (optical potential) in the dissociative coordinate [16]. Analytic continuation is also used in various approaches such as complex scaling [17] or CAP/CI [18]. As discussed above, the calculations were performed under the assumption that the effective Hamiltonian did not depend on the energy. The effective Hamiltonian $H^{\text{eff}}(z)$ was constructed for the value $z = 67$ cm^{-1} which is near the mean energy of the two resonances. We have checked that the observables do not depend on this choice and that they are also independent, at large extent, on the parameters of the absorbing potential. A nice advantage of the present approach is that it can handle simultaneously two or, in general, several interacting resonances and provides within a unified scheme both the density of states which can be compared with spectroscopic data and the associated autocorrelation functions which describe the dynamics.

Table 1. Three matrix representations of the effective Hamiltonian: (a) in the basis $|\phi_1\rangle = |35,0\rangle$, $|\phi_2\rangle = |34,4\rangle$. (b) In the representation which cancels the real part of the coupling. (c) in the diagonal representation which provides the poles of the Green operator (Siegert states). All matrix elements are in cm^{-1}.

(a)	$\begin{pmatrix} -68.20 - \mathrm{i}\,0.82 & -1.21 - \mathrm{i}\,0.07 \\ -1.21 - \mathrm{i}\,0.07 & -67.63 - \mathrm{i}\,0.02 \end{pmatrix}$
(b)	$\begin{pmatrix} -69.19 - \mathrm{i}\,0.58 & \mathrm{i}\,0.37 \\ \mathrm{i}\,0.37 & -66.67 - \mathrm{i}\,0.25 \end{pmatrix}$
(c)	$\begin{pmatrix} -69.16 - \mathrm{i}\,0.59 & 0 \\ 0 & -66.73 - \mathrm{i}\,0.25 \end{pmatrix}$

In the following, the initial state $|\phi\rangle$ may be any normalized linear combination of $|\phi_1\rangle$ and $|\phi_2\rangle$. Although in the present case only $|\phi\rangle = |\phi_1\rangle$ is a realistic choice because the transition dipole is a flat function of the Ne–I_2 coordinate, we will consider four cases to illustrate general situations. Let us examine the physical information contained in the effective Hamiltonian for the three representations (a), (b) and (c) reported in Table 1. The complex symmetric matrices are the fingerprints of the underlying dynamics of the decaying resonances. In the basis of the states $|\phi_1\rangle$ and $|\phi_2\rangle$, the matrix representation (a) shows that the static interaction between the two states is about 1 cm^{-1} which is much larger than the imaginary part -0.07 cm^{-1} of the coupling. The diagonal representation (c) provides the complex energies of the Siegert states specifying their position and width, while the intermediate representation (b) gives the most illustrative representation describing the system in terms of two dynamically weakly-coupled resonances. In representation (b) the real part of the coupling was suppressed by a real rotation of the basis functions $|\phi_1\rangle$ and $|\phi_2\rangle$ within the model space. The remaining purely imaginary interaction term characterizes the coupling through the continua between the two resonances [19] whose energies and widths remain close to those of the Siegert states. This imaginary term measures the deviation from Lorentzian profiles and therefore contains a true physical information. As usual when mainly one continuum channel is involved in the dissociation, $v = 33$ in the present case, its value is very close to the square root of the product of the two widths. Thus the dynamics of these van der Waals states can be described in terms of two weakly-interacting resonances, the parameters of which were here directly extracted from the Hamiltonian without any empirical or semiempirical parameterization [19]. In textbooks, resonances are often investigated by means of model Hamiltonians with real coupling terms whereas, from our study, a purely imaginary coupling emerges which can be obtained only by analytical continuation [20].

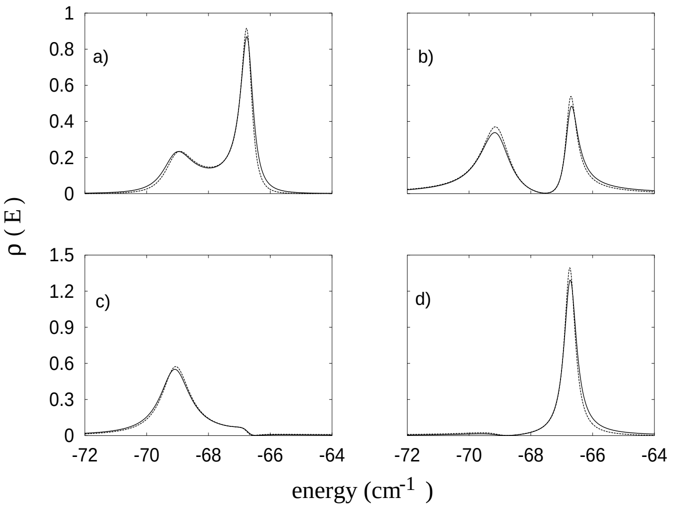

Fig. 2. Density of states for four initial conditions: (a) $|\phi\rangle = |\phi_1\rangle$, (b) $|\phi\rangle = |\phi_2\rangle$, (c) $|\phi\rangle = (|\phi_1\rangle + |\phi_2\rangle)/\sqrt{2}$, (d) $|\phi\rangle = (|\phi_1\rangle - |\phi_2\rangle)/\sqrt{2}$. Full line: effective resolvent method, equations (5, 6); dotted line: close-coupling calculation.

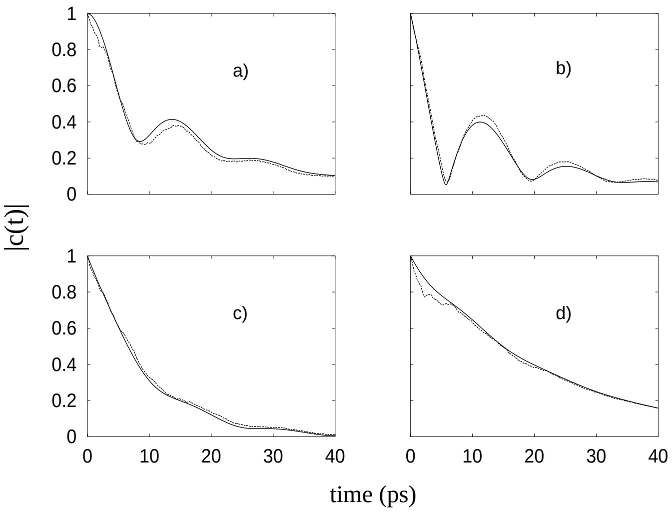

Fig. 3. Modulus of the autocorrelation function for the four initial conditions of Figure 2. Full line: effective resolvent method, equations (7, 8); dotted line: wave packets propagation.

Since our approach provides simultaneously data relevant for spectroscopy and for dynamics, we have represented on the same footing in Figures 2 and 3, the density of states and the moduli of the associated autocorrelation functions proceeding from four distinct initial conditions. We have clearly non-Lorentzian shapes related to non-exponential decays. The effective resolvent results are compared, in Figure 2, to accurate close-coupling calculations [21] in the energy domain (absorption spectrum) and, in Figure 3, to a direct determination of the autocorrelation function from wave packet propagations in the time domain [22]. There is an excellent agreement between the results obtained independently by the various methods, the small discrepancies coming essentially from computational details. This agreement illustrates the numerical accuracy of our method and grounds it for other realistic applications.

About the computational cost, it is the lowest for the present method where the main effort consists in calculating the wave operator, which has taken about 10 minutes on a personal computer. A similar time was necessary for the close-coupling calculation but at each initial condition and it do not yield the dynamics, whereas the wave packet propagation, performed with a usual optimized Chebyshev propagator, required several hours. Therefore our approach combines the advantages of the smallest computational effort and the above underlined capabilities of a direct interpretation of spectroscopic and dynamical observables.

Conclusions

Unlike scattering theory which privileges asymptotic states and phase shifts due to the resonances and continua, our approach focuses on localized quasi bound states. The theory, the computational techniques and the interpretation schemes are a direct generalization of standard methods which were found to be so successful for bound states. The method of moments (Lanczos recursion algorithm) provides also stable and accurate results and is able to determine many interacting resonances. Our method is also general. Besides the two resonances presented above, it was easy to extend the calculations to several resonances and their couplings arising from many quasi bound states in I_2Ne. We do not present them here, because it does not essentially provide any new information. The methods of moments basically use repeated matrix by vector multiplications without any discrimination among the energies. A great computational advantage of the perturbation-iteration method with respect to the method of moments, or similar methods, is that the number of iterations is typically 20, instead of, for example, several thousands reported in reference [23], where, however, many more resonances were determined. An important interest of our approach is to focussed the calculation on a restricted number of resonances, almost without loss of accuracy. In conclusion, the power of the method is to combine computational efficiency with the simultaneous determination of the main observables characterizing the resonances in the energy range of interest. In addition, the effective resolvent produces appealing physical insight. Therefore, we consider that the method offers an elegant and efficient alternative to the usual close-coupling and time-dependent wave-packet approaches.

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