Resonance states by the generalized complex variational method

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Resonance states by the generalized complex variational method

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The resonance states are presented as the complex stationary solutions of generalized secular equations. The study of the analytical behaviour of the complex stationary solutions of these equations as a function of a coupling parameter λ in the hamiltonian yields the following.

(1) Criteria to distinguish between the complex stationary solutions that describe the resonances and the complex solutions that may be obtained as a result of the restrictions on the basis set.

(2) Criteria and a computational procedure for judging the stability of results obtained within the framework of the complex coordinate method. On this basis it is pointed out that the enhanced stability of the resonant eigenvalue when a complex basis function is added to the real basis set is due to the fact that the expectation value of the second derivative of the hamiltonian with respect to the scaling parameter can be negative while for a real basis set it is equal to the kinetic energy and therefore gives positive values only.

1. INTRODUCTION

Any real atom and molecule (with more than one electron) has quasibound states (resonances) that are important for understanding their dynamics. The resonance states are associated with non-normalized solutions of the time independent Schrödinger equation and thus appeared to require techniques similar to those of quantum scattering theory. However, the complex co-ordinate method as established by the fundamental work of Aguilar, Balslev, Combes and Simon [1] enables us to isolate the states of finite lifetime (like the autoionization and the predissociation resonances) from the other states in the continuum and enables us to obtain the resonance position and lifetime by the widely used procedures for bound states.

In the complex coordinate method the internal coordinates of the hamiltonian $H(\mathbf{r})$ which describes many particle systems are transformed by

$$\mathbf{r} \to \mathbf{r}/\eta \qquad (1)$$

where

$$\eta = |\eta| \exp(-i\theta). \qquad (2)$$

Thereby a complex Schrödinger equation is obtained

$$\hat{H}(\mathbf{r}/\eta)\phi_K(\mathbf{r}) = E_K \Phi_k(\mathbf{r}). \qquad (3)$$

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The resonance states are identified with the complex solutions E_K that are *independent* of η. The complex eigenvalue yields the resonance position E_r and width Γ (the inverse of the lifetime)

$$E_K = E_r - \frac{i}{2}\,\Gamma. \tag{4}$$

For large enough θ (see equation (2)) the resonance wavefunction becomes square integrable and therefore ϕ_K can be described within a complete set of square integrable real and orthogonal functions (ϕ_i)

$$E = \sum_{i,j}^{\infty} C_i C_j H_{ij} \Big/ \sum_{i,j}^{\infty} C_i C_j \delta_{ij} \tag{5}$$

where

$$H_{ij} = \int \phi_i(\mathbf{r})\hat{H}(\mathbf{r}/\eta)\phi_j(\mathbf{r})\,d\mathbf{r}.$$

The linear parameters are obtained by the requirement of [2]

$$\partial E/\partial C_i = 0. \tag{6}$$

By truncating the basis set, (3) is replaced by an eigenvalue matrix equation

$$(\mathbf{H}(\eta) - E_K \mathbf{1})\mathbf{C}_K = 0. \tag{7}$$

Within the finite matrix approximation all the eigenvalues E_K of (7) are *functions* of η. The resonance states are obtained when the complex scaling parameter η is chosen such that

$$[\partial E_K/\partial \eta]_{\eta = \eta_0} = 0. \tag{8}$$

These types of solutions satisfy the complex virial theorem that has been derived by Brandas and Froelich [3] and was applied to electron scattering of atoms by Moiseyev et al. [2, 4].

The complex coordinate method has been applied to various physical phenomena : atomic (see for example [5]) and molecular [6, 7] autoionization resonances ; shape (see for example [2]) and Feshbach [8] predissociation resonances ; resonances where the autoionization and the predissociation channels are coupled to one another [9] ; resonances of atoms in electric fields [10] ; rotational predissociation resonances of van der Waals molecules [11] ; and resonances obtained by elastic scattering of positronium-hydrogen [12]. However, in spite of the successful application of the complex coordinate method to different types of resonance phenomena, several numerical diffi-culties were observed in the application of this method. In the complex coordinate method the basis sets required to stabilize the variational solutions are much larger in the case of resonance states than in the case of bound states. In order to make the complex variational solution of a molecular hamiltonian more stable for a smaller basis set, it was suggested by Rescigno and McCurdy to optimize the positions of the basis functions in the complex plane, in addition to the optimization of the scaling factor [7]. Recently it was proposed to use the real hamiltonian with a basis set containing only one or two complex basis functions ([13, 14] and references therein). When all the non-linear parameters are complex optimized to give a stationary solution, then all these procedures are identical. The inclusion of complex basis functions yields different results

only because of the restrictions on the variational space. Therefore, the resonance states can be defined by the generalized secular equations

$$(\mathbf{H}(\boldsymbol{\gamma}) - E_K \mathbf{I}) \mathbf{C}_K = 0 \tag{9}$$

rather than by (7). Here $\boldsymbol{\gamma}$ stands for the complex optimized non-linear parameters of the basis functions, that is $\partial E / \partial \gamma_i = 0$. If the scaling factor is the only complex optimized parameter then (9) is identical with (7) that has been derived by the complex coordinate method within the finite matrix approach. The secular equations presented in (9) are general in the sense that there is a freedom in selecting the pattern in which the conventional variational solutions are analytically continued to the complex plane. Namely, anyone of the non-linear parameters of the given basis functions can be taken as the complex variational variable. In this paper we study these generalized complex secular equations, addressing ourselves to the following questions.

(1) Under what conditions are complex stationary solutions of (9) obtained ?

(2) How can we distinguish between the complex variational solutions that describe the resonance and the complex solutions that may be obtained as a result of the restrictions on the basis set ?

(3) What are the reasons for the necessity of large basis sets to calculate resonance states by the complex coordinate method and why does the inclusion of only one complex function in the real basis, without the use of rotated coordinates, show enhanced stability of the resonant eigenvalue ?

2. RESONANCE STATES OBTAINED BY THE GENERALIZED VARIATIONAL METHOD

Resonances may be obtained for an arbitrary hamiltonian, $\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$, when the coupling parameter λ is larger than some λ_0. By varying λ a bound state of $\hat{H}$ can be shifted to the continuum as was pointed out by Reinhardt [15] and Stillinger [16]. If for $\lambda = \lambda_0$ the energy of a bound state is equal to the threshold energy then a resonance *may* be obtained. Examples are :

(a) in the case of the helium isoelectronic system λ is the inverse of the nuclear charge ($1/Z$ perturbation) and atomic autoionization resonances are obtained for $\lambda > \lambda_0$ where $\lambda_0 = 0$, that is the resonances can be obtained even if $Z \to \infty$ [17] ;

(b) in the case of atoms in electric fields λ is the intensity of the field and $\lambda_0 = 0$ [10] ;

(c) in the case of rotational predissociation λ is the rotational quantum number J and $\lambda_0 \neq 0$ [9].

As was discussed in the introduction the resonance states are associated with the complex solutions of the Schrödinger equation. These complex solutions of an arbitrary hamiltonian can be obtained by the complex coordinate method (3) only for dilatation-analytic hamiltonians. However, in the framework of the finite matrix approximation the complex coordinate (see (7)) is applicable to non-dilatation analytic potentials as well. This is justified by the successful applications of the complex coordinate method to non-dilatation-analytic problems such as the autoionization of H_2^- [6], the Stark effect [10] and, in the present case, the anharmonic oscillator.

In the finite matrix representation of the hamiltonian the critical value λ_0 for which a bound state becomes a resonance is associated with the appearance of complex solutions of (9). Since it is most likely that the complex solutions of (9) will be obtained when two real solutions of the *conventional* secular equations coalesce, λ_0 can be considered as a branch point. This statement is a simple result of the fact that the secular equations for homogeneous potential functions can be written as a power series of the scaling factor η. The complex roots of an analytical power series appear when at least two real solutions of a polynomial coalesce. Therefore, we can use the basic assumption that in general the complex solutions appear when two real solutions of the conventional secular equations coalesce. This occurs by varying the coupling parameter in the hamiltonian. Support for this assumption is given by the numerical study and analysis of the harmonic oscillator model hamiltonian presented here as an example.

Because of the limitations on the variational space, $|\lambda_0|$ which is obtained by truncating the basis set, is greater than the exact absolute value $|\lambda_0(\text{exact})|$ that is obtained for the complete basis set. In the range of

$$|\lambda_0| > |\lambda| > |\lambda_0(\text{exact})| \tag{10}$$

bound states rather than resonances are obtained (for a more detailed discussion on a bound state in the continuum see [18]). As an example we solved the secular equations (7) for the anharmonic oscillator $\hat{H} = -\frac{1}{2}(d^2/dx^2) + (x^2/2) + \lambda x^4$, with the basis set truncated to N harmonic wavefunctions (19). The bound state energies were obtained by satisfying the virial theorem, that is, $\partial E/\partial \eta = 0$. The results for the optimized η as a function of λ are given in figure 1 (a). The bound state solutions are associated with the optimized positive scaling parameters. When $-\lambda_0 < \lambda < \lambda_0$ and $\eta > 0$ two stationary solutions were obtained. One of the stationary solutions is associated with a local minimum of the energy (the thick line in figure 1 (a)) and the second solution is associated with a local maximum of the energy (the fine line in figure 1 (a)). At $\lambda = \lambda_0$ the two extremal solutions coalesce, $(\partial E/\partial \eta)_{\lambda = \lambda_0} = 0$, and two complex conjugated solutions are obtained (schematic representation of the complex stationary solutions is given by the dashed lines in figure 1 (a)). Figure 1 (b) shows that improvement of the variational space (by taking a large basis set) reduces the deviation of λ_0 (obtained by a limited basis set) from the exact value. The two solutions coalesce at a certain value of λ_0 if and only if one of the solutions corresponds to a minimum point in the variational space, $(\partial^2 E/\partial \eta^2) > 0$, whereas the other one corresponds to a maximum point and $(\partial^2 E/\partial \eta^2) < 0$. These two extremal solutions for the anharmonic oscillator are presented in figure 2. By decreasing the value of λ the two solutions presented by the dark dots in figure 2 approach one another. A coalescence of the two solutions yields two complex conjugated eigenvalues, where the resonance state is associated with the complex stationary solution for which $\text{Im } E = E_i < 0$. The resonances are obtained for $\lambda < \lambda_0$ by optimizing the complex scaling factor, $\eta = |\eta| \exp(i\theta)$ such that, $(\partial E_r/\partial \theta)_{\theta_{\text{opt}}} = (\partial E_r/\partial |\eta|)_{|\eta_{\text{opt}}|} = 0$. The resonance solution is therefore represented by the cusps [20] in figures 3 (a) and (b).

Following the above analysis λ_0 can be obtained by satisfying the condition

$$\left.\frac{d^2 E}{d\eta^2}\right|_{\eta_0} = \infty \quad \text{and} \quad \left.\frac{dE}{d\eta}\right|_{\eta_0} = 0, \tag{11}$$
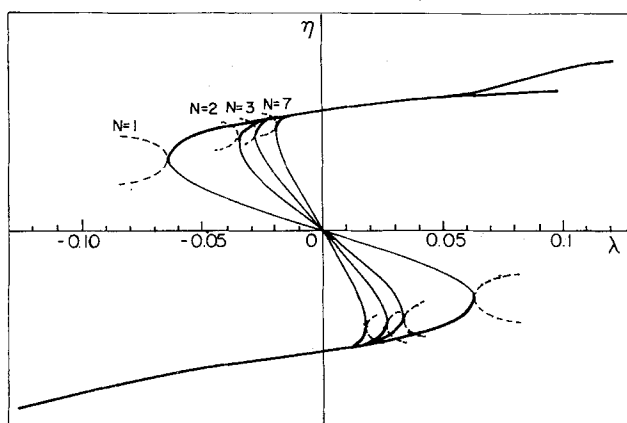
(a)
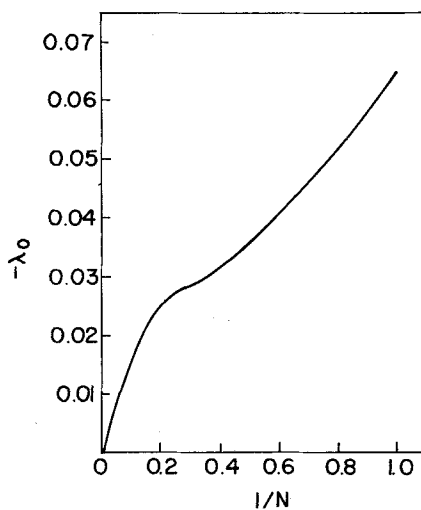
(b)

Figure 1. (a) Location of the extremal values of η. N denotes the number of basis functions. The dashed line represents the complex solutions that are obtained as a result of the coalescense of the two extremal values of η. The thick lines represent the values of η for each a local minimum of the energy is obtained whereas the fine lines represent η which yield a maximum solution. (b) The critical anharmonicity parameter at which the extremal solutions coalesce versus the size of the basis set.

where

$$\frac{d^2 E}{d\eta^2} = \mathbf{C}^{\mathrm{T}}[\partial^2 \mathbf{H}/\partial\eta^2]C - |a| \tag{12}$$

and

$$|a| = \frac{\mathbf{D}^+(\mathbf{H} - E\mathbf{I})\mathbf{D}}{\mathbf{D}^+\mathbf{D}}, \quad \mathbf{D} = \frac{\partial\mathbf{C}}{\partial\eta}. \tag{13}$$
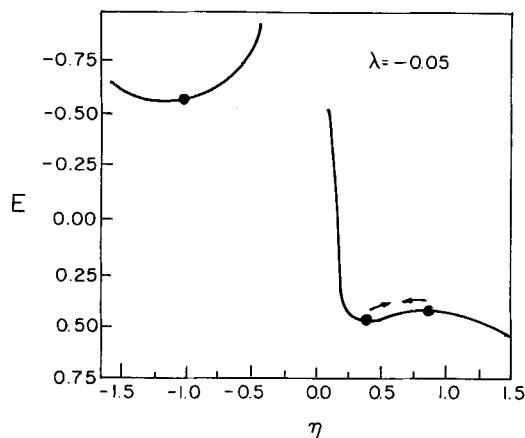
Figure 2. The local minima and maximum of the energy for a negative anharmonicity parameter, obtained for a minimal basis set of one gaussian. The arrows indicate the direction of motion of the two extrema solutions with increasing the number of the basis functions.

(a)   (b)
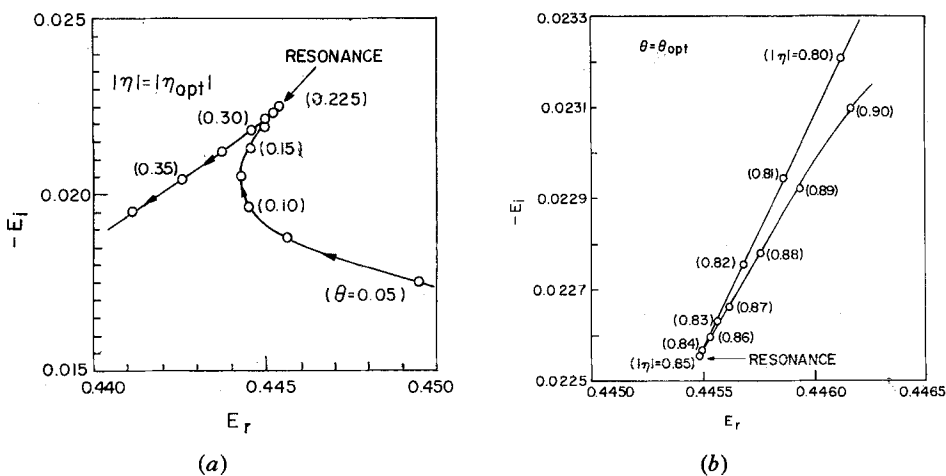
Figure 3. (a) $|\eta|$ trajectory for fixed $\theta = 0.23$, ten basis functions and $\lambda = -0.05$. The solution at the cusp satisfies the complex virial theorem. (b) θ-trajectory for fixed $|\eta| = 0.85$, ten basis functions and $\lambda = 0.05$. The arrows indicate the direction of motion of the eigenvalues with increasing θ.

The conditions presented by (11) are obtained from the relation $E \sim (\eta - \eta_0)^{3/2}$ when η_0 is the stationary point in which two eigenvalues of the hamiltonian matrix coalesce ([21] and references therein). The proof of (12) is as follows. By taking the product of the first derivative of (9) with respect to a non-linear parameter γ with $\mathbf{D} = d\mathbf{C}/d\gamma$ one can get

$$- \mathbf{D}^{\mathrm{T}}(d\mathbf{H}/d\gamma - dE/d\gamma \mathbf{I})\mathbf{C} = \mathbf{D}^{\mathrm{T}}[\mathbf{H}(\gamma) - E\mathbf{I}]\mathbf{D}. \qquad (14)$$

The product of the second derivative of the matrix Schrödinger equation with $\mathbf{C}$ results in

$$-2\mathbf{C}^{\mathrm{T}}(d\mathbf{H}/d\gamma - dE/d\gamma \mathbf{I})\mathbf{D} = \mathbf{C}^{\mathrm{T}}(d^2 \mathbf{H}/d\gamma^2)]\mathbf{C} - d^2 E/d\gamma^2. \qquad (15)$$

Consequently

$$\frac{d^2 E}{d\gamma^2} = \mathbf{C}^{\mathrm{T}} \left(\frac{d^2 \mathbf{H}}{d\gamma^2} \right) \mathbf{C} - |a| \tag{16}$$

where

$$|a| = 2\mathbf{D}^{\mathrm{T}}(\mathbf{H} - E\mathbf{I})\mathbf{D} > 0. \tag{17}$$

Note that if γ stands for any real parameter occurring in the hamiltonian then (12) is an extention of the proof for the upper bound relation $(\partial^2 E/\partial\gamma^2) < \langle \psi | \partial^2 H/\partial\gamma^2 | \psi \rangle$ to the variational solutions. (For the upper bound relation, see [21] and references therein.) Note that (11) and (12) are valid for *any* non-linear parameter γ and not only for the special cases where γ is identified with the scaling factor η. The knowledge of the value of λ_0 helps to distinguish between the complex stationary solutions which describe the resonance states, and those that may be obtained because of the restrictions on the variational space. *The resonance statet are associated with the complex stationary solutions that are lying on a branch that becomes a bound state at $\lambda = \lambda_0$ as λ is decreased.* In the case of the anharmonic oscillator for example (see figure 1 (*a*)) complex stationary points are obtained also for *positive* λ. However, these complex solutions do not lie on a complex branch that is obtained as a result of the coalescence of one of the vibrational energy level (obtained for $\lambda > 0$) with another stationary solution (maximum of the energy with respect to the non-linear variational parameter) and therefore are not interpreted as resonance states. From the value of the branch point one can estimate the radius of convergence of the perturbational series [22], when the perturbation is taken to be the operator that couples discrete energy levels with the continuum and λ is the strength parameter of the perturbation. Consequently, we conclude that the *smallest value of $|\lambda|$ for which resonances can be obtained determines the radius of convergence of the perturbation expansion.*

We shall study explicitly this statement by the analysis of the example of the *anharmonic oscillator*

The complex rotated hamiltonian is

$$H = \frac{\eta}{2} \frac{d^2}{dx^2} + \frac{\omega^2 x^2}{2\eta} + \frac{\lambda}{\eta^2} x^4. \tag{18}$$

The resonance state is approximated by a trial function ψ_n and the resonance position and width are estimated from the complex energy

$$E_n = \int_{-\infty}^{\infty} \psi_n \hat{H} \psi_n \, dx \bigg/ \int_{-\infty}^{\infty} \psi_n^2 \, dx, \tag{19}$$

where η is chosen to satisfy the condition [2, 4]

$$\frac{dE_n}{d\eta} = 0. \tag{20}$$

By making use of the Hellman–Feynman theorem [23], (18)–(20) can be summarized by the following cubic equation

$$\eta^3 - b\eta - c = 0, \tag{21}$$

where

$$b = \frac{\omega^2}{2} \int_{-\infty}^{\infty} \psi_n x^2 \, \psi_n \, dx \Bigg/ \int_{-\infty}^{\infty} \psi_n \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) \psi_n \, dx \equiv \frac{\omega^2}{2} \langle x^2 \rangle / \langle T \rangle \qquad (22)$$

and

$$c = 2\lambda \langle x^4 \rangle / \langle T \rangle. \qquad (23)$$

As was pointed out in the analysis presented above, a complex stationary solution (a *resonance*) is obtained when two solutions of (21) (one corresponding to a minimum energy and the other one corresponding to a maximum energy) coalesce at

$$\lambda = \lambda_0. \qquad (24)$$

In the case of the anharmonic oscillator from (21) to (23) one can get that

$$\lambda_0{}^2 = \frac{[(\omega^2/2)\langle x^2 \rangle]^3}{27 \langle x^4 \rangle^2 \langle T \rangle}. \qquad (25)$$

Since λ_0 is a point in which *two* roots of (19) coalesce, it is expected that [22]

$$E_n \propto (\lambda - \lambda_0)^{1/2}. \qquad (26)$$

However, from (25) we can see that $\lambda = -\lambda_0$ is also a branch point. Consequently, in the neighbourhood of the critical value of λ where resonance states appear

$$E_n \propto [(\lambda - \lambda_0)(\lambda + \lambda_0)]^{1/2}. \qquad (27)$$

If ψ_n is taken in a zeroth order approximation as the nth harmonic oscillator wavefunction, then

$$\lambda_0 = \frac{\omega^2}{6\sqrt{3}} \frac{\langle x^2 \rangle}{\langle x^4 \rangle} \qquad (28)$$

and for large n

$$\lambda_0 \propto \frac{\omega^3}{n}. \qquad (29)$$

Equation (29) shows that the infinite sequence of branch points has a limit point at $\lambda = 0$. At that limit the Hermite polynomials are the exact solutions of the Schrödinger equation and therefore it is expected that (29) yields the exact behaviour for large n. This conclusion and (27), (29), that were obtained here by the analysis of the complex coordinate method, are in complete agreement with the results that were obtained recently by Katriel ([24] and references therein) who has studied the radius of convergence of the perturbation expansion of the anharmonic oscillator using the generalized Bose operators.

3. The complex coordinate method and the stabilization method of Junker [13]

In the stabilization method of Junker complex square-integrable functions, which do not impose explicitly any boundary condition, are added to the basis set. In the introduction we pointed out that if all the non-linear parameters are complex optimized to give a stationary solution, then the procedure of Junker is equivalent to the complex coordinate method. However, the non-linear parameters are usually not optimized and therefore different results are

obtained by the two methods for any given finite basis set. Within the finite matrix approximation, the complex coordinate method can be applied without rotating the internal coordinates of the hamiltonian to the complex plane (as it is in the stabilization method of Junker) if the basis functions are complex scaled. In this section we shall study the reasons for the enhanced stability of the resonant eigenvalue when a complex basis function is added to the real basis set, while the hamiltonian is unrotated.

As was indicated in the previous section, the resonances are associated with the complex solutions of the secular equations. The complex solutions are obtained as a result of the coalescence of two *real* eigenvalues of (9) as any parameter λ in the hamiltonian is varied. One of the two real stationary solutions has to correspond to a maximum in the variational space, whereas the other one should correspond to a minimum.

From (11) we get that

$$\mathbf{C}^{\mathrm{T}}[\partial^2 \mathbf{H}/\partial\gamma^2]\mathbf{C} < 0 \tag{30}$$

is a sufficient (though not necessary) condition to yield a maximal stationary solution of the energy with respect to γ. As λ is varied, a complex stationary solution is obtained whenever a maximum stationary solution of the energy (obtained by varying the non-linear variational parameter) coalesces with a local minimum stationary solution. Therefore, (30) is a sufficient condition to get a complex stationary solution in the variational calculations.

In the case that the complex coordinate method is applied to atomic auto-ionization resonances, γ stands for the scaling factor η. Then

$$H_{ij} = \langle \psi_i(\mathbf{r}\eta) | \hat{H}(\mathbf{r}) | \psi_j(\mathbf{r}\eta) \rangle$$
$$= \langle \psi_i(\mathbf{r}) | \hat{H}(\mathbf{r}/\eta) | \psi_j(\mathbf{r}) \rangle. \tag{31}$$

In view of the quadratic dependence of the atomic hamiltonian on η, $H_{ij} = \eta^2 T_{ij} + \eta V_{ij}$

$$\partial^2 H_{ij}/\partial\eta^2 = 2T_{ij} \quad \text{and} \quad \mathbf{C}^{\mathrm{T}}\mathbf{T}\mathbf{C} > 0. \tag{32}$$

Consequently, (30) is not satisfied and the maximum stationary solution of the energy obtained as the non-linear parameter is varied, is due to the dependence of the linear parameters $\mathbf{C}$ on η ($\mathbf{D}$ in (13)) and a large number of basis functions are required to get a stable solution. (Note that for a small basis set both maxima and minima may be obtained. However, these extrema would be strongly affected by η since this is true for the linear parameters $\mathbf{C}$.) Following the above analysis it is clear why poor estimates of the atomic autoionization resonances have been obtained for small basis sets even though they may yield very accurate results for the resonance position [25]. However, this is not the case when a complex basis function is added to the real basis set [13]. In his work Junker complex optimized the non-linear parameters of only one or two basis functions. Since not all of the basis functions are complex optimized [24], the equality presented in (31) is not valid and

$$\partial^2 H_{ij}/\partial\gamma^2 = f_{ij}(\gamma) \neq T_{ij}. \tag{33}$$

Note that (33) is valid even if all basis functions are complex optimized so long as there are at least two different complex scale factors. For certain values of

γ, $\mathbf{C}^T\mathbf{f}\mathbf{C} < 0$ and the sufficient condition, presented by (30), to obtain a complex stationary solution in the variational space is satisfied. Therefore in the procedure of Junker (30) is satisfied and a maximum of the energy can be obtained even when the linear parameters are held fixed or for a minimal basis set of two functions ϕ and χ. Here ϕ is a real function which yields a good estimate for the resonance position and χ is the function of which the non-linear parameter γ is complex optimized.

Table 1. The resonance position E_r and width $-2E_i$ of the anharmonic oscillator, $\lambda = -0.05$, obtained by the complex coordinate method. The real basis set is constructed of N Hermite polynomials and was complex scaled by $\eta_{opt} = |\eta| \exp(-i\theta)$ to yield a complex stationary solution, that is $(\partial E_r/\partial \theta) = (\partial E_i/\partial \theta) = 0$.

N	E_r	$-E_i$	$|\eta|$	θ
1	$\begin{cases} 0.45387 \text{ min} \\ 0.49590 \text{ max} \end{cases}$	0 \ 0	0.786 \ 0.339	0 \ 0
2	0.43745	0.01905	0.800	0.306
5	0.44454	0.02373	0.868	0.259
10	0.44548	0.02255	0.847	0.234
15	0.44550	0.02275	0.854	0.233
20	0.44548	0.02278	0.855	0.234
25	0.44548	0.02279	0.856	0.234

In the case of the anharmonic oscillator, some of the hamiltonian matrix elements are homogeneous functions of the third order and therefore (32) is not valid also when the complex coordinate method is used. Therefore, a maximum of the energy for $\lambda > \lambda_0$ or a complex stationary solution for $\lambda < \lambda_0$ can be obtained even for one basis function. At $\lambda = -0.05$, for example, a basis set of two functions is large enough to describe the lowest resonance state. In table 1 the estimates of the resonance position and width of the anharmonic oscillator, which were obtained for different large basis sets, are presented. The weak dependence of the results on the number of the basis functions supports our proof that, if $\mathbf{C}^T(\partial^2 H/\partial \eta^2)\mathbf{C} < 0$ for $\lambda < \lambda_0$, a complex stationary solution can be obtained even when the linear variational parameters are independent or weakly dependent on η. Therefore, in such a case the resonance position and width can be estimated for $\lambda < \lambda_0$ from a relatively small basis set.

When the linear parameters are held fixed only three stationary solutions can be obtained (21) if the complex coordinate method is applied to the anharmonic oscillator. However, when a complex basis function is included in the basis [13] more stationary solutions may be obtained by solving the following equation

$$\frac{\partial E}{\partial \gamma} = \int_{-\infty}^{\infty} \frac{\partial \chi(\gamma x)}{\partial \gamma} \hat{H}(x)[\phi(x) + 2C\chi(\gamma x)] \, dx = 0, \qquad (34)$$

where the variational function is defined by $\psi = \phi(x) + C\chi(\gamma x)$. It has already been observed [26] that as more complex stationary solutions which are describing the same resonance state are obtained for a given basis set, then the corresponding complex eigenvalues are more stable and less affected by the

variational non-linear parameters. Therefore, one can expect that the results obtained by the stabilization method of Junker would be more stable and less sensitive to the number of basis functions and to the value of the complex non-linear parameter γ than the resonance solutions obtained by the complex co-ordinate method (that is complex scaling of all the internal coordinates of the hamiltonian by η). This conclusion supports the idea that, in the case of a shape resonance which corresponds to an electronic configuration with one electron outside a closed shell, a smaller basis set can be used to determine the resonances. This can be performed if the open-shell basis functions are complex scaled while the inner-shell orbitals are kept unscaled, rather than scaling all basis functions by the same factor. The numerical results we have obtained for the anharmonic oscillator is in agreement with the above analysis.

At $\lambda = 0.035$ for two basis functions *no* complex stationary solution that describes the lowest resonance state can be obtained by the complex coordinate method. However, a *good* estimate for the resonance position and width was obtained for two basis functions when the method of Junker was used, that is, $E_r = 0.4577$ and $E_i = -0.0044$. This result is in harmony with the estimate of the resonance position and width, $E_r = 0.4602$ and $E_i = 0.0058$, that was obtained by the complex coordinate method when ten harmonic wavefunctions were taken as a basis set. The two basis functions which were used when the pro-cedure of Junker was applied to the anharmonic oscillator were

$$\phi = \sum_{i=1}^{10} C_i^{(0)} H_{2i-2}(x) \exp\left(\frac{-\alpha_0 x^2}{2}\right) \qquad (35)$$

and

$$\chi = \exp\left(-\gamma x^2\right) ; \quad \gamma = \beta - ik. \qquad (36)$$

The fixed linear parameters $\mathbf{C}^{(0)}$ and $\alpha_0 = 0.8237$ were obtained by optimizing the ten harmonic oscillator functions to yield a real stationary solution, at $E_r = 0.4580$, from which the resonance position is estimated. The weak depen-dence of the complex energy on β is presented in table 2. These results were obtained by the addition of one complex basis function χ to a real basis set consisting of five harmonic oscillator functions (note that in this case also the linear parameters of the real basis functions $\mathbf{C}^{(0)}$ in (30) were freely optimized).

Table 2. The resonance position E_r and width $-2E_i$ of the anharmonic oscillator, $\lambda = -0.05$, obtained by the stabilization method of Junker. The basis set was con-structed of five real Hermite polynomials (scaled by $\alpha_0 = 0.868$) and a primitive gaussian complex scaled by $\gamma = (\beta - 0.9i)$. The non-linear parameters α_0 and γ were optimized to give stationary solution of the complex energy.

E_r	$-E_i$	β
0.4357	0.0159	0.02
0.4354	0.0173	0.10
0.4383	0.0205	0.20
0.4390	0.0261	0.30

4. DISCUSSION

The resonance position E_r and width $-2E_i$ are presented as the complex eigenvalues of the conventional secular equations that are generalized by letting one (or more) of the exponential parameters γ of the basis functions to be a complex number. Since we require that

$$\partial E_r / \partial |\gamma| = 0 = \partial E_i / \partial |\gamma| \qquad (37)$$

then the resonances can be considered as the complex solutions that are obtained as results of the analytical continuation of the conventional variational solutions to the complex plane. The complex stationary solutions are obtained while one of the parameters in the hamiltonian λ is varied to give a branch point in which two (or more) eigenvalues of the real hamiltonian matrix coalesce. This exploration of the conditions in which complex stationary solutions are obtained leads us to the following suggestion, that helps one to distinguish between the resonant complex eigenvalues and the other complex non-physical eigenvalues that are obtained as well.

The complex eigenvalues should be calculated as functions of λ. The resonances are associated with the complex eigenvalues that are lying on the branches that are linked to the real eigenvalues (the optimized λ gets a real value in spite of the fact that the variational space is complex) that describe the bound states of the given hamiltonian (see figure 1 for example). On the basis of the above analysis it was pointed out that the enhanced stability of the resonant eigenvalue when a complex basis function is added to the real basis set is due to the fact that the expectation value of the second derivative of the hamiltonian

Table 3. Iterative virial-scaling procedure for the lowest anharmonic oscillator resonance $\lambda = -0.05$, illustrating the speed of convergence when (a) the basis set is constructed of five Hermite polynomials, (b) the basis set is constructed of twenty five Hermite polynomials.

Iteration	E_r	$-E_i$	η
1	0·45066	0·02585	$0·9727 - 0·2319\,i$
5	0·44483	0·02501	$0·8836 - 0·2548\,i$
10	0·44445	0·02381	$0·8336 - 0·2077\,i$
15	0·44453	0·02373	$0·8394 - 0·2264\,i$
20	0·44454	0·02373	$0·8402 - 0·2203\,i$

(a)

Iteration	E_r	$-E_i$	η
1	0·45087	0·02607	$0·9727 - 0·2319\,i$
5	0·44201	0·01907	$0·7813 - 0·3017\,i$
10	0·44548	0·02278	$0·8324 - 0·1978\,i$
15	0·44548	0·02278	$0·8317 - 0·1981\,i$
20	0·44548	0·02278	$0·8317 - 0·1981\,i$

(b)

Table 4. The complex eigenvalues obtained by the application of the stabilization method of Junker to the anharmonic oscillator, $\lambda = 0.05$, illustrating the sensitivity of the resonant eigenvalue to the scaling of the ten real basis functions by α_0 while the complex variational parameter $\gamma = \beta - 0.6i$ (defined by (36) in the text) has a weak effect on the results.

β	$E_r(\alpha_0 = 1.0)$	$-E_i(\alpha_0 = 1.0)$	$E_r(\alpha_0 = 0.8)$	$-E_i(\alpha_0 = 0.8)$
0.02	0.45034	0.00290	0.43681	0.02761
0.04	0.45038	0.00291	0.43974	0.02645
0.06	0.45043	0.00292	0.44171	0.02506
0.08	0.45048	0.00293	0.44308	0.02384
0.10	0.45052	0.00295	0.44413	0.02286

with respect to γ is negative. However, in this context we should mention the computational advantages of the complex coordinate method. For homogeneous potential functions the complex coordinate method gives an algebraic equation for the optimized complex scaling factor η that can be solved by any of the conventional numerical procedures and thereby simultaneously the optimized values of the real and the imaginary parts of η are obtained. In the case of the anharmonic oscillator these computational advantages were found to be very helpful in finding the complex stationary solutions (convergence of E_r, E_i and the optimized η were achieved in several iterations, (see table (3)), whereas when the stabilization method of Junker was used the resonant eigenvalues were very sensitive to the values of the exponential parameter of the real basis set, α_0 in (30), which had to be obtained variationally (see table 4).

The anharmonic oscillator was studied as a numerical example. It is interesting that resonance eigenvalues were obtained by the complex coordinate method within the finite matrix approach in spite of the fact that the anharmonic hamiltonian contains a x^4 potential term and therefore does not have a spectrum. The successful application of the complex coordinate method to the anharmonic oscillator supports the assumption resulting from previous applications to the Stark effect in atoms [10] and to a singular potential [27] that the resonant eigenvalues are invariant under a complex coordinate scaling even in cases where the potentials do not give a physically scattering theory.

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