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Resonances by complex nonsimilarity transformations of the Hamiltonian

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A set of complex scaling schemes which enable one to calculate resonance positions and widths is introduced. Although these scaling procedures are not equivalent to the complex-coordinate method, they change the asymptotic behavior of resonance wave functions from exponentially diverging to square integrable. Coupled to a Padé-approximation-extrapolation procedure, these nonsimilarity transformations enable one to obtain the complex resonance energies of the original Hamiltonian. A study of these scaling schemes, their influence on the spectrum, and the limitations of the method is presented. The use of some of these procedures, especially a kinetic-energy-scaling scheme where $\hbar \rightarrow \hbar e^{-i\phi}$, is most attractive from the computational point of view, and permits the use of currently existing programs for the calculation of potential-energy matrix elements.

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I. INTRODUCTION

Metastable resonance states are of primary importance in many areas of chemistry and physics. Resonances are associated with complex eigenvalues of the time-independent Schrödinger equation, where the corresponding eigenfunctions have the asymptotical behavior of divergent outgoing plane waves.

Several methods have been used in order to obtain these complex eigenvalues. The most well known is the complex-coordinate method (CCM) [1–5], which is equivalent to a similarity transformation [5] of the Hamiltonian which causes the resonance wave functions to become square integrable. In the CCM the similarity transformation is the complex scaling operator, which amounts to rotating the internal coordinates of the Hamiltonian into the complex plane, according to $x \rightarrow x e^{i\theta}$. The CCM is based on rigorous mathematical foundations—the Balslev-Combes theorem [6–8] and the works of Aguilar, Combes, and Simon [6–10]. The theory states that under the scaling transformation the eigenvalues associated with bound states remain on the real axis of the complex energy plane, at the positions that they occupied before scaling. The eigenvalues that are associated with metastable resonance states appear as complex eigenvalues unrelated to the scaling angle $-\theta$ used, when it is larger than a critical angle, and eigenvalues that are associated with continuum states appear as complex eigenvalues which are dependent on the scaling angle in the form

$$E_{\text{cont}} = E^0_{\text{cont}} \exp(e^{-2i\theta}) ,$$

where E^0_{cont} are the eigenvalues representing the continuum prior to scaling.

The eigenfunctions representing the bound states remain square integrable under complex rotation, and the continuum eigenfunctions retain their bounded asymptotic behavior. The eigenfunctions associated with resonances, however, change their asymptotic behavior under scaling, from an exponentially divergent behavior before scaling, to square integrable after the transformation. The CCM, as developed by Aguilar, Balsev, Combes, and Simon, requires the complex rotation of *all* coordinates into the complex plane, and is applicable, in principle, only to dilation-analytic Hamiltonians. (In practice it works well for nondilation-analytic cases as well.) Apart from the CCM, other procedures are also used in order to obtain the complex resonance energies. Some of these procedures are expansions of the CCM to cases which the original analytical dilation theory does not treat. Such procedures include the widely used method of scaling only the reaction coordinate [11–15]; a procedure in which the Hamiltonian matrix elements are analytically continued into the complex plane, after they have been formulated for a nonrotated Hamiltonian and a real basis set [11,12]; the complex stabilization technique [16,17], in which nonlinear parameters in the basis set are scaled while the Hamiltonian operator is kept real; and the exterior scaling method [18,19], in which only the asymptotic part of coordinate space is scaled. Also used is the Junker stabilization method [20], which involves the inclusion of a few complex basis functions in the basis set, without imposing explicitly any boundary conditions. The Siegert method [21–23] does explicitly impose boundary conditions. In this method the resonance wave function contains terms which describe an exponentially outgoing wave in the open channels. A relatively novel procedure is the use of the optical-potential method [24–27], in order to calculate resonance positions and widths. In this method an imaginary potential is added in the physically asymptotic region in order to induce localization in the resonance wave functions and expose the complex nature of resonance eigenvalues and eigenfunctions. When applying the optical-potential method, care must be taken in order to make sure that the optical potential does not affect the physically significant region of coordinate space and is smooth enough to preserve the outgoing character of the wave function.

Thus, all methods described above enable us to obtain the complex resonance energies by imposing, explicitly or not explicitly, specific boundary conditions on resonance wave functions; resonances are associated with wave functions that are exponentially divergent prior to scaling (or otherwise perturbing the system) and become square integrable as a result of scaling (or as a result of the perturbation we introduce). In all cases, the energy spectrum we get remains the spectrum of the physical problem under investigation.

Some time ago, Lefebvre and Garcia-Sucre [28] made the observation that an optical potential applied abruptly [say, $V_{\text{opt}}(r)=-iA$ for $r_0 \leq r$] outside the range of the physical potential induces a large perturbation in the eigenenergies associated with the localizable wave functions. However, if such calculations are repeated for a number of values of the parameter A, it is possible to build a Padé approximant $E(A)$ giving the energy as an analytic function of A. This approximant can be used to extrapolate $E(A)$ to $E(0)$, that is, for a situation where *no optical potential is present,* while the energy $E(0)$ is that of a resonance state. This can be interpreted as a procedure to access the non-Hermitian domain of the Hamiltonian. A similar idea was used to calculate photoionization or photodissociation cross-sections by using complex photon frequencies. A Padé approximant is used to extrapolate to real photon frequencies [29]. Such ideas are somewhat related to the use of imaginary electric-field intensities in the description of Stark ionization in order to circumvent the difficulties related to the divergent character of the Rayleigh-Schrödinger perturbation expansion [30,31].

In this work we further investigate the possibilities and limitations of procedures similar to the one suggested by Lefebvre and Garcia-Sucre. We will try to find out which transformations can be carried out, and why, and look at the influence of these transformations on the bound and continuous spectrum. The transformations we study, in contrast to previously used transformations, consist of scaling parameters that influence the kinetic energy of the system, such as $\hbar$, and mass μ, and the threshold energy E_{th}, and *not* potential parameters. It is therefore easy to examine their influence on the asymptotic behavior of resonance wave functions.

II. RESONANCES BY NONSIMILARITY TRANSFORMATIONS OF THE HAMILTONIAN

For a potential that decays to a constant in the asymptotic regions of coordinate space,

$$V \to E_{\text{th}} \quad \text{as } x \to \infty \ ,$$

the asymptotic form of resonance wave functions in the open channel is of the Siegert outgoing type,

$$\psi^{\text{res}}_{x\to\infty} \to A(E)\exp\left[\frac{i\sqrt{2\mu(E-E_{\text{th}})}}{\hbar}x\right] .$$

It is easy to see that scaling either μ, $\hbar$, or E_{th} ($\mu \to \mu e^{2i\phi}$ $\hbar \to \hbar e^{-i\phi}$ or $E_{\text{th}} \to E_{\text{th}}e^{2i\phi}$) in the *open* channels changes the asymptotic behavior of the wave functions and causes localization, in the same manner that scaling the coordinate x does so in the CCM (we denote by θ the CCM scaling angle and by ϕ the scaling angle of the non similarity transformations presented in this paper). We shall see later that scaling closed-channel parameters may also cause some localization, through coupling to the open channels. Scaling of these parameters, though, affects not only the asymptotic region, but also those regions of space which contain physical information. We therefore expect the energies of bound and resonance states to be shifted in comparison to the energies of the physical Hamiltonian.

However, if we repeat the calculation with a set of ϕ values, fit a Padé approximant to the function $E(\phi)$, and use this approximant to find the limit of the function as the perturbation goes to zero, we expect to obtain the complex energies of the unperturbed Hamiltonian which are associated with localizable wave functions—the resonance energies $\lim_{\phi\to 0}E(\phi) \to E_{\text{res}}$.

It is worthwhile noting that *unlike* in the CCM, the energies of the bound and resonance states obtained by the scaling procedures described above are *intrinsically* ϕ dependent, since the scaling constitutes a perturbation of the Hamiltonian. In actual CCM calculations, on the other hand, the dependence of the bound and resonance energies on the scaling angle results from the truncation of the basis sets used.

The effect of the transformations on eigenvalues describing the continuum can be deduced by an examination of the asymptotic form of continuum wave functions. For $V_{x\to\infty} \to E_{\text{th}}$,

$$\psi^{\text{cont}}_{x\to\infty} \to A(E)\exp\left[\frac{i\sqrt{2\mu(E-E_{\text{th}})}}{\hbar}x\right] + B(E)\exp\left[\frac{-i\sqrt{2\mu(E-E_{\text{th}})}}{\hbar}x\right] ,$$

for complex μ, $\hbar$, or E_{th}, and real energy E, one of these exponentials diverges. In order to retain the boundedness of the continuum wave functions, the energies must become complex in a manner that cancels the imaginary part of the perturbation:

$$(E_{\text{cont}}-E_{\text{th}}) \to (E_{\text{cont}}-E_{\text{th}})e^{-2i\phi} \quad \text{for } \hbar \to \hbar e^{-i\phi} ,$$

$$(E_{\text{cont}}-E_{\text{th}}) \to (E_{\text{cont}}-E_{\text{th}})e^{-2i\phi} \quad \text{for } \mu \to \mu e^{2i\phi} ,$$

$$E_{\text{cont}} \to E_{\text{cont}} - i\sin(2\phi)E_{\text{th}} \quad \text{for } E_{\text{th}} \to E_{\text{th}}e^{2i\phi} .$$

Thus, the scaling of either $\hbar$ or μ causes *rotation* of the continuum into the complex plane by an angle of 2ϕ, just as is the case in the CCM, and for the same reasons, whereas scaling the threshold energy causes a translation of continuum energies into the complex plane by an amount $\sin(2\phi)E_{\text{th}}$. This expectation is fulfilled by our results, which are presented in Fig. 1.

III. METHODS AND MODELS

We applied our method to several model systems, using either a basis-set method or a matching method [32]. In the basis-set method, the Hamiltonian matrix is built of basis functions φ_i, representing all of the system coordi-

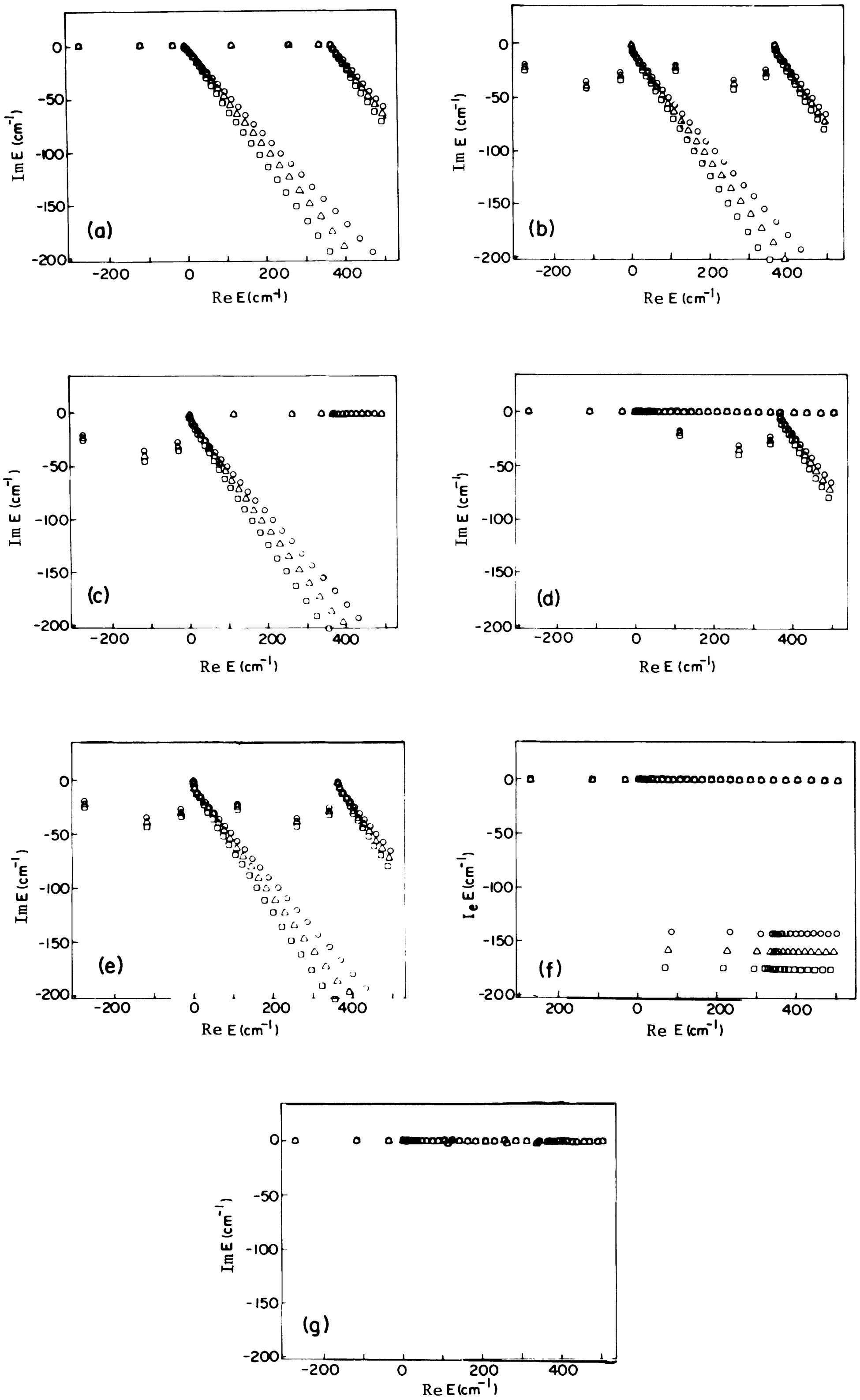

FIG. 1. The shape of the spectrum (real and imaginary parts of the eigenvalues) of the van der Waals rotational predissociation model for a set of scaling transformations. All calculations were performed with the basis-set method, for scaling angles of $\phi=0.2$, 0.225, 0.25 rad. (a) Complex-coordinate scaling $x \rightarrow xe^{i\phi}$; (b) scaling of the kinetic energy in all channels $\hbar \rightarrow \hbar e^{-i\phi}$; (c) scaling of the kinetic energy in the open channel only; (d) scaling of the kinetic energy in the closed channel only; (e) scaling of the kinetic-energy term and the centrifugal barrier $\mu \rightarrow \mu e^{2i\phi}$; (f) scaling of the threshold $B_{\rm rot} \rightarrow B_{\rm rot} e^{2i\phi}$; and (g) scaling of the centrifugal barrier only.

nates, in the form

$$\mathbf{H}_{ij}=\langle \varphi_i|\hat{H}|\varphi_j\rangle \ ,$$

where the operator $\hat{H}$ is scaled in an appropriate way. After being formulated, the Hamiltonian matrix is diagonalized to obtain the system eivenvalues.

In the matching method, $\mathbf{U}^0(r)$ and $\mathbf{U}^i(r)$ are matrices with columns representing N independent solutions of N coupled equations, which fulfill given boundary conditions at small r and large r. In the Fox-Goodwin method [33] one builds the two matrices

$$\mathbf{P}^0(r+h)=\mathbf{U}^0(r)\mathbf{U}^0(r+h)^{-1}$$

and

$$\mathbf{P}^i(r-h)=\mathbf{U}^i(r)\mathbf{U}^i(r-h)^{-1} \ ,$$

which are obtained from two propagation formulas,

$$\mathbf{P}^0=[2\underline{\beta}(r)-\underline{\alpha}(r-h)\mathbf{P}^0(r)]^{-1}\underline{\alpha}(r+h) \ ,$$

$$\mathbf{P}^i(r-h)=[2\underline{\beta}(r)-\underline{\alpha}(r+h)\mathbf{P}^i(r)]^{-1}\underline{\alpha}(r-h) \ .$$

and $\underline{\alpha}(r)$ and $\underline{\beta}(r)$ are the Numerov matrices

$$\underline{\alpha}(r)=h\left[\mathbf{1}+\frac{h^2}{12}[E\mathbf{1}-\mathbf{V}(r)]\right] \ ,$$

$$\underline{\beta}(r)=\left[\mathbf{1}-\frac{5h^2}{12}[E\mathbf{1}-\mathbf{V}(r)]\right] \ ;$$

h is the propagation step; and $\mathbf{V}(r)$ is the potential matrix. The matching relation, which is a quantization condition for the energy, is

$$\frac{d}{dr}\{P^i(r_m)-[P^0(r_{m+1})]^{-1}\}=0 \ .$$

r_m is the matching point and r_{m+1} is r_m+h.

The boundary condition on both ends $-r_1$ and r_p of the integration range are for a bound-state wave function, or a resonance wave function localized by the scaling

$$\mathbf{P}^0(r_1+h)=\mathbf{U}^0(r_1)\mathbf{U}^0(r_1+h)^{-1}=0 \ ,$$

$$\mathbf{P}^i(r_p-h)-\mathbf{U}^i(r_p)\mathbf{U}^i(r_p-h)^{-1}=0 \ .$$

With the matching method we applied a procedure in which only the kinetic energy of the system was scaled. This is done by defining the Numerov matrices

$$\underline{\alpha}'(r)=h\left[\mathbf{1}e^{-2i\phi}+\frac{h^2}{12}[E\mathbf{1}-\mathbf{V}(r)]\right] \ ,$$

$$\underline{\beta}'(r)=h\left[\mathbf{1}e^{-2i\phi}+\frac{5h^2}{12}[E\mathbf{1}-\mathbf{V}(r)]\right] \ .$$

After performing the calculation with a certain scaling scheme for a number of scaling angles ϕ, we fit a Padé approximant to the 1 values which correspond to the resonance eigenvalue at each angle. The identification of these eigenvalues does not pose a problem since, just as in spectra which appear in the CCM, the eigenvalues associated with resonances behave in an entirely different manner than eigenvalues associated with the continuum. This observation holds even in cases where the scaling transformation causes large shifts in the position and width of resonance eigenvalues. This phenomenon can be observed, for a model describing van der Waals rotational predissociation resonances, in Fig. 1. After the Padé approximant is fit to the resonance eigenvalues, the function is evaluated at $\phi=0$ to obtain the eigenvalue of the unperturbed Hamiltonian.

We have used two of the point Padé methods described by Schlessinger [34]. One of the methods [let us call it method (a)] is a direct fit of the input values of a function $f(z)$ to a ratio of two polynomials:

$$f(z_i)=\frac{P_{m_2}(z_i)}{Q_{m_1}(z_i)} \ , \tag{1}$$

with

$$P_{m_2}(z_i)=\sum_{k=1}^{m_2} p_k z_i^k$$

and

$$Q_{m_1}(z_i)=1+\sum_{\iota=1}^{\mu} q_l z_i^l \ .$$

The z_i's are the input values of the variable. The number of unknown coefficients p_k and q_k being m_1+m_2+1, one needs this number of input values $f(z_i)$ to determine them. Relations (1) lead to a set of inhomogeneous linear equations with a solution requiring a matrix inversion.

Another method [method (b)] consists of using a truncated continued fraction of the form

$$C_N(z)=\cfrac{f(z_1)}{1+\cfrac{a_1(z-z_1)}{1+\cfrac{a_2(z-z_2)}{\begin{matrix}\vdots\\ a_n(z-z_n)\end{matrix}}}} \ .$$

The coefficients a_i are chosen such that

$$C_N(z_i)=f(z_i) \ , \quad i=1,2,\ldots,N \ .$$

Expressions for the a_i's are given by Schlessinger. In both methods it is usful to examine the convergence of the extrapolated function

$$f(z_e)=\frac{P_{m_2}(z_e)}{Q_{m_1}(z_2)} \quad \text{or} \quad C_N(z_e)$$

calculated for z_e outside the input range of the z_i's, when the numbers m_1+m_2+1 or N are increased. This amounts to taking into account an increasing number of input data. As discussed in several textbooks (see, for example, Stoer [35], better results are obtained when the degrees of the polynominals in the numerator and denominator of expression (1) are close to one another. In method (b) this is automatically ensured, since the truncated continued fraction is equivalent to a ratio of polynomials with either $m_1=m_2$ (with an even number of a_i's or $m_1=m_2+1$ (with an odd number of a_i's). In method (a) we have imposed this rule on the two numbers m_1 and

m_2. The approximation is very sensitive to the exact values of the input data, and it is important to apply the Padé procedure to data which are accurately determined. It is our experience that increasing the orders of the polynomials beyond values around 5 or 6 decreases the accuracy of the Padé approximation. This can be easily detected in method (a), where a matrix inversion is required. One finds that trying to recover the original matrix as $[(A)^{-1}]^{-1}$ gives poor results for high orders.

A. van der Waals rotational predissociation resonances

A model Hamiltonian describing rotational predissociation resonances in van der Waals molecules was suggested by Levine, Johnson, Muckerman, and Bernstein [36] and is often used as a testing ground for the study of new methods and approaches [13–15]. The model consists of a rigid rotor BC, and a structureless atom A. The parameters are chosen to fit the He-H_2 system.

The system Hamiltonian is

$$H(R,\gamma)=\frac{1}{2\mu}\left[-\hbar^2\frac{\partial}{\partial R^2}+\frac{l^2(\hat{\mathbf{R}})}{R^2}\right]+B_{\text{rot}}j^2(\hat{\mathbf{r}})+V(R,\gamma)\ ,$$

where μ is the reduced mass of the complex, B_{rot} is the rotational constant of the diatom, l^2 is the orbital angular momentum of BC and A about each other, j is the rotational angular momentum of the diatom, R is the distance between A and the center of mass of BC, r is the distance between B and C (fixed in this model at the equilibrium distance), and γ is the angle between the vectors $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}\cos\gamma=\hat{\mathbf{r}}\cdot\hat{\mathbf{R}}$. The potential is expressed as a sum of two Legendre polynomials [36]:

$$V(V,\gamma)=V_0(R)+V_2(R)P_2(\cos\gamma)\ ,$$

$$V_0(R)=4\varepsilon\left[\left[\frac{\sigma}{R}\right]^{12}-\left[\frac{\sigma}{R}\right]^{6}\right]\ ,$$

$$V_L(R)=0.6\varepsilon\left[\frac{\sigma}{R}\right]^{2}\ .$$

With the parameters $\sigma=3.0$ Å $\varepsilon=384.097\ \text{cm}^{-1}$, $B_{\text{rot}}=60.967\ \text{cm}^{-1}$, and $\mu=1.340\,15$ a.u., the system has three bound states for the lowest channel, $j=0$, which become three resonance states in each even $j>0$ channel as a result of the coupling with the continua of the lower even channels. (The odd channels are not coupled to the even ones due to the symmetry of the potential and hence are ignored.) We investigated the effect of the nonsimilarity transformations on the lowest resonance, located at $\sim 114\ \text{cm}^{-1}$ and describing a state localized in the $j=2$ channel and dissociating into the $j=0$ channel.

The eigenvalues of the system were obtained both by the matching method, with 2000 grid points, with a step of 0.006 in reduced units $\tilde{R}$ such that

$$\frac{-\hbar^2}{2\mu hc}\frac{\partial^2}{\partial R^2}=-\frac{\partial^2}{\partial\tilde{R}^2}\ ,$$

and by a basis-set method, using 150 particle-in-a-box basis functions with box size of 28 a.u. for R—the distance between A and the center of mass of BC—and two Legendre polynomials P_0 and P_2 for the angular coordinate γ.

With the basis-set method, various scaling schemes were tried: scaling the kinetic-energy term by scaling $\hbar$ ($\hbar\rightarrow\hbar e^{-i\phi}$), scaling the kinetic energy and the centrifugal barrier by scaling μ, ($\mu\rightarrow\mu e^{2i\phi}$), scaling of the centrifugal barrier only, scaling the threshold by scaling B_{rot} to $B_{\text{rot}}e^{2i\phi}$, and scaling the kinetic energy in the closed channel only, or in the open channel only. With the matching method we used scaling of the kinetic-energy term, by scaling $\hbar$. For each scaling scheme 10 or 11 calculations, with different scaling angles, were carried out, with angles in the range of $\phi=0.2$–0.25 rad.

B. 1D shape-type resonances

The second model we investigated was the one-dimensional Bardsley potential [37,38] with Hamiltonian

$$H(R)=-\frac{d^2}{dr^2}+15r^2e^{-r}\ .$$

The system was studied by the matching technique with 6000 grid points, with a grid step of 0.005 a.u. For this system scaling of the kinetic energy was carried out.

C. Helium autoionization resonances

The third case studied was that of the autoionization resonances of the helium atom [39]. The Schrödinger equation for this system was solved by a basis-set method, using 36 Hylleraas-type basis functions of the form

$$\phi_{lmn}(a,b)=(1+P_{12})r_1^l r_2^m r_{12}^n\exp(-ar_1-br_2)\ ,$$

where $a=b=2.0$, P_{12} permutes the particle labels, r_1 and r_2 are the scalar distances from the nucleus, r_{12} is the interelectronic distance, and $0\leq[l,m]\leq 2$ and $0\leq n\leq 5$.

The resonance studied is positioned at ~ 0.777 hartree. For this system also, only scaling of the kinetic-energy term was carried out.

IV. RESULTS AND DISCUSSION

A. van der Waals rotational predissociation model

Figure 1 shows the shape of the spectrum (real and imaginary parts of the eigenvalues) for a range of scaling angles for the various scaling schemes. The corresponding wave-function components in the open channel are plotted as a function of R, the distance between the atom and the diatom, in Fig. 2 the functions were drawn for $\phi=0.2$.

The corresponding extrapolations of the Padé approximations to $\phi=0$ are summarized in Table I. In all cases but the one denoted by an asterisk, the results are those given by method (a) for the highest-order Padé approximation derived from 11 points ($m_1=5$, $m_2=5$) (as can be seen from Table II, both methods give practically the same results, and the results were usually stable with respect to increase in m_1 and m_2). In the case of scaling the kinetic energy in the closed channel only, the results

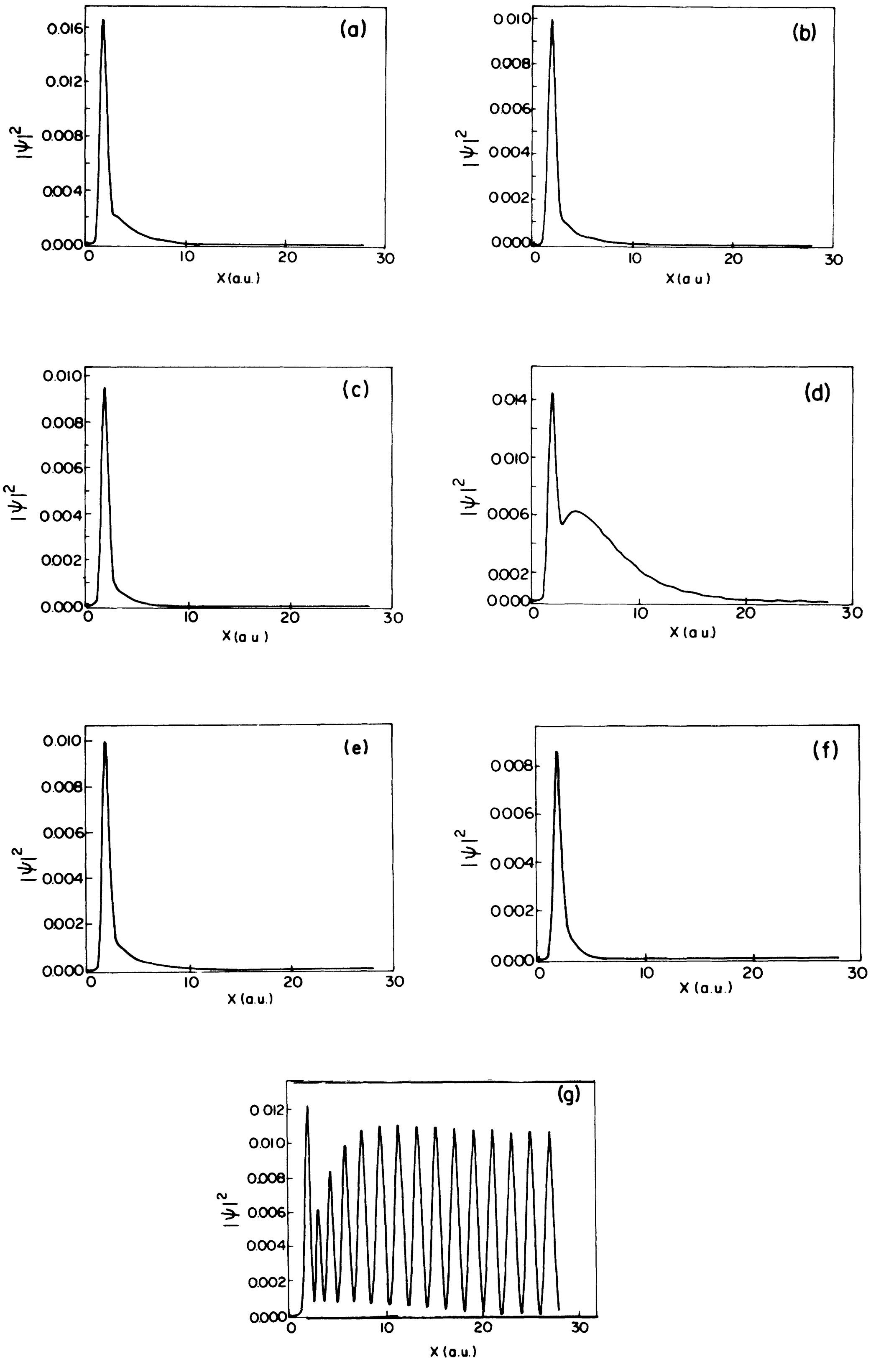

FIG. 2. The shape of the resonance wave function component in the open channel ($j=0$) of the van der Waals rotational predissociation model, for the various scaling schemes (a)–(g), as described for Fig. 1. Calculations were done with the basis-set method and for a scaling angle of $\phi=0.2$ rad.

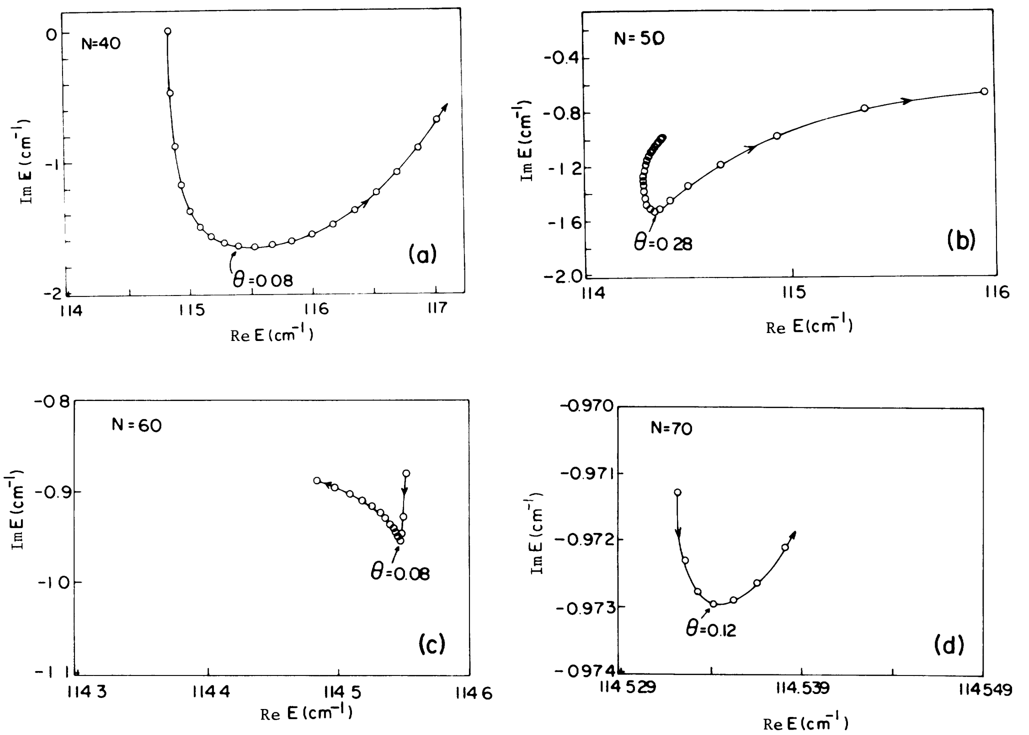

FIG. 3. Complex-coordinate θ trajectory calculations for the lowest resonance energy of the van der Waals rotational predissociation model, for a varying number of basis functions: (a) $N=40$ (b) 50, (c) 60, (d) 70. θ values are given in radians.

of various order Padé approximations fluctuate, and the result cited is that of the $m_1=2$, $m_2=5$ approximation.

The sign of the imaginary part of the energy is devoid of physical meaning and depends on the sign of the scaling angles used. Changing the form of scaling from $e^{i\phi}$ to $e^{-i\phi}$ causes the solution to converge to a pole in either the upper or lower halves of the complex energy plane. In Table II the dependence of the results on the order of the polynomials used—m_1 and m_2— is given for both Padé methods. This table is taken from calculations done

TABLE I. Extrapolation of the Padé approximants to $\phi=0$, for the lowest bound state and lowest resonance, of the van der Waals rotational predissociation model, for a variety of scaling transformations. The Padé approximants were constructed from a set of eigenvalues of Hamiltonians scaled by angles of $\phi=0.2-0.25$ rad. All the results were obtained by the basis-set method, except the one denoted by two asterisks, which was obtained by the matching method. Padé approximants were constructed with method (a). The result denoted by one asterisk was not very stable with respect to the order of the Padé approximant used.

	Extrapolation of the Padé approximant to $\phi=0$	
Scaling transformation	First bound state	First resonance
Scaling the kinetic-energy term in both open and closed channels ($\hbar \rightarrow \hbar e^{-i\phi}$)	-273.238 $+0.158\times10^{-4}i$ -273.239 $+0.105\times10^{-4}i$**	114.527 $-0.972i$ 114.529 $-0.970i$**
Scaling the kinetic-energy term in the open channel only	-273.238 $-0.122\times10^{-4}i$	114.530 $-0.970i$
Scaling the kinetic-energy term in the closed channel only	-273.238 $-0.715\times10^{-5}i$	114.151 $-0.789i$*
Scaling both the kinetic energy and the centrifugal barrier ($\mu \rightarrow \mu e^{2i\phi}$)	-273.238 $+0.124\times10^{-3}i$	114.524 $-0.974i$
Scaling the threshold ($B_{\mathrm{rot}} \rightarrow B_{\mathrm{rot}} e^{2i\phi}$)	-273.238 $+0.510\times10^{-4}i$	114.530 $-0.969i$
Scaling the centrigfugal barrier only	-273.238 $+0.408\times10^{-4}i$	114.550 $+0.475i$
Complex-coordinate Method ($x \rightarrow xe^{i\theta}$)	-273.238 $-0.645\times10^{-4}i$	114.530 $-0.970i$
No scaling	-273.238 $+0.0i$	114.552 $+0.0i$

TABLE II. Estimates of the lowest resonance energy of the van der Waals rotational predissociation model obtained by extrapolating the Padé approximation constructed from the kinetic-energy scaling procedure, with angles $\phi=0.2-0.25$ rad to $\phi=0$. Estimates are presented for both methods of construction of the Padé approximants [(a) and (b)] and for different polynomial orders used for the fit. Calculations were done by the matching method.

Order of Padé polynomials			
m_1	m_2	Resonance estimate method (a)	Resonance estimate method (b)
1	1	$114.51826-1.0363024i$	$114.51826-1.0363024i$
2	1	$114.52709-0.96841194i$	$114.52709-0.96841194i$
2	2	$114.52975-0.97001071i$	$114.52975-0.97001071i$
3	2	$114.52980-0.97038712i$	$114.52980-0.97038709i$
3	3	$114.52943-0.97021103i$	$114.52943-0.97020869i$
4	3	$114.52981-0.97036012i$	$114.52981-0.97036012i$
4	4	$114.52983-0.97042668i$	$114.52983-0.97043589i$
5	4	$114.52981-0.97032404i$	$114.52981-0.97035674i$

Exact value: $114.52986-0.97041i$.

with the matching method. As can be seen from Table I and from looking at Fig. 2, all transformations which cause strong localization in the open-channel wave function produced fine estimates for resonance position and width. Scaling of the kinetic-energy term in the *closed* channel causes weak localization in the open-channel wave function, through the coupling between the channels, and gives a much worse estimate for the resonance position and width. This result, denoted by an asterisk in Table I, was, as mentioned before, not very stable with respect to the order of Padé approximations. Scaling of the centrifugal barrier only does not cause localization in the open-channel wave function, and the extrapolation to zero perturbation of the Padé approximation of $E(\phi)$ yields exactly the result we obtain with no scaling whatsoever. It seems evident from these results that the adequacy of a transformation in yielding the correct complex resonance energy rests on its ability to cause localization in resonance wave functions in the open channels.

The asymptotic behavior of the bound-state wave functions is unaffected by the transformations we perform, and the extrapolation of the Padé approximations of $E(\phi)$ to $\phi=0$ yields the correct bound-state energy (the small imaginary part of the bound-state energies is mainly due to the size of the basis set used, and to numerical errors in the Padé extrapolation).

Note that the Padé approximations give good results even when the perturbed values deviate very much from the correct resonance energy (in the case of scaling the threshold, for example, we base the Padé approximation on values as far off as $70-175i$ cm^{-1} and yet extrapolate back to the correct result).

The dependence of the results on the range of scaling angles used was checked for the kinetic-energy scaling procedure, and is presented in Table III. For each calculation, 11 ϕ values in the given range were used to construct the Padé approximant. As can be seen from Table V, it is crucial to choose ϕ large enough to cause sufficient localization of the resonance wave function. For a large range of ϕ values $(0.2-0.6)$, the results of the extrapolation to $\phi=0$ are little dependent on the range of ϕ values used to construct the Padé approximant; these results were also stable with respect to the order of the Padé approximants used. For very large ϕ values, we extrapolate back a long way, and the results become less accurate and also less stable with respect to the order of the Padé approximants used. As can be seen from the last two entries of Table III, increasing the span of angles considered in the calculation, while restricting oneself to the range of angles which give stable results, increases the accuracy, probably due to the fact that we are giving a more loyal description of the function $E(\phi)$.

It is interesting to examine the shape of the spectra obtained for the various transformations (Fig. 1). For all transformations we can see that, as in spectra obtained with the CCM, it is easy to distinguish between bound or resonance states and continuum states. In contrast to the case in the CCM, however, the bound states also move into the complex plane under these transformations; also, the resonance states might appear with imaginary parts either smaller or *larger* than the continuum energies. The dependence of continuum energies on the form of scaling and on the scaling angle follows the expectations discussed in Sec. II: rotation into the complex plane by an angle of 2ϕ, for scaling of either μ or $\hbar$, and translation by an amount $\sin2\phi$ for scaling the threshold energy.

TABLE III. Estimates of the lowest resonance energy of the van der Waals rotational predissociation model obtained by extrapolating the Padé approximations to $\phi=0$, as a function of the range of angles ϕ used to construct the Padé approximants. The entry denoted by an asterisk was not stable with respect to the order of Padé approximant used.

Range of scaling angles	Resonance estimate
0.02–0.12	$114.55+0.05i^*$
0.13–0.23	$114.5-0.9i$
0.24–0.34	$114.529-0.968i$
0.35–0.45	$114.530-0.969i$
0.46–0.56	$114.529-0.967i$
0.57–0.67	$114.527-0.96i$
0.68–0.78	$114.53-0.95i$
0.79–0.89	$114.5-0.9i$
0.2–0.5	$114.53-0.97i$
0.3–0.5	$114.531-0.9704i$

In the case of scaling μ or $\hbar$, the continuum is rotated not about the real threshold energy, but about a slightly shifted complex energy "threshold." The exact origin of this shift is not yet completely understood.

An interesting side remark is that when we form a Padé approximation of the CCM $E(\theta)$ results for large enough scaling angles θ (since we use a finite basis set, the CCM results are θ dependent) and extrapolate to $\theta=0$, we get, in most cases, better estimates for the resonance position and width than we got from the stationary point in the plot of $E(\theta)$ for a given basis set. Figure 3 depicts the θ trajectory plots for the van der Waals rotation predissociation model $\sim 114\text{-cm}^{-1}$ resonance, for a set of basis-set sizes $N=40,50,60,70$. In Fig. 4 we show the same trajectories extrapolated from 11 θ values in the range $\theta=0.3$–0.4 rad (namely a Padé approximation was fit to the 11 θ-values in the range $\theta=0.3$–0.4 rad, then extrapolated to $\theta=0$, 0.001, 0.002, ..., 0.4 rad). It can be seen from Fig. 4 that the extrapolated trajectories follow the CCM trajectories very closely, and accurately represent the stationary points. Then, at $\theta=0$, they converge to a better value than the one obtained from the stationary point. The difference between the two values decreases rapidly with the increase in basis-set size.

This phenomenon can be easily understood if we recall that for a small basis set, complex scaling can be regarded as a perturbation and it is a well-documented fact that large basis sets are needed when using the CCM, unless nonlinear basis-set parameters are adequately optimized [17,40]. Just as in the case of other transformations, then, the Padé extrapolation to $\theta=0$ serves to minimize the perturbation while retaining asymptotic behavior, and improves the estimate. For large basis sets, this effect is negligible. Note that with $N=60$ we find a sharp cusp at the CCM θ trajectory. For this case *only*, the stationary point obtained from the Padé extrapolation deviates slightly from the CCM stationary point, and the energy estimate obtained by extrapolation to $\theta=0$ is slightly *worse* than the stationary-point estimate. We found this phenomenon to occur also in the case of the Hamiltonian of helium autoionization, which also has a sharp cusp, and it seems to indicate the inability of the Padé approximation to represent adequately a function demonstrating such a nonsmooth behavior.

B. 1D shape-resonance model

The results obtained by applying the kinetic-energy scaling procedure to the Bardsley model Hamiltonian described in Sec. III are given in Table IV. Those results were calculated using the matching method. As can be seen from Table IV, accurate results are obtained by this method for this model also. The results are very close for both Padé methods, and are stable with respect to an increase in the order of the polynomials used for constructing the Padé approximants.

As for the previous model, we also tried carrying the Padé-approximation-extrapolation procedure for the CCM results of this model. In the matching method, complex resonance energies can be obtained in two

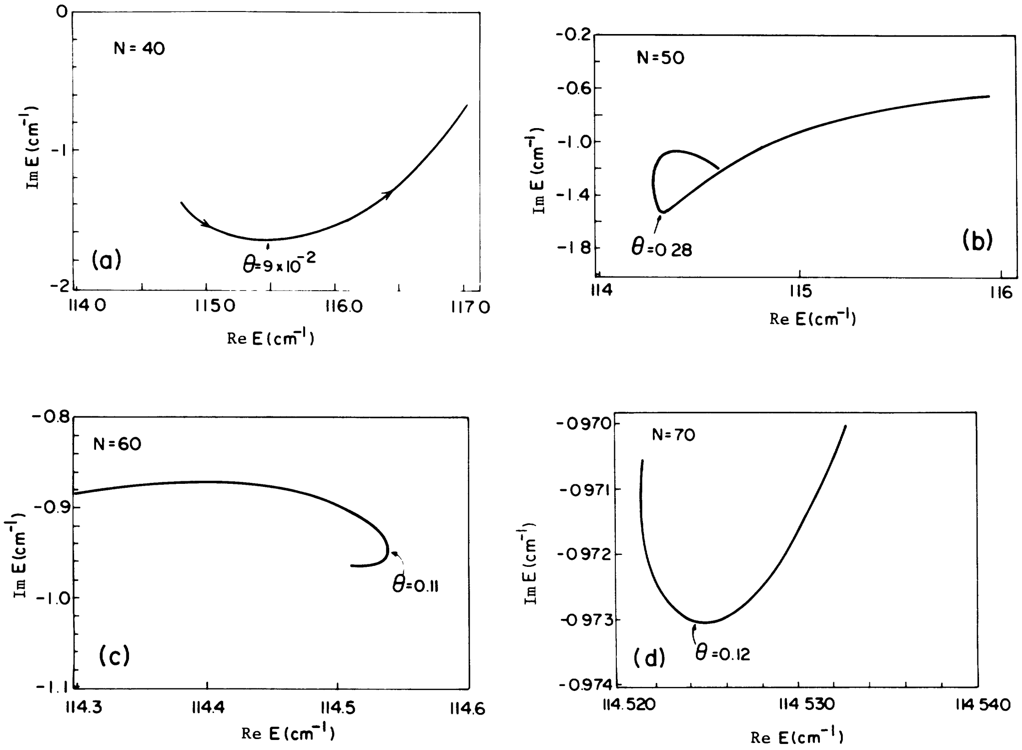

FIG. 4. The Padé-approximant $E(\theta)$ fit to the eigenvalues of the lowest resonance of the van der Waals model. The approximants were constructed from a fit to eigenvalues calculated with scaling angles $\theta=0.3$–0.4 rad and for a varying number of basis functions (a) $N=40$, (b) 50, (c) 60, (d) 70.

TABLE IV. Estimates of the resonance energy of the 1D shape-resonance model obtained by extrapolating the Padé approximation constructed from the kinetic-energy scaling procedure, with angles $\phi=0.2$–0.25 rad to $\phi=0$. Estimates are presented for both methods of construction of the Padé approximants [(a) and (b)] and for different polynomial orders used for the expansion. Calculations were done by the matching method.

Order of Padé polynomials			
m_1	m_2	Resonance estimate method (a)	Resonance estimate method (b)
1	1	6.953 099 4−0.067 976 679*i*	6.953 099 4−0.067 976 679*i*
2	1	6.842 839 2−0.037 337 698*i*	6.842 839 2−0.037 337 698*i*
2	2	6.856 254 2−0.018 948 584*i*	6.856 254 2−0.018 948 584*i*
3	2	6.852 243 8−0.026 431 957*i*	6.852 243 8−0.026 431 957*i*
3	3	6.852 504 1−0.025 076 761*i*	6.852 504 1−0.025 076 701*i*
4	3	6.852 707 6−0.025 706 763*i*	6.852 707 6−0.025 706 768*i*
4	4	6.852 744 7−0.025 547 433*i*	6.852 744 7−0.025 547 522*i*
5	4	6.852 861 0−0.025 683 349*i*	6.852 860 9−0.025 683 36*i*

Exact value: 6.852 780 62−0.025 549 76*i*.[a]

[a] Reference [38].

ways—one can either scale the coordinate and look for solutions with asymptotic square-integrable behavior (a CCM procedure) or leave the Hamiltonian unscaled and look for solutions with Siegert-type boundary conditions.

In Table V we compare the resonance estimates obtained by the CCM stationary point, by the direct requirement of outgoing asymptotic behavior, and by the procedure of fitting a Padé approximant to a series of CCM energies calculated for large θ, and extrapolating to $\theta=0$, for calculations with a varying number of grid points. It can be seen from Table V that the results obtained by the latter method are closer to the resonance estimates obtained by a direct requirement of Siegert-type asymptotic behavior and to the exact value than the estimates obtained from CCM stationary points. As we increase the number of grid points, the difference between the estimated values becomes smaller. These observations further consolidate the conclusion that for not very accurate integration schemes (few grid points, few basis functions), the resonance estimates obtained from the stationary points in a CCM calculation can be improved using the Padé-approximation-extrapolation procedure.

By carrying out the Padé-approximation-extrapolation procedure on CCM results obtained by integrating along the complex contour, we get the results that have been obtained with the same number of grid points by integrating along the *real* axis and requiring divergent boundary behavior. These results are better than the estimates obtained from the CCM stationary points, since the integration along a complex contour requires a more exact calculation (more grid points in our case). This is in harmony with the experience gathered during calculations done within the framework of the finite basis-set approximation.

C. Autoionization resonances of helium

For Coulombic potentials it is easy to find analytically the connection between CCM eigenvalues obtained by scaling the whole Hamiltonian and eigenvalues obtained by scaling the kinetic energy only, due to the simple form of the ratio between the factor by which the kinetic and potential energies are scaled.

If the Hamiltonian is

$$\hat{H}(R)=\hat{T}+\hat{V}_{\text{Coul}} ,$$

then

TABLE V. Estimates of the resonance energy of the 1D shape-resonance model, obtained by various methods (the CCM stationary point, extrapolation of the Padé approximation of the CCM scaling results to $\theta=0$, and a direct requirement of Siegert-type asymptotic behavior) as a function of the number of grid points used in the matching calculation.

	Resonance estimates obtained by		
Number of grid points	CCM stationary point	Extrapolating to $\theta=0$ the Padé approximants constructed from $\theta=0.4$–0.5	$\theta=0$ calculation with Siegert-type asymptotic behavior
50	6.853 −0.0327*i*	6.847 −0.0253*i*	6.847 −0.025 24*i*
75	6.8527−0.026 93*i*	6.8514 −0.025 47*i*	6.8514 −0.025 48*i*
100	6.852 77 −0.025 989*i*	6.852 34 −0.025 522*i*	6.852 34 −0.025 527*i*
500	6.852 780 6 −0.025 549 67*i*	6.852 780 6−0.025 549*i*	6.852 779 9 −0.025 549*i*
1000	6.852 780 62 −0.025 549 006*i*	6.852 7806 −0.025 548 9*i*	6.852 780 6 −0.025 548 9*i*

Exact value: 6.852 780 62 −0.025 549 76*i*.

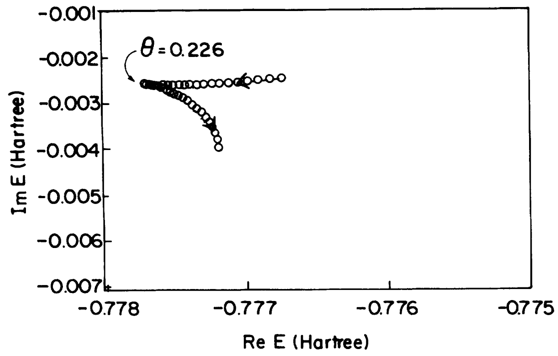

FIG. 5. The complex-coordinate θ trajectory calculation for the He autoionization ~ -0.777-hartree resonance, with 36 Hylleraas-type basis functions. θ is given in radians.

$$\hat{H}(R\eta)=\frac{1}{\eta^2}\hat{T}+\frac{1}{\eta}\hat{V}\ ,$$

where

$$\eta=|\eta_0|e^{i\theta}$$

and the Schrödinger equation is

$$\left[\frac{1}{\eta^2}\hat{T}+\frac{1}{\eta}\hat{V}\right]\psi=E\psi\ .$$

Multiplying by η, we obtain

$$\left[\frac{1}{\eta}\hat{T}+\hat{V}\right]\psi=(E\eta)\psi\ ,$$

which is exactly the form of a kinetic-energy-scaled Hamiltonian, with scaling angle $\phi=\theta/2$.

This is, therefore, a case where the spectrum of the nonsimilarity transformed Hamiltonian can be related to the spectrum of the similarity transformed CCM Hamiltonian in a simple manner. The resonance energy of a kinetic-energy-scaled Hamiltonian is the energy of a CCM Hamiltonian scaled by an angle twice as large, multiplied by $|\eta_0|e^{2i\phi}$. It seems reasonable to expect then that no problems would be encountered by applying the scaling-extrapolation procedure described at the beginning of this section to the helium Hamiltonian. When actually applying the procedure, we find that we get estimates which are far from being correct, and are also unstable with respect to the order of the Padé approximation used. Fitting the Padé approximation to the CCM energies themselves and extrapolating to $\theta=0$ also gives poor and unstable results (the stationary point can, however, be easily reproduced by extrapolating to the cusp angle). As in the case of $N=60$ for the H_2-He model, we trace the problem to the existence of a very sharp cusp (Fig. 5) in the θ trajectory of the problem, a fact which makes the Padé approximation of the function much more difficult.

V. CONCLUDING REMARKS

We have presented in this paper a set of complex scaling nonsimilarity transformations which have the property of changing the asymptotical behavior of resonance wave functions into a square-integrable behavior. These scaling procedures enable one to add resonance energies to the spectrum of energies which can be obtained by standard techniques which were originally developed for bound systems, and hence require square-integrable boundary behavior of the solution. The perturbation which these scaling procedures cause in the physical spectrum is eliminated by extrapolating the function describing the energy as a function of the perturbation to zero perturbation.

This procedure illustrates that the essential requirement from any scaling transformation is that it causes localization in resonance wave functions. The numerical application of these procedures, especially of the procedure involving scaling the kinetic-energy term only, is very simple; one needs only to divide kinetic-energy matrix elements by a constant, while potential-energy matrix elements are left untouched. This enables the straightforward application of the method of existing computer codes. Care must be taken, though, in cases where sharp cusps occur in the graph of $E(\theta)$, since the existence of such cusps severely hampers the use of the Padé extrapolation.

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