

Competition Among Molecular Fragmentation Channels Described with Siegert Channel Pseudostates

Edward L. Hamilton and Chris H. Greene

Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440

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To describe multiple interacting fragmentation continua, we develop a method in which the vibrational channel functions obey outgoing wave Siegert boundary conditions. This paper demonstrates the utility of the Siegert approach, which uses channel energy eigenvalues that possess a negative imaginary part. The electron scattering energy in each such channel is rotated upward, giving it an equal and opposite imaginary part. This permits a natural inclusion of vibrational continua without requiring them to appear as explicit channels in the scattering matrix. Calculations illustrate the application of this theory to photoionization, photodissociation, and dissociative recombination.

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In this Letter, we propose a general method for describing coupling between electronic and dissociative continua, based on a Siegert pseudostate basis representation of the vibrational degree of freedom. The underlying rationale for this idea traces back to the recognition by Kapur and Peierls [1] that the narrow resonances of a scattering spectrum can be described in terms of a complex energy eigenstate, with the imaginary part of the energy defining a resonance width parameter. This proposal was further developed by Siegert [2] in two important ways. First, Siegert showed that for any Hamiltonian a set of eigenstates may be chosen to satisfy pure incoming or outgoing wave boundary conditions in the asymptotic limit. Second, and of importance to our work, Siegert's derivation allowed for overlapping resonances of arbitrary width. Siegert eigenstates formally correspond to S -matrix poles in the complex plane. Sharply resonant features associated with bound states can be identified with poles lying on the real axis, while broad background scattering can be described by closely spaced complex eigenstates that serve as a discretized approximation to the true continuum.

Traditionally, the use of Siegert states has been complicated by the nonlinearity of the associated eigenvalue

problem. Because the wave number appears linearly in the boundary condition but quadratically (as the energy) in the eigenvalue, the eigenproblem is quadratic, and in the past could only be solved iteratively. Tolstikhin *et al.* [3,4] recently demonstrated how this difficulty may be circumvented using finite range *Siegert pseudostates*.

Initially, the true asymptotic boundary condition is replaced by a finite range approximation,

$$\left(\frac{d}{dR} - ik\right)\phi(R) \Big|_{R=R_0} = 0, \quad (1)$$

where R_0 indicates the range of the potential. We expand into a primitive basis set,

$$\phi(R) = \sum_{j=1}^N c_j y_j(R), \quad 0 \leq R \leq R_0. \quad (2)$$

Here N is the dimension of our basis, and we have selected a nonorthogonal B -spline basis for the $y_j(R)$. Inserting this into the Schrödinger equation, premultiplying by $y_{j'}$, and employing the boundary value (1), we find a matrix equation for the coefficients c_j ,

$$\sum_{j=1}^N \left(\frac{1}{2} \int_0^{R_0} \frac{dy_{j'}}{dR} \frac{dy_j}{dR} dR - \frac{ik}{2} y_{j'}(R_0) y_j(R_0) + \int_0^{R_0} y_{j'}(R) \mu [V(r) - E] y_j(R) dR \right) c_j = 0. \quad (3)$$

Note that we have used a Green's theorem identity, and that the Hamiltonian has been multiplied through by the reduced mass μ . Written more concisely in matrix notation, we have a system of the form

$$(\tilde{\mathbf{H}} - ik\mathbf{L} - k^2\mathbf{O})\tilde{\mathbf{c}} = 0, \quad (4)$$

where $L_{j,j'}$ is the surface matrix $y_j(R_0)y_{j'}(R_0)$, $\tilde{H}_{j,j'}$ is the matrix $2\mu H_{j,j'} + y_j(R_0) \frac{d}{dr} y_{j'}(R_0)$, and \mathbf{O} is the overlap matrix for the spline basis set.

This equation is manifestly nonlinear, but the method of Tolstikhin *et al.* allows it to be "linearized" by recast-

ing it as a new eigensystem in a basis of doubled dimension ([5,6] discuss related techniques for solving differential equations where the eigenvalue appears in a boundary condition). We define $d_i = ikc_i$, yielding a trivial second equation $ik\mathbf{O}\tilde{\mathbf{c}} = \mathbf{O}\tilde{\mathbf{d}}$. Substituting this into the original eigenequation now gives a linear equation in the doubled basis space,

$$\begin{pmatrix} \tilde{\mathbf{H}} & 0 \\ 0 & -\mathbf{O} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{c}} \\ \tilde{\mathbf{d}} \end{pmatrix} = ik \begin{pmatrix} \mathbf{L} & -\mathbf{O} \\ -\mathbf{O} & 0 \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{c}} \\ \tilde{\mathbf{d}} \end{pmatrix}. \quad (5)$$

This is an equation for the eigenvalue $\lambda = ik$, giving $2N$ solutions lying either on the $(\text{Re } \lambda)$ axis or in conjugate pairs in the right half of the complex plane.

In their work, Tolstikhin *et al.* used completeness properties of the Siegert state set to construct a Green's function of the Hamiltonian, a scattered solution, and the associated scattering matrix, for a variety of single channel model problems. For systems with multiple channels, we instead appeal to the well-understood machinery of multichannel quantum defect theory (MQDT).

For resonance series corresponding to high electronically excited intermediates (Rydberg states) of diatomic molecules, the most natural description of the system is one with quantum defect parameters defined in terms of a fixed internuclear distance R and a well-defined projection of the orbital angular momentum Λ onto the axis of symmetry. This is because the electron spends most of its time far from the nuclear core and, when it does penetrate into the core, it gains enough speed from falling through the Coulomb potential that the nuclei are essentially frozen on the time scale of its motion. The quantum defect functions $\mu_\Lambda(R)$ in this representation, the so-called "body frame," may either be calculated from highly accurate *ab initio* techniques, or extracted from a semi-empirical fitting of experimental data [7]. In order to connect them with the true asymptotic ionization channels defined in terms of Siegert pseudostates of the residual core, $j = \{v^+, N^+\}$, a *frame transformation* must be performed [8,9], where N^+ is the ionic rotational momentum, and v^+ is the vibrational quantum number of the pseudostates. In our procedure, we directly evaluate the S matrix by the frame transformation integral,

$$S_{j,j'} = \sum_{\Lambda} \langle N^+ | \Lambda \rangle \int_0^{R_0} \phi_j(R) e^{2i\pi\mu_\Lambda(R)} \phi_{j'}(R) dR \langle \Lambda | N^{+'} \rangle + i \sum_{\Lambda} \langle N^+ | \Lambda \rangle \frac{\phi_j(R_0) e^{2i\pi\mu_\Lambda(R_0)} \phi_{j'}(R_0)}{k_j + k_{j'}} \langle \Lambda | N^{+'} \rangle. \quad (6)$$

The surface term in (6) also arises in the orthonormality relation [3]. A similar transformation converts the body-frame transition dipole elements $D_\Lambda(R)$ into reduced dipole matrix elements in the same S -matrix representation,

$$D_j^S = (2J + 1) \sum_{\Lambda} \langle \Lambda | J_0 \rangle^{(j)} \langle \Lambda | N^+ \rangle \times \int_0^{R_0} \phi_0(R) D_\Lambda(R) e^{i\pi\mu_\Lambda(R)} \phi_j(R) dR. \quad (7)$$

Here $\phi_0(R)$ is the initial vibrational wave function, and J_0 and J are the total angular momenta of the initial and final states of the system, respectively. Note that the Siegert pseudostates are *never* conjugated in these expressions, even when they formally belong to the dual ("bra") space. This means that the quantity labeled as $\tilde{D}^{S\dagger}$ below is calculated by conjugating only $e^{i\pi\mu_\Lambda(R)}$ in the definition above, and not the dipole matrix elements directly.

At this stage of the calculation, no information about the long-range behavior of the channels has yet been included, and since the body-frame quantum defects are nearly energy independent, the resulting S matrix is typically a smooth and fairly weak function of energy. The method of *channel elimination* [10,11] systematically eliminates flux in all electronic channels below the energy threshold for electron escape (the "closed-channel subspace") to form a "physical" S matrix, S^{phys} , by taking the proper linear combination of short-range solutions that ensures exponential decay at infinity. For a long-range Coulomb potential, this procedure gives

$$S^{\text{phys}} = S_{oo} - S_{oc}(S_{cc} - e^{-2i\beta})^{-1}S_{co}. \quad (8)$$

Here, β is a diagonal matrix of the usual Coulomb long-range phase parameter $\pi(\nu_j)$, where ν_j is the (possibly complex) effective quantum number in the j th channel, S is the scattering matrix, and the subscripts indicate partitions of the matrices into closed and open subspaces [11].

For a Siegert state basis, this physical scattering matrix is in general *not* unitary, but rather subunitary, reflecting the loss of flux at the boundary R_0 via coupling to the Siegert pseudocontinuum states. It may be used to calculate partial cross sections by means of conventional formulas, but with the departure from unitarity, $1 - \sum_j |\mathbf{S}_{j,j'}^{\text{phys}}|^2$, identified as the probability $|\mathbf{S}_{d,j'}^{\text{phys}}|^2$ for scattering into the dissociative continuum. This method also provides all quantities necessary to find the partial photoionization cross section into any open channel, σ_j ; see Eq. 2.59 of [11] for further details. The contributions from all open channels may then be summed to give the total cross section for photoionization.

Alternatively, the total photoabsorption cross section may be found directly from a "*preconvolution*" formula first derived by Robicheaux to handle the energy smoothing of densely spaced resonances [12,13],

$$\sigma_{\text{total}}(E) = \frac{4\pi^2\alpha\omega}{3(2J_0 + 1)} \text{Re } \tilde{D}^{S\dagger} \frac{1 + \mathbf{S}e^{2i\beta}}{1 - \mathbf{S}e^{2i\beta}} \tilde{D}^S \quad (9)$$

where Re signifies taking the real part of everything that follows, and the \dagger here conjugates only the operator, not the entire matrix element. The diagonal matrix written as $e^{-2i\beta}$ has a nontrivial definition in terms of the quantum defect parameters, it may be approximated quite well by taking $\beta_j = i\infty$ for "closed" channels with $(E) < \text{Re } E_j$, and $\beta_j = \pi\nu_j$ for "open" channels with $(E) > \text{Re } E_j$. Here E is the total energy of the system, E_j is the threshold energy for channel j , and $\nu_j = 1/\sqrt{2(E_j - E)}$ on the branch where $\text{Im } \nu > 0$. The utility of this expression lies in recognizing that the value of the cross section at a complex energy in the above formula is equivalent to the cross section at a real energy, smoothed over a channel-dependent width $\Gamma_j = 2 \text{Im } \epsilon_j$. In the Siegert state formulation, the electron energy $\epsilon_j = E - E_j$ will take on a complex value in any channel where the channel eigenenergy E_j is complex, while E remains real.

Given \mathbf{S} and ϵ_j , either of the two cross-section formulas above may be evaluated, with appropriate allowances for the possibility of complex energy eigenvalues. Note that the first procedure simply gives a sum over the flux into specific ionization channels, while the second gives a single value for the total photoabsorption cross section. This means that the latter will contain information about the solution wave function along the $R = R_0$ boundary not contained in any of the open ionization channels. In general, the value of σ_{total} will be equal to or greater than the sum over the individual σ_j , and any difference may be attributed to the effect of coupling to high-lying Siegert states in the continuum. Thus, the difference between these two formulas yields the dissociative cross section.

In order to test the validity of this hypothesis, we have defined a set of Siegert pseudostates for the H_2^+ internuclear potential. The eigensolutions fall into three classes, as shown in Fig. 1. Those lying on the positive ($\text{Im } k$) axis are associated with negative eigenenergies on the physical sheet of the E plane, the bound states of the potential. These are the channel thresholds to which the Rydberg autoionization series of the ionization spectrum converge, and so we include all of their states. The solutions along the negative ($\text{Im } k$) axis lie on the unphysical energy sheet, and we reject them as anti-bound states arising from the doubling of the dimension space. The remainder of the solutions fall above and below the ($\text{Re } E$) axis, corresponding to conjugate solution pairs of the eigenvalue parameter $\lambda = ik$. We select only those with negative $\text{Im } E_j$, ensuring that they obey outgoing wave boundary conditions. (This amounts to selecting only those states that contribute to the retarded, rather than the advanced, Green's function. See [14] for a related discussion.) For MQDT matrix elements, one may also reject states lying high in the continuum, since their Franck-Condon overlap with the bound states is negligible.

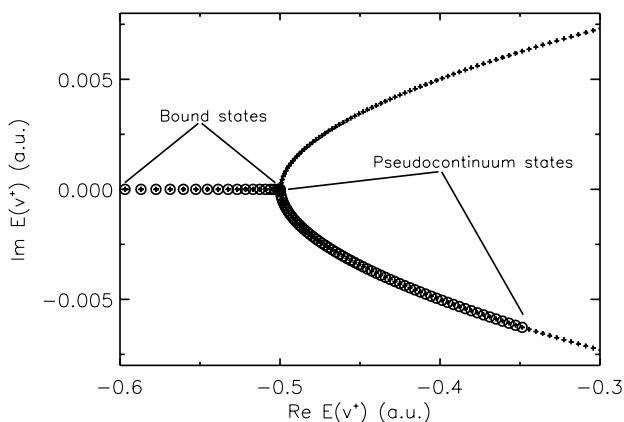


FIG. 1. Distribution of H_2^+ vibrational Siegert pseudostate energies in the complex energy plane for angular momentum $N^+ = 1$. Only the circled states are included as channels in the scattering matrix.

Tolstikhin *et al.* discuss the unusual completeness relation obeyed by the full set of Siegert pseudostates, with an additional factor of 2. Our restricted subset of Siegert pseudostates does not, of course, obey that doubled completeness relation. We have confirmed through numerical tests, however, that our restricted subset behaves similar to a complete set, to at least 10^{-12} accuracy, for representing either L^2 functions confined within the boundary or functions with purely outgoing wave character at the boundary. For an impressive demonstration (in a somewhat different context) of the convergence properties of a similarly truncated Siegert basis also used to describe smooth continuum physics, see [15].

In the region of the ungerade H_2 spectrum between 127 200 and 127 800 cm^{-1} , there are several strongly predissociated resonances, members of the $np\pi, v^+ = 8$ and $np\pi, v^+ = 5$ series. In each case, our calculated spectrum correctly reproduces them in the total absorption cross section, but shows them as weak or absent in the ionization. Comparisons of our results with other theoretical and experimental values [7,16] for selected resonances appear in Table I. Note particularly that we are able to correctly describe the strong rotational dependence of the $4p\pi, v^+ = 5$ branching ratio, a nontrivial consequence of subtle channel interactions.

As a test of the method in an entirely different energy regime, we considered the problem of dissociative photoionization, a three-body breakup channel accessible only at much higher energies. Experimental measures of the ratio between pure ionization and dissociative ionization have been performed since the 1970s by a number of researchers [17–19], along with at least one early theoretical calculation [20]. Since our ionization spectrum is a sum over individual channels, we can easily distinguish between contributions from channels above and below the dissociative threshold. Our results, plotted against those of past experiment and theory, are presented in Fig. 2.

TABLE I. Photoionization and photodissociation yields for select ungerade resonances in H_2 for which the relative yields have been experimentally observed [16].

State	Source	Energy	% Ion.	% Diss.
$3p\pi, v^+ = 8, R(0)$	Observed	127 248.2	10(5)	95(5)
	Theory [7]	127 246.9	1	99
	Present	127 242.2	1	99
$5p\sigma, v^+ = 4, R(0)$	Observed	127 599.4	90(10)	10(10)
	Theory [7]	127 602.2	88	12
	Present	127 606.8	76	24
$4p\pi, v^+ = 5, R(0)$	Observed	127 667.6	82(5)	18(5)
	Theory [7]	127 665.4	93	7
	Present	127 666.6	97	3
$4p\pi, v^+ = 5, R(1)$	Observed	127 599.4	30(10)	70(10)
	Theory [7]	127 758.4	17	83
	Present	127 759.5	29	71

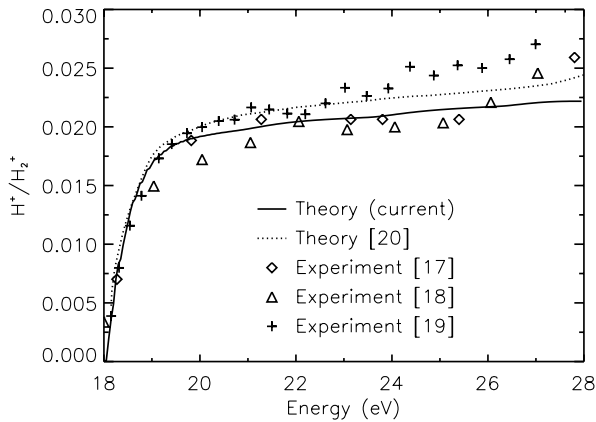


FIG. 2. Dissociative photoionization cross section, as a ratio to the total photoionization cross section.

Finally, we have performed a model calculation demonstrating the utility of our method for treating dissociative recombination, particularly in systems where indirect channels (those involving scattering into intermediate autodissociating Rydberg states) play an important role. Figure 3 shows the dissociative recombination spectrum of a simplified H_2 model potential (neglecting rotation and with R -independent quantum defects), compared with the O'Malley approximation for smooth background scattering by direct processes [21]. Our spectrum accurately reproduces this background, and also describes complex interference effects from the series of resonances converging to each Rydberg threshold.

Some aspects of the Siegert MQDT method remain poorly understood, and would benefit from greater clarification. For example, the utility of a subset of the Siegert basis for MQDT depends on ability of that subset to represent all energetically accessible regions of the continuum. While this requirement appears from our numerical tests to be reasonably easy to satisfy, we have not yet rigorously derived it from the relevant completeness relations. Also, it is not presently clear how to extend the energy-smoothed formula to include non-Coulombic long-range electronic potentials.

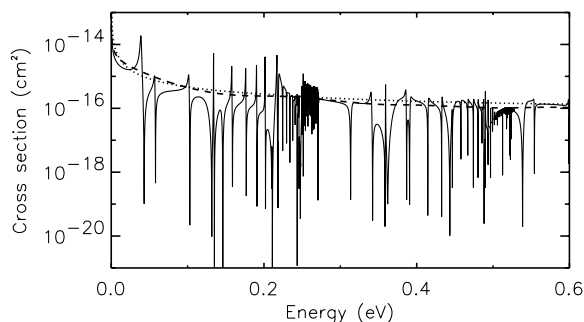


FIG. 3. Dissociative recombination cross section for the model potential, unconvolved (solid) and convolved with a Lorentzian of width 0.1 eV (dashed line), compared to that resulting from the O'Malley formula (dotted line).

Other avenues of investigation could provide insight concerning the applicability of our method to more complex systems. Polyatomic molecules, for example, might be handled either by reduction to hyperspherical coordinates [22], or by a multidimensional generalization of the Siegert state boundary conditions on an arbitrary hypersurface. Since our method yields a full solution to the Schrödinger equation along the boundary at R_0 , it should also be possible to project onto the continuum functions of different dissociative channels, and explicitly resolve partial dissociation cross sections [23]. Even in its current form, however, we believe the Siegert MQDT method offers a simple description of the flux escaping into dissociative channels, by working within a channel basis that obeys a physically motivated boundary condition.

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