PHYSICAL REVIEW LETTERS

VOLUME 41 | 10 JULY 1978 | NUMBER 2

Stark Effect Revisited

I. W. Herbst
Department of Mathematics, University of Virginia, Charlottesville, Virginia 22903

and

B. Simon
Departments of Mathematics and Physics, Princeton University, Princeton, New Jersey 08540
(Received 8 May 1978)

We extend the rigorous theory of complex scaling to atoms in constant electric field. This allows one to give a precise mathematical definition of resonance and leads to several results about the perturbation series: Borel summability at nonreal field and a relation between the asymptotics of the perturbation coefficients for large n and the width of the resonance for small field.

Most quantum mechanics texts present three examples of time-independent perturbation theory as typical and important applications of the method: the x^4 anharmonic oscillator, the Zeeman effect in atoms, and the Stark effect in atoms. Ironically, all three perturbation series are divergent![1,2] It is natural to ask whether the right answer is not somehow computable nonetheless from the series by some procedure more subtle than straightforward summation, and Borel summability is a natural candidate.[3,4] For several years, now, we have known that the anharmonic oscillator is Borel summable[5] to the correct eigenvalue, and recently the same has been proven for the Zeeman effect.[6] For the Stark problem, straightforward summation cannot give the "right" answer which should be a resonance, and hence nonreal. That the Stark problem in hydrogen is nevertheless Borel summable in a suitable sense has been discovered by Graffi and Grecchi[7] who claim summability about *pure imaginary* field and analytic continuability back to the real-field region where the answer will be nonreal.

Our purpose in this Letter is to announce three sets of results whose details will be presented elsewhere[8,9]: (1) Rigorous extension[8] of the complex scaling method[10,11] to Stark problems. This is important because the standard approach[10] is not applicable although the method has been formally used as a basis of extensive numerical calculation of resonance positions in Stark problems[12]; we provide a rigorous underpinning for their calculation and also a precise mathematical definition of the position of the resonance. (2) A rigorous proof of Borel summability of the Stark series at imaginary field in arbitrary atoms. It seems quite difficult to do this with the methods of Ref. 7 which rely on the separability of the hydrogenic Stark problem in parabolic coordinates. (3) A rather striking relation between the width of the resonance and the perturbation coefficients [see Eq. (2) below].

Let us describe our results in slightly more detail. (1) In complex scaling of atoms in zero electric field, one has the familiar phenomenon[10] that as the argument of the scaling parameter is changed from zero, the continuous spectrum swings into the complex plane about the various scattering thresholds and uncovers resonances. In the Stark problem, there are not thresholds (this is seen most clearly for potentials which are also translation analytic[13] and therefore it appears there is no natural place for the continuous spectrum to go. For this reason, one might conclude that complex scaling is unlikely to be of much validity in these problems. However, if there is no natural place for it, there is a natural thing it can do: It can disappear! For simplicity, we describe the purely atomic case[14] where $H = T + V + \epsilon X$ with T the kinetic energy, V the Coulomb potential, ϵ the field strength, and X the position of the center of charge. The formally scaled Hamiltonian is

$$H(\theta, \epsilon) = e^{-2\theta}T + e^{-\theta}V + \epsilon e^{\theta}X. \quad (1)$$

Theorem 1 (Refs. 8 and 9).—If $0 < \mathrm{Im}\theta < \pi/3$ and ϵ is real and nonzero, then $H(\theta, \epsilon)$ has a purely discrete spectrum which lies in the lower half-plane and which is θ independent. Moreover, for any dilation analytic vector (there are a dense set), φ, the function $F(z) = (\varphi, [H(0, \epsilon) - z]^{-1}\varphi)$ defined for $\mathrm{Im}z > 0$ has a meromorphic continuation into the entire complex plane with poles possible only at the eigenvalues of $H(\theta, \epsilon)$ (for θ in the above region).

This result depends on the fact discovered by one of us[8] that $-\Delta + \alpha x$ has an empty spectrum(!) if $\mathrm{Re}\alpha \neq 0$.[15] Once one has the dilation analytic machinery, one can use the stability methods of Ref. 6 to prove the following:

Theorem 2 (Refs. 8 and 9).—Fix θ with $\mathrm{Im}\theta$ in $(0, \pi/3)$ and let E_0 be a nondegenerate[16] eigenvalue of $H(\theta = 0, \epsilon = 0)$ below its lowest threshold. Then for all sufficiently small positive reals ϵ, $H(\theta, \epsilon)$ has exactly one eigenvalue $E(\epsilon)$ near E_0; it is nondegenerate and it has an *asymptotic* series

$$\sum_{n=0}^{\infty} a_{2n}\epsilon^{2n}$$

with the a_{2n} the *real* Rayleigh-Schrödinger coefficients. In particular, the width $\Gamma(\epsilon) = -2\,\mathrm{Im}E(\epsilon)$ goes to zero faster than any power. Moreover,[17] for small nonzero ϵ, Γ is strictly positive.

(2) Borel summability comes from analyticity properties and Watson's theorem:

Theorem 3 (Ref. 9).—The function $E(\epsilon)$ of theorem 2 defined for ϵ small and positive has an analytic continuation into the region

$$\{\epsilon \,|\, 0 < |\epsilon| < R_\delta;\ -\tfrac{1}{2}\pi + \delta < \arg\epsilon < \tfrac{3}{2}\pi - \delta\}$$

(Ref. 18). Moreover, the Rayleigh-Schrödinger series is asymptotic in the whole region with error bounded by $|Az|^{N+1}(N+1)$! In particular, the series[19] $\sum (a_n i^n) z^n$ has a Borel transform analytic in the region $\mathrm{Re}w > 0$ and the inverse Borel transform for $|\arg z| < \frac{1}{2}\pi - \delta$ and $|z| < R_\delta$ is $E(iz)$.

Theorem 3 is proven by using the freedom to vary θ and $\arg\epsilon$ separately in (1). This argument is very reminiscent of the use of complex scaling in the study of the anharmonic oscillator.[20,2]

(3) Finally, we note a remarkable formula relating the width $\Gamma(\epsilon) = -2\,\mathrm{Im}E(\epsilon)$ (ϵ real) and the Rayleigh-Schrödinger coefficients, a_n:

Theorem 4 (Ref. 9).—For the eigenvalue $E(\epsilon)$ of Theorem 2, one has[21]

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

Formula (2) is proven by writing

$$E(\epsilon) = \frac{1}{\pi i}\oint \frac{zE(z)}{z^2 - \epsilon^2}dz,$$

where ϵ is in the upper half-circle $\{z \,|\, 0 < |z| < R;\ 0 < \arg z < \pi\}$ and the integral is around the boundary of this region. Theorem 4 is motivated by analogous results for the anharmonic oscillator: Simon[20] noted that the Rayleigh-Schrödinger coefficients in that case are moments of a measure related to the imaginary part of an analytically continued eigenvalue. Subsequently, Bender and Wu[22] interpreted this imaginary part as the width for a certain unphysical problem; the big difference here is that the width is a physical one.

Equation (2) sets up a direct relation[23] between the asymptotics of a_{2n} for n large and that of $\Gamma(x)$ for x small; in particular the $(2n)!$ growth of a_{2n} which we believe to occur is directly related to the $e^{-1/x}$ behavior of Γ computed by Oppenheimer.[24]

It is a pleasure to thank W. Reinhardt and J. Howland for stimulating discussions and S. Graffi and V. Grecchi for correspondence and copies of their preprints. This work was supported in part by the National Science Foundation, Grant No. MPS-75-11864.

---

[1]One expects $n!$ growth of the Rayleigh-Schrödinger coefficients on the basis of the following argument: Unless there is a miraculous cancellation, the nth term of the perturbation series should look more or less like $(\psi_0, V[(H_0 + E)^{-1}V]^n\psi_0)$ where ψ_0 is the unper-

turbed eigenvector, V the perturbation, H_0 the unperturbed Hamiltonian, and E some point not in the spectrum of H_0. In the x^4 oscillator, $V \sim x^4$ and $(H_0+E)^{-1}$ has an x^{-2} falloff at spatial infinity. Since $\psi_0 \sim e^{-x^2}$ we get $n!$ growth. In the Stark and Zeeman problems, $V \sim \epsilon x$ and $V \sim x^2 B^2$, respectively, while $(H_0+E)^{-1}$ has no x-space falloff. Since $\psi_0 \sim e^{-|x|}$ we again get $n!$ growth (for n even; in the Stark problem the expectation value is zero for n odd by symmetry if ψ_0 is nondegenerate). This argument can be made into a rigorous *upper* bound on the coefficients of the form $A^{n+1} n!$.

[2]C. Bender and T. T. Wu, Phys. Rev. 184, 1231–1260 (1969), have rigorously proven divergence of the series in the x^4 case by using the fact that one can write the coefficients as a sum of Feynman diagrams which all have the same sign. One consequence of the work we report here is a rigorous proof of the divergence in the Stark case. A rigorous proof of the divergence of the perturbation series in the Zeeman case is still lacking.

[3]We say that a formal series $\sum a_n z^n$ is Borel summable if (1) the Borel transform $g(w) = \sum a_n w^n/n!$ has a finite radius of convergence and an analytic continuation to a neighborhood of $(0,\infty)$; (2) for z small and positive the integral $f(z) = \int_0^\infty g(wz) e^{-w} dw$ is absolutely convergent. If one *formally* interchanges the sum in g and the integral, one sees that *formally* $f \sim \sum a_n z^n$. A celebrated theorem of Watson [see Godfrey H. Hardy, *Divergent Series* (Oxford Univ. Press, Oxford, 1949)] gives sufficient conditions for a function $f(z)$ to be recoverable from its asymptotic series by Borel summation.

[4]There has been considerable recent interest, in the quantum-field-theory literature, in the method of Borel summation; see N. Khuri, Bull. Am. Phys. Soc. 23, 551 (1978); L. N. Lipatov, to be published; E. Brézin, J. C. Le Guillou, and J. Zinn-Justin, Phys. Rev. D 15, 1544, 1558 (1977); E. Brézin, G. Parisi, and J. Zinn-Justin, Phys. Rev. D 16, 408 (1977); C. Itzykson, G. Parisi, and J. B. Zuber, Phys. Rev. Lett. 38, 306 (1977), and Phys. Rev. D 16, 996 (1977); G. Parisi, Phys. Lett. 66B, 167, 382 (1977); J. C. Collins and D. Soper, to be published; G. Auberson, G. Mennessier, and G. Mahoux, to be published.

[5]S. Graffi, V. Grecchi, and B. Simon, Phys. Lett. 32B, 631–634 (1970).

[6]J. Avron, I. Herbst, and B. Simon, Phys. Lett. 62A, 214–216 (1977), and to be published.

[7]S. Graffi and V. Grecchi, to be published.

[8]I. Herbst, "Dilation analyticity in constant electric field. I. The two-body problem" (to be published).

[9]I. Herbst and B. Simon, "Analyticity in constant electric field. II. The N-body problem, Borel summability" (to be published).

[10]J. Aguilar and J. M. Combes, Commun. Math. Phys. 22, 269 (1971); E. Balslev and J. M. Combes, Commun. Math. Phys. 22, 280 (1971); C. van Winter, J. Math. Anal. Appl. 47, 633 (1974), and 48, 368 (1974).

[11]This method has been used extensively to locate resonance positions; see, e.g., R. A. Bain *et al.*, J. Phys. B 7, 2189 (1974); G. Doolen *et al.*, Phys. Rev. A 10, 1612 (1974); G. Doolen, J. Phys. B 8, 525 (1975); R. J. Drachman and S. K. Houston, Phys. Rev. A 12, 885 (1975); A. P. Hickman *et al.*, Chem. Phys. Lett. 37, 63 (1976); Y. K. Hu, J. Phys. B 10, L373 (1977); E. Brändas and S. Froelich, Phys. Rev. A 16, 2207 (1977); B. R. Junker and C. L. Huang, to be published.

[12]W. P. Reinhardt, Int. J. Quantum Chem. Symp. 10, 359–367 (1976); C. Cerjan, W. Reinhardt, and J. Avron, J. Phys. B 11, L201 (1978); C. Cerjan, R. Hodges, C. Holt, W. Reinhardt, K. Scheiber, and J. Wendoloski, "Complex Coordinates and the Stark effect" (to be published).

[13]J. Avron and I. Herbst, Commun. Math. Phys. 52, 239–254 (1977).

[14]Our methods (Refs. 8 and 9) deal with a large class of potentials, including superpositions of Yukawa potentials.

[15]In fact, one can show (Ref. 8) that for fixed α with $\mathrm{Re}(i\alpha^{-1}) > 0$, $\| \exp[-it\alpha^{-1}(-\Delta + \alpha x)] \| = \exp(-Dt^3)$ so that the formula for the resolvent is $(-\Delta + \alpha x - z)^{-1} = i\alpha^{-1} \int_0^\infty \exp(i\alpha^{-1} zt) \exp[-it\alpha^{-1}(-\Delta + \alpha x)] dt$ converges for all t. Nevertheless the problem is very singular. For example, if $h(\epsilon) = -\Delta - i\epsilon x$ then $1+i$ is not in the spectrum of $h(\epsilon)$ for any $\epsilon > 0$ (since there is no spectrum) nor for $\epsilon = 0$ (when the spectrum is real) but (Ref. 8) $\| [h(\epsilon) - 1 - i]^{-1} \|$ diverges at least as fast as $c\epsilon^{-1/6} \exp(1/6\epsilon)$ as $\epsilon \downarrow 0$.

[16]We intend to study the degenerate case in detail in Ref. 9. If the degeneracy is removed by restriction to a fixed $\vec{L} \cdot \hat{e}$, where $\hat{e}$ is the direction of the field (as is the case if there is a single angular momentum, l, and total degeneracy $2l+1$), then our results hold without change.

[17]For the hydrogenic case, Γ is always strictly positive by results of E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second Order Differential Equations* (Oxford Univ. Press, Oxford, 1958); S. Agmon, in Proceedings of the International Conference on Function Analysis and Related Topics, Tokyo, 1969 (Mathematical Society of Japan, Univ. of Tokyo Press, 1970); and Ref. 13. For the case of general atoms, we extend methods of E. Balslev, Arch. Rat. Mech. Anal. 59, 343 (1975); B. Simon, Math. Ann. 207, 133 (1974).

[18]Where δ may be taken arbitrarily small and R_δ is δ dependent.

[19]One can ask what distinguishes i from $-i$ in a problem which is clearly initially invariant under complex conjugation. Our choice to take $\mathrm{Im}\theta > 0$ leads to $\mathrm{Im}E(\epsilon) < 0$ and no singularities in an upper half-circle.

[20]B. Simon, Ann. Phys. (N.Y.) 58, 76 (1970); J. J. Loeffel *et al.*, Phys. Lett. 30B, 656 (1969).

[21]Here R is any number less than some R_δ with $\delta < \frac{1}{2}\pi$.

[22]C. Bender and T. T. Wu, Phys. Rev. Lett. 16, 461 (1971), and Phys. Rev. D 7, 1620 (1973).

[23]For the anharmonic oscillator, Bender and Wu (Ref. 22) exploited the analog of (2) to obtain the asymptotics of a_n from a calculation of Γ.

[24]J. Oppenheimer, Phys. Rev. 31, 66 (1928). One consequence of the work described in this Letter is to provide a precise definition of the width of a Stark resonance in hydrogen so that a rigorous investigation of Oppenheimer's formula is possible in principle.