

Chapter 5

Siegert states

Progress toward a truly general theory of molecular systems excited at continuum energies depends on the ability to describe all accessible continua concurrently. Modern experiments routinely probe energy regimes where multiple channels of both ionizing and dissociative types are in competition [10]. The philosophy of multichannel quantum defect theory outlined in Chapter 2 is naturally suited to the description of physics in the asymptotic region, where channel indices correspond to the quantum numbers of the separated system, and complicated short-range scattering dynamics are reduced to a minimal set of interaction parameters. In principle, the problems of predissociation and preionization are based on exactly the same interaction parameters, since they both hinge on the coupling between the electronic excitation of the Rydberg electron and the rovibronic excitation of the core. In preionization, sufficient energy is transferred from the core to the electron to promote it into the continuum of the separated electron-ion system; in predissociation the reverse process occurs, with energy transferring from the electron into vibrational excitation, dissociating the molecule.

5.1 Dissociative channels in molecular MQDT: General considerations

The extension of quantum defect theory to include a nuclear continuum is not naturally suggested by the form of the channel expansion on which the theory relies,

because the usual theory has only ionization channels represented explicitly (see Eq. 2.2 in Chapter 2). The time-independent Schrödinger wavefunction is conventionally expanded using a solution *ansatz* form that distinguishes the channel states (discrete, and usually calculated numerically) from the asymptotic states of the scattering coordinate (continuous, and usually known analytically at large separations). The necessity of selecting one coordinate set to serve as the “channels” inevitably entails a preimposed bias as to which coordinate should be considered to correspond to the reactive dynamics of the fragmenting particles. From that perspective, the very notion that MQDT could be of utility in double continuum problems may appear on the surface to be questionable.

At the same time, much of the conceptual appeal of quantum defect methods for single continuum studies is retained or even enhanced by the computational challenges of working within a two-continuum problem. The physics of the system is still dominated by a finite set of energetically open channels, and the selection of an expansion form that incorporates those channel states directly will still greatly reduce computational labor. Some coordinates and asymptotically “good” quantum numbers refer to coordinates that obey periodic rather than asymptotic boundary conditions, such as the angular electronic coordinates or the rotational eigenvalues; it would be a great waste of computational resources to solve for wavefunctions already known in advance, such as when the ionization occurs via a few partial waves or into a small number of product rotational states. Moreover, the transition from single continua systems to multiple continua only complicates the necessity of efficiently describing the coupling between metastable resonant states and the continua in which they are embedded. Since the short-range interaction physics to which resonant processes are sensitive is relatively indifferent to the number of different continua or types of continua that are simultaneously open, the same quantum defects and phase shifts that characterize the single-continuum case still ought to contain all necessary information for handling any associated multiple-continuum generalizations of the same system.

5.2 Established methods for handling dissociative channels

The extension of quantum-defect-style techniques to the description of dissociative channel physics was initially pursued in the late 1970s by Schneider, Burke, and other co-workers [112, 113, 114, 115], in the context of electron scattering from neutral molecules. Their calculations were based on the Born-Oppenheimer approximation, and neglected all non-adiabatic coupling effects. This allowed for an adequate handling of dissociative attachment and vibrational excitation processes of neutrals, but could not be extended to electron scattering from positive ions (or the associated half-scattering processes of neutral molecule photoionization and photodissociation), which involve an essentially non-adiabatic coupling interaction with electronic Rydberg states. Still, Schneider *et al.* were able to demonstrate that their R-matrix method gave results formally equivalent to that of the Fano frame transformation formulas (see the concluding discussion of [115]). Other applications of quantum defect theory to the dissociative spectra of diatomic molecules were later developed by Giusti [116] and [117]. These methods are analogous to the standard one-dimensional formulation of quantum defect theory, but with the electronic coordinate replaced by the nuclear degree of freedom. (For an extended discussion of the extension of MQDT to non-Coulombic long-range potentials, see [43, 118, 119].) These methods are rigorous, but naturally involve no reference to electronic physics except at the level of relying on adiabatic or diabatic potential curves.

5.2.1 Jungen eigenphase method

One of the earliest attempts to apply multichannel quantum defect theory to the problem of competing dissociation and ionization processes was carried out by Christian Jungen [53]. Jungen adopted an approach inspired by the utility of Fano's approach [45] in treating the "recoupling" transformation between the short-range interaction of the Rydberg electron with the core, and the long-range Coulombic forces of the Rydberg

states. For escape into an electronic continuum only, the result of this procedure is the orthogonal frame transformation already discussed in Chapter 2. To represent the dissociative physics, the vibrational basis must be augmented in some way that permits a finite value of the wavefunction on the fixed- R boundary between the inner region (where the wavefunction is unknown) and the outer region (where it can be expanded in dissociative channels). R , as before, refers to the internuclear separation, as opposed to r , the radial coordinate of the electron. The assumption is made that the potential in the outer region vanishes except for a constant that defines the channel energy threshold. Note that while the boundary condition of the electronic coordinate r is formally applied at infinity, the boundary condition for the nuclear coordinate R is necessarily imposed at some finite boundary R_0 that delineates the range over which the inner region vibrational basis is defined. Outside the region the solution is a linear combination of the regular and irregular vibrational continuum functions, $F_{n\Lambda} \cos \delta - G_{n\Lambda} \sin \delta$, multiplied by the channel function that describes the state of the dissociating atoms or molecular fragment pair, with the Rydberg electron in a low- n electronic state.

Figure 5.1 shows the inner and outer regions, the boundaries between them, and the form of the solutions in each region, as found in [53]. Solutions with finite amplitude in region II correspond to ionization, and solutions with finite amplitude in region III correspond to dissociation. Solutions in region IV, which would describe dissociative ionization, are not possible in the current version of Jungen’s method.

If a vibrational basis for the molecular ion H_2^+ is generated in accordance with a fixed logarithmic derivative boundary condition at R_0 , which all functions in the basis must satisfy, then the (discrete) basis consists a ladder of energy levels that begin to resemble the eigenstates of a particle in a one-dimensional box as soon as they rise high enough in energy to exceed the dissociation threshold; they shall be referred to as the “box states”, in contrast to the ordinary vibrationally bound states that vanish as $R \rightarrow \infty$. For an arbitrary choice of the logarithmic derivative, it is unlikely

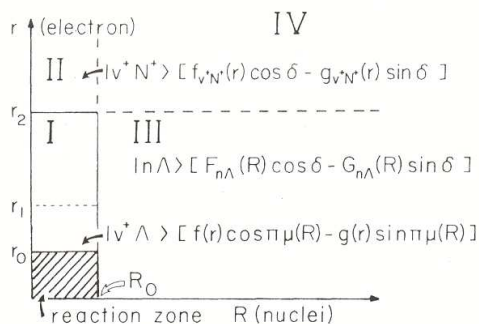


Figure 5.1: Partition of configuration space into inner and outer regions, taken from the work of Ch. Jungen [53].

that the wavefunction expansion constructed using the box states (which all share the same boundary condition) will have an energy at precisely the right value to correspond to the true (energy-conserving) continuum state. The selection of a single logarithmic derivative discretizes the continuum values available for continuum-like H_2^+ channel states, and this also restricts the continuum H_2 states to a finite range of discrete values. Thus, the system must be solved iteratively, with a systematic variation of the logarithmic derivative from $-\infty$ to ∞ that causes the locations of the energy levels to scan across the position of the true dissociative state energy. This is accomplished by casting the eigenequation system normally as for the ionization-only R-matrix approach [120] approach, but including the box state channels as “strongly closed” channels with phase parameters that depend implicitly on the logarithmic derivative. These additional strongly closed channels produce exactly one extra solution, corresponding to the dissociative continuum state of proper energy. This and the other eigenphase solutions are then projected back onto the channel basis, defining the usual smooth, short-range reaction matrix (or scattering matrix). From this point, channel elimination can be performed, usually to close off the “weakly closed” channels associated with the true vibrationally bound states of the molecular ion potential that give rise to the ionization Rydberg series structure.

As originally developed, this method is encumbered by the need to recalculate the eigensolution coupling matrix elements at each new logarithmic derivative. Since the values at which the linear eigensystem possesses an eigensolution are dependent on energy, this means that the system must be solved repeatedly at each energy until the result has iteratively converged to the desired accuracy. Moreover, the method, as originally conceived, functions only for a single dissociative channel per Λ symmetry, and only in the energy regime below dissociative ionization. The reaction matrix contains an explicit channel for dissociation, reflecting the constraint that the solution must vanish either at infinity in all ionization channels, or else at the boundary in the dissociation channel.

More recently [121], Jungen and Ross generalized their method to allow for multiple dissociative channels, and to remove the necessity for iteration. The standard frame transformation calculation is done first for the normal basis set (vanishing at R_0 , and it is then repeated with a different logarithmic derivative for each dissociation channel. The eigenchannel solutions for all the different boundary condition choices are combined into a single generalized basis, and the asymptotic boundary conditions then give a generalized eigenvalue problem for the full two-dimensional eigenphases and eigensolution vectors. As before, this gives a short-range reaction matrix with “weakly closed” channels, which may be then eliminated with the usual algebra. This method has provided the most accurate theoretical results currently available, and is in the process of being extended to other systems [122]. It does depend, however, on a physically motivated choice of the “additional” logarithmic derivatives; the accuracy of the results reflects the extent to which an energy in the vibrational basis appears close to the energy at which the calculation is being performed. In effect, this optimization condition amounts to a semi-iterative procedure that must be adjusted “by hand” in different energy ranges. This is easily accomplished for the study of a single peak at some specified energy, but could be potentially quite inconvenient for the calculation of a continuously

energy-dependent spectrum with many peaks over a wide energy range. Moreover, it remains unclear how to extend this method to energies above the dissociative ionization threshold.

5.2.2 Stephens-Greene box averaging method

A more conceptually direct approach to the representation of coupling to a dissociative continuum is that of box size averaging [54]. As in the Jungen method, the dissociative continuum is discretized by allowing the vibrational basis to extend far above the ionic dissociation threshold, to include many box states. Instead of looking at the variation of these state energies with logarithmic derivative, one may instead consider their sensitivity to variations in the box radius R_0 . As the box increases in size, the box state levels shift to lower energies, passing smoothly through all continuum energies. The coupling between these fictitious channels and the physical ionization channels provides a measure of the extent to which flux can be expected to pass into those dissociation channels. The positions of resonances with strong dissociative character will be perturbed significantly by the introduction of these additional box states, and the variation in this perturbation as a function of R_0 is thus a measure of the coupling strength between the dissociative continuum and the ionization channel associated with that resonance.

In order to quantitatively interpret this effect, the standard MQDT frame transformation procedure must be performed sequentially for a series of closely spaced box radius parameter values. The cross-sections arising from each individual value of the box radius are then averaged together, giving a cross-section in which the linewidths of dissociation-sensitive peaks have been broadened. The range of R_0 values used in the calculation is determined by the separation between box state energy levels in the vicinity of the energy for which coupling to the dissociative continuum is anticipated to be important; roughly speaking, it is necessary to change R_0 by exactly enough to

shift all the levels down by one cycle, such that the $n + 1$ -th level is lowered to the position initially occupied by the n -th level. Since the eigenvalues of a particle in a box have a relative spacing itself proportional to n , the selection of an appropriate reference value for n is essential for producing an evenly weighted average. This is a trivial choice at low total energies, where only one dissociative channel is accessible; if there are multiple competing dissociative product channels open at once, however, the criterion becomes more difficult to specify, and if the cycle periodicities are fundamentally incommensurate, potentially impossible.

5.2.3 Two-dimensional R-matrix method

R-matrix techniques derive their name from the original formulation of Wigner and Eisenbud [123], who first recognized that the matrix of generalized logarithmic derivatives on the surface bounding a continuum system of interacting particles could be written as an expansion over resonant terms located at the eigenenergies of the bounded system¹. This approach demonstrated good utility for the semi-empirical characterization of small collections of known nuclear resonances in terms of a minimal parameter set, but it was not applied widely for *ab initio* computation in its original form, owing to its poor convergence properties. Although it is possible to improve convergence through the inclusion of certain correction schemes, such as the Buttle correction, this can only be accomplished at the expense of some amount of conceptual clarity and computational efficiency.

An alternate version of the R-matrix theory was introduced by Fano and Lee [120], based on transformation to the eigenchannel representation. Rather than selecting a single arbitrary value for the surface logarithmic derivative and solving the Schrödinger equation subject to that condition, the eigenchannel representation provides a set of solutions, each of which has a different logarithmic derivative that is common to all of its

¹ For a review of early applications of R-matrix theory to problems in nuclear physics, see [124].

physical channel components. Since the boundary condition is itself the undetermined eigenvalue parameter, it is permissible to express the matrix equation in a basis set that uses basis functions with a range of different logarithmic derivatives, improving the convergence properties of the final R-matrix expression. This comes at the expense, however, of requiring an iterative solution procedure. For an application of this approach to photoionization, see [125].

The eigenchannel approach may be recast in a noniterative form by means of a variational principle first discovered by Kohn [126]. In contrast to the more traditional bound state applications of the calculus of variations to quantum systems, which apply the Rayleigh-Ritz method to determine a stationary value of the energy for a given basis set, Kohn's principle gives a stationary value for the logarithmic derivative in terms of a fixed scattering energy. For continuum systems this is conceptually advantageous, in that it reflects an awareness that the total energy is typically a controllable input parameter for scattering experiments. This simplification was first proposed for a field-perturbed atomic system by Greene [127], and shortly thereafter extended to molecular photoionization [128]. Although this approach successfully combines the stable convergence of the eigenchannel method with the non-iterative efficiency of the traditional Wigner-Eisenbud theory, it still suffers from the disadvantage of requiring the eigensystem to be solved again at each new energy. This disadvantage may be reduced by use of a modified "streamlined" solution technique for the generalized eigenequation, although for larger basis sets (e.g., such as those commonly required for the two-dimensional R-matrix method), the computational advantage is limited by the inability to efficiently diagonalize the Γ matrix in the closed-closed subspace [129, 44]. Additionally, the energy dependence of the R-matrix elements over small energy ranges is frequently smooth enough that they may be interpolated from a limited number of data points, provided sufficient care is taken with respect to the handling of divergences in the logarithmic derivative eigenvalues.

A detailed review of the variational R-matrix method may be found in [129]. Here, we will focus specifically on the specialization of this method to the problem of photoionization and photodissociation in diatomics. For a system with two dissimilar modes of fragmentation, as is the case for competing dissociation and ionization, the variational principle must be adjusted to account for the nonequivalence of the kinetic energy terms of the Hamiltonian. Assume the potential within a two-dimensional box bounded by surfaces at the axes and at $r = r_0$ and $R = R_0$ may be written as $V(r, R)$. Then the time independent Schrödinger equation requires

$$\left(-\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + V(r, R) \right) \psi(r, R) = E\psi(r, R). \quad (5.1)$$

The mass factors μ_r and μ_R denote the reduced masses for electronic and nuclear motion, respectively. The angular degrees of freedom have already been separated in spherical coordinates, such that the full solution in the inner region is given by

$$\Psi(\vec{r}, \vec{R}) = \frac{1}{rR} \psi(r, R) \Phi(\Omega). \quad (5.2)$$

The notation Ω represents all angular degrees of freedom. In general, the possibility of additional electronic symmetries and partial wave components would require a sum over multiple Φ channels, although for the *ungerade* photodissociation spectrum of molecular hydrogen it suffices to assume that only the p-wave channel is active; the R coordinate, however, is strictly confined to s-wave scattering by conservation of momentum. The partition of configuration space that defines the inner region is identical to that of Jungen's work as previously shown in Figure 5.1, with Jungen's radius r_2 corresponding to the box boundary labeled here as r_0 .

The mass factors may be temporarily absorbed by a change of variables, $x = \sqrt{\mu_r}r$ and $X = \sqrt{\mu_R}R$, to recast the Hamiltonian in a more symmetric form. Then the differential equation is transformed into the usual matricial form by the taking of an

inner product over the enclosed box volume,

$$E \int dx dX \psi^* \psi = \int dx dX \psi^* \left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial X^2} + \tilde{V}(x, X) \right) \psi \quad (5.3)$$

followed by the application of Green's theorem,

$$E \int dx dX \psi^* \psi = \int dx dX \left(\frac{1}{2} \frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} + \frac{1}{2} \frac{\partial \psi^*}{\partial X} \frac{\partial \psi}{\partial X} \right) \quad (5.4)$$

$$+ \int dx dX \psi^* \tilde{V}(x, X) \psi \quad (5.5)$$

$$- \frac{1}{2} \int_0^{x_0} dx \psi^*(x, X_0) \frac{\partial \psi}{\partial X} \Big|_{x=x_0} \quad (5.6)$$

$$- \frac{1}{2} \int_0^{X_0} dX \psi^*(x_0, X) \frac{\partial \psi}{\partial X} \Big|_{X=X_0}. \quad (5.7)$$

The logarithmic derivative is defined based on an outward normal with respect to the appropriate scaled variable along each surface,

$$\frac{\partial \psi}{\partial X} \Big|_{X=X_0} = -b\psi, \quad \frac{\partial \psi}{\partial x} \Big|_{x=x_0} = -b\psi.$$

After rearrangement and restoration of the original variables, the variational quantity b may finally be expressed as

$$b = \frac{\sqrt{\mu_r \mu_R} \int dr dR \left(2E - \frac{1}{\mu_r} \left| \frac{\partial \psi}{\partial r} \right|^2 - \frac{1}{\mu_R} \left| \frac{\partial \psi}{\partial R} \right|^2 - 2V(r, R) |\psi|^2 \right)}{\sqrt{\mu_r} \int_0^{r_0} dr |\psi|^2 + \sqrt{\mu_R} \int_0^{R_0} dR |\psi|^2} \quad (5.8)$$

Note that the boundary parameter b is not the logarithmic derivative itself, but rather the mass-rescaled logarithmic derivative; to recover the usual logarithmic derivative, b must be multiplied by the appropriate $\sqrt{\mu}$ factor.

Proceeding from this relation, the solution is expanded in a two-dimensional basis,

$$\psi = \sum_i \sum_j c_{i,j} u_i(r) v_j(R)$$

,

to produce the usual generalized eigenvalue equation,

$$\mathbf{\Gamma}\vec{c} = b\mathbf{\Lambda}\vec{c}, \quad (5.9)$$

where $\mathbf{\Gamma}$ is the matrix representation of the numerator of 5.8 and $\mathbf{\Lambda}$ is the matrix representation of the denominator of 5.8 (i.e., the overlap matrix for that basis). Each eigensolution will have a common boundary parameter value b_β on both surfaces. Outside the box boundary, the scattered eigenchannel solutions can be written as a channel decomposition of the regular and irregular solutions [44],

$$\psi_\beta(r, \omega) = \sum_i \frac{1}{r} \Phi_i(\omega) (f_i(r) I_{i\beta} - g_i(r) J_{i\beta}). \quad (5.10)$$

The symbol ω includes all degrees of freedom necessary to describe the channel, including R and all angular coordinates Ω . This wavefunction requires a formal antisymmetrization, but for sufficiently large r_0 this can usually be neglected. For the solutions asymptotic in R , the variable r is replaced by R wherever it appears, and the Coulomb functions f_i and g_i are replaced by the regular and irregular vibrational continuum functions, which can be found by the Milne method [118, 130] or else by similar numerical techniques. The matching condition of continuity for the wavefunction and its derivative permits the determination of \mathbf{I} and \mathbf{J} in terms of Wronskians,

$$I_{i\beta} = -\frac{W(g_i, \psi_{i\beta})}{W(f_i, g_i)}$$

and

$$J_{i\beta} = -\frac{W(f_i, \psi_{i\beta})}{W(f_i, g_i)},$$

and this suffices to define either the reaction matrix $\mathbf{K} = \mathbf{I}\mathbf{J}^{-1}$ or the scattering matrix $\mathbf{S} = (\mathbf{I} + i\mathbf{J})(\mathbf{I} - i\mathbf{J})^{-1}$. The notation $\psi_{i\beta}$ refers to the projection of the solution ψ_β onto the i -th channel function at the appropriate matching surface.

The variational R-matrix method requires an explicit form for the potential energy function within the two-dimensional box. In principle, the potential energy of molecular

hydrogen as a bivariate function of r and R is quite complicated, reflecting short-range electron correlation effects that are challenging to define for the highly excited pseudo-continuum states that characterize the R-matrix eigenspectrum. Instead, we have opted to work with a simplified two-dimensional model potential that reproduces the features of the exact H_2 intermolecular potential to reasonable quantitative accuracy. A separate potential form is utilized for each Λ -space symmetry, with several parameters that may be optimized through a one-dimensional R-matrix procedure to reproduce the known body-frame quantum defects $\mu_\Lambda(R)$. For the Σ symmetry, this procedure yields (in atomic units)

$$V(r, R) = -\alpha_1 \left(1 - \tanh \frac{\alpha_2 - R - \alpha_3 R^4}{7} \right) \tanh(R/\alpha_4)^4 \frac{e^{-r^2/3}}{r} \quad (5.11)$$

where $\alpha_1 = 1.6435$, $\alpha_2 = 6.2$, $\alpha_3 = 0.0125$, and $\alpha_4 = 1.15$. For the Π symmetry, the optimization gives

$$V(r, R) = \alpha_1 \sqrt{R} \left(e^{-(R-\alpha_2)^2/\alpha_3} \right) \frac{e^{-r^2/3}}{r} \quad (5.12)$$

with $\alpha_1 = 0.480$, $\alpha_2 = 3.35$, and $\alpha_3 = 6.5$. The resulting model potential curves are shown in 5.2. Note that the model potential begins to break down for Σ states of low n , owing to the neglected energy dependence of the Σ quantum defect which is not described by this fitted potential. The shape of the 2Σ potential is not even qualitatively correct, a reflection of the inability of a $^1\Sigma_u^+$ state to dissociate into two ground state hydrogen atoms [40]. This is a problem common to all QDT techniques that use an energy-independent quantum defect, but since the $n=2$ state lies so low in energy as to be inactive for scattering or photoabsorption processes near the ionization threshold, this does not constitute a serious defect for the purpose of using the model as a test system.

As mentioned above, the R-matrix procedure is computationally expensive to re-

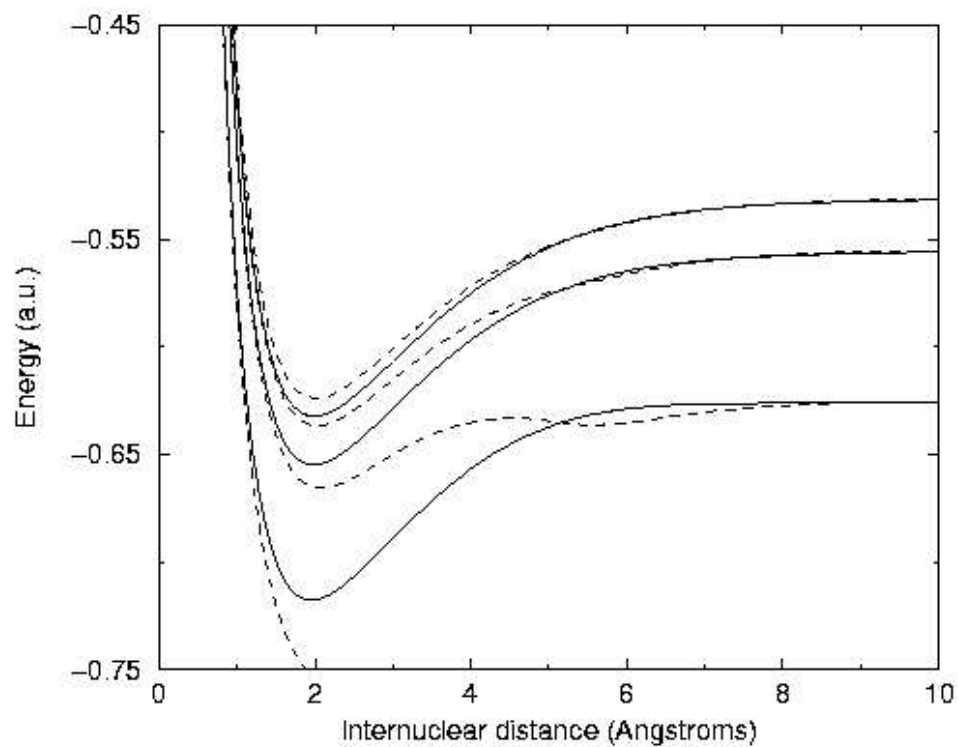


Figure 5.2: Potential curves generated from the model Hamiltonian using Eqs. 5.11 and 5.12. Potentials drawn with a dashed curve are of $1\Sigma_u$ symmetry, and those with a solid curve are of $1\Pi_u$ symmetry. (These may be compared with the exact curves for H_2 shown in Figure 2.1.)

peat at each new energy (unless the basis set is small enough to use the streamlined version). Fortunately, the quantities \mathbf{I} and \mathbf{J} are only weakly and smoothly energy dependent, and can be interpolated from data computed on a coarser energy grid. Because they incorporate relative phase information, and because the phase is ambiguous with respect to a shift of π , the eigenvector solutions are susceptible to branch discontinuities associated with the underlying trigonometric functions; these must be repaired before the interpolation is applied. Given the interpolated reaction matrix values, the only remaining step that must be performed at each energy is the elimination of closed channels according to the conventional channel elimination procedure. Note that this method results in the appearance of channels in the S-matrix that are explicitly labeled as either ionization or dissociation channels.

Results of the R-matrix calculation, and a comparison with experimental data, are summarized in Table 5.1 (aside from the $v^+ = 2$ resonance series, for which the peaks are exclusively ionized, and occur within a wavenumber or two of the correct position). The photoionization, photodissociation, and total cross-sections are shown in Figures 5.3, 5.4, and 5.5. The photoionization and photodissociation portions of the cross-section are separated by summation over only the appropriate physical channels. Note that since this calculation is based on a model potential, and resonance features are often highly sensitive to small variations in the form of the short-range potential, the comparison is not expected to be quantitative. A comparison with the Siegert method (below) using the same model potential, however, suggests that only errors in the positions (as opposed to widths or relative yields) of the peaks are likely to be a consequence of the failure of the model approximations. The inability of the relative yields to reproduce experiment in anything beyond a general qualitative correspondence is disappointing, and may reflect either a fundamental weakness of the technique, or some undetected error in the implementation. Moreover, the dissociation spectrum reveals an unassignable peak at 786 Å; this may be an artifact related to the anomalous

shape of the $2p\sigma$ and $3p\sigma$ potential curves. This method probably merits further study before any definite conclusions are drawn concerning its capabilities and limitations.

Table 5.1: Positions and fractional yields for select *ungerade* $J=0$ resonances in H_2 .

		Model	Obs. (H_2)
$3p\pi, v = 8$	Position (cm^{-1})	127295.7	127248.2
	Width (cm^{-1})	3.9	3.4
	% Ionization	0.1	≤ 2
	% Dissociation	99.9	≥ 98
$5p\sigma, v = 4$	Position (cm^{-1})	127622.0	127599.4
	% Ionization	0.42	0.77
	% Dissociation	0.58	0.10 ± 0.10
$4p\pi, v = 5$	Position (cm^{-1})	127701.4	127667.6
	% Ionization	0.998	0.85
	% Dissociation	0.002	0.18 ± 0.05

The two-dimensional R-matrix method, unlike the MQDT approaches, works directly from the potential energy function, rather than incorporating that information through intermediate parameters such as the quantum defects. Its advantage is that it does not rely on the vibrational frame transformation method, and thus serves well as a benchmark calculation. In situations where the short-range potential can be described in full quantitative detail, it provides a “brute force” alternative to the more approximate quantum defect methods, with a controlled convergence behavior relative to the variation of geometric parameters like the number of channels and the box dimensions. This can be of potential utility for testing other methods, or studying representative model systems. For experimental spectra, however, the reproduction of accurate high-resolution spectra at the sub-wavenumber level is much more easily attained by the inclusion of semi-empirical parameter adjustments that naturally account for small correction effects.

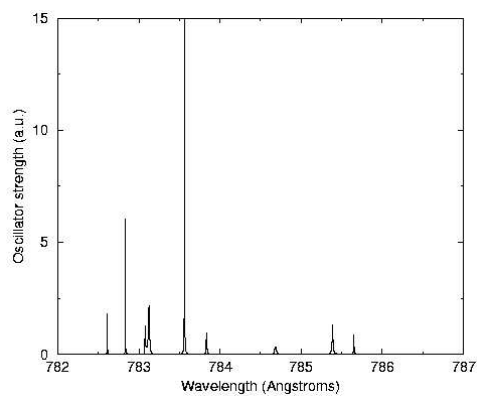


Figure 5.3: Infinite resolution photoionization cross-section calculated using the two-dimensional R-matrix technique.

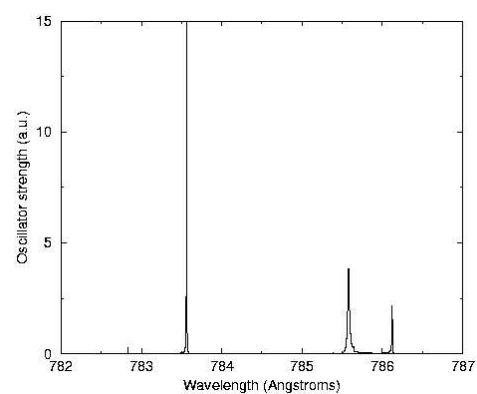


Figure 5.4: Infinite resolution photodissociation cross-section calculated using the two-dimensional R-matrix technique.

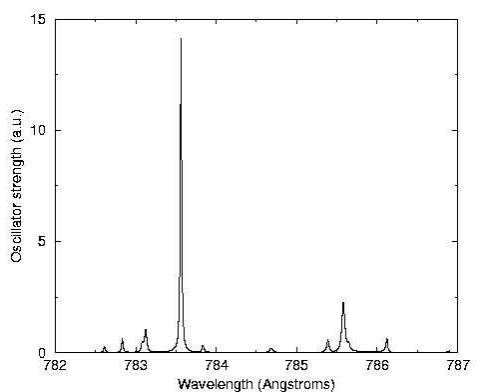


Figure 5.5: Infinite resolution total photoabsorption cross-section, taken from the summation of Figures 5.3 and 5.4.

5.3 Siegert pseudostates: Basic concepts

The difficulties of the Stephens-Greene box-averaging stems from its inability to represent a true outgoing wave solution. With the box averaging method, for example, the inner region solutions are fixed by normalization in such a way as to guarantee conservation of the probability within the box radius; the solution cannot have a finite flux at the boundary, but can only “bounce”. As such, the shape of an averaged peak can be broadened, but the total integrated area can never be reduced. This is a necessary consequence of flux conservation. For methods that incorporate the dissociative channel as if it were an additional ionic channel, on the other hand, the solution forces flux to be conserved despite distribution over all channels; this neglects the possibility that the true solution may be coupled to both types of continua at once, implying a failure when the first threshold for dissociative ionization is crossed; it is simply not possible in these methods for flux to be outgoing in both channel types at once. Despite the ability of MQDT to provide, in principle, the true two-dimensional solution within a finite region of space, the use of a conventional basis fails to provide sufficient flexibility to characterize a wavefunction with outgoing wave form in both the asymptotic electronic coordinate (controlled by the assumed asymptotic form of the outer region solutions) and the finite-bounded nuclear coordinate simply in terms of a single set of channel states. Thus, methods such as the treatment of Ross-Jungen [121] must explicitly supplement the basis using additional sets of basis functions obeying non-Dirichlet boundary conditions, with the logarithmic derivative of each new set selected in a somewhat arbitrary and *ad hoc* manner.

The construction of outgoing-wave solutions for a given Hamiltonian can be accomplished by analytically generalizing the energy eigenvalue spectrum of that Hamiltonian into the complex plane. Because outgoing wave states behave asymptotically as exponential functions of a complex argument, they cannot be described in terms of the

usual boundary conditions encountered in Sturm-Liouville theory, since neither their values nor their first derivatives vanish at any point in space; thus, the hermiticity of the Hamiltonian operator is no longer sufficient to guarantee that the eigenvalues are confined to real axis. The physical interpretation of complex eigenenergies was first explored by Gamow [131], who recognized that the lifetime τ of a resonance state was inversely proportional to the imaginary part of its complex energy. Subsequent work by Wiesskopf and Wigner [132] related the lifetime τ to the linewidth parameter $\Gamma = 1/\tau$, at least at the level of the approximation of their theory.

The definition of resonance states in terms of the solutions of the Schrödinger equation may be approached from two somewhat different perspectives. The first theory, developed by Kapur and Peierls [133], was based on the partitioning of the Hamiltonian into an outer region (with a continuous spectrum) and an inner region (with a discrete spectrum), treated as two interacting coupled channels. The Kapur-Peierls eigenstates are defined as the eigenfunctions of an effective Hamiltonian defined by inverting the projection of the resolvent operator onto the inner channel. Since this is an energy-dependent operator, with the wavenumber of the outer channel continuum state as a free parameter of the Hamiltonian, the eigensolution set itself has a parametric dependence on the scattering energy. Although the Kapur-Peierls functions have the advantage of well-behaved orthogonality and completeness properties, they are inconvenient for use in any calculation which involves a range of scattering energies; because they have such a complicated parametric dependence on the energy, they are quite difficult to evaluate except by re-diagonalizing the effective Hamiltonian at each new energy.

An alternate, parameter-free version of the resonance states was developed by Siegert [134]. Siegert states are defined, in a much more intuitive way, as the eigen-solutions of the Hamiltonian that vanish at the origin and have pure outgoing wave character in the asymptotic limit $R \rightarrow \infty$. Siegert's derivation, notably, allowed for overlapping resonances of arbitrary width, giving a smooth background term in the

cross-section. 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 eigenstates with finite imaginary parts that serve as a discretized approximation to the true continuum. The Siegert states offer several advantages over the Kapur-Peierls theory. First, they correctly describe long-lived resonances in the sense that they pass smoothly over into bound states; any states that lie lower in energy than the continuum threshold of a potential are guaranteed to correspond to the usual (real-valued) bound states. For the Kapur-Peierls formulation, this only occurs for a fortuitous selection of the partitioning radius. Moreover, the Siegert bound states are guaranteed to be correctly normalized and orthogonal. Second, the Siegert states are uniquely defined for a given Hamiltonian at any scattering energy. This allows them to serve as an expansion basis for other functions, including the Green's function. (A more detailed survey of the relations between the Siegert and Kapur-Peierls theories may be found in [135].) In addition to their identification as poles of the scattering matrix, one may note from the Siegert boundary conditions at 0 and ∞ that the Siegert eigensolutions are proportional to the Jost solution $f_{\pm}(k, R)$ [136], and the eigenvalues are equivalent to the zeroes of the Jost function $J_{\pm}(k) = f_{\pm}(k, 0)$ in the complex plane [137].

A renewed interest in Siegert functions during the 1970s was stimulated by the realization that they could be applied to the direct calculation of total [138] or partial [139, 140] linewidth parameters in many-electron multichannel systems. These methods do not calculate cross-sections, but extract the resonance eigenvalues directly as poles of the scattering matrix; they are closely related to the various complex coordinate scaling methods [141]. The utility of Siegert states for numerical calculations is compromised by their rapid exponential divergence for increasing r . One of several approaches for circumventing divergence-related instabilities was developed by Meyer and Walter [137],

who confined the range of the Siegert states to a finite radius, and solved for their eigenspectrum within an L^2 primitive basis set using variational calculus. That is, they replaced the exact Siegert boundary condition

$$\left(\frac{d}{dR} - ik\right)\phi(R)\Big|_{R=\infty} = 0 \quad (5.13)$$

with the finite range boundary condition

$$\left(\frac{d}{dR} - ik\right)\phi(R)\Big|_{R=R_0} = 0. \quad (5.14)$$

(As a historical note, it is the latter definition that actually corresponds to that of Siegert's original paper, which was only concerned with very short-range nuclear interaction potentials.) This method allowed a single formalism to yield all the bound, virtual, and resonance states of the potential, a significant accomplishment.

A complication of the method involves the necessity of differentiating the ‘‘cut-off’’ resonances, a string of closely spaced poles in the complex plane arising from the truncation of the potential at a finite cut-off radius, from the true physical resonances. These are not artifacts, but rather the direct scattering states associated with that modified potential. They are highly sensitive to the shape of the potential tail and the location of the cut-off discontinuity, even if the tail is exponentially small in that region. This is a general peculiarity of the analytical properties of Siegert states in any infinite-range potential, even one that decays exponentially rapidly— they invariably display a pathological sensitivity to the asymptotic potential behavior, preventing all but a finite subset of the Siegert states for cut-off potentials (SSCPs) from converging to exact Siegert states. From the standpoint of rigorous mathematical formalism, it is important to consider all further discussion in light of this recognition. Since all realistic physical potentials have a tail behavior that decays more *slowly* than exponentially, the ultimate test of any Siegert method, including the elegant work of [142], is whether or not

the derived observable quantities (cross-sections and S-matrices) are numerically stable with respect to variation of the box radius parameters. Since scattering observables in atomic physics are in general *not* sensitive to weak long-range potential terms (except in sufficiently low energy scattering regimes that such terms can no longer be considered weak), however, the pathological behavior of the SSCPs is expected not to have physical significance for any realistic system; even with two very different eigenvalue spectrums, an expansion-based expression for an observable should converge to exactly the same value in both cases.

Even methods based on the SSCPs still suffer from the serious drawback of being computationally dependent on iterative procedures, either in diagonalizing the full matrix [138], or the secular equation resulting from a variational principle [137], or most recently, a partitioned submatrix reduced to the dimension of the open channels [143]. The solution must be iterated many times to converge on every individual eigenvalue. While this is potentially practical for “direct” methods, in which the only objective is the determination of a finite number of true resonant states and perhaps a representative topology of the surrounding scattering (cut-off) resonances, it would be impossible to calculate all the wavefunctions of the infinite series of SSCPs, which are necessary components of any complex basis vector expansion, such as would be used (for example) to construct the Green’s function by means of the Mittag-Leffler expansion theorem. In principle, all of the information describing the continuum resonance features and state densities should be contained in these eigenvectors, thus bypassing the need for approximating any integrals over the continuum. Turning that promise into a computational reality requires a careful study of the relationship between the SSCPs, and their representation in any finite basis, as well as a way of finding *all* of the eigensolutions defined by that basis selection without the need for cumbersome and potentially unstable iterative searches for eigenvalues in the complex plane.

Both of these difficulties were resolved recently by Tolstikhin *et al.* in their study

of the Siegert pseudostates (SPSs) [144, 142], the set of N eigenstates the result from solving the Hamiltonian with Siegert boundary conditions on the interval $[0, R_0]$ for an N -dimensional basis set. Tolstikhin *et al.* assume orthonormality of the basis functions, but most of their expressions can be straightforwardly generalized to a non-orthogonal basis, and we will lift that assumption except where otherwise noted. Regardless of orthogonality, the basis is in general not assumed to be complete except in the limit of $N \rightarrow \infty$. The SPS basis representation allows the derivation of completeness and normalization properties of the Siegert state functions to be replaced by linear algebra operations, which are then related to the true properties of the SSCPs by investigation of the $N \rightarrow \infty$ limiting behavior.

We seek a solution expanded in terms of some primitive basis set

$$\phi(R) = \sum_{j=1}^N c_j y_j(R), \quad 0 \leq R \leq R_0. \quad (5.15)$$

Here N is the dimension of our basis, and we have selected a non-orthogonal b-spline basis [145, 146] for the $y_j(R)$. Inserting this into the Schrödinger equation, premultiplying by $y_{j'}$, integrating with an integration by parts, and employing the boundary value 5.14, we find a matrix equation for the coefficients c_j

$$\sum_{j=1}^N \left(\frac{1}{2} \int_0^{R_0} \frac{dy_{j'}}{dR} \frac{dy_j}{dR} dR - \frac{ik}{2} y_{j'}(R_0) y_j(R_0) \right) \quad (5.16)$$

$$+ \int_0^{R_0} y_{j'}(R) \mu [V(r) - E] y_j(R) dR \Big) c_j = 0. \quad (5.17)$$

$$(5.18)$$

Note that we have used a Green's theorem identity before substituting in the boundary condition, 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

$$(\tilde{\mathbf{H}} - ik\mathbf{L} - k^2\mathbf{O})\vec{c} = 0, \quad (5.19)$$

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 recasting it as a new eigensystem in a basis of doubled dimension. ([147, 148] discuss related techniques for solving differential equations where the eigenvalue appears in a boundary condition.) We continue by defining $d_i = ikc_i$, yielding a trivial second equation $ik\mathbf{O}\vec{c} = \mathbf{O}\vec{d}$. Substituting this into the original eigenequation now gives a linear equation in the doubled basis space

$$\begin{pmatrix} \tilde{\mathbf{H}} & 0 \\ 0 & -\mathbf{O} \end{pmatrix} \begin{pmatrix} \vec{c} \\ \vec{d} \end{pmatrix} = ik \begin{pmatrix} \mathbf{L} & -\mathbf{O} \\ -\mathbf{O} & 0 \end{pmatrix} \begin{pmatrix} \vec{c} \\ \vec{d} \end{pmatrix}. \quad (5.20)$$

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 λ -plane. The solutions (plotted here in the k plane, rather than the λ -plane) are shown in Figures 5.6 and 5.7.

An atypical feature of the SPS eigensystem should be noted here— the eigenvalue parameter is proportional to the wavenumber k , rather than the energy. Since the energy has a k^2 functional dependence, the energy spectrum itself will need to be mapped onto a two-sheet Riemann surface in order to become single-valued, with a branch point at the origin and the cut following the positive real semiaxis. States with k in the upper half- k -plane will be mapped onto the first sheet of the Riemann surface on which the energy eigenspectrum is defined, and those with k in the lower half-plane will map to the second sheet. Since the bound state eigenvalues (that is, those which exponentially decay as $R \rightarrow R_0$) lie on the first sheet, this will be termed the “physical” sheet. The only states that can lie on the physical sheet are bound states (although if a discrete state is embedded in the continuum, it will be located on top of the cut line). Thus, all resonance states, whether they are near the real energy axis and related to real observable resonances, or deeper in the complex plane and related to smooth background

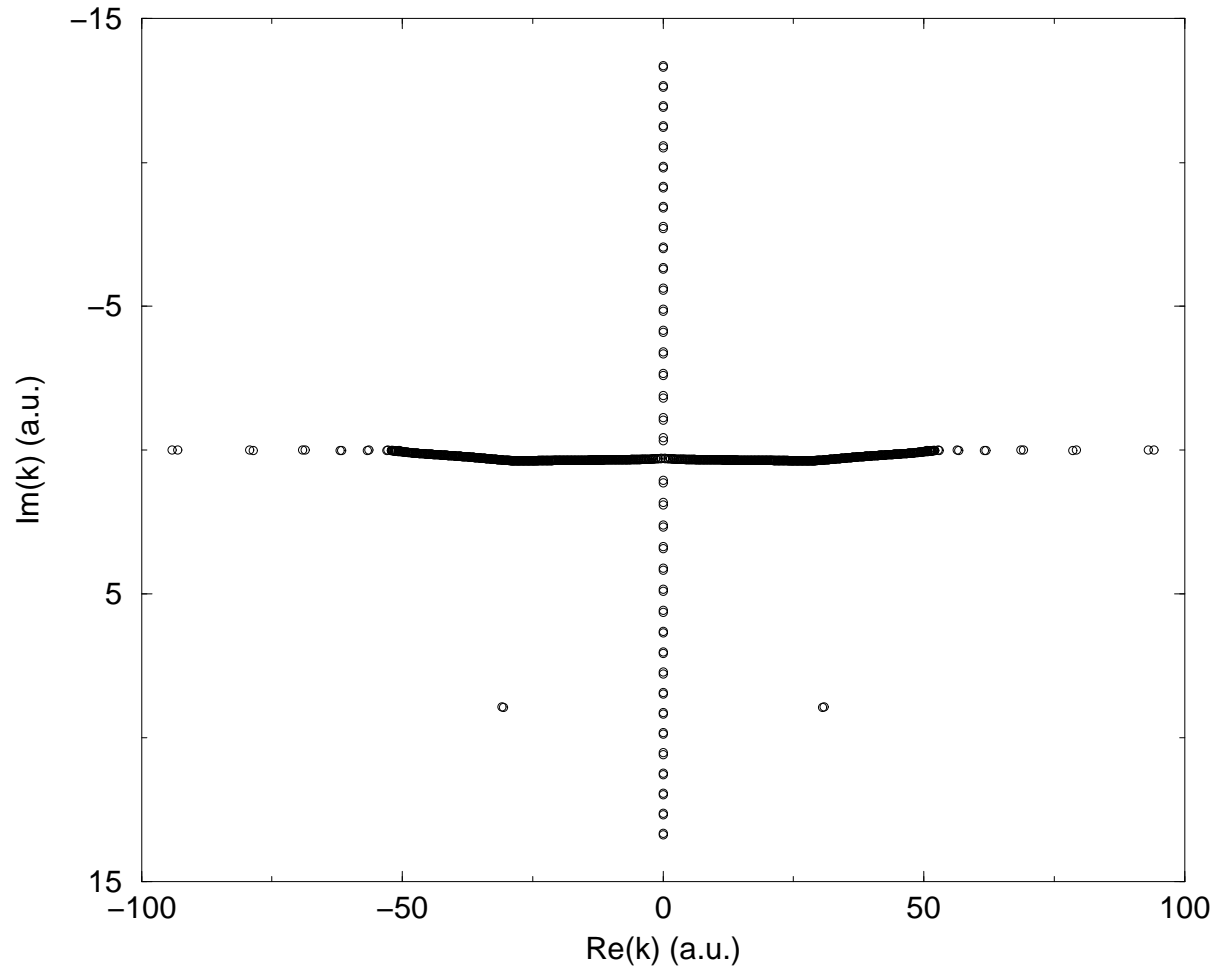


Figure 5.6: Siegert pseudostate eigenspectrum resulting from the solution of Equation 5.20. Note that the eigenstates have been transformed from λ to k , corresponding to a rotation in the complex plane by 90 degrees. States above the real axis all lie on the imaginary axis, and are identified as the bound states of the potential. States on the complex axis below the real axis are unphysical antibound states.

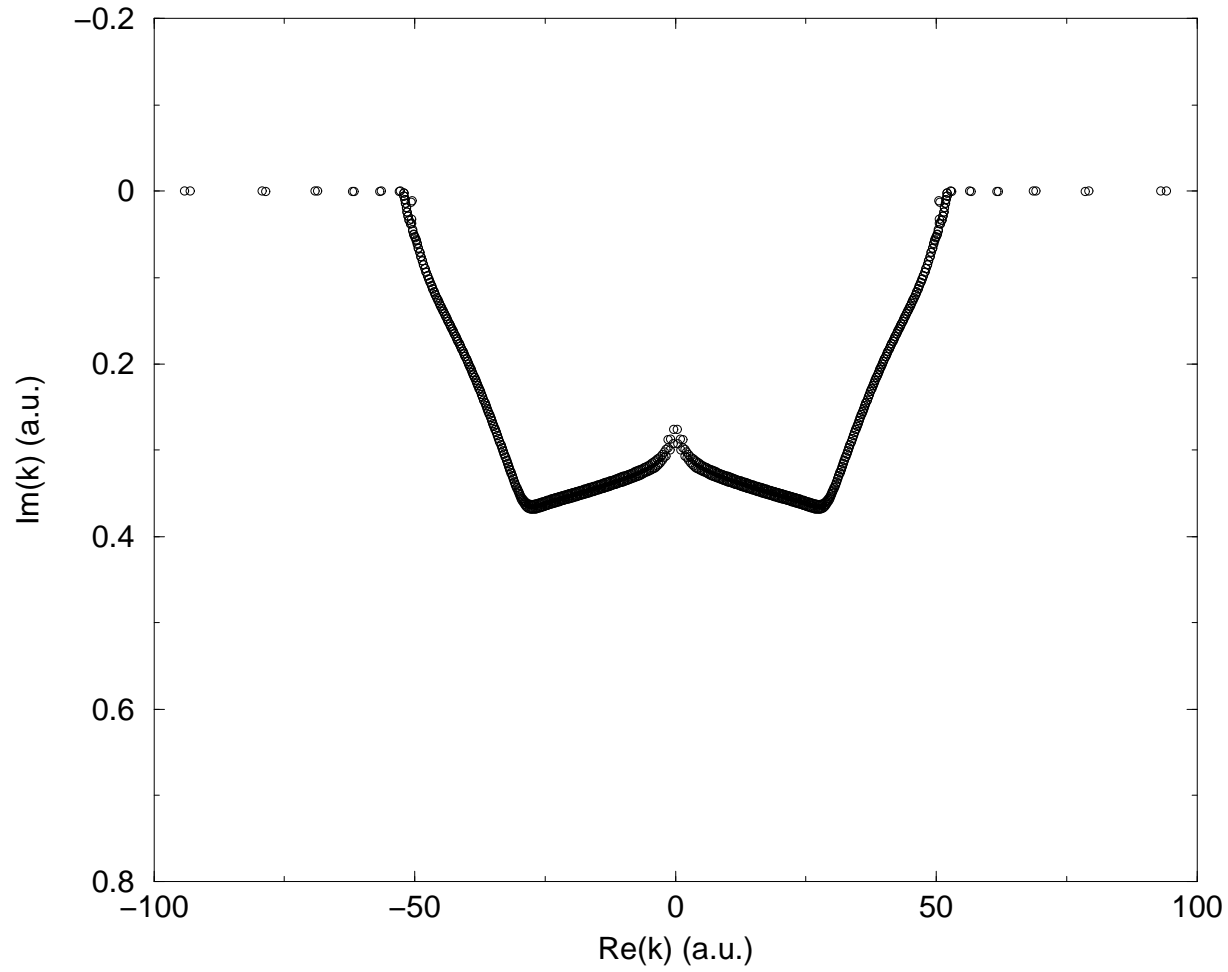


Figure 5.7: Enhanced detail of the spectrum in the vicinity of the real axis, showing states that correspond to the Seigert discretized continuum. Note that the “kink” in the spectrum occurs for values of k that oscillate too quickly to be represented in the primitive spline basis.

scattering, are exclusively on the unphysical sheet of the multisheet Riemann surface.

The Siegert states are known to obey unconventional orthogonality, normalization, and completeness relations, and this has historically been a source of controversy in the literature, with several competing schemes for regularizing the non-square-normalizable continuum-like states. In the SPSs, however, the origin of these questions become simpler to understand by working within the doubled dimension space. If the eigenvalues of Equation 5.20 are nondegenerate, then it may be easily shown (noting that the matrices are symmetric, not Hermitian) that the eigenvectors are symmetric with respect to the weighting matrix that appears on the right hand side,

$$\begin{pmatrix} \vec{c}^{(n)T} & \vec{d}^{(n)T} \end{pmatrix} \begin{pmatrix} \mathbf{L} & -\mathbf{O} \\ -\mathbf{O} & 0 \end{pmatrix} \begin{pmatrix} \vec{c}^{(m)} \\ \vec{d}^{(m)} \end{pmatrix} = 0, \quad \forall n \neq m. \quad (5.21)$$

The normalization condition may be derived by examining the behavior of the exponentially decaying bound states, and imposing unit normalization on them in the limit that R_0 is made sufficiently large that their amplitude on that boundary vanishes. We begin from the orthonormality expression with an undetermined normalization constant,

$$\begin{pmatrix} \vec{c}^{(n)T} & \vec{d}^{(n)T} \end{pmatrix} \begin{pmatrix} \mathbf{L} & -\mathbf{O} \\ -\mathbf{O} & 0 \end{pmatrix} \begin{pmatrix} \vec{c}^{(m)} \\ \vec{d}^{(m)} \end{pmatrix} = \alpha \delta_{nm}. \quad (5.22)$$

By the definition of \vec{d} , this condition reduces to an equivalent version in the original N -dimensional basis,

$$-(\lambda_n + \lambda_m) \vec{c}^{(n)T} \mathbf{O} \vec{c}^{(m)T} + \vec{c}^{(n)T} \mathbf{L} \vec{c}^{(m)T} = \alpha \delta_{nm}, \quad (5.23)$$

or in the position-space representation,

$$-(\lambda_n + \lambda_m) \int_0^{R_0} \phi_n(R) \phi_m(R) dR + \phi_n(R_0) \phi_m(R_0) = \alpha \delta_{nm}. \quad (5.24)$$

For bound states in the limit $R_0 \rightarrow \infty$, where the surface term vanishes, we must recover the conventional unit normalization

$$\int_0^\infty \phi_n(R)\phi_m(R)dR = \delta_{nm}. \quad (5.25)$$

This requirement uniquely determines the normalization constant $\alpha = -(\lambda_n + \lambda_m)$ for all states. Note that since all the states on the unphysical sheet, the eigenfunction diverges exponentially for increasing R , and thus the normalization condition 5.24 amounts to a cancellation of two exponentially growing terms; this is a potential source of numerical instability as the box size increases.

The orthonormality relation 5.22 implies an associated completeness relation in the doubled dimension space,

$$\sum_{n=1}^{2N} \frac{1}{2\lambda_n} \begin{pmatrix} \vec{c}^{(n)} \\ \vec{d}^{(n)} \end{pmatrix} (\vec{c}^{(n)T} \vec{d}^{(n)T}) = \begin{pmatrix} -\mathbf{L} & \mathbf{O} \\ \mathbf{O} & 0 \end{pmatrix}^{-1}, \quad (5.26)$$

which yields a set of multiple completeness relations upon reduction to the original N -dimensional basis:

$$\sum_{n=1}^{2N} \frac{1}{\lambda_n} c^{(n)} c^{(n)T} = 0 \quad (5.27)$$

$$\sum_{n=1}^{2N} c^{(n)} c^{(n)T} = 2\mathbf{O}^{-1} \quad (5.28)$$

$$\sum_{n=1}^{2N} c^{(n)} c^{(n)T} = 2\mathbf{O}^{-1}\mathbf{L}\mathbf{O}^{-1} \quad (5.29)$$

In fact, an infinite list of such completeness relations, generated by changing the power of λ_n in the weighted sum, may be derived on the basis of a recursion relation based on the Schrödinger equation 5.19, as shown in [142].

5.4 Siegert pseudostates: Single channel Green's function method

For a single-channel system with a finite-range potential, the SPS eigenstates serve as a complete expansion set for the Mittag-Leffler expansion theorem. Unlike the true Siegert states, for which convergence of this representation is problematic (see More and Gerjuoy [135] for an extended discussion), the SPS Green's function is guaranteed to converge, owing to the completeness relations given above. The derivation proceeds entirely by linear algebra [142], and requires no assumptions about the analytical properties of the exact Green's function in the limit $N \rightarrow \infty$.

The form of the Green's function depends on the choice of boundary conditions. The Green's function is required in all cases to vanish at the origin,

$$G(0, R'; k) = 0. \quad (5.30)$$

For a conventional (i.e. eigenvalue-independent) outer boundary condition, the Schrödinger Green's function equation

$$(H - E)G(R, R'; k) = \delta(R - R') \quad (5.31)$$

yields the solution

$$G(R, R'; k) = \sum_{n=1}^{2N} \frac{\phi_n(r)\phi_n(r')}{k_n^2 - k^2}. \quad (5.32)$$

This function is identifiable as the principle value Green's function; it displays neither incoming nor outgoing wave character on the boundary. On the other hand, the Siegert boundary condition

$$\left(\frac{d}{dR} - ik \right) G(R, R'; k) \Big|_{R=R_0} = 0 \quad (5.33)$$

has the same quadratic matrix equation representation as 5.19, and gives the alternate solution form

$$G(R, R'; k) = \sum_{n=1}^{2N} \frac{\phi_n(r)\phi_n(r')}{k_n(k_n - k)}. \quad (5.34)$$

This is the outgoing wave Green's function. Both forms are solutions to the same Hamiltonian, and differ only by a homogeneous solution of the Schrödinger equation.

These Green's functions require *all* $2N$ SPS solutions to be included in the summation; the omission of even one state (or pair of states) will give a totally incorrect solution. Since some of the pseudostates lie very far from the axis, their exponential growth at the outer boundary may be extremely rapid. This is a potential cause of serious numerical instability, as noted first in [149]; because the normalization of the Siegert pseudostates 5.24 involves a cancellation of an exponentially large integral with an exponentially large surface term, an exponential growth factor that exceeds the inverse of the machine precision will effectively destroy any orthonormality of the basis set, and thus the completeness relations on which the derivation of the Green's function depends.

Fortunately, the scattering matrix may be analytically derived directly from the Green's function expansion, giving either a "sum formula"

$$S(k) = e^{2ikR_0} \left[1 + ik \sum_{n=1}^{2n} \frac{[\phi_n(R_0)]^2}{k_n(k_n - k)} \right] \quad (5.35)$$

or the "product formula"

$$S(k) = -e^{2ikR_0} \prod_{n=1}^{2N} \frac{k_n + k}{k_n - k}. \quad (5.36)$$

The second result, rather remarkably, allows the S-matrix to be written entirely in terms of the eigenvalues; this completely bypasses the difficulty of numerical instability associated with the rapid exponential breakdown of the orthonormality relation for increasing value of R_0 , as discussed in [149].

The partitioning of configuration space into inner and outer regions for the SPS

eigenvalue and the subsequent symmetrization of the Hamiltonian by use of the Bloch operator are both reminiscent of the eigenvalue R-matrix method. Further, the derivation of the sum and product formulas shown above involves the surface value of the Green's function, $G(R_0, R_0; k)$, which is known to be proportional to the R-function (the one-dimensional R-matrix) [124]. This suggests that there should be some natural relationship between the SPS formulation and the R-matrix formulation. In fact, Baye *et al.* [149] have shown that for the same finite basis set representation, the methods are formally equivalent.² This homology provides an alternate expression for the S-matrix based on R-matrix theory, working directly from the primitive basis and the matrices in its representation without any need to find the complete set of SPS eigenstates. Of course, it may still be useful to find SPSs that correspond to the true physical Siegert states, for the sake of extracting their width and shape parameters, but for only a few states this can be easily accomplished by using the iterative approach. For the task of constructing the scattering matrix, the usefulness of the SPS formalism appears to be subsumed by the more general applicability of the R-matrix formalism; the latter is not susceptible to the Siegert states' noted susceptibility to long-range potential tails, and the multichannel version of R-matrix theory is far simpler than that for the Siegert state case.

Although the Green's function SPS theory is completely rigorous, it is severely restricted in utility. The limitations discussed in the last two sections of this chapter may be summarized: First, the SPS technique is best suited for single channel problems. An extension to even two-channel problems presents considerable challenge, and depends on the motivated selection of a fortuitously simple uniformization transformation [150]. Such a transformation is necessary to map the multi-valued function defined on the entire multisheet Riemann surface into a single-valued (but potentially quite complicated)

² This is already anticipated in the discussion of Lane and Thomas, who note that the Wigner-Eisenbud theory is "absolutely equivalent" to the Kapur-Peierls resonance theory [124], which in turn is related to the Siegert theory by the renormalization procedure suggested by More and Gerjuoy [135].

function of some new variable. For a two-channel system, the Riemann surface has four sheets (arising from two branch cuts, with branch points at each of the threshold energies) and the uniformized matrix eigenequation is quartic in the transformed variable. More generally, a N -channel problem will have a 2^N -sheet Riemann surface, and there is no known method for uniformization beyond the two-channel case.

Second, the derivation of the SPS Green's function expressions shown above is considered only for one dimensional model systems in the work of Tolstikhin *et al.* It remains a matter of untested conjecture whether or not there exists a multidimensional generalization of the requisite completeness relations, or whether the derivation yields a comparably simple closed form. At the approximate level, one might imagine an expansion in hyperspherical coordinates [151]; this treatment is only of utility, however, if the fragmentation modes are qualitatively similar. For the solution of competing ionization and dissociation channels, involving the coupling between fundamentally distinct degrees of freedom, an entirely different approach is necessary. This problem is further compounded by the possibility that one set of channels (e.g., the ionization channels in the hydrogenic system) may have Coulombic long-range interaction or a centrifugal effective potential term associated with finite angular momentum. In this case, the SPS formalism is not simply non-rigorous, but involves increasingly complicated corrections to the boundary condition that must be expressed at the level of a Taylor expansion.

In the conclusion of their work, Tolstikhin *et al.* hinted at the possibility of an entirely different philosophy for application of the Siegert states to scattering physics: "The SPS formulation also has advantages as a method of discretization of the continuum." Their suggestion called for the use of the SPSs as a basis for a time-dependent close-coupling calculation, with the recognition that this would "enable one to distinguish between the excitation of a resonance state and the underlying continuum scattering." This idea was implemented shortly thereafter by Yoshida and coworkers [152, 153] to describe the reflectionless loss of wavepacket probability by flux across a bounding

surface.

In fact, the ability of Siegert states to serve as a finite basis approximation to the continuum had already been demonstrated some time earlier in the work of Seideman and Miller [154], in the context of exploring the semiclassical analysis of transition state theory in nonperturbative regimes. If the wavefunction describing reaction dynamics in the vicinity of a harmonic transition state are expanded in terms of the normal mode frequencies, with the reaction coordinate naturally acquiring an imaginary frequency, then the Hamiltonian expanded in normal mode coordinates becomes complex symmetric. If this Hamiltonian is solved by direct diagonalization, instead of perturbative corrections to the semiclassical solution, then the spectrum contains a set of complex eigenvalues identifiable as Siegert states. These states do not represent resonant complex formation, but are instead the discretization of the reaction coordinate continuum, and give smooth and structureless contributions to the transition probability. Ryaboy and Moiseyev [155] showed that this set of states could be equivalently generated by a complex coordinate scaling in which the “white” (non-resonant) continuum was rotated off into the complex plane to uncover the Siegert eigenvalues and make their states square integrable in the scaled coordinates.

In the next section, we follow the approach of Seideman and Miller, rather than the more rigorous theory of Tolstikhin *et al.*, and begin from the hypothesis that the Siegert pseudostates can be usefully appropriated as a basis set for representing the discretized continuum of a channel expansion. In effect, this creates an additional (potentially infinite) set of complex-energy channels that extend arbitrarily high into the vibrational continuum. As Ryaboy and Moiseyev note, so long as these channels are associated with poles of the scattering matrix that are separated in the complex plane by “distances” (i.e., the difference between the real parts of the eigenvalues) that are smaller than the corresponding widths (i.e., the sum of the imaginary parts of the eigenvalues), the contribution to the observable scattering parameters (phase shift,

cross-section, etc.) can be sufficiently smooth to completely represent the background elastic scattering. In effect, the coupling to the continuum has been broken up into a sequence of broad, overlapping Lorentzian resonances which may be summed together to give a slowly varying baseline that reflects direct coupling to the continuum. If any physical resonance states are present, they will normally have poles much closer to the real axis, and thus their Siegert eigenstate widths will be much sharper and narrower, and their contribution to the spectrum will be manifestly resonant.

5.5 Extending MQDT to a Siegert pseudostate basis: Theory

Since the Siegert pseudostate basis consists of two branches of narrowly-spaced continuum-like complex eigenstates, in addition to the same rovibrational eigenstates they share with a more conventional basis with fixed logarithmic derivatives on the box boundary, they appear at first glance to include exactly the basis set contribution needed to give the wavefunction outgoing flux across that boundary. In principle, we would like to have a solution state located at precisely the energy of the vibrational continuum state into which the molecule is dissociating at that energy, with an imaginary part corresponding to the width of the predissociating resonance. In practice, if we have an artificial discretized continuum of sufficiently dense pseudostates with the property of being complete (or at least, complete with respect to the subset of continuum states one is attempting to represent), then the lack of a state at exactly the right energy and width is immaterial, and accommodated at the level of a complex basis expansion. This is quite different from the original method Jungen described above, where producing a pseudo-continuum state at precisely the correct energy (by varying a parameter iteratively in [53]) was of paramount importance for the success of the solution. (It is more similar to the later method of Ross and Jungen, which augments the basis by including additional sets that do not vanish, although even in this case the choice of additional sets must be optimized by the choice of a boundary condition resembling the boundary

condition of the real solution wavefunction. This cannot typically be known in advance, but must be optimized by hand for different resonances for best results, whereas the Siegert method avoids the need to readjust any parameters throughout an entire energy region.) There are, to be sure, numerical concerns to be addressed before this approach should be naively trusted, especially in light of the known peculiarities of the Siegert states, including their exponential divergence for increasing argument (on the “unphysical” sheet of the Riemann surface) and their innate overcompleteness. For the sake of devising a useful basis, however, it suffices that these concerns be resolved merely to the level of numerical accuracy (i.e., convergence of the calculated cross-section) under certain specified parameters that reflect relevant real-world conditions. This is a much weaker requirement than the one necessary for implementation by the more rigorous approach of Tolstikin *et al.*

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 [121]. 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 [45, 37], where N^+ is the ionic rotational momentum, and v^+ is the vibrational quantum number of the pseudostates. In the Siegert MQDT procedure, it is necessary to directly evaluate the S-matrix by the frame transformation integral

$$\begin{aligned}
S_{j,j'} = & \sum_{\Lambda} \langle N^+ | \Lambda \rangle \int_0^{R_0} \phi_j(R) e^{2i\pi\mu_{\Lambda}(R)} \phi_{j'}(R) dR \langle \Lambda | N^{+'} \rangle \\
& + i \sum_{\Lambda} \langle N^+ | \Lambda \rangle \frac{\phi_j(R_0) e^{2i\pi\mu_{\Lambda}(R_0)} \phi_{j'}(R_0)}{k_j + k_{j'}} \langle \Lambda | N^{+'} \rangle.
\end{aligned} \tag{5.37}$$

The surface term in 5.38 is new, but it is included because also arises in the orthonormality relation [142]. A similar transformation converts the body-frame transition dipole elements $D_{\Lambda}(R)$ into reduced dipole matrix elements in the same S-matrix representation,

$$\begin{aligned}
D_j^S = & (2J + 1) \sum_{\Lambda} \langle \Lambda | J_0 \rangle^{(J)} \langle \Lambda | N^+ \rangle \\
& \times \int_0^{R_0} \phi_0(R) D_{\Lambda}(R) e^{i\pi\mu_{\Lambda}(R)} \phi_j(R) dR.
\end{aligned} \tag{5.38}$$

Here $\phi_0(R)$ is the initial vibrational wavefunction, and J_0 and J are the total angular momenta of the initial and final states of the system, respectively. (Note that the surface term is omitted here because $\phi_0(R)$ is assumed to be negative on the surface.)

Note that the Siegert pseudostates are *never* conjugated in these expressions, even when they formally belong to the dual (“bra”) space. In particular, this means that the quantity labeled as $\vec{D}^{S\dagger}$ below is calculated by conjugating only $e^{i\pi\mu_{\Lambda}(R)}$ in the definition above, and not the dipole matrix elements directly. The unconventional nature of the inner product in a Siegert basis may be understood from a somewhat more intuitive perspective by means of an appeal to the symmetry properties of the Green’s function in the complex k plane, as first presented by More and Gerjuoy [135]. To briefly sketch this argument, we begin by noting that the Green’s operator formed by eigenvector expansion over a resonance state basis such as the Siegert pseudostates obeys the identity

$$G^{\dagger}(k) = G(-k^*). \tag{5.39}$$

This relation follows rigorously from the fact that the Green's operator is real for negative energies (i.e., for pure imaginary values of k), via the Schwartz reflection principle. (This is in contrast to the more usual case of the reflection principle, defined for functions which are real when their argument is real.) This nonstandard symmetry also applies to the left eigenvector states $\tilde{\phi}_j$ and right eigenvector states ϕ_j

$$\tilde{\phi}_j(R; k) = \phi_j(R; -k^*) = \phi_j^*(R; k). \quad (5.40)$$

In other words, if $\langle \tilde{\phi}_j |$ is a left eigenvalue of the Green's operator $G(k)$, then $|\tilde{\phi}_j\rangle$ is a right eigenvalue of $G(-k^*)$. Since both the transformation between left and right eigenvectors *and* the transformation between the bra and ket space representations both involve a conjugation, the net effect is that the functions of the dual space are unconjugated.

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* [156, 44] systematically eliminates flux in all electronic channels below the energy threshold for electron escape (the “closed-channel subspace”) to form a “physical” S-matrix \mathbf{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

$$\mathbf{S}^{phys} = \mathbf{S}_{oo} - \mathbf{S}_{oc}(\mathbf{S}_{cc} - e^{-2i\beta})^{-1}\mathbf{S}_{co}. \quad (5.41)$$

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, \mathbf{S} is the scattering matrix, and the subscripts indicate partitions of the matrices into closed and open subspaces [44].

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 pseudo-continuum states. It can be used to calculate the total cross-section for dissociative recombination by means of conventional formulas, but with the departure from unitarity, $1 - \sum_j |\mathbf{S}_{j,j'}^{phys}|^2$, identified as the probability $|\mathbf{S}_{d,j'}^{phys}|^2$ 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 [44] for further details. The contributions from all open channels can 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 [48], but expressed here in the equivalent but more symmetrical form of Granger [157, 158],

$$\sigma_{total}(E) = \frac{4\pi^2\alpha\omega}{3(2J_0 + 1)} \text{Re} \vec{\mathbf{D}}^{\text{S}\dagger} \left[\mathbf{1} - \mathbf{S} \mathbf{e}^{2i\beta} \right]^{-1} \left[\mathbf{1} + \mathbf{S} \mathbf{e}^{2i\beta} \right] \vec{\mathbf{D}}^{\text{S}} \quad (5.42)$$

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 $\beta_j = \pi\nu_j$ for “closed” channels with $E < \text{Re} E_j$, and $\beta_i = i\infty$ 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 $\Gamma_j = 2 \text{Im} \epsilon_j$. Within the Siegert state formulation, the electron energy $\epsilon_j = E - E_j$ will naturally take on a complex value in any channel where the channel eigenenergy E_j is itself complex, while E remains real.

Given \mathbf{S} and ϵ_j , either of the two cross-section formulas above can 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 wavefunction 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 formulae at any energy provides the photodissociation cross-section.

In order to test the validity of this hypothesis, we will start by defining a set of Siegert pseudostates for the H_2^+ internuclear potential. The eigensolutions fall into three classes, as shown in Figure 5.8. Those lying along 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 antibound 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 $\text{Im } E_j$, a decision that can be justified conceptually on the grounds that these states display a time dependence in which total probability decreases over time, corresponding to decay into the continuum. (For a much more sophisticated discussion of this topic, see the extensive discussion of [159, 160, 161], which arrives at the same conclusion for complex expansions of the Green's function using far more rigorous formal arguments.) For MQDT matrix elements it is also acceptable to reject states lying very high in the continuum, since their Franck-Condon overlap with the bound states is negligible.

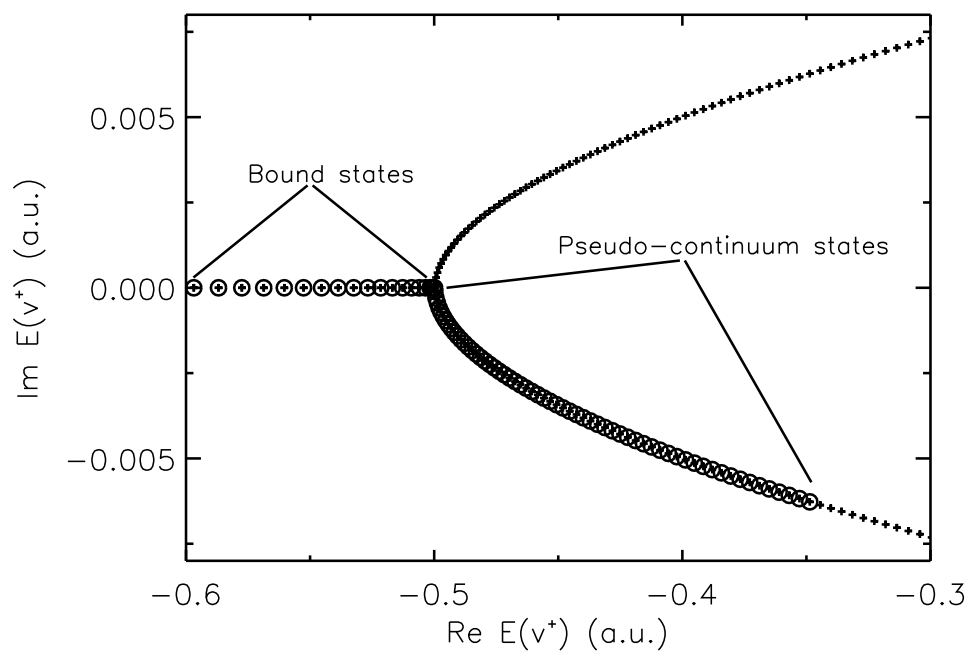


Figure 5.8: Distribution of H_2^+ vibrational Siegert pseudostate energies in the complex energy plane for angular momentum $N^+=1$. Only the circled states are included as channels in the scattering matrix.

Tolstikhin *et al.* discuss the unusual completeness relation obeyed by the full set of Siegert pseudostates, which has 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 this restricted subset behaves like 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. The ability to represent L^2 functions diminishes somewhat for extremely narrow functions, for which the primary contribution must come from shorter wavelength pseudocontinuum functions. For example, when expanding in terms of a truncated set with a maximum $\text{Re}(k)$ of about 50 a.u., only features broader than $\frac{1}{7}k=0.02$ a.u. in width can be well- represented. When using this truncated set numerically, a Gaussian of the form $e^{-\alpha(R-R_{eq})^2}$ can be only represented to 10^{-6} accuracy when $\alpha=100$ (i.e., a Gaussian of width 0.14 a.u.), has a relative error of over 10% for $\alpha=1000$ (i.e., a Gaussian of width 0.045 a.u.), and fails entirely for $\alpha=10000$ (i.e., a Gaussian of width 0.014 a.u., smaller than the wavelength of the highest excited state included in the basis). 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 [154].

5.6 Extending MQDT to a Siegert pseudostate basis: Results and discussion

In the region of the ungerade H_2 spectrum between 127200 and 127800 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 cross-section. Comparisons of our results with other theoretical and experimental values [55, 121] for the relative yields of selected resonances appear in Table 5.2. Note particu-

larly that this method is able to correctly describe the strong rotational dependence of the $4p\pi, v^+ = 5$ branching ratio, a nontrivial consequence of subtle channel interactions.

Table 5.2: Photoionization and photodissociation yields for select *ungerade* resonances in H_2 for which the relative yields have been experimentally observed [55].

State	Source	Energy	% Ion.	% Diss.
$3p\pi, v = 8, R(0)$	Observed	127248.2	10(5)	95(5)
	Theory ^[121]	127246.9	1	99
	Present	127242.2	1	99
$5p\sigma, v = 4, R(0)$	Observed	127599.4	90(10)	10(10)
	Theory ^[121]	127602.2	88	12
	Present	127606.8	76	24
$4p\pi, v = 5, R(0)$	Observed	127667.6	82(5)	18(5)
	Theory ^[121]	127665.4	93	7
	Present	127666.6	97	3
$4p\pi, v = 5, R(1)$	Observed	127599.4	30(10)	70(10)
	Theory ^[121]	127758.4	17	83
	Present	127759.5	29	71

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 measurements of the ratio between pure ionization and dissociative ionization have been performed since the 1970s by a number of researchers [162, 163, 164], along with at least one early theoretical calculation [165]. Since our ionization spectrum is a sum over individual channels, one 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 5.9.

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. 5.10 shows the dissociative recombination spectrum of a simplified H_2 model potential (neglecting rotation and with R-independent quantum defects), compared with the familiar approximation of O'Malley for smooth background scatter-

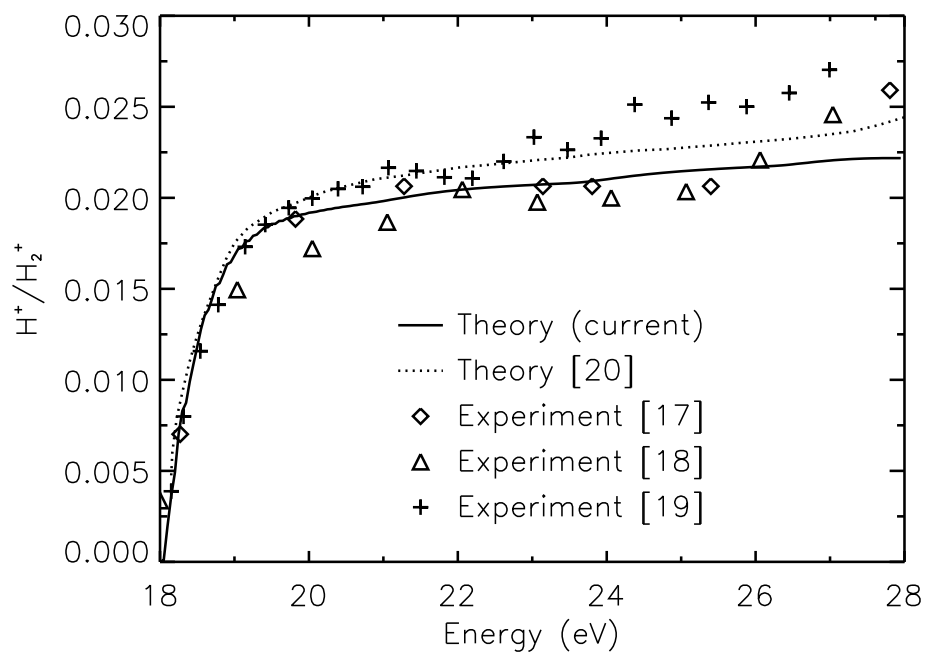


Figure 5.9: Dissociative photoionization cross-section, as a ratio to the total photoionization cross-section. The solid line is the current theory, the dotted line is an earlier theory [165], and the points are data from various experimental measurements [162, 163, 164].

ing by direct processes [166]. This spectrum accurately reproduces the background, and also describes complex interference effects from the series of resonances converging to each Rydberg threshold.

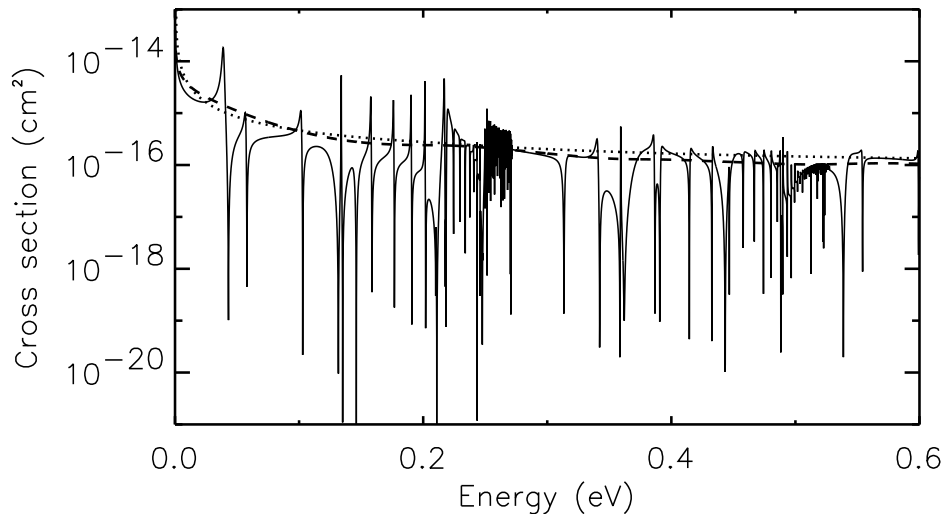


Figure 5.10: Dissociative recombination cross section for the model potential, unconvolved (solid) and convolved with a Lorentzian of width 0.1 eV (dashed), compared to that resulting from the O'Malley formula (dotted).

The extension of the Siegert MQDT method to polyatomic systems might be attempted in several ways. First, by transforming the nuclear coordinates to a hyperspherical coordinate system, a multidimensional problem is effectively reduced to a single scattering coordinate (the hyperradius), allowing the formulas above to be adapted with minimal alteration. This has already been demonstrated for the dissociative recombination of H_3^+ [28], with results that appear to correctly reproduce broad features in the experimental spectrum, although the theory appears not to be sufficiently precise to describe detailed resonance structures. Alternatively, it might be possible to recast the Siegert eigenproblem in a generalized form that admits arbitrary dimension. Even if the completeness relations and matrix inversion identities required for the derivation

of the Green's function (as in the Tolstikhin papers) were no longer possible to write out analytically in multiple dimensions, the ability to construct a "locally complete" representation of the multidimensional continuum would still be sufficient to provide appropriate channel states for the MQDT channel expansion.