Exponential Decay of Quantum Wave Functions

I've no doubt that for ODEs, the questions and techniques for exponential decay of solutions go back a long way, maybe even to the nineteenth century. For one body systems with decaying potential, I think they are at least in Titchmarsh's book. For ODEs with explicit polynomially growing potentials there are precise asymptotics going back to the at least the middle of the twentieth century.

My work concerns N–body systems and qualitative polynomially growth where instead of exact asymptotics on the potential one supposes lower bounds on the growth.

Slaggie-Wichmann [45] used integral equation ideas to prove some kind of exponential decay in certain three body systems with decaying potentials. I gave looking at N–body systems to Tony O'Connor, my first graduate student (who began working with me when I was a first year instructor). He had the idea of looking at analyticity of the Fourier transform and obtains results in the L^2 sense (i.e. $e^{a|x|}\psi \in L^2$) that were optimal in that you couldn't do better in terms of isotropic decay. Here $|x|$ is a mass weighted measure of the spread of the N particles, explicitly if $X = \sum_{j=1}^N m_j x_j / \sum_{j=1}^N m_j$ is the center of mass, then $|x|^2 = \sum_{j=1}^N m_j (x_j - X)^2 / \sum_{j=1}^N m_j$.

His paper [33] motivated Combes–Thomas [15] to an approach that has now become standard of using boost analyticity. Independently of O'Connor, Ahlrichs [4] found pointwise isotropic bounds but his result was not optimal and restricted to Coulomb systems since he used the explicit $|r|^{-1}$ form.

All these results, except Ahlrichs, obtained L^2–decay. In three papers [37, 38, 39], I looked at getting pointwise bounds. In the first paper, I obtained optimal pointwise isotropic bounds for N–body systems. In the second paper, I considered the case where V goes to infinity at infinity and proved pointwise exponential decay by every exponential (Sch'nol [36] earlier had a related result). In the third paper, I assumed $|x|^{2m}$ lower bounds and got $\exp(-|x|^{m+1})$ pointwise upper bounds. When one has an upper bound on V of this form, one gets lower bounds of the same form on the ground state. Papers 1-2 were written during my fall 1972 visit to IHES, one of my most productive times when Lieb and I did most of the Thomas–Fermi work and I developed new aspects of correlation inequalities and Lee–Yang for EQFT.

Two of my students used these bounds in their work. Jay Rosen [35] needed them in his thesis proof of supercontractive estimates. Harrell [19, 20] while a postdoc followed my suggestions to study 1D double wells using these bounds and he and I [21] then used his techniques to prove the Oppenheimer formula for the width of the Stark Hamiltonian and the Bender–Wu formula for the asymptotics of the anharmonic oscillator perturbation coefficients.

Optimal decay estimates for N–body systems were obtained in the fourth paper in my series [17] jointly with Deift, Hunziker and Vock.

1982 saw two big breakthroughs. Agmon [1] introduced his metric as a way to compute the optimal upper bound for fairly general situations. Froese–Herbst [18] proved the remarkable theorem if ψ is an L^2 solution of $H\psi = E\psi$ for a multiparticle Hamiltonian, then $\sup\{\alpha^2 + E \,|\, e^{-\alpha|x|}\psi \in L^2\}$ is either a scattering threshold or is $+\infty$ and used this to show absence of positive eigenvalues.

The Agmon metric could be used to understand the results of Deift et al. [17]. I used it to in my Annals paper on instanton formulae for multidimensional double wells [42]. At about the same time as papers IV-VI, the Hoffmann-Ostenhofs (sometimes jointly with Ahlrichs and/or Morgan) [5, 6, 7, 23, 24, 25, 26, 27]found bounds on atomic wave functions and they and I interacted on these questions. Both Ahlrichs and Thomas Hoffmann–Ostenhof were in Chemistry departments but they approached the world like mathematical physicists.

****

Here is a more detailed discussion of these papers (leaving discussion of [41]) to another commentary [TK]. I note that several of my other papers have connections to the subject of this commentary [3, 12, 44, 29, 43]. There are six papers in a single titled series, [37, 38, 39, 17, 13, 30]. Common to all six is the notion of pointwise decaying estimates - for papers I and II, I had L^2–estimates (i.e. $e^f\psi \in L^2$) and proved L^∞ estimates while papers III-VI prove both L^2 and L^∞ estimates. A brief overview of the six papers:

(I) O'Connor had proven "optimal" L^2–isotropic estimates for N–body quantum systems, $e^{\alpha|x|}\psi \in L^2$ if $\alpha^2 < (\Sigma - E)$ where $\Sigma = \inf \sigma_{\text{ess}}(H)$, $H\psi = E\psi$ and $|x|$ is a mass weighted distance of the particles from their center of mass. This paper proved for such α that $e^{\alpha|x|}\psi \in L^\infty$.

(II) This proved a pointwise bound $e^{\alpha|x|}\psi \in L^\infty$ for all α if V goes to ∞ at ∞ so that H has empty essential spectrum.

(III) This proved that $\exp(c|x|^\beta)\psi \in L^\infty$ if $V(x) \geq d|x|^m - c$, $\big(\beta = \frac{1}{2}m + 1\big)$ and complementary lower bounds if $\psi > 0$ and $V(x) \leq d|x|^m + c$. If $V(x)|x|^{-m}$ has a limit and $\psi > 0$, one finds the existence and value of $\lim_{|x|\to\infty} |x|^{-\beta} \log \psi(x)$ from these bounds.

(IV) This paper (joint with Deift, Hunziker and Vock; Deift had been my student and we continued working on this while he was a postdoc. I learned that Hunziker was looking at similar questions so we joined forces – Vock was his master's student) explored non–isotropic bound for N-body systems. We found a critical differential inequality that if f obeys it, then $e^f\psi \in L^\infty$ and in some cases were able to find explicit formula for the optimal f (but only in a few simple situations). Later, Agmon [1] found the optimal solution of the differential inequality as a geodesic distance in a suitable Riemann metric (discontinuous in the case of N–body systems) – this is now called the Agmon metric, a name that appeared first in Carmona–Simon [13], which also proved lower bounds for the ground state complementary to Agmon's upper bounds proving that if $\psi(x)$ is the ground state and $\rho(x)$ the Agmon metric distance from x to 0, then $\lim_{|x|\to\infty} -\log|\psi(x)|/\rho(x) = 1$. In some ways this paper is made obsolete by [1, 13] although the explicit closed form for ρ in some cases remains of significance.

(V) Due to my book on Functional Integration [40], Herbst–Sloan [22] and Carmona [10, 11], there was a revolution in using path integrals and Schrodinger semigroup to study eigenfunctions (eventually reviewed in [41]). A key lemma in this approach goes back to Khasmin'skii [28], and was rediscovered by Portenko [34] and Berthier–Gaveau [9] (the last one motivated Carmona and me). With this lemma, the standard hypotheses one needs are that $V_- \equiv \max(-V, 0)$ lies in the Kato class, K_ν and the that $V_+ \equiv \max(V, 0)$ lies in $K_{\nu,\text{loc}}$ (this includes all the various L^p conditions; see [41, 16] and [TK] for more on K_ν). Paper V, joint with René Carmona (who visited me in Princeton) applied semigroup and path integral ideas to study eigenfunction decay. We interpreted Agmon's geodesic distance as a minimum action and then applied the theory of large deviations in path space to get lower bounds. This paper influence my tunnelling paper [42].

(VI) This paper, joint with Elliot Lieb, studied asymptotic behavior of N–body ground states in the special two cluster region where $x = (\zeta_1, \zeta_2, R)$ where ζ_j is an internal coordinate for cluster j and R is the distance between the center of masses of the clusters. When the bottom of the essential spectrum comes from this two cluster breakup, if ψ is the ground state of the full system and η_j of cluster j, and if $E = \Sigma - \kappa^2/2\mu$ with $(\mu = M_1M_2/(M_1 + M_2))\,, M_j =$ mass of cluster j, then as $R \to \infty$, $|\zeta_j|$ bounds, we have, when $x_j \in \mathbb{R}^3$, that

$$\psi(\zeta_1, \zeta_2, R) = c\eta_1(\zeta_1)\eta_2(\zeta_2)e^{-\kappa R}R^{-1}(1 + \mathrm{O}(\mathrm{e}^{-\gamma \mathrm{R}})$$

We end with a brief discussion of the modern view of the two main issues studied in these papers: the passage from L^2 to L^∞ bounds and the formulation and proof of optimal L^2 upper bounds (lower bounds are a different matter). We look first at the passage from L^2 to L^∞ bounds. This is handled in paper I in an ad hoc way and more systematically in papers II-IV until the ultimate technique is used in paper V. A *subsolution* is a function, φ, obeying $(H - E)\varphi \geq 0$. By Kato's inequality (that as distributions $\Delta|\psi| \geq \overline{\psi}|\psi|^{-1}\Delta\psi$), one sees that if $(H - E)\psi = 0$, then $|\psi|$ is a subsolution. For any Schrödinger operator with $V_- \in K_\nu$, there is a constant C depending only on $R > 0, E, \nu$ and Kato class norms of V_- so that subsolutions obey:

$$|\varphi(x)| \leq C \int_{|y-x|\leq R} |\varphi(y)| d^\nu y$$

This immediately implies that $e^f\psi \in L^2 \Rightarrow e^f\psi \in L^\infty$ so long as $\sup_{|x-y|\leq R} |f(x) - f(y)| < \infty$ which is true for the N-body situation and that $e^f\psi \in L^2 \Rightarrow e^{(1-\epsilon)f}\psi \in L^\infty$ so long as $\sup_{|x-y\leq 1} |f(x)/f(y)| \to 1$ as $|x| \to \infty$ as holds for the $\exp(x^\beta)$ bounds.

Subsolution estimates go back to Trudinger [47] who treated general elliptic operators but with stronger hypotheses than K_ν (he used ideas of Stampacchia [46] and Moser [32]) and were pushed by the Hoffmann–Ostenhofs [7, 23, 24, 25, 26, 27] for Schrödinger operators.

A probabilistic approach goes back to Chung-Rao [14] but they supposed locally bounded V. The general K_ν result (by probabilistic methods) is from Aizenman–Simon [3]. This approach uses the Fenyman–Kac formula and stopping times and cannot be summarized in a few lines.

A simpler approach to eigenfunction bounds when $|f(x) - f(y)| \leq |x - y|$ and $f(x) \geq \epsilon|x| - D$ depends on proving that

$$|e^{-tH}(x, y)| \leq C|e^{t\Delta}(x, y)|^{1/2} \tag{1}$$ eq1

Given this, one uses $|\psi(x)| \leq e^{tE} \int e^{-tH}(x, y)|\psi(y)|d^\nu y$. Given the Gaussian decay of $|e^{t\Delta}(x, 0)|$, the contribution of the integral from those y with $|x - y| \geq |x|^{3/4}$ is $\mathrm{o}\left(\mathrm{e}^{-\mathrm{f}}\right)$ and the L^2 bounds control the integral over those y with $|x-y| \leq |x|^{3/4}$. To prove (1), one notes that by a Schwarz inequality in path space and the Feynman–Kac formula (or by a Trotter approximation), one has that

$$|e^{-tH}(x, y)| \leq |e^{t\Delta}(x, y)|^{1/2}|e^{-(-\Delta+2V)}(x, y)|^{1/2}$$

For $W_- \in K_\nu$, one can prove (see, e.g. Aizenman–Simon [3]) that $|e^{-(-\Delta+W)}(x, y)|$ is bounded proving (1).

We turn finally to L^2 bounds. Combes–Thomas [15] notes that $e^{a|x|}\psi \in L^2$, if and only if for any unit vector, $\hat{e}$, $\psi_z \equiv \exp(iz\hat{e}\cdot x)\psi(x)$ has an analytic continuation from $z \in \mathbb{R}$ to $\{z \,|\, |\mathrm{Im} z| < a\}$. Similarly if f is a non-negative function and $U(s)$ is the unitary operator of multiplications by e^{isf}, then for $e^{(1-\epsilon)f}\psi \in L^2$, it suffices that $U(s)\psi$ have an analytic continuos to $Q \equiv \{s \,|\, |\mathrm{Im} s| < 1\}$. By ideas going back to Combes et. al. [2, 8] (see also [TK]), this is true if $H(s)$ has an analytic continuation to Q so that E is an isolated eigenvalue of $H(iy), 0 \leq y < 1$.

If $V \to \infty$ at ∞, then for s real, $H(s)$ has compact resolvent and by the arguments in [2, 8], it suffices to show that $H(s)$ has an analytic continuation to Q. Since $\mathrm{Re}(H(iy) - H) = y^2(\nabla f)^2$ this is true if $(\nabla f)^2 \leq V + c$ with $c = 1 - \inf(V(x))$. The optimal solution of this inequality is the geodesic distance in the Riemann metric $(V(x) + c)(dx)^2$. For eigenfunction decay, this is a realization of Lithner [31] and Agmon [1].

For N-body systems, an analysis of the essential spectrum of $H(iy)$ using geometric spectral analysis (see [TK]) shows that f has to obey the bound $(\nabla f)^2 \leq \Sigma(x) - E$. For any $x = (x_1, \ldots, x_N)$, an N-body coordinate let $C(x)$ be the clustering defined by putting i and j in the same cluster if and only if $x_i = x_j$ so $C(x)$ is N singlets for all x except for planes of codimension at least ν. Then $\Sigma(x)$ is the inf of the essential spectrum of $H(C(x))$ the Hamiltonian obtained by dropping all potentials between clusters. The inequality is essentially in paper IV but it was

Agmon [1] who realized that the solution was the geodesic distance in the discontinuous Riemann metric $(\Sigma(x) - E)(dx)^2$. Geodesics from x to 0 are piecewise linear with the lines in a plane with $C(y)$ constant. Essentially the special hyperplanes where $C(y)$ has fewer than N clusters are superhighways where one can go faster and the geodesic is the path that takes the least time. Paper IV has explicit formula for this distance in some special cases.

References

Agmon [1] S. Agmon, *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations*, Princeton University Press, Princeton (1982).

AC [2] J. Aguilar and J.M. Combes, *A class of analytic perturbations for one-body Schrödinger Hamiltonians.* Comm. Math. Phys. **22** (1971), 269–279.

AizSi [3] M. Aizenman and B. Simon, *Brownian motion and Harnack's inequality for Schrödinger operators*, Commun. Pure Appl. Math. **35** (1982), 209–273. Paper 135

Ahl [4] R. Alrichs, *Asymptotic behavior of atomic bound state wave functions*, J. Math. Phys. **14**, (1973) 1860–1863.

AHO1 [5] R. Alrichs, M. Hoffmann–Ostenhof, and T. Hoffmann–Ostenhof, *Bounds for the long range behaviour of electronic wave functions*, J. Chem. Phys. **68** (1978), 1402–1410.

AHO2 [6] R. Alrichs, M. Hoffmann–Ostenhof, and T. Hoffmann–Ostenhof, *"Schrödinger inequalities" and asymptotic behaviour of many electron densities*, Phys. Rev. **A18** (1978), 328–334.

AHOM [7] R. Alrichs, M. Hoffmann–Ostenhof, T. Hoffmann–Ostenhof, and J. Morgan, *Bounds on the decay of electron densities with screening*, Phys. Rev. **A23** (1981), 2106–2116.

BC [8] E. Balslev, and J.M. Combes, *Spectral properties of many-body Schrödinger operators with dilatation-analytic interactions.* Comm. Math. Phys. **22** (1971), 280–294.

BG [9] A. Berthier and B. Gaveau, *Critère de convergence des fonctionelles de Kac et applications en mechanique et en géométrie*, J. Funct. Anal. **29** (1978), 416–424.

Car1 [10] R. Carmona, *Regularity properties of Schrödinger and Dirichlet semigroups*, J. Funct. Anal. **17** (1974), 227–237.

Car2 [11] R. Carmona, *Pointwise bounds for Schrödinger eigenstates*, Comm. Math. Phys. **62** (1978), 97–106.

Si210 [12] R. Carmona, W. Masters and B. Simon, *Relativistic Schrödinger operators: Asymptotic behavior of the eigenfunctions*, J. Funct. Anal. **91** (1990), 117–142. Paper 210

PB5 [13] R. Carmona and B. Simon *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems, V. Lower bounds and path integrals*, Commun. Math. Phys. **80** (1981), 59–98. Paper 133

CR [14] K. Chung and K. Rao, *Sur la théorie du potentiel avec la fonctionelle de Feynman-Kac*, C. R. Acad. Sci. Paris Sér. A **290** (1980), 629–631.

CT [15] J. Combes and L. Thomas, *Asymptotic behavior of eigenfunctions for multiparticle Schrödinger operators*, Comm. Math. Phys. **34** (1973), 251–270.

SiX [16] H. Cycon, R. Froese, W. Kirsch and B. Simon *Schrdinger Operators with Application to Quantum Mechanics and Global Geometry*, Springer Verlag, (1987) Book X

PB4 [17] P. Deift, W. Hunziker, B. Simon, and E. Vock, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems. IV*, Comm. Math. Phys. **64** (1978/79), 1–34. Paper 95

FH [18] R. Froese and I. Herbst, *Exponential bounds and absence of positive eigenvalues for N-body Schrödinger operators*, Commun. Math. Phys. **87**, 429–447 (1982).

H1 [19] E. Harrell, *On the rate of asymptotic eigenvalue degeneracy*, Comm. Math. Phys. **60** (1978), 73–95.

H2 [20] E. Harrell, *Double wells*, Comm. Math. Phys. 75 (1980), 239–261.

HS [21] E. Harrell and B. Simon, *The mathematical theory of resonances whose widths are exponentially small.* Duke Math. J. **47** (1980), 845–902. Paper 105

HerbSl [22] I. Herbst and A. Sloan, *Perturbations of translation invariant positivity preserving semigroups in* $L^2(\mathbb{R})$, Trans. Amer. Math. Soc. **236** (1978), 325–360.

HO1 [23] M. Hoffmann–Ostenhof, and T. Hoffmann–Ostenhof, *"Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules*, Phys. Rev. **A16** (1977), 1782–1785.

THO1 [24] T. Hoffman–Ostenhof, *Lower and upper bounds to the decay of the ground state one-electron density of helium-like systems*, J. Phys. **A12** (1979), 1181–1187.

THO2 [25] T. Hoffman–Ostenhof, *A comparison theorem for differential inequalities with applications in quantum mechanics*, J. Phys. **A13** (1980), 417–424.

HO2 [26] T. Hoffman–Ostenhof and M. Hoffman–Ostenhof, *Exponentially decreasing upper bounds to the electron density of atoms,* Phys. Lett. **A59** (1976), 373-374.

HO3 [27] T. Hoffman–Ostenhof and M. Hoffman–Ostenhof, *Bounds to expectation values and exponentially decreasing upper bounds to the one electron density of atoms*, J. Phys. **B11** (1978), 17–24.

Khas [28] R. Khas'minskii, *On positive solutions of the equation $Uu + Vu = 0$*, Theory Probab. Appl. **4** (1959), 309–318.

LaSi [29] Y. Last and B. Simon, *Eigenfunctions, transfer matrices, and absolutely continuous spectrum of one-dimensional Schrödinger operators*, Invent. math. **135** (1999), 329–367. Paper 263

PB6 [30] E. Lieb and B. Simon, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems, VI. Asymptotics in the two-cluster region*, Adv. Appl. Math. **1** (1980), 324–343. Paper 134

Li [31] L. Lithner, *A theorem of Phragmón Lindelöf type for second order elliptic operators*, Ark. Mat. **5** (1965), 281–285.

Moser [32] J. Moser, *On Harnack's theorem for elliptic differential equations*, Comm. Pure Appl. Math. **14** (1961), 577–591.

TO [33] A. O'Conner, *Exponential decay of bound state wave functions*, Comm. Math. Phys. **32** (1973), 319–340.

Port [34] N. Portenko, *Diffusion processes with unbounded drift coefficient*, Theory Probab. Appl. **20** (1976), 27–37.

JR [35] J. Rosen, *Sobolev inequalities for weight spaces and supercontractivity*, Trans. Amer. Math. Soc. **222** (1976), 367–376.

Schnol [36] E. Sch'nol On the behavior of the eigenfunctions of Schrödinger's equation, Mat. Sb. (N.S.) **42** (1957), 273–286.

PB1 [37] B. Simon *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems, I*, Proc. Amer. Math. Soc. **42** (1974), 395–401. Paper 43

PB2 [38] B. Simon, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems, II*, Proc. Amer. Math. Soc. **45** (1974), 454–456. Paper 46

PB3 [39] B. Simon, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems, III*, Trans. Amer. Math. Soc. **208** (1975), 317–329. Paper 51

FuncInt [40] B. Simon, *Functional Integration and Quantum Physics*, Academic Press (1979), Second Edition: AMS Chelsea Publishing (2005). Book IX

SchSmgp [41] B. Simon, *Schrödinger semigroups*, Bull. Amer. Math. Soc. **7** (1982), 447–526. Review Article xxi

Tun [42] B. Simon, *Semiclassical analysis of low lying eigenvalues. II. Tunneling*, Ann. of Math. **120** (1984), 89–118. Paper 162

SiR28 [43] B. Simon, *Boundedness of continuum eigenfunctions and their relation to spectral problems*, in *Linear and Complex Analysis Problem Book: 199 Research Problems* (ed. V. Havin, S. Hruscev, and N. Nikol'skii), Lecture Notes in Mathematics **1043**, Springer, (1984), 113–115 Review Paper xxviii

Si253 [44] B. Simon, *Bounded eigenfunctions and absolutely continuous spectra for one-dimensional Schrödinger operators*, Proc. Amer. Math. Soc. **124** (1996), 3361–3369 Paper 253

SW [45] E. Slaggie, and E. Wichmann, *Asymptotic properties of the wave function for a bound nonrelativistic three-body system*, J. Mathematical Phys. **3** (1962) 946–968.

Stamp [46] G. Stampacchia, *Le problem de Dirichlet par les equations elliptiques du second order à coefficients discontinue*, Ann. Inst. Fourier (Grenoble) **15** (1969), 189–258.

Trud [47] N. Trudinger, *Linear elliptic operators with measurable coefficients*, Ann. Scuola Norm. Sup. Pisa Sci. Fis. Mat. **27** (1973), 255–308.