

# HAMILTONIAN MATRIX REPRESENTATIONS FOR THE DETERMINATION OF APPROXIMATE WAVE FUNCTIONS FOR MOLECULAR RESONANCES

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**Abstract:** Wave functions obtained using a standard complex Hamiltonian matrix diagonalization procedure are square integrable and therefore constitute only approximations to the corresponding resonance solutions of the Schrödinger equation. The nature of this approximation is investigated by means of explicit calculations using the above method which employ accurate diabatic potentials of the B  $^1\Sigma^+$  - D'  $^1\Sigma^+$  vibronic resonance states of the CO molecule. It is shown that expanding the basis of complex harmonic oscillator functions gradually improves the description of the exact resonance wave functions out to ever larger internuclear distances before they take on their unwanted bound-state characteristics. The justification of the above matrix method has been based on a theorem that states that the eigenvalues of a complex-scaled Hamiltonian  $H(Re^{i\Theta})$  are associated with the energy position and linewidth of resonance states ( $R$  is an internuclear coordinate and  $\Theta$  is a real number). It is well known, however, that the results of the approximate method can be obtained directly using the unscaled Hamiltonian  $H(R)$  in real coordinates provided a particular rule is followed for the evaluation of the corresponding matrix elements. It is shown that the latter rule can itself be justified by carrying out the complex diagonalization of the Hamiltonian in real space via a product of two transformation matrices, one of which is unitary and the other is complex orthogonal, in which case only the *symmetric* scalar product is actually used in the evaluation of all matrix elements. There is no limit on the accuracy of the above matrix method with an un-rotated Hamiltonian, so that exact solutions of the corresponding Schrödinger equation can in principle be obtained with it. This procedure therefore makes it unnecessary to employ a complex-scaled Hamiltonian to describe resonances and shows that any advantages which have heretofore been claimed for its use are actually non-existent.

**Keywords:** molecular resonance states; complex basis function method; Hamiltonian matrix representation; complex rotation; Schrödinger equation; Born-Oppenheimer Approximation

## 1. Introduction:

Resonance wave functions differ from their bound-state counterparts in at least two essential ways: 1) they are not square-integrable and 2) they correspond to complex (non-real) eigenvalues of the Hamiltonian [1-3]. First attempts to obtain approximate solutions of this type involved use of convergence factors in order to regularize integral evaluations [4] as well as the use of complex coordinate rotations [5]. Based on a theorem by Aguilar and Combes [6] and Balsev and Combes [7], Simon [8] gave a proof that the eigenvalues  $W=E-i\Gamma/2$  of a complex-scaled Hamiltonian  $H(Re^{i\Theta})$  correspond to the energy position  $E$  and line-width  $\Gamma$  of resonance states. Yaris, Lovett and Winkler [9] introduced a technique that they refer to as the Direct Siebert Method that makes use of a cancellation of divergent integrals and thereby retains the use of a Hamiltonian in real coordinate space. Complex-rotated Hamiltonians [5] on the other hand presented additional difficulties, despite the fact that square-integrable functions can be used in principle to form their matrix representations. Specifically, it was shown that only dilation analytic potentials could be treated successfully on this basis within the Born-Oppenheimer Approximation.

Moiseyev and Corcoran [10] later introduced the complex-rotation (CR) method to carry out approximate calculations of resonances. In practice, a back-rotation method is used to avoid any problems with dilation analyticity, whereby the square-integrable basis functions employed are complex-scaled rather than the Hamiltonian itself. The general conclusion from this work has been that it is absolutely necessary to work with a complex-scaled Hamiltonian to obtain *exact* solutions for resonances, but that the CR method allows one to obtain useful approximations to such results while using the conventional un-rotated Hamiltonian within the

Born-Oppenheimer Approximation. In the following discussion the above premise will be examined in detail. For this purpose it will be helpful to examine the results of an application of the CR method in which vibrational resonance wave functions for the B-D'  $^1\Sigma^+$  band system of the CO molecule [11] have been obtained.

## 2. The complex-scaling equivalence relations:

The main motivation for using a complex-scaled Hamiltonian to describe resonances is to deal with the fact that the corresponding energy eigenvalues are complex, that is, have a non-zero imaginary component. This is necessary in order to explain the spontaneous exponential decay of meta-stable states that result from solution of the Schrödinger equation for a time-independent Hamiltonian:

$$H(\Theta)\Psi(\Theta) = W\Psi(\Theta) \quad (1)$$

In this equation  $H(\Theta)$  is a conventional Hamiltonian whose coordinates have been subjected to the complex scaling  $R \rightarrow Re^{i\Theta}$  mentioned above and  $\Psi(\Theta)$  is a resonance eigenfunction with complex energy eigenvalue  $W$ . The un-scaled Hamiltonian  $H(0)$  is related to  $H(\Theta)$  through the linear transformation  $T(\Theta)$ , whereby  $T^{-1}(\Theta) = T(-\Theta)$ :

$$H(\Theta) = T(-\Theta)H(0)T(\Theta) \quad (2)$$

Substitution of this expression in eq. (1) and making use of the definition,

$$\Psi(0) = T(\Theta)\Psi(\Theta), \quad (3)$$

leads to a corresponding Schrödinger equation for the un-scaled Hamiltonian  $H(0)$ :

$$H(0)\Psi(0) = W\Psi(0), \quad (4)$$

with the same eigenvalue  $W$ .

This result shows that there is a one-to-one correspondence between the respective eigenfunctions of the two Hamiltonians with the same energy eigenvalue. It holds for both bound states and for resonances. This relationship is an example of the key characteristic of quantum mechanical theory that its equations are invariant with respect to coordinate transformations in general. The equations take on a different form as a result of such transformations, but the *physical significance* of their solutions is completely independent of which set of coordinates is used explicitly in a given theoretical treatment. In particular, there is never a case where a solution exists for one set of coordinates without their being a completely equivalent solution for any other set of coordinates. The equivalence relationships implied by eqs. (1-4) can nonetheless be used to great advantage in seeking solutions to specific quantum mechanical equations. For example, there may be singularities for one set of coordinates (representation) that make it quite difficult or even impossible to obtain the desired solutions directly in a given application. A coordinate transformation can be found that removes such singularities, thereby allowing for a straightforward solution of the corresponding differential equation. The point to be emphasized in the present discussion is that once a solution has been obtained in this manner, it is always possible to convert its results quantitatively to those that would have been obtained in the original representation had a direct path to the solution been available in this case.

The reason that efforts to obtain quantum mechanical resonances have concentrated on using complex-scaled/rotated coordinates is not because equivalent solutions do not exist for the un-scaled Hamiltonian  $H(0)$  and corresponding Schrödinger equation, but rather because there are computational advantages in doing so, or at least it was perceived that this is the case. This conclusion was based primarily on the fact that the resonance wave function for the un-scaled Hamiltonian is not square-integrable because it does not vanish at infinity. Rotating the coordinates in the complex plane by a sufficient angle produces a corresponding solution that does not have this undesirable characteristic. It was therefore possible to employ well-established techniques for bound-state functions in the search for resonances, such as is done in the CR method [10], for example. On the other hand, this procedure leads to a new problem that is not present when one uses the un-scaled coordinates to set up the problem, namely a singularity in the potentials resulting from use of the Born-Oppenheimer Approximation for the treatment of molecular systems. This circumstance led to the introduction of an exterior scaling procedure [12-13] that limits the range of inter-nuclear distance for which coordinate rotation is actually applied.

All of the above relationships also hold for matrix representations of the operators in eqs. (1-4) when a finite basis is employed. Indeed,  $H(\Theta) = H(0)$  in this case when the respective basis sets employed are related by the same complex-coordinate scaling as for the Hamiltonian operators themselves. This result follows from the fact

that corresponding matrix elements can be converted into one another by a change of variables in the respective integrations. It needs to be emphasized in this connection that *the path in the complex plane* along which integration is actually carried out is also changed as a result of the coordinate scaling. *Indeed, when the scaled and un-scaled functions are evaluated along their respective integration paths, the perceived distinction disappears entirely.*

Diagonalization of  $H(\Theta)$  and  $H(0)$  therefore leads to identical eigenvector (coefficient) matrices,  $\Psi(\Theta)$  and  $\Psi(0)$ . As a result, any *approximate* solution obtained by employing complex-scaled coordinates in a matrix formalism can be converted into a perfectly equivalent wave function with the same complex energy eigenvalue that is obtained by working exclusively with the un-rotated Hamiltonian expressed in real coordinates. One can make use of this identity as a test for the associated computer codes. One simply scales the basis functions employed to construct the matrix representation in exactly the same manner as for the Hamiltonian operator itself [10, 11, 14]. This fact raises an interesting point, however: *Is there any computational advantage whatsoever in employing complex-coordinate scaling to obtain resonance wave functions and energies at any level of approximation?* In order to study this question in detail, it is helpful to consider the results of specific calculations that have made use of the complex-scaling methodology.

### 3. Description of unbounded wave functions using square-integrable basis functions:

An application of the complex-scaling method employing a basis of complex solutions of the one-dimensional harmonic oscillator has been reported earlier for the B-D'  $^1\Sigma^+$  band system of the CO molecule [11]. Very good agreement was obtained with the work of other authors who employed both the close coupling and optical potential methods. Comparisons were made for the energy locations  $W$  and predissociation linewidths  $\Gamma$  of the  $v=0-10$  vibronic levels. It was found that the complex-scaling results agreed almost perfectly with those employing the optical potential method, which in turn performed better than its close coupling alternative, particularly for vibronic states with quite high  $\Gamma$  values. No consideration was given to the appearance of the associated vibronic wave functions in the previous study [11], however.

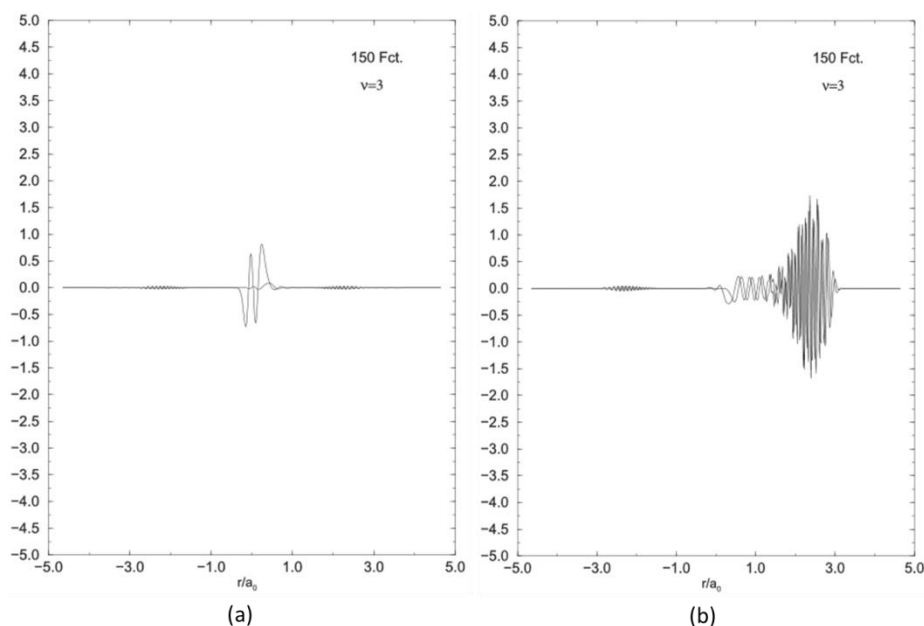


Figure 1: Real and imaginary components of the wave function for the  $v=3$  resonance state in the B  $^1\Sigma^+$  - D'  $^1\Sigma^+$  band system of the CO molecule obtained by employing a basis set of 150 complex-rotated ( $\Theta= 4.0$  deg) harmonic oscillator solutions for each of the vibrational functions  $\Phi_i(r)$  in multiplying a) the bound electronic state  $\psi_1(R, r)$  and b) the repulsive electronic state  $\psi_2(R, r)$ . Note that  $r=0$  corresponds to the equilibrium bond distance of the bound potential  $H_{11}$ .

In view of the discussion in Sect. II, it is important to mention that the above calculations were actually carried out using the unscaled Hamiltonian  $H(0)$ . Formally, the treatment employs a complex-scaled potential and a basis of *real* harmonic oscillator functions  $\{\chi(R)\}$ , but the actual calculations make use of the Cauchy-Coursat

theorem [15] for integration of a complex analytical function. An identity that takes advantage of the fact that the above basis functions are square-integrable is employed to convert the matrix elements for the original complex-scaled Hamiltonian to corresponding integrals using a real potential and *complex-scaled basis functions*  $\{\chi(\text{Re}^{-i\Theta})\}$ . The resulting procedure is therefore seen to be an application of eq. (4) in this special case, in which approximate eigenfunctions of  $H(0)$  are constructed as linear combinations of basis functions with complex exponents. The above identity simply makes clear that the resulting solutions can be transformed to their counterparts in eq. (1) by rotating the basis functions back to their original real form. The corresponding expansion coefficients are left unchanged in this procedure since they do not depend on  $\Theta$ . The eigenvalue  $W$  is not affected for the same reason, so the one-to-one correspondence between the respective eigenfunctions of  $H(0)$  and  $H(\Theta)$  expected from the general discussion in Sect. II is obtained explicitly from these calculations.

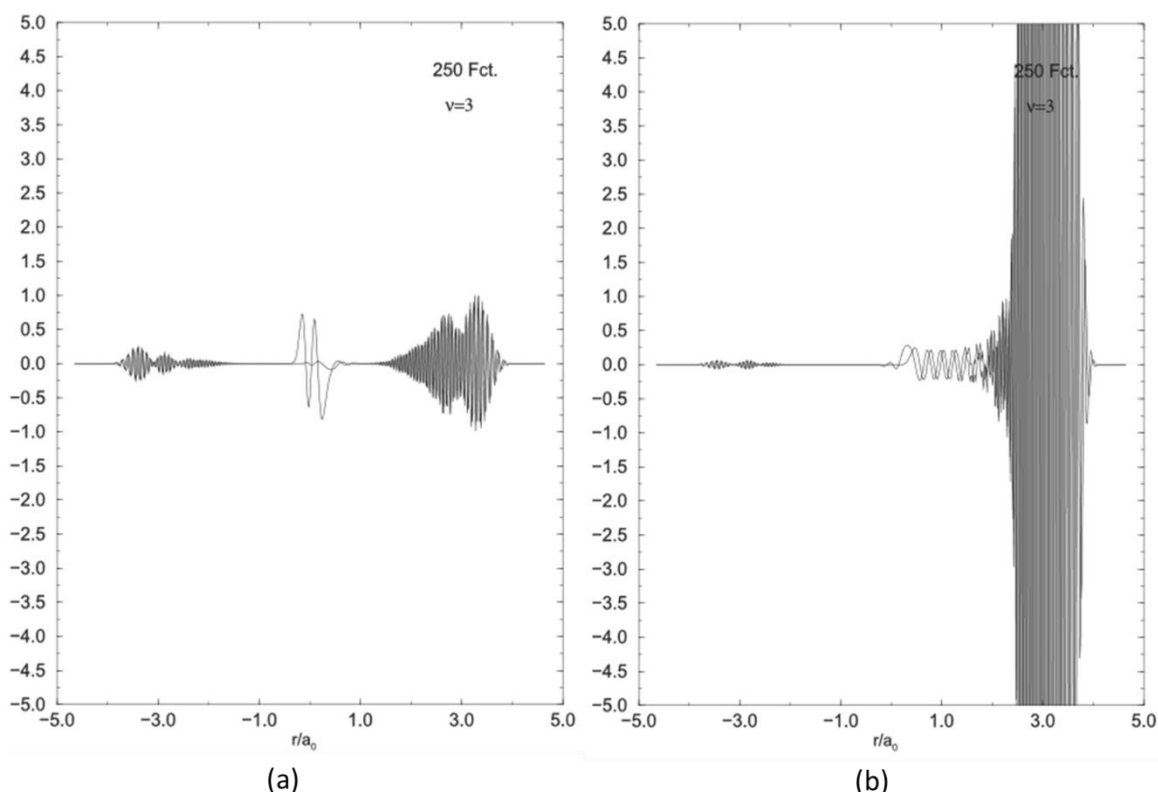


Figure 2: Real and imaginary components of the wave function for the  $v=3$  resonance state in the  $B^1\Sigma^+ - D^1\Sigma^+$  band system of the CO molecule obtained by employing a basis set of 250 complex-rotated ( $\Theta= 4.0$  deg) harmonic oscillator solutions for each of the vibrational functions  $\Phi_i(r)$  in multiplying a) the bound electronic state  $\psi_1(R, r)$  and b) the repulsive electronic state  $\psi_2(R, r)$ . Note that  $r=0$  corresponds to the equilibrium bond distance of the bound potential  $H_{11}$ .

There is another aspect of the above theoretical treatment that requires further scrutiny, however. The values of  $\Theta$  employed in these calculations fall generally in the 0-5 deg range. The new basis functions  $\{\chi(\text{Re}^{-i\Theta})\}$  formed by scaling the coordinates of the real harmonic oscillator basis functions  $\{\chi(R)\}$  are therefore still square-integrable. How does this mesh with the requirement that the exact resonance wave functions  $\Psi(0)$  of eq. (4) must be unbounded? This question is best answered by looking at some specific examples of computed wave functions for the CO vibronic resonances [11], beginning with the results for different basis set sizes for the  $v=3$  state shown in Figs. 1a-b and 2a-b. Convergence of the energy and line-width values with respect to the number of complex harmonic oscillator functions in the basis set is found to be quite satisfactory. The same cannot be said for the vibronic functions themselves, however. Both the real (a) and imaginary (b) parts of the wave functions are shown in each case. Note that a phase convention is chosen so that the part of the function associated with the typical harmonic oscillator character is real. There is almost no imaginary part in the equilibrium region ( $R=0$ ) and the real part in this region is quite similar in both cases, showing the expected variations for a  $v=3$  solution (two minima and two maxima). The behavior at large  $R$  values changes significantly as the size of the basis is increased, however. In the 150 function case, both the real (Fig. 1a) and

imaginary (Fig. 1b) parts start to oscillate rapidly near  $R=1.50 a_0$ . A maximum is reached in each case at  $R=2.5 a_0$ , and then the oscillations die down until both the real and imaginary parts have essentially zero values from  $R=3.0 a_0$  onwards. The latter behavior is expected from the exclusively bound character of the present basis functions, and is unavoidable for any application of the CR method after a certain point. It also should be pointed out that there are many extraneous roots of the secular equations in the above three treatments that have no physical significance whatsoever and are simply ignored in the present discussion. It is impossible to locate a stabilization angle for any of them and the number of such roots simply increases with the size of the basis set.

The corresponding results for 250 functions (Figs. 2a-b) agree very closely with those for 150 functions in the  $R=0$  region in which the characteristic form of the  $v=3$  wave function is observed. In the neighborhood of  $R=1.50 a_0$ , however, significant differences emerge between the two sets of vibronic solutions. The results for 250 basis functions show much greater variations beyond  $R=2.0 a_0$ , reaching a maximum of  $30 a_0^{-1.5}$  near  $R=3.1 a_0$ . Despite these differences in the three  $v=3$  wave functions, however, the corresponding energy eigenvalues are scarcely affected by the increase in basis set. The real part changes by only  $0.002 \text{ cm}^{-1}$  in going from 150 to 250 functions ( $E_r=6784.09 \text{ cm}^{-1}$  [11]), while  $E_i$  varies by  $0.0005 \text{ cm}^{-1}$  about its value of  $45.45 \text{ cm}^{-1}$ . The wave functions are each normalized to unity, from which it is clear that the large differences in the intermediate region of bond distance, where the respective (absolute) values are increasing exponentially, are simply compensated for by correspondingly large changes after the maximum value has been reached in each case.

Further inspection of these diagrams shows that the various representations of the resonance wave functions exhibit a well delineated  $e^{ikR}$  dependence over the intermediate region of  $R(k=k_r+ik_i, k_r>0 \text{ and } k_i<0)$ . Starting at about  $R=0.5 a_0$  in each case, there are nearly parallel variations in the real and imaginary parts of the wave functions. This behavior is expected for the case when the real part of  $k$  is notably larger than the corresponding imaginary part. Each peak in the real part ( $k_r$ ) is followed closely by a corresponding peak in the imaginary part ( $k_i$ ). In the 250 function case (Fig. 2a-b), it is possible to identify four such maxima and minima before the wave functions start to oscillate between wider ranges. If we define the difference in  $R$  separating successive real and imaginary parts as  $\Delta$ , this means that we can obtain a relatively accurate value for  $k_r$  as  $\pi/2\Delta$ . The exponentially increasing part of the wave function allows one to compute the value of  $k_i$  to similar accuracy based on the envelope formed by ignoring the oscillatory behavior of the function as a whole. Note that this value is fairly sensitive to the number of basis functions, however.

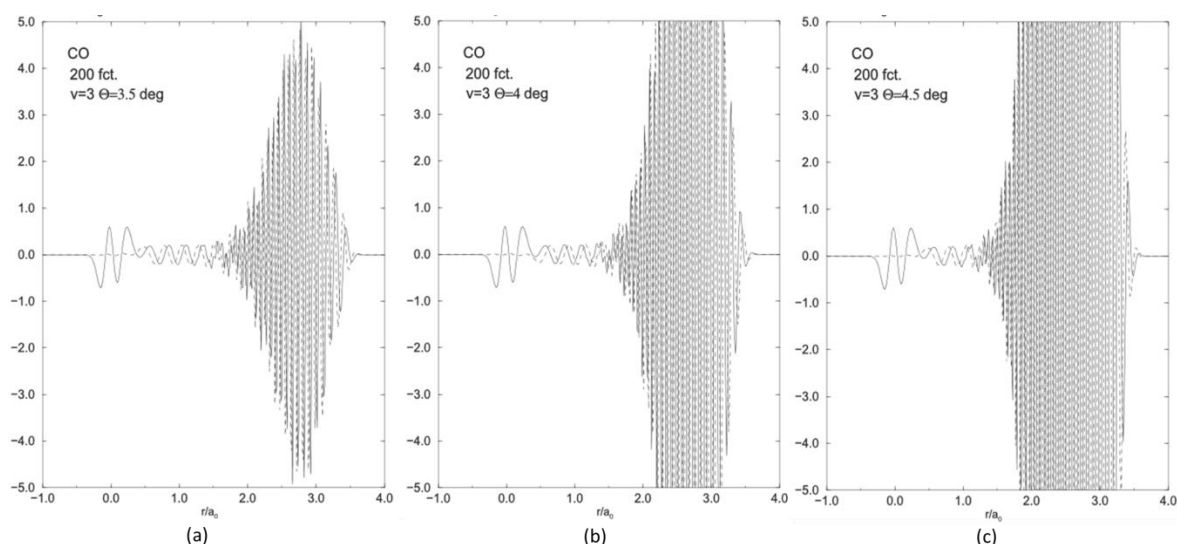


Figure 3: Real and imaginary components of the wave function for the  $v=3$  resonance state in the  $B \ 1\Sigma^+ - D' \ 1\Sigma^+$  band system of the CO molecule obtained by employing a basis set of 200 complex-rotated harmonic oscillator solutions for the vibrational function multiplying each electronic state [see eq. (1) for definitions] for different values of the scaling parameter: a)  $\Theta= 3.5 \text{ deg}$ , b)  $\Theta= 4.0 \text{ deg}$  and c)  $\Theta= 4.5 \text{ deg}$ .

In Figs. 1-2,  $\Theta=4^\circ$  has been used for the scaling procedure in each case. Corresponding results for neighboring values of  $\Theta$  ( $3.5^\circ$  and  $4.5^\circ$ ) as well as for  $4.0^\circ$  are shown in Figs. 3a-c for the case with 200 basis functions. Comparison of these diagrams shows that the long-range part of the  $v=3$  wave function ( $R=1-4 a_0$ ) is by no means independent of the parameter  $\Theta$ , even though the corresponding value of the complex energy  $W$  is very

nearly constant over the same range. Not surprisingly, the magnitude of the oscillations gradually increases with the value of  $\Theta$ . When  $\Theta=0$ , the basis is real by definition, and so only real values of both the energy eigenvalues and associated eigenfunctions can ensue in this case, for example. In practice, the final (stabilization) value of  $\Theta$  is determined by demanding that the complex energy  $W$  be stationary relative to variations in this quantity. This condition is easily satisfied [11] when such large basis sets are used as in the present one-dimensional vibronic application, but it is considerably more difficult to achieve this objective when multidimensional Hamiltonians are employed [14].

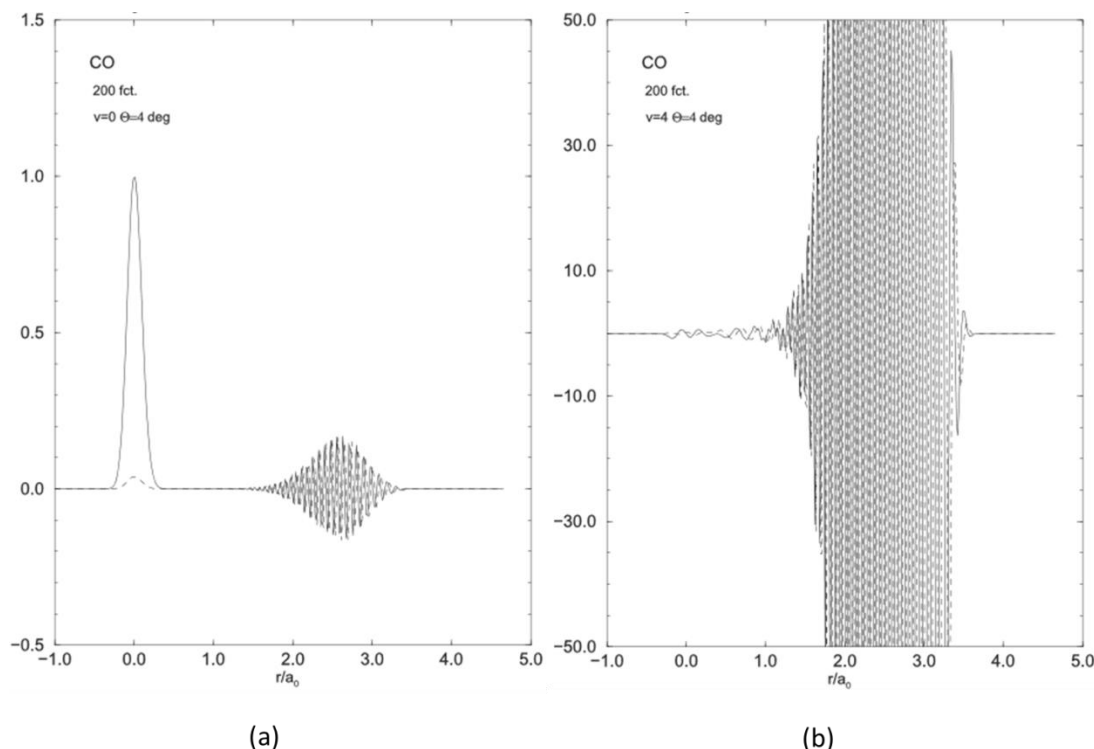


Figure 4: Real and imaginary components of the wave functions for the a)  $v=0$  and b)  $v=4$  resonance states in the  $B\ ^1\Sigma^+ - D'\ ^1\Sigma^+$  band system of the CO molecule obtained by employing a basis set of 200 complex-rotated ( $\Theta=4.0$  deg) harmonic oscillator solutions for the vibrational function multiplying each electronic state.

The characteristics of the  $v=3$  resonance wave functions discussed above are mirrored in the results obtained with the same method (200 basis functions) for other vibrational quantum numbers. The real and imaginary parts of the  $v=0$  and 4 wave functions are shown in Fig. 4a-b, respectively. The  $\Gamma$  values that are obtained in the latter two cases (0.0 and  $801.8\text{ cm}^{-1}$ ) [11] differ significantly from that of  $v=3$ . One needs a large amount of magnification to see that there is complex oscillatory behavior in the  $v=0$  resonance, but it is clear from Fig. 4a that a similar pattern of monotonically increasing values of the wave function occurs up to a certain  $R$  value, corresponding to the expected  $e^{ikR}$  asymptotic behavior in this range. Otherwise, the familiar shape of the  $v=0$  harmonic oscillator solution is apparent in the  $R=0$  region. Near  $R=2.7\ a_0$ , however, the values of the real and imaginary parts begin to decrease until they are completely damped out beyond  $R=3.2\ a_0$ , again as required by the use of exclusively bound, albeit complex, harmonic oscillator basis functions. The  $v=4$  wave function differs mainly in its behavior around  $R=0$  and the value of their respective stabilization angle. It also shows the characteristic “tropical fish” pattern in the  $R=1.5\text{-}3.5\ a_0$  region before finally taking on a null value beyond this point.

One of the traditional arguments for the coordinate-rotation procedure is the possibility of transforming away the unbounded character of the resonance wave function by scaling both it and the Hamiltonian by  $R \rightarrow R e^{i\Theta}$ . In the above discussion, we have seen that the computed vibronic resonance wave functions that result from use of the un-scaled Hamiltonian  $H(0)$  always take on the general form of the product of a sinusoidal and exponential function:  $e^{aR} e^{ibR}$ , with  $a>0$ , in an intermediate region of  $R$  before being damped to zero after a certain point (Figs. 1-4). If the angle of rotation  $\Theta$  is defined as  $\tan^{-1}(a/b)$ , it appears from the present calculations that the above scaling procedure with this angle or larger will indeed transform the original unbounded wave function

into one that is square-integrable, but certainly not eliminate its oscillatory characteristics (as mentioned above, however, even this difference goes away once one takes account of the fact that the two functions are to be evaluated along different rays in the complex plane). The above discussion has shown that the values of  $a$  and  $b$  ( $-ik_i$  and  $k_r$ , respectively) are not very stable with respect to expansions of the basis set, however. These parameters therefore have very little connection with the complex energy eigenvalue  $W$ , which is seen to converge far more quickly with the size of the basis. The latter is determined almost exclusively by the short-range behavior of the computed wave function and is all but unaffected by its corresponding asymptotic character.

Returning to the main theme of the present section, however, the effect of complex scaling the vibrational coordinate in these calculations is simply to generate a perfectly equivalent resonance wave function in each case as defined in eq. (3) for the exact results. This is the case no matter what the size of the basis set may be in a given approximate treatment and it also holds by extension to the limit of complete basis sets for the exact solutions of eqs. (1,4).

#### 4. Hermiticity and scalar products:

The discussion in the previous sections has left out an important detail, namely what scalar product to use in constructing individual matrix elements. Since the Hamiltonian operator for electronic structure applications is hermitian, it is clear that only real energy eigenvalues can result for square-integrable (bound-state) solutions of the Schrödinger equation. As discussed in the previous section, it is nonetheless possible to obtain accurate complex energy eigenvalues, i.e. with non-zero imaginary components, for resonance states with a computational method that employs exclusively square-integrable basis functions to construct the matrix representation of the conventional un-rotated Hamiltonian  $H(0)$ . It is natural to assume that any such matrix representation must be accomplished through use of the hermitian scalar product, that is, where the bra function is complex conjugated:  $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle = \int \Phi_i^* H \Phi_j d\tau$ , but this procedure excludes any possibility of obtaining complex energy eigenvalues because of the hermitian character of  $H(0)$ .

The CR method [10] avoids this problem by employing a mixed scalar product. The radial parts of basis functions are not subjected to complex conjugation, whereas the angular parts (including spin) are. This procedure has been followed in the CO vibronic calculations discussed above, but since there are no angular variables in this application, however, one can just as well say that the *symmetric* scalar product  $H_{ij} = \int \chi_i H(0) \chi_j dR$  has been used instead.

The theoretical justification of the mixed scalar product mentioned first has been considered by various authors [10, 12-13,16-18], and a consensus has been reached that it requires use of the hermitian scalar product in all cases but with different basis functions in the bra and ket positions of the Hamiltonian matrix elements. There are difficulties with this procedure in practice, however. The main problem is that it does not give a clear prescription of how to proceed for all types of basis functions. For example, in electronic structure calculations the basis sets employed in standard codes (Gaussian- or Slater-type atomic orbitals) are defined exclusively in terms of Cartesian coordinates, making it impossible to make the required distinction between angular and radial coordinates. One might attempt to circumvent this problem by transforming the basis so that it consists of complex spherical harmonics, for which a distinction can be made for each atomic basis function, but it is not clear how this would work in the case of a general polyatomic molecule in which no axis of symmetry exists.

In any event, the normal procedure in CR molecular calculations is to apply the complex-coordinate rotations to exclusively real basis functions and to then evaluate matrix elements over the scaled basis without applying any complex conjugation whatsoever (other than in integrations over spin coordinates). This procedure is clearly the same as has been used in the CO vibronic resonance calculations discussed above. It also suffers from the same deficiency as that employing the mixed scalar product, however, in that it is not clear how to apply it in the general case when one has to compute matrix elements for *linear combinations* of such complex-rotated functions. Specifically, when must one apply complex conjugation to the corresponding coefficients and when not? Above all, the choice of scalar product must be consistent with accepted procedures for bound-state functions, in which case the hermitian scalar product is assumed to be both necessary and sufficient.

It needs to be pointed out, however, that there is no compelling reason to use the hermitian scalar product exclusively in forming matrix representations of a Hamiltonian merely *because it satisfies the definition of a hermitian operator*. The latter designation simply means that it is *possible* to form a hermitian matrix

representation as long as the corresponding basis functions satisfy certain conditions, for example, being square-integrable in the present case, and the hermitian scalar product is used for each matrix element. To show that this is a meaningful distinction, let us consider the case when a set of *real* orthonormal basis functions is employed to form the matrix representation. If the Hamiltonian is real and only square-integrable basis functions are employed, the result is a real symmetric matrix. The latter can be diagonalized by a real orthogonal matrix  $O$  ( $OO^T=E$ ). If the Hamiltonian contains imaginary terms, as for example when the spin-orbit interaction is included, a Hermitian matrix will result, again assuming that exclusively real orthonormal square-integrable basis functions are employed. In this case one needs a unitary matrix  $U$  ( $UU^\dagger=E$ ) to diagonalize the Hamiltonian. One can use the properties of a hermitian matrix to simplify the procedure computationally, however, namely that it can be brought into real symmetric form ( $H_r=H_r'$ ) by carrying out a *preparatory* unitary transformation with  $U_p$ . The resulting matrix can then be diagonalized with a real orthogonal matrix  $O$  ( $OO^T=E$ ) as before. The author and coworkers [19] have used this two-step procedure to treat Breit-Pauli terms in the molecular Hamiltonian for heavy systems containing lead and bismuth, for example:

$$H_d = O^T H_r O = O^T U_p^\dagger H U_p O . \tag{5}$$

The latter matrix operation requires that one apply the complex conjugation operation in forming  $U_p^\dagger$  from  $U_p$ . Since real basis functions are employed throughout, *this is the only operation that involves complex conjugation in the entire procedure*. One can arrive at the same result in principle if the product matrix  $X=U_p O$  is formed. By construction,  $X$  is also unitary since  $O$  is real, so alternatively one could accomplish the diagonalization in one step:

$$H_d = X^\dagger H X , \tag{6}$$

in which case again, the only complex conjugation operation to be applied occurs in forming  $X^\dagger$  from  $X$ , *thereby avoiding use of the Hermitian scalar product entirely*.

It is interesting to consider the above matrix operations for a particular choice of  $U_p$ , namely the transformation that changes the basis from real to complex spherical harmonics. One can also look upon this as a change from Cartesian to polar coordinates in the original real basis, whereby complex conjugation is necessary only for the resulting functions that depend on the angular coordinates when they appear in the bra position of the Hamiltonian matrix elements. This is because the basis functions that result from transforming the original real basis can be factored into products of radial and angular functions, of which only the latter have imaginary parts. This state of affairs allows one to look upon the above (mixed) scalar product feature in the CR method [10,17,18] in a different light. There is actually no need to distinguish between functions of radial and angular coordinates in performing the integrations over basis functions required to construct the Hamiltonian matrix representation. One can either a) carry out the entire calculation in a basis that results exclusively by complex-rotating real functions and then use only the symmetric scalar product to evaluate the matrix elements, or b) first transform to a basis of complex spherical harmonics with  $U_p$  before complex-rotating them and also use the symmetric scalar product in evaluating matrix elements, but with the proviso that  $U_p^\dagger$  be used in the basis transformation when the resulting functions appear in the bra position, as prescribed in eq. (5). Avoiding the use of the Hermitian scalar product in the above procedure does not change the fact that exclusively real energy eigenvalues result from the diagonalization of  $H(0)$  if either a *real* square-integrable basis is employed directly or one that *only differs from it by a unitary transformation*. In both cases  $H(0)$  is a hermitian matrix by reason of the fact that a) the corresponding operator  $H(0)$  is hermitian, b) the basis is square-integrable and c) *the bra vector in each matrix element is the complex conjugate of one of the basis functions in all cases*.

The situation is different when a complex-rotated square-integrable basis is used, however. In that case *only the first two* of the latter conditions are fulfilled, and this is sufficient to prevent  $H(0)$  from being a Hermitian matrix. Indeed, when the Hamiltonian operator  $H(0)$  contains imaginary terms, this means that the  $H(0)$  matrix is *neither symmetric nor Hermitian*, and thus a more complicated procedure is required to diagonalize it than in the case discussed first. The two-step transformation procedure described above can also be used effectively for such matrices, however. First of all, it is clear that the same unitary matrix  $U_p$  that was used to produce a real symmetric Hamiltonian matrix  $H_r$  in eq. (5) can be used to produce a *complex symmetric* Hamiltonian matrix  $H_c$  from  $H(0)$  in the present case in which a complex-rotated version of the original real (orthonormal) basis set is employed:

$$H_c = U_p H(0) U_p , \tag{7}$$

where  $H_c=H_c'$  and  $H_c \neq H_c^*$ .



This matrix in turn can be diagonalized with a complex orthogonal matrix  $O_c$  ( $O_c O_c' = E$ ):

$$H_d = O_c' H_c O_c = O_c' U_p^\dagger H(0) U_p O_c. \tag{8}$$

As in the case for which only real square-integrable basis functions are employed, the only place in this entire procedure where the complex-conjugation operation is used is in the formation of  $U_p^\dagger$ , and hence only for linear coefficients, not for the basis functions themselves. As a result, the *hermitian scalar product is avoided entirely* in this diagonalization procedure, exactly as for the corresponding bound-state treatment employing eqs. (5,6). Note, however, that unlike the case in eq. (6), it is not possible to define a matrix product  $X = U_p O_c$  that can then be used to obtain  $H_d$  by means of a single unitary transformation. Clearly,  $X^\dagger X \neq E$  because  $O_c$  is not unitary, contrary to the case for  $O$  in eq. (5). One can obtain something comparable to eq. (6) in the present case by defining a new matrix  $X^+ = O_c' U_p^\dagger$ , so that

$$H_d = X^+ H X. \tag{9}$$

Expectation values of resonance eigenstates for other quantum mechanical operators  $Q$  can then be obtained from their respective matrix representations  $Q$  for the complex-scaled basis by means of the analogous transformation with  $X^+$  and  $X$  (note that these matrix elements will also generally be complex).

In practical terms it is necessary to develop a straightforward means of deriving the  $X^+$  matrix from  $X$ . To illustrate this procedure it is helpful to first compute the matrix elements of  $X$  by expanding a resonance solution  $\Psi_k$  of the Schrödinger equation with complex energy eigenvalue  $W_k$  in a basis of orthonormal (formerly real) complex-rotated square-integrable functions  $\{e_i\}$ :

$$\Psi_k = \sum(i) x_{ik} e_i. \tag{10}$$

The matrix elements can be obtained as:

$$x_{ik} = \int e_i \Psi_k d\tau, \tag{11}$$

i.e., by using the symmetric scalar product, not the hermitian. In order to compute  $X^+$ , it is necessary to introduce a particular unitary transformation  $U_p$  as defined above which satisfies eq. (7), that is, which converts the Hamiltonian matrix  $H(0)$  in the  $\{e_i\}$  basis to the complex-symmetric form of  $H_c$ . By definition,  $X = U_p O_c$  in eq. (9), which allows us to obtain first  $O_c$  and then  $X^+$  directly from  $X$ :

$$O_c = U_p^\dagger X \tag{12}$$

$$X^+ = O_c' U_p^\dagger. \tag{13}$$

The matrix elements of  $X^+$  are then used to expand a conjugate solution  $\Psi_k^+$  as

$$\Psi_k^+ = \sum(j) x_{kj}^+ e_j \tag{14}$$

Expectation values  $Q_{kk}$  are then obtained as

$$Q_{kk} = \int \Psi_k^+ Q \Psi_k d\tau = \int \sum(j) x_{kj}^+ e_j Q \sum(i) x_{ik} e_i d\tau = (X^+ Q X)_{kk}, \tag{15}$$

which in the special case ( $Q=H$ ) of eq. (5) gives  $H_{kk}=W_k$ . Complex conjugation is only used in forming  $U_p^\dagger$  in eqs. (8,9), so there is no question of scaling one kind of spatial coordinates differently than another as is the case in the definition of the conjugate operator in Reinhardt's formalism [17,18].

As has already been pointed out above, this is a key consideration in the case of molecular potentials, where the distinction between radial and angular coordinates cannot generally be drawn. All calculations are carried out exclusively in real coordinate space, and complex energy eigenvalues nonetheless result in the limit of complete sets. This occurs because the symmetric rather than the hermitian scalar product is used in evaluating matrix elements of the Hamiltonian as well as of all other quantum mechanical operators. In the case of bound states,  $O_c=O$  is real and thus  $O_c'=O_c^\dagger$ ; hence,  $X^+=X^\dagger$  in eq. (13) and  $\Psi_k^+=\Psi_k^*$  in eq. (14), so that the standard expression for matrix elements in this type of application is also obtained from eq. (15).

The above discussion has concentrated on the use of a particular type of basis set for applications of the complex coordinate method, namely functions that result by complex scaling commonly used sets of *real* square-integrable functions. This is really not a severe restriction, especially for molecular Hamiltonians, in which case it is standard practice to work with either real Gaussian or exponential (Slater-type) orbitals. When one speaks of complete sets of such functions, it is necessary to stipulate that only bound states (with zero natural linewidths) can be represented with such a basis, that is, no resonances can result from their use according to the strict definition of these quantities. On the other hand, one can form a *conjugate* basis by scaling such real

functions by  $R \rightarrow Re^{-i\Theta}$ . There is clearly a one-to-one relationship between the two sets, which we will refer to as  $\{R_0\}$  and  $\{R_\Theta\}$ , respectively. The two sets of functions have non-zero overlaps with one another, but it is still possible to think of them as being mutually exclusive in the sense that all bound states can be perfectly described with only functions from  $\{R_0\}$ , whereas to describe resonances we only need functions from  $\{R_\Theta\}$ . One value of  $\Theta$  will do in the latter case for one-dimensional problems in the limit of a complete set.

In treating multidimensional problems such as arise in the description of atomic and molecular autoionization processes, it is clear that different one-electron basis sets need to be used for inner-shell and valence occupied orbitals than that mainly responsible for the instability. In particular, one can choose standard basis sets of type  $\{R_0\}$  for the former and a complex-rotated set for the latter. There is no conceptual difficulty with this approach, since it ultimately only involves the optimization of exponents and other parameters that define the orbitals occupied in the electronic wave function. The Hamiltonian employed is a function of exclusively real coordinates  $[H(0)]$  and the calculations can be carried out entirely within the standard Born-Oppenheimer approximation commonly used for bound states, i.e. the necessity of an external coordinate scaling does not arise [10, 12, 13].

As in the calculations of the last section, the value of the parameter  $\Theta$  is chosen so as to satisfy the stationary principle, specifically that  $dE_r/d\Theta = dE_i/d\Theta = 0$ . This requirement is the main reason why complex scaling calculations for multidimensional potentials are significantly more difficult to carry out successfully for metastable states than they are for bound states. In principle, the energy should be stable with respect to variations in all non-linear parameters, but in practice this condition can usually be relaxed so that at most one or two such quantities in addition to  $\Theta$  are optimized in this way [14].

The matrix operations with  $U_p$  in eqs. (5,7-8) correspond to a transformation from the original orthonormal basis sets  $\{R_0\}$  and  $\{R_\Theta\}$ . They show that it is always possible to choose orthonormal sets  $\{R_0'\}$  and  $\{R_\Theta'\}$  spanning the same linear spaces which lead to symmetric representations of the Hamiltonian ( $H_{ij} = H_{ji}$ ) because of its hermitian character. The two sets can be merged and transformed to a mutually orthonormal set  $\{R''\}$ , thereby making it possible to obtain both bound and resonance states from the same matrix representation of the unrotated Hamiltonian  $H(0)$ , i.e. one that is expressed in exclusively real coordinates. Taken to the limit of complete sets, this procedure therefore makes it possible in principle to describe all solutions  $\{\Psi_i\}$  of the corresponding Schrödinger equation to arbitrary accuracy, that is, which satisfy the relation:

$$H\Psi_k = W_k\Psi_k, \tag{16}$$

whereby  $\Psi_k = \sum(i)c_{ik}R_i''$  [note that  $U_p^\dagger$  must be used in the bra position while constructing matrix representations with the  $\{R'\}$  and  $\{R''\}$  basis sets; see eqs (5-9)]. The stationary principle ( $\delta W_k = 0$ ) employed above to optimize the scaling parameter  $\Theta$  can be derived by employing eq. (16) in connection with the normalization condition:  $S_{kk} = \int \Psi_k^* \Psi_k dt$ , i.e.  $\delta H_{kk} = W_k \delta S_{kk} = 0$ . It also can be shown on this basis that eigenstates with different eigenvalues (and therefore bound and resonance states in particular) are mutually orthogonal.

#### 4. Conclusion:

The belief that the complex scaling of spatial coordinates can lead to more accurate solutions of the Schrödinger equation for resonances overlooks an important fact. There is a one-to-one correspondence between eigenfunctions of the scaled and unscaled Hamiltonians with the same eigenvalue, and these functions can be converted into one another by the same transformation that connects the two Hamiltonians. This situation holds for any level of approximation, up to and including the exact solution of the Schrödinger equation. It manifests itself in a particularly striking manner in the complex-rotation (CR) method of Moiseyev and Corcoran [10], which leads to *identical* matrix representations of the scaled and unscaled Hamiltonian so long as the respective square-integrable basis sets employed are related by the same change in coordinates as the two operators. One therefore obtains completely equivalent eigenvalue and corresponding eigenvector coefficient results from the two theoretical treatments regardless of the size of basis set employed.

The rationale for complex scaling in spite of the above equivalence relations has been that this somehow overcomes a basic problem, namely the fact that the resonance wave functions are not square-integrable. This only appears to be the case, however, because one has to keep in mind that the rotated functions *are no longer evaluated on the real axis*. Consistent with the above equivalence relations, it is seen that once this fact is taken into account, *the eigenfunctions of the complex-scaled Hamiltonian are no more bounded than their un-scaled counterparts*.

This does not mean that resonance eigenfunctions cannot be described to useful accuracy by employing exclusively square-integrable basis functions to form a matrix representation of the un-rotated Hamiltonian, however. Consideration of the results of calculations of vibronic resonances for the CO B-D' band system has shown that the corresponding complex energy eigenvalues converge relatively quickly with respect to increasing the size of the basis. The same is true for the short-range parts of the associated wave functions, whereas their behavior far away from the equilibrium bond distance is much less settled. As more and more functions are added, it is clear that the resonance solutions slowly take on their expected exponentially increasing character in the intermediate range of internuclear distance (Figs. 1a-b), but at a certain point a maximum is reached in each case. Beyond this point, the functions start to degenerate and ultimately approach the null values that are inevitable in view of the square-integrable characteristics of the basis in which they are expanded.

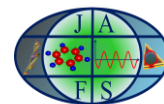
The conclusion is that the asymptotic behavior of resonance wave functions is not critical in the determination of their complex energy eigenvalues. In particular, the imaginary component that determines the time constant for exponential decay of resonances is all but independent of the long-range characteristics of their computed wave functions. For all practical purposes, one need only achieve a high level of accuracy for the *short-range part* of these solutions in order to obtain good agreement with experimental observations. It is certainly not surprising that use of square-integrable basis functions is quite adequate for this limited purpose, and thus the fact that they are fundamentally incapable of describing the unbound asymptotic characteristics of such wave functions is all but irrelevant in the theoretical treatment.

The fact that a quantum mechanical operator is hermitian does not require that its spectrum consist exclusively of real eigenvalues. This will be the case only if two conditions are both satisfied in forming its matrix representation: the basis functions must be square-integrable and the *hermitian scalar product* must be employed in the calculation of its matrix elements. To obtain the complex energy eigenvalues required for resonances while still using a Hamiltonian operator that is hermitian [for example,  $H(0)$ ], it is sufficient to violate either one of these conditions. Since there are great computational advantages to working with a square-integrable basis, it is best not to change this aspect of the theoretical treatment, however. That leaves open the possibility of working with *complex-scaled* square-integrable functions such as have been used in ref. [11] but using a *symmetric scalar product* in lieu of its hermitian counterpart.

A computational scheme has therefore been developed which makes exclusive use of the symmetric scalar product in forming matrix representations of the un-rotated Hamiltonian  $H(0)$ . Two types of square-integrable basis sets are employed: a) one with exclusively real functions to describe bound states, the other, b) a complex-rotated set ( $R \rightarrow Re^{i\Theta}$ ) with exponential parameters that depend explicitly of the scaling angle  $\Theta$ . Formally, diagonalization of the resulting Hamiltonian matrices occurs with the aid of a product of two linear transformations, one unitary and the other orthogonal (either real or complex depending on the type of basis employed). A preparatory unitary transformation with  $U_p$  is carried out first for both types of basis sets in order to bring the respective Hamiltonian matrix to symmetric form. This is always possible because of the hermitian character of the operator. In this procedure complex conjugation is only used to form the hermitian conjugate matrix  $U_p^\dagger$  to be used in the bra position of the matrix elements, hence only for linear coefficients and not for the basis functions themselves. Since the basis functions for bound states are real (not complex-rotated), this means that the transformed Hamiltonian matrix must also be real-symmetric and therefore only have real energy eigenvalues, as required. If the basis functions are complex rotated (type b), however, the transformed Hamiltonian matrix will be complex-symmetric and therefore lead to the desired complex energy eigenvalues that are necessary to describe the spontaneous decay of the associated resonance states. The quantum mechanical description of resonance states is thus reduced to a variational treatment in real coordinate space in which both real and complex exponent values are to be optimized in accordance with a stationary principle.

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