Sharp Regularity Results for Coulombic Many-Electron Wave Functions

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Abstract: We show that electronic wave functions \( \psi \) of atoms and molecules have a representation \( \psi = F \phi \), where \( F \) is an explicit universal factor, locally Lipschitz, and independent of the eigenvalue and the solution \( \psi \) itself, and \( \phi \) has second derivatives which are locally in \( L^\infty \). This representation turns out to be optimal as can already be demonstrated with the help of hydrogenic wave functions. The proofs of these results are, in an essential way, based on a new elliptic regularity result which is of independent interest. Some identities that can be interpreted as cusp conditions for second order derivatives of \( \psi \) are derived.

1. Introduction

1.1. Motivation and results. The non-relativistic quantum mechanical Hamiltonian of an \( N \)-electron molecule with \( L \) fixed nuclei is given by

\[
H_{N,L}(X, Z) = -\Delta + V(X, Z) + U(X, Z),
\]

where \( V \), the Coulombic potential, is given by

\[
V \equiv V(X, Z) = -\sum_{j=1}^{N} \sum_{k=1}^{L} \frac{Z_k}{|X_k - x_j|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}, \tag{1.1}
\]

and the internuclear repulsion \( U \) by

\[
U(X, Z) = \sum_{1 \leq k < \ell \leq L} \frac{Z_k Z_\ell}{|X_k - X_\ell|}.
\]
The latter is merely an additive term that will be neglected in the sequel and we will henceforth consider

\[ H \equiv H_{N,L}(X, Z) - U(X, Z). \]  

(1.2)

Above, \( x = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^3 \) denotes the positions of the \( N \) electrons, with \( x_j = (x_{j1}, x_{j2}, x_{j3}) \in \mathbb{R}^3 \) the position of the \( j^{th} \) electron. The positions of the \( L \) nuclei with the positive charges \( Z = (Z_1, Z_2, \ldots, Z_L) \in \mathbb{R}_+^L \) are denoted by \( X = (X_1, X_2, \ldots, X_L) \in \mathbb{R}^{3L} \), where \( X_k = (X_{k1}, X_{k2}, X_{k3}) \in \mathbb{R}^3 \) is the (fixed) position of the \( k^{th} \) nucleus with charge \( Z_k \), and it is assumed that \( X_\ell \neq X_k \) for \( \ell \neq k \).

The Laplacian corresponding to the \( j^{th} \) electron is \( \Delta_j = \sum_{i=1}^3 \frac{\partial^2}{\partial x_{j,i}^2} \) and so the Laplacian on \( \mathbb{R}^{3N} \) is given by \( \Delta = \sum_{j=1}^N \Delta_j \). We also introduce the \( 3N \)-dimensional gradient by \( \nabla = (\nabla_1, \ldots, \nabla_N) \).

The operator \( H \) is selfadjoint on \( L^2(\mathbb{R}^{3N}) \) with operator domain \( D(H) = W^{2,2}(\mathbb{R}^{3N}) \) \([14]\), and it depends parametrically on \( X \) and \( Z \). In the case of an \( N \)-electron atom with (one) nucleus of charge \( Z \) fixed at the origin \( 0 \in \mathbb{R}^3 \), (1.2) becomes

\[ H \equiv H_N(Z) = -\Delta + V \]  

(1.3)

\[ = \sum_{j=1}^N \left( -\Delta_j - \frac{Z}{|x_j|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}. \]

Generations of chemists and physicists have devoted a good part of their research to the analysis of various problems related to \( H_{N,L}(X, Z) \). Most of the present day understanding of atoms and molecules is based on the analysis of problems directly related to this operator; see any textbook in atomic and molecular quantum mechanics.

One of the central problems is the eigenvalue problem

\[ H \psi = E \psi, \quad E \in \mathbb{R}, \quad \psi \in L^2(\mathbb{R}^{3N}). \]  

(1.4)

Since the electrons are Fermions the \( N \)-electron wave function \( \psi \) has to satisfy the Pauli Principle. This can be achieved in a spinless formulation by requiring that \( \psi \) transforms according to certain irreducible representations of the symmetric group \( \mathfrak{S}^N \). Our present work will not require any symmetry assumptions on \( \psi \). More precisely, we will consider local properties of distributional solutions (locally \( L^1 \)) in a domain \( \Omega \subset \mathbb{R}^{3N} \) to \( H \psi = E \psi \), where \( E \) can be any real number.

Within mathematics and mathematical physics Schrödinger operators as (1.2) are studied mostly from an operator theoretical point of view, see the textbooks \([1, 14, 18, 22]\) as well as the recent survey \([21]\).

The PDE-aspects of (1.4) have been studied in relatively few works. We first note the following: Let \( \Sigma(X) \) denote the set of points in \( \mathbb{R}^{3N} \) where the potential \( V \) defined in (1.1) is singular. The function \( V \) is real analytic in \( \mathbb{R}^{3N} \setminus \Sigma(X) \) and hence by classical results (see \([11, \text{Sect. 7.5, pp. 177-180}]\)), so is \( \psi \).

Therefore a basic question is how to characterize the effect of the singularities of \( V \) on the local behaviour of a solution \( \psi \) of (1.4).

In 1957 Kato \([13]\) showed that a solution \( \psi \) satisfying (1.4) is continuous in all of \( \mathbb{R}^{3N} \) with first derivatives locally in \( L^\infty \), i.e., \( \psi \) is locally Lipschitz. He also analyzed how \( \psi \) behaves near the so-called two-particle coalescence points, i.e., those points in \( \Sigma(X) \) where exactly one term in the sums representing \( V \) (see (1.1)) is unbounded.