Geometric Analysis and the singularities of Schrödinger operator eigenfunctions (periodic potentials)

Joint work with

Jorge O. Sofo and Eugenie Hunsicker

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Victor Nistor, Penn State U.

www.math.psu.edu/nistor/

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Abstract

We study the **eigenvalues** of **Schrödinger–type operators** of the form

$$-\Delta u + Vu \text{ on } \mathbb{R}^3,$$

V potential potential with *Coulomb type singularities* in a class of potentials closed under Hartree's iteration.

Example: one electron systems and DFT.

Motivation (short): the *Hartree and DFT* (Density Functional Theory) methods to approximate the **eigenvalues** and **eigenvectors** of the Schrödinger operator of a **multi-electron system**. For a multi-electron system (atom or molecule) the direct methods are extremely expensive.

Methods from analysis on manifolds with conical singularities/cylindrical ends ($V =$ lower order perturbation).

Multi-particle systems: Lie manifolds, methods of Geometric Analysis.

Plan

1. Motivation (*Review of:* Schrödinger's Equation(s), Hydrogen atom, Rayleigh quotients, Ground states).

2. Approximation of eigenvalues (Total effort, Problems, Born–Openheimer approximation, Hartree and DFT Methods, Formulation of the Problem)

3 Periodic potentials (Bloch's theorem).

4. Eigenvalue estimates (Results: well-posedness and regularity results, regularity of eigenfunctions in weighted Sobolev spaces, optimal approximation results, a class of potentials closed under Hartree's iteration).

5. Conclusions and future work

Motivation: Quantum theory

Rutherford and col.: a model of the atom as a miniature solar system with a small, central nucleus about which the much lighter electrons cluster. The bonding forces are electrostatic, instead of gravitational.

Problem: *decay due to energy radiation*.

Bohr: quantization of *phase integral* ($\int pdq = nh$) and discrete set of possible orbits for the electrons were imposed.

This can be used to justify the emission spectrum of the Hydrogen atom:

$$h\nu = c(n^{-2} - m^{-2}), \quad n, m \in \mathbb{N}.$$

($n = 2$ and $m = 3, 4, 5, 6$ form the *Balmer's series*, which is in the visible spectrum, so it is observed.)

Planck & **Einstein:** energy quanta, $E = h\nu$.

Schrödinger's equation

The form of the discrete emission and absorbtion spectrum of other atoms (other than H) could not be justified classically by Bohr's model.

Schrödinger (building on work of **de Broglie** and others), formulated a wave equation for a particle moving in a force field with potential V:

$$\imath \partial \psi / \partial t = H \psi, \quad H = T_{kin} + V.$$

$|\psi(x)|^2$ is the probability density for the given particle to be at position x. Moreover, $\psi \sim \lambda \psi$, for $|\lambda| = 1$.

The *time independent Scrödinger equation* (stationary solutions)

$$H \psi = E \psi,$$

and describes the possible **bound states** of the system, with E the *energy* of that state.

The **radiation *emitted*** by the system is then

$$\nu = (E_{init} - E_{fin})/h.$$

The Hydrogen atom (suitable coordinates and units):

$$H = -\frac{1}{2}\Delta - \frac{1}{r}.$$

Simplest operator of the type we study.

Hydrogen atom: explicit calculations are possible.

Schrödinger has computed the eigenvalues (discrete spectrum) of the Hydrogen atom Hamiltonian H:

$$E_n = -\frac{1}{2n^2}$$

This is in spectacular agreement with the observed spectrum of the Hydrogen atom.

Hydrogen Eigenfunctions

The E_n–eigenfunctions of the Hydrogen atom are

$$\phi_{n,\beta}(x) = P_\beta(x) L_\beta(r) e^{-r/n}, \quad r = |x|,\ x \in \mathbb{R}^3$$

where p and L are polynomials with total degree

$$\deg(p) + \deg(L) \leq n - 1.$$

$\phi_{n,\beta}$ is *not smooth* at the origin.

$\phi_{n,\beta}(rx')$ is *smooth* in $(r, x') \in [0, \infty) \times S^2$, (generalized polar coordinates).

One of our main results will generalize this smoothness in generalized polar coordinates

The theory (but not the explicit calculations) extend to multi-electron systems.

Successes of QM theory have lead to ...

... Dirac's famous 1929 quote

"The general theory of quantum mechanics is now almost complete, [...].

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equation much too complicated to be soluble."

"It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, [...]"

Dirac, *Quantum mechanics of many-electron systems*, 1929 (courtesy of **Jim Anderson**, Chemistry, PSU).

Multi-electron systems

- M **nuclei** with *charges* Z_α and masses m_α
- N **electrons** (atomic units $m_e = 1$, $e = -1$).

$$H_{full} = -\sum_{\alpha=1}^{M} \frac{1}{2m_\alpha}\Delta_{y_\alpha} - \sum_{k=1}^{N} \frac{1}{2}\Delta_{x_k} + V_{full},$$

$\Delta_z =$ **Laplace** operator in the $z \in \mathbb{R}^3$ variable.

$V_{full} = V_{nn} + V_{ne} + V_{ee} =$ potential.

$$V_{ne}(x) = -\sum_k \underbrace{\sum_\alpha Z_\alpha |x_k - y_\alpha|^{-1}}_{-v(x_k)} = \sum_k v(x_k)$$

$$V_{ee} = \sum_{k<l} |x_k - x_l|^{-1}$$

The red terms are often omitted **(Born–Openheimer approximation)**.

The Ground State

A **fundamental problem** is to find the eigenvalues E_n and eigenfunctions of H (energy levels, spectra, evolution, ...).

For $E_1 := \min E_n$ we get the ground state of H.

For example, the ground state energy E is given by minimizing the **Rayleigh quotient:**

$$E_1 := \min E_n = \inf_{\psi \neq 0} \frac{(H\psi, \psi)}{(\psi, \psi)}$$

To find E_2, we then restrict to $\psi \perp \psi_1$, where ψ_1 is the ground state, ...

Impossible to do exactly: approximate methods.

Approximation

In *principle*, a good approximation of $E_1 := \min E_n$ can be obtained by minimizing $(H\psi, \psi)/(\psi, \psi)$ over a well-chosen, finite dimensional subspace V:

$$E_1 \simeq E_{1V} := \inf_{\psi \in V \setminus 0} \frac{(H\psi, \psi)}{(\psi, \psi)}$$

This can, of course, be continued with an approximation of E_2, ...

The amount of work needed to find the minimum E_{1V} depends on the dimension of V, so *we would like V to be as small as possible.*

We thus need V to "almost contain" the first few eigenfunctions of H.

We need good information on the eigenvalues.

Work

$\epsilon =$ desired precision, and

$m =$ order of approximation.

Typical approximations: $\dim V \sim \epsilon^{-3(M+N)/m}$,

So the work (effort) is

$$\text{Work} \simeq C\Big(\epsilon^{-3(M+N)/m}\Big)^q, \quad C = C_{M+N,m,q}.$$

Problems:

- Linear algebra improves q, but $q \geq 1$.
- The high dimension $M + N$ of the space;
- For standard methods, the *singularities* of the eigenfunctions ϕ of H *will limit* m (polution).

(The "pollution phenomenon," extensively studied: **Apel, Arnold, Babuška, Bramble, Dauge, Guo, Melenk, Oden, Osborn, Schatz, Strang, Schwab, Wahlbin, Xu, ...**).

Born–Openheimer approximation

The idea behind the Born–Openheimer approximation is that, since $m_\alpha >> 1$, the nuclei are much more localized, so we freeze them at some fixed values y_α.

We drop the red terms in $H_{full} =$

$$= -\sum_{\alpha=1}^{M} \frac{1}{2m_\alpha}\Delta_{y_\alpha} - \sum_{k=1}^{N} \frac{1}{2}\Delta_{x_k} + \underbrace{V_{nn} + V_{ne} + V_{ee}}_{V_{full}},$$

We obtain the *simplified Hamiltonian*:

$$H = -\sum_{k=1}^{N} \frac{1}{2}\Delta_{x_k} + V_{ne} + V_{ee} \quad \text{on } \mathbb{R}^{3N}.$$

Still, only $N \leq 3$ can be handled by this method.

Hartree and DFT

Hartree's method: Decompose

$$H - V_{ee} = -\sum_{k=1}^{N} \frac{1}{2}\Delta_{x_k} + V_{ne}$$

$$= -\sum_{k=1}^{N} \Big(\frac{1}{2}\Delta_{x_k} + \underbrace{\sum_{\alpha} Z_\alpha |x_k - y_\alpha|^{-1}}_{-v(x_k)}\Big) = \sum_{k=1}^{N} H_k$$

with

$$H_k \text{"="} \tilde{H} := -\frac{1}{2}\Delta + v,$$

acting only on the $x_k \in \mathbb{R}^3$ variables

$$v(x) = -\sum_{\alpha} Z_\alpha |x - y_\alpha|^{-1}$$

We shall concentrate on operators similar to $\tilde{H}$.

The eigenvalues of $\tilde{H}$ will determine the eigenvalues of $H - V_{ee}$.

Let q_j be the *eigenfunctions* of $\tilde{H} = -\Delta/2 + v$.

Roughly, *Hartree's method* consists in trying to approximate the ground state of H with

$$\psi(x_1, \dots, x_N) = q_1(x_1) q_2(x_2) \dots q_N(x_N).$$

Incorporating ψ in the calculations, will amount to find the eigenfunctions of $-\frac{1}{2}\Delta + v + \Phi$, where Φ is a sum of terms of the form

$$c \int |x-y|^{-1} |q_j(y)| dy = \Delta^{-1} |q_j|^2.$$

We then repeat with v replaced with $v + \Phi$.

We define inductively $V_0 = v$.

Then, if V_{n-1} was defined, **we compute** (!) the first N eigenfunctions of $-\Delta/2 + V_{n-1}$ and form Φ_{n-1} by adding terms of the form $\Delta^{-1}|q_j|^2$.

Finally we define

$$V_n = v + \Phi_{n-1} := v + \sum c_j \Delta^{-1} |q_j|^2.$$

v contains the singularities. (**Hartree's iteration**.)

Natural Questions:

• Find a class of potentials V that is closed under the Hartree iteration.

• Show good approximation properties for the eigenfunctions of these potentials.

Main Results: We answer these questions in the periodic case.

Bloch's Theorem

We consider $H = -\Delta/2 + V$, acting on $\mathbb{R}^3$.

V has only Coulomb singularities and is periodic (for some period lattice $\mathcal{L}$).

$\mathbb{T} := \mathbb{R}^3/\mathcal{L} \simeq (S^1)^3$, a three dimensional torus.

$\mathcal{S} \subset \mathcal{T}$ the finite set of singularities of V.

Bloch's Theorem, we need to consider $\mathbf{k} = (k_1, k_2, k_3)$

$$H_{\mathbf{k}} := -\sum_{j=1}^{3} (\partial_j + \imath k_j)^2/2 + V,$$

acting on $\mathbb{T} := \mathbb{R}^3/\mathcal{L}$ (i.e. on *periodic* functions).

(Our results are to a large extend independent of $\mathbf{k}$.)

To state our results we need ...

... Classes of potentials

We denote by $\overline{M}_{\mathcal{S}}$ the set obtained by replacing each $Q \in \mathcal{S}$ with a small sphere around it (blow up).

(Ex. $\mathbb{R}^3$ is replaced with $[0, \infty) \times S^2$, if we replace the origin in $\mathbb{R}^3$ with a sphere.)

This introduces "generalized polar coordinates" (r, x') in the neighborhood of each point $Q \in \mathcal{S}$.

Denote by r the distance to $\mathcal{S}$ (smoothed outside $\mathcal{S}$).

"Coulomb type singularity" means that rV belong to one of the following classes:

$$\mathcal{C}^\infty(\mathbb{T}) \subset \mathcal{C}^\infty(\overline{M}_{\mathcal{S}}) \subset W^{\infty,\infty}.$$

Results

Theorem. (Hunsicker-Sofo-N.) Assume $rV \in \mathcal{C}^\infty(\overline{M}_\mathcal{S})$ and $u \in L^2(\mathbb{T})$ is an *eigenfunction* of $H_\mathbf{k}$:

$$H_\mathbf{k} u := -\sum_{j=1}^{3} (\partial_j + \imath k_j)^2 u/2 + Vu = \lambda u.$$

Then $u \in \mathcal{C}^\infty(\overline{M}_\mathcal{S})$.

This theorem can be used to justify *Taylor–type expansions* of u close to the singularity (*Kato's cusp condition*, Hoffmann-Ostenhof).

However, $\mathcal{C}^\infty(\overline{M}_\mathcal{S})$ is *not closed* under Hatree's iteration.

We introduce a **larger class** of potentials $W^{\infty,\infty}$.

Except for the above theorem, all the following results hold for this larger class of potentials.

Functions spaces

Weighted Sobolev spaces:

$$\mathcal{K}^m_a(\mathbb{T}) := \{v,\ r^{|\alpha|-a}\partial^\alpha v \in L^2(\mathbb{T}),\ \forall\ |\alpha| \le m\}.$$

Similarly,

$$W^{m,\infty}_b(\mathbb{T}) := \{v,\ r^{|\alpha|}\partial^\alpha v \in L^\infty(\mathbb{T}),\ \forall\ |\alpha| \le m\}.$$

As usual:

$$\mathcal{K}^\infty_a := \cap_m \mathcal{K}^m_a(\mathbb{T}),$$

and $W^{\infty,\infty} := \cap_m W^{m,\infty}(\mathbb{T})$.

From now on we assume:

$$rV \in W^{\infty,\infty} \supset \mathcal{C}^\infty(\overline{M}_{\mathcal{S}}) \supset \mathcal{C}^\infty(\mathbb{T}).$$

Theorem. (H.-S.-N.) $H_{\mathbf{k}}$ is self-adjoint on $L^2(\mathbb{T})$ with domain $H^2(\mathbb{T})$ and with compact resolvent.

In particular, we can find an orthonormal basis of $L^2(\mathbb{T})$ consisting of eigenfunctions of $H_{\mathbf{k}}$.

Theorem. (H.-S.-N.) Let $H_{\mathbf{k}}u = \lambda u$, $u \in L^2(\mathbb{T})$. Then

$$u \in H^{5/2-\epsilon}(\mathbb{T}) \cap \mathcal{K}^{\infty}_{3/2-\epsilon} \cap W^{\infty,\infty},$$

and $\Delta^{-1}|u|^2 \in W^{\infty,\infty}$.

The last results shows that our class of potentials is **closed under Hartree's iteration**.

Regularity of eigenfunctions, analogous to classical results.

How well can we compute the eigenvalues?

Recall that (effort) is

$$\text{Work} \simeq C\epsilon^{-3q/m}, \quad N = 1, M = 0.$$

For standard methods (quasi-uniform meshes), $m < 5/2$, since $u \notin H^{5/2}$ (recall e^{-r}).

We need better approximation spaces: (non quasi-uniform meshes, GFEM, ...)

Piecewise polynomial approximations

Let $\mathcal{T}$ be a triangulation of $\mathbb{T}$ (mesh) and $S(\mathcal{T}, m)$ be the space of continuous functions on $\mathbb{T}$ that are polynomials of degree $\le m$ on each tetrahedron of the mesh.

There exists a simple refining procedure (divide each edge closer to the singularity) that yields inductively a sequence of meshes $\mathcal{T}_n$ with the following property.

Theorem. (H.-S.-N.) Let $u \in \mathcal{K}^{m+1}_{3/2-\epsilon}(\mathbb{T} \smallsetminus \mathcal{S}) \cap H^2(\mathbb{T})$. Then, if $S_{n,m} = S(\mathcal{T}_n, m)$

$$\text{dist}_{\mathcal{K}^1_1}(u, S_{n,m}) \le C(u)\text{dim}(S_{n,m}^{-m/3},$$

$C(u) = C_0(\|u\|_{\mathcal{K}^{m+1}_{3/2-\epsilon}} + \|u\|_{H^2(\mathbb{T})})$.

For our meshes, no restriction on m in the estimate of the amount of work. The sequence $S(\mathcal{T}, m)$ yields optimal convergence rates. **Classically**, $m \le 5/2$.

Some details

$H_{\mathbf{k}} : \mathcal{K}^{m+1}_{a+1} \to \mathcal{K}^{m-1}_{a-1}$ is continuous and satisfies elliptic regularity.

$H_{\mathbf{k}} + \Delta : \mathcal{K}^{m+1}_{a+1} \to \mathcal{K}^{m}_{a}$ is of "lower order".

$\mathcal{K}^{m}_{a} \to \mathcal{K}^{m-1}_{a-1}$ is compact, $\Rightarrow$ $H_{\mathbf{k}}$ is self-adjoint with domain the domain of Δ, that is $H^2(\mathbb{T})$.

$H_{\mathbf{k}}$ and Δ are Fredholm for $a - 1/2 \notin \mathbb{Z}$.

It is essential to compute their index.

$\Delta : \mathcal{K}^{m+1}_{a+1} \to \mathcal{K}^{m-1}_{a-1}$ is an isomorphism for $a \in (-1/2, 1/2)$ on functions with mean zero ($\Delta 1 = 0$).

This is **not true** for $a \notin (-1/2, 1/2)$.

Sobolev embedding: $\mathcal{K}^{\infty}_{a+1} \subset W^{\infty,\infty}$ for $a \geq 1/2$ (**Ammann–Ionescu–N.**). (**Not** in the above range.)

We need a refined *well–posedness* result.

Refined well–posedness result

$\forall\, Q \in \mathcal{S}$, we fix $\chi_Q \in \mathcal{C}^\infty(\mathbb{T})$,

$\chi_Q = 1$ in a neighborhood of Q,

$\chi_Q = 0$ in a neighborhood of each singular point $Q' \neq Q$.

Let $W_s := \{\sum_Q c_Q \chi_Q\}$, a space of dimension the number of nuclei.

Refined well–posedness result (using an index calculation):

Theorem. (H.-J.-N.) The map

$$\Delta : (\mathcal{K}^{m+1}_{a+1} + W_s) \cap \{1\}^\perp \to \mathcal{K}^{m-1}_{a-1} \cap \{1\}^\perp$$

is an **isomorphism** for $a \in (1/2, 3/2)$.

We have $\mathcal{K}^\infty_{a+1} + W_s \in W^{\infty,\infty}$ for $a \geq 1/2$.

Summary

We have studied operators of the form

$$H_{\mathbf{k}} := -\sum_{j=1}^{3} (\partial_j + \imath k_j)^2/2 + V$$

(solid state physics, band structure of the spectrum).

For a large class of potentials, $rV \in W^{\infty,\infty}$, we have proved full regularity of eigenfunctions in weighted Sobolev spaces. (The regularity is limited in the usual Sobolev spaces.)

This enough to obtain optimal approximability of the eigenfunctions of $H_{\mathbf{k}}$.

This class of potentials is closed under the Hartree iteration.

Singularities similar to the ones in polygonal domains.

Methods: Analysis on non-compact manifolds.

Future work

Numerical tests.

Direct approximation for the Helium atom and, hopefully larger atoms or molecules.

Singularities similar to those in polyhedral domains in three or more dimensions.

We used methods from analysis on manifolds with conical singularities/cylindrical ends.

$V =$ lower order perturbation.

Multi-particle systems: we plan to use Lie manifolds, methods of Geometric Analysis.

(Regensburg Lectures for Geometric Analysis)