Complex Coordinate Scaling and the Schrödinger Equation

Robert J. Buenker

Fachbereich C-Mathematik und Naturwissenschaften,
Bergische Universität Wuppertal, Gaussstr. 20,
D-42119 Wuppertal, Germany

Abstract

The complex rotation method (CRM) for the description of quantum mechanical resonance states is critically analyzed by noting that quantum mechanical eigenvalues are not affected by a change in spatial coordinates. On this basis it is concluded that equivalent solutions of the Schrödinger equation for a complex-rotated Hamiltonian H (Θ) can be obtained without loss of accuracy by using the un-rotated Hamiltonian H (0) in its place. Despite the fact that the latter operator is hermitean, it is possible to obtain a complex symmetric matrix representation for it by following a few simple rules: a) the square-integrable basis functions must have complex exponents, i.e. with non-zero imaginary components, and b) the symmetric scalar product must be employed to compute matrix elements of H (0). The nature of this approximation is investigated by means of explicit calculations which are based on diabatic RKR potentials for the B $^1\Sigma^+$ - D' $^1\Sigma^+$ vibronic resonance states of the CO molecule.

I. Introduction

The original tests of the Schrödinger equation [1] dealt exclusively with bound states for a variety of potentials. Such states are characterized by time-independent charge distributions and thus have infinite decay lifetimes. Gamov [2] and Siegert [3] later showed that there could be other solutions of the Schrödinger equation corresponding to meta-stable states with a finite lifetime. The condition for this type of (resonance) state is that it must possess a complex energy eigenvalue E. In that case the product of the time-dependent part of the wave function [Φ (t) = exp (-iEt)] with its complex conjugate is no longer constant and thus would in principle correspond to a charge distribution which decays over time. One of the outgrowths of this idea was the common belief that only a non-hermitean Hamiltonian operator can have eigenfunctions that have other than real energy eigenvalues. This conclusion in turn led to the complex rotation method (CRM) for the description of resonance states. Accordingly, the Hamiltonian of such a theoretical treatment must differ from the standard operator employed for bound states by rotating the original real spatial coordinates into the complex plane with the mapping: $R \rightarrow R \exp (i\Theta)$. The working hypothesis of the CRM is therefore that for each resonance state there is a *unique* (real) value of the scaling parameter Θ that defines a Hamiltonian H (Θ) of which the state is an eigenfunction. The corresponding complex energy eigenvalue E (Θ) can then be used to determine both the energy position of the resonance as well as its lifetime. The question that will be considered in the following is whether this hypothesis is correct or if in fact the desired characteristics of resonances can be obtained directly by solving the Schrödinger equation on the real axis with the unscaled Hamiltonian H (0).

II. Complex Rotation of Resonance Eigenfunctions

According to the CRM, the following time-independent Schrödinger equation holds for the complex rotated Hamiltonian H (Θ) described above:

$$H(\Theta)\,\Psi(\Theta) = E(\Theta)\,\Psi(\Theta). \tag{1}$$

The key assumption is that if the eigenfunction Ψ (Θ) corresponds to a resonance, the parameter Θ must have a unique real value and the energy eigenvalue E (Θ) must be complex, i.e. it must contain a non-zero imaginary component. To test this assertion it is useful to apply a further complex-coordinate scaling to each of the quantities in this equation: $R \rightarrow R \exp(i\Theta')$. This means that the original Hamiltonian operator H (0) defined on the real axis is rotated by the sum of the two angles, i.e. by Θ + Θ’. We can therefore express the result of the combined rotation as H (Θ + Θ’). Since the wave function Ψ (Θ) in eq. (1) also depends on the spatial coordinates R, it follows that it is also changed by the complex scaling and the result can be similarly expressed as Ψ (Θ + Θ’). However, the eigenvalue E (Θ) is by definition a constant and therefore its value is not changed by the added scaling. We are thus led to the following result which also has the form of a Schrödinger equation with the same eigenvalue as before:

$$H(\Theta + \Theta')\,\Psi(\Theta + \Theta') = E(\Theta)\,\Psi(\Theta + \Theta'). \tag{2}$$

All that has been done is to *systematically* change the coordinates used to define a differential equation and thereby obtain a different but equivalent form for it. This is a quite standard procedure that is used as a matter of course in this field of mathematics. In short, the assertion of the CRM that the Hamiltonian of the Schrödinger equation corresponding to a given resonance is uniquely defined by a specific complex rotation angle is patently false. Any rotation angle will lead to the same complex energy eigenvalue, including the special case of $\Theta + \Theta' = 0$. If eq. (1) is correct for a given resonance, it therefore must be possible to obtain both its energy eigenvalue and wave function by solving the corresponding Schrödinger equation *on the real axis*.

It should not come as a great surprise that the physical content of eq. (1) is not affected by complex scaling. From a purely mathematical point of view, there is no essential difference between multiplying coordinates with a complex constant or a real one. In the latter case it is clear that one would merely be changing the unit of distance in the theoretical formulation, changing from bohr to Ǻ, for example. Once one has obtained a solution to a given Schrödinger equation, it is a straightforward matter to express the resulting wave function in any other set of units, complex or otherwise. Since the energy eigenvalue itself is not a function of the spatial coordinates, it is obvious that it will not change as the result of any such scaling procedure. The only possible conclusion is therefore that if a solution of eq. (1) exists for a complex energy eigenvalue for any value of Θ, then *exactly the same physical information* must result from solution of the corresponding Schrödinger equation *defined on the real axis* that is routinely used for bound states of the system.

III. Use of Standard Matrix Techniques to Describe Resonances

The above conclusion needs to be reconciled with the fact that the Hamiltonian defined on the real axis, i.e. H(0), is hermitean. One often reads in the literature that the eigenvalues of any hermitean matrix are real, for example, in Goldstein's treatise on classical mechanics [4]. This statement might seem to contradict the conclusion that the H (0) operator can possess complex energy eigenvalues, but that is not the case. The reason it is not is that the hermitean property for a linear operator *only holds in general for a specific set of basis functions*. In the case of quantum mechanical operators this set consists *exclusively of square-integrable functions*. As a result, there is no *a priori* reason to conclude that the spectrum of such an operator only consists of real eigenvalues. In the present case, the hermitean character of H (0) requires that any and all eigenfunctions with complex energy eigenvalues *do not belong to the class of square-integrable functions.* This is a clear distinction between conventional bound states on the one hand, and resonances on the other.

The most effective means of obtaining approximate solutions for bound states is to represent them as linear combinations of square-integrable functions, and thus one would like to employ similar techniques for their resonance counterparts. However, in order to accomplish this goal in an optimal manner, it is necessary to deal with the fact that in this case the exact wave functions are themselves unbounded at infinity. Moiseyev and Corcoran [5] designed a computational method that has been quite successful in describing resonances in terms of a basis of square-integrable functions, but it is based on the proposition that the corresponding exact solution can only be obtained using a complex-rotated Hamiltonian consistent with the CRM of eq. (1). Since the discussion in Sect. II shows that the equivalent solutions for resonances can be obtained by solving the Schrödinger equation on the real axis, there is merit in considering how such wave functions can be approximated to a suitable degree of approximation while avoiding complex-coordinate scaling entirely. For this purpose it is necessary to decide which scalar product to use in constructing the required H (0) matrix representation and how to choose the square-integrable basis functions on which it is based.

This brings us to the crux of the problem for calculating resonances. According to eq. (2), it should be possible to obtain wave functions Ψ_{res} for meta-stable states by solving the Schrödinger equation on the real axis:

$$H(0)\,\Psi_{res}(0) = E_{res}\,\Psi_{res}(0), \qquad (3)$$

even when the Hamiltonian is a real operator, i.e. $H(0) = H(0)^*$, as is commonly the case. It is clear that under these circumstances, the only way that the eigenvalue $E_{res} \equiv E_r + iE_i$ can have other than a real value is for the eigenfunction $\Psi_{res}(0)$ to possess a non-zero imaginary component. Simply expanding it in terms of linear combinations of real basis functions cannot produce the desired result because the eigenvalues of a hermitean matrix are invariant to a linear transformation. Using such a transformed real basis must therefore give the same eigenvalues as if the H (0) matrix were expanded in terms of the original real basis functions themselves, i.e still yielding only real values.

That still leaves open the possibility of employing square-integrable basis functions with non-linear complex parameters to achieve the desired end. For example, one can use complex exponents for harmonic oscillator functions or the types of exponential basis functions commonly employed in electronic structure calculations. However, since these functions are square-integrable and H (0) is a hermitean operator in Schrödinger's theory, one would still have a hermitean matrix representation using these functions as basis *if the standard hermitean scalar product is used to evaluate the matrix elements*. One is therefore forced to choose another scalar product than the hermitean one in order to have any possibility of obtaining complex eigenvalues upon diagonalization of H(0). There is indeed a simple alternative available, however, namely the symmetric scalar product, that is, one in which the bra and ket functions in each matrix element are treated equivalently:

$$<\psi\, H\, (0)\, \varphi> \;=\; \int \psi\, H\, (0)\, \varphi\, d\tau \qquad (4)$$

This choice produces a complex symmetric matrix when the above complex exponential type of basis is employed, and this in turn does lead to complex eigenvalues upon diagonalization, i.e. with potentially non-zero imaginary components.

There is a fundamental question that arises when this is done, however, namely how can the use of a symmetric scalar product be justified in the treatment of resonances when in other applications of quantum mechanics, the hermitean scalar product is assumed to be essential, i.e. where the bra function is complex conjugated in evaluating the integral of eq. (4). To answer it, it is helpful to go back and consider how the scalar product enters into the theory in the first place. The Schrödinger equation itself does not require one since it only involves a linear operator and its eigenstates. If Ψ is an exact solution of eq. (3), the following general relationship holds for any form of the scalar product:

$$<\Psi\ H\ (0)\ \Psi > / <\Psi\ \Psi > = <\Psi\ E\ \Psi > / <\Psi\ \Psi > = E <\Psi\ \Psi > / <\Psi\ \Psi > = E. \qquad (5)$$

It is completely immaterial what one chooses as scalar product to evaluate the integrals implied in this equation as long as Ψ is an exact solution of the eigenvalue problem. It is not even necessary to carry out the integrations over all space to arrive at the above result. The role of matrix techniques in such an analysis is to obtain suitable approximations for both the wave function and the associated eigenvalue in the most efficient way possible. In principle, any scalar product may be used for this purpose, but obviously where one version has a clear advantage over the other it is only common sense to employ that one instead of its less effective counterpart. A complex energy eigenvalue can result from use of a hermitean scalar product when the exact solution is inserted into eq. (5), but that fact is of no use when finite basis sets are employed to obtain an approximate value for this quantity because only a real eigenvalue is possible under these circumstances. By contrast, use of a symmetric scalar product produces a complex eigenvalue for the simplest of basis sets. There is therefore at least the possibility by using it that accurate estimates of such quantities can be obtained with an acceptable outlay of computational resources. In short, there is no *a priori* reason for avoiding the symmetric scalar product in theoretical treatments of resonances, only an obvious impediment for the use of its hermitean counterpart.

The reason that the hermitean scalar product has gained favor has to do with a misunderstanding of the role of complex spherical harmonics in bound-state treatments of atoms. One could use exclusively real basis functions for such calculations, in which case it is clear that there is no difference between the use of the symmetric and hermitean scalar products. Complex conjugation in the bra position comes into play when spherical harmonics are used because they result from a unitary transformation of real (Cartesian) basis functions [6]. It is therefore necessary to use complex conjugation of *the linear coefficients* in the bra position, consistent with the definition of a unitary transformation. The transformed basis still consists of functions defined in terms of the real Cartesian coordinates of the atom, even though one can also claim that the calculations are actually based on spherical coordinates (and therefore angular variables) when this change of basis is employed. The advantage to making this distinction between complex conjugation of linear coefficients as opposed to a specific type of spatial coordinate is that there is no ambiguity in deciding which variables are radial and which are angular when calculations for polyatomic molecules are considered. In any event, it is perfectly consistent to claim that only the symmetric scalar product need be used in quantum mechanical matrix methods, regardless of whether bound or resonance states are under consideration. One simply must be aware of the fact that when a complex unitary transformation of real functions is used to define the basis set for the matrix representations, it is necessary to employ complex conjugation for the corresponding linear coefficients of these functions in the bra position [6].

IV. The Role of the Stationary Principle in Resonance Calculations

In order to use matrix methods effectively in treating resonance states, it is not sufficient to simply choose a complex basis and compute the eigenvalues that result from diagonalizing the corresponding Hamiltonian matrix (i.e. solving a secular equation). A criterion is needed on which to base the optimization of resonance wave functions and also to eliminate *spurious roots* which do not have any physical meaning but often appear in the results of the matrix diagonalization. To this end, it is helpful to note that exact solutions of the Schrödinger equation are *stationary* with respect to all variations *under the restriction of a constant normalization factor* $<\Psi\ \Psi>$:

$$\delta W = \delta < \Psi\ H\ \Psi > = E\ \delta <\Psi\ \Psi> = 0. \qquad (6)$$

This characteristic is especially useful in the present context because it applies to *all states* of a given system, not just the ground state. It also should be noted that approximate resonance wave functions can conveniently be normalized to unity since they are expanded in a square-integrable basis.

In the case of resonances, the above condition requires that both the real and imaginary components of the approximate energy eigenvalue $E \equiv E_r + i\ E_i$ must have vanishing derivatives *for the same value of each independent variable* and this turns out to be rather difficult to satisfy on a general basis. The situation is quite workable in the case of one-dimensional potentials, where one can effectively saturate the basis and still carry out the necessary matrix diagonalizations. Such an example has been reported for the resonances that occur because of the non-adiabatic interactions of the B $^1\Sigma^+$ and D $^1\Sigma^+$ states in the spectrum of the CO molecule [7]. The basis consists of a series of up to 250 harmonic oscillator functions, each of whose Gaussian exponents are scaled by an exp (iΘ) factor (it should be noted that the unscaled Hamiltonian H (0) is being used in these calculations, so the method employed is clearly distinct from complex-coordinate scaling despite the common use of the above exponential factor).

Two types of solutions are found, those with complex energy eigenvalues that satisfy the stationary principle to a satisfactory degree and thus are classified as resonances, and those that definitely do not satisfy it and are simply spurious (diffuse) roots of the H (0) diagonalization. States in the former category have E_r and E_i values that are *nearly independent of Θ over a wide range* and thus there is no difficulty in determining the corresponding energy eigenvalue for any of the 14 cases studied. These results are also found to agree quantitatively with those of other calculations [7], and so there is no doubt that diagonalization of H (0) is quite effective in the computation of resonance states, achieving the same level of accuracy that is normal for bound states. The corresponding wave function necessarily vanishes at large C-O distance because of the exclusive use of square-integrable basis functions (see Figs. 1a,b). However, at intermediate C-O distances it is evident that the approximate wave function has an exponentially increasing envelope similar to what one expects for a true (unbounded) resonance [8]. The indication is that increasing the size of the basis further would have very little influence on the complex energy eigenvalue, but that it would lead to an improved description of the wave function out to ever larger C-O bond distances.

The stationary principle also proves beneficial in the identification of spurious roots of the H (0) secular equation. There are many such examples in the results of Ref. 7. The variation of the E_r and E_i values with Θ for one of these roots is shown in Table 1, and these results clearly underscore the distinction between a resonance and a spurious root in the computations. It is possible to find a fairly stable value for the real component of the energy eigenvalue, but the corresponding E_i value is seen to vary linearly with Θ so that it is *impossible to satisfy the stationary criterion in this case*. Note that the root number also varies with Θ, making even the identification of corresponding energy values somewhat uncertain. *Such roots do not correspond to true solutions of the Schrödinger equation and have no physical significance*.

The C-O vibronic resonance calculations also illustrate a more general point that is closely related to the arguments of Sect. II. The theoretical treatment has also been carried out with a complex-rotated Hamiltonian and the same matrix representation is obtained as with H (0) when the harmonic oscillator basis functions are rotated by the same amount. This result is justified by the Cauchy-Coursat theorem for complex variables [9]. The fact that the Hamiltonian matrix representation is independent of the scaling angle Θ obviously means that the energy eigenvalues resulting from the diagonalization procedure are also unaffected by the coordinate scaling. The corresponding eigenvector coefficient matrices are also independent of Θ. One can thus make the same argument for such complex Hamiltonian matrices as is commonly used for the real matrices employed in conventional bound-state calculations. *In the limit of a complete set, the results of the theoretical treatment must approach the exact values obtained by direct solution of the corresponding Schrödinger equation.* Hence, the Cauchy-Coursat theorem is seen to be perfectly consistent with the result of eq. (2), thereby justifying the exclusive use of eq. (3) to obtain exact resonance solutions, as well as their bound-state counterparts, by directly employing the H (0) operator defined on the real axis in the Schrödinger equation and therefore avoiding complex-coordinate rotations entirely in the theoretical treatment.

In principle, the matrix approach described above can also be used to treat many-electron problems as well. It is not possible to employ basis sets that are comparable to those used in one-dimensional calculations, however, and so one normally has to make a number of approximations that are not required for vibronic resonances. It is nonetheless helpful in dealing with many-electron systems to recognize that the basic approach is to solve the Schrödinger equation on the real axis in accord with eq. (3). This has distinct advantages over the complex-coordinate scaling method when it comes to making decisions about the theoretical treatment to be used. For example, when the Born-Oppenheimer Approximation is to be applied for molecular systems [10,11], there is no doubt as to which Hamiltonian is to be used. By contrast, in a complex-scaling approach, one has to ask very basis questions about how the nuclear coordinates are to be scaled. The complex-scaling method of Ref. 5 overcomes this difficulty with some rather complicated arguments that lead to the same result as when H (0) is simply used in its original form, but in the end there is absolutely no distinction between the two approaches in this regard.

By not employing complex scaling, one also is much freer in deciding on the appropriate basis sets that are to be used for many-electron interactions. For example, it seems obvious that the inner-shell electrons of the system will have nearly the same charge distribution for low-energy resonances as they do for bound states. If only the exponents of the basis functions are to be scaled, it is clear how to handle this situation, namely to simply scale those basis functions that are likely to be involved in the description of the outer-valence orbitals whose occupation is clearly responsible for the observed meta-stable characteristics. Again, a method which claims that complex coordinate rotation is essential in the theoretical treatment of resonances must justify the use of a limited scaling that does not affect inner-shell electrons in a much more convoluted way than if the goal is simply to employ basis sets that are specifically designed to obtain optimal descriptions of resonances using the un-rotated H (0) operator in the associated Schrödinger equation.

There is still merit in using a limited scaling procedure for the complex exponents in treatments based on eq. (3), however. This greatly simplifies the application of the stationary principle to the optimization process, since the condition of simultaneously vanishing derivatives of E_r and E_i with respect to a single variable is already difficult enough. At this level of treatment, the complex-coordinate approach of Ref. 5 is basically indistinguishable from one employing a matrix representation of H (0). The computational results are the same, but the theoretical justification is quite different.

V. Time Reversal and Resonance Energy Eigenvalues

One of the most interesting aspects of the theory of resonances presented above is the fact that a *time-dependent charge distribution* results from use of a *time-independent Hamiltonian*. Formally, this comes about by first separating variables in the associated time-dependent Schrödinger equation:

$$H\,(0)\,\Psi\,(r,t) = i\,\partial\,\Psi\,(r,t)\,/\,\partial t, \qquad (7)$$

which leads to the one-dimensional equation $i\, d\varphi(t)/dt = E\varphi$ with the solution, $\varphi(t) = \exp(-iEt)$. It is commonplace to read in textbooks that the charge distribution given in Schrödinger's theory by the product $\varphi\varphi^*$ is nonetheless independent of time, and this is what one should expect because of the lack of time dependence in the associated Hamiltonian operator. This result only holds when E is real, however, which is ultimately the basis for the conclusion [2,3] that a resonance state must be characterized by a non-zero imaginary component for its energy eigenvalue ($E_r + i\, E_i$). In this case, $\varphi\varphi^* = \exp(2E_i t)$, from which one concludes that E_i must be negative for a resonance state so that its charge distribution is exponentially decaying rather than increasing with time.

It might be thought that a negative value for E_i is essential for a true resonance state. Indeed, this was the case for each of the resonances obtained in the calculations mentioned above [7,10,11]. This conclusion is actually false, however, because it overlooks a basic fact about the time-dependent Schrödinger equation, namely that there is an equivalent version:

$$H(0)\, \Psi(r, t) = -i\, \partial\, \Psi(r, t) / \partial t. \tag{8}$$

It is related to eq. (7) by the time-reversal operation ($t \rightarrow -t$) and its solutions have exactly the same physical significance as the latter [12]. In fact, for every resonance eigenfunction of eq. (3) with a negative E_i value, there is an equivalent one with a positive value for this quantity. One simply has to change the basis set so that the sign of all imaginary components of the exponents of the functions is reversed. An example for this behavior can be seen from Table 1, which shows the value of E_r to be the same for the scaling factors $\Theta = 1$ deg and -1 deg, but that for E_i to be equal but opposite in sign. In evaluating the time-dependence of the associated charge distribution, one simply has to choose the correct Schrödinger equation on which to base this determination. The corresponding time-dependent function for eq. (8) is seen to be $\varphi(t) =$

exp (i E t) instead of the result for eq. (7) discussed first with the opposite sign for its exponent. In this case the charge distribution $\varphi\varphi^* = \exp(-2E_i t)$, and hence a positive E_i value is necessary for the resonance to be exponentially decaying, but with the same absolute value as in the other case. The corresponding wave functions are also interrelated by changing the sign of all imaginary components. In effect, time reversal is accounted for by simply changing the value of i to –i wherever it appears in the results of the respective calculations. Consequently, the solutions of both eq. (3) and the corresponding matrix equation used in the approximate theoretical treatment always come in equivalent pairs. Application of the time-reversal operation changes the form of the resonances without altering their physical interpretation in any way.

VI. Conclusion

The scaling of coordinates does not affect the eigenvalues of a given Schrödinger equation, only its Hamiltonian operator and the corresponding eigenvectors. Complex coordinate scaling therefore does not affect the spectrum of the Hamiltonian. This applies to the complex energy eigenvalues of resonance states, so if there is such a solution for the rotated Hamiltonian operator H (Θ) of eq. (1) there is also an equivalent solution for all other angles of rotation. The conclusion is that all resonance states for a given system can be obtained by solving the Schrödinger equation for the un-rotated Hamiltonian H (0) defined on the real axis. Because of the hermitean property of the latter operator, it follows that all resonance eigenfunctions must be un-bounded, i.e cannot be square-integrable.

It is nonetheless possible to obtain resonance wave functions to any degree of approximation in terms of an exclusively square-integral basis. For this purpose it is essential that at least some of the exponents in standard basis sets employed to construct matrix representations of H (0) have non-zero imaginary components. In addition, a symmetric scalar product needs to be used in computing the matrix elements, so that a complex symmetric matrix results which therefore can have other than real energy eigenvalues. In the limit of complete sets, the hermitean scalar product could be used just as well, but for finite basis sets only real energy eigenvalues can result from its use because of the hermitean character of H (0) and thus this type of scalar product must be avoided if resonance wave functions are to be computed.

A one-dimensional treatment for the vibronic resonances of the C-O B-D band system is used to illustrate the above matrix method. The basis set consists of harmonic oscillator functions defined on the real axis but with non-zero imaginary components for the exponents of their Gaussian functions. It is required that the eigenvalues be stationary with respect to exponent variations for both the real and imaginary components of the energy. This condition is necessary for optimization of the complex values of the exponents as well as to identify spurious roots of the resulting secular equations that do not correspond to resonances but rather are quasi-continuum functions having no physical significance. Application of the above matrix method for many-electron problems is hampered by the sizes of basis sets that can be used for such problems, in which case the stationary principle takes on an especially critical role in the theoretical treatment.

Finally, it is pointed out that two completely equivalent solutions are found for each root with a non-zero imaginary component of the energy. This duality is traced to the time-reversal phenomenon and the existence of two completely equivalent time-dependent Schrödinger equations differing only in the sign of the associated energy operator.

Acknowledgement

The financial support of the Deutsche Forschungsgemeinschaft in the form of Grant No. Bu 450/22-1 is hereby gratefully acknowledged.

(Jan. 16, 2010)

References

1) E. Schrödinger, Ann. D. Phys. **79**, 361 (1926); 489 (1926).
2) G. Gamov, Der Bau des Atomkernes und die Radioaktivitaet (S. Hirzel Verlag: Leipzig, 1932).
3) A. J. F. Siegert, Phys. Rev. **56**, 750 (1939).
4) H. Goldstein, Classical Mechanics (Addison-Wesley, Reading MS, 1950), p. 153.
5) N. Moiseyev and C. Corcoran, Phys. Rev. A **20**, 614 (1979).
6) R. J. Buenker, "Hamiltonian Matrix Representations for the Determination of Approximate Wave Functions for Molecular Resonances," to be published.
7) Y. Li, O. Bludsky, G. Hirsch, and R. J. Buenker, J. Chem. Phys. **107**, 3014 (1997).
8) R. J. Buenker, Y. Li, and H.-P. Liebermann, "Use of Gauss-Hermite Quadrature to Approximate the Asymptotic Behavior of Vibronic Resonance Wave Functions," to be published.
9) F. P. Greenleaf, Introduction to Complex Variables (Saunders, Philadelphia, 1972).
10) M. Honigmann, R. J. Buenker, and H.-P. Liebermann, J. Chem. Phys. **125**, 234304 (2006).
11) M. Honigmann, R. J. Buenker, and H.-P. Liebermann, J. Chem. Phys. **131**, 034303 (2009).
12) D. G. Truhlar and C. A. Mead, Phys. Rev. A **42**, 2593 (1990).

Table 1. Variation of the real (E_r) and imaginary (E_i) components of the energy eigenvalue (in units of cm^{-1}) for a quasi-continuum (diffuse) state as a function of the complex-scaling parameter Θ (in deg). The root number in each secular equation is also given. Note that E_i varies linearly with Θ and that the values for +1 and -1 deg are equal except for sign.

Θ	root no.	E_r	E_i
1	6	1242	-20.26
2	6	1240	-40.49
4	8	1235	-81.42
6	11	1225	-117.94
10	30	1237	-196.00
-1	6	1242	+20.26

Fig.1a

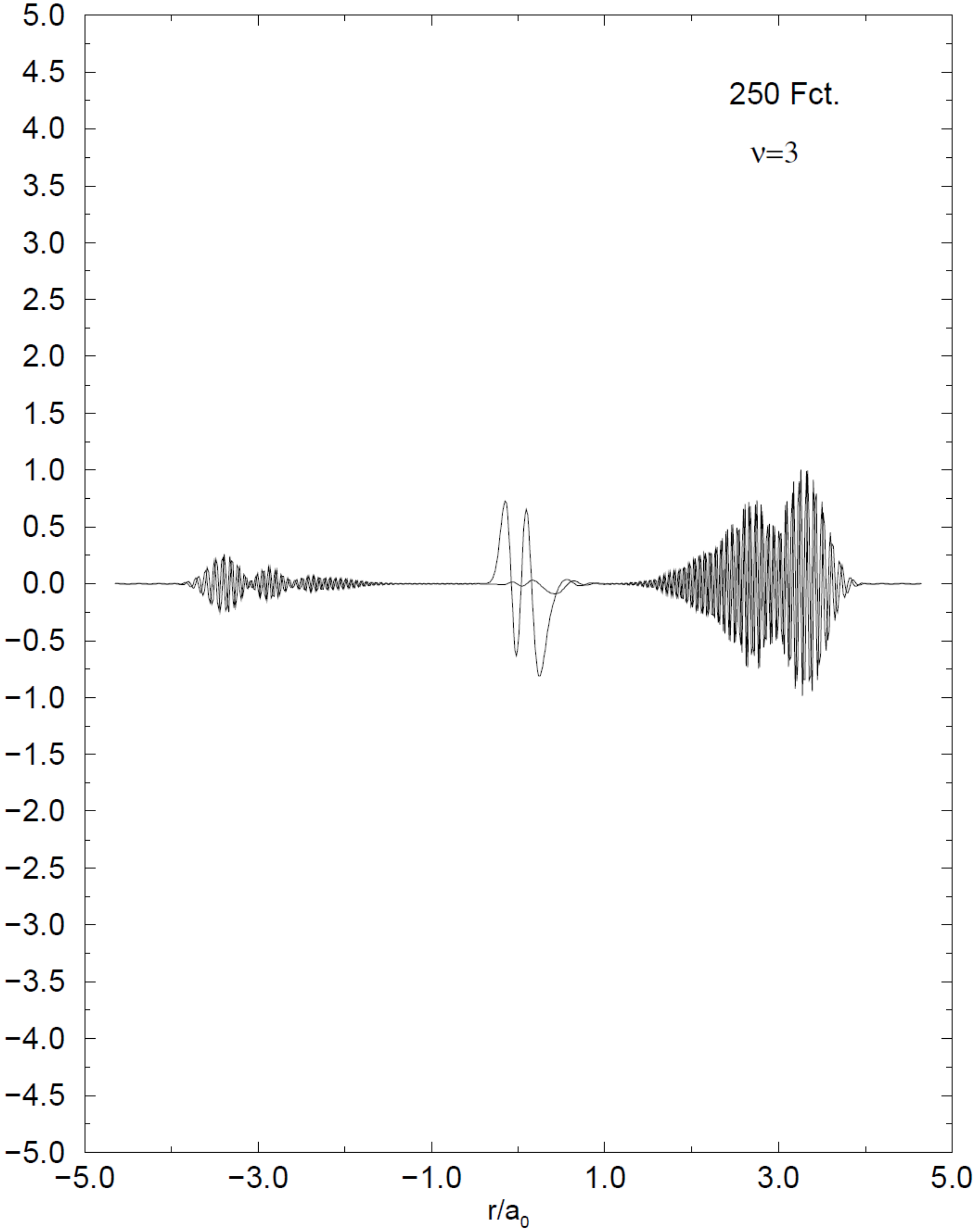
250 Fct.
ν=3
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
−3.5
−4.0
−4.5
−5.0
−5.0
−3.0
−1.0
1.0
3.0
5.0
r/a₀

Fig.1b

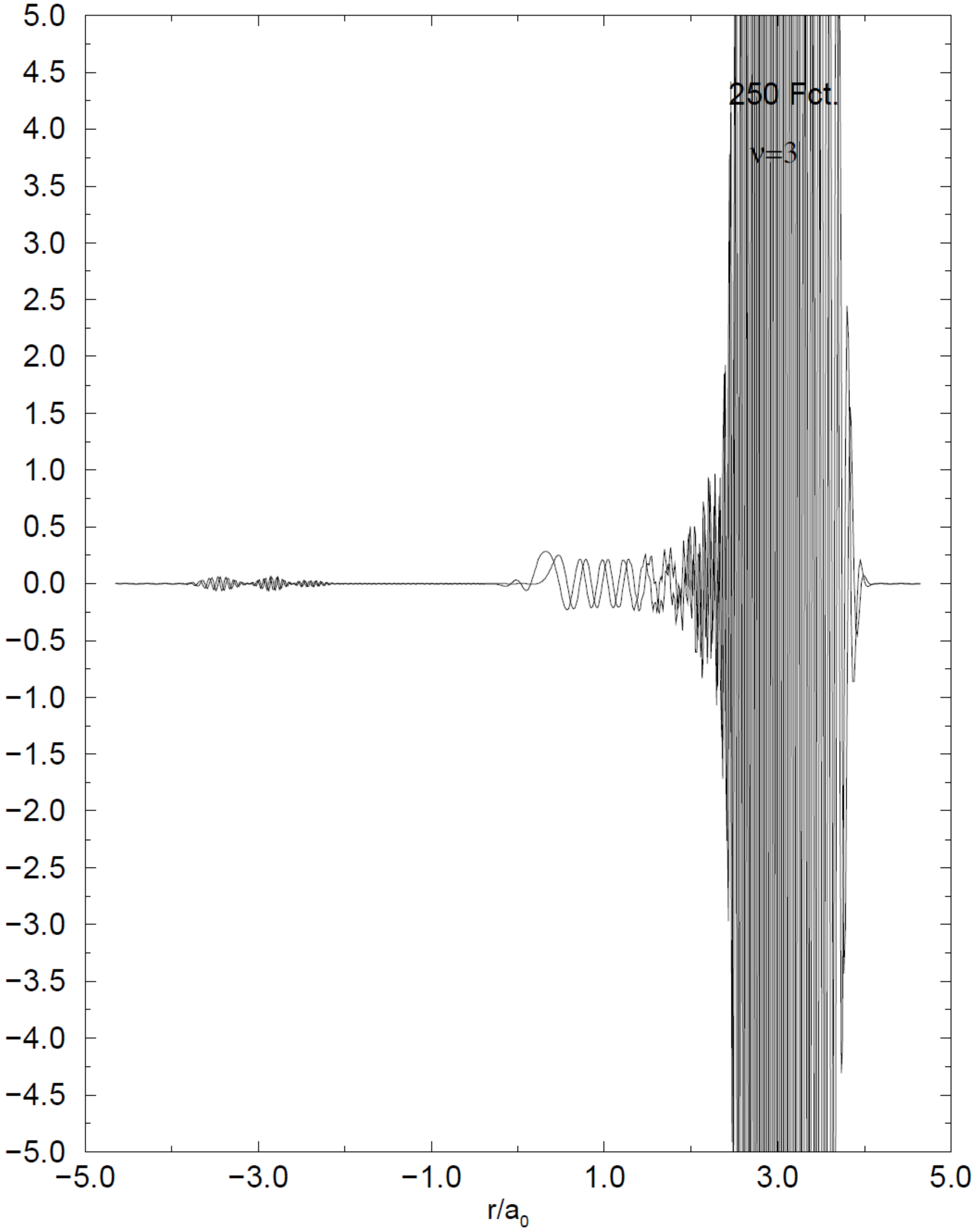

Figure 1. Real and imaginary components of the wave function for the v=3 resonance state in the B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by employing a basis set of 250

complex-scaled (Θ= 4.0 deg) harmonic oscillator solutions for the vibrational functions multiplying a) the bound electronic state ψ_1 and b) the repulsive electronic state ψ_2 (see ref. 7 for definitions). Note that r=0 corresponds to the equilibrium bond distance of the bound potential H_{11}.