Method of Complex Coordinates: Application to the Stark Effect in Hydrogen*

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Abstract

The method of complex coordinates as applied to calculation of resonance parameters for dilatation analytic operators is discussed, and numerical evidence is presented that although the Stark potential is not dilatation analytic, many of the results of the theory seem to hold. In particular, Stark widths and shifts for the H atom ground state in weak and strong fields are calculated in spherical coordinates using only $L_z^2$ basis functions, giving results in excellent agreement with those of methods applying detailed boundary conditions in parabolic coordinates.

1. Introduction: Dilatation Analytic Operators

Very few results in scattering theory can be extended rigorously from the case of one-body potential scattering to multiparticle interacting systems. However, in the special case of nonrelativistic particles interacting via pairwise analytic potentials, many strong and reasonably specific results pertaining to the analytic structure of matrix elements of the resolvent, $(z - H)^{-1}$, and to the spectrum, $\sigma(H)$, of the Hamiltonian are becoming available. In the potential scattering case results are easily obtained via analysis of the Jost regular and irregular solutions by construction of the Jost function [1]. That is, the analysis is based on well understood properties of the solutions of second-order ordinary differential equations [2]. No correspondingly simple theory of the solutions of partial differential equations exists, and the most recent results have been obtained using techniques of functional analysis applied to the operators themselves. Functional analysis allows the spectra of closely related operators to be compared directly without detailed discussion of coordinate or permutation boundary conditions of the wave function. A useful class of comparison operators are those related to the usual nonrelativistic Hamiltonian $H(r)$ by the dilatation (or dilation) transformation $r \rightarrow e^{i\theta} r$, $\theta > 0$ and real. This transformation “rotates” the coordinates of H into the complex r plane. For example, the atomiclike Hamiltonian

$$H = H(r) = \sum_{i=1}^{N} \left( -\frac{1}{2} \frac{d^2}{dr_i^2} + \frac{L_i^2}{2r_i^2} \right) + \frac{1}{2} \sum_{i \neq j}^{N} V(r_{ij})$$

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* This paper is dedicated to the memory of George J. Schulz whose infectious interest in resonances and resonance phenomena in atomic and molecular processes stimulated a whole generation of theorists.
† Camille and Henry Dreyfus Teacher-Scholar.

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DILATATION TRANSFORMATION,
\[ H \rightarrow H(\theta) \]
\[ \sigma(\mathbf{H}) \rightarrow \sigma(\mathbf{H}(\theta)) \]

\[ r \rightarrow r e^{i\theta} \]

ONE BODY PROBLEM

Figure 1. Effect of the coordinate rotation \( r \rightarrow e^{i\theta}r \) on the spectrum of a one-body dilatation analytic Hamiltonian. The bound states are invariant, while the continuum "rotates" by an angle \( 2\theta \) about the scattering threshold.

\[ H \rightarrow H(\theta) \]
\[ \text{THERRESHOLD} \rightarrow \text{BOUND STATE IN CONTINUUM} \]
\[ \text{BOUND STATES} \rightarrow \text{BOUND STATES} \]
\[ \text{BOUND STATES} \rightarrow \text{BOUND STATES} \]

MANY-BODY CASE

Figure 2. Effect of the coordinate rotation \( r \rightarrow e^{i\theta}r \) on the spectrum \( \sigma(H) \) of a many-body dilatation analytic Hamiltonian. Bound states, whether isolated or embedded in a continuum, are invariant under the transformation. Real thresholds are also invariant, while the continua associated with them "rotate" by an angle \( 2\theta \) into the lower half complex energy plane. Isolated complex eigenvalues in the lower half-plane correspond to poles of the analytically continued resolvent \( (z - H(\theta))^{-1} \) and are identified with resonances. Although not shown in the figure, complex thresholds with associated cuts can appear for more than three particles interacting via pairwise Coulomb potentials.

becomes

\[ H(\theta) \equiv H(e^{i\theta}r) = e^{-2i\theta} \sum_{i=1}^{N} \left( -\frac{1}{2} \frac{d^2}{dr_i^2} + \frac{L_i^2}{2r_i^2} \right) + \frac{1}{2} \sum_{i \neq j}^{N} V(e^{i\theta}r_{ij}) \]  \( (2) \)

under the transformation. In particular, if the potential \( V \) is the Coulomb interaction,

\[ H(\theta) = e^{-2i\theta}T(r) + e^{-i\theta}V(r) \]  \( (3) \)

where \( T \) and \( V \) are the usual kinetic and Coulomb potential energies, respectively. The Coulomb Hamiltonian, Equation (3), falls into a class of many-particle operators called "dilatation analytic," a term introduced by Combes and coworkers [3, 4]. For our purposes the most important results of the theory of dilatation analytic operators have been given by Balslev and Combes [4]. The analysis of the Balslev–Combes paper is rather forbidding, but the results are fairly simple to state, and have been clearly expounded in a review, intended for physicists and chemists, by Simon [5].

Results of the theory of dilatation analytic operators, which apply directly to problems of nonrelativistic atomic and molecular quantum theory, relate to the deformation of the spectrum, \( \sigma(H) \) as \( \theta \) takes on nonzero real values. In the one-particle case the spectrum maps as shown in Figure 1, namely, discrete eigenvalues are invariant to the transformation, while the continuous spectrum is "rotated" by the angle \( 2\theta \). Figure 2 shows the corresponding result for a many-body Hamiltonian. In the many-body case as \( \theta \) increases
discrete real or complex eigenvalues of the non-Hermitian $H(\theta)$ may be “exposed.” Balslev and Combes have shown that the matrix elements $\langle \phi | (z - H(\theta))^{-1} | \phi \rangle$, for suitable $\phi$, provide the analytic continuation of the projected resolvent, $\langle \phi | (z - H)^{-1} | \phi \rangle$, into the lower half $z$ plane, and thus that the discrete complex eigenvalues of $H(\theta)$ correspond to poles of the projected resolvent on higher Riemann sheets, and may be identified with resonances. The real and imaginary parts of the complex eigenvalues give the resonance position $E_{\text{res}}$ and width $\Gamma/2$, respectively. The theory of dilatation analyticity thus provides a well-defined, albeit non-Hermitian, eigenvalue problem for the determination of resonance parameters.

After brief reviews, in Sections 2 and 3, of previous atomic applications of dilatation analyticity and of the Stark problem, we present in Section 4 a discussion of Stark broadening based on the ideas discussed above.

2. Previous Applications—A Brief Review

The results of dilatation analyticity (often referred to as the “coordinate rotation” or “complex coordinate” technique) have seen many applications in the past few years. Doolen, Nuttall, and Stagat [6] and, independently, Bardsley and Junker [7] have used the method to locate the lowest $1S$ resonance below the $n = 2$ threshold in $e$-H scattering. Similar results have been obtained by Hickman, Isaacson, and Miller [8]. Doolen [9] has presented a study of the numerical convergence problems associated with the method. From a more formal point of view, Simon [10] has used dilatation analyticity to prove that there are no positive energy bound states for $N$-body Coulomb systems. Doolen [11] has discussed the relevance of this result for the $H^a$ resonances seen by Peart and Dolder [12], and investigated numerically by Taylor and Thomas [13].

The coordinate rotation technique has been used as a computational method in scattering theory by, among others, Nuttall and Cohen [14] and Rescigno and Reinhardt [15, 16]. Rescigno, McCurdy, and McKoy [17] have used complex coordinates to investigate photoabsorption.

The computational advantages of the complex coordinate technique are obvious for resonances: resonance “searches” are reduced from solution of an energy-dependent scattering problem to a bound state type of eigenvalue problem, where spatial boundary conditions need not always be explicitly enforced. The advantages arising in calculation of scattering or photoabsorption cross sections follow from the fact that the resolvent $(z - H(\theta))^{-1}$ is not singular for real $z$ if $\theta \neq 0$, unlike the usual operator $(z - H)^{-1}$ appearing in the kernel of the Lippmann–Schwinger equation.

3. The Stark Effect

The problem of an atom in an electric field is a classic example of a nonanalytic perturbation. For arbitrarily small field strength $F$ the spectrum of the Stark Hamiltonian

$$H^{\text{Stark}} = H^{\text{atomic}} + Fz$$

has no discrete eigenvalues, and a continuous spectrum running from $-\infty$ to $+\infty$. However, in the limit that $F$ is identically zero we regain the usual discrete, or bound-state, spectrum of the atomic Hamiltonian $H^{\text{atomic}}$. This aspect of the Stark problem has been discussed by, among others, Titchmarsh [18], Kato [19], Rellich [20], Fredrichs [21], Rejtö [22] in terms of the possible meaning of ordinary perturbation theory as it applies
to such a nonanalytic perturbation and with respect to the concept of “spectral concentration” [5, 18] as a mathematical technique for discussing the experimental fact that quasidiscrete atomic states are still obtained up to very high fields, and at lower fields seem to have rather well-defined energies.

Many computational methods for calculation of Stark shifts and widths have been proposed. Citing only recent work, Stark parameters have been calculated by Alexander [23], using a polynomial expansion technique coupled with a WKB type asymptotic form; by Hirschfelder and Curtiss [24] who have directly integrated the Stark differential equation in parabolic coordinates; and by Hehenberger, McIntosh, and Brändas [25] using the Weyl “m method” to directly calculate the spectral concentration. All these methods essentially treat the Stark effect as a scattering problem, and thus all require at least an approximate specification of the coordinate space asymptotic form of the wave function. Methods which are independent of specification of an asymptotic boundary condition are the minimum variance method [26, 27] recently applied to the Stark problem by Froelich and Brändas [28], and the complex coordinate approach discussed below.

4. Application of the Complex Coordinate Technique to the Stark Problem—A Numerical Experiment

In spherical coordinates the appropriate Hamiltonian describing an H atom in a constant electric field of strength $F$ (a.u.) is

$$H_{\text{Stark}}(r) = H^0(r) + Fr \cos \alpha$$

where $H^0$ is the Coulomb Hamiltonian, and $\alpha$ is the angle between the radius vector and the field. $H_{\text{Stark}}$ is not spherically symmetric and couples all $l$ values, although the $Fr \cos \alpha$ coupling connects only adjacent $l$ blocks (usual dipole coupling). The H-atom Stark problem is separable in parabolic coordinates, but for applications to more complex atomic systems it will probably be advantageous to work in spherical coordinates where the atomic problem itself is more easily handled.

One might expect that under the dilatation transformation

$$H_{\text{Stark}}(r) \rightarrow H_{\text{Stark}}(\theta) \equiv H^0(e^{i\theta}r) + Fe^{i\theta}r \cos \alpha$$

the theory described in the Introduction would immediately allow identification of particular complex eigenvalues of the non-self-adjoint operator $H_{\text{Stark}}(\theta)$ with the Stark broadened and shifted states of $H^0$. This is not the case. First of all it is not immediately clear what happens to the continuous spectrum of $H^0$ under the transformation. Rather than a simple rotation of the continua by angles of $2\theta$ into the lower half-plane, as in the examples of Figures 1 and 2, in the Stark case the branch points themselves move to $-\infty$ for any finite field strength. This is yet another symptom of the fact that the application of the Stark field does not give an ordinary scattering problem, where it would always be possible to define threshold energies (onsets of continua) entirely in terms of $H^0$. This nonanalytic motion of the branch point as a function of $F$ does not contradict any results of the theory of dilatation-analytic operators, they simply do not apply. $Fr \cos \alpha$ is not bounded at infinity and thus does not meet the criteria for application of either the potential scattering or Balslev–Combes results. However, lack of a rigorous theoretical justification does not prevent the carrying out of experimental calculations. We present numerical evidence that $H_{\text{Stark}}(\theta)$ has complex eigenvalues whose real parts represent the Stark shifts of the hydrogenic energy levels, and whose imaginary parts represent
the widths of these levels which have only a finite lifetime, $\tau \approx 1/\Gamma$, due to the possibility of ionization by the field. The Stark resolvent, $\langle (z - H^\text{Stark})^{-1} \rangle$ will correspondingly have a complex pole at $z = E^{\text{res}} - i\Gamma/2$ on a higher nonphysical Riemann sheet as has been discussed by Titchmarsh [29].

To investigate the eigenvalues of $H^\text{Stark}(\theta)$ the spectrum was discretized by use of the orthonormal Laguerre type basis [30]

$$\phi_{n,l} = C_{n,l}(\lambda_l)r^{l+1}e^{-(\lambda_l/2)r}\lambda^{l+2}_n(\lambda_l)r$$

$c_{n,l}(\lambda)$ being a normalization coefficient. $H^0(\theta)$ is block diagonal in this basis, with the $l$th block connected to the $(l\pm 1)$th block via matrix elements of the form

$$e^{i\theta}\mathcal{A}(l,l \pm 1)\langle \phi_{n,l}|\phi_{n,l\pm 1}\rangle$$

where $\mathcal{A}(l,l \pm 1)$ arises from the angular integrations [31]. For simplicity of calculation, and to systematize convergence studies, each $l$ block was taken to be of dimension $N$, and all the $\lambda_l$s were taken to be equal. Convergence was then studied for each fixed value of $F$ as a function of $\theta, N, \lambda$, and $l_{\text{max}}$, $l_{\text{max}}$ being the maximum angular momentum used in a given calculation. The dimension of the discretized $H^\text{Stark}$ is thus $N \times (l_{\text{max}} + 1)$ in the following.
Figures 3 and 4 show convergence of the shifted and broadened hydrogenic 1s energy level as a function of $N$ for fixed $\lambda$, $l_{\text{max}}$, and $\theta$, for a field $F = 0.1$ a.u. ($5.4 \times 10^6$ V/cm). Convergence to the complex eigenvalue is systematic and follows the spiral pattern which seems to be characteristic of asymptotic convergence to a complex eigenvalue in many discretized one-dimensional problems. Inspection of the figures reveals that the rate of convergence is strongly dependent on the rotation angle $\theta$, convergence being considerably faster for $\theta = 0.2$ than for $\theta = 0.1$. To investigate the rate of convergence as a function of $\theta$, a series of calculations were carried out for fixed $N$, $l_{\text{max}}$, and $\lambda$. Typical results are shown in Figure 5, where the “$\theta$ trajectories” of the complex eigenvalue are shown (note the greatly expanded scale) for $20 \times 20$ and $40 \times 40$ calculations, again for $F = 0.1$ a.u. The behavior of these $\theta$ trajectories is typical of that discussed by Doolen [11]. Near the “converged” result the trajectories “pause,” and $\theta$ trajectories arising from different basis sets intersect or approach one another closely. The $\theta$ trajectories of Figure 5 suggest that an optimal value of $\theta$ is 0.4 or 0.5 radian for $F = 0.1$ and $\lambda = 1.5$, as used in the present calculations. Calculations performed as a function of $N$ and $l_{\text{max}}$ for $\theta = 0.4$ indeed converged rapidly. Typical results are shown in Table I. Convergence was equally satisfactory for smaller fields, as is indicated by the results shown in Table II.

5. Summary and Discussion

Although the Stark perturbation $F r \cos \alpha$ does not fit into the class of potentials which allows immediate application of the results of dilatation analyticity, we have presented
Figure 5. \( \theta \) trajectories of a complex eigenvalue of \( H^{\text{Stark}}(\theta) \) corresponding to the 1s state of hydrogen for a field of 0.1 a.u. The location of a resonance is indicated by a "stationary point" in a trajectory as a function of \( \theta \), as discussed in [11]. Note that the scale has been greatly expanded in comparison with Figures 3 and 4. \( I_{\text{max}} = 3 \) and \( \lambda = 1.5 \) in these calculations.

Numerical evidence that \( H^{\text{Stark}}(\theta) \) has complex "resonance" eigenvalues which give the shifts and widths of hydrogenic energy levels in a dc electric field. Possible advantages of the present method are that no coordinate space boundary conditions need be enforced, and that only finite matrix techniques are employed. This leads one to hope that the method can be extended to treatment of complex atoms and molecules in intense electric fields.

**Table I.** Convergence of the complex eigenvalue representing the shifted and broadened 1s state of hydrogen in a field \( F = 0.1 \) a.u. as a function of \( N \) and \( I_{\text{max}} \).

<table>
<thead>
<tr>
<th>( N )</th>
<th>( I_{\text{max}} = 3 )</th>
<th>( I_{\text{max}} = 4 )</th>
<th>( I_{\text{max}} = 5 )</th>
<th>( I_{\text{max}} = 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(-0.527313 - 0.7465 \times 10^{-3}i)</td>
<td>(-0.527381 - 0.7154 \times 10^{-3}i)</td>
<td>(-0.527404 - 0.7225 \times 10^{-3}i)</td>
<td>(-0.527335 - 0.7259 \times 10^{-3}i)</td>
</tr>
<tr>
<td>8</td>
<td>(-0.527349 - 0.7469 \times 10^{-2}i)</td>
<td>(-0.527392 - 0.7237 \times 10^{-2}i)</td>
<td>(-0.527429 - 0.7289 \times 10^{-2}i)</td>
<td>(-0.527415 - 0.7273 \times 10^{-2}i)</td>
</tr>
<tr>
<td>10</td>
<td>(-0.527367 - 0.7450 \times 10^{-2}i)</td>
<td>(-0.527395 - 0.7234 \times 10^{-2}i)</td>
<td>(-0.527428 - 0.7270 \times 10^{-2}i)</td>
<td>(-0.527417 - 0.7271 \times 10^{-2}i)</td>
</tr>
<tr>
<td>12</td>
<td>(-0.527346 - 0.7449 \times 10^{-2}i)</td>
<td>(-0.527396 - 0.7234 \times 10^{-2}i)</td>
<td>(-0.527427 - 0.7270 \times 10^{-2}i)</td>
<td>(-0.527417 - 0.7270 \times 10^{-2}i)</td>
</tr>
</tbody>
</table>

\( N \) is the number of basis functions per \( l \) value; partial waves with \( l = 0, 1, \ldots, I_{\text{max}} \) are coupled by the field. The shift \( \Delta E = (E_{\text{res}} - (E_n^N)) \) and width \( \Gamma/2 \) calculated by Alexander [23] are \(-0.027\) and \(-0.75 \times 10^{-2}\) a.u., respectively; and as calculated by Hehenberger and coworkers [25], \(-0.0274\) and \(-0.725 \times 10^{-2}\) a.u. \( \theta = 0.4 \) in these calculations.
TABLE II. Convergence of the complex eigenvalue $E_{\text{res}} - i\Gamma/2$ of $H_{\text{Stark}}(\theta)$ representing the shifted and broadened hydrogenic 1s state in a Stark field with $F = 0.03$ a.u. as a function of $N$ and $l_{\text{max}}$ for $\theta = 0.1$ radian.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$l_{\text{max}} = 7$</th>
<th>$l_{\text{max}} = 9$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{res}}$</td>
<td>$-\Gamma/2$</td>
</tr>
<tr>
<td>6</td>
<td>-0.502707425</td>
<td>$+9.96 \times 10^{-9}$</td>
</tr>
<tr>
<td>7</td>
<td>-0.502707420</td>
<td>$-1.080 \times 10^{-8}$</td>
</tr>
<tr>
<td>8</td>
<td>-0.502707427</td>
<td>$-1.106 \times 10^{-8}$</td>
</tr>
<tr>
<td>9</td>
<td>-0.502707427</td>
<td>$-1.112 \times 10^{-8}$</td>
</tr>
<tr>
<td>10</td>
<td>-0.502707427</td>
<td>$-1.117 \times 10^{-8}$</td>
</tr>
<tr>
<td>12</td>
<td>-0.502707427</td>
<td>$-1.1184 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

The shift $\Delta E = (E_{\text{res}} - E_{1s})$ and width $\Gamma/2$ calculated by Alexander [11] are $-2.074273 \times 10^{-3}$ and $1.15 \times 10^{-4}$, a.u., respectively.

Acknowledgment

The author gratefully acknowledges the computational assistance of Shih-I Chu who performed the convergence studies shown in Figure 5 and Table 1. Many thanks are also due to Messrs. Löwdin, Ohrn, and Brändas for their superb organization of the Sanibel Symposium.

This work was partially supported by the National Science Foundation under Grants MPS72-05169 A02 and MPS74-19605, and by ERDA.

Bibliography


Received March 2, 1976