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Perturbation Theory and Atomic Resonances Since Schrödinger's Time

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Abstract. Quantum theory makes a sharp distinction between bound states and scattering states, the former associated with point spectrum and the latter with continuous spectrum. Resonances associated with quasi-stationary states bridge this distinction, and have posed mathematical challenges since the beginning of the Schrödinger theory. Here the development of the mathematical underpinnings of resonance theory in atomic physics is reviewed, with particular reference to the rôle of the (DC) Stark effect, and time-independent perturbations of bound states in the two-body problem in atomic and molecular physics.

This review is dedicated to Barry Simon, whose vision in [**160**] laid out a program of more than thirty years of rigorous mathematical research on resonances and perturbation theory.

Contents

1. Resonances in the Early Days of the Schrödinger Theory

It was a perturbation calculation that convinced physicists that Schrödinger's theory was superior to the earlier quantum theory of Bohr and Sommerfeld based on phase integrals. The old quantum theory provided an explanation for the spectral lines of isolated hydrogen, but there was no easy or systematic procedure to handle perturbations of exactly integrable models. Schrödinger considered the Stark effect [**175, 116, 108**], the shifts caused to hydrogen's emission spectrum by the

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application of a constant electric field, in 1926 [**153**]. In Schrödinger's model the energies are eigenvalues of the hydrogen Stark Hamiltonian, which in scaled units reads

$$-\nabla^2 + \frac{1}{r} + \kappa x_1. \tag{1}$$

Schrödinger adapted Rayleigh's [**146**] procedure for generating the Taylor series in powers of κ for the eigenvalues and eigenfunctions of a family of linear operators of the form $H_0 + \kappa W$. At first order he recaptured the formulae of Epstein [**45, 46**] for the shifts in the spectral lines, and with the more systematic procedure he was able to obtain second-order corrections and better agreement with experiment. Although the Stark Hamiltonian was known to be separable in parabolic coordinates, and to correspond to an integrable classical system [**45, 46**], it was clear from Schrödinger's procedure that separability and integrability played no essential rôle in the calculation, and that perturbative corrections could be calculated to arbitrary order. Due to this first major success of the Schrödinger theory, both Schrödinger's equation and his perturbation scheme were swiftly adopted, and the old quantum theory was soon scrapped [**33, 127**]. (Notoriously reluctant to accept the new theory was Stark [**176**] himself.) To this day the perturbation expansions of Rayleigh and Schrödinger are easier to calculate and more successful than the perturbation methods used in classical mechanics, on which the Bohr–Sommerfeld theory was cobbled together.

Given the impact of Schrödinger's analysis on the development of modern physics, it is ironic to note much later proofs that:

- The operator (1) has no eigenvalues at all as soon as $\kappa > 0$ [**181, 182, 15**]; and
- The Taylor coefficients according to Schrödinger's prescription follow a precise asymptotic law [**58, 68**], and the radius of convergence of the series is 0.

The quantum states observed in the Stark effect are not truly bound, but are instead resonance phenomena, although Schrödinger did not recognize this in [**153**]. While resonances of classical oscillators formed part of the tool-kit of every physicist at the dawn of quantum mechanics, it took some time for physicists to address or even articulate the basic questions about quantum resonances:

1. What is the definition of a resonance energy?
2. Is there a "resonance state," and how is it defined?
3. How can the resonance energy be calculated?
4. How can the time-decay of a resonance be quantified?

The first step was taken by Oppenheimer, in one of his earliest works [**137**]. Oppenheimer stated that the Stark Hamiltonian (1) had no eigenvalues, and rather cavalierly cited an article of Weyl [**187**] with a loose connection to this claim. He then attempted to calculate the rate of decay of the wave function associated with the ground state of unperturbed hydrogen by approximating a solution to the Schrödinger equation including the electric field and estimating a matrix element connecting this state to the unperturbed hydrogen state. Although Oppenheimer did not use the term "resonance," he addressed the fourth question for the first time within quantum theory, and implicitly considered something one could regard as a resonance state, a special non-normalized solution of Schrödinger's equation.

Not long thereafter Weisskopf and Wigner [**186**] defined a resonance as a bump in the graph of the scattering amplitude and explicitly connected it to the presence of a pole in the analytic continuation of the scattering amplitude, located close to the real frequency axis. The analogy they made was with a system of classical damped oscillators, in which the Fourier transform of the displacement has a pole in the complex plane at position $\omega_0 - i\frac{\Gamma}{2}$, contributing a Lorentzian line shape proportional to

$$\frac{1}{(\omega - \omega_0)^2 + \frac{\Gamma^2}{4}} \tag{2}$$

in the response function. From the shape of the graph, Γ is referred to as the *width* of the resonance.

With this analogy and the observed exponential decay in time of a radioactive species, early resonance theorists attempted to fit the probability of decay of a resonance state, perhaps as coupled to a radiation field, to an exponential function, assuming that

$$|\,\langle \Psi_0, \exp(-itH)\Psi_0\rangle\,|^2 \sim C\exp(-\Gamma t), \tag{3}$$

where Ψ_0 is some sort of resonance state. (In contrast, for generic scattering states, polynomial decay in time is the most that can be expected [**96, 92**].) If the ansatz of exponential decay in time is accepted, then formal arguments lead one to expect that the Γ in (3) should be comparable to the Γ in (2) and given by a version of the *Fermi Golden Rule* [**47**], according to which to leading order Γ is proportional to the square of a matrix element coupling the resonance state to the continuum.

A criticism of the usual formal arguments for (3) is to be found in [**161, 148**]. Although early arguments for the exponential-decay ansatz were rather vague about what constitutes the resonance state Ψ_0, in practice it was often chosen as an eigenstate of an unperturbed H_0, or as such an eigenstate corrected to some finite order in perturbation theory. Alternatively, the left side of (3) might be replaced by the projection of $\exp(-itH)\Psi_0$ onto a set of continuum states localized near the energy of Ψ_0. A difficulty with (3) is that it is one of those deep truths that are clearly false! For small t the expression in (3) should behave as $1-O(t^2)$, which is inconsistent with exponential decay. On the other hand, it can be shown that if (3) holds for some $\Psi_0 \in \mathcal{H}$ as $t \to \infty$, then $\sigma(H) = \mathbf{R}$: Following Herbst [**75**] (see also [**161**]), observe that (3) would imply that the spectral measure $d\mu_{\Psi_0} := \left\langle \Psi_0, P_{(-\infty,\lambda]}\Psi_0\right\rangle$ is absolutely continuous and has an analytic continuation to the strip $\left\{\mathrm{Im} < \frac{\Gamma}{2}\right\}$. If the support of $d\mu_{\Psi_o}$ were not the whole real axis, then analytic continuation would imply that $d\mu_{\Psi_0} = 0$ identically on the strip. Although exponential decay in time is possible for the Stark effect Hamiltonian (1), for which the spectrum is $\mathbf{R}$, it is consequently excluded in typical situations where the Hamiltonian is bounded from below, and the most that can be hoped for is transient exponential decay according to (3). A more realistic expectation for the decay law is

$$\langle \Psi_0, \exp(-itH)\Psi_0\rangle = \exp(-i(E - i\Gamma/2)t) + b(t), \tag{4}$$

where the remainder $b(t)$ is small for intermediate times but relatively significant for small t and dominant for large t.

The physical mechanism of most resonances has generally been understood to be the existence of a quasi-stationary state [**24, 142**] caused by perturbation of a true bound state. Two variants of this mechanism are encountered:

1. Shape resonances, which correspond to confinement of a particle by a barrier, through which tunneling occurs, as in Gamow's model of alpha emission [**54**], in which the potential energy was a radial function proportional to $\chi_{\{a\leq r\leq b\}}$. The Stark effect may also be viewed as a kind of shape resonance: Although the strength of the electric field may be small, the perturbation interaction remains large somewhere far from the origin. Conceptually, a shape resonance arises as a classical bound state liberated by tunneling. Its signature is a very slow decay, with a characteristic time identifiable with the reciprocal of Γ in (2).
2. Embedded bound states [**134, 43**] that "dissolve into the continuum" under a slight perturbation. The most important model is that of the Auger effect in helium. If the nucleus is treated as fixed in space and the electron-electron interaction is neglected, then the helium spectrum is the set sum of two scaled Balmer (hydrogen) spectra, consisting of negative bound states at $\left\{-\frac{Z}{4n^2}\right\}$ and a continuum covering the non-negative real values. The continuous spectrum of this operator begins at $-\frac{z}{4}$ and overlaps many eigenvalues and thresholds. The introduction of the electron-electron interaction destroys the symmetry of the operator and the embedded eigenvalues are expected to couple to the continuum and disappear. The decay of resonances associated with embedded eigenvalues is not as slow as that of shape resonances.

Other mechanisms can arise if the interaction depends on time (e.g., [**190**]), but will not be pursued here.

There is a unified way to understand resonances and true eigenvalues of a quantum Hamiltonian, namely, as poles of the resolvent operator $(H-\lambda)^{-1}$ or its integral kernel, the Green function. If the pole occurs on the real energy axis, it corresponds to an eigenvalue in the usual way, but additional poles may occur when the resolvent is analytically continued onto an "unphysical sheet." Schrödinger Hamiltonians are supposed to be self-adjoint and therefore have only real spectra, but the non-real poles in the continued resolvent might be located at the eigenvalues of some related non-self-adjoint operator. Non-real eigenvalues had been introduced into physics as early as 1884 by Thomson [**180**], as a way to understand resonances in electromagnetic theory, and they appeared in quantum scattering theory since the 1950's [**115, 49**], somewhat artificially. The idea of finding poles in the resolvent as continued analytically across a branch cut on the real energy axis was introduced by Schwinger in [**155**]. Although quite plausible, the connection between resonances defined as poles of a continued resolvent and those defined as poles in the scattering amplitude or zeroes in the Jost function was initially murky. (Theorems equating them in some generality have been proved in, e.g., [**66, 18**].)

The next section of this review will recount some rigorous mathematical approaches to atomic resonances that were elaborated in one-dimensional and highly symmetric models in the 1970's and 80's. Section 3 will describe later developments in which assumptions of symmetry were abandoned as more sophisticated methods of scattering theory and PDEs became available. Finally, some alternative approaches to resonance theory that have been developed will be mentioned.

2. Mathematical Foundations of Quantum Resonance Theory and the Analysis of One-Dimensional and Separable Models

In the 1930's and 40's, the work of Rellich [**151**] and Kato [**101**] put time-independent perturbation theory for non-relativistic quantum theory on a firm mathematical footing, particularly for Hamiltonians with discrete spectra. Families of operators depending on a coupling constant κ were understood as analytic functions of a complex variable, taking values in an operator algebra. Most often the family of operators has the form $H_\kappa := H_0 + \kappa W$, and if W is relatively bounded, in the sense that $D(W) \supseteq D(H_0)$ and there are constants a and b such that for all $f \in D(H_0)$,

$$\|Wf\| \leq a\|H_0 f\| + b\|f\|, \tag{5}$$

then the spectral projectors of H_κ for isolated subsets of the spectrum depend analytically on κ, and consequently the eigenvalues of H_κ can be analytically continued, provided that they do not meet other parts of the spectrum.

Wave operators were introduced by Møller in [**126**], which enabled Kato [**102**] and Birman [**22**] to lay the mathematical foundations of quantum scattering theory over the following decades (see [**41, 147, 9, 135, 143, 82, 189**]). Møller's work was also the starting point for the development of acoustic scattering theory in the hands of Lax and Phillips [**113**]. In the early period rigorous results about resonance scattering were rare. One of the first topics connected with resonances to receive attention was the mechanism whereby an eigenvalue could dissolve into the continuum. In [**50**] Friedrichs discussed some simple models in which an eigenvalue embedded in the continuum dissolves under a perturbation, and made connections with quantum scattering theory. Soon afterwards Titchmarsh attempted to make sense of the perturbation series that Schrödinger had developed for the Stark effect. In [**181**] he showed for the first time rigorously that a version of the Stark Hamiltonian does not have any eigenvalues, and introduced the notion of *spectral concentration*.

Definition 1. Let H_n be a sequence of self-adjoint operators with spectral projectors $E_n(S)$. Let T and $\{S_n\}$ be subsets of $\mathbf{R}$. Then the part of the spectrum of H_n in T is *concentrated on* S_n provided that

$$E_n(T - S_n) \to 0$$

in the strong sense. (The notation of [**103**] is followed here.)

Titchmarsh showed that the asymptotic series for Stark "eigenvalues," as derived by Schrödinger, defines nested intervals on which the spectrum of (1) is concentrated [**182**]. Spectral concentration gave some insight into the third basic question of how the resonance energy can be calculated, at least in an asymptotic sense.

Titchmarsh's analysis was extended by Conley and Rejto [**34**] and by Riddell [**152**]. Howland also analyzed spectral concentration in a variety of contexts [**85, 86, 87, 88**]. In [**133**], Nenciu showed under wide circumstances that if the unperturbed operator has finitely degenerate eigenvalues in a given interval, then there is spectral concentration near those eigenvalues to order p if and only if there is an asymptotic basis of pseudo-eigenvectors to order p. Nenciu's analysis included general Stark Hamiltonians. Nenciu also showed that if there are pseudo-eigenvectors to order p, then they remain quasi-stationary for a correspondingly long time. A

perturbative treatment of resonances seemed, however, to offer little hope of a precise estimate of the rate of decay of a shape resonance, for which Γ is not merely "several million times" smaller than ω_0, as Weisskopf and Wigner marveled more than once in [**186**], but, as an exponentially small function of κ, identically 0 in perturbation theory.

In addition to the limitations of spectral concentration for quantitative calculations, it was not even clear that spectral concentration could adequately be used to define quantum resonance. Indeed, in 1975 Howland [**89**] showed that although resonances imply spectral concentration, it is possible for spectral concentration to occur in the absence of a corresponding singularity in a continued resolvent.

Howland is also credited with a fundamental insight about possible definitions of a resonance. In contrast to Occam's razor, which cuts away complications in scientific theory, *Howland's razor* cuts away simplicity. As formulated in [**161**], this principle states:

> No satisfactory definition of a resonance can depend only on the structure of a single operator on an abstract Hilbert space.

For example, the family of Stark Hamiltonians (1) is unitarily equivalent for all non-zero real κ [**15**]. How could the energy or lifetime of the resonance depend on κ, if the definition were a unitary invariant?

Two key techniques opened the way to making sense of the perturbation series for resonances and precisely calculating resonance widths in the 1960's and 70's: complex scaling and summability methods. The inspiration of Aguilar, Balslev, and Combes [**6, 17**] was to complexify Euclidean symmetry groups and to use analytic continuation to define resonance energies as non-real eigenvalues of the family of operators produced by conjugating the Hamiltonian with the complexified groups. In the original version of complex scaling, Aguilar, Balslev, and Combes exploited symmetry under dilatations. The unitary group of dilatations depends on a real parameter θ such that $\mathbf{x} \in \mathbf{R}^\nu \to e^\theta \mathbf{x}$, hence $[U(\theta)f](\mathbf{x}) := e^{\nu\theta/2} f\left(e^\theta \mathbf{x}\right)$. For suitable potentials one can treat θ as a complex variable and regard $H_\theta := U^*(\theta) H U(\theta)$ as an analytic family of operators. An easy calculation shows that if θ is continued off the real axis, the essential spectrum of the complex-scaled one-particle Laplacian is simply rotated in the complex plane. Correspondingly, for a many-particle free Hamiltonian, the essential spectrum becomes the union of rays in the complex plane emanating from threshold energies. Assuming relative compactness for the potential energy function, the same will be true for $\sigma_{\rm ess}(H_\theta)$. Meanwhile, by Kato–Rellich perturbation theory, isolated eigenvalues of H_θ are analytic in θ and can be continued as long as they remain isolated. The kicker is that variations of θ in real directions correspond to unitary transformations of H_θ, so the spectrum is constant with respect to such variations. An eigenvalue is therefore constant as a function of θ on any connected component of its domain of regularity. It follows that for "dilatation-analytic" potentials, *eigenvalues are independent of θ except that they may appear or disappear when the essential spectrum passes over them.* Resonances correspond to non-real eigenvalues of the complex-scaled operator. The complex-scaling definition of a resonance thus complies with Howland's razor, but without special dependence on the introduced parameter. Resonance eigenvalues may well depend on perturbation parameters κ occurring in H, but in the usual situations they are isolated and non-degenerate, and hence accessible to well-controlled perturbation expansions in powers of κ. Complex scaling also offers a definition of a

resonance state as the eigenfunction corresponding to a non-real eigenvalue and its analytic continuation in θ.

In an influential article [**160**], Simon synthesized and clarified the theory of resonances and dilatation analyticity, showing that it applies to important physical models, including Coulomb and Yukawa interactions. This article cemented the importance of complex scaling as a tool in quantum physics [**31**], and it has become a standard reference in the physical literature for the mathematical underpinnings of the technique (e.g., [**150, 99, 23, 84, 27, 125, 40**]). For mathematical physicists, Simon articulated the challenge of a better understanding of the time-decay of resonance and related matters:

> The goals of the time-dependent theory are much more ambitious than merely proving certain eigenvalues dissolve .... The time-dependent theory is supposed to compute a characteristic lifetime τ, for the decay of a state ... It turns out to be a very hard problem to define the lifetime directly.

Simon identified a suitable interpretation of the Fermi Golden Rule for Γ in (3) and (4) as an estimate of the imaginary part of the Taylor coefficient a_2 of a resonance eigenvalue associated with a bound state at $\kappa = 0$. (The coefficient a_1 is real by first-order perturbation theory.) Using Stone's formula and second-order perturbation theory, one can express the resonance width for a perturbed non-degenerate discrete bound state as

$$\frac{\Gamma}{2} = 2\pi \frac{d}{d\lambda} \left\langle \Phi_0, W\tilde{P}(\lambda)W\Phi_0 \right\rangle \Big|_{\lambda=\lambda_0}, \tag{6}$$

where Φ_0 is the unperturbed eigenfunction and $\tilde{P}(\lambda)$ is the spectral projector for $(-\infty, \lambda) \setminus \{\lambda_0\}$, cf. [**148**].

In the period around and following [**160**], analytic function theory helped to clarify the issues raised in [**160**] and to unify the understanding of high-order perturbation theory, resonances, and complex scaling. Inspiration was drawn from the detailed understanding of the eigenvalues $\lambda_k(\kappa)$ of the one-dimensional anharmonic oscillator

$$p^2 + x^2 + \kappa x^4 \tag{7}$$

and their analytic continuations that had been achieved beginning with the work of Bender and Wu [**19**]. Bender and Wu had observed that the perturbation coefficients for an eigenvalue $\lambda(\kappa)$ as functions of κ can be efficiently calculated with a difference equation, and the perturbation series diverges. They also tied the analysis of the functions $\lambda_k(g)$ to the WKB approximation of semiclassical quantum mechanics (more accurately called the Liouville–Green approximation [**114, 64, 136**]).

At that time a popular method for interpreting divergent series was Padé approximation, and in [**119**] it was proved that the diagonal Padé approximants for the anharmonic oscillator perturbation series converge to the eigenvalues. Afterwards, Graffi, Grecchi, and Simon [**61**] noted that an understanding of the domain of analyticity of the eigenvalues [**159, 118**] and control on the growth in n of a_n allow the use of Borel summation to define a unique analytic function $f(\kappa)$ to which the series is asymptotic in a sector. (The Borel sum works by summing the series with a_n replaced by $\frac{a_n}{(n-1)!}$, then analytically continuing onto the positive real axis, and recovering $f(\kappa)$ with a Laplace transform.) The Borel sum became a standard method that in due course was adapted for many other classic models where the perturbation series diverges, including the Zeeman effect [**14, 13, 16**], and

the hydrogen molecular ion [**38, 60**], which resemble the anharmonic oscillator in that discrete eigenvalues remain discrete under singular perturbation. The idea of a "Bender–Wu theory" relating high-order perturbation theory, summation methods, and tunneling for the complex eigenvalues in resonance models [**19, 20, 21**] was made plausible by considering (7) when κ is continued to negative values, in which case, at least at the formal level, the model exhibits non-real eigenvalues and quasi-stationary states. In [**159**] Simon showed that Taylor coefficients a_n are proportional to the moments on the negative κ axis of the imaginary part of the continued anharmonic oscillator eigenvalues. In resonance models, given the ability to displace the essential spectrum and analytically continue the resolvent to a second sheet, where resonances can be defined as eigenvalues, an analogous formula can often be derived with Cauchy's theorem. For the Stark effect it reads [**77, 68**]

$$a_{2n} = -\frac{1}{\pi}\int_0^R \kappa^{-2n-1}\Gamma(\kappa)d\kappa + O(R^{-2n}).$$

In the remainder of the 1970's, the vision of a perturbation theory of resonances advanced rapidly, with

- Avron and Herbst's analysis of Stark Hamiltonians using translation and dilatation analyticity [**15, 74**];
- A Bender–Wu analysis of high-order perturbation theory and summability for Stark resonances [**77, 58, 161, 158, 59, 78**]; and
- Precise tunneling asymptotics for the resonance widths for the Stark effect, i.e., the (corrected) Oppenheimer formula [**191, 68**],

among other mileposts. By the end of the decade, most of the standard models of quantum resonance brought about by perturbations of eigenvalues were mathematically well-understood. The general theory, however, left much to be desired. Dilatation analycity was an oddly strict condition to put on the potential energy for a number of reasons. First, from the point of view of operator theory, the resolvent $(H-\lambda)^{-1}$ is already an analytic function of λ on the resolvent set of H, without regard to the details of H, such as whether its coefficients depend analytically on auxiliary parameters in H that have nothing to do with λ. It does not help much that some such parameter, like θ in the dilatation argument, is introduced *ad hoc*, even if resonance eigenvalues are independent of θ, but for whether or not they exist. Second, the special assumptions needed to achieve the magical results of complex scaling excluded some of the simplest models, like those where the potential is radial and of compact support, in which case the original version of dilatation-analyticity is not able to encompass the familiar use of the Sommerfeld outgoing radiation condition [**174**] to define a resonance state. In [**162**] Simon proposed the method of exterior complex scaling to respond to this shortcoming. Many other variants of complex scaling, relying on other symmetries or localizing in other ways, were introduced in due course (e.g., [**81, 71**]). The method reached its culmination in the 1980's in the hands of Hunziker [**90, 82**].

The really sharp results attained by 1980 on high-order perturbation theory and estimates of exponentially small quantities like Γ were restricted to one-dimensional, separable, or otherwise highly symmetric Hamiltonians, usually for one particle. This restriction was not so much due to a shortcoming of the theory of resonances as it was due to the method of calculation. In a circumstance where Γ is exponentially small, the difficulty is to disentangle it from the perturbation expansion

for the energy, despite Γ being smaller than the perturbative error at all orders. A successful strategy for accomplishing this is to use integral identities for Γ in terms of an identifiable resonance eigenfunction, and then estimate the exponential growth of the latter with sufficient accuracy.

For example, suppose that one has identified a resonance with a non-real eigenvalue $\lambda - i\frac{\Gamma}{2}$ and, with the aid of complex scaling, has picked out a canonical "resonance solution" Φ_r solving $(-\Delta + V(\mathbf{x}))\Phi_r = (\lambda - i\frac{\Gamma}{2})\Phi_r$, where V is a real-valued potential function. Of course Φ_r is not normalizable in L^2, but one can multiply by $\overline{\Phi_r}$ and integrate over a finite region S. With Green's identity, it is easily calculated that

$$\Gamma \int_S |\Phi_r|^2 d^\nu x = 2 \int_{\partial S} \mathrm{Im}\left(\overline{\Phi_r}\Phi_r\right) d^{\nu-1}x. \tag{8}$$

Thus with a good choice of S and uniform control on the resonance solution Φ_r, an estimate of Γ can be obtained, which is accurate in proportion to the pointwise accuracy with which Φ_r is known.

In that period, excellent techniques were available for uniform approximation of solutions to ordinary differential equations (e.g., [**136**]), including ones that grew or decayed exponentially, but not for partial differential equations. Not only are geometric complications minimal for ordinary differential equations, but, most usefully, the solution space of the time-independent Schrödinger equation is two-dimensional. With the Wronski identity, variation of parameters, etc., a plethora of explicit relations can be found for special solutions, whether for their dependence on the position x or on a spectral parameter. In the case of the Stark effect and other separable problems, uniform approximation of solutions of ordinary differential equations enabled the proof of "tunneling" formulae like the corrected Oppenheimer formula [**68**].

One of the earliest canonical models of the subject, shape resonance, was relatively late to receive rigorous mathematical analysis. This model was introduced in the 1920's by Gamow [**54**] and by Gurney and Condon [**65**] to understand alpha emission. A particle is supposed to be confined in a potential well surrounded by a high potential barrier, outside of which the potential is zero, or at least tends to zero. In the radially symmetric case one can separate variables and study the operator

$$-\frac{d^2}{dr^2} + U(r) + \beta V(r) \tag{9}$$

on $L^2(\mathbf{R}^+)$ with a Dirichlet boundary condition at the origin. The barrier V may be supposed non-negative and strictly positive a.e. on its support, a finite interval such as $[1, 2]$. The operator (9) is considered in the strong-coupling limit, and as $\beta \to \infty$ it tends formally to

$$-\frac{d^2}{dr^2} + U(r) \tag{10}$$

for $r < 1$, with a Dirichlet condition at $r = 1$. Outside the finite region, the time-independent Schrödinger equation is identical to the Helmholtz equation obtained by separating the wave equation, and Gamow imposed an outgoing radiation condition on (9) equivalent to that used earlier by Sommerfeld [**174**] in his analysis of the wave equation. (Thomson [**180**] had an even earlier version of an outgoing radiation condition.) The outgoing condition was specifically connected with the notion of a quantum resonance by Kapur and Peierls [**100, 141**] and Siegert [**156**],

and is perhaps the most common way to define resonance states in the physical literature (e.g., [**192, 108**]). The outgoing radiation condition is precisely recovered in the shape-resonance problem for compactly supported radial potentials when the method of exterior complex scaling is brought to bear.

Ashbaugh and Harrell [**11**], using uniform approximation of solutions of ODEs and the implicit function theorem, established in this situation that the eigenvalues of (10) turn into eigenvalues or resonances of (9). A systematic perturbation theory was developed, in fractional powers of β, and exponentially small resonance widths were calculated, using a version of (8).

Around this time another model that became popular was known as the Stark–Wannier Hamiltonian, in which a periodic background potential is combined with that of a constant electric field. Wannier introduced this model in 1960 [**185**], and mathematical analysis was initiated by Herbst and Howland in [**76**]. Resonances in this model occur in infinite evenly spaced "ladders," and were studied with perturbative methods analogous to those used for the more venerable canonical models [**2, 94, 62, 106, 10, 63, 29**]

Estimates of the density and distribution of resonances go back in the physical literature to Regge [**149**]. In one dimension, theorems of this form were obtained by Melrose [**122**] and Zworski [**193, 194, 195**], who chose to define resonances as poles of the analytic continuation of the S-matrix and obtained a Weyl-type distribution result; and by Froese [**51, 52**], who preferred the Birman–Schwinger kernel $K(\kappa)$ of $|V(x)|^{1/2}\mathrm{sgn}\,(V(x))\left(H_0+\kappa^2\right)^{-1}|V(x)|^{1/2}$. Actually, due to the special features of ordinary differential equations, there are close connections among Birman–Schwinger kernels, S-matrices, phase shifts, Jost functions, m-functions, and Green functions, and consequently in one dimension resonances can be defined more or less equivalently in terms of singularities or zeroes of complex functions concocted from any of these. This point was brought out, for example, in an article of Simon [**164**], which unified the results of Froese, Melrose, and Zworski by focusing on the properties of the Fredholm determinant

$$d(\kappa) := \det\left(1+K(\kappa)\right),$$

the zeroes of which correspond to resonances [**122, 7, 56, 57, 194**]. In addition to estimates of the distribution of resonances of several one-dimensional models, Simon obtained distribution estimates for antibound states.

3. Quantum Resonance Without Symmetries

In the last two to three decades the mathematical theory of quantum resonance has broken free of the symmetries and special circumstances needed to make the canonical models accessible. Advances have depended on three important developments: Better estimates of the growth properties of solutions of elliptic PDEs; an application of the Schur complement of matrix theory to Schrödinger operators, known in the trade as the *Livšic–Feshbach matrix*; and Mourre theory in scattering.

The understanding of solutions of the multidimensional Schrödinger equation advanced in the 1980's. The notion of an Agmon metric, as expounded in [**3**], allows estimates of the exponential decay in space of Schrödinger wave functions without separation of variables or other uses of symmetry. This construction is quite general; for example, for a Schrödinger operator H, if one can find a function

$\Lambda(\mathbf{x}) > 0$ such that

$$H - \mu \geq \Lambda(\mathbf{x}) > 0 \tag{11}$$

in the sense of quadratic forms, then solutions are governed by a metric ρ_A defined by $ds_A^2 = \Lambda(\mathbf{x})|d\mathbf{x}|^2$. Agmon's essential result was that if (11) holds and a solution ψ of $H\psi = \mu\psi$ has controlled growth in the sense that on an exterior domain Ω,

$$\int_\Omega |\psi|^2 \exp\left(-2(1-\delta)\rho_A(\mathbf{x})\right) dx < \infty,$$

then on average it decays exponentially in the sense that

$$\int_\Omega |\psi|^2 \exp\left(2(1-\epsilon)\rho_A(\mathbf{x})\right) dx < \infty.$$

With epsilonic loss, Agmon's theorem shows that when integrated, solutions of the time-independent Schrödinger equation satisfy exponential-growth estimates much like the familiar tunneling formulae in one dimension. Moreover, the function $\Lambda(\mathbf{x})$ provides flexibility to adapt the method to particular circumstances. Similar estimates have been proved on adapted regions, such as exterior sectors [**3**], applied to Green functions [**39**], etc.

Agmon's techniques made estimates like (8) tractable in the absence of separability. In the hands of Helffer and Sjöstrand [**72**], Simon [**163**], and others, systematic asymptotic expressions for solutions of multidimensional Schrödinger equations were developed in semiclassical limits, whether as a parameter $\hbar \to 0$ or in other circumstances with a large or small parameter. Quantum resonances figured among the semiclassical phenomena on which these microlocal techniques were brought to bear (e.g., [**73**]). Many articles of Helffer, Sjöstrand, and collaborators are synopsized in [**70, 165, 107**].

In the late 1980's and 90's, a number of the results on canonical models that had been obtained with one-dimensional methods were re-obtained without symmetry assumptions. Among these results were perturbation theory and width estimates for shape and Stark resonances [**73, 157, 95, 165, 71**], and stability, resolvent estimates, and perturbation theory for shape resonances without radial symmetry [**32, 81, 82**]. In the same period, the notion of a resonance state as satisfying an outgoing condition, or a truncated version of such a state, was further developed in the multidimensional setting, and conditions were found under which exponential decay in time (4) could be proved for such states [**170, 171, 172, 91, 105, 112**].

One of the earliest to appreciate the value of the Livšic–Feshbach matrix in the theory of quantum resonances was Howland, who, in a somewhat overlooked article [**89**], used it to develop a perturbation theory for resonances of self-adjoint Schrödinger operators, arising from embedded eigenvalues. (Livšic had introduced the matrix in relation to non-real eigenvalues of explicitly non-self-adjoint operators [**115**]. Feshbach independently developed similar ideas in an article on resonance theory for nuclear physics [**49**].) The power of the Livšic–Feshbach technique is that the analysis of the spectrum of an infinite-dimensional operator is replaced by that of a finite-dimensional operator, albeit one that depends on the spectral parameter.

Definition 2. Let H be self-adjoint and let P be a finite-dimensional projector (normally the projector onto the unperturbed eigenvector ψ_0 of a reference operator H_0). The *Livšic–Feshbach matrix* is the finite-dimensional operator $B(z)$ acting on

$\mathcal{K} := \operatorname{Ran} P$ such that

$$(B(z) - z\mathbf{1})^{-1} = P(H - z\mathbf{1})^{-1}P, \tag{12}$$

when the right side is "compressed" to $\mathcal{K}$.

The matrix-valued function $B(z)$ is meromorphic on the complement of the essential spectrum of H and has only real singularities [**89**]. Provided that $\mathcal{K} \subset D(H)$, the Hamiltonian H can be written as a block-partitioned operator with respect to $\mathcal{K}$ and $\mathcal{K}^\perp$, and $B(z) - z$ is, in the terminology of matrix theory, the *Schur complement of* $(\mathbf{1} - P)(H - z)(\mathbf{1} - P)$ *in* $H - z\mathbf{1}$ [**154, 36, 42**].

It follows by a calculation from (12) that, with $\bar{P} := (\mathbf{1} - P)$ and $\bar{H} := \bar{P}H\bar{P}$,

$$B(z) = PHP - PH\bar{P}(\bar{H} - z)^{-1}\bar{P}HP. \tag{13}$$

(Again, this formula is to be interpreted as compressed to $\mathcal{K}$.) Replacing H by $H_0 + \kappa W$ and taking P as the orthogonal projector corresponding to an eigenvalue $\lambda_0 \in \sigma_p(H_0)$ with normalized eigenvector Φ_0 yields the *Feshbach formula*

$$B(z, \kappa) = \lambda_0\mathbf{1} + \kappa PWP - \kappa^2 F(z, \kappa),$$

where $F(z, \kappa) = PW\bar{P}(\bar{H} - z)^{-1}\bar{P}WP$ [**49**]. When P is one-dimensional, $B(z, \kappa)$ and F reduce to scalar functions that satisfy

$$B(z, \kappa) = \lambda_0 + \kappa \langle \Phi_0, W\Phi_0 \rangle - \kappa^2 F(z, \kappa). \tag{14}$$

Observe that the first-order term is identical to that of Rayleigh–Schrödinger perturbation theory for the first-order correction to a non-degenerate eigenvalue, and that $-\kappa^2 F(z, \kappa)$ resembles the second-order correction. From (14) the leading-order expression for the resonance width is found to be

$$\frac{\Gamma}{2} = -\mathrm{Im}F(\lambda_0 + i\epsilon, 0). \tag{15}$$

In [**89**] Howland observed that the Livšic–Feshbach matrix allows an analogue of Kato's regular perturbation theory for non-isolated eigenvalues of a family of operators $H(\kappa)$, and he demonstrated that this theory embraces not only the situation of an isolated eigenvalue, but also perturbations of certain embedded eigenvalues and resonances of complex-scaled Hamiltonians as in [**160**].

Howland's work on the Livšic–Feshbach matrix was extended in the 1985 dissertation of Orth and a related article [**138**]. There, a resonance is defined in the model case of a non-degenerate unperturbed eigenvalue λ_0 as follows:

Definition 3. Suppose that there exists a dense subspace $\mathcal{H}_+$ containing $\mathcal{K}$, $W(\mathcal{K})$, and all possible eigenvectors of $H(\kappa)$. If for λ in some neighborhood of λ_0 and κ near 0, $((\mathbf{1}-P)H(\kappa)(\mathbf{1}-P)-\mathbf{1})^{-1}$ can be continued analytically in z to the real axis as a bounded operator from $\mathcal{H}_+$ onto its dual $\mathcal{H}_-$, and the continuation is Lipschitz continuous with Lipschitz constant $O(\kappa^{-2})$, then $B(z, \kappa)$ can likewise be continued to the real axis, and the *resonance eigenvalue* near λ_0 is the fixed point of the equation

$$\lambda(\kappa) = B(\lambda(\kappa), \lambda).$$

With this definition, Orth showed that resonances are associated with spectral concentration, as in [**89**], and proved the existence of resonances for a large class of many-body potentials. Orth required no *ad hoc* analyticity of the potential with respect to dilatations. Instead, the dilatation group makes its appearance in an assumption that products of its generator and the one-body potentials are

bounded maps between appropriate Sobolev spaces. According to Mourre theory [**128, 97**], this allows control on resolvents, localized in energy and space. Hence the subspace $\mathcal{H}_+$ can be taken as $D(A^2)$, where A is the symmetrized generator of dilatations, $\frac{i}{2}(x\cdot\nabla+\nabla\cdot x)$. The Howland–Orth definition of a resonance for $H(\kappa)$ has become widely accepted.

Mourre theory refers to the use of local commutator estimates to prove that quantum scattering is well-behaved. The role of commutators in scattering theory dates from the 1960's, when Putnam [**145**] showed that if there is a bounded self-adjoint operator A such that $B := i[H, A] \geq 0$, and 0 is not an eigenvalue of B, then the spectrum of H is purely absolutely continuous. Putnam's theorem led to many further developments, notably the theory of smooth perturbations in the hands of Kato [**104**], Lavine [**109**], and others. Mourre's innovation in [**128**] was to localize Putnam's condition in energy: Suppose that the commutator B satisfies certain technical conditions, and that on some real interval Δ there exists a positive number α and a compact operator K, such that

$$P_\Delta B P_\Delta \geq \alpha P_\Delta + K. \tag{16}$$

Mourre discovered that under this condition H has no singular continuous spectrum in Δ, and only finitely many eigenvalues in any compact subset of Δ. Moreover, if $K = 0$, then the expression

$$\|(|A|+1)^{-1}(H-\lambda-i\delta)^{-1}(|A|+1)^{-1}\| \tag{17}$$

remains bounded for $\lambda \in \Delta$ as $\delta \to 0^+$ (see also [**53, 144**]). Mourre's method was extended to higher-order commutators and higher powers of resolvents in [**97**]. An exposition of Mourre theory is to be found in [**37**].

Connections between Mourre theory and quantum resonances were first made by Orth [**138**] in his many-body analysis, and by Herbst and Skibsted in the context of the Stark effect [**80**]. Later, Soffer and Weinstein [**173**] posited an outright hypothesis on the time-decay of $\exp(-iH_0t)$, when localized in space and in energy, and under that assumption proved that embedded eigenvalues away from thresholds dissolve into the continuum as resonances and decay according to a version of (4), provided that Γ, as given by (6), satisfies a certain bound from below. (Agmon, Herbst, and Skibsted had earlier shown in [**5**] that embedded eigenvalues are generically unstable against perturbations.) The decay hypothesis of Soffer and Weinstein is a familiar consequence related to (17) of a Mourre inequality, and therefore holds under wide circumstances away from thresholds.

Soffer and Weinstein focused more on the notion of a resonance state than did Howland and Orth. In particular, with the decay hypothesis on the propagator, the decay law (4) is shown to apply to all initial functions in the range of a smoothed version of the spectral projector onto an interval Δ containing an unperturbed eigenvalue but no other part of the point spectrum of H_0. Most earlier analyses of resonance states and their the time-evolution had defined them with outgoing radiation conditions, and were consequently more restrictive. Some technical assumptions of Soffer and Weinstein were relaxed in [**35**]. In particular, given sufficient regularity of the unperturbed resolvent, Γ was required in [**35**] merely to be positive rather than bounded away from zero in a specific way. Making similar assumptions, Merkli and Sigal [**124**] considered the nature of a metastable state, showing that any state suitably localized in energy can be written as the sum of a

resonant part and a dispersive part. The resonant part will stay near the unperturbed state for a long time, and then decay according to (4).

In [**98**], Jensen and Nenciu recently considered how an eigenvalue E at a (nondegenerate) threshold of H_0 becomes a resonance of $H_0+\kappa W$, in the Howland–Orth sense, when the first-order correction to E is positive. Jensen and Nenciu carry out an asymptotic analysis of the Livšic–Feshbach matrix, and with the aid of an expansion of the resolvent at zero energy, they derive a modified Fermi Golden Rule for the width Γ, proportional to $\kappa^{m/2}$ with m odd.

In another recent article [**30**], Cattaneo, Graf, and Hunziker synthesize the current state of quantum resonance theory under rather basic assumptions, *viz.*: That Mourre's inequality (16) holds for $H(\kappa)$ and an auxiliary operator A; that the multiple commutators of A with $H(\kappa)$ and W exist up to some finite order N; and that $D(H)$ is mapped by $\exp(isA)$ into itself. Their main theorem is that if N is sufficiently large, and if $\Gamma > 0$, then for some smoothed spectral projector g onto an interval Δ containing λ_0,

$$\langle \phi, \exp(-iH(\kappa)t)g(H(\kappa))\phi\rangle = e^{-i\lambda(\kappa)t}(1+O(\kappa^2)) + b(\kappa,t), \tag{18}$$

where b is an error term vanishing suitably as $\kappa \to 0$ and decaying polynomially in time. Boundary values of the resolvent are also shown to be regular in Δ.

Concurrently with the evolution of resonance theory as described above, with the focus on perturbations and the exponential-decay law (4), important mathematical work was done on resonances from some independent points of view. Although Lax and Phillips stated in the introduction to their monograph [**113**] that their subject was "classical—in contrast to quantum mechanical scattering theory," a section on the Schrödinger equation with compactly supported potential was included. Observing the simple relationship between the Schrödinger S-matrix for compactly supported potential energy and an "acoustic" scattering matrix for the wave equation with a compact obstacle, Lax and Phillips showed in [**113**] that the Schrödinger scattering matrix has a meromorphic continuation onto the nonphysical sheet, poles of which constitute resonances in their set-up. The counterpart for the wave equation of semiclassical analysis for the time-dependent Schrödinger equation is the propagation of wave fronts along rays. Correspondingly, the Lax–Phillips approach to scattering has brought out connections between resonances and rays that are trapped. An obstacle is said to be *trapping* if there exist rays reflecting according to Snell's law that are either closed or of arbitrary long duration. For problems with a potential, trapping requires trajectories of the classical flow at some energy E, that do not tend to infinity in time, around which one can construct quasi-modes [**167, 178**]. Physical intuition argues that if rays can be trapped, then there will be quasi-stationary wave packets, whereas in the absence of trapping, scattering should take place without delays, and consequently the poles in the analytic continuation of the S-matrix ought to be relatively far from the real axis.

With or without trapping, there are universal, non-asymptotic lower bounds to shape-resonance widths, which show exponential dependence if parameters like Planck's constant are introduced. Such resonance-free regions were first found for one-dimensional shape resonances by Harrell in [**67**], using ODE comparison theorems and integral identities. A similar result was obtained in higher dimensions by Fernandez and Lavine [**48**] for states satisfying a strict outgoing radiation condition. Related semiclassical bounds were then studied by Helffer and Sjöstrand [**73**], Briet

et al. [**25**], and Burq [**28**], who allowed long-range potentials. Other restrictions on the location of individual resonances have been obtained with various methods in [**69, 131, 117, 12, 1**].

If the potential is assumed non-trapping, the expectation is that resonances should be few and weak. Under non-trapping assumptions, Melrose, Zworski, and others have delineated resonance-free regions and estimates of the numbers and distribution of resonances [**122, 193, 130, 194, 123, 83, 195, 121**]. In contrast, it can be proved that if the potential is trapping, or if quasi-modes are assumed, then there are resonances exponentially close to the real axis; for results of this sort, see [**32, 26, 55, 166, 167, 177**]. Theorems about the distribution of resonances in many dimensions generally lack the detail of the results in one dimension [**122, 193, 194, 51, 52, 164**], and often they distinguish between even and odd dimensions, a familiar circumstance for the wave equation that is less compelling for the Schrödinger equation. For example, Sjöstrand and Zworski [**168**] proved a distribution theorem for resonances only in odd dimensions, which was also valid in even dimensions, although that was proved only much later [**167**].

Broadly viewed, the acoustic resonance theory of Lax and Phillips follows the same strategy as quantum resonance theory, of reducing the subject to analytic Fredholm theory for families of compact operator. Variants of this strategy have been developed by a number of authors (e.g., [**56, 139, 57, 140**]), and most currently by Agmon [**4**], who regarded the resolvent $(H-\lambda)^{-1}$ as an operator from $\mathcal{H}$ to some larger space. Assuming that the resolvent can be continued as a meromorphic function of λ, Agmon extracts in a canonical way an operator with discrete spectrum corresponding to the poles of the resolvent.

A conceptually distinct approach to resonance theory takes quasi-stationary time-evolution of the wave function as the starting point. A persistent advocate of this point of view has been Lavine [**110**], who stressed the notion of the *sojourn time* of a quantum state, closely related to the Eisenbud–Wigner time-delay [**44, 188, 120, 93, 135, 132, 8**]. Lavine prefigured Mourre by using commutators with the generator A of dilatations, and in particular derived a formula for the sojourn time in terms of $B := i[H, A]$. (See [**111, 93, 8, 129, 183, 184**] for further developments connected with sojourn times and time-delays.)

The program laid out out by Simon in [**160**] has largely come to fruition, as the questions laid out in that article about resonances are now answered not only in special models but in wide generality. The mathematical methods developed in the interim are suitable for making numerical calculations of resonance energies and decay rates, and are in the process of joining Rayleigh–Schrödinger theory and complex scaling in the arsenal of physicists for everyday calculation.

In the mature phase of the theory of quantum resonances, there will continue to be challenging problems to analyze. For example: Can the restriction to odd dimensions in articles such as [**98**] be relaxed? Can the asymptotics of resonances in many dimensions be estimated with an exactness approaching that of the one-dimensional case [**122, 193, 194, 51, 52, 164**]? The most interesting possibilities on the horizon, however, may be a full merger of the different conceptual approaches to resonances, whether under an abstract umbrella like Agmon's theory [**4**], or one beginning with a time-delay and proceeding from that to information about the analysis of continued resolvents.

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