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Full-angular-momentum, three-dimensional, smooth-exterior complex dilated, finite-element method for computing resonances in triatomic molecules: Application to a model of the NeICl van der Waals complex

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By combining a total-angular-momentum representation, the smooth-exterior complex dilation technique and a three-dimensional finite-element code, a study of some resonances in a model of an electronic surface of the van der Waals complex NeICl was performed. For zero angular momentum, our results show good agreement with earlier calculations. Using the present formalism we believe that we are able to report a fully quantum-mechanical calculation of predissociation widths for a triatomic molecule.

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Resonant states have for a long time been suspected and have very recently been shown to play an important role in chemical reaction dynamics [1]. Studies of van der Waals complexes provide important information on intermolecular forces and on intermolecular energy transfer [2]. Several experimental studies have accordingly been conducted in electronically excited states of triatomic systems involving a rare-gas atom and two halogen atoms [3,4].

The energy interval between two close rotational levels of many triatomic molecules are less than 1 cm^{-1}. Thus, the influence of nonzero-momentum levels should be accounted for when comparing theory and experiment. The present letter reports a method that will allow such studies.

A number of theoretical studies of the zero angular momentum levels of the NeICl system have been performed during the last few years [5–9] using the same potential. Previously, quantum-mechanical studies of predissociation phenomena in triatomic molecules do not, to our knowledge, use a Hamiltonian that has a nonzero total angular momentum.

Tennyson and coworkers [10–15] solve the same equations as we do but have not yet, to our knowledge, treated any predissociation problems. Kendrick *et al.* [16–18] use a symmetrized hyperspherical-coordinate discrete-variable and finite-basis representation method to compute cross sections including nonzero angular momentum levels in the H_2D collision complex. Castillo and Manoloppoulos [19] use an exact hyperspherical-coordinate method that involves nonzero angular momenta for the collision complex to compute cross sections for the F+HD reaction. The adiabatic rotation approximation method of Carter and Bowman [20] plus a complex $\mathcal{L}^2$ modification have, on the other hand, been used to compute rovibrational energies and widths in the HCO [21,22] and HOCl [23–25] molecules. While both we and Tennyson *et al.* [10] include the exact Hamiltonian in our formalism, the latter authors [20] use an approximate method that they have analyzed and motivated.

With this paper we want to demonstrate how a recently developed method [26,27] based on an exact Hamiltonian is capable of computing eigenenergies, associated predissociation widths, and eigenvectors for rovibrational levels associated with a single electronic surface of a triatomic molecule. We first show that this method is capable of producing complex energies for first three rotationless vibrational levels associated with the ICl, $B\,{}^3\Pi_{0^+}$, $v=2$ vibrational level of a Morse potential model of the NeICl molecule in good agreement with previously published studies [8,9]. Energies and predissociation widths for the three lowest nonzero angular momenta (J) including all their projections (M) of the above mentioned three vibrational levels are then presented.

The total wave function Ψ^{JM} of any system with the angular momentum J and its projection M can be expanded in terms of Wigner D-functions $D^J_{Ms}(\alpha,\beta,\gamma)$ [28,29]:

$$\Psi^{JM}_{\tau}=\sum_{s}^{J}\frac{1}{\sqrt{2+2\delta_{s0}}}[D^J_{Ms}+\tau(-1)^s D^J_{M-s}]\psi^{(Js)}_{\tau}(\mathbf{R}). \tag{1}$$

The Euler angles α, β, and γ define a rotation of the body fixed frame with respect to the laboratory fixed one and $\mathbf{R}$ is a three-dimensional coordinate in the body fixed frame. The index s varies as $s=0,1,\ldots,J$ for the positive parity $\tau=+1$ and as $s=1,\ldots,J$ for $\tau=-1$. In the following, we omit the parity for sake of simplicity.

To describe the body fixed coordinate $\mathbf{R}$, we have here chosen Jacobi coordinates. Let particles 1, 2, and 3 represent the Ne, I, and Cl atoms, respectively. Then x is the distance between particles 2 and 3 (i.e., Cl and I atoms), y is the distance between particle 1 (Ne atom) and the center of mass of pair (23) and ϕ is the angle between $\mathbf{x}$ and $\mathbf{y}$.

After substituting expansion (1) into the Schrödinger equation and using an orthogonality relation for D function [28], one can derive the system of equations [29]:

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$$\begin{aligned}
&-\imath\sqrt{1+\delta_{s1}}\frac{\lambda_-(J,s)}{\mu_{1,23}y^2}\left[\frac{\partial}{\partial\phi}+(1-s)\cot\phi\right]\psi^{(Js-1)}\\
&-\left[\frac{1}{\mu_{1,23}}\left(\frac{1}{y}\frac{\partial^2}{\partial y^2}y-\frac{J(J+1)-2s^2}{y^2}\right)+\frac{1}{\mu_{23}}\left(\frac{1}{x}\frac{\partial^2}{\partial x^2}x\right)\right.\\
&+\left(\frac{1}{\mu_{1,23}y^2}+\frac{1}{\mu_{23}x^2}\right)\left(\frac{\partial^2}{\partial\phi^2}+\cot\phi\frac{\partial}{\partial\phi}-\frac{s^2}{\sin^2\phi}\right)\\
&\left.+V(x,y,\phi)-z\right]\psi^{(Js)}-\imath\sqrt{1+\delta_{s0}}\,\frac{\lambda_+(J,s)}{\mu_{1,23}y^2}\\
&\times\left[\frac{\partial}{\partial\phi}+(1+s)\cot\phi\right]\psi^{(Js+1)}=0, \qquad (2)
\end{aligned}$$

where $\lambda_\pm(J,s)=[J(J+1)-s(s\pm1)]^{1/2}$ and $\psi^{(J-1)}\equiv0$. The reduced masses μ have been defined in terms of the particle masses m_i as $\mu_{23}=m_2m_3/(m_2+m_3)$, $\mu_{1,23}=m_1(m_2+m_3)/[m_1+(m_2+m_3)]$. The components $\psi^{(Js)}$ must satisfy the boundary conditions with respect to the angle ϕ so that

$$\psi^{(Js)}(x,y,\phi)=\sin^s\phi\,\tilde{\psi}^{(Js)}(x,y,\phi), \qquad (3)$$

where $\tilde{\psi}^{(Js)}(x,y,\phi)$ is a bounded function of its arguments. A most important property of the set of equations (2) is that they couple the three components $\psi^{(Js-1)}$, $\psi^{(Js)}$, and $\psi^{(Js+1)}$ only.

The total potential $V(x,y,\phi)$ is the sum of three pair atom-atom pair potentials of the Morse type [5].

To calculate resonant energies $z=E-\imath(\Gamma)/(2)$ with the complex scaling (CS) method, we should replace the real-valued three-dimensional coordinate **R** by its complex analogue. In fact, only the magnitudes x and y of the vectors have to be scaled [30]. In the present case it is sufficient to scale the Ne-ICl coordinate, y, since the ICl subsystem remains bound. We define the transformation of x as follows [31]:

$$x\rightarrow\xi(x)=x+\lambda g(x),$$

where

$$g(r)=\begin{cases}0, & r\leqslant R_0\\ (r-R_0)\{1-\exp[-\sigma(r-R_0)^2]\}, & r>R_0\,.\end{cases} \qquad (4)$$

Here, $\lambda=\exp(\imath\theta)-1$, θ is a rotation angle, R_0 is the external radius, and σ is the curvature parameter. Both the function and its derivative are continuous at R_0. The angular variable ϕ is obviously not changed by the transformation. The representation of the Hamiltonian in these complex coordinates can be found in Ref. [27].

It is well known that positions and widths of resonances are independent of the rotation angle θ. When a numerical approximation is used, resonances become θ dependent. In this case, their positions E and widths Γ are defined by means of the complex variational principle [32].

TABLE I. Parameters of two-body Morse potentials. The masses adopted are $m_{Ne}=20.18$ amu, $m_I=126.9$ amu, and $m_{Cl}=34.97$ amu.

	$D(\mathrm{cm}^{-1})$	β (Å^{-1})	r^{eq} (Å)
Ne-I	26.0	1.80	5.40
Ne-Cl	34.7	1.90	3.61
I-Cl	1270.4	3.96	2.66

Numerically we have realized Eq. (2) using the finite-element method (FEM). A detailed description of our FEM implementation can be found elsewhere [33–35]. The accuracy of the present method has earlier been tested in studies of the helium atom [27] and the antiprotonic helium system [26,36].

The mesh used in the calculations was fixed to meet convergence criteria. The one-dimensional basis functions of the angular variable $c=\cos\phi$ were chosen to be associated Legendre polynomials $P_i^s(c)$ for each component $\psi^{(Js)}$. Then the boundary conditions (3) are correctly taken into account. For the Ne-ICl (y) direction we chose to have exponentially weighted Legendre polynomials on 28 elements within the interval $y_{min}=4$ a.u., $y_{max}=32$ a.u.. The maximum polynomial degree in y direction was fixed to be 6. One single element was used to describe the ICl coordinate (x). It covered $x_{min}=4$ a.u. to $x_{max}=6.5$ a.u. In this direction we used four Morse type functions. In convergence studies, we used up to eight Morse type functions. The external radius R_0 coincides with one of the box boundary and is equal to 16.6 a.u. When properly chosen [27], the curvature parameter σ weakly influences the results. We use the value $\sigma=1.0$.

The formalism, discussed above, yielded sparse matrices of dimension 11 900 with a total bandwidth of 1074 for each component. The code development work were performed on a DEC/Alpha 433 a.u. workstation using 64 bit precision. The final results were obtained on a parallel IBM SP2 Nighthawk 8 node computer with the same precision. While the total computer time for the DEC/Alpha 433 a.u. workstation was of the order of 24 hours for obtaining a few eigenvalues, the IBM SP Nighthawk requires only about three hours for the same task.

Let us now discuss the NeICl resonances. The parameters of potential are taken from Ref. [5] and given in Table I. To facilitate comparison with the results of Refs. [8,9], we relate the computed resonance energies to the energy of the $v=0,J=0$ level of ICl system. The $v=0$, 1, and 2 levels of this system lie at 108.269 cm^{-1}, 310.343 cm^{-1}, and 493.132 cm^{-1}, respectively, above the zero of ICl potential.

In Table II, we present our results for the first ten resonances of a total of 30 reported in Refs. [8,9]. For zero angular momentum, we are in close agreement with results obtained by the complex scaling discrete variable representation method [8], the modified stabilization method [8], and the optical potential discrete variable representation method [9]. Small differences exist in the second decimal of the real part with one exception for the tenth resonance. Although the real parts almost coincide with each other, the imaginary part varies considerably.

TABLE II. Comparison of our results E_n^{our} for $J=0$ and the results of (a) the complex scaling discrete variable representation method (CSC-DVR) [8], (b) the modified stabilization method (Mod.St.) [8], and (c) the optical potential discrete variable representation method (OP-DVR) [9]. Numbers in square brackets denote powers of 10.

E_n^{our}	Γ_n	$E_n^{a,b,c}$	$\Gamma_n^{\text{CSC-DVR}}$	$\Gamma_n^{\text{Mod. St.}}$	$\Gamma_n^{\text{OP-DVR}}$
342.531	2.52[−3]	342.544	1.83[−3]	2.07[−3]	2.02[−3]
350.033	1.77[−3]	350.072	9.83[−4]	1.17[−3]	1.08[−3]
354.516	1.20[−3]	354.540	8.61[−4]	9.51[−4]	8.91[−4]
358.522	1.42[−3]	358.551	1.41[−3]	1.73[−3]	1.60[−3]
362.565	1.19[−3]	362.541	6.19[−4]	6.79[−4]	6.41[−4]
364.539	3.16[−3]	364.541	2.64[−3]	2.99[−3]	3.01[−3]
366.631	7.52[−4]	366.659	6.80[−4]	9.00[−4]	7.09[−4]
367.290	1.84[−4]	367.284	2.21[−4]	3.67[−4]	2.43[−4]
368.055	3.66[−4]	368.035	5.75[−4]	7.82[−4]	6.49[−4]
369.126	5.40[−4]	369.047	9.10[−4]	9.65[−4]	1.00[−3]

Both previous studies [8,9] involve representations of the ICl motion in form of basis set expansions fitted to give a correct eigenvalues for the ICl subsystem. Here we use Morse-type functions that are the analytical solutions of the two-body ICl Hamiltonian. Hence, they provide both accurate eigenenergies and eigenfunctions. We further used 4–6 Morse-type functions, representing $v=0,1,2,\ldots,5$ in the expansion of the ICl motion within the NeICl molecule. We find that we get converged results for four Morse functions already.

Nonzero angular-momentum results corresponding to the three lowest levels are presented in Table III. We show the results obtained with the solution of the entire set of equations (2). This implies that the Js component is coupled to the $Js\pm1$-components that in turn are coupled to the $Js\pm2$-components, etc. The nonzero angular-momentum levels were calculated on the same mesh as the corresponding zero angular momentum levels. Note that the present method and code was used to compute energy for high-angular momentum ($J\approx40$) energy levels of antiprotonic helium [26]. These results yielded transition energies that predicted measured, corrected to the zero pressure, experimental transition energies within the experimental accuracy of 4 ppm. Hence, the obtained here absolute accuracy for nonzero NeICl angular momentum levels is the same as for the zero angular momentum levels within the present NeICl model. To our knowledge, there are no data available from other studies with which we can compare these results. We present the results for the three lowest resonances that are well separated (in comparison with higher-resonance states) and almost noninterfere with each other. The energy-level spectrum obtained has a form that agrees in general with common ex-

TABLE III. Nonzero angular-momentum energy levels with the total angular momentum J, parity τ, and the helicity quantum number s. Numbers in square brackets denote powers of 10.

$J(\tau)$	s	E_1	Γ_1	E_2	Γ_2	E_3	Γ_3
0(+)	0	342.531	2.52[−3]	350.033	1.77[−3]	354.516	1.20[−3]
1(−)	1	342.823	2.48[−3]	350.563	1.80[−3]	356.022	1.44[−3]
1(+)	0	342.585	2.52[−3]	350.083	1.76[−3]	354.563	1.20−3]
	1	342.820	2.48[−3]	350.561	1.81[−3]	356.019	1.44[−3]
2(−)	1	342.866	2.50[−3]	350.605	1.79[−3]	356.066	1.42[−3]
	2	343.646	2.32[−3]	351.808	1.95[−3]	357.878	1.48[−3]
2(+)	0	342.691	2.52[−3]	350.183	1.75[−3]	354.657	1.19[−3]
	1	342.923	2.48[−3]	350.659	1.81[−3]	356.115	1.43[−3]
	2	343.625	2.32[−3]	351.787	1.94[−3]	357.863	1.48[−3]
3(−)	1	342.984	2.50[−3]	350.716	1.79[−3]	356.177	1.40[−3]
	2	343.769	2.32[−3]	351.926	1.95[−3]	357.997	1.46[−3]
	3	344.942	2.12[−3]	353.560	2.10[−3]	359.909	1.48[−3]
3(+)	0	342.851	2.52[−3]	350.332	1.73[−3]	354.798	1.18[−3]
	1	343.079	2.48[−3]	350.807	1.81[−3]	356.259	1.42[−3]
	2	343.786	2.32[−3]	351.941	1.95[−3]	358.015	1.46[−3]
	3	344.914	2.12[−3]	353.535	2.10[−3]	359.889	1.48[−3]

perimental spectra of asymmetric top triatomic molecules [37,38]. The widths for the same parity depend smoothly on the helicity number *s* and are almost independent of the total angular momentum *J*. The full material including higher *J* levels for the series presented in Ref. [9] will be reported in a more extensive forthcoming paper.

In conclusion, we report here a method by which we can accurately compute energy levels and their predissociation widths for a single potential triatomic problem. Widths obtained so far show a smooth variation with the rotational quantum numbers, the parity, and the helicity quantum number for the lowest resonance states.

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