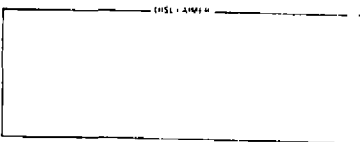# Recent Developments in
Complex Scaling

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I. INTRODUCTION

My objective in this talk will be to discuss some recent developments in the use of complex basis function techniques to study resonance, as well as certain types of non-resonant, scattering phenomena. Complex scaling techniques and other closely related methods have continued to attract the attention of computational physicists and chemists and have now reached a point of development where meaningful calculations of many-electron (more than two!) atoms and molecules are beginning to appear feasible. The field has evolved very rapidly over the past few years and I will not attempt anything like an exhaustive review of the subject. I can refer the interested reader to the review article by McCurdy[1] and to a volume of the International Journal of Quantum Chemistry[2] devoted entirely to the subject. These sources give an excellent summary of both mathematical and computational techniques in complex scaling through 1978. The scope of this talk will be limited to several developments since 1978 with which I have been connected.

The first of these developments i. a discussion of direct methods for computing _partial_ resonance widths.[3] The imaginary part of the complex resonance energy computed by any direct method gives only the total resonance width, but it can be shown that the eigenfunction associated with the complex resonance eigenvalue can be used to provide partial width information - a simple consequence of the separable nature of the S-matrix near a resonance.

The recent use of complex scaling methods for studying molecular resonances has stimulated considerable interest in generalizations which are applicable to other continuum processes.[4, 5] In Section III of this talk, I will review methods for computing resolvent matrix elements - and molecular photoionization cross sections in particular - within the framework of the Born-Oppenheimer approximation. This discussion will also serve to establish a connection between two methods proposed for treating molecular problems[6, 7] and will focus attention on certain numerical complications that must be dealt with.

Finally, in Section IV, I will review some very recent work on how complex scaling ideas can be used to adapt simple SCF theory to the study of negative ion shape resonances in atoms and molecules.

II. PARTIAL WIDTHS

Consider the scattering of a structureless particle by an idealized target with no rearrangements and with a potential which does not couple partial waves. These restrictions can be relaxed at the cost of substantially more cumbersome notation. The asymptotic form of the scattering wave function for partial-wave ℓ is given by

$$\psi^{+}_{\alpha,k_{\alpha},\ell}(r,x) \xrightarrow[r \to \infty]{} \frac{1}{(2\pi k_{\alpha})^{1/2}}$$

$$\sum_{\beta} \left\{ (-1)^{\ell} \delta_{\alpha\beta} \frac{e^{-ik_{\alpha}r}}{k_{\alpha}^{1/2}\, r} - S^{\ell}_{\beta,\alpha}(E) \frac{e^{ik_{\beta}r}}{k_{\beta}^{1/2}\, r} \right\} \phi_{\beta}(x) \tag{1}$$

where $\phi_{\beta}(x)$ is the target wave function for channel β, and $S^{\ell}_{\beta}(E)$ is the partial wave S matrix. The channel momenta k_{γ} are related to the total energy E and target energy ε_{γ} by

$$k_{\gamma} = \left[2\mu(E-\varepsilon_{\gamma}) \right]^{\frac{1}{2}} \tag{2}$$

At a resonance eigenvalue ε_R, all non-vanishing S matrix elements $S_{\beta\alpha}(E_R)$ have a pole. Thus at large r, the wave function with k^{R}_{α} given by

$$k^{R}_{\alpha} = \left[2\mu(\varepsilon_R - \varepsilon_{\alpha}) \right]^{\frac{1}{2}} \tag{3}$$

has only outgoing waves in each open channel and satisfies the
asymptotic boundary condition

$$\Psi_{\alpha'k^R_\alpha,\ell}(r,x) \sim \sum_\beta D^\alpha_\beta \frac{e^{ik^R_\beta r}}{r} \phi_\beta(x); \quad D^\alpha_\beta \equiv -S^\ell_{\beta,\alpha}/k^{\frac{1}{2}}_\beta \tag{4}$$

For a problem with M open channels, we use a trial variational
function of the form

$$\psi_t = \sum_{i=1}^{N-M} C_i \phi_i(r,x) + \sum_\beta C_\beta \theta_\beta(r,x) \tag{5}$$

where the functions $\phi_i(r,x)$ are square-integrable basis
functions and the sum over β is limited to open channels. The
functions θ_β are given by

$$\theta_\beta = g(r) \frac{e^{ik_\beta r}}{r} \phi_\beta(x) \tag{6}$$

where $g(r)$ is a cutoff function satisfying

$$g(r) \underset{r \to 0}{\sim} r^{\ell+1} \quad ; \quad g(r) \underset{r \to \infty}{\longrightarrow} 1 \tag{7}$$

The coefficients C_i and C_β are determined by making the
functional

$$I[\Psi_t] = \iint \psi_t(r,x)(H_\ell(r,x)-E) \psi_t(r,x) r^2 dr dx \tag{8}$$

where $H_\ell(r,x)$ is the partial-wave Hamiltonian, stationary with
respect to variation of the coefficients.

Bardsley and Junker[8] proposed an iterative scheme for
solving a single-channel version of Eq. (8) for resonances by
varying the (complex) values of k^R_α in the trial function until
Eq. (3) is satisfied for a particular eigenvalue.

There is an important point to note about Eq. (8). The free-
free elements of $(H_\ell - E)$, i.e., matrix elements between two
functions of the form of θ_β, are in general not well defined for
values of the channel momenta in the lower half-plane. This
difficulty depends specifically on the form of the interaction

potential since the definition of the channel momenta in Eq. (2) guarantees that the contribution at large r from the kinetic energy to the free-free matrix elements of $(H_\ell - E)$ does not lead to divergences. The matrix is therefore defined, for a particular choice of basis, as the analytic-continuation of that matrix from the upper half-k plane (physical sheet of the E plane). This analytic continuation can be performed using analytic formulas for the free-free matrix elements, if they are available, or numerically as discussed by Isaacson et al.[9]

The coefficients of the continuum functions, θ_β, in Eq. (5) are determined by diagonalizing the secular matrix obtained from Eq. (8). There is, in general, no way to arrange for these coefficients to coincide with the D_β^α chosen in Eq. (4). We denote the vector which connects the two sets of coefficients as $\vec{a}$:

$$C_\beta = \sum_\alpha a_\alpha D_\beta^\alpha \tag{9}$$

A single diagonalization of a multichannel Hamiltonian in a set of basis functions which do not fix the asymptotic normalization of the wave function does not provide eigenvectors from which complete scattering information can be obtained in the general nonresonant situation.[10] The resonance case is considerably simpler; complete information, that is, partial as well as total widths, can be obtained without requiring the mixing coefficients $\vec{a}$.

We can demonstrate this very simply. The partial-wave S matrix is given in terms of the partial-wave T matrix by

$$S_{\beta\alpha}^\ell = \delta_{\beta\alpha} - 2\pi i\mu \, k_\alpha^{\frac{1}{2}} \, k_\beta^{\frac{1}{2}} \, T_{\beta\alpha}^\ell \tag{10}$$

Since we are considering a problem with no partial-wave coupling, we can write $T_{\beta\alpha}^\ell$ as a matrix element of the T operator between functions of the form $\phi_\alpha(x)X_\ell(k_\alpha\vec{r})$, where

$$X_\ell(k_\alpha\vec{r}) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} i^\ell \frac{\hat{J}_\ell(k_\alpha r)}{k_\alpha r} Y_{\ell m}(\hat{r}) \tag{11}$$

and $\hat{J}_\ell$ is the regular Ricatti-Bessel function

$$T_{\beta\alpha}^\ell = \left\langle \phi_\beta(x)X_\ell(k_\beta\vec{r}) \middle| T(E) \middle| \phi_\alpha(x)X_\ell(k_\alpha\vec{r}) \right\rangle \tag{12}$$

We can establish the behavior of $T_{\beta\alpha}^{\ell}$ near a resonance by recalling that $T(E)$ satisfies the operator equation for all E,

$$T(E) = V + VG(E)V \tag{13}$$

where V is the full potential and $G(E)$ is the full Green's function (operator) for the system. The central point of the proof hinges on the fact that the T operator is a separable operator at the complex resonance energy. We can define the resonance wave function $|\psi_R\rangle$ and the corresponding function in the dual space $\langle\tilde{\psi}_R|$ (not merely the complex conjugate) in terms of the residue of the Green's function at the resonance pole

$$|\psi_R\rangle \langle\tilde{\psi}_R| = \lim_{E \to \epsilon_R} (E-\epsilon_R) G(E) \tag{14}$$

More and Gerjuoy[11] have discussed the fact that Eq. (14) fixes the normalization of the resonance wave function and also derive the relationship between $|\psi_R\rangle$ and $|\tilde{\psi}_R\rangle$. With the definition in Eq. (13) we can easily see the residue of $T(E)$ at a resonance pole is a separable operator:

$$\lim_{E \to \epsilon_R} (E-\epsilon_R) T(E) = V|\psi_R\rangle \langle\tilde{\psi}_R|V. \tag{15}$$

The definition of $S_{\beta\alpha}^{\ell}$ in terms of $T_{\beta\alpha}^{\ell}$ Eq. [(10)] and Eqs. (11) and (12) can be used to evaluate the singular term in $S_{\beta\alpha}^{\ell}$. Combining all other contributions to the S matrix into a background term $S_{\beta\alpha}^{bg,\ell}$, the form of $S_{\beta\alpha}^{\ell}$ near a resonance is

$$S_{\beta,\alpha}^{\ell} = S_{\beta,a}^{bg,\ell} - i \frac{\tilde{\gamma}_\beta \gamma_\alpha^*}{E-\epsilon_R} \tag{16}$$

where the factors of the residue are

$$\gamma_\beta \equiv (2\pi\mu k_\beta^R)^{\frac{1}{2}} \langle\phi_\beta X_\ell(k_\beta^R \vec{r})|V|\psi_R\rangle \tag{17}$$

$$\tilde{\gamma}_\alpha \equiv (2\pi\mu k_\alpha^R)^{\frac{1}{2}*} \langle\phi_\alpha X_\ell(k_\alpha^R \vec{r})|V|\tilde{\psi}_R\rangle$$

If we now follow the usual argument for a narrow resonance,[12] which is based on the unitarity of $S_{\beta\alpha}^{\ell}$ for all real energies, we are led to the usual result for the partial widths for decay into open channels Γ_α that if Γ_α is defined by

$$\Gamma_\alpha = |\gamma_\alpha|^2 \tag{18}$$

and the total width is defined by

$$\epsilon_R \;=\; E_R - 1\Gamma/2 \tag{19}$$

where E_R is the real part of ϵ_R, the partial widths sum to the total width

$$\Gamma = \sum_\alpha \Gamma_\alpha \tag{20}$$

Although the identification of the total width as the sum of the partial widths 'Eq. 18) is exact only in the case of a narrow resonance, it is important to note that the resonance form expressed in Eq. (16) is exact and that an unambiguous definition of both the complex resonance energy ϵ_R and the residue factors is provided by the (analytically continued) matrix elements defined in Eq. (17).

It is not convenient to use the definition of γ_β in Eq. (16) to compute the partial widths, because we have not fixed the normalization of ψ_1 to match that of ψ_R. However, because of the particular form of ψ_t chosen in Eq. (5) we can derive a simple prescription for the ratio of the partial widths in two channels. Recalling the definition in Eq. (9), it is easy to see that, with the form of the S matrix in Eq. (16), the coefficients C_β in the definition of ψ_t are proportional (in the limit of a complete basis) to the amplitudes γ_β according to

$$C_\beta \;=\; \frac{1\gamma_\beta}{k_\beta^{\frac{1}{2}}} \sum_\alpha a_\alpha \tilde{\gamma}_\alpha{}^* \tag{21}$$

Thus the ratio of partial widths for any pair of open channels is given by

$$\frac{\Gamma_\beta}{\Gamma_\alpha} \;=\; \left| \frac{k_\beta}{k_\alpha} \frac{C_\beta}{C_\alpha} \right|^2 \tag{22}$$

Since the partial widths must sum to the total width, and the Siegert eigenvalue computed together with ψ_t yields the total width, we can use Eqs. 19) and (22) together to determine all of the partial widths for decay into open channels.

The formalism outlined here was applied to a model three-channel square-well problem. The computational details can be

found in reference 3. The results of this study confirmed the
conclusions reached above and showed that the use of complex
"Siegert" functions combined with purely L^2 functions provides
a convenient method for obtaining quantitative information about
partial as well as total resonance widths. The procedure we have
outlined above is applicable to any direct method which provides
an accurate representation of the eigenfunction associated with
the resonance eigenvalue. However, if one were to employ a trial
function without reference to a particular asymptotic form, as in
the complex coordinate method for example, one would also have to
project onto the resonance eigenfunction with the unperturbed
states $\phi_\alpha(x)X_\ell(k_\alpha r)$, evaluated at complex coordinates, to extract
the coefficients which would play the same role as C in Eq. (21).
We refer the reader to the recent work of Noro and Taylor for
further details.[13]

III. COMPLEX-COORDINATE PROCEDURES FOR MOLECULES AND MOLECULAR PHOTOIONIZATION

Two computational techniques have been proposed to date for
extending complex scaling techniques to molecular resonance
problems. In an earlier study, McCurdy and Rescigno[6] proposed
the use of ordinary floating Gaussian basis functions which are
made complex by simply scaling the orbital exponents by a phase
factor. It was argued that such functions, when used to form a
matrix representation of the Born-Oppenheimer Hamiltonian with a
complex-valued scalar product, would effectively provide an
asymptotic scaling of the electronic coordinates and that such a
scaling would be sufficient to render a resonance eigenfunction
L^2; this supposition was supported by several illustrative
calculations. More recently, Moiseyev and Corcoran[7] have
described a procedure which superficially appears to be identical
to the transformation $r \rightarrow \theta r = \lambda r e^{i\omega}$ that can be applied to the
electronic coordinates of a dilatation analytic Hamiltonian.
This simple analogy is complicated, however, by the fact that the
branch-point singularities in the electron-nuclear attraction
terms of the Born-Oppenheimer Hamiltonian render it a nonanalytic
function of electron coordinates. In addition to these numerical
studies, the formal work of Simon[14] establishes that complex
scaling in the Born-Oppenheimer picture can be put on firm
mathematical ground through the use of what Simon calls the
method of "exterior complex scaling" in which the magnitudes of
all electronic coordinates are only scaled outside a sphere which
is large enough to enclose all the nuclei.

A recent development in this area was the observation by
McCurdy[4] that the Moiseyev-Corcoran procedure[7] could be

formally related to Simon's exterior complex scaling. This
observation also led to a procedure for calculating the matrix
elements of the resolvent needed to evaluate photoionization
cross sections.[4,]   I will not repeat the rather lengthy
arguments needed to establish the formal connections between the
various methods. These can be found in references 4 and 5. I
will content myself here with a brief comparison of the
McCurdy-Rescigno (MR)[6] and Moiseyev-Corcoran (MC)[7] procedures
and their use in photoionization calculations.

The MR procedure employs basis functions which effectively
scale $\vec{r}$ by θ asymptotically while avoiding the nonanalyticity
problem at the nuclear centers. This is accomplished by forming
a matrix representation of the unscaled Born-Oppenheimer
Hamiltonian in a basis set of complex Cartesian Gaussians of the
form

$$\psi^{\theta}_{lmn}(\alpha, \vec{r}, \vec{A}) = N_{lmn}(x - A_x)^l(y - A_y)^m(z - A_z)^n \qquad (23)$$

$$e^{-\alpha\theta^{-2}(\vec{r} - \vec{A})^2}$$

We have argued that using such a basis is equivalent to using
rotated coordinates in the Hamiltonian asympototically.

It is instructive to compare the behavior of the analytically
continued matrix elements in the MR and MC procedures,
particularly the matrix elements of the nuclear attraction
potential. We will consider a matrix element of one term of the
nuclear potential between two S-type Gaussians [l=m=n=0 in Eq.
(23)] both centered at position $\vec{A}$:

$$I = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \int d^3r \; e^{-\alpha(\vec{r} - \vec{A})^2} \frac{1}{\sqrt{(\vec{r} - \vec{R})^2}} \; e^{-\beta(\vec{r} - \vec{A})^2}$$

$$(24)$$

$$= \left(\frac{32}{\pi}\right)^{1/2} \frac{(\alpha\beta)^{3/4}}{(\alpha+\beta)} F_0((\alpha + \beta)(\vec{R} - \vec{A})^2)$$

where $F_0(z)$ is the entire function of z,

$$F_0(z) = 1/2 \sqrt{\frac{\pi}{z}} \; \text{erf} \; (z) .$$

The MC procedure replaces $(\vec{r} - \vec{R})^2$ with $(\vec{r}\theta - \vec{R})^2$ in Eq. (24)
and obtains a formula for I by factoring θ^{-1} out of the

integrand. Evaluating the result at complex 0 gives

$$I^{MC} = \frac{e^{-i\phi}}{\lambda} \left(\frac{32}{\pi}\right)^{1/2} \frac{(\alpha\beta)^{3/4}}{(\alpha + \beta)} F_0\left((\alpha + \beta)\left(\frac{\vec{R}e^{-i\phi}}{\lambda} - \vec{A}\right)^2\right) . \quad (25)$$

In the M procedure, we simply multiply α and β in Eq. (24) by 0^{-2}, giving

$$I^{MR} = \frac{e^{-i\phi}}{\lambda} \left(\frac{3\lambda}{\pi}\right)^{1/2} \frac{(\alpha\beta)^{3/4}}{(\alpha + \beta)} F_0\left(\frac{(\alpha + \beta)e^{-2i\phi}}{\lambda^2}(\vec{R} - \vec{A})^2\right) (26)$$

It is now clear from comparing Eqs. (25 and (26) that the MR procedure can be related to the MC procedure; if the basis functions are simply shifted from center $\vec{A}$ to $\vec{A}9^{-1}$ in the latter, it reduces to the McCurdy-Rescigno prescription.

Note that as the orbital exponents α and β become small, I^{MC} and I^{MR} limit to the same numerical value since $\lim_{z\to 0}F_0(z)\to 1$. Furthermore, since the asymptotic behavior of the eigenfunctions is determined by the most diffuse functions, it is clear that both procedures should yield the same spectrum in the limit of a complete expansion. However, since the behavior of the matrix elements for large values of α and β is quantitatively very different in the two procedures, one may expect to find significant differences between the two methods in numerical applications. In fact, we expect to see substantial numerical differences between the two approaches for the following reason. In a complex-coordinate calculation, the cusps that appear in the wavefunction because of the nuclear sigularties in the Born-Oppenheimer Hamiltonian are moved to complex centers. Recalling that the M procedure can be derived from the MC prescription by translating the basis functions to complex centers 0^{-1} $\vec{A}$, we see immediately that the MR method allows the complex cusps in the molecular wave functions to be approximated by Gaussians of large exponents on the cusp centers, while the MC method effectively centers basis functions elsewhere. For this reason we expect the MR procedure to have better convergence properties.

We have applied both the MR and MC procedures to the calculation of the photoionization cross section of H_2^+. We make use of the fact that the cross section $\sigma(\omega)$ can be expressed as a matrix element of the resolvent:[15]

$$\sigma(\omega) = \lim_{\varepsilon\to 0} \frac{4\pi\omega}{c} \, Im \left\langle \psi_0 \left| \mu \frac{1}{H-E_0-\omega-i\varepsilon} \mu \right| \psi_0 \right\rangle \quad (27)$$

where ψ_0 is the wave function for the target in its initial state with energy E_0, μ is the dipole operator, and ω is the photon frequency. Under complex-scaling, the continuous spectrum of the atomic Hamiltonian is rotated off the real axis. This makes it possible to obtain convergent approximations to Eq. (27) by inverting a finite matrix representation of the scaled Hamiltonian obtained over a set of normalizable functions, whereas such a representation could not be used directly at real energies in the continuum for the unscaled Hamiltonian.[16]

An approximation to Eq. (27) is obtained as (see references 4 and 5 for details):

$$\sigma(\omega) = 4\pi\omega/c \ \text{Im} \ \theta^3 \ \vec{f}(\underline{E_0 + \omega - H})^{-1} \ \vec{f}, \tag{28}$$

where the inverse $(\underline{E_0 + \omega - H})_\theta^{-1}$ is simply formed from the analytically continued matrix elements obtained either from the MR or MC procedures and the elements of $\vec{f}$ are given by

$$f_\alpha = \theta^{-3} \sum_\beta d_\beta \int d^3r \chi_\beta(\vec{r}) u(\vec{r}\theta) \chi_\alpha(\vec{r}) \tag{29}$$

The expansion coefficients d_β in Eq. (29) make up the eigenvector corresponding to ψ_0 and are determined by diagonalizing $H_{\alpha,\beta}(0)$ over basis functions $\{\chi_\alpha\}$ of the initial-state symmetry. The matrix inverse $(\underline{E_0 + \omega - H})_\theta^{-1}$ is then constructed over a set of functions of opposite parity, $\{\chi_\alpha\}$.

To facilitate our comparisons, we have used large basis sets both to calculate the $1s\sigma_g$ ground-state eigenfunction and to represent the matrix $(\underline{E_0 + \omega - H})_\theta$ for the σ_u continuum. In this way, we are able to use the same basis sets for both methods while avoiding the criticism that the basis set was optimum for one method but not for the other. After choosing the basis-set exponents, one may optimize the scaling parameter θ in a given basis set because the results are formally independent of θ when converged. The usual procedure in atomic calculations is to fix the magnitude of θ at unity and vary the argument to find the region of greatest stability. We did that using the MR prescription for computing $H_{\alpha,\beta}(\theta)$, making no attempt to optimize the magnitude of θ. Figure 1 shows a superposition of five plots of the photo-ionization cross sections obtained by setting $\theta = \exp(i\pi\phi/180.0)$ and varying ϕ in $2.5°$ increments over a $10°$ interval centered approximately at the most stable point in ϕ. The results are stable within a few percent and agree essentially exactly with the exact values of Bates and Öpik.[17]
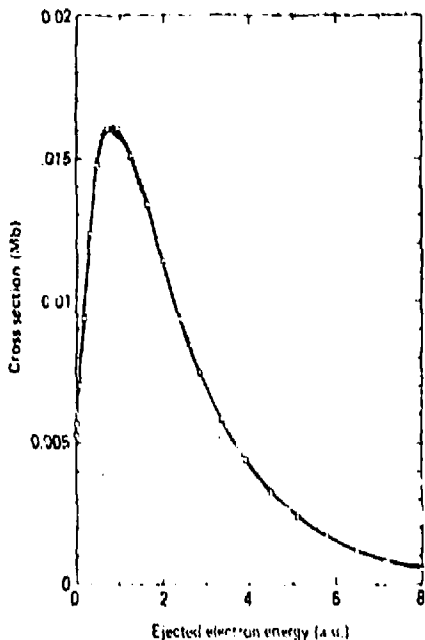
Fig. 1. Superposition of results for the parallel component
of the photoionization cross section of H_2^+ computed using
the method of Ref. 6 to analytically continue the Hamiltonian
matrix elements. The superimposed curves are for ϕ varying over
the most stable region (15° to 25°) in 2.5° increments.

We repeated this calculation with the procedure of Moiseyev
and Corcoran. However, no recognizable region of stability could
be found with $|\phi| = 1$, and we therefore varied $|\theta|$ to find a more
optimum value. It is not surprising that this was necessary
considering the behavior of nuclear attraction integrals with
large exponents which Moiseyev and Corcoran point out and which
we discussed earlier. We find the most favorable value of $|\theta|$ to
be approximately 0.6, with little sensitivity for values varying
between 0.5 and 0.8. Figure 2 shows a superposition of five
plots for the photoionization cross sections obtained with
$\theta = 0.6 \exp(i\phi/180.0)$ for values of ϕ in 2.5° increments over a
10 interval, again approximately centered in the region of
greatest stability. Comparison of Fig. 1 and 2 shows that the
Moiseyev-Corcoran technique is substantially less stable in this
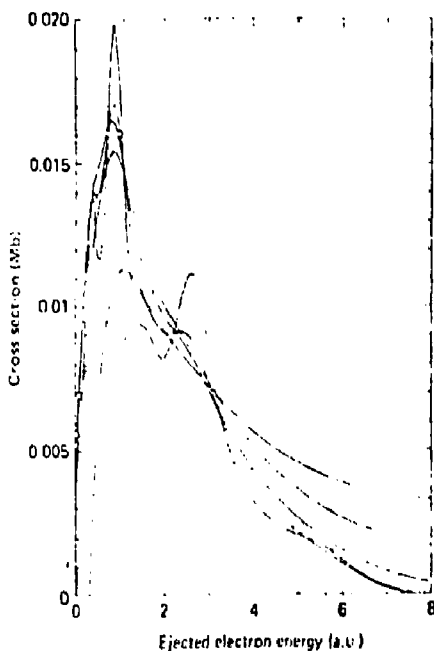application than that of McCurdy and Rescigno.

FIG. 2. As in Fig. 1, but using the method of Ref. 7 to
analytically continue the Hamiltonian matrix elements. The
magnitude of the scaling parameter is 0.6 and ϕ varies from
5° to 15° in 2.5° increments.

In comparing the two methods, we have concentrated on the
behavior of the matrix elements of the nuclear attraction terms,
since their non-analytic behavior has hindered the application of
complex scaling techniques to molecular probelms. Moiseyev and
Corcoran have also emphasized that the computation of two-
electron matrix elements, which is the most time-consuming part
of integral evaluation, is simpler with their procedure since the
integrals are simply scaled by constants and need not be
recomputed when the scale parameters are changed. It is note-
worthy, however, that several applications of complex scaling
techniques to atomic problems involving more than two electrons

have shown that accurate results can only be achieved when the orbitals referring to tightly bound core electrons are left unscaled and the outer valence electron orbitals made complex.[18] We have adopted a similar procedure for molecules, which I will illustrate in the next section. With this mix of real and complex orbitals, the two-electron integrals no longer scale simply and the computational details involved in implementing either method are comparable.

IV. COMPLEX SCF TECHNIQUES
   A. Formulation

Almost all of the previous calculations using complex basis functions have relied on direct diagonalization of the Hamiltonian with many-electron basis states. In conventional structure calculations on bound states, a Hartree-Fock wavefunction is frequently generated as a starting point for more accurate treatments. It is logical to assume that the basic mathematics of SCF theory should also be applicable to the square-integrable resonance eigenstates of an analytically continued complex Hamiltonian. We have recently shown that, for the case of shape resonances in atoms and molecules, this is indeed the case.

The basic idea[19, 20] underlying our discussion of the SCF equations for resonances is that by beginning with the complex atomic Hamiltonian, $H(\{\sigma r_j\})$, and following (essentially) the same variational arguments used to derive the bound state SCF equations, we can derive complex SCF equations appropriate for resonance states. This procedure is successful because the resonance eigenfunctions of the complex Hamiltonian are square-integrable. In that sense these eigenfunctions are sufficiently like bound state wavefunctions to allow treatment by the SCF methods currently employed in many bound state calculations.

We will specialize our discussion to the simple case of a shape resonance which corresponds to an electronic configuration with one electron outside a closed shell. The ^2P shape resonance encountered in e^- - beryllium scattering is an example of such a case; the $^2\Pi_g$ resonance state of N_2^- is a well known molecular example.

Starting with a trial variational wavefunction which is a single Slater determinant of spin orbitals

$$\Phi = \det |\psi_1 \bar\psi_1 \psi_2 \bar\psi_2 \cdots \psi_k \bar\psi_k \psi_\mu| \; .$$

(30).

where each spin orbital, ψ_i, is the product of a spatial
orbital ϕ_i (depending on the coordinates of one electron) and a
spin function, and $\bar{\psi}_i$ denotes the spin orbital with opposite
spin, we derive the SCF equations for the orbitals, ϕ_i, by
setting to zero the first variations with respect to those
orbitals of a particular functional. For the ordinary bound
state problem that functional consists of the expectation value
of the Hamiltonian with respect to ψ plus Lagrange multiplier
terms which serve to apply the orthonormality constraint among
the orbitals, ϕ_i. In our case we must generalize this
expression slightly. Since the Hamiltonian, $H(\{\cdot r_j\})$, is not
hermitian, its eigenfunctions form a biorthogonal set, and the
complex conjugate of the wavefunction which appears in the usual
expectation value is not appropriate. Thus the functional we
have chosen is

$$I = \int \phi \, H(\{\vec{r}_j, \theta\})\phi \, d\tau_1 \, d\tau_2 \ldots d\tau_{2k+1}$$

$$- \sum_{i,j=1}^{k} \lambda_{ij} \int \phi_i(\vec{r})\phi_j(\vec{r}) d^3r$$

$$- 2 \sum_{i=1}^{k} \lambda_{i\mu} \int \tilde{\phi}_i(\vec{r})\phi_\mu(\vec{r}) d^3r$$

$$- \epsilon_\mu \int \phi_\mu(\vec{r})\phi_\mu(\vec{r}) d^3r$$

$$(31)$$

where the matrix, λ_{ij}, of Lagrange multipliers is complex
ymmetric and the redundant terms in the first sum are for
convenience only. As the scale factor, θ, approaches unity the
SCF equations must approach the usual Hartree-Fock equations in
which the orbital Hamiltonians are hermitian. The equations we
drive using Eq. (31) have this property only if the orbitals,
ϕ_i, in the trial wavefunction are real when $\theta=1$, because
otherwise the Coulomb and exchange operators as defined below are
nonhermitian. In practice, this simply means that we are
constructing the correct analytic continuation of the working
equations of the ordinary real valued SCF calculations of quantum
chemistry. Note that in defining the functional in equation
(31), we have in mind a class of problems which, in the $\theta=1$
limit, can be formulated in terms of real orbitals. If, for
example, the orbitals of Eq. (31) were expressed as products of
radial functions and spherical harmonics, the functional we would
then use would have the complex conjugate of the angular
variables of the left hand orbitals appearing in all the scalar
products, but not the radial variables.

By setting the functional derivatives, $\delta I/\delta \phi_i$ and $\delta I/\delta \phi_u$, of equation (31) with respect to the open and closed shell orbitals to zero, we obtain the SCF equations. If we define the Fock operators by

$$\hat{F}_o = h_\theta + \theta^{-1} \sum_{j=1}^{k} (2\hat{J}_j - \hat{K}_j) + \theta^{-1}(\hat{J}_\mu - \tfrac{1}{2}\hat{K}_\mu)$$

$$\hat{F}_\mu = h_\theta + \theta^{-1} \sum_{j=1}^{k} (2\hat{J}_j - \hat{K}_j) \tag{32}$$

where the one electron Hamiltonian, h_θ, is (atomic units)

$$h_\theta = -\frac{\theta^{-2}}{2} \nabla^2 - \frac{2\theta^{-1}}{r} \tag{33}$$

and the Coulomb and exchange operators are

$$\hat{J}_j = \int \frac{\phi_j(\vec{r}_2)\phi_j(\vec{r}_2)}{r_{12}} d^3r_2 \tag{34}$$

$$\hat{K}_j \phi_1 = \phi_j(r_1) \int \frac{\phi_j(\vec{r}_2)\phi_1(\vec{r}_2)}{r_{12}} d^3r_2$$

the complex SCF equations can be written

$$2\hat{F}_o \phi_1 = \sum_{j=1}^{k} \lambda_{j1}\phi_j + \lambda_{\mu 1}\phi_\mu \tag{35}$$

$$\hat{F}_\mu \phi_\mu = \sum_{j=1}^{k} \lambda_{\mu j}\phi_j + \epsilon_\mu \phi_\mu$$

$$\lambda_{1j} = \lambda_{j1}$$

The usual SCF procedure is to find a set of equivalent matrix equations by multiplying equation (35) by the orbitals and integrating. All the matrices appearing in these calculations

are complex symmetric. Finally, we note that the value of the complex resonance energy from this procedure is the complex SCF energy, E_{CSCF}

$$
\begin{aligned}
E_{CSCF} &= \int \phi H \ (\{\vec{r}_j \theta\}) \phi d\tau_1 \ldots d\tau_{2k+1} \\
&= \sum_{i=1}^{k} \int \phi_i (h_\theta + \hat{F}_o) \phi_i d^3r \\
&\quad + \frac{1}{2} \int \phi_\mu (h_\theta + \hat{F}_\mu) \phi_\mu d^3r
\end{aligned}
\tag{36}
$$

B. Atomic Example

The [2]P shape resonance in e-beryllium scattering is an example of a resonance which the complex SCF approach should describe well. We have performed two sets of calculations on this system,[19] the first of which employs a (14s/16p) basis of real valued Gaussians chosen as follows. The complex SCF equations were solved in matrix form and E_{CSCF} from this calculation with $\theta = \exp(i\alpha)$ is plotted in Figure 3 for a range of α values between .3 and .5 radians. We were unable to converge the SCF equations for values of α less than .3. The trajectory of E_{CSCF} as a function of α is somewhat surprising in view of what has been observed in complex coordinate CI calculations.

In a configuration interaction calculation using the complex Hamiltonian, $H(\{\theta r_j\})$, there is a well known behavior to be expected of the complex resonance eigenvalue as a function of θ. That behavior, which can be shown to be a consequence of the complex version of the virial theorem,[21] is that for a given basis set the resonance eigenvalue, E_{res}, has a stationary point with respect to variation of θ so that, at some value of θ, $dE_{res}/d\theta$ vanishes. The stationary point does not necessarily occur with $|\theta| = 1$, but if a CI calculation is performed with $\theta = \exp(i\alpha)$ a sharp cusp in the complex value of E_{res} is often found as α is varied. The curve in Figure 3 corresponding to the (14s/16p) real basis function calculation does not show such a cusp, nor is E_{CSCF} particularly stable as α is varied. This is a troublesome point because the stationary value of E_{res} is usually taken to be the best approximation to the resonance energy.

The main curve in Figure 3 shows little evidence of stationarity with respect to variations in α. This problem is

due entirely to an inadequate description of the orbitals which make up the Be core, particularly the tight 1s orbital. The problem has been discussed in detail elsewhere[18] and can be solved by using Gaussian basis functions with complex exponents given by $\theta \xi_i$ where ξ_i is real to expand the core orbitals (1s and 2s in this case). Thus we performed a second set of
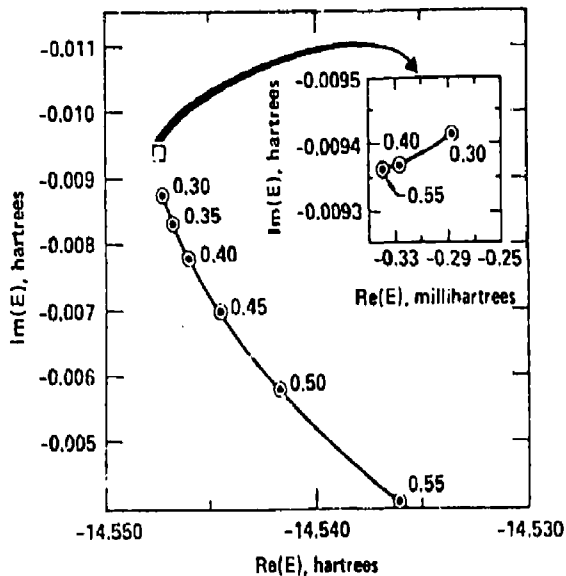

Figure 3. E_{CSCF} for Be⁻ as a function of α in the scaling parameter $\theta = \exp(i\alpha)$. The main cirve is calculated with real basis functions, and the insert is the complex basis function result for the same range of α. The real part of the energy scale in the insert is relative to -14.547 Hartrees.

calculations with only the s-functions scaled by θ. The results of this calculation are plotted in the inset to Figure 3. The stability of E_{CSCF} as a function of α is remarkable in this calculation, but still no sign of clear cusp behavior was observed. Fortunately E_{CSCF} is so stable that it is unnecessary to find a stationary point of E_{CSCF} in order to find the resonance energy. Choosing a value of α near the center of the range plotted in Figure 3 ($\alpha=0.4$) we find $E_{CSCF} = 14.54733 - .00137i$. The value for the width of the resonance is therefore 0.51 eV or about half the value from a static exchange calculation.[18] To get an estimate of the position of the resonance it seems most reasonable to subtract the Hartree-Fock value of the ground state energy of Be from E_{CSCF} for Be⁻,

because one of the solutions of the complex SCF equations (a
nonresonant, continuum solution) is the Hartree-Fock wavefunction
for Be with the remaining electron in a continuum p orbital with
(in a limiting sense) zero energy. The resonance position so
obtained is 0.70 eV, only slightly lower that the static exchange
value.[18]

There is a practical note which concerns the use of complex
basis functions. In an earlier publication[18] we made use of
the identity, written here for the radial part of a one electron
problem,

$$\int \phi_i(r)H(r\theta)\phi_j(r)r^2 dr = \theta^{-3}\int \phi_i(r\theta^{-1})H(r)\phi_j(r\theta^{-1})r^2 dr \quad (37)$$

to perform a rotated coordinate calculation by diagonalizing the
real Hamiltonian, $H(r)$, using complex basis functions, $\phi_i(r\theta^{-1})$.
It is in fact more convenient to use the same device in complex
SCF calculations. Thus the second of our calculations[19] on Be⁻ was
actually performed with unscaled Fock operators and complex p basis
functions of the form $\phi_i(r\theta^{-1})$ and real s basis functions, instead
of scaled Fock operators with real p and complex s basis functions
as described above. These two forms of the calculation are
completely equivalent, but the prescription of unscaled Fock
operators plus complex basis functions requires fewer complex two
electron integrals and, more importantly, is a more convenient
starting point for the extension to molecular problems.

B. Molecular Example

The $^2\Pi_g$ resonance state of N_2^- has been well characterized
experimentally through extensive studies of vibrational excitation by
electrons between 1 and 5 eV[2] and has also been the subject of
numerous theoretical treatments.[23-27] We felt that this system
would provide a good indication of whether the "method of complex
basis functions" is an accurate and practical way to proceed with
complex SCF studies on molecules.

The open-shell SCF equations for $N_2^-(^2\Pi_g)$, which has
the electronic configuration $(1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g)\ ^2\Pi_g$,
were solved in a mixed basis set of real and complex Cartesian
Gaussian functions.[20] For these calculations, we use a real
valued Hamiltonian again and Gaussian basis functions in which
the exponents are scaled by θ^{-2}. The non-resonant core orbitals
(all but $1\pi_g$) were again expanded solely in terms of real
functions, for the same physical reasons which are discussed at
length in reference 18. We also carried out several numerical
tests to check the adequacy of the core-orbital basis. These are
be discussed below.

The $1\pi_g$ orbital was expanded in terms of both real and complex Gaussians. The latter were chosen following the prescription of McCurdy and Rescigno (reference 6) by complex-scaling the orbital exponents of the Gaussian basis functions and keeping the associated nuclear centers real.

The core orbitals were expanded in a nuclear-centered (9s 5p)/[5s 3p] contracted basis, augmented with two d-polarization functions (α = 1.0 and .4). Several choices for the π_g orbital space were tested. A preliminary set of calculations was done using a (4p) basis, augmented with additional diffuse d_π functions placed at the center-of-mass. All π_g functions were complex scaled. These calculations produced a complex total energy for $N_2^-(^2\Pi_g)$ which depended strongly on and varied monotonically with the rotation angle ϕ, the resonance width varying by roughly 40% over the range $15° \leq \phi \leq 25°$. A simple test was devised to demonstrate that this instability was due to the inadequacy of the π_g orbital basis and not the core orbital basis. The total SCF energy for $N_2^-(^2\Pi_g)$ can be written as $E = E_{core} + {}^\epsilon\Pi_g$ where E_{core} is the core-orbital contribution to the total energy and ${}^\epsilon\Pi_g$ is the orbital energy of $1\pi_g$. A series of "static-exchange" calculations was performed at different angles with the core orbitals frozen. It was found that changes in ${}^\epsilon\Pi_g$ were precisely equal to the variations noted earlier in the SCF calculations.

The addition of several real p_π functions to the π_g orbital space greatly reduced the sensitivity of the energy to the rotation angle. The final π_g basis we used consisted of the (5p 2d)/[3p 2d] set of real functions, four nuclear-centered p_π functions with exponents .6, .26, .125, and .05 and six complex d_π functions placed at the center-of-mass with exponents ranging from .2 to .002 in a geometric series. The total energy as a function of rotation is shown in Figure 4 for an internuclear separation of 2.068 a.u., the equilibrium bond distance of N_2. The resonance width is found to vary by roughly % within a range of angles between $28° \leq \theta \leq 38°$. An average of the data over this range gives a resonance lifetime of .44 eV and an energy of 3.19 eV, when referenced to the SCF energy of ground state N_2 in the same basis. Table I compares these results to those of other recent theoretical calculations.

These preliminary results[20] are an encouraging indication that the complex SCF method, with properly chosen basis functions, can provide useful information about the lifetimes of certain types of molecular metastables and should provide a convenient starting point for further complex configuration-interaction studies.
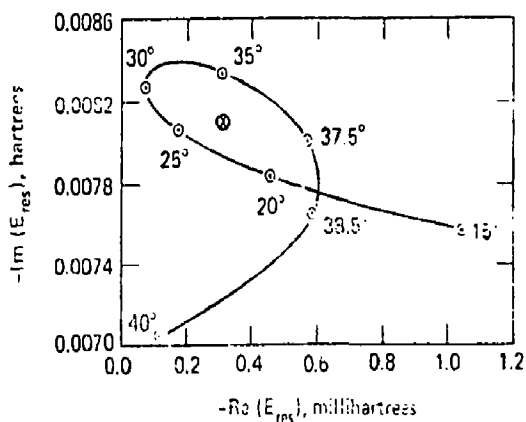
Figure 4. SCF Resonance energy of $N_2^-(^2\Pi_g)$ as a function of rotation angle. The real part of the energy scale is given relative to -108.8494 Hartrees. The internuclear separation is 2.068 a.u.

Table I. Comparison of electron resonance parameters for $N_2^-(^2\Pi_g)$. Energies and widths are in electron volts and $R_0 = 2.068$ a.u.

	$\epsilon_r(R_0)$	$\Gamma(R_0)$
Complex SCF[20]	3.19	.44
Krauss and Mies[24] (stabilization)	3.26	.8 .3
Schneider et al[25] (R-matrix)	2.15[a]	.34
Hazi et al[26]	3.23 (2.16[a])	.42
Levin and McKoy[27]	2.19[a]	.36

[a] Resonance energy relative to the energy of a fictitous N_2 neutral core made up with N_2^- orbitals.

It is worth noting that the simple SCF approach outlined above is
not applicable in the case of a Feshbach resonance (for example,
He (2s 2p) ^3P) because the complex SCF equations so derived
have solutions which yield a real value for E_{CSCF} and
consequently give no information about the resonance width. The
decay of a Feshbach resonance is a correlation effect which
cannot be described by a simple SCF treatment. MCSCF theory
might offer an effective way to treat these cases.

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