

Resonance properties of complex-rotated hamiltonians†

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The fundamental work of Balslev, Combes, and Simon has provided a mathematical foundation for the description of atomic and molecular resonances by the complex-rotation method. In the present paper we discuss some formal properties of the complex-rotated hamiltonian operators and the variational criteria for the approximation of their resonance eigenvalues. These criteria are employed in numerical studies of the complex-rotation method, which is illustrated and compared with various stabilization procedures in an application to a simple model potential. We propose a virial-scaling procedure for determining variationally optimal estimates of the resonance position and lifetime and apply the technique to the helium $(2s)^2$ auto-ionizing resonance. Our results lend support to the idea that resonance features in the continuous spectrum can be successfully described by techniques similar to those employed for bound states.

1. INTRODUCTION

Recent mathematical developments have clarified the theoretical situation with respect to the description of certain *non-stationary* properties of atoms and molecules, such as the auto-ionizing resonances lying above an ionization threshold [1]. These resonances are among a class of quasi-stationary states which seem to be more easily characterized by experiment than by theory [2-4]. Time-dependent perturbation theory has traditionally been used to calculate the lifetime τ of an unperturbed prepared state which decays exponentially under the effect of a perturbation [5], but difficulties may arise concerning the form of perturbation [2], the appropriate procedure for broader (short-lived) resonances, or for non-exponential decay. Resonances have also been treated by scattering techniques [6], where they appear as rapid changes in the phase shift, or by variational principles [7], based on features of the wave-function that might be expected near a resonance energy.

Recently Simon [8] has shown, based on an important theorem of Balslev and Combes [9], that the energy E and width Γ ($=\tau^{-1}$) of such resonance states may be associated with the complex eigenvalues

$$W = E - \frac{i}{2} \Gamma \quad (1.1)$$

of a certain analytically continued hamiltonian operator H_θ . The appropriate

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operator results from the ordinary self-adjoint hamiltonian $H(\mathbf{r}) = T(\mathbf{r}) + V(\mathbf{r})$ when the position vectors \mathbf{r} are rotated upward into the complex coordinate plane

$$\mathbf{r} \rightarrow \mathbf{r} \exp(i\theta), \quad \theta > 0, \text{ real} \quad (1.2)$$

to give the complex-rotated hamiltonian

$$H_\theta(\mathbf{r}) = H(\mathbf{r} \exp(i\theta)). \quad (1.3)$$

For a broad class of potentials V (including coulombic), it was shown [9] that the time-independent Schrödinger equation for the rotated operator,

$$H_\theta(\mathbf{r})\psi_k(\mathbf{r}) = W_k\psi_k(\mathbf{r}), \quad (1.4)$$

has, in addition to ordinary *real* eigenvalues of bound states, two classes of *complex* eigenvalues, one of which (rotating branch cuts emanating from thresholds) depends on the rotation angle θ , and another which does not (see figure 1). It is the latter solutions, occurring as isolated points of finite multiplicity on a second Riemann sheet of the complex energy plane, which in Simon's analysis are to be identified with resonances.

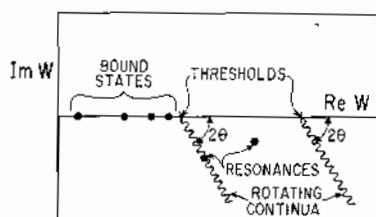


Figure 1. Schematic representation of the eigenvalues of the complex-rotated hamiltonian H_θ , according to the theorem of Balslev and Combes [9].

Since the resonance eigenfunctions are square-integrable (unlike corresponding continuum solutions of the unrotated H), the rotated eigenvalue problem of equation (1.4) can be approximated by conventional bound-state techniques. The latter permit one to dispense with the coordinate-space asymptotic terms which occur in the eigenfunctions of the unrotated problem, and which greatly complicate numerical calculations of atomic and molecular continuum properties. Variational complex-rotation procedures were initially explored by Nuttall, Doolen and co-workers [10], and such calculations were subsequently carried out for low-lying resonances in H^- , He, and related systems by several groups [11].

The complex-rotated hamiltonians have many unusual formal properties, and numerical studies indicate a pronounced dependence on rotation angle θ (in addition to the usual dependence on basis size, non-linear variational parameters, etc.) which has no counterpart in the ordinary hermitian case. In the present paper we discuss some simple properties of the complex-rotated H_θ in terms which are analogous to those of the unrotated H . Included in the discussion are the complex (non-hermitian) analogues of several bound-state theorems, including virial and hypervirial relations, the Hellmann-Feynman theorem, and generalized stationary (variational) principles which are useful

in analysing both exact and numerical properties of the resonance solutions. Some numerical aspects of approximate resonance solutions are discussed in these terms in §§ 3 and 4 and illustrated for a model one-dimensional potential. An iterative virial-scaling procedure is proposed in § 5 for accelerated variational optimization of resonance parameters, and illustrated for the helium $(2s)^2$ resonance. Section 6 concludes with a brief summary.

2. PROPERTIES OF COMPLEX-ROTATED HAMILTONIANS

2.1. The c -product

In order to discuss the properties of the complex-rotated operators H_θ of (1.3), it is convenient to introduce the c -product $(f|g)$,

$$(f|g) = \int_{\text{all space}} f(\mathbf{r})g(\mathbf{r}) d\mathbf{r}, \quad (2.1)$$

of the general (complex) wave-functions f and g . In this expression, $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_n)$ is a collective variable denoting the positions of the n particles of the system, and the usual integration over spin variables is implicitly understood. The c -product given by equation (2.1) is to be distinguished from the ordinary scalar product $\langle f|g \rangle$,

$$\langle f|g \rangle = \int_{\text{all space}} f^*(\mathbf{r})g(\mathbf{r}) d\mathbf{r}, \quad (2.2)$$

of such functions. For example, while the c -product is symmetric and distributive,

$$(f|g) = (g|f), \quad (2.3 a)$$

$$(f|g+h) = (f|g) + (f|h), \quad (2.3 b)$$

the c -product $(f|f)$ of f with itself may be complex (and may have negative real or imaginary parts), whereas $\langle f|f \rangle$ is strictly real and positive for any non-zero f . Thus, the symbol $(f|g)$ is not a metric scalar product. We shall assume that f and g are square-integrable in the ordinary Hilbert-space sense, i.e. that

$$\langle f|f \rangle < \infty \quad \text{and} \quad \langle g|g \rangle < \infty, \quad (2.4)$$

so that by the inequality

$$|(f|g)|^2 \leq \langle f|f \rangle \langle g|g \rangle, \quad (2.5)$$

the c -products $(f|g)$ are also of finite modulus. The motivation for introducing these symbols is that the c -product given by equation (2.1) facilitates the discussion of theorems for the rotated (non-hermitian) operator H_θ which are analogous to those for H , whereas the scalar hermitian product given by equation (2.2) does not†.

† The c -product is provisional in that it does not yet satisfactorily accommodate all hamiltonians of physical interest, neither does it permit the use of basic functions for the unrotated H (such as a Y_{lm} spherical harmonic for the angular dependence) which, while unnecessary, are sometimes convenient. We consider it preferable to have a specific symbol for the c -product, rather than employ strained notation such as $\langle f(-\theta)^*|g(\theta) \rangle$, and the like.

We shall say that the functions f and g are c-orthogonal if

$$(f|g) = 0. \quad (2.6)$$

Similarly, if $(f|f) = |a| \exp(i\phi)$ is non-zero, one can define the corresponding c-normalized function $\hat{f} = |a|^{-1/2} \exp(-i\phi/2) f$ satisfying

$$(\hat{f}|\hat{f}) = 1. \quad (2.7)$$

If f has real and imaginary parts, f_r and f_i respectively, it will be seen that f is c-normalizable unless both

$$(f_r|f_r) = (f_i|f_i) \quad (2.8 a)$$

and

$$(f_r|f_i) = 0. \quad (2.8 b)$$

In contrast to the hermitian norm, $\langle f|f \rangle$, it is entirely possible that a non-zero function f can have vanishing c-norm, $(f|f) = 0$.

2.2. Complex-rotated hamiltonians

We shall consider the system of interest to be described by a real, self-adjoint hamiltonian operator $H = T + V$ incorporating no magnetic field variables (see footnote, page 1615),

$$H = H^\dagger = H^*. \quad (2.9)$$

The corresponding complex-rotated operator is

$$H_\theta = T_\theta + H_\theta = \exp(-2i\theta)T + V(\mathbf{r} \exp(i\theta)) \quad (2.10)$$

where, for example, $V(\mathbf{r} \exp(i\theta)) = \exp(-i\theta)V(\mathbf{r})$ for a Coulomb potential.

Since T is real and self-adjoint, and V is often a multiplicative function of coordinates, it follows for the cases of principal interest that $H_\theta^\dagger = H_\theta^*$. Hence, for general complex wave-functions f and g ,

$$(f|H_\theta g) = \langle f^* | H_\theta g \rangle = \langle H_\theta^\dagger f^* | g \rangle = \langle (H_\theta f)^* | g \rangle = (H_\theta f | g)$$

and H_θ is therefore symmetric (satisfies the turn-over rule) with respect to the c-product,

$$(f|H_\theta g) = (H_\theta f | g) = (g | H_\theta f). \quad (2.11)$$

From the turn-over property, it follows immediately that eigenfunctions ψ_k and ψ_l belonging to non-degenerate eigenvalues W_k and W_l are c-orthogonal,

$$(\psi_k | \psi_l) = 0 \quad \text{if } W_k \neq W_l, \quad (2.12)$$

since, by using equation (2.11),

$$(\psi_l | H_\theta \psi_k) - (\psi_k | H_\theta \psi_l) = (W_k - W_l)(\psi_k | \psi_l) = 0.$$

Note that equations (2.11) and (2.12) are generally untrue if angular brackets (hermitian product) are taken to replace parentheses (c-product), unless both f and g are real, and $\theta = 0$. In this sense the c-product is proper to the intrinsic symmetry $H_\theta^\dagger = H_\theta^*$ of the complex-rotated operators.

It should be noted that an eigenfunction ψ_k is always associated with some particular θ , since hamiltonians H_θ and $H_{\theta'}$ for distinct angles will generally

fail to commute. It should also be noted that the eigenfunctions of a general c-symmetric operator need *not* form a complete set [12]. For example, the 3×3 matrix

$$A = \begin{bmatrix} 6 & i & -1 \\ i & 5 & 2i \\ -1 & 2i & 1 \end{bmatrix} \quad (2.13 a)$$

has only *two* distinct eigenvectors,

$$W_1 = 6, \quad \psi_1 = \begin{bmatrix} 1 \\ i/3 \\ -1/3 \end{bmatrix}; \quad W_2 = 3, \quad \psi_2 = \begin{bmatrix} 0 \\ 1 \\ i \end{bmatrix} \quad (2.13 b)$$

only the first of which is c-normalizable. This has serious implications for the variational approximation of the eigenvalues W_1 and W_2 . Let $\bar{W}(\Phi) = (\Phi|A\Phi)/(\Phi|\Phi)$ denote the usual Rayleigh functional for a c-normalizable approximation Φ , $(\Phi|\Phi) \neq 0$, and consider the application of the variational principle $\delta\bar{W} = 0$ to each solution.

- (1) For the ordinary solution ψ_1 , the variational functional for a trial $\Phi = \psi_1 + \epsilon\chi$ gives the correct stationary result for the eigenvalue

$$\bar{W}(\Phi) = W_1 + \mathcal{O}(\epsilon^2),$$

but the eigenvector ψ_1 *cannot* be uniquely determined from the criterion $\delta\bar{W} = 0$. In fact, if $\Phi = c_1\psi_1 + c_2\psi_2$, one finds that $\bar{W}(\Phi) \equiv W_1$ for *any* non-zero coefficients c_1 and c_2 .

- (2) For the second (non-c-normalizable) solution, the variational criterion $\delta\bar{W} = 0$ will not even give the correct eigenvalue. Taking $\Phi = \psi_2 + \epsilon\chi$, one finds the *wrong* eigenvalue ($\bar{W} = W_1 + \mathcal{O}(\epsilon^2)$) whenever $(\chi|\psi_2) = 0$, and a *non-stationary* result ($\bar{W} = W_2 + \mathcal{O}(\epsilon)$) when $(\chi|\psi_2) \neq 0$.

We shall *assume* that (complex-rotated) atomic and molecular hamiltonians do not exhibit the pathologies of the example above. In particular, we assume that eigenfunctions of the exact H_θ form a complete set. This implies that non-degenerate eigenfunctions are c-normalizable, for if $(\psi_k|\psi_k) = 0$, the completeness assumption (together with equation (2.12)) leads to

$$\begin{aligned} \langle \psi_k | \psi_k \rangle &= (\psi_k | \psi_k^*) = \sum_l (\psi_k | \psi_l) (\psi_l | \psi_k^*) \\ &= (\psi_k | \psi_k) (\psi_k | \psi_k^*) = 0, \end{aligned}$$

which would imply that $\psi_k \equiv 0$. Although the completeness assumption is plausible, and seems to underlie all numerical applications of Balslev-Combes theory, we are not aware that its truth is yet established. Note that pathologies such as equations (2.13) could arise in finite-basis variational calculations, even if the *exact* complex-rotated hamiltonians were known to have c-normalizable eigenfunctions. Indeed, if $\chi_1(\mathbf{r})$ and $\chi_2(\mathbf{r})$ are chosen basis functions for some particular H_θ , then it is generally possible to find a new scale factor α and rotation angle θ' for which the 2×2 matrix $(X'_i | H_{\theta'} X'_j)$ in the scaled basis $X'_i = \chi_i(\alpha\mathbf{r})$

has an incompleteness pathology similar to equations (2.13). Presumably, such accidental pathologies are rare.

With this background, we turn to the analogues for the rotated operators H_θ of some elementary theorems of hermitian hamiltonians. Since the proofs of these theorems generally follow the same lines as in the unrotated case, we shall in most cases omit them.

2.3. Complex-analogue theorems

From the turn-over rule (2.11) for the complex-rotated hamiltonian, it follows immediately that commutators of H_θ have vanishing c-expectation values in any eigenstate ψ_k given by

$$(\psi_k | [H_\theta, \Lambda] \psi_k) = 0. \quad (2.14)$$

This *hypervirial theorem* [13, 14] holds for a wide class of operators Λ , whether hermitian or not. In particular, if Λ is chosen to be $\mathbf{r} \cdot \nabla$ (or a sum of such terms in a many-particle system), and if the potential V is a homogeneous function of coordinates of degree m , equation (2.14) reduces to the ordinary *virial theorem*

$$(\psi_k | T_\theta \psi_k) = \frac{m}{2} (\psi_k | V_\theta \psi_k), \quad (2.15)$$

relating the (complex) kinetic and potential energies. An alternative proof of the complex virial theorem, based on the (assumed) stationary property of the resonance eigenvalues, will be sketched below. Another proof of this theorem, recently given by Froehlich *et al.* [15], was based on a complex-rotated time-dependent Schrödinger equation. The present treatment has the virtue of requiring no assumptions to be made about the time evolution of complex-rotated eigenfunctions, nor on their completeness.

If the eigenfunctions of H_θ form a complete c-normalizable set, as we assume, then it is easy to verify that the Rayleigh quotient

$$\tilde{W}(\Phi) = \frac{(\Phi | H_\theta \Phi)}{(\Phi | \Phi)} \quad (2.16)$$

provides a stationary approximation to the true eigenvalue W_k when Φ is a c-normalizable approximation that is close to ψ_k ; that is,

$$\Phi = \psi_k + \mathcal{O}(\epsilon) \quad \text{implies} \quad \tilde{W} = W_k + \mathcal{O}(\epsilon^2). \quad (2.17)$$

This complex *variation principle* is, however, a stationary principle rather than an upper or lower bound for either the real or imaginary part of the complex eigenvalue. As noted above, even this stationary property fails if the eigenfunctions are not c-normalizable.

If a trial function Φ is scaled by the complex scale factor $\eta = \alpha \exp(-i\theta')$,

$$\Phi_\eta(\mathbf{r}_1, \dots, \mathbf{r}_n) = \eta^{3n/2} \Phi(\eta \mathbf{r}_1, \dots, \eta \mathbf{r}_n), \quad (2.18)$$

one can carry through the c-product analogue of the well-known argument [16] to obtain

$$\tilde{W}(\Phi_\eta) = \eta^2 (\Phi | T_\theta \Phi) + \eta^{-m} (\Phi | V_\theta \Phi). \quad (2.19)$$

Stationary values of this functional occur when

$$\frac{\partial \tilde{W}}{\partial \eta} = 2\eta(\Phi | T_\theta \Phi) - m\eta^{-m-1}(\Phi | V_\theta \Phi) = 0. \quad (2.20)$$

In particular, $\eta = 1$ must satisfy this equation when Φ is the true eigenfunction ψ_k , which provides an alternative statement of the c-virial theorem (2.15). However, equation (2.20) is also a useful criterion for the optimal choice of scale in approximate resonance wave-functions†.

It is also possible to establish the complex analogue of the Hellmann–Feynman theorem [18] for a rotated hamiltonian $H_\theta = H_\theta(\zeta)$ containing an embedded parameter ζ . Suppose Φ depends on M variational parameters c_i (including any explicit reference to ζ itself). Variationally optimal values of these parameters must satisfy the relation

$$\left(\frac{\partial \tilde{W}}{\partial c_i} \right)_{c, \zeta} = 0, \quad i = 1, 2, \dots, M. \quad (2.21 a)$$

However, for c-normalized Φ ,

$$\frac{d\tilde{W}}{d\zeta} = \left(\Phi | \frac{\partial H_\theta}{\partial \zeta} \Phi \right) + \sum_{j=1}^M \left(\frac{\partial \tilde{W}}{\partial c_j} \right)_{c, \zeta} \frac{dc_j}{d\zeta} \quad (2.21 b)$$

and thus, if Φ is variationally optimal (at least with respect to the explicit ζ dependence),

$$\frac{d\tilde{W}}{d\zeta} = \left(\Phi | \frac{\partial H_\theta}{\partial \zeta} \Phi \right). \quad (2.22 a)$$

If Φ is an exact eigenfunction ψ_k , this becomes

$$\frac{dW_k}{d\zeta} = \left(\psi_k | \frac{\partial H_\theta}{\partial \zeta} \psi_k \right), \quad (2.22 b)$$

the complex form of the Hellmann–Feynman theorem. In particular, if ζ is chosen to be the rotation angle θ , the Balslev–Combes theorem (which implies that $dW_k/d\theta = 0$ for a resonance eigenvalue) leads to yet another derivation of the virial theorem (2.15). However, ζ may also be identified with nuclear charge, internuclear distance, or other physical parameters of the hamiltonian to give many special cases [19].

3. VARIATIONAL CALCULATION OF RESONANCE EIGENVALUES

In the variational solution of the complex eigenvalue equation (1.4), the trial function Φ of the Rayleigh ratio (2.16) is expanded in a linear combination of N basis functions $\{\chi_\mu(\alpha)\}$,

$$\Phi = \sum_{\mu=1}^N c_\mu \chi_\mu(\alpha), \quad (3.1)$$

where α denotes an embedded non-linear scale parameter. These functions

† As this manuscript was being completed, we learned of a paper [17] in which the virial theorem is employed in a very similar spirit. However, the discussion it contains is based on a derivation of the complex virial theorem which does not take account of anomalies such as those in equation (2.13) and [12, 13].

may be chosen to be real and c-orthonormal without loss of generality :

$$\chi_{\mu}^* = \chi_{\mu} \quad (3.2 a)$$

$$(\chi_{\mu} | \chi_{\nu}) = \delta_{\mu\nu}. \quad (3.2 b)$$

The resonance eigenvalue is stationary if (complex) coefficients c_{μ} can be found to satisfy the finite matrix eigenvalue problem

$$(\mathbf{H} - W_k)\mathbf{c}_k = 0, \quad k = 1, 2, \dots, N, \quad (3.3)$$

where for a Coulomb potential V the hamiltonian matrix elements are

$$\begin{aligned} (\mathbf{H})_{\mu\nu} &= (\chi_{\mu} | H_{\theta} \chi_{\nu}) \\ &= \exp(-2i\theta)(\chi_{\mu} | T \chi_{\nu}) + \exp(-i\theta)(\chi_{\mu} | V \chi_{\nu}). \end{aligned} \quad (3.4)$$

The complex eigenvalues W_k obtained from the finite secular equations (3.3), in contrast to the true resonance eigenvalues, will generally depend on α , N and the rotation angle θ :

$$W_k = W_k(\alpha, \theta, N). \quad (3.5)$$

This leads to an ambiguity in the choice of a best resonance estimate from a series of such calculations, which has usually been resolved by one of two procedures.

- (1) In earlier work (see, for example, Doolen *et al.* (1974 [10]) and Reinhardt (1976, [11])), the non-linear scale α and rotation angle θ were given fixed (essentially arbitrary) values, and the basis was enlarged. The resonance eigenvalue was observed to *spiral* inward towards a limiting position, which could be taken as the best estimate of the true resonance location.
- (2) Doolen (1975, [10]; many examples are also to be found in [11]) subsequently suggested the procedure of fixing α and N while varying the rotation angle θ until the resonance eigenvalue slows down along its θ trajectory. The trajectory $W_k(\theta)$ is found to undergo loops, kinks or bends as the true resonance position is approached. Figure 3 illustrates such behaviour for the simple model potential depicted in figure 2 (discussed in § 4). On changing the value of α , new θ trajectories are obtained which, however, tend to slow down in the same region as before.

A related procedure, apparently uninvestigated, is to fix θ and N while varying the scale factor α to obtain a corresponding α trajectory. However (as we show in § 4), such α trajectories are necessarily related to θ trajectories in the sense of exhibiting bends and slowing down in the same region of the complex energy plane.

It is evident that the complex variational theorem (2.15) and the complex Hellmann-Feynman theorem (2.22) provide a unique criterion for choosing optimum resonance parameters within a given basis set†. The Balslev-Combes theorem [9] establishes that $dW_{\text{true}}/d\theta = 0$ for a true resonance, and equation (2.22 a) shows that the approximate W will have this same stationary property

† It should be noted that the complex variational theorem establishes only the *stationary* (rather than the extremum) character of the variational integral, so that increased numbers of basis functions do not necessarily give a numerical result lying closer to the true resonance position and width.

if the trial Φ satisfies the relation

$$\left. \frac{dW_{\text{opt}}}{d\theta} \right|_{\theta_{\text{opt}}} = \left(\Phi_{\text{opt}} \left| \frac{\partial H_{\theta}}{\partial \theta} \right. \Phi_{\text{opt}} \right) = 0, \quad (3.6)$$

which in turn implies that the virial theorem is satisfied. If Φ does not satisfy the virial theorem (2.20), it is evidently not possible to make the resonance position and width simultaneously stationary with respect to a single value of θ . Yet the variational principle singles out those angles θ_r and θ_i as optimal which make the resonance position and width individually stationary; that is, with $W = E_r + iE_i$, the resonance position E_r should be evaluated at the particular angle θ_r defined by

$$\left. \frac{dE_r}{d\theta} \right|_{\theta_r} = 0, \quad (3.7 a)$$

while the width $\Gamma = -2E_i$ should be evaluated at the angle θ_i for which

$$\left. \frac{dE_i}{d\theta} \right|_{\theta_i} = 0. \quad (3.7 b)$$

As the basis is extended, or as the scale is optimized to more nearly satisfy the virial theorem, these angles coalesce towards the limiting value θ_{opt} of equation (3.6), corresponding to the resonance estimate which is variationally optimal (most stationary) within the available basis set. If the basis set is badly out of scale for the resonance state, one or both of equations (3.7) may have no solution. In this case, variational re-scaling of the approximate Φ by the procedure of equations (2.18)–(2.21) is indicated, so that solutions to equations (3.7) appear once more.

It is evident that the stationary angles θ_r and θ_i in equation (3.7) will tend to occur where the θ trajectory undergoes a bend, kink or loop of the type sought in Doolen's procedure (see figure 3). As the resonance eigenvalue slows and bends more sharply, the stationary points θ_r and θ_i approach one another, and the resonance location is better defined. Thus, the heuristic Doolen procedure, which has been used to select a specific angle on the θ trajectory, should generally coincide with the specific values given by equation (3.7) and singled out by the variational theorem. However, equations (3.7) suggest that the resonance position and width should be evaluated at *different* points on the θ trajectory when a sub-optimal choice of scale (failure to satisfy the virial theorem) makes it impossible to satisfy them simultaneously.

Since each point of a θ trajectory requires solution of a matrix eigenvalue equation, it is evident that determination of the best estimate of the resonance eigenvalue can become computationally laborious, particularly when such trajectories are required for several values of the non-linear α . In addition, the procedure must be repeated for each new resonance state, since values of α_k and θ_k which prove optimal for eigenvalue W_k will not be so for estimating W_l . We return to this problem in § 5.

4. MODEL POTENTIAL CALCULATIONS

Variational calculations by the complex-coordinate method can be illustrated by a one-dimensional model potential

$$V(x) = (\frac{1}{2}x^2 - J) \exp(-\lambda x^2) + J \quad (4.1)$$

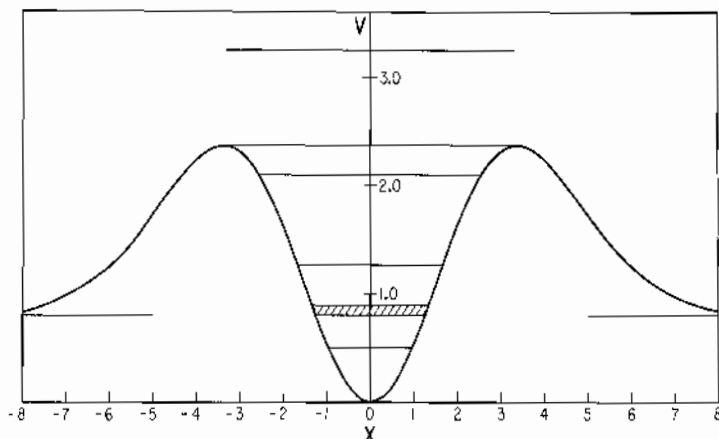


Figure 2. The model potential $V(X) = (\frac{1}{2}x^2 - J) \exp(-\lambda x^2) + J$ for $J=0.8$ and $\lambda=0.1$. Shown superimposed are the lowest eigenvalues of the potential (as calculated with 10 gaussian basis functions).

which has the form shown in figure 2. (This potential exhibits pre-dissociating resonances analogous to those found in diatomic molecules. Even though the inhomogeneous nature of the potential precludes the straightforward application of the virial theorem, the complex-rotated eigenvalues appear to have the same properties as are found in the case of the Coulomb potential.) With the parameter values (in atomic units[†]) $J=0.8$ and $\lambda=0.1$, this potential has a single bound state near $E=0.5$, a continuous spectrum beginning at $E_{\text{threshold}}=0.8$, and a broad resonance just below the lip of the potential near $E_r=2.1$. As basis functions, we chose a set of gaussian functions,

$$\chi_k = \exp(-\alpha_k x^2), \quad k=1, 2, \dots, N, \quad (4.2a)$$

with even-tempered exponential parameters α_k , given by

$$\alpha_k = \alpha(0.45)^{k-1}, \quad (4.2b)$$

where α is the variable scale parameter. In this section we compare the complex-coordinate procedure with some other variational methods for the model potential given by equation (4.1), employing the same basis set for each.

4.1. Complex-coordinate method

We computed θ trajectories for various values of α as described in the previous section, obtaining the results shown in figure 3. The angles θ_r and θ_i , defined by equation (3.7), are most nearly coincident for $\alpha \approx 0.61$, for which one finds that $\theta_r \approx \theta_i \approx 0.31$ rad. With these parameters, the resonance eigenvalue W is calculated to be

$$W = E_r - \frac{i}{2} \Gamma = 2.124 - \frac{i}{2} (0.037) \quad (4.3)$$

where $\alpha=0.61$, $\theta=0.31$ and $N=10$. As figure 3 shows, the various θ trajectories all pause in the general neighbourhood of this value for a range of values of α .

[†] a.u. of length (bohr) $\approx 0.52918 \times 10^{-10}$ m; a.u. of energy (hartree) ≈ 4.3598 aJ ≈ 27.212 eV.

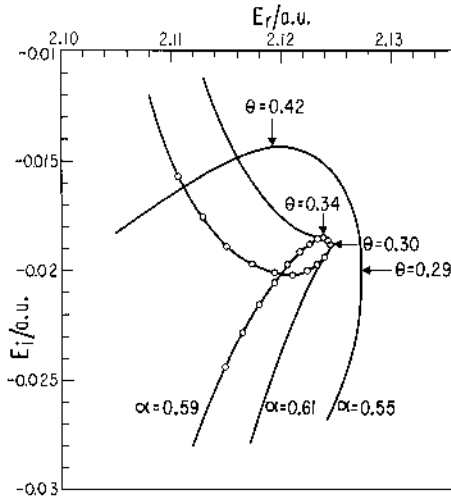


Figure 3. θ Trajectories, showing the dependence of the complex resonance eigenvalue on the rotation angle θ (for fixed $N=10$, and various α s). Each circle indicates an angular increment $\Delta\theta=0.02$ rad, and the arrows indicate the angles at which real or imaginary parts of the eigenvalue are stationary.

With θ fixed at 0.31, we also varied α to obtain the α trajectory shown in figure 4. A comparison of figures 3 and 4 shows that this procedure leads to precisely the same estimate, given by equation (4.3), of the resonance parameters. It is easy to understand this behaviour on the basis of the properties discussed in § 2. The resonance eigenvalue is evidently an analytic function of the complex scale factor $\eta = \alpha \exp(-i\theta)$,

$$W = W(\eta) = W(\alpha \exp(-i\theta)), \tag{4.4}$$

as follows from the identities (see equations (2.18)–(2.21))

$$W(\eta) = (\Phi_\alpha | H_\theta \Phi_\alpha) = (\Phi_\eta | H \Phi_\eta) \tag{4.5}$$

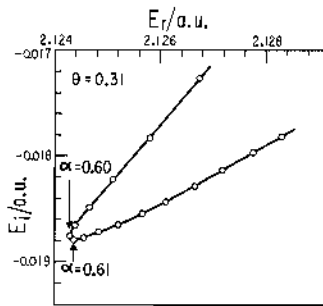


Figure 4. α trajectory showing the dependence of the complex resonance eigenvalue on the scale parameter α (for fixed $N=10$ and $\theta=0.31$). The circles correspond to increments $\Delta\alpha=0.01$, and the arrows mark the values at which $\text{Re } W$ or $\text{Im } W$ are stationary.

and the observation that Φ is an analytic function of \mathbf{r} . The *Cauchy–Riemann* conditions for analytic $W(\eta)$ then require that

$$\frac{\partial E_r}{\partial \alpha} = \frac{1}{\alpha} \frac{\partial E_i}{\partial \theta}, \quad (4.6 a)$$

$$\frac{\partial E_i}{\partial \alpha} = -\alpha \frac{\partial E_r}{\partial \theta}; \quad (4.6 b)$$

a related observation is made in a very recent article [20]. It is evident that the conditions (3.7) for the resonance parameters on a θ trajectory must therefore lead to corresponding stationary points on the associated α trajectory. At the resonance position equations (4.6) give the relationship between the real and imaginary parts of the complex stationary condition $\partial W/\partial \eta = 0$ of equation (2.21).

Figure 5 shows the spiralling convergence of the resonance eigenvalue as N is increased (up to $N=20$ basis functions) for fixed α and θ . The numerical convergence is evidently quite satisfactory.

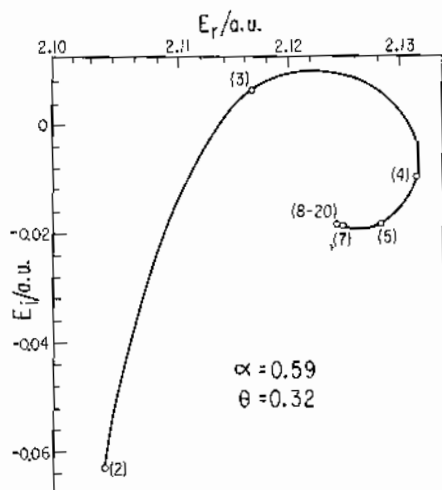


Figure 5. Spiralling convergence of the complex resonance eigenvalue with increasing number N of basis functions. For this calculation $\alpha=0.59$ and $\theta=0.32$.

4.2. Stabilization methods

In a study of H^- , Temkin [1] found that when the basis set was enlarged, new eigenvalues in the continuum region tended to hover in the neighbourhood of a resonance before dropping down to add to the dense manifold of eigenvalues near the continuum threshold. Figure 6 illustrates such behaviour for our model potential. The resonance clearly manifests itself in the range $E_r \approx 2.1$ – 2.4 , which is in good agreement with the previous result given in equation (4.3). A related stabilization method, as employed by Holøien and Midtdal [21], is to look for near-stationary behaviour of the continuum eigenvalues as a function of α . These procedures are also related to the Hazi–Taylor stabilization method which, however, is based on overlaps rather than energies [23]. Figure 7 depicts this behaviour for $N=10$ eigenvalues in our model problem over the

range $0 \leq \theta \leq 2$. Evidence for the resonance can again be seen in the energy region defined by equations (2.1)–(2.3). A disadvantage of such methods is that the resonance appears only indirectly from a characteristic numerical behaviour, which may be difficult to observe in the case of broad or overlapping resonances.

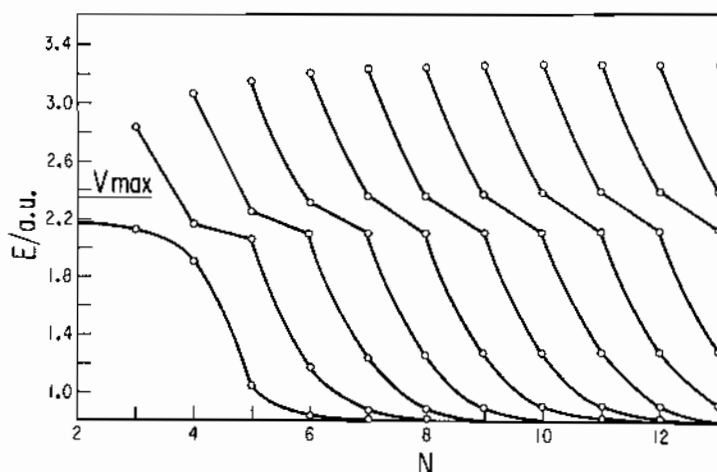


Figure 6. Variational eigenvalues for the model potential of figure 2 plotted for increasing number N of basis functions, showing the stabilization of eigenvalues in the neighbourhood ($E \approx 2.2$) of the resonance.

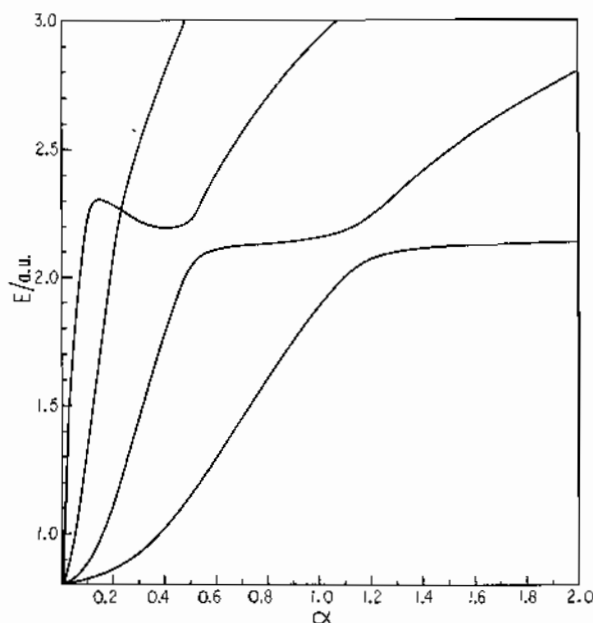


Figure 7. The four highest roots of the 10×10 secular equation (for the model potential of figure 2) as a function on the scale factor α , showing the stabilization of eigenvalues in the resonance region.

4.3. Modified stabilization method

Recently, Liebman *et al.* [24] have proposed a modified stabilization method in which a resonance eigenvalue is distinguished from ordinary scattering eigenvalues by its behaviour when an additional positive definite operator, kx^s , is added to the hamiltonian. In their example the energies of the scattering states were sharply raised by this perturbation, while the bound states and the resonant state were not significantly affected.

Table 1. Eigenvalues E of the model potential given by equation (4.1) perturbed by a term kx^s , as suggested by the modified stabilization method [21]. The first four columns give the lowest few eigenvalues for a range of non-zero k values, with those eigenvalues underlined that are close to one of the unperturbed ($k=0$) eigenvalues of the fifth column, as expected of a resonance. The sixth column lists the $\langle x^2 \rangle$ expectation value of each unperturbed eigenvector as a measure of spatial extent. All values are in atomic units, and were calculated in a basis of 10 even-tempered gaussian functions.

k					
10^{-4}	10^{-5}	10^{-6}	10^{-7}	0	$\langle x^2 \rangle$
0.502	0.502	0.502	0.502	0.502	0.54
<u>2.254</u>	<u>2.165</u>	<u>2.133</u>	<u>2.006</u>	0.801	2436.5
<u>6.083</u>	<u>3.223</u>	<u>2.730</u>	<u>2.181</u>	:	:
117.8	13.765	3.582	3.050	0.805	292.1
3357	336	34.925	4.858	1.271	110.9
88782	8879	889	89.8	2.104	9.8
				2.380	30.6
				3.254	14.0

We have applied this procedure to our model potential, given by equation (4.1), for different values of k (with $s=8$), obtaining the results shown in table 1. For each k , we have underlined the eigenvalues which are relatively unaffected by the additional kx^s term. From this table one can see the difficulty that arises because the resonance state is not always uniquely selected out. If k is chosen to be too small, even the scattering levels are unaffected, and will appear as spurious resonances, while if k is too large, all the eigenvalues, including that associated with the true resonance, will be affected [24]. Unless one has a reliable criterion for choosing the correct k , the distinction between resonance and scattering eigenvalues may therefore remain ambiguous. The final column of table 1 gives the unperturbed expectation value $\langle x^2 \rangle$, which was suggested [24] as a measure of the spatial extent of the eigenvectors. While some scattering states can be clearly distinguished as such by their large $\langle x^2 \rangle$ values, it is less certain how many of those with smaller $\langle x^2 \rangle$ should be attributed to resonances. Nevertheless, with properly chosen k ($\approx 10^{-6}$), one obtains an estimate of the resonance position (≈ 2.1), in reasonable agreement with those found by other methods, with modest computational effort.

In summary, the complex-rotation method, while giving general agreement with various stabilization methods for this model potential, seems more able to locate the resonance position consistently and precisely. In addition, it alone gives a clearly defined expression for the resonance lifetime.

5. VIRIAL STATIONARY POINTS

It was argued in §3 that one should choose the rotation angle θ and any adjustable parameters of the resonance wave-function to satisfy the complex virial theorem. This criterion allows an optimal resonance wave-function to be found without resorting to detailed computation of θ trajectories (or α trajectories). Moreover, such a criterion should permit one to extract accurate resonance parameters from smaller variational basis sets than might otherwise seem necessary. Here we describe two alternative approaches to such virial determination of resonance eigenvalues and vectors, and illustrate them by a simple but realistic example.

One procedure is to use the virial theorem in an iterative fashion to estimate an optimal α_1 and θ_1 from an initial guess, α_0 and θ_0 (as was recently suggested by Froehlich *et al.* [15]). Suppose $\Phi_0 = \Phi_0(\alpha_0 \mathbf{r})$ is the initial resonance approximation for H_{θ_0} , with

$$W_0 \equiv (\Phi | H_{\theta_0} \Phi) \equiv (\Phi_0 | H_{\theta_0} \Phi_0). \quad (5.1)$$

In general, the estimate W_0 is not a stationary point on a θ (or α) trajectory, and does not satisfy the c-virial theorem at angle θ_0 :

$$(\Phi | T_{\theta_0} \Phi)_0 \neq -\frac{1}{2} (\Phi | V_{\theta_0} \Phi)_0. \quad (5.2)$$

However, one can choose a new scale α_1 , such that

$$\Phi_1(\mathbf{r}_1, \dots, \mathbf{r}_N) = \alpha_1^{3N/2} \Phi_0(\alpha_1 \mathbf{r}_1, \dots, \alpha_1 \mathbf{r}_N) \quad (5.3)$$

and, simultaneously, a new rotation angle θ_1 for which the corresponding resonance estimate

$$W_1 = (\Phi | H_{\theta_1} \Phi)_1 \equiv (\Phi_1 | H_{\theta_1} \Phi_1) \quad (5.4)$$

has the desired stationary property. In terms of the complex scale factor

$$\eta_1 = \alpha_1 \exp(-i\theta_1), \quad (5.5)$$

equation (5.4) is rewritten as

$$W_1 = \eta_1^2 (\Phi | T_{\theta_0} \Phi)_0 + \eta_1 (\Phi | V_{\theta_0} \Phi)_0 \quad (5.6)$$

and the desired stationary behaviour, $\partial W_1 / \partial \eta_1 = 0$, is obtained when η_1 satisfies the relation

$$\eta_1 = -\frac{1}{2} \frac{(\Phi | V_{\theta_0} \Phi)_0}{(\Phi | T_{\theta_0} \Phi)_0}. \quad (5.7)$$

The new values, α_1 and θ_1 , can thus be estimated from the ratio of (complex) kinetic and potential energies for the unscaled estimate, equation (5.1). However, when the trial Φ contains other adjustable parameters \mathbf{c}_0 (e.g. linear variational coefficients), which were chosen with respect to α_0 and θ_0 , it will be necessary to find new values \mathbf{c}_1 which are optimal with respect to the new α_1 and θ_1 . The re-optimized $\Phi(\alpha_1, \theta_1, \mathbf{c}_1)$, although no longer satisfying the virial theorem, can be taken as an unscaled estimate for the next iteration of equations (5.1)–(5.7).

By this means one may successively approximate the optimal α_{opt} and θ_{opt} for which W_{opt} is truly stationary with respect to all permissible variations. Such an iterative procedure, if convergent, obviates the need for trajectory studies. Of course, the basic objective is to find simultaneous solutions of $\partial W/\partial \eta = 0$ and $\partial W/\partial \mathbf{c} = 0$. If the iterative method is non-convergent, one should consider alternative methods for solving the implied non-linear equation, such as Newton-Raphson procedures.

However, a more direct procedure is suggested. The primary objective is to satisfy the virial theorem, which occurs when the equations $\partial W/\partial \eta = 0$ and $\partial W/\partial \mathbf{c} = 0$ have simultaneous solutions. When the virial theorem is satisfied, the resonance eigenvalue W coincides with the virial estimate W_{vir} (see equations (5.6) and (5.7))

$$W_{\text{vir}} = -\frac{1}{2} \frac{(\Phi | V_{\theta} \Phi)^2}{(\Phi | T_{\theta} \Phi)} \quad (5.8)$$

for $\Phi = \Phi(\alpha, \mathbf{c})$. Accordingly, one may seek to numerically minimize the virial error

$$\Delta_{\text{vir}} = |W - W_{\text{vir}}| = \Delta_{\text{vir}}(\alpha, \theta, \mathbf{c}) \quad (5.9)$$

by direct search methods, starting from an initial guess based on α_0 , θ_0 and \mathbf{c}_0 . Such algorithms will often have better convergence characteristics than the simple iteration procedure outlined above.

We illustrate these procedures by an application to 1S autoionizing resonances in two-electron atoms, for which extensive experimental and theoretical comparisons are available. (Froehlich *et al.* [15] recently applied the iterative procedure successfully to the H-atom Stark effect.) Previous calculations of the lowest 1S e-He⁺ scattering resonance, employing 60 [11] and 80 [20] variational functions, had not corresponded to the complex stationary points where the virial theorem is precisely satisfied. We calculated the position and width of this resonance with a basis set of 20 Hylleraas-type functions†, and searched for stationary virial solutions by both the iterative procedure, and the Powell method [25] (method of conjugate directions) for directly minimizing the virial error given by equation (5.9).

With the initial guesses $\alpha_0 = 1.0$ and $\theta_0 = 0.3$, both the iterative and Powell procedures converged to limiting values of $\alpha = 0.59$ and $\theta = 0.14$, as shown for the iteration procedure in table 2. The resulting resonance parameters,

$$E_r = 58.03 \text{ eV} \quad \text{and} \quad \Gamma = 0.12 \text{ eV},$$

are in quite satisfactory agreement with previous theoretical values calculated from much larger basis sets, and indicate that reasonable positions and widths might be obtained from fairly modest basis sets and fairly small numbers of matrix diagonalizations. In this case, both the iterative and Powell procedures converged in a comparable number of steps.

However, the Powell procedure performs satisfactorily in several instances in which the iterative procedure is poorly convergent or non-convergent. For example, in searching for the second 1S resonance, the Powell algorithm (with

† The basis functions were of the form $(1 + P_{12})r_1^l r_2^m r_{12}^n \exp[-\beta_1 r_1 - \beta_2 r_2]$, where P_{12} permutes the electron labels, the maximum values of l , m and n were 3, 3 and 1 respectively, and $\beta_1 = 1.5$ and $\beta_2 = 2.5$.

initial guesses $\alpha_0=0.32$ and $\theta_0=0.2$) converged in 15–20 steps to the values

$$E_r=63.47 \text{ eV} \quad \text{and} \quad \Gamma=0.09 \text{ eV},$$

whereas the iteration method converged smoothly, and erroneously, to the real axis, $\theta=0$. In fact, the iterative procedure cannot be applied at all to this resonance, for even when the procedure was started from the *exact* optimized α and θ values, successive iterations led to increasing (!) virial errors, and to eventual convergence on the real axis. Our experience suggests that the direct procedure is always to be preferred over the iterative procedure, when the complex stationary point must be accurately located.

Details of these and related applications will be described more completely in a future paper [26].

Table 2. Iterative virial-scaling procedure for lowest 1S $e\text{-He}^+$ scattering resonance, illustrating the convergence of the resonance eigenvalue $W=E_r+iE_1$ and scale factor $\eta=\alpha \exp(-i\theta)$ with increasing iterations. Energy values are in atomic units, θ in rad. Parenthesized numbers under the virial error Δ_{vir} indicate the power of 10 by which the entry should be multiplied.

Iteration	E_r	E_1	α	θ	Δ_{vir}
1	-0.76735	+0.00322	0.500	0.300	0.19 (-2)
2	-0.77102	+0.00356	0.526	0.309	0.20 (-2)
5	-0.77192	-0.00125	0.569	0.240	0.20 (-3)
10	-0.77143	-0.00198	0.584	0.192	0.30 (-4)
15	-0.77133	-0.00214	0.591	0.171	0.95 (-5)
20	-0.77128	-0.00217	0.594	0.157	0.37 (-5)
25	-0.77126	-0.00218	0.594	0.148	0.16 (-5)
30	-0.77125	-0.00217	0.593	0.142	0.63 (-6)
35	-0.77125	-0.00216	0.591	0.140	0.25 (-6)
40	-0.77125	-0.00216	0.590	0.139	0.92 (-7)
	-0.7767	-0.00215	(Hickman <i>et al.</i> [11], 60 terms)		
Previous values	-0.7716	-0.00271	(Winkler [20], 80 terms)		
	-0.7781	-0.00228	(Burke†, close coupling)		

† Burke, P. G., 1968, *Adv. atom. molec. Phys.*, **4**, 173.

6. CONCLUSION

We have described in this paper exploratory studies on the complex-rotated hamiltonian operators H_θ , whose isolated point eigenvalues in the complex-energy plane can be rigorously associated with the positions and widths of resonances in the cross-sections for electron scattering, photo-ionization and related processes. Our results support the idea that these complex eigenvalues can be characterized by techniques highly analogous to those employed for ordinary bound states. On the basis of the complex-rotation formalism, one may anticipate further progress in developing numerical techniques which apply

both above and below break-up thresholds and which thereby permit a more unified picture of bound-state and continuum properties of atoms and molecules.

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