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COMPLEX COORDINATES IN THE THEORY OF ATOMIC AND MOLECULAR STRUCTURE AND DYNAMICS

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INTRODUCTION

During the past ten years there has been rapid development and application of a theory variously known as *complex scaling*, *complex coordinates*, *coordinate-rotation*, and *dilatation analyticity*, to problems of resonances in atomic and molecular physics and in chemistry. Resonances are ubiquitous. A few examples:

1. an excited species radiates;
2. a multiply excited atom autoionizes;
3. an atomic or molecular system in an external field is subject to field or multiphoton ionization;
4. an appropriately excited molecule dissociates unimolecularly;
5. electrons attach to molecules and the resulting quasibound molecular ions dissociate into stable ionic and neutral subsystems.

Each of these processes is typified by the formation and decay of an intermediate state, or *resonance*, which is a nonstationary (or quasibound) state with a lifetime long enough to be well characterized, and long enough to make its explicit recognition of experimental and theoretical importance. The simplest, and most naive, mathematical description of such states is that they resemble bound stationary states in that they are "localized" in space (at $t = 0$), and their time evolution is

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given by (1–3)

$$\psi_R(t) = \exp(-iE_R t/\hbar)\psi_R(0) \tag{1.}$$

which is the usual stationary state time dependence, except that now the energy, E_R, of the resonant state is complex:

$$E_R = E_{res} - i\Gamma/2 \tag{2.}$$

where E_{res} and Γ are real, and $\Gamma \geqslant 0$. The presence of the "$-i\Gamma/2$" forces exponential decay, if we accept Eq. 1, thus allowing description of a decaying state. If we assume for the moment that such a simple description of the time evolution is adequate (it very often is), *a priori* calculation of the real and imaginary parts of E_R allows prediction of the formation energies and lifetimes of intermediate species, and thus is an important task. However, an immediate question arises: If the Hamiltonian for the system at hand is Hermitian, how can a "complex eigenvalue" such as E_R ever occur? Hermitian operators have real eigenvalues! This observation has led to almost continuous discussion and dispute since 1930. Refs. (1–7) contain sensible discussions. Many others do not. However, even without detailing any of this discussion, it is straightforward to state that one of the major purposes of the introduction of complex coordinates in nonrelativistic quantum theory is to produce exactly those (non-Hermitian) operators which have the complex energies of Eq. 2 among their actual eigenvalues. That the procedure for constructing these new operators is, at first glance, totally trivial is certainly a reason for the popularity and utility of the method. A pleasant bonus is that the eigenfunctions associated with these complex resonance eigenvalues are square integrable (henceforth, L^2) and thus satisfy our feeling that resonances are localized, at least at complex values of the coordinates.

Thus, one result of the use of complex coordinates is calculation of the energies and lifetimes of decaying systems, be they atoms or molecules, and for all types of decay mechanisms. As the formalism is developed, it will also emerge that use of complex coordinates by no means implies a particular a priori assumption as to the actual time evolution: it might be exponential for all times, t, of physical interest, $\tau_{short} \lesssim t \lesssim \tau_{long}$ [for example, (5) and (6) contain discussions of the origin of the mandatory existence of long-time departures from pure exponential decay] or it might be strongly nonexponential, and not at all well described by a single complex eigenvalue for any reasonable length of time. Another use of the technique is the production of rigorous mathematical results governing what we can expect Schrödinger theory to predict for bound state and scattering dynamics of atoms and molecules. The third major use of the method is in the area of computational scattering theory. In the flurry of successful activities relating to calculation of resonance properties, many workers have overlooked an original motivation for interest in the method: namely, direct calculation of scattering and photoabsorption cross sections *without detailed enforcement of boundary conditions*. The ability to develop computational methods that flout the usual channel-by-channel accounting of multichannel scattering theory is essential as the number of channels increases (or becomes infinite as in impact ionization or collisional dissociation) and was a dominant interest of many of the early workers attempting to apply complex coordinates in atomic and molecular physics (8–18). These three areas—resonances, results of rigorous theory, and potential for development of techniques that ignore usual scattering boundary conditions—form the body of the review, and are interwoven with discussion of applications.

Before proceeding a few additional comments are in order. The status of theory and computation as of early 1978 are well represented in the proceedings (19) of a March 1978 Sanibel Workshop. An extensive discursive review of computational aspects relating mainly to atomic electronic resonance structure, and, in particular, use of complex basis functions has been prepared by Junker (20). The present review is intended for physical chemists, which is taken to imply that there is usually no need for the great mathematical precision that can be found in abundance in much of the cited literature. Thus, for example, the *spectrum* of an operator is taken to consist of the set of its eigenvalues; we assume that square integrable bound state eigenfunctions correspond to discrete eigenvalues, and that δ-function normalized scattering, or continuum, eigenfunctions correspond to eigenvalues in the continuous spectrum: this is the usual language of physicists.

CONCEPTUAL AND MATHEMATICAL BACKGROUND

Before stating the results of the theory of many-particle analytically continued Hamiltonians developed by Aguilar & Combes (21), Balslev & Combes (22), Reed & Simon (7), Simon (23, 24), and van Winter (25), it is useful to give a little qualitative background and motivation. (Experts may skip the next two subsections.)

How Can Coordinates Be Complex?

We take the view of Heisenberg: Only observables are subject to physical interpretation, and observables are matrix elements and eigenvalues.

Consider the hydrogen atom Hamiltonian (in a.u.) for s-states ($l=0$)

$$\mathcal{H} \equiv \mathcal{H}(r) = -\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{1}{r} \tag{3.}$$

r being the radial variables in spherical polar coordinates. The expected value of the energy is thus

$$\langle E\rangle = \int_0^\infty R(r)\left[-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{1}{r}\right]R(r)r^2\,dr \Big/ \int_0^\infty R^2(r)r^2\,dr \tag{4.}$$

assuming that the state function is $\Psi(r,\theta,\phi) = R(r)/\sqrt{4\pi}$, and that $R(r)$ is real, as it may always be taken (s-states are nondegenerate). It is usually assumed that the integration in Eq. 4 is over the real range of r from 0 to ∞, and that the radial coordinate of Eq. 3 is real. However, if $R(r)$ is analytic in r (e.g. a combination of actual hydrogenic functions, or Slater functions, or Gaussian radial functions) we can rewrite, using Cauchy's theorem, Eq. 4 in terms of contour integrals

$$\langle E\rangle = \int_C R(\rho)\left(-\frac{1}{2}\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho} - \frac{1}{\rho}\right)R(\rho)\rho^2\,d\rho \Big/ \int_C R^2(\rho)\rho^2\,d\rho \tag{5.}$$

without changing the value of $\langle E\rangle$. Three possible contours, C, are shown in Figure 1. If we take $R(r) = 2e^{-r}$ (the exact radial 1s function), the contour need not even return to the real axis at ∞, as long as ρ has a positive real part at ∞ insuring convergence of the integral. Thus, for

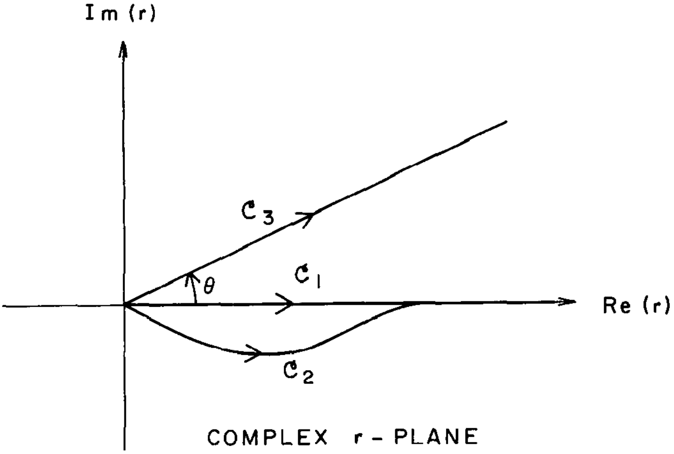

Figure 1 Complex r integration contours. The integral in Eq. 6 has the same value on each of these. C_1 is the usual real axis contour, C_2 is asymptotically real, and C_3 heads off into the complex plane even as $\rho \to \infty$.

example, taking[1] $\rho = re^{i\theta}$ (θ real, for the moment), which "scales" r by the complex factor $e^{i\theta}$, we have

$$\langle E\rangle = \frac{\int_0^\infty e^{-re^{i\theta}}\left(-\frac{e^{-2i\theta}}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{e^{-i\theta}}{r}\right)e^{-re^{i\theta}}\left(e^{i\theta}r\right)^2e^{i\theta}\,dr}{\int_0^\infty \left(e^{-re^{i\theta}}\right)^2\left(e^{i\theta}r\right)^2e^{i\theta}\,dr}, \qquad 6.$$

which may be directly evaluated, giving the usual value, $-1/2$. Thus the expected energy is not altered if we use the complex scaled wave function

$$R(re^{i\theta}) = 2e^{-re^{i\theta}} \qquad 7.$$

along with the scaled operator

$$\mathcal{H}(\theta) \equiv \mathcal{H}(re^{i\theta}) = -e^{-2i\theta}\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{e^{-i\theta}}{r} \qquad 8.$$

integrated with the scaled measure $e^{3i\theta}r^2\,dr$. Note also that just as $R(r) = 2e^{-r}$ is an eigenfunction of the $\mathcal{H}(r)$ of Eq. 3, with eigenvalue $-1/2$, $2e^{-e^{i\theta}r}$ is an eigenfunction of $\mathcal{H}(re^{i\theta})$, with the same eigenvalue, as is easily checked by substitution, or more laboriously, by usual power series techniques (26, 27). As Eqs. 6–8 give the same matrix element and eigenvalue as $2e^{-r}$ with Eqs. 3 and 4, no predictions are changed. Whether we prefer to think of the coordinate r in $R(r)$ as real, or as a scaled complex coordinate $\rho = e^{i\theta}r$, makes no difference in this example as long as the following hold:

1. r is not itself an observable. (This is usually true—think about it, spectroscopy and scattering experiments do not give "r" directly).
2. The operators are also appropriately scaled.
3. We note that as Eqs. 5–8 arose from Eq. 4 by changing the radial integration contour via Cauchy's theorem, there is no complex conjugation of the $e^{i\theta}$ arising from the scale transformation, whether it occurs on the left or right of the operator. On the other hand, if $R(r)$ for r real (i.e. $\theta = 0$) is intrinsically complex (e. g. $R(r) = re^{-r} + ie^{-2r}$) then the complex conjugation of the usual definition of expectation value does apply to (but only to) the intrinsically complex part of the function. Thus, for example, the spherical harmonics, $Y_{l,m}$, are conjugated as usual.

Thus, without changing any observable properties of the system, we can work with a complex radial variable. The only care that need be taken is

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[1] The "angle" θ defining the complex scaling factor $e^{i\theta}$ is not to be confused with the θ of usual (r, θ, ϕ) coordinates. This will always be clear in context.

with regard to Condition 3 above, as not all "i"s are treated alike in forming expectation values—an odd rule unless it turns out to be useful. Finally, we note that the $e^{3i\theta}$, arising as $r^2\,dr \to e^{3i\theta} r^2\,dr$ when $r \to re^{i\theta}$, is often included with the scaled functions, leaving the "measure" $r^2\,dr$ unchanged thus

$$\langle E\rangle = \frac{\int_0^\infty \left(e^{i3\theta/2} e^{-re^{i\theta}}\right)\left(-\frac{e^{-2i\theta}}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{e^{-i\theta}}{r}\right)\left(e^{i3\theta/2}e^{-re^{i\theta}}\right) r^2\,dr}{\int_0^\infty \left(e^{i3\theta/2}e^{-re^{i\theta}}\right)^2 r^2\,dr}. \qquad 9.$$

In this case the $e^{i3\theta/2}$, as well as the $re^{i\theta}$, are not complex conjugated. But, again, any intrinsically complex functions are treated as usual. The reason for this last rearrangement becomes clear below, when a unitary transformation is introduced to effect the scale transformation: Everyone knows that operators don't "act" on the integration measure, so the $e^{i3\theta/2}$'s have to be stuck in! The ideas of this subsection are taken far more seriously in Refs. (8, 10, 28–32), where they are referred to as contour distortion techniques.

So far, much complexity, a peculiar set of operations for performing expectation values (not all is are equivalent!) and no new results, but:

What About Boundary Conditions?

Boundary conditions determine whether an operator has eigenvalues, and whether the corresponding eigenfunctions are L^2 (bound states) or non-L^2, δ-function-normalized, scattering states. What happens to boundary conditions as $r \to re^{i\theta}$? For our example of $R(r) = 2e^{-r}$, which is certainly L^2, there is no problem. $R(re^{i\theta}) = 2\exp(-r\exp(i\theta))$ is also L^2, unless $|\theta| \geqslant \pi/2$, a restriction that must be observed. Thus the boundary condition of square integrability is preserved. Conversely, no new square integrable eigenfunctions with real eigenvalues suddenly appear as $r \to re^{i\theta}$ and $\mathcal{H}(r) \to \mathcal{H}(re^{i\theta})$. That is $\mathcal{H}(r)$ and $\mathcal{H}(re^{i\theta})$ have the same real bound state eigenvalues.

What about scattering states? This is where things begin to happen. Scattering wave functions are non-normalizable, but they remain finite as $r \to \infty$. Thus, unless the potentials are too long ranged, radial scattering solutions look like linear combinations $(e^{+ikr})/r$ and $(e^{-ikr})/r$ as $r \to \infty$. k is the momentum (in units of $\hbar$) and $E = k^2/2$. To preserve this (bounded) asymptotic form as $r \to re^{i\theta}$ we must simultaneously take $k \to ke^{-i\theta}$. If we don't, one of the exponentials will grow exponentially at ∞, violating the boundary condition of everywhere finite wave functions.

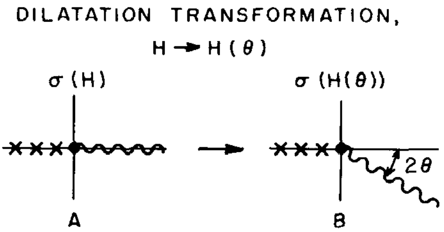

Figure 2 Effect of the transformation $r \rightarrow r\exp(i\theta)$ on the spectrum "σ" of a one-body problem. Bound states are invariant as is the threshold where the continuum begins. The continuous spectrum "rotates" about the threshold by -2θ, exposing a higher Riemann sheet of the resolvent.

If $k \rightarrow ke^{-i\theta}$, then $E = k^2/2 \rightarrow e^{-2i\theta}k^2/2$, for the allowed scattering eigenenergies. This suggests immediately: the complex scaled Hamiltonian $\mathcal{H}(\theta)$ of Eq. 8 has the same bound state eigenvalues as does the original of $\mathcal{H}$ (Eq. 3), but the scattering states have energies $Ee^{-2i\theta}(0 \leqslant E < \infty)$. The continuum is then *rotated* into the lower half complex energy plane, as shown in Figure 2. This is the correct result even though for the Coulomb problem the asymptotic forms aren't quite $(e^{\pm ikr})/r$. It is the fact that the continuous spectrum of $\mathcal{H}(\theta)$ is different from that of $\mathcal{H}$ which is the key to the utility of the $r \rightarrow re^{i\theta}$ transformation. With this very qualitative motivation, we now simply state the results of the full theory.

Spectral Theory of Dilatation Analytic Hamiltonians

This section contains the mathematical results of the theory of complex scaling. The basic result is that if, for an N-body Coulomb system, we take (θ real and postive, to simplify the discussion)

$$\mathcal{H}(\theta) = -e^{-2i\theta}\frac{\nabla_N^2}{2} + e^{-i\theta}V_N^{coul}, \qquad 10.$$

where $e^{-2i\theta}, e^{-i\theta}$ are complex numbers which scale the ordinary N-body kinetic energy $-\nabla_N^2/2$, and N-body Coulomb potential energy V_N^{coul}, $\mathcal{H}(\theta)$ has complex eigenvalues with L^2 eigenfunctions (for certain ranges of θ) which we *associate* [a carefully chosen word, see (33) and below] with resonances. Those wishing to see applications before investing the energy to follow a fuller statement of the theory may look at Figures 2 and 3, and then proceed to the applications sections, having noted that Eq. 10 is just Eq. 8 scaled up to N-particles.

The rigorous theory (7, 21–25) that follows gives results for eigenvalues of complex scaled N-body nonrelativistic Coulomb Hamiltonians, and their behavior under the complex scale transformation $r \rightarrow re^{i\theta}$. The parallel results for the analytic structure of Hilbert space matrix elements of the *resolvent* $(z-\mathcal{H})^{-1}$ are also stated. Rather than by direct use of Cauchy's theorem and the contour distortions of the previous sections, the rigorous theory is compactly formulated in terms of unitary transformations called dilatation transformations (dilate $\equiv$ dilatate $\equiv$ stretch), conveying the idea that stretching scales the system but does not change angles. We thus define a unitary operator $U(\theta)$ whose action on *wave functions* is defined in configuration space for three dimensions

$$U(\theta)\psi(\vec{r}) \equiv e^{i3\theta/2}\psi(\vec{r}e^{i\theta}) \qquad 11.$$

for a two-body system, $\vec{r}$ being the relative center-of-mass coordinate vector (see Eq. 9 and following equations). For N-body systems, if $\psi^N(\vec{r})$ is the corresponding function $\vec{r} \equiv (\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N)$, where only $N-1$ of the $\vec{r}_i$ are independent in center-of-mass coordinates, we have

$$U(\theta)\psi_N(\vec{r}) \equiv e^{i3(N-1)\theta/2}\psi(\vec{r}e^{i\theta}). \qquad 12.$$

The corresponding transformation on the N-body *operators*, exemplified by the Hamiltonian, is

$$\mathcal{H}_N(\theta) \equiv \mathcal{H}_N(\vec{r}e^{i\theta}) \equiv U(\theta)\mathcal{H}_N(\vec{r})U(\theta)^{-1} \qquad 13.$$

For the case of the N-body Coulomb problem

$$\mathcal{H}_N \equiv \mathcal{H}_N(\vec{r}) = -\frac{\nabla_N^2}{2} + V_N^{coul}(\vec{r}) \qquad 14.$$

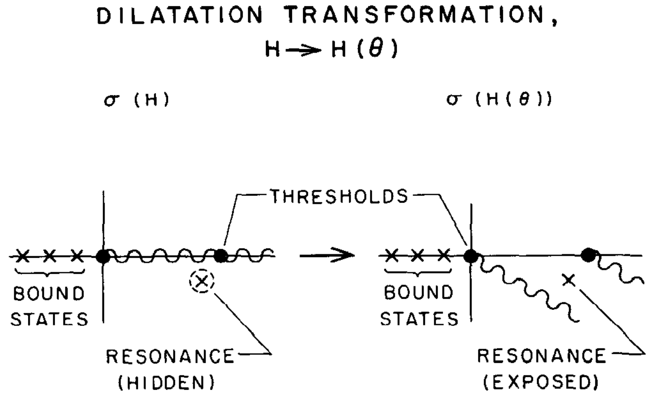

Figure 3 Effect of dilatation transformation on a many-body Hamiltonian. Again bound states and thresholds are invariant. However, as the continua rotate, complex resonance eigenvalues may be exposed. Such eigenvalues correspond to poles of the resolvent $R_\phi(z)$, but are "hidden" on a higher sheet if $\theta=0$, and will be exposed if the cuts are appropriately moved.

and

$$\begin{aligned}\mathcal{H}_N(\theta) \equiv U(\theta)\mathcal{H}_N(\vec{r})U(\theta)^{-1} = \mathcal{H}(\vec{r}e^{i\theta}) \\ = -e^{-2i\theta}\frac{\nabla_N^2}{2} + V_N^{coul}(\theta) \\ = -e^{-2i\theta}\frac{\nabla_N^2}{2} + e^{-i\theta}V_N^{coul}. \end{aligned} \quad 15.$$

That is, for N-body systems with only pair-wise Coulomb interactions, the scaled Hamiltonian $\mathcal{H}(\theta)$ is obtained by simply multiplying the total relative kinetic energy by $e^{-2i\theta}$, and the potential energy by $e^{-i\theta}$. Note that this is precisely the analog of Eq. 8, as obtained by contour distortion. Not only does the Coulomb potential scale in a simple manner; the Coulomb interaction belongs to a special class of potentials called *dilatation analytic*, a more restrictive condition than simple analyticity in the interparticle coordinates, which the Coulomb potential has (except at $r_{ij}=0$, which causes no difficulty). The precise definition, and determination of which potentials are or are not dilatation analytic, is a nontrivial mathematical technicality (see Refs. 7, 21–25, 34–36), into which we shall not delve. That the N-body Coulomb potential is dilatation analytic allows us to state at once (suppressing the "N" in $\mathcal{H}_N$):

1. Bound state eigenvalues of $\mathcal{H}(\theta)$ are independent of θ, and identical to those of $\mathcal{H}$ for $|\theta| \leqslant \pi/2$.

2. Scattering thresholds corresponding to the possibility of fragmentation of different subsystems in differing states of excitation are also independent of θ, $|\theta| \leqslant \pi/2$.

3. The segments of continua beginning at each scattering threshold rotate by an angle 2θ into the lower half plane ($\theta \geqslant 0$), each about its individual threshold. (This follows from the fact that the continua are related to the kinetic energy, not the potential.)

Points 1, 2, and 3 mimic the simplistic analysis of the preceding subsection (see Figure 2); now, additionally:

4. New, complex, discrete eigenvalues of $H(\theta)$ may appear in the lower half complex energy plane, in the sector $0 > \arg(z - E_0^{\text{thresh}}) \geqslant -2\theta$ where z is the complex energy, and E_0^{thresh} is the lowest energy-scattering threshold. These are the complex eigenvalues that we associate with resonances. The corresponding eigenfunctions $\chi(\theta)$ are L^2, as befits their association with discrete eigenvalues. Note that the $\chi(0)$ obtained by taking $\lim_{\theta\to 0}\chi(\theta)$ will not be L^2, unless its eigenvalues were real to begin with, and it represents a bound state. The discrete complex eigenvalues of $H(\theta)$ are independent of θ as long as they remain isolated from parts of the continuum. As the continua rotate as a function of θ,

discrete complex eigenvalues may appear or disappear as the continua sweep by, and:

5. All discrete eigenvalues of $\mathcal{H}(\theta)$ are of finite multiplicity, and can accumulate only at thresholds (i.e. only near a threshold is it possible to have an infinite number of discrete, bound state, or resonance eigenvalues, in an arbitrarily small region of the complex plane).

These changes in the spectrum (the set of eigenvalues) "σ" of $\mathcal{H}(\theta)$ as a function of θ, are illustrated in Figures 2 and 3.

An important reinterpretation of Figures 2 and 3 is in terms of the resolvent. Consider a matrix element of the resolvent $(z-\mathcal{H})^{-1}$:

$$R_\phi(z) \equiv \langle \phi, (z-\mathcal{H})^{-1}\phi \rangle \qquad 16.$$

as a function of the complex variable z. For all but exceptional L^2 vectors ϕ, in our N-body Hilbert space, $R_\phi(z)$ has well-known properties: it is analytic in z everywhere off the real axis $[\mathcal{H}=\mathcal{H}(\vec{r})$ is Hermitian]; it has (simple) poles corresponding to bound state eigenvalues; and, has branch points corresponding to thresholds, with the segments of continua running to $+\infty$ from the various thresholds acting as branch cuts. The branch cuts force $R_\phi(z)$ to be carefully interpreted as z approaches the real axis if $Re(z) \geqslant E_0^{\text{thresh}}$, the lowest scattering threshold energy. Thus we associate points of nonanalyticity of $R_\phi(z)$ with the spectrum (eigenvalues) of the operator. Thus $R_\phi(z)$ is analytic for $Im(z) \neq 0$, as the spectrum of $\mathcal{H}$ is real.

What about the resolvent $(z-\mathcal{H}(\theta))^{-1}$? How is it related to $(z-\mathcal{H})^{-1}$? This is where the utility of defining the complex scale transformations via the unitary transformations of Eqs. 12 and 13 becomes apparent. Consider

$$\begin{aligned} R_\phi^\theta(z) &\equiv \langle \phi, U(\theta)^{-1}U(\theta)(z-\mathcal{H})^{-1}U(\theta)^{-1}U(\theta)\phi\rangle \\ &= \langle \phi(\theta), (z-\mathcal{H}(\theta))^{-1}\phi(\theta)\rangle. \end{aligned} \qquad 17.$$

Using our association of the singularity structure of a resolvent with the spectrum of the operator, we see that the analytic structure of $R_\phi^\theta(z)$ is the same as that of $R_\phi(z)$ except that the *branch cuts* of $R_\phi^\theta(z)$ are rotated into the lower half plane, by angle 2θ. As $R_\phi^\theta(z) = R_\phi(z)$ in the upper half z-plane, these two functions are simply different integral representations of the same more general multisheeted analytic function. Each representation has its own domain of validity, as the cut locations give the natural boundaries of the representation. Thus in Figures 2 and 3, $R_\phi(z)$ is valid for $0 \leqslant \arg(z) \leqslant 2\pi$; $R_\phi^\theta(z)$ is valid for $-2\theta \leqslant \arg(z) \leqslant (2\pi - 2\theta)$. The two representations are not equal on the segment $0 \leqslant \arg(z) \leqslant -2\theta$, where $R_\phi^\theta(z)$ provides the (unique) analytic continuation of

$R(z)$ into the lower half z-plane. This geometric interpretation involving the Riemann sheet structure makes the statements 1, 2, and 4, above, transparent. All follow from the fact that poles (bound states or resonances) and branch points (thresholds) are intrinsic singularity properties of an analytic function. As long as a representation restricted to a cut plane "exposes" these singularities, they are independent of cut location; but, as soon as the cuts move in such a way as to hide singularities, they are (suddenly) no longer seen in a specific representation. The cuts themselves, of course, are not singularities of the analytic function, but only boundaries of a representation, and we may attempt to place them as we wish. Those who prefer to see these properties exemplified in terms of explicitly soluble model problems, rather than as following from analytic function theory, should look at such solved problems in (20, 37, 38a, b), where complex coordinates have been explicitly included, and (39), where it would be a useful exercise to do so.

Finally, many computational results, such as those involving atoms in fields and molecular structure and dynamics (discussed below), indicate that similar properties of spectra and resolvents exist for systems that interact via nondilatation analytic potentials [see also Yaris et al (40)]. The restrictive requirements of dilatation analyticity are thus too strong. What is the appropriate generalization of the concept of dilatation analyticity? Where will results differ from those for dilatation analytic potentials? If the past continues to be a guide to the future, positive results of computation will be an important guide to mathematicians as to the potential existence of theorems waiting to be discovered.

Theoretical Applications of Spectral Theory

Many quite strong additional theoretical results that apply to the dynamics of atomic and molecular electronic structure have been demonstrated using the dilatation analyticity of the N-body Coulomb Hamiltonian. Briefly, dilatation analyticity has been used in the following cases:

1. In combination with its cousin Boost Analyticity to establish dispersion relations (41, 42) in e^+-H scattering, and to suggest their nonutility in e^--H scattering, contrary to earlier conjecture (43 and references therein).
2. To prove (24, 44, 45) nonexistence of discrete eigenvalues (real or complex) of $\mathcal{H}(\theta)$ with $Re(E) \geqslant 0$. In this theorem $E=0$ is the threshold for total breakup. A very simple proof was later found (33, 46) and warrants inspection.

3. In derivation and discussion of the usual Born-Oppenheimer approximation (47). Are diatomic potentials analytic in the internuclear distance, R?
4. In establishing fundamental results about convergence and summability of Rayleigh-Schrödinger perturbation theory for resonances (48 and references therein) and time-dependent perturbation theory (24, 49).
5. In establishing the possible behavior of $E(1/Z)$, the ground state energy of an atomic system in $1/Z$ perturbation theory (50), forcing the conclusion that conjectured (50, 51 and references therein) bound states in the continuum are likely to occur only on sets of measure zero in $1/Z$.
6. In setting rigorous bounds on the rate of fall off in coordinate space of bound state wave functions (52, 53) and on the rate of fall off in time of resonant time evolution (54).

Other more technical mathematical results are discussed by Reed & Simon (7) and Simon (33). However, it is important to note at this point that for the N-body Coulomb problem the relationship of poles of $\langle\phi(\theta),(z-\mathcal{H}(\theta))^{-1}\phi(\theta)\rangle$ to poles of scattering amplitudes, and thus to observables, is not fully established. This general point is discussed by Simon (33). More recently Nuttall & Singh (55) have given a proof of the connection for e^- atom scattering for energies below the lowest three-body (the collisional dissociation or impact ionization) threshold. Thus there are open theoretical questions, in contrast to the two-body case (e.g. 56 and references therein) and the N-body case with shorter ranged potentials (e.g. 57 and references therein). The importance of such a gap in the mathematical foundations is well illustrated by an experiment of Peart & Dolder (58) observing a resonance (albeit very broad) in H^{2-} above $E=0$. If observed resonances are in one-to-one correspondence with complex eigenvalues of $\mathcal{H}(\theta)$, this observation contradicts 2, above, and we could conclude the experiment to be an artifact. This puzzling situation is discussed by Doolen (59) and Nuttall (60). It is especially unclear how to interpret the stabilization calculation of an H^{2-} resonance with E well above zero (61) as this relates directly to the original Hamiltonian, as do eigenvalues of $\mathcal{H}(\theta)$, not even to the (remote) possibility that $\mathcal{H}(\theta)$ has no eigenvalue corresponding to an S-matrix pole.

COMPUTATIONAL APPLICATIONS

Applications to atomic and molecular autoionization, atomic structure in ac and dc fields, molecular predissociation, and calculation of cross sections are discussed under this heading. The discussion of atomic electronic structure is sufficiently detailed to reflect the changes in computational strategy as they have developed since 1972.

Atoms: The Direct Approach

From a purely computational point of view the simplest way to implement the theoretical developments for N-body systems is to use standard configuration interaction or other variational techniques which produce a real symmetric matrix representation of the usual electronic Hamiltonian,

$$(\overline{\mathcal{H}})_{ij}=\langle\chi_i(\vec{r})|\mathcal{H}(\vec{r})|\chi_j(\vec{r})\rangle.$$

Then

$$\overline{\mathcal{H}}=\overline{KE}+\overline{PE} \qquad 18.$$

where $\overline{KE}$ and $\overline{PE}$ are the real symmetric representations of the kinetic and potential energies in the variational basis. Rayleigh-Ritz theory now directs us to find the eigenvalues of $\overline{\mathcal{H}}$ as equivalent to a linear variation in our space of trial functions. The extension to $\mathcal{H}(\theta)$, and thus to direct determination of resonance eigenvalues as first suggested by J. Nuttall in 1972 (private communication), is to take (as follows at once from Eq. 18)

$$\overline{\mathcal{H}}(\theta)=e^{-2i\theta}\,\overline{KE}+e^{-i\theta}\,\overline{PE} \qquad 19.$$

where $\overline{KE}$ and $\overline{PE}$ are the same real symmetric matrices as in Eq. 18, although we might expect to choose the trial function space differently. Solution of the complex symmetric matrix eigen-problem

$$\overline{\mathcal{H}}(\theta)\bar{c}_i=E_i\bar{c} \qquad 20.$$

then yields the complex eigenvalues E_i, and the complex vectors $\bar{c}_i$. All of the burden of trying to represent a complex valued wave function is placed on these vectors of expansion coefficients. We note at once that as $\overline{\mathcal{H}}(\theta)$ is not Hermitian, its spectral resolution involves both its left and right eigenfunctions (62). However, elementary manipulation gives the results that the left eigenfunction $\bar{d}_i$ corresponding to eigenvalue E_i is just $(\bar{c}_i)^T$ where T is the transpose. (Note that the transpose is not the usual Hermitian conjugate, which is the transpose complex conjugate.) Thus

$$\overline{\mathcal{H}}(\theta)=\sum_i E_i(\bar{c}_i)(\bar{c}_i)^T.$$

This is a bi-orthogonal expansion (62, 63) and $(\bar{c}_i)^T(\bar{c}_j)=\delta_{ij}$ (rather than the usual $(\bar{c}_i)^\dagger(\bar{c}_j)=\delta_{ij}$ for Hermitian problems).

The ansatz of Eq. 19 is very attractive as it implies that standard, existing variational codes may be used to generate $\overline{\mathcal{H}}(\theta)$, leaving only the problem of solution of Eq. 20, which is almost always straightforward. This is, in spite of the limitations discussed in the following subsection, still an attractive feature for exploratory calculations. One can determine whether the method will be of any utility without much work on code development. We refer to the use of Eqs. 19 and 20 with real symmetric representations of $\overline{KE}$ and $\overline{PE}$ as the *Direct Approach*.[2]

The most important question about the Direct Approach is: Does it work? This is answered affirmatively by Doolen et al (64, 65). Next, how can we optimize the choice of θ, given that in a finite variational expansion the resonance eigenvalues are not independent of θ (although in a complete basis they would be)? This is answered in an empirical manner by Doolen (66). Doolen observed, for a fixed L^2 expansion basis, that approximate complex resonance eigenvalues, when plotted as a function of θ (note that in the Direct Approach no new matrix elements need be calculated as θ is changed!), followed trajectories (henceforth θ-trajectories) that *paused* for certain values of θ, suggesting some sort of stationary property. This is illustrated in Figure 4 in a calculation of E_{res} and $\Gamma/2$ for the lowest ^1S resonance in helium $(2s^2)$. The approximate stationarity, easily observed in the figure, is even more dramatic for larger basis sets (66). The analytic theory of the morphology of these θ-trajectories has been given by Moiseyev et al (67), and the existence and interpretation of such stationarity analyzed in terms of an extension of the usual virial theorem to complex scalings by Brändas et al (68, 69), Canuto & Goscinski (70), Winkler & Yaris (71, 72), Yamabe et al (63, 73), Certain (74), and Moiseyev et al (75–78). Application of the virial results require that θ in the $e^{i\theta}$ scaling be itself a complex number, thus allowing optimization of $Re\theta$ and $Im\theta$, to ensure simultaneous stationarity of both the real and imaginary parts of the resonance eigenvalue. This is completely consistent with the general theory of dilatation transformations; the restriction to real θ in our earlier discussions was simply for convenience.

A very large number of workers have used the θ-trajectory techniques as the basis of computational algorithms to locate resonances. Winkler & Yaris (79, 80) and Weinhold (81a) have shown that low-order perturbation theory may sometimes be used to avoid repetition of eigenvalue computations as a function of θ, although Moiseyev & Certain (81b) have demonstrated that such a theory may not be expected to have a large radius of convergence.

Applications of the Direct Approach to resonance structure of few body atomic systems have been notably successful. A highly selective

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[2] Ironically, the first published results (112) ostensibly using complex coordinates to locate a resonance (following Nuttall's suggestion) were by a different method, to be discussed below.

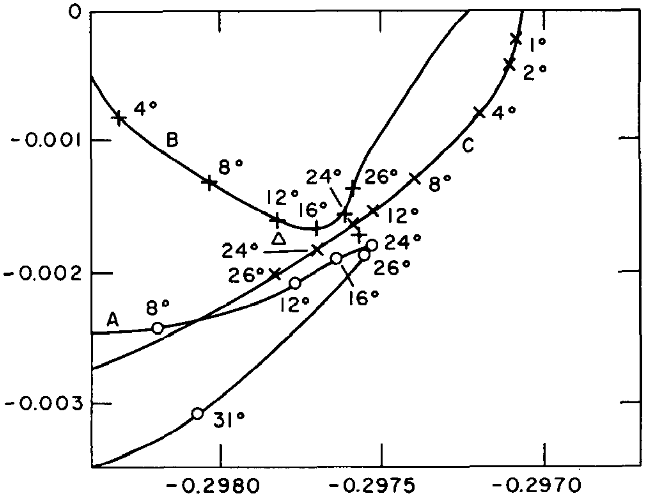

Figure 4 θ-trajectories for location of the complex eigenvalue corresponding to the lowest ^1S Feshbach resonance in He. Trajectories show behavior of complex eigenvalue as a function of the complex scaling angle θ, for three choices of nonlinear parameters in a Hylleraas-type basis. The trajectories kink, or pause near values of θ approximately consistent with the Virial Theorem. Figure reproduced from (66), with permission.

sampling of recent papers (containing references to earlier work) follows: Ho, in an extensive series of papers, has looked at autoionizing resonance structure in He and H^- associated with higher ($n > 2$) excitation thresholds in He^+ and H (82–85). Ho (86) and Moiseyev & Weinhold (87), have examined a large number of isoelectronic series of resonances from $Z = 1$ to 10; the latter authors, using data of Ho (82), have examined correlation in the resonances as a function of $1/Z$. Doolen et al have established the existence of a very narrow Feshbach resonance in e^+-H scattering (88). Similarly, resonances in the (e^-, e^+, e^-) system (89) and in the scattering of positronium (e^+, e^-) from H-atoms have been found (90, 91).

Atoms in Fields: The Direct Approach

The Direct Approach has been applied to problems involving the dc Stark (electric field) and Zeeman (magnetic field) problems, and to multiphoton ionization. The dc Stark Hamiltonian (for hydrogen)

$$\mathcal{H}^{\text{Stark}} = -\frac{\nabla^2}{2} - \frac{1}{r} + \vec{F}\cdot\vec{r} \qquad 21.$$

has no bound states, but for small fields ($\vec{F}$) has long-lived states which may be treated as resonances. Using the Direct Approach ansatz,

$$\overline{\mathcal{H}}(\theta) = e^{-2i\theta}\,\overline{KE} + e^{-i\theta}\,\overline{PE} + e^{+i\theta}\,\overline{\vec{F}\cdot\vec{r}}, \qquad 22.$$

Reinhardt (92) obtained excellent positions and widths of Stark broadened hydrogenic states for $n=1$, with subsequent extensions to $n=2$ states (93). Many others have subsequently used the Stark problem as a test case, for example (68, 94–96). The same techniques were then applied to the Stark broadening of autoionizing states by Wendoloski & Reinhardt (97); to the combined Stark-Zeeman effect by Chu (98); and to the multiphoton (ac Stark) ionization by Chu & Reinhardt (99), Reinhardt (100), Chu (101, 102, and references therein), and Preobrazhensky & Rapoport (103) for the case of an oscillatory classical field, and for quantized fields by Grossman & Tip (104). Many of these results were obtained before there was any real theoretical justification for the use of the dilatation transformation. The field coupling $\vec{F}\cdot\vec{r}$ is not well behaved at ∞, and is not encompassed by the standard theory of Refs. (7, 21–25). Qualitative mathematical results were obtained by Cerjan et al (105) and the whole theory finally put on a firm mathematical footing by Herbst (106, 107) and Herbst & Simon (108a, b, 109). The clear lesson is that there are many things to be discovered via computations, and that in particular the numerical utility of complex scale transformations is often ahead of rigorous mathematical foundation.

Critique and Extensions of Computational Technique

The Direct Approach has the following advantages:

1. Boundary conditions are ignored—often a nontrivial fact: for example, for resonances near the $n=4$ threshold (85) in, say, He, where a sufficiently large number of open and almost open channels are present as to make use of other methods problematic; or for the problem of Stark broadening of the ${}^1P2s2p$ shape resonance (97) in H^-, which lies above the $n=2$ threshold, and in the presence of the field a minimum of 12 important open channels are strongly coupled, ignoring the problem of enforcing Stark boundary conditions. In these cases, both of which were motivated by concurrent experimental work, no other computational techniques have even yet been quantitatively applied.
2. It is possible to take existing codes and put them into the service of the direct method without reprogramming integrals or integral transformations. This means that exploratory calculations are easily undertaken.

But there are problems. The Direct Approach very often requires solution of large eigenproblems: in (85), Ho used Hylleraas bases of up to 165 terms, in (88) Doolen et al used bases ranging from 286 to 680 Hylleraas terms. This latter is an extreme case, and quantitative results were obtained for a very narrow resonance ($\Gamma/2 \sim 7\times 10^{-5}$ a.u.), very slightly below the $n=2$ threshold in e^{+}-H scattering, and where other computational methods were not able to come to decisive conclusions. In general, that widths are usually quite small implies the need for fairly high precision. However, use of a large basis is aesthetically offensive to some, and one can ask: Can some asymptotic information be included to speed convergence? More fundamentally, the Direct Approach simply runs out of steam for e^{-}-atom resonances involving several shells of atomic electrons. In the Direct Approach the *inner shells* cause grave difficulties. The origin of this difficulty, illustrated by our elementary discussion of the H atom, is that for a bound state, if

$$\mathcal{H}(r)R(r)=ER(r), \quad \text{then} \quad \mathcal{H}(re^{i\theta})R(re^{i\theta})=ER(re^{i\theta}).$$

Thus, if an inner shell is orbital in, say, neon is well represented by $2e^{-Zr}$, with an effective Z of about 9, the corresponding 1*s* orbital for the scaled Hamiltonian $\mathcal{H}(\theta)$, will be $2e^{-9re^{i\theta}}$. This is highly oscillatory and will be quite difficult to represent in the basis of real radial functions of the Direct Approach, where, again, the expansion coefficients themselves bear the whole burden of the fact that $\mathcal{H}(\theta)$ is not $\mathcal{H}$. This is all the more frustrating as in e^{-}-Ne scattering resonance, the 1*s* orbital probably plays no real role in the resonance formation. Apparently somewhat different, but in fact closely related, methods for solving this inner-shell problem have been introduced. The simplest to describe is:

METHOD OF COMPLEX BASIS FUNCTIONS A matrix element of the scaled Hamiltonian

$$I=\langle \chi_i(\vec{r})|\mathcal{H}(\theta)|\chi_j(\vec{r})\rangle,$$

which might occur in the Direct Approach, might well employ basis functions of the form

$$\chi_i(\vec{r})=A\big(\phi_{i(1)}(\vec{r}_1)\phi_{i(2)}(\vec{r}_2)\ldots\phi_{i(N+1)}(\vec{r}_{N+1})\big) \qquad 23.$$

in scattering of an electron from an N electron atom, A being an appropriately normalized antisymmetrizer. In the Direct Approach the $\phi_{i(1)}(\vec{r}_1)$ are of the form $R_i(r_1)Y_{lm}(\Omega_1)$ with $R_i(r_1)$ a real radial function. A moment's reflection indicates that the variable change $\vec{r}\rightarrow \vec{r}e^{-i\theta}$ in the matrix element leaves it invariant:

$$I=\langle \chi_i(\vec{r}e^{-i\theta})|\mathcal{H}|\chi_j(\vec{r}e^{-i\theta})\rangle$$

and thus, it is possible to reinterpret the Direct Approach as keeping the unscaled (normal) Hamiltonian, $\mathcal{H}$, but working with the complex radial functions $R_j(re^{-i\theta})$ implicit in

$$\chi_i(\vec{r}e^{-i\theta}) = A\left(\phi_{i(1)}(\vec{r}_1e^{-i\theta})\phi_{i(2)}(\vec{r}_2e^{-i\theta})\dots\phi_{i(N+1)}(\vec{r}_{N+1}e^{-i\theta})\right). \qquad 24.$$

However, as realized in a slightly different context by Rescigno & Reinhardt (15, 16, 18), the use of complex basis functions with the unscaled Hamiltonian is more flexible than the Direct Approach if we scale the different $\phi_j(\vec{r}_j)$ differently. The method is in general no longer equivalent to the spectral theory of dilatation analyticity, as it may well not correspond to an easily derived variable scaling of the operator. Thus, in introducing the method of complex basis functions for resonance determination, Rescigno & McCurdy (110, 111) have chosen to take $\mathcal{H}$ unscaled and to take

$$\begin{aligned}\chi_i = A\big(&\phi_{i(1)}(\vec{r}_1)\phi_{i(2)}(\vec{r}_2)\dots\phi_{i(k)}(\vec{r}_k)\phi_{i(k+1)}\\ &\times(\vec{r}_{k+1}e^{-i\theta})\dots\phi_{i(N+1)}(\vec{r}_{N+1}e^{-i\theta})\big)\end{aligned} \qquad 25.$$

where orbitals $i(1)$ through $i(k)$ correspond to a subspace of orbitals important for the static interaction, polarization, and correlation, and $i(k+i)$ through $i(N+1)$ correspond to the orbitals involved in resonance formation and scattering. Thus, inner shells are simply not scaled, thus avoiding the aforementioned inner-shell problem. This idea of not scaling "tight" orbitals and scaling "loose, or scattering" type orbitals is intuitively related to the concept of exterior scaling discussed below. The method has been applied to e$^-$-Be scattering in the static exchange approximation (111) and works well. More recently, K. T. Chung and B. Davis (private communication, 1981) have used an explicit multichannel version of this technique: They use $\mathcal{H}(\theta)$ and a trial function of the form

$$\begin{aligned}\Psi = A\Bigg(&\psi_1(\vec{r}_1e^{i\theta},\dots,\vec{r}_Ne^{i\theta})\\ &+\sum_i^{\substack{\text{open}\\ \text{channels}}}\phi_i^{\text{Target}}(\vec{r}_1e^{i\theta},\dots,\vec{r}_{N-1}e^{i\theta})\phi_N(\vec{r}_N)\Bigg)\end{aligned} \qquad 26.$$

where $\psi_1(\vec{r}e^{i\theta},\dots,\vec{r}_Ne^{i\theta})$ is just an L^2 eigenfunction of $\mathcal{H}(\vec{r})$, which approximates the resonance, with the indicated variable changes, and $\phi_i(\vec{r}_N)$, which represents the scattering electron, is expanded in Slaters. While this appears to differ from the Rescigno-McCurdy ansatz, note that the change of variables $\vec{r}\rightarrow\vec{r}e^{-i\theta}$, in both $\mathcal{H}(\theta)$ and Ψ, yields the former type ansatz. K. T. Chung and B. Davis have obtained results of exceptional stability for doubly excited states of He using this method.

METHOD OF COMPLEX SIEGERT FUNCTIONS Bardsley et al (112, 113), Junker & Huang (27, 114, 115), Junker (20, 116, 117), and Nicolaides et al (118–121) have implemented a method closely related to the Siegert method (3). The Bardsley & Junker paper (112) was the first computational application of any type of complex scaling to a resonance calculation. The use of complex coordinates was suggested to them by Nuttall, who was rather surprised by the way they used his suggestion: he had expected them to attempt a Direct Approach calculation.

Siegert proposed that one solve $\mathcal{H}\psi(r)=E\psi(r)$ with the boundary condition $\psi(r)\rightarrow e^{+ikr}/r$. With this unusual boundary condition, resonance solutions with complex E and k are found, but, k has a negative imaginary part implying that $\psi(r)$ diverges as $r\rightarrow\infty$, making the method problematic for computations. However, simply looking for formal solutions of the Schrödinger equation, if

$$\mathcal{H}\psi(r)=E\psi(r), \quad \text{then} \quad \mathcal{H}(\theta)\psi(re^{i\theta})=E\psi(re^{i\theta})$$

by simply regarding r as a dummy variable. Thus applying the Siegert condition amounts to solving

$$\mathcal{H}(\theta)\psi(re^{i\theta})=E\psi(re^{i\theta})$$

with the rotated Siegert condition

$$\psi(re^{i\theta})\rightarrow e^{ikre^{i\theta}}/(re^{i\theta})$$

which, if θ is large enough, is a decaying function even for k complex in the lower half k plane: a far more palatable boundary condition for actual applications. Thus if $k=pe^{-i\alpha}$ (p, α, real and positive), as long as $\theta>\alpha$, an L^2 Siegert function may be found. Thus, an L^2 eigenfunction in a sense suddenly "appears" as θ increases from 0 and finally becomes larger than α; this is highly reminiscent of the dilatation analyticity spectral theory, where a discrete eigenvalue "suddenly" appears as a cut rotates far enough into the lower half plane.

In fact, both methods have found the same L^2 eigenfunction, a fact recognized (and often exploited) by numerous workers, in addition to the above: for example, Nuttall (60); Atabek et al (122–124), the latter of these (124) containing an interesting discussion of optimization of θ; Isaacson et al (125, 126); Simons (127, 128). In particular, McCurdy & Rescigno (129a), Yaris & Taylor (129b), and Bačić & Simons (130) have been able to determine partial resonance widths (i.e. fractional decay into different open channels) via relationships involving Siegert boundary conditions, an alternative method to that of Noro & Taylor (131). Thus, excellent results for many atomic resonances are obtained using a trial function of the approximate form (written here for a single open channel)

$$\Psi = A\Big(\sum_i a_i\chi_i(\vec{r}_1e^{i\theta},\vec{r}_2e^{i\theta},\ldots,\vec{r}_{N+1}e^{i\theta}) + \phi^{\text{target}}(\vec{r}e^{i\theta})f(r_{N+1}e^{i\theta})\Big) \qquad 27.$$

where $f(re^{i\theta}) \rightarrow e^{ikre^{i\theta}}/re^{i\theta}$ asymptotically, is used in diagonalization of $\mathcal{H}(\theta)$ (not $\mathcal{H}$). In some cases k is determined self-consistently, in others (27) the method is generalized by using k as a complex variational parameter.

The two methods (complex coordinates and complex Siegert functions) are not as dissimilar as they appear. The trial function, Ψ, of Eq. 27 is employed with $\mathcal{H}(\theta)$. If both Ψ and $\mathcal{H}(\theta)$ are subject to the transformation $r_j \rightarrow r_je^{-i\theta}$ (for all j) and $k \rightarrow ke^{-i\theta}$, a trial function of the form of Eq. 25 is obtained, which is to be used with $\mathcal{H}$, just as in the Rescigno-McCurdy ansatz. The only difference is the expansion basis used for the term $f(\vec{r}_{N+1})$, which in both methods will be an L^2 function for θ large enough. Thus both methods solve the inner-shell problem in the same way. Moiseyev et al (132) have carried out a study of the two methods using a newly defined criterion for stabilized complex eigenvalues, with the conclusion that neither method works well. This is in strong contrast to the findings of other workers, and the origins of the differences should be resolved as soon as possible.

COMPLEX VARIATIONAL THEORY The observation that (Eqs. 22, 24)

$$\langle\chi_i(\vec{r})|\mathcal{H}(\theta)|\chi_j(\vec{r})\rangle = \langle\chi_i(\vec{r}e^{-i\theta})|\mathcal{H}|\chi_j(re^{-i\theta})\rangle$$

for all (i, j) implies that scaling all basis coordinates $\vec{r} \rightarrow \vec{r}e^{-i\theta}$ and leaving $\mathcal{H}$ unscaled is identically equivalent to a dilatation transform and has an identical spectral theory, provided only that the basis functions analytically continue. Thus, if a Direct Approach calculation gives a stabilized complex eigenvalue $E_R(\theta)$ at $\theta = \tilde{\theta}$, and

$$\Psi_R(\tilde{\theta}) = \sum_i c_i(\tilde{\theta})\chi_i(\vec{r}) \qquad 28.$$

$\bar{c}(\tilde{\theta})$ being an eigenfunction of the matrix representation of $\mathcal{H}(\theta)$ in the $\chi_i(\bar{r})$ basis, then the corresponding function in the rotated basis is

$$\tilde{\Psi}_R(\tilde{\theta}) \equiv \sum_i c_i(\tilde{\theta})\chi_i(\vec{r}e^{-i\tilde{\theta}}) \qquad 29.$$

[with the identical $c_i(\tilde{\theta})$] as $\bar{c}(\tilde{\theta})$ is automatically an eigenfunction [with the same $E_R(\tilde{\theta})$] of the matrix representation unscaled Hamiltonian $\mathcal{H}$, in the $\chi_i(\vec{r}e^{-i\theta})$ basis. As the spectral theory tells us to expect $\Psi_R(\tilde{\theta})$ to be L^2, $\tilde{\Psi}_R(\tilde{\theta})$ is also L^2, establishing the complete equivalence of the pairs $\{\mathcal{H}(\theta)$ with basis $\chi_i(\vec{r})\}$ and $\{\mathcal{H}$, with basis $\chi_i(\vec{r}e^{-i\theta})\}$ as far as computations are concerned. This is the old rotation group (physical rotations in this single occurrence!) duality: Do we rotate objects, or do we rotate the coordinates?

If coordinates corresponding to different electrons are scaled differently, however, [as in Rescigno et al (111)] a new flexibility is obtained. Further, if even coordinates in the radial expansion of a *single electron* are scaled differently

$$\left(\text{e.g.}\quad R(r)=re^{-\alpha r}+r^{2}e^{-\beta x},\quad \text{with}\quad \alpha\to\alpha e^{-i\theta_1},\beta\to\beta e^{-i\theta_2}\right)$$

use of complex basis functions gives still more flexibility. Note that even in this most general case, as only radial (rather than angular) coordinates are scaled, a stretching of coordinates (albeit nonuniform) is occurring without any angular distortion. We thus call this most general type of transformation a generalized dilatation transformation (GDT). It is defined by its action on the wave function. How are we to use this flexibility? Stillinger et al (133a, b) and Herrick et al (133c, 134, 135), beginning in the mid 1970s, have implicitly used a variational principle for resonances based on locating complex energy stationary points of the GDT functional (note that $\mathcal{H}$ is unscaled)

$$E^{GDT}(\Psi)\equiv\frac{\int(\Psi)^{GDT(*)}\mathcal{H}\Psi\,d\tau}{\int(\Psi)^{GDT(*)}\Psi\,d\tau}. \qquad 30.$$

The new quantity $\Psi^{GDT(*)}$ we define as the generalized dilatation transformation complex conjugate: GDT(*) implies that only those quantities (such as spherical harmonics) not involved in the GDT are conjugated. That is, only those quantities that would be conjugated in the absence of a GDT. The new GDT notation is introduced to indicate the generality of the variational theory implied. A simple example will make this clear. Given a one-dimensional radial Hamiltonian $\mathcal{H}(r)$, which might support both bound states and resonances, we write

$$R(r,\{\alpha_i\})=\sum_i c_i re^{-\alpha_i r}$$

and take

$$E^{GDT}\{c_i\alpha_i\}=\frac{\int_0^\infty R(r,\{\alpha_i\})\mathcal{H}(r)R(r,\{\alpha_i\})r^2\,dr}{\int_0^\infty R(r,\{\alpha_i\})^2 r^2\,dr} \qquad 31.$$

with no conjugates at all in this one-dimensional problem. We now vary all of the c_i and α_i independently, including independent complex variations. As the (possible) complex values of the c_i and α_i are associated with the GDT they are not involved in complex conjugation. This is clearly far more general than simply assuming, as would be the case in application of the method of complex coordinates [as in (111)] to a one-dimensional problem, that the trial function be of the form

$$R\left(re^{i\theta},\{\alpha_j\}\right)=\sum_j c_j\left(re^{-i\theta}\right)e^{-\alpha_j re^{-i\theta}},$$

with real α_j, which would then be made stationary without conjugation of the $e^{-i\theta}$'s. It is also more general than the variational theories discussed in (68, 70, 73), for example. Such a variation can only give stationarity, rather than the usual variational upper bound (which would be regained were ordinary *'s reinserted) even for the (real) ground state. Herrick attempted to publish an explicit discussion of these points (D. R. Herrick, 1978 preprint, 1981 private communication), but the complex-coordinate community was not yet prepared to understand the real import of his remarks: his 1978 paper was rejected. Quite independently, Junker (20, 96, 136, 137 and references therein) intuitively rediscovered the utility of Eq. 30 and applied it to several systems. Junker's broad grasp of the many forms of complex basis functions led him to the correct conclusions, even though one is confused by his implication (20, 96) that $\tilde{\Psi}_R(\tilde{\theta})$ of Eq. 29 is the continuation of $\Psi_R(\tilde{\theta})$ to $\theta \rightarrow 0$. It simply isn't, unless all the c_i's are independent of θ: they are not. This misinterpretation does not affect his conclusions. Junker calls the method of Eq. 30 *complex stabilization*, from its similarity to ordinary stabilization (138), and he cogently points out that the method can wreak havoc with boundary conditions. Additionally, Junker has, in a very successful series of calculations (20, 96), applied the method to a model problem, a e^--Be resonance, and to the Stark effect, and has pointed out that an earlier e^--Be calculation by Donnelly & Simons (140) also exemplifies the method. [Taylor & Yaris (139a) and Simons et al (139b,c) have discussed aspects of the relationship of various complex coordinate methods to the usual stabilization techniques.] Perhaps the most spectacular example is that of McCurdy et al (141), in which, in an SCF calculation of a Ca^- resonance employing real basis functions and a real Hamiltonian, use of the scalar product implicit to Eq. 30 with respect to the radial expansion coefficients (which are part of the GDT) gave a complex eigenvalue from the otherwise ordinary SCF equations. This is clearly a very powerful method, although its limitations are not yet defined. What is the distribution of eigenvalues for a large basis? The GDT(*) conjugation has clear origins in contour distortion and dilatation transformation theory, but its use as outlined in this section is of far greater generality.

Molecular Electronic Structure: Real Axis Clamped Nuclei

The spectral theory of Refs. (7, 21–25) is immediately valid for the full molecular problem, treating all nuclei and electrons as mobile particles. It is also immediately consistent with the Born-Oppenheimer approximation, but with a twist. Consider the H_2^+ Hamiltonian, with nuclei at $\vec{R}_\alpha$ and $\vec{R}_\beta$ in the Born-Oppenheimer approximation (no nuclear kinetic energies) and $\vec{r}_1$ denoting the electron coordinate

$$\mathcal{H} = -\frac{\nabla_1^2}{2} - \frac{1}{|\vec{r}_1 - \vec{R}_\alpha|} - \frac{1}{|\vec{r}_1 - \vec{R}_\beta|}. \qquad 32.$$

Can we simply take

$$\mathcal{H}(\theta) = -e^{-2i\theta}\frac{\nabla_1^2}{2} - e^{-i\theta}\left(\frac{1}{|\vec{r}_1 - \vec{R}_\alpha|} + \frac{1}{|\vec{r}_1 - \vec{R}_\beta|}\right) \qquad 33.$$

and, if so, what is its interpretation? This is transparently answered by inspection of the Hamiltonian in confocal elliptic coordinates (e.g. 142). If $r_\alpha = |\vec{r}_1 - \vec{R}_\alpha|$ and $r_\beta = |\vec{r}_1 - \vec{R}_\beta|$, and R is the scalar distance between nuclei, then

$$\mathcal{H} = -\frac{2}{R^2(\xi^2 - \eta^2)}\left[(\xi^2 - 1)\frac{\partial^2}{\partial \xi^2} + 2\xi\frac{\partial}{\partial \xi} + (1 - \eta^2)\frac{\partial^2}{\partial \eta^2} - 2\eta\frac{\partial}{\partial \eta} + \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2}\right)\frac{\partial}{\partial \phi^2}\right] - \frac{2}{R(\xi + \eta)} - \frac{2}{R(\xi - \eta)} \qquad 34.$$

where ϕ is the azimuthal angle and $\xi = (r_\alpha + r_\beta)/r$ and $\eta = (r_\alpha - r_\beta)/R$ are dimensionless. In these variables the expected scaling $e^{-i2\theta}KE$, $e^{-i\theta}PE$ can only arise if ξ, η are unscaled, and $R \rightarrow Re^{i\theta}$. That is, under the simultaneous scalings $r_\alpha \rightarrow r_\alpha e^{i\theta}$, $r_\beta \rightarrow r_\beta e^{i\theta}$ and $R \rightarrow Re^{i\theta}$. The conclusion is that, for an N-electron molecule with arbitrarily many nuclei, the naive transformation

$$\mathcal{H} \rightarrow \mathcal{H}(\theta) = e^{-2i\theta}KE + e^{-i\theta}PE$$

is consistent with the Born-Oppenheimer Approximation, but at complex internuclear distances. We call this the CCBOA (Complex Coordinate Born-Oppenheimer Approximation). There is absolutely nothing wrong with this, as observables are always matrix elements of transition operators over appropriate vibrational functions, and we can distort the contours! Thus, for a diatom, a transition moment between vibrational states $\psi_i(R), \psi_j(R)$ might be written in the form

$$\left| \int_0^\infty \psi_i(Re^{i\theta}) M(Re^{i\theta}) \psi_j(Re^{i\theta}) d(Re^{i\theta}) \right|^2. \qquad 35.$$

The electronic transition moment $M(Re^{i\theta})$ in Eq. 35 is exactly what would follow (automatically) from the use of $e^{-2i\theta}KE + e^{-i\theta}PE$. These points have been noted by Bardsley (143), Junker (136), and informally by the author and others (private communications from T. N. Rescigno, C. W. McCurdy, V. McKoy, J. Simons). However, no calculations of the CCBOA type have been carried out. There is an incredibly strong (and largely irrational, in most cases) resistance to thinking of complex R. What is done instead is to clamp the nuclei on the real axis, and only scale the electronic coordinates. We refer to this as the CCRACNA (Complex Coordinate Real Axis Clamped Nuclei Approximation); it initially caused no end of difficulty. Note carefully that the CCRACNA is not simply the Born-Oppenheimer approximation, which is not at all inconsistent with the simple scaling

$$\mathcal{H}(\theta) = e^{-2i\theta}KE + e^{-i\theta}PE.$$

The problems in the CCRACNA arise from the fact that if nuclear coordinates are left real, and an electronic coordinate $\vec{r}_i$ is scaled $\vec{r}_i \rightarrow \vec{r}_i e^{i\theta}$, the nuclear-electron interaction

$$\sum_\alpha |\vec{r}_i e^{i\theta} - \vec{R}_\alpha|^{-1}$$

is nonanalytic, (33), as the argument of the absolute value can vanish for a continuous range of values such that

$$|\vec{r}_i| = |\vec{R}_\alpha|, \hat{r}_i \cdot \hat{R}_\alpha = \cos\theta,$$

giving rise to a continuous line of square root branch points. McCurdy & Rescigno (144), and independently Moiseyev & Corcoran (145), nevertheless established that the CCRACNA could be made to work. In (144) in application to H_2^+ and a model problem this was done by the method of complex basis functions discussed above. Diffuse basis functions (only) were scaled $r \rightarrow re^{-i\theta}$, in a sense performing the scaling for $|\vec{r}_i| > |\vec{R}_\alpha|$ and avoiding the singularities. In (145) in applications to autoionizing states of H_2 and H_2^-, matrix elements of the RACNA Hamiltonian were analytically continued [see especially footnote 12 of (145) for an important remark on stability of this method for the Gaussian bases used in both (144) and (145)]. The success of these calculations prompted a quick response by Simon (146), who suggested use of an exterior scaling, as illustrated in Figure 5, where the coordinates are kept on the real r-axis long enough to get past any interior nonanalyticities. This is an old idea [Figure 5 is reproduced from (32)] but one that fills the bill, in that it allows formulation of a solid mathematical foundation for the CCRACNA. McCurdy (147) and Morgan & Simon (148) have analyzed the relationship between actual computations and the complex exterior scaling concept. Qualitatively, phrased in the language of GDT's, if we scale the diffuse basis functions, but not tight ones, a relationship (not an identity) can be established between the idea of Figure 5 and actual computations. This idea is implicit in the Siegert work of Isaacson & Miller (126). More recently, Deguchi & Nishikawa (149, 150), using the generator coordinate formulation of Lathouwers (151), have suggested a related approach, which has the very attractive feature that through generator coordinates nonadiabatic effects might well be included, although this has not yet been explored. Actual computational applications to molecules is a developing field. At present the only real electronic structure results are the following: the He+H Penning ionization calculations of (126); the H_2 and H_2^- work of (145); a calculation by Rescigno et al (152) of an N_2^- shape resonance [using a complex SCF formalism developed by McCurdy et al (153, 154) and concurrently by Froelich (see 155)]; and the work on competition between dissociation and autoionization of Moiseyev (156, 157).

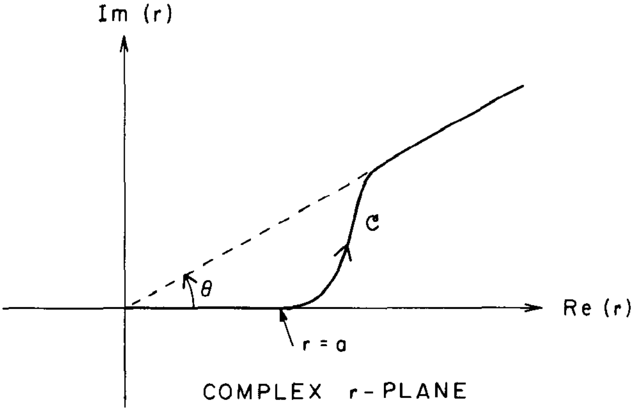

Figure 5 Exterior scaling contour for r distortion appropriate to a situation where for $r < a$ the potential is nonanalytic. As $r \rightarrow re^{i\theta}$ as $r \rightarrow \infty$, the spectral theory is unchanged, as the spectrum of $\mathcal{H}(\theta)$ is determined by asymptotic boundary conditions. Reproduced from (32), with permission.

Molecular Predissociation

All applications discussed so far (except the CCRACNA) have consisted of systems with one- and two-body interactions that scale as $PE \rightarrow e^{-i\theta}PE$ (or $PE \rightarrow e^{+i\theta}PE$ for the Stark problem); however, the general techniques have much greater applicability. For nuclear motion on a Born-Oppenheimer potential surface $V(\vec{r}_1,\ldots,\vec{r}_N)$

$$\mathcal{H}(\theta)=e^{-2i\theta}KE(\vec{r})+V\left(\vec{r}_1e^{i\theta},\vec{r}_2e^{i\theta}\ldots\vec{r}_Ne^{i\theta}\right). \qquad 36.$$

But where does one find $V(\vec{r}e^{i\theta})$? In a model this is simple; however, for an ab initio surface it perhaps seems a formidable problem. It isn't: We note with amusement that precisely this potential function of complex internuclear distance $(\vec{r}_1e^{i\theta},\ldots,\vec{r}_Ne^{i\theta})$ is that which would be immediately obtained from the simple ansatz of the CCBOA, rather than from the CCRACNA. Given such an $\mathcal{H}(\theta)$, one can, for example, look at rotational predissociation of diatoms (e.g. (158, 159) or at various predissociating channels in a tri-atom, say Ar(H_2). Chu (160) and Chu & Datta (161) have looked at rotational predissociation of van der Waals com-

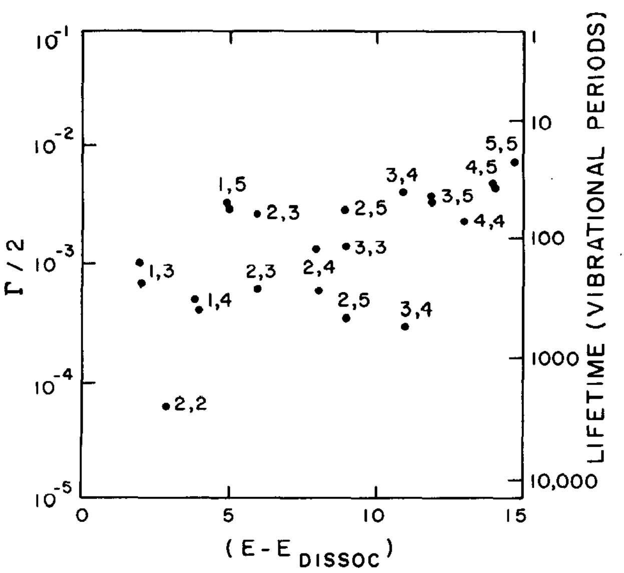

Figure 6 Imaginary parts of complex eigenvalues as a function of energy above dissociation for two coupled Morse oscillators. Parameters have been chosen to mimic interacting symmetric and antisymmetric stretches in H_2O. The states where lifetimes are shown are resonances corresponding to doubly excited states of the unperturbed oscillators. The lifetimes of these states are certainly nonstatistical. The complex eigenvalues were obtained by R. Hedges and W. P. Reinhardt using a spline basis.

plexes via $\mathcal{H}(\theta)$ of Eq. 36 as a Direct Application, i.e. diagonalization in a basis with no boundary conditions except square integrability. Chu has subsequently extended the method to consider molecular dynamics in strong laser fields (162).

Atabek & Lefebvre (163–165) and Bačić & Simons (130, 166) have developed multichannel Siegert-like formalisms which when used with complex coordinates allow use of square integrable boundary conditions using an L^2 expansion (130, 166) or numerical solutions (163–165) of the multichannel problem (see also 167). Model problems, usually involving linear triatoms or van der Waals predissociation, have been solved by these authors. Waite & Miller (168) and R. Hedges and W. P. Reinhardt (unpublished), using the Direct Approach, have examined resonance eigenvalue distributions for vibrational predissociation of very strongly coupled triatom systems and investigated the effect of potential surface on RRKM or non-RRKM (i.e. mode specific) decay rates. Typical complex eigenvalues obtained by R. Hedges and W. P. Reinhardt for a coupled Morse oscillator problem, modeling the symmetric and antisymmetric stretch in H_2O, are shown in Figure 6, where strongly nonstatistical behavior is seen for a sequence of multiply excited states above the dissociation limit. These results contrast with the results of (168) for the Henon-Heiles model problem, but are in rough consonance with a second model problem considered by Waite & Miller, where some mode specificity was observed.

CONCLUSIONS: THE FUTURE

Use of complex coordinate techniques in various guises is now widespread for determination of complex resonance eigenvalues in all types of physical situations: electronic autoionization, field ionization, molecular predissociation. Progress has been made in sorting out the amplitudes for decay into each of several decay channels when competing mechanisms exist. The computational theory for carrying out such calculations is becoming clearly defined. New computational variants, such as use of complex coordinates with many-body optical potentials (169–172), are continually appearing. What lies beyond?

Time Dependences

In many applications exponential decay is not a reasonable approximation. General time dependences are given by

$$|t\rangle = e^{-i\mathcal{H}(\theta)t/\hbar}|0\rangle \qquad 37.$$

where $\mathcal{H}(\theta)$ may be replaced by its biorthogonal spectral resolution, and thus

$$e^{-i\overline{\mathcal{H}}(\theta)t/\hbar} \cong \sum_j e^{-iE_j t/\hbar}\bar{c}_j\bar{c}_j^T \qquad 38.$$

where the E_j are complex. Equation 38 is a quadrature of continuum time dependence and exponential decay, as appropriate. This would seem to require that all vectors/eigenvalues of $\mathcal{H}(\theta)$ be found, a prohibitive task for large systems. However, this is not necessarily the case. Figure 7, prepared by the author for this discussion, shows time evolution of the probability of an H atom leaving the 1*s* state, on sudden application of a strong dc field. There is much *nonexponential* structure due to the sudden turn on. However, the most important feature of the results is that they have been obtained by a sequence of simple power expansion of Eq. 37 and Padé resummations: no eigenvalues or eigenvectors of $\overline{\mathcal{H}}(\theta)$ were even estimated. Converged results for short times were even found for $\theta = 0$! These results illustrate the capability of complex coordinate methods to handle complex time evolution, and indicate that systems of

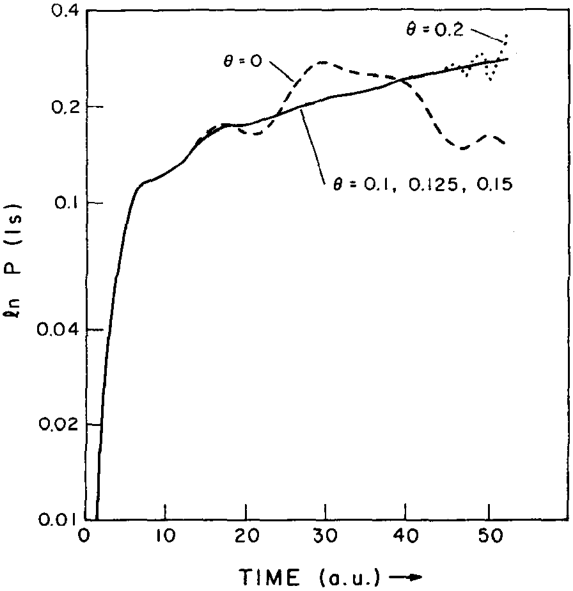

Figure 7 Time evolution of the probability of leaving the 1*s* state of atomic hydrogen under the influence of a suddenly applied dc electric field as computed by expansion of the exponential $\exp(-i\mathcal{H}(\theta)t/\hbar)$, without explicit determination of eigenparameters. This technique allows the use of very large matrix representations, and thus should allow extension to calculation of time evolution (and thus spectra) in molecular systems. The method has no great difficulty in coping with a multi-timescale decay process.

many degrees of freedom may well be approached, as time evolution can be calculated directly, without solution of large complex eigenproblems.

Scattering

As mentioned in the introduction, early motivation for moving branch cuts off the real axis was to make discretized solution of many-particle scattering problems tractible. Except for application to photoabsorption (173–176), a problem which can be reformulated as a complex eigenvalue problem in any case (99), this aspect has not been actively pursued. Why? Simply because scattering amplitudes of the form

$$\langle k|V(r)(z-H)^{-1}V(r)|k\rangle,$$

the $|k\rangle$'s being plane wave states, do not survive insertion of our unitary transform $U(\theta)U(\theta)^{-1}$ unless $V(r)$ is exponentially damped, apparently excluding the long-range interactions of atoms, molecules, and especially charged systems such as ions and electrons. However, if mathematical difficulties of this type had been taken too seriously many of the computations discussed in this review would not have been even attempted. One can only agree with the remarks of Taylor & Yaris (139a) that there are many ways to by-pass this apparent obstacle. Thus, a parting conjecture: Ways will soon be found to harness the power of complex coordinate techniques for solution of atomic and molecular scattering problems, as well as for determination of resonance parameters, and of time evolution of initially bound systems.

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