Distributed complex Gaussian basis sets: A useful function space for the solution of predissociation problems via the complex eigenvalue Schrödinger equation. Application to the isotope effect of NeH, NeD

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A method is presented for the solution of the complex eigenvalue Schrödinger equation for predissociation resonances, employing a basis set of complex Gaussians, with centers distributed along the internuclear axis. Application to the predissociation of the $v=0$ level of the $A\,^2\Sigma^+$ state of HeH, $v=0$–4 level of the $A\,^2\Sigma^+$ state of NeH and all the vibrational levels of he $A\,^2\Sigma^+$ state of NeD have yielded widths that are in very good agreement with the available experimental values and the recent observations [Devynck, Graham, and Peterson, J. Chem. Phys. **91**, 6880 (1989)] of the strong suppression of predissociation in NeD as compared to that of NeH.

INTRODUCTION

The predissociation phenomenon is associated with a nonstationary molecular state decaying via a nonradiative transition into a vibrational continuum. The corresponding intrinsic observables, the energy and the width (lifetime), are computable from a complex eigenvalue Schrödinger equation with outgoing-wave boundary conditions that can be made square-integrable by perturbing the boundary condition in the asymptotic region via the transformation[1–4]

$$R \rightarrow \rho = Re^{i\theta}. \tag{1}$$

The transformation (1) does not, of course, alleviate the necessity of handling real molecules in terms of advanced computational methods that treat reliably the electronic structure problem (potential energy surfaces and wave functions plus coupling) in addition to that of the continuous spectrum. The present paper presents a method for the study of predissociation in diatomic molecules and an application to decaying states of NeH and NeD.

According to the state-specific, complex-eigenvalue theory (SSCET) of resonances,[1,2,9–12] the important element for the analysis and efficient solution of the multiparticle complex-eigenvalue Schrödinger equation (CESE) is the possibility of defining and separately optimizing square-integrable function spaces representing the localized and the asymptotic components of the resonance. A good choice of such function spaces allows the reliable computation of the unshifted real energy and its analytic continuation into the complex energy plane.[1,2,4]

Recently,[13] we implemented the SSCET for the study of polyelectronic predissociating states of diatomic molecules. In this method the basis set consisted of Gaussian-type orbitals (GTO) of the form

$$\Phi_l(\rho) = \left(\frac{2^{l+1}\sqrt{2A_i}^{\,2l+1}}{(2l+1)!!\pi}\right)^{1/2} \times (Re^{i\theta})^l \exp\left(-A_l e^{2i\theta}R^2\right), \quad \begin{matrix} 0<R<\infty, \\ 0\leqslant\theta\leqslant\pi/4, \end{matrix} \tag{2}$$

centered at the origin and all the integrals were evaluated from zero to infinity. With this type of basis there is the restriction that at most 14–15 functions may be used since the numerical accuracy of any double precision computer is inadequate for the satisfactory orthonormalization of more than 15 functions. A calculation of the predissociation of the $v=0$ level of the $A\,^2\Sigma^+$ state of HeH (Ref. 13) showed that a number of 10–12 functions sufficed for stabilization. However, in general, a numerically imposed limitation of 15 functions is undesirable.

A type of basis set that can avoid such restrictions is the Distributed Gaussian Type Orbitals[14–17] (DGTO) basis set

$$\varphi_i(R) = (2A_i/\pi)^{1/4} \times \exp[-A_i(R-R_i)^2], \quad -\infty<R<+\infty, \tag{3}$$

where the overlap integrals among these functions may be controlled from the coefficients A_i, A_j of the exponents and the difference $(R_i - R_j)$ between the centers of the ith and jth function, respectively,

$$\begin{aligned} S_{ij} &= \langle\varphi_i(R)|\varphi_j(R)\rangle \\ &= [4A_iA_j/(A_i+A_j)^2]^{1/4} \\ &\quad \times \exp\left[-(A_iA_j/(A_i+A_j))(R_i-R_j)^2\right]. \end{aligned} \tag{4}$$

Making the simple observation that the complex rotated functions

$$\varphi_i(Re^{i\theta}) = (2A_i/\pi)^{1/4} \times \exp\left[-A_i(Re^{i\theta}-R_i)^2\right], \quad \begin{matrix} -\infty<R<\infty, \\ 0\leqslant\theta\leqslant\pi/4, \end{matrix} \tag{5}$$

have the same overlap as the unrotated ones,[1] the considerations regarding the linear dependence problems also hold for Rotated Distributed Gaussian Type Orbitals (RDGTO) which are required for the continuum part of the resonance.

Using these RDGTO for a basis set, we have developed a practical method for the solution of the CESE along the lines of our previous work.[13] We applied this new basis set to the

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predissociation problem of the $v=0$ level of the $A\,^2\Sigma^+$ state by the $X\,^2\Sigma^+$ state of HeH as well as of several vibrational levels of the $A\,^2\Sigma^+$ state of NeH and NeD. Previous calculations,[18,19] based on the golden rule formula, found a very strong isotope effect in the above systems with a rate of predissociation in NeH almost two orders of magnitude larger than in NeD. Recent experimental observations[20] are in general agreement with the theoretical results.

It is thus of interest to calculate the predissociation rates in NeH and NeD by the present new method in order to make a comparison with the aforementioned findings and establish its level of efficiency and reliability.

II. METHOD

The total zeroth-order molecular wave function is written as a product of the electronic and the nuclear components following the Born–Oppenheimer approximation,

$$\Psi = \Psi_{\rm el}\Psi_{\rm nu}, \tag{6}$$

while the total Hamiltonian is expressed as a sum of the electronic and nuclear Hamiltonian

$$H = H_{\rm el} + H_{\rm nu}. \tag{7}$$

The nuclear part of the wave function is calculated in the adiabatic potential provided by the solution of the electronic Schrödinger equation. The interaction between two product functions of Eq. (6) is given by

$$M_{12} = \langle \Psi^1_{\rm nu} | \langle \Psi^1_{\rm el} | H^{\rm int}(R) | \Psi^2_{\rm el}\rangle | \Psi^2_{\rm nu}\rangle, \tag{8}$$

where the inner integral involving the electronic wave functions must be evaluated for many values of the internuclear coordinate R. The coupling operator $H^{\rm int}(R)$ involves interactions that have not been included in the operator H of Eq. (7) such as radial coupling, spin-orbit, rotational electronic coupling, etc.

The resonance wave function is separated into two parts.[1,2,9–12]

$$\Psi(\rho) = \alpha(\theta)\Psi_0(\rho) + b(\theta)\chi(\rho), \tag{9}$$

with

$$\rho = Re^{i\theta}, \quad 0<\theta<\pi/2,$$

where Ψ_0 is the initially localized component of the wave function corresponding to a vibrational level of a bound electronic state and X is the "scattering" (unbound) part of Ψ. By rotating the coordinates in the complex plane, the resonance wave function becomes square-integrable. Then, since Ψ_0 is also square-integrable, the "scattering" function $X(\rho)$ can be expanded in a basis of square-integrable functions with real coordinates[10–12]

$$X(\rho) = \sum_i c_i(\theta)\varphi_i(R). \tag{10}$$

The complex coefficients that appear in Eqs. (9) and (10) now can be determined by the solution of the non-Hermitian matrix eigenvalue problem in the basis of the functions $\{\Psi_0(\rho),\varphi_i(R)\}$,

$$\mathbf{HC} = z\mathbf{SC}, \tag{11}$$

with $\mathbf{S}$ = the overlap matrix and the eigenvalue z corresponding to the resonance,

$$z = E_0 + \Delta - i(\Gamma/2), \tag{12}$$

where E_0 is the energy of the vibrational level described by the Ψ_0 wave function, Δ is the energy shift, and Γ is the total linewidth of this level due to the interaction [Eq. (8)] of the vibrational level with the adjacent continuum of a repulsive electronic state.

Using the identity,[1]

$$\langle \Psi_i(\rho)|H(\rho)|\Psi_j(\rho)\rangle = \langle \Psi_i(R)|H(R)|\Psi_j(R)\rangle, \tag{13}$$

where Ψ_i,Ψ_j are square-integrable functions, and the back rotation transformation (Refs. 4,10,11) is $\theta\to-\theta$, we have the following expressions for the Hamiltonian matrix elements.

(a) The first diagonal matrix element involving only Ψ_0,

$$H_{11} = \langle \Psi_0(\rho)|H_b(\rho)|\Psi_0(\rho)\rangle = \langle \Psi_0(R)|H_b(R)|\Psi_0(R)\rangle = E_0, \tag{14}$$

where for the calculation of $\Psi_0(R)$ we employ an expansion in a basis set of equally distributed real Gaussian functions[14] [Eq. (3)]. The Hamiltonian operator is

$$H_b(R) = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + V_b(R), \tag{15}$$

where V_b refers to the adiabatic bound potential and μ is the reduced mass of the system. Analytic fits to the calculated points in a basis set of sin and cos functions are employed for $V_b(R)$. The matrix elements over the basis of DGTO [Eq. (3)],

$$V^b_{ij} = \langle \varphi_i(R)|V_b(R)|\varphi_j(R)\rangle, \quad i,j=1,N, \tag{16}$$

are evaluated by the Hermite quadrature method.[14] Analytic formulas are employed for the overlap matrix elements

$$S^b_{ij} = \langle \varphi_i(R)|\varphi_j(R)\rangle \tag{17}$$

and also for the nuclear kinetic energy matrix elements

$$T^b_{ij} = \left\langle \varphi_i(R)\left| -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}\right|\varphi_j(R)\right\rangle \quad i,j=1,N. \tag{18}$$

(b) The interaction matrix elements between Ψ_0 and the continuum functions $\{\varphi_i\}$,

$$H_{1i} = H_{i1} = \langle \Psi_0(\rho)|H^{\rm int}(\rho)|\varphi_{i-1}(R)\rangle = \langle \Psi_0(R)|H^{\rm int}(R)|\varphi_{i-1}(\rho^*)\rangle, \tag{19}$$

where ρ^* is the complex conjugate of ρ and $\varphi(\rho)$ has been defined in Eq. (5). In the present development radial coupling between the adiabatic states will be considered:

$$H^{\rm int}(R) = -\frac{1}{\mu}A(R)\frac{\partial}{\partial R} \tag{20}$$

and

$$A(R) = \left\langle \Psi^b_{\rm el}\left|\frac{\partial}{\partial R}\right|\Psi^r_{\rm el}\right\rangle, \tag{21}$$

where b stands for "bound" and r for "repulsive." Fitting the $A(R)$ operator in a basis set of Slater-type orbitals (STO) we obtain

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$$H_{1i}^{\text{int}} = \sum_{j=1} C_{1j} \left(\frac{4A_iA_j}{(A_i + A_je^{2i\theta})^2} \right)^{1/4} 2A_je^{i(3\theta/2)} \left[\sum_{k=1}^{\text{NSTO}} C_K^0 \exp\left(\frac{[2(A_iR_i + A_jR_je^{i\theta}) - \alpha_k^0]^2}{4(A_i + A_je^{2i\theta})} - (A_iR_i^2 + A_jR_j^2) \right) \times \left(R_j - \frac{e^{i\theta}}{(A_i + A_je^{2i\theta})} \frac{2(A_iR_i + A_jR_je^{i\theta}) - \alpha_k^0}{2} \right) \right], \quad (22)$$

where C_k^0 and α_k^0 are the coefficients of the STO expansion and the coefficients of the STO exponents, respectively.

(c) Matrix elements involving the repulsive potential only,

$$H_{ij} = H_{ji} = \langle \varphi_{i-1}(R) | H_r(\rho) | \varphi_{j-1}(R) \rangle = \langle \varphi_{i-1}(\rho^*) | H_r(R) | \varphi_{j-1}(\rho^*) \rangle, \quad i,j \neq 1, \quad (23)$$

where $H_r(R)$ is as $H_b(R)$ [Eq. (15)] but with $V_r(R)$, the repulsive adiabatic potential, instead of $V_b(R)$.

So for the kinetic energy we have the analytic expression

$$T_{ij}^r = \frac{e^{2i\theta}S_{ij}}{\mu} \frac{A_iA_j}{(A_i + A_j)} \left(1 - 2\frac{A_iA_j}{(A_i + A_j)} (R_i - R_j)^2 \right), \quad (24)$$

where S_{ij} is given by Eq. (4), while for the potential energy, after a fit with STO for the $V_r(R)$ operator,

$$V_{ij}^r = \left(\frac{4A_iA_j}{(A_i + A_j)^2} \right)^{1/4} \sum_{K=1}^{\text{NSTO}} C_K^r \times \exp\left(\frac{[2e^{i\theta}(A_iR_i + A_jR_j) - \alpha_k^r]^2}{4(A_i + A_j)e^{2i\theta}} - (A_iR_i^2 + A_jR_j^2) \right), \quad (25)$$

where C_k^r and α_k^r are the coefficients from the STO fit. The matrix element of the overlap S in Equation (11) are

$$S_{11} = \langle \Psi_0(R) | \Psi_0(R) \rangle \langle \Psi_{\text{el}}^b | \Psi_{\text{el}}^b \rangle = 1, \quad (26)$$

$$S_{1i} = S_{i1} = \langle \Psi_0(R) | \varphi_{i-1}(R) \rangle \langle \Psi_{\text{el}}^b | \Psi_{\text{el}}^r \rangle = 0, \quad i \neq 1, \quad (27)$$

$$S_{ij} = \langle \varphi_{i-1}(R) | \varphi_{j-1}(R) \rangle \langle \Psi_{\text{el}}^r | \Psi_{\text{el}}^r \rangle, \quad i,j \neq 1, \quad (28)$$

where the analytic expression for Eq. (28) is given by Eq. (4).

From the above development the advantages of the present method are evident. We are using a well-established basis[14] to calculate the "bound" part of the resonance wave function Ψ_0. Hence, in order to obtain total resonance function we have to search for a function space appropriate for the continuum part of the problem only. Knowledge of E_0 facilitates this search and makes the final identification of the proper complex root reliable.

The other advantage of the method is that only the asymptotic part need be complexified.[1,2,10] In this way the technical problems involved with the rotation of the fitted potentials and the interaction $A(R)$ are avoided, making the calculations for a real system straightforward.

The generalization of the method to multi-channel problems[1,9-12] and for different interaction operators for various channels, is straightforward, since they can all be included in the secular equation.

III. APPLICATIONS

A. Predissociation of the $A\,^2\Sigma^+$ state ($v=0, j=0$) of HeH by the repulsive ground state $X\,^2\Sigma^+$

This problem has been studied by analytic methods with the use of real[18] and complex[13] basis sets giving a linewidth of 4.27 and 2.94 cm^{-1} respectively, while the experimental value[21] is $3.1 \pm 1.0\,\text{cm}^{-1}$. For the present work, we took the potential energy curves and coupling matrix element computed earlier.[22]

For the calculation of Ψ_0 we used 50 equally distributed GTO from 0.8 to 4.0 bohr with scale factor (Ref. 14) of 0.6, while for the continuum, 99 RDGTO were used equally distributed from 1.0 to 5.0 bohr with scale factor of 1.0. We fitted the repulsive potential and the $\langle A\,^2\Sigma^+ | \partial/\partial R | X\,^2\Sigma^+ \rangle$ operator using 10 STOs and a nonlinear optimization procedure. The calculated energy shift and half-width for various values of the rotation angle θ are given in Table I. As one can see, the resonance is revealed immediately even at a rotation angle of 1°, where a very good estimate of the final stabilized complex eigenvalue is obtained. As shown in Table I, for a particular choice of Ψ_0 the stabilization appears for a large number of decimals (e.g., values for θ of 3° and 4°), eight and five decimals for the energy shift and the width, respectively. The present calculations yielded a linewidth of 2.34 cm^{-1} for the $v=0$, $J=0$ level of the $A\,^2\Sigma^+$ state of HeH, which is within the error limits of the experimental value.[21] For rotation angles larger than 5° there is no stabilization.

TABLE I. Calculated energy shift (Δ) and half-width ($\Gamma/2$) in a.u. for five rotation angles for the $v=0$, $J=0$ level of the $A\,^2\Sigma^+$ state of HeH.

	Δ	$\Gamma/2$
−1°	0.378 241 45 (−5)[a]	−0.526 71 (−5)
−2°	0.377 589 93 (−5)	−0.532 66 (−5)
−3°	0.377 581 52 (−5)	−0.532 68 (−5)
−4°	0.377 581 52 (−5)	−0.532 68 (−5)
−5°	0.377 528 91 (−5)	−0.532 39 (−5)

[a] The number enclosed in parentheses indicates the exponent of a multiplicative factor of 10.

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TABLE II. Calculated energy shifts in (a.u.$\times 10^{-5}$) for the six rotation angles for $v=0$, $J=0$ level of the $A\,^2\Sigma^+$ state of NeH, for different numbers of functions for the expansion of the Gamow continuum function.

θ	Number of RDGTO				
	40	50	60	80	99
$-1°$	0.422 025	0.422 020	0.422 019	0.422 020	0.422 020
$-2°$	0.422 019	0.422 020	0.422 019	0.422 019	0.422 019
$-3°$	0.422 023	0.422 023	0.422 021	0.422 019	0.422 019
$-4°$	0.422 038	0.422 059	0.422 048	0.422 019	0.422 019
$-5°$	0.422 077	0.422 369	0.422 000	0.422 020	0.422 019
$-6°$	0.422 095	0.422 934	0.356 463	0.422 096	0.422 019

B. Predissociation study of the $J=0$ first five vibrational levels of the $A\,^2\Sigma^+$ state of NeH by the repulsive ground state, $X\,^2\Sigma^+$

The predissociation of the $A\,^2\Sigma^+$ state has been studied theoretically previously[18] by the golden rule method. In this work, we examined how the complex eigenvalue changed with the number of the RDGTO functions as well as with the rotation angle. Electronic potentials and interaction matrix elements were obtained from Ref. 23. In Table II, the calculated energy shifts of the $v=0$, $J=0$ level of the $A\,^2\Sigma^+$ state of NeH are listed for different angles of rotation, from $-1°$ to $-6°$, and for different numbers (from 40 to 99) of rotated basis functions. The corresponding half-widths are listed in Table III. For these calculations Ψ_0 was obtained using 40 DGTO in the region from 1.0 to 4.0 a.u. with a scale factor of 0.6. The different number of RDGTO were distributed in the region 0.7 – 5.0 a.u. and the scale factor was 1.0. From Tables II and III we can see that we achieve stable energy shift and half-width for the $v=0$ level with basis set expansions of 60 functions or more and for the first five degrees of rotation. The calculated half-width is 0.1417×10^{-8} a.u., which is in agreement with the previous theoretical result[18] of 0.10×10^{-8} a.u. The calculated energy shifts and half-widths for the levels $v=0$–4 are listed in Tables IV and V, respectively. For these calculations 99 RDGTO have been employed. The half-widths for the 1,2,3, and 4 vibrational levels are 0.5311×10^{-8}, 0.1072×10^{-7}, 0.1725×10^{-7}, and 0.2216×10^{-7} a.u., respectively, in good agreement with the corresponding quantities from the previous work[18] 0.34×10^{-8}, 0.67×10^{-8}, 0.22×10^{-7} and 0.32×10^{-7} a.u.

TABLE III. Calculated half-widths in (a.u.$\times 10^{-8}$) for the first six rotation angles for $v=0$, $J=0$ level of the $A\,^2\Sigma^+$ state of NeH, for different numbers of functions for the expansion of the Gamow continuum function.

θ	Number of RDGTO				
	40	50	60	80	99
$-1°$	-0.1165	-0.1430	-0.1406	-0.1410	-0.1417
$-2°$	-0.1367	-0.1419	-0.1417	-0.1417	-0.1417
$-3°$	-0.1273	-0.1446	-0.1419	-0.1417	-0.1417
$-4°$	-0.0369	-0.1759	-0.1183	-0.1417	-0.1417
$-5°$	0.6195	-0.5861	1.5913	-0.1427	-0.1417
$-6°$	5.3002	-7.1671	99.944	-0.4139	-0.1408

C. Predissociation of the $A\,^2\Sigma^+$ state of NeD by the repulsive ground state $X\,^2\Sigma^+$

An experimental study[20] of the NeH and NeD system has found that there is a strong suppression of the predissociation for the $A\,^2\Sigma^+$ state of NeD compared to predissociation in NeH, much bigger than what would be expected from the difference in the reduced mass factors. The relevant numbers calculated in the present work are given in Table VI. A comparison of the calculated widths for NeH (Table V) with those of NeD (Table VI) shows that the present results also find a strong suppression of predissociation in NeD. The predissociation rates (in s^{-1}) corresponding to the half-widths of Table VI are, 7.6×10^5, 5.6×10^6, 1.5×10^7, 3.29×10^7, and 5.77×10^7 for the first five vibrational levels, respectively. The corresponding radiative rates are (Ref. 18) 3.12×10^7, 2.51×10^7, 2.17×10^7, 2.14×10^7, 2.42×10^7, and 3.09×10^7. Thus, for $v>3$ predissociation dominates radiative dissociation, which is in agreement with the experimental findings[20] that predissociation in NeD occurs at high vibrational levels that are scarcely populated, and thus leads to an observation of an overall low predissociation peak.

IV. CONCLUSION

We have presented a method for the computation of predissociating resonances, based on the SSCET.[1,2,9–12] The basis set we use for the real axis calculations is the distributed Gaussian-type orbitals (DGTO).[14] Rotating this basis set by a few degrees in the complex plane and using a proper number of RDGTO, reveals the predissociation resonances. In all the applications, a calculation with a number of 60 or more RDGTO and a small rotation angle of 2° or 3° was enough to give the final result. The precision of the method for a given fit of the operators and a good description of the bound part of the resonance eigenfunction is very high (stabilization for a few angles of eight decimals for the energy shift and five for the half-width) and increases with the number of RDGTO. Applications to the $A\,^2\Sigma^+$ states of HeH and NeH gave results that are in excellent agreement with the experiment[20,21] and previous theoretical work,[13,18] while the calculations on the $A\,^2\Sigma^+$ state of NeD support the observation[20] of the strong suppression of predissociation in NeD in relation to the NeH system.

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TABLE IV. Calculated energy shifts in (a.u.$\times 10^{-5}$) for the first six rotation angles for $J=0$ and $v=0$–4 vibrational levels of the $A\,^2\Sigma^+$ state of NeH.

θ	Vibrational level 0	1	2	3	4
$-1°$	0.422 020 25	0.919 717 99	1.258 664 05	1.491 926 17	1.544 602 32
$-2°$	0.422 019 42	0.919 716 29	1.258 667 85	1.491 929 53	1.544 593 65
$-3°$	0.422 019 42	0.919 716 29	1.258 667 86	1.491 929 54	1.544 593 64
$-4°$	0.422 019 42	0.919 716 29	1.258 667 86	1.491 929 52	1.544 593 64
$-5°$	0.422 019 41	0.919 716 31	1.258 667 95	1.491 928 11	1.544 597 75
$-6°$	0.422 018 58	0.919 700 17	1.258 705 75	1.491 498 01	1.533 767 06

TABLE V. Calculated half-widths in a.u. for the first seven rotation angles for $J=0$ and $v=0$–4 vibrational levels of the $A\,^2\Sigma^+$ state of NeH.

θ	Vibrational level 0	1	2	3	4
$-1°$	$-0.141\,739(-8)$	$-0.533\,375(-8)$	$-0.107\,543(-7)$	$-0.171\,861(-7)$	$-0.221\,929(-7)$
$-2°$	$-0.141\,665(-8)$	$-0.531\,106(-8)$	$-0.107\,186(-7)$	$-0.172\,543(-7)$	$-0.221\,629(-7)$
$-3°$	$-0.141\,666(-8)$	$-0.531\,096(-8)$	$-0.107\,183(-7)$	$-0.172\,539(-7)$	$-0.221\,617(-7)$
$-4°$	$-0.141\,668(-8)$	$-0.531\,093(-8)$	$-0.107\,180(-7)$	$-0.172\,533(-7)$	$-0.221\,607(-7)$
$-5°$	$-0.141\,668(-8)$	$-0.531\,129(-8)$	$-0.107\,152(-7)$	$-0.172\,586(-7)$	$-0.221\,827(-7)$
$-6°$	$-0.140\,760(-8)$	$-0.490\,254(-8)$	$-0.100\,833(-7)$	$-0.181\,734(-7)$	$-0.296\,087(-6)$
$-7°$	$0.262\,949(-6)$	$0.139\,387(-4)$	$0.820\,168(-5)$	$-0.896\,865(-6)$	$-0.101\,398(-1)$

Given its intrinsic structure and the present results, it appears possible to apply the SSCET to predissociation problems with many channels[10–12] and also to polyatomics provided a vibrational and fragmentation coordinate analysis is possible.

TABLE VI. Calculated energy shifts (Δ) and half-linewidths ($\Gamma/2$) in a.u. for all the vibrational levels with $J=0$ of the $A\,^2\Sigma^+$ state of NeD.

v	E_0[a]	Δ	$\Gamma/2$
0	$-0.922\,922$	$0.146\,343(-5)$	0.920×10^{-11}
1	$-0.914\,409$	$0.349\,429(-5)$	0.677×10^{-10}
2	$-0.906\,570$	$0.499\,338(-5)$	0.181×10^{-9}
3	$-0.899\,185$	$0.618\,772(-5)$	0.398×10^{-9}
4	$-0.892\,178$	$0.712\,541(-5)$	0.698×10^{-9}
5	$-0.885\,600$	$0.763\,377(-5)$	0.120×10^{-8}
6	$-0.879\,693$	$0.745\,961(-5)$	0.163×10^{-8}
7	$-0.874\,602$	$0.711\,961(-5)$	0.199×10^{-8}
8	$-0.869\,907$	$0.729\,479(-5)$	0.260×10^{-8}
9	$-0.865\,696$	$0.632\,150(-5)$	0.266×10^{-8}
10	$-0.862\,332$	$0.566\,760(-5)$	0.285×10^{-8}

[a] Energy of the vibrational levels with respect to $-128.000\,000$ hartree.

[1] C. A. Nicolaides and D. R. Beck, Int. J. Quantum Chem. **14**, 457 (1978); in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), p. 383.

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[3] Reference 1 refers explicitly to the problem of predissociation in terms of complex scaling of the nuclear coordinates and of separation of the function spaces of which the localized part, Ψ_0, remains unscaled in the actual computation [Eq. (9) of the present paper]. Accordingly, with the view of using Gaussian functions for molecular dissociation problems, the harmonic oscillator results were shown to be invariant under coordinate rotation.

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