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On the regularity of the electronic Schrödinger equation in Hilbert spaces of mixed derivatives

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Summary. The electronic Schrödinger equation describes the motion of electrons under Coulomb interaction forces in the field of clamped nuclei and forms the basis of quantum chemistry. The present article is devoted to the regularity properties of the corresponding wavefunctions that are compatible with the Pauli principle. It is shown that these wavefunctions possess certain square integrable mixed weak derivatives of order up to $N + 1$ with N the number of electrons, across the singularities of the interaction potentials. The result is of particular importance for the analysis of approximation methods that are based on the idea of sparse grids or hyperbolic cross spaces. It indicates that such schemes could represent a promising alternative to current methods for the solution of the electronic Schrödinger equation and that it may even be possible to reduce the computational complexity of an N-electron problem to that of a one-electron problem.

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1 Introduction

The physics of atoms and molecules (and therefore nearly all of chemistry) is largely governed by the quantum mechanical many body problem in which the electrons and nuclei interact by Coulomb attraction and repulsion forces. As the nuclei are much heavier than the electrons, the electrons almost instantaneously follow their motion. Already in the early days of quantum mechanics, Born and Oppenheimer therefore proposed treating molecules as quantum-classical systems in which only the motion of the electrons is determined by the laws of quantum theory, but the nuclei move according to

classical physics. The core of the Born-Oppenheimer procedure and of most quantum-chemical computations up to the present day consists in finding the eigenvalues and eigenfunctions of the electronic Hamilton operator

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|x_i - x_j|} \tag{1.1}$$

written down here in dimensionless form. It acts on functions with arguments $x_1, \ldots, x_N \in \mathbb{R}^3$, the coordinates of given N electrons. The positions $a_1, \ldots, a_K \in \mathbb{R}^3$ of the nuclei are kept fixed. The positive values Z_ν are the charges of the nuclei in multiples of the electron charge.

The spectral theory of Hamilton operators like (1.1) is a huge field to which many mathematicians made important contributions. Starting point was Kato's work [14] in which he has shown that such Hamilton operators fit into the abstract framework of quantum mechanics that has been laid by von Neumann [21]. Another breakthrough was the Hunziker-van Winter-Zhislin theorem, which essentially states that the spectrum of an atom or molecule consists of isolated eigenvalues $\lambda_0 \le \lambda < \Sigma$ of finite multiplicity between a minimum eigenvalue λ_0 and a ionization bound Σ and an essential spectrum $\lambda \ge \Sigma$. Comprehensive surveys on the mathematical theory of Schrödinger operators and the quantum N-body problem in particular are [12] and [18]. The basic textbook reference still is [17].

The present article deals with the regularity properties of the eigenfunctions of the Hamilton operator (1.1). The basic reference in this field is another work [15] of Kato, in which he derived the famous cusp conditions that establish a connection between the function values and certain first order directional derivatives at the points where two particles meet and the corresponding interaction potential becomes singular. For newer developments in this direction, see [5], [10], and [11]. In contrast to the work of Kato or to these papers, we do not direct our attention primarily to the local behavior of the eigenfunctions near the singular points of the interaction potentials, but show that the eigenfunctions possess global, square-integrable weak derivatives of partly very high order.

Our results fundamentally depend on symmetry properties of the eigenfunctions. These symmetry properties cannot be understood without taking the spin of the electrons into account. Basically, the eigenfunctions

$$\psi : (\mathbb{R}^3)^N \times \{-1/2,\ 1/2\}^N \to \mathbb{C} : (x, \sigma) \to \psi(x, \sigma) \tag{1.2}$$

do not only depend on the space coordinates $x_i \in \mathbb{R}^3$ of the electrons, but also on their spin coordinates $\sigma_i = \pm 1/2$. As the Hamilton operator (1.1) disregards the spin-orbit coupling and does not act upon the spin variables, the components

$$u : (\mathbb{R}^3)^N \to \mathbb{C} : x \to \psi(x, \sigma) \tag{1.3}$$

of the full eigenfunction (1.2) represent eigenfunctions of H for every fixed σ. The Pauli principle, one of the fundamental principles of quantum mechanics, states that only those eigenfunctions (1.2) are physically relevant that change their sign under a simultaneous exchange of the space coordinates x_i and x_j and the spins σ_i and σ_j of two electrons i and j, that is, behave like

$$\psi(Px, P\sigma) = \operatorname{sign}(P)\psi(x, \sigma) \tag{1.4}$$

under an arbitrary simultaneous permutation $x \to Px$ and $\sigma \to P\sigma$ of the electron coordinates and spins.

The Pauli principle strongly restricts the form the spatial parts (1.3) of the eigenfunctions can attain. For a given fixed σ, let

$$\mathcal{I}_- = \{\, i \mid \sigma_i = -1/2 \,\}, \quad \mathcal{I}_+ = \{\, i \mid \sigma_i = +1/2 \,\} \tag{1.5}$$

denote the subsets of the indices $1, \ldots, N$ for which the spin coordinates σ_i take the values $+1/2$ and $-1/2$, respectively. Let P be a permutation that leaves $\mathcal{I}_-$ and $\mathcal{I}_+$ invariant. Then $P\sigma = \sigma$, so that (1.4) implies

$$\psi(Px, \sigma) = \operatorname{sign}(P)\psi(x, \sigma). \tag{1.6}$$

The spatial eigenfunction (1.3) therefore is both antisymmetric under the exchange of electron coordinates x_i and x_j with indices i and j in $\mathcal{I}_-$ and antisymmetric under the exchange of electron coordinates x_i and x_j with indices i and j in $\mathcal{I}_+$. Particularly, for systems with more than two electrons completely symmetric spatial eigenfunctions (1.3) are ruled out. The other extreme form spin correlated states in which all spins σ_i take the same value and for which already the corresponding spatial components (1.3) of the eigenfunctions are antisymmetric.

We will consider eigenfunctions $u : \mathbb{R}^{3N} \to \mathbb{R}$ of the Hamilton operator (1.1) that are antisymmetric under the exchange of electron coordinates x_i and x_j with indices $i \neq j$ in given subsets $\mathcal{I}$ of the indices $1, \ldots, N$. The regularity properties of these eigenfunctions depend on these sets $\mathcal{I}$. Our main result is: Their weak partial derivatives of order $|\mathcal{I}|$ with $|\mathcal{I}|$ the number of elements in $\mathcal{I}$, that act only onto the electron coordinates x_i with $i \in \mathcal{I}$ and that are of first order in every single such x_i, do not only exist as L_2-functions on the whole domain of definition of the wavefunctions including the singular points of the interaction potentials, but themselves even have square-integrable first order weak derivatives. The larger $\mathcal{I}$ is, the higher the regularity. As discussed above, the indices $1, \ldots, N$ always split into two such sets $\mathcal{I}$ for physically admissible eigenfunctions. The admissible eigenfunctions therefore possess very high order weak partial derivatives for systems consisting of many electrons.

The maximum regularity is reached for purely antisymmetric eigenfunctions u. The regularity theorem then expresses that the integral

$$\int \Big(1 + \sum_{i=1}^{N} |\omega_i|^2\Big)\Big(1 + \prod_{i=1}^{N} |\omega_i|^2\Big)|\widehat{u}(\omega)|^2 d\omega \tag{1.7}$$

remains finite. In the case of general eigenfunctions that are compatible with the Pauli principle, one can bound the integral

$$\int \Big(1 + \sum_{i=1}^{N} |\omega_i|^2\Big)\Big(1 + \prod_{i=1}^{N} |\omega_i|\Big)|\widehat{u}(\omega)|^2 dw, \tag{1.8}$$

which is less, but still suffices for the purpose we have in mind.

Our theory is based on careful estimates of the Coulomb interaction operators in (1.1) within the scale of the chosen solution spaces, on the fact that integration by parts across the corresponding singularities is possible in certain cases, and on standard arguments from Hilbert space theory and Fourier analysis. The structure of the interaction potentials is utilized on a massive scale as well as the fact that functions which are antisymmetric under the exchange of two electron coordinates take the value zero at the singular points of the interaction potential of these electrons. In which way our regularity theorem is connected with the regularity results mentioned above remains an open question. Higher order mixed derivatives can presumably only be bounded in weighted L_2-spaces.

The intention of this article is to lay a mathematical foundation for the construction of numerical methods to compute the lowest eigenvalues and corresponding eigenfunctions of electronic Schrödinger operators. This problem is inevitably connected with the problem to approximate very high-dimensional functions. If one wants to avoid that the computational complexity of such procedures degrades with an increasing space dimension or here an increasing number of electrons, the regularity must grow sufficiently fast with the number of space dimensions. As shown in this article, this is surprisingly the case for the eigenfunctions of electronic Schrödinger operators. This fact together with the symmetry properties of the eigenfunctions resulting from the Pauli principle may enable the construction of numerical methods for the solution of the electronic Schrödinger equation the rate of convergence of which in the number of degrees of freedom does not deteriorate with the number of electrons.

Recent attempts of this kind are based on the idea of sparse grids or hyperbolic cross spaces [4], [6], [8], [13]. Such constructions have a long tradition in approximation theory and go back to the Russian literature [1], [19]. They became popular in numerical mathematics through the work of Zenger [23] who recognized their potential; see [2] and [7] for newer developments and

the literature cited therein. Similar constructions are possible with wavelets; see [3], for example. The advantage of such approximation spaces is that their dimension grows tremendously much slower in the number of independent variables than usual when increasing the accuracy, in particular, if symmetry or antisymmetry are taken into account [8]. The present regularity theorems let expect that properly designed approaches based on such ideas could work in the case of the electronic Schrödinger equation as well. They make them a promising alternative to current methods like Hartree-Fock [9], [20] or density functional theory [16], which more resemble simplified models than true discretization procedures.

2 The underlying function spaces

The eigenvalue problem for the Hamilton operator (1.1) is of purely formal nature as long as no solution space is specified. This solution space must be a subspace of $H^1(\mathbb{R}^n)$ with $n = 3N$ here. The Hilbert space $H^1(\mathbb{R}^n)$ consists of the one times weakly differentiable functions $u : \mathbb{R}^n \to \mathbb{R}$ for which the H^1-norm $\|u\|_1$ composed of the L_2-norm

$$\|u\|_0 = \left(\int |u(x)|^2 \, dx \right)^{1/2} \tag{2.1}$$

and of the H^1-seminorm

$$|\, u \,|_1 = \left(\int |\nabla u(x)|^2 \, dx \right)^{1/2} \tag{2.2}$$

takes a finite value. Interpreting its elements as wavefunctions, it is the largest space for which the total position probability (2.1) remains finite and for which the expectation value

$$-\frac{1}{2} \sum_{i=1}^{N} \int u \, \Delta_i u \, dx = \frac{1}{2} \sum_{i=1}^{N} \int |\nabla_i u|^2 \, dx \tag{2.3}$$

of the kinetic energy can be given a meaning. In Sect. 4, it will be discussed why the operator equations

$$(H + \mu I)u = f \tag{2.4}$$

indeed have a unique weak solution $u \in H^1(\mathbb{R}^{3N})$ for sufficiently large positive constants μ and corresponding right-hand sides f. Correspondingly, a solution of the eigenvalue problem

$$Hu = \lambda u \tag{2.5}$$

for the Hamilton operator (1.1) is a weak solution $u \neq 0$ in $H^1(\mathbb{R}^{3N})$ of the operator equation (2.5).

Let $\mathcal{D}$ be the space of the infinitely differentiable functions

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : (x_1, \ldots, x_N) \to u(x_1, \ldots, x_N) \tag{2.6}$$

having a bounded support. The functions in $\mathcal{D}$ form a dense subset of $H^1(\mathbb{R}^{3N})$ or shortly H^1, so that $H^1(\mathbb{R}^{3N})$ coincides with the space $H_0^1(\mathbb{R}^{3N})$, the closure of $\mathcal{D}$ in $H^1(\mathbb{R}^{3N})$. Most estimates in this paper will first be proved for functions in $\mathcal{D}$ and are then extended to $H^1(\mathbb{R}^{3N})$ or other Hilbert spaces. The H^{-1}-norm on $\mathcal{D}$ is defined as

$$\|f\|_{-1} = \sup\left\{(f, v) \,\middle|\, v \in \mathcal{D},\ \|v\|_1 = 1\right\} \tag{2.7}$$

where (f, v) denotes the L_2-inner product inducing the norm (2.1). The completion of $\mathcal{D}$ under this norm is the space $H^{-1}(\mathbb{R}^{3N})$ and can be identified with the space of the bounded linear functionals on $H^1(\mathbb{R}^{3N})$.

Another dense subspace of H^1 is the Schwartz space $\mathcal{S}$ of the rapidly decreasing functions. This space is somewhat larger than $\mathcal{D}$ and consists of the infinitely differentiable functions that tend, together with all their derivatives, faster to zero for $|x| \to \infty$ than any polynomial grows. The Fourier transform is a one-to-one mapping from $\mathcal{S}$ onto itself. This fact will play a decisive role in our argumentation.

As mentioned in the introduction, the regularity of the eigenfunctions largely depends on their symmetry properties under the exchange of the electron coordinates. In the given context, these symmetry properties are determined by a subset

$$\mathcal{I} \subseteq \{1, \ldots, N\}, \quad \mathcal{I} \neq \emptyset, \tag{2.8}$$

of the indices $i = 1, \ldots, N$. We keep this set fixed in the sequel and denote by $|\mathcal{I}|$ the number of its elements.

By $\mathcal{D}_\mathcal{I}$ we denote the space of the functions (2.6) in $\mathcal{D}$ that are antisymmetric under the exchange of electron coordinates $x_i,\ x_j \in \mathbb{R}^3$ for indices $i \neq j$ in the given index set $\mathcal{I}$. The functions in this space vanish at the singular points x with $x_i = x_j$, $i \neq j$ in $\mathcal{I}$, of the electron-electron interaction potential in (1.1). The completion of $\mathcal{D}_\mathcal{I}$ in H^s, $s = -1$, 0 or 1, is denoted by $H^s_\mathcal{I}$. The subspace $\mathcal{S}_\mathcal{I}$ of the space $\mathcal{S}$ of rapidly decreasing functions is defined correspondingly to $\mathcal{D}_\mathcal{I}$.

With the given set $\mathcal{I}$ of indices, we associate the set $\mathcal{I}^*$ of the mappings

$$\alpha : \mathcal{I} \to \{1, 2, 3\}. \tag{2.9}$$

To every $\alpha \in \mathcal{I}^*$, we attribute the differential operator

$$L_\alpha = \prod_{i \in \mathcal{I}} \frac{\partial}{\partial x_{i,\alpha(i)}} \tag{2.10}$$

where x_{i1}, x_{i2} and x_{i3} denote the components of the electron coordinate $x_i \in \mathbb{R}^3$. The differential operator (2.10) has order $|\mathcal{I}|$ and acts only on the variables x_i, $i \in \mathcal{I}$. It is of first order in the components of a given such electron coordinate. It is

$$\sum_{\alpha \in \mathcal{I}^*} L_\alpha^2 = \prod_{i \in \mathcal{I}} \Delta_i \tag{2.11}$$

where Δ_i again denotes the Laplace operator acting upon the variable x_i.

On the space $\mathcal{D}$ of the infinitely differentiable functions with compact support, we introduce the norms

$$\|u\|_{\mathcal{I},s} = \Big(\|u\|_s^2 + \sum_{\alpha \in \mathcal{I}^*} \|L_\alpha u\|_s^2 \Big)^{1/2} \tag{2.12}$$

for $s = -1$, 0 or 1. The completion of $\mathcal{D}_\mathcal{I}$ under the norm (2.12) is denoted as $X_\mathcal{I}^s$. The Hilbert spaces $X_\mathcal{I}^s$ have to be distinguished from the spaces $H_\mathcal{I}^s$ introduced above, which are much bigger and which consist of the functions in H^s only having the corresponding symmetry properties. The notations

$$| u |_{\mathcal{I},0} = \Big(\sum_{\alpha \in \mathcal{I}^*} \|L_\alpha u\|_0^2 \Big)^{1/2} \tag{2.13}$$

and correspondingly

$$| u |_{\mathcal{I},1} = \Big(\sum_{\alpha \in \mathcal{I}^*} |L_\alpha u|_1^2 \Big)^{1/2} \tag{2.14}$$

will often be used to reflect the nature of estimates better.

Our primary aim is to prove that, for $f \in X_\mathcal{I}^{-1}$ and μ chosen sufficiently large, the weak solution $u \in H^1$ of the equation (2.4) is contained in $X_\mathcal{I}^1$. Although we will proceed somewhat differently in the end to keep the norms small, an induction argument then already shows that the eigenfunctions of the Hamilton operator (1.1) that behave correspondingly under the exchange of electron coordinates are located in the same space.

3 Properties of the interaction potentials

The regularity of the wavefunctions is restricted by the singular behavior of the electron-electron interaction potential

$$V_{ee} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|x_i - x_j|} \tag{3.1}$$

and of the nucleus-electron interaction potential

$$V_{ne} = -\sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} \tag{3.2}$$

with the a_ν the fixed positions of the nuclei and the Z_ν their charges. The aim of the present section is to study the integrals

$$\sum_{\alpha\in\mathcal{I}^*}\int L_\alpha(V_{ee}u)L_\alpha v\,dx\,,\quad \sum_{\alpha\in\mathcal{I}^*}\int L_\alpha(V_{ne}u)L_\alpha v\,dx \tag{3.3}$$

for functions u and v in the space $\mathcal{D}_\mathcal{I}$ of infinitely differentiable functions with bounded support that are antisymmetric under the exchange of the given electron coordinates. To simplify notation a little bit, we restrict ourselves to the case of neutral atoms or molecules and exclude ions. The general case, however, can be treated in the same way. The fact that the interaction potentials are Coulomb potentials is of fundamental importance and is utilized on a massive scale. The results of this section form the analytic background for the abstract treatment of the operator equation (2.4) in Sect. 4 and Sect. 5 and represent the foundation of the regularity proof.

The single parts of the electron-electron interaction potential (3.1) involve only two electron coordinates x_i and x_j in $\mathbb{R}^3$. For ease of presentation, we suppress the variables except for x_i and x_j for a while and rename the two remaining variables in $\mathbb{R}^3$ to x and y. The quantities x_1, x_2 and x_3 and y_1, y_2 and y_3 then denote the components of the vectors x and y for the time being and not electron coordinates. We set

$$\phi(x,y) = \frac{1}{|x-y|} \tag{3.4}$$

for abbreviation and at first estimate and transform expressions like

$$\sum_{i,j=1}^{3}\int\frac{\partial^2}{\partial x_i\partial y_j}(\phi u)\,\frac{\partial^2 v}{\partial x_i\partial y_j}\,d(x,y) \tag{3.5}$$

with u and v being infinitely differentiable functions that have a compact support and u vanishing on the singular set $x = y$ of the potential ϕ.

The key to the mathematical treatment of Hamilton operators like (1.1) are Hardy-type estimates like the following ones. They represent a standard tool in the field, but to keep the presentation self-contained we prove them.

Lemma 1 *For all infinitely differentiable functions v in the variable $x \in \mathbb{R}^3$ that have a compact support,*

$$\int\frac{1}{|x|^2}\,v^2\,dx \;\le\; 4\int|\nabla v|^2\,dx\,. \tag{3.6}$$

Proof. Let $d(x) = |x|$ for abbreviation and assume at first that v vanishes on a neighborhood of the origin. Using the relation

$$\frac{1}{d^2} \;=\; -\,\nabla\Big(\frac{1}{d}\Big)\cdot\nabla d\,,$$

and partial integration one obtains

$$\int \frac{1}{d^2}\,v^2\,dx \;=\; \int \frac{1}{d}\,\nabla\cdot(v^2\nabla d)\,dx$$

or, using $\Delta d = 2/d$ and resolving for the left-hand side, the representation

$$\int \frac{1}{d^2}\,v^2\,dx \;=\; -\,2\int \frac{1}{d}\,v\,\nabla d\cdot\nabla v\,dx$$

of the integral to be estimated. The Cauchy-Schwarz inequality yields

$$\int \frac{1}{d^2}\,v^2\,dx \;\le\; 2\Big(\int \frac{1}{d^2}\,v^2\,dx\Big)^{1/2}\Big(\int |\nabla d\cdot\nabla v|^2\,dx\Big)^{1/2}$$

and, using $|\nabla d| = 1$, finally the estimate (3.6) for functions v vanishing near the origin. To treat the general case, let $\omega : \mathbb{R}^3 \to [0,\,1]$ be a smooth function with $\omega(x) = 0$ for $|x| \le 1/2$ and with $\omega(x) = 1$ for $|x| \ge 1$. Set

$$v_k(x) = \omega(kx)v(x).$$

The estimate (3.6) then holds for the functions v_k as just proved. Using

$$|\,\omega(kx)| \le 1, \quad |\,k\,(\nabla\omega)(kx)| \le \frac{c}{|x|}$$

with a constant c independent of k and the local integrability of

$$x \to \frac{1}{|x|^2},$$

the proposition follows with the dominated convergence theorem. □

For smooth functions in the variables $x,\,y \in \mathbb{R}^3$ having a compact support, the estimate (3.6) takes the form

$$\int \frac{1}{|x-y|^2}\,v^2\,d(x,\,y) \;\le\; 2\,\|\nabla v\|_0^2 \tag{3.7}$$

where ∇v now is the gradient with respect to x and y. The estimate (3.7) is proved rewriting the integral on the left-hand side with Fubini's theorem and then applying Lemma 1 to the inner integrals.

The counterpart of Lemma 1 for functions vanishing at the origin is:

Lemma 2 *For all infinitely differentiable functions v in the variable $x \in \mathbb{R}^3$ that have a compact support and that vanish at the origin,*

$$\int \frac{1}{|x|^4}\, v^2\, dx \;\le\; 4 \int \frac{1}{|x|^2}\, |\nabla v|^2\, dx\,. \tag{3.8}$$

Proof. The proof proceeds as with the first lemma starting from the relation

$$\frac{1}{d^4} \;=\; -\,\frac{1}{3}\,\nabla\Big(\frac{1}{d^3}\Big)\cdot\nabla d\,.$$

To transfer (3.8) from the functions v that vanish on a whole neighborhood of the origin to functions v for which only $v(0) = 0$ holds, one has to utilize that there exists a constant K with

$$|v(x)| \le K|x|$$

and then can again apply the dominated convergence theorem. □

It should be noted that the condition $v(0) = 0$ is essential in Lemma 2 because the function $x \to 1/|x|^4$ is not locally integrable in three space dimensions. A consequence of Lemma 1 and Lemma 2 and of Fubini's theorem is the estimate

$$\int \frac{1}{|x-y|^4}\, v^2\, d(x,y) \;\le\; 16 \sum_{i,j=1}^{3} \int \Big(\frac{\partial^2 v}{\partial x_i\, \partial y_j}\Big)^2\, d(x,y) \tag{3.9}$$

for infinitely differentiable functions v in the variables $x, y \in \mathbb{R}^3$ having a compact support and vanishing on the singular set $x = y$. At this place, the antisymmetry of the functions in the solution space for the operator equation (2.4) will finally enter.

We now come to a group of three lemmata that will form the basis for the estimates of the integrals (3.3).

Lemma 3 *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support and let u vanish for $x = y$. Then*

$$\begin{aligned} \sum_{i,j=1}^{3} \int \frac{\partial^2}{\partial x_i\, \partial y_j}(\phi u)\, \frac{\partial^2 v}{\partial x_i\, \partial y_j}\, d(x,y) \\ \le\; C \Big\{ \sum_{i,j=1}^{3} \Big\| \frac{\partial^2 u}{\partial x_i\, \partial y_j} \Big\|_0^2 \Big\}^{1/2} \Big\{ \sum_{i,j=1}^{3} \Big| \frac{\partial^2 v}{\partial x_i\, \partial y_j} \Big|_1^2 \Big\}^{1/2} \end{aligned} \tag{3.10}$$

with a constant C nearer specified in the proof.

Proof. Because

$$\frac{\partial^2}{\partial x_i \partial y_j}(\phi u) \;=\; \frac{\partial^2 \phi}{\partial x_i \partial y_j}\, u + \frac{\partial \phi}{\partial x_i}\frac{\partial u}{\partial y_j} + \frac{\partial \phi}{\partial y_j}\frac{\partial u}{\partial x_i} + \phi\, \frac{\partial^2 u}{\partial x_i \partial y_j}\,,$$

the integral on the left-hand side of (3.10) naturally splits into four different parts that are estimated separately. Introducing the notation $\phi = 1/d$, using

$$\sum_{i,j} \Big(\frac{\partial^2 \phi}{\partial x_i \partial y_j}\Big)^2 \;=\; \frac{6}{d^6}\,,$$

and applying the Cauchy-Schwarz inequality first to the sum over the indices i and j and then to the resulting integral, the first part can be estimated by the expression

$$\Big(\int \frac{1}{d^4}\, u^2\Big)^{1/2} \Big(\sum_{i,j} \int \frac{1}{d^2} \Big(\frac{\partial^2 v}{\partial x_i \partial y_j}\Big)^2\Big)^{1/2} \tag{3.11}$$

up to the factor $\sqrt{6}$. Similarly, starting from the relations

$$\sum_i \Big(\frac{\partial \phi}{\partial x_i}\Big)^2 \;=\; \frac{1}{d^4}\,, \quad \sum_j \Big(\frac{\partial \phi}{\partial y_j}\Big)^2 \;=\; \frac{1}{d^4}\,,$$

the second part can be estimated by

$$\Big(\sum_j \int \frac{1}{d^2} \Big(\frac{\partial u}{\partial y_j}\Big)^2\Big)^{1/2} \Big(\sum_{i,j} \int \frac{1}{d^2} \Big(\frac{\partial^2 v}{\partial x_i \partial y_j}\Big)^2\Big)^{1/2} \tag{3.12}$$

and the third part correspondingly by

$$\Big(\sum_i \int \frac{1}{d^2} \Big(\frac{\partial u}{\partial x_i}\Big)^2\Big)^{1/2} \Big(\sum_{i,j} \int \frac{1}{d^2} \Big(\frac{\partial^2 v}{\partial x_i \partial y_j}\Big)^2\Big)^{1/2}. \tag{3.13}$$

Finally, the fourth part is estimated by

$$\Big(\sum_{i,j} \int \Big(\frac{\partial^2 u}{\partial x_i \partial y_j}\Big)^2\Big)^{1/2} \Big(\sum_{i,j} \int \frac{1}{d^2} \Big(\frac{\partial^2 v}{\partial x_i \partial y_j}\Big)^2\Big)^{1/2}. \tag{3.14}$$

The first integral in (3.11) satisfies the estimate

$$\int \frac{1}{d^4}\, u^2 \;\le\; 16 \sum_{i,j} \int \Big(\frac{\partial^2 u}{\partial x_i \partial y_j}\Big)^2$$

as follows from inequality (3.9). This is the place where the fact that the function u vanishes for $x = y$ enters. Fubini's theorem and Lemma 1 yield

$$\sum_j \int \frac{1}{d^2} \Big(\frac{\partial u}{\partial y_j}\Big)^2 \;\le\; 4 \sum_{i,j} \int \Big(\frac{\partial^2 u}{\partial x_i \partial y_j}\Big)^2$$

for the integral involving u in (3.12) and

$$\sum_i \int \frac{1}{d^2} \Big(\frac{\partial u}{\partial x_i}\Big)^2 \;\le\; 4 \sum_{i,j} \int \Big(\frac{\partial^2 u}{\partial x_i \partial y_j}\Big)^2$$

for the corresponding term in (3.13). Thus, the left-hand side of (3.10) can be estimated by the expression (3.14) up to the factor $5+4\sqrt{6}$. Applying (3.7) to the integrals in (3.14) involving v, the proposition follows with the constant $C = (5+4\sqrt{6})\sqrt{2}$. □

A to Lemma 3 closely related estimate, which involves only first order derivatives and therefore does not rely on the property that u vanishes on the diagonal $x = y$, is:

Lemma 4 *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support. Then*

$$\sum_{i=1}^{3} \int \frac{\partial}{\partial x_i}(\phi u)\, \frac{\partial v}{\partial x_i}\, d(x,y) \;\le\; C \Big\{ \sum_{i=1}^{3} \Big\| \frac{\partial u}{\partial x_i} \Big\|_0^2 \Big\}^{1/2} \Big\{ \sum_{i=1}^{3} \Big| \frac{\partial v}{\partial x_i} \Big|_1^2 \Big\}^{1/2} \tag{3.15}$$

with a constant C nearer specified in the proof.

Proof. Because

$$\frac{\partial}{\partial x_i}(\phi u) \;=\; \frac{\partial \phi}{\partial x_i}\, u + \phi\, \frac{\partial u}{\partial x_i}\,,$$

the integral on the left-hand side of (3.15) splits into two distinct parts that are again estimated separately. Using the same notation as in the proof of the preceding lemma, the first part can be estimated by the expression

$$\Big(\int \frac{1}{d^2}\, u^2 \Big)^{1/2} \Big(\sum_i \int \frac{1}{d^2} \Big(\frac{\partial v}{\partial x_i}\Big)^2 \Big)^{1/2} \tag{3.16}$$

and the second part correspondingly by

$$\Big(\sum_i \int \Big(\frac{\partial u}{\partial x_i}\Big)^2 \Big)^{1/2} \Big(\sum_i \int \frac{1}{d^2} \Big(\frac{\partial v}{\partial x_i}\Big)^2 \Big)^{1/2}. \tag{3.17}$$

The integral involving the function u in (3.16) is estimated using Fubini's theorem and Lemma 1. Up to the factor 3, the left-hand side of (3.15) can therefore be estimated by the expression (3.17). Estimating the integral involving v in (3.17) with (3.7), the proposition follows with $C = 3\sqrt{2}$. □

The last estimate in this series is easily proved using the Cauchy-Schwarz inequality and (3.7). It reads:

Lemma 5 *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support. Then*

$$\int \phi u \, v \, d(x, y) \;\leq\; \sqrt{2}\, \|u\|_0 |\, v \,|_1. \tag{3.18}$$

The next two lemmata will allow to transform the integrals (3.3) by partial integration and to shift all derivatives to the function v. In a sense, they correspond to Lemma 3 and Lemma 4 and are again based on the Hardy-type inequalities from Lemma 1 and Lemma 2, respectively.

Lemma 6 *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support and let u vanish for $x = y$. Then*

$$\int \frac{\partial^2}{\partial x_i \partial y_j}(\phi u)\, v \, d(x, y) \;=\; \int \phi u \, \frac{\partial^2 v}{\partial x_i \partial y_j}\, d(x, y) \tag{3.19}$$

for all indices $i, j = 1, 2, 3$.

Proof. The problem is that, because of the singularity of ϕ on the diagonal $x = y$, one cannot simply integrate by parts. To overcome this difficulty, let $\varphi(r)$ be a twice continuously differentiable function of the real variable $r \geq 0$ with $\varphi(r) = 1/r$ for $r \geq 1$ and $\varphi(r) = \text{const}$ for $r \leq 1/2$. Let

$$\phi_k(x, y) \;=\; k\, \varphi(k\, |x - y|), \quad k \in \mathbb{N}.$$

Then ϕ_k coincides with ϕ for $|x - y| \geq 1/k$. Partial integration leads to

$$\int \frac{\partial^2}{\partial x_i \partial y_j}(\phi_k u)\, v \, d(x, y) \;=\; \int \phi_k u \, \frac{\partial^2 v}{\partial x_i \partial y_j}\, d(x, y)\,.$$

The integral on the left-hand side of this equation then again splits, because

$$\frac{\partial^2}{\partial x_i \partial y_j}(\phi_k u) \;=\; \frac{\partial^2 \phi_k}{\partial x_i \partial y_j}\, u + \frac{\partial \phi_k}{\partial x_i}\frac{\partial u}{\partial y_j} + \frac{\partial \phi_k}{\partial y_j}\frac{\partial u}{\partial x_i} + \phi_k \, \frac{\partial^2 u}{\partial x_i \partial y_j}\,,$$

into four parts that can be examined separately. Because of the estimates

$$\Big|\frac{\partial^2 \phi_k}{\partial x_i \partial y_j}\Big| \leq \frac{c}{|x - y|^3}, \quad \Big|\frac{\partial \phi_k}{\partial x_i}\Big| \leq \frac{c}{|x - y|^2}, \quad \Big|\frac{\partial \phi_k}{\partial y_j}\Big| \leq \frac{c}{|x - y|^2},$$

for the first- and second order derivatives of the ϕ_k and because

$$|\phi_k| \;\le\; \frac{c}{|x-y|}$$

with a c independent of k and since the function u can be estimated as

$$|u(x,y)| \;\le\; K|x-y|\,,$$

the local integrability of the function

$$(x,y) \;\to\; \frac{1}{|x-y|^2}$$

and the dominated convergence theorem assure that

$$\lim_{k\to\infty} \int \frac{\partial^2}{\partial x_i \partial y_j}(\phi_k u)\, v\, d(x,y) \;=\; \int \frac{\partial^2}{\partial x_i \partial y_j}(\phi u)\, v\, d(x,y)\,.$$

Correspondingly,

$$\lim_{k\to\infty} \int \phi_k u\, \frac{\partial^2 v}{\partial x_i \partial y_j}\, d(x,y) \;=\; \int \phi u\, \frac{\partial^2 v}{\partial x_i \partial y_j}\, d(x,y)$$

holds, which proves the proposition. □

Lemma 7 *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support. Then*

$$\int \frac{\partial}{\partial x_i}(\phi u)\, v\, d(x,y) \;=\; -\int \phi u\, \frac{\partial v}{\partial x_i}\, d(x,y) \tag{3.20}$$

for all indices $i = 1, 2, 3$.

Proof. The proof is based on the same argumentation as the proof of the preceding lemma and starts from the relation

$$\int \frac{\partial}{\partial x_i}(\phi_k u)\, v\, d(x,y) \;=\; -\int \phi_k u\, \frac{\partial v}{\partial x_i}\, d(x,y)$$

in the notation introduced there and the splitting of the left integral into the two terms arising from

$$\frac{\partial}{\partial x_i}(\phi_k u) \;=\; \frac{\partial \phi_k}{\partial x_i}\, u + \phi_k\, \frac{\partial u}{\partial x_i}\,.$$

The dominated convergence theorem then again proves the proposition. □

Note that, in contrast to the preceding lemma, no assumptions need to be made on the behavior of u on the diagonal $x = y$. As with Lemma 4, an analogous result holds for the partial derivatives with respect to the components of y. Lemma 6 and Lemma 7 state that the partial derivatives

$$\frac{\partial^2}{\partial x_i \partial y_j}(\phi u)\,, \quad \frac{\partial}{\partial x_i}(\phi u)\,, \quad \frac{\partial}{\partial y_j}(\phi u) \tag{3.21}$$

do not only exist as classical derivatives outside the set of the singular points of the potential ϕ, but also as global weak derivatives across this set.

We now return to the full set of electron coordinates $x_1, \ldots, x_N \in \mathbb{R}^3$ and to the old notation. The results obtained so far are now merged into the two following theorems that form the key to our entire theory.

Theorem 1 *The functions $u \in \mathcal{D}_{\mathcal{I}}$ and $v \in \mathcal{D}$ satisfy the estimate*

$$\sum_{\alpha \in \mathcal{I}^*} \int L_\alpha (V_{ee} u) L_\alpha v \, dx \;\leq\; C N^{3/2} |\, u \,|_{\mathcal{I},0} |\, v \,|_{\mathcal{I},1} \tag{3.22}$$

with N the number of electrons and C independent of N.

Proof. We first turn our attention to the interaction potential

$$\phi_{ij}(x) = \frac{1}{|x_i - x_j|}$$

of two electrons $i \neq j$ and estimate the expression

$$\sum_{\alpha \in \mathcal{I}^*} \iint L_\alpha (\phi_{ij} u) L_\alpha v \, dx_i dx_j \,.$$

All first order partial derivatives of which the differential operators L_α are composed commute with the multiplication by ϕ_{ij}, except for those acting upon the components of the electron coordinates x_i and x_j. Depending on whether both indices i and j or only one or none of these indices belong to the given index set $\mathcal{I}$ fixing the symmetry properties of u, two, one or none of these first order partial derivatives remain. The first case is the most delicate. In this case, u itself and all partial derivatives of u with respect to the components of the other variables x_l are antisymmetric under the exchange of x_i and x_j. Particularly, they take the value zero where $x_i = x_j$. Therefore the sum above can be estimated with help of Lemma 3. Lemma 4 and Lemma 5, respectively, apply to the other two cases. In all three cases,

$$\begin{aligned} \sum_{\alpha \in \mathcal{I}^*} \iint L_\alpha (\phi_{ij} u) L_\alpha v \, dx_i dx_j \;\leq\; & C \left(\sum_{\alpha \in \mathcal{I}^*} \iint |L_\alpha u|^2 \, dx_i dx_j \right)^{1/2} \\ & \times \left(\sum_{\alpha \in \mathcal{I}^*} \iint \left\{ |\nabla_i L_\alpha v|^2 + |\nabla_j L_\alpha v|^2 \right\} dx_i dx_j \right)^{1/2} \end{aligned}$$

with C the largest constant occurring in the lemmata. Integration with respect to the remaining variables and the Cauchy-Schwarz inequality yield

$$\sum_{\alpha\in\mathcal{I}^*}\int L_\alpha(\phi_{ij}u)L_\alpha v\,dx \;\le\; C\,|\,u\,|_{\mathcal{I},0}\left\{|\nabla_i v|^2_{\mathcal{I},0}+|\nabla_j v|^2_{\mathcal{I},0}\right\}^{1/2}.$$

Using the trivial estimate

$$\frac{1}{2}\sum_{i,j}\left(\eta_i^2+\eta_j^2\right)^{1/2}\le\;\frac{1}{\sqrt{2}}\,N^{3/2}\left(\sum_i\eta_i^2\right)^{1/2},$$

summation over all particle pairs gives the proposition. □

Theorem 2 *The functions $u\in\mathcal{D}_\mathcal{I}$ and $v\in\mathcal{D}$ satisfy the relation*

$$\sum_{\alpha\in\mathcal{I}^*}\int L_\alpha(V_{ee}u)L_\alpha v\,dx \;=\; (-1)^{|\mathcal{I}|}\sum_{\alpha\in\mathcal{I}^*}\int V_{ee}u\,L_\alpha^2 v\,dx \tag{3.23}$$

where $|\mathcal{I}|$ denotes the number of elements in the index set $\mathcal{I}$.

Proof. Again, the potential V_{ee} is decomposed into the interaction potentials ϕ_{ij} of the single electrons. Depending on whether both indices i and j or only one or none of these indices belong to the index set $\mathcal{I}$, one applies Lemma 6, Lemma 7, or simply partial integration to show that

$$\int L_\alpha(\phi_{ij}u)L_\alpha v\,dx \;=\; (-1)^{|\mathcal{I}|}\int\phi_{ij}u\,L_\alpha^2 v\,dx\,.$$

Summation over all i and j and then over all α finishes the proof. □

To prove that the equation (2.4) is well-posed in H^1, we still need the following estimate that directly results from the Hardy inequality (3.7).

Theorem 3 *The functions u and v in $\mathcal{D}$ satisfy the estimate*

$$\int V_{ee}u\,v\,dx \;\le\; CN^{3/2}\|u\|_0|\,v\,|_1 \tag{3.24}$$

with $C=1$ independent of the number N of electrons.

The estimates from Theorem 1 and Theorem 3 as well as the partial integration formula from Theorem 2 transfer to the nucleus-electron interaction potential (3.2). The estimate corresponding to (3.22) reads

$$\sum_{\alpha\in\mathcal{I}^*}\int L_\alpha(V_{ne}u)L_\alpha v\,dx \;\le\; 6\,ZN^{1/2}|\,u\,|_{\mathcal{I},0}|\,v\,|_{\mathcal{I},1}\,, \tag{3.25}$$

and the estimate corresponding to (3.24)

$$\int V_{ne} u\, v\, dx \;\leq\; 2\, Z N^{1/2} \|u\|_0 |\, v\,|_1 \tag{3.26}$$

with $Z = \sum_\nu Z_\nu$ the total charge of the nuclei or $Z = N$ in the case of neutral atoms or molecules as assumed here. We do not elaborate the proofs in detail because they are considerably simpler than the proofs of the corresponding results for the electron-electron interaction potential. The decisive difference is that the parts of which the nucleus-electron interaction potential is composed depend only on a single electron coordinate x_i and not on two such coordinates x_i and x_j. Therefore only first order derivatives of the single parts of the potential have to be mastered, and therefore no particular behavior whatever of the function u at the singular points $x_i = a_\nu$ of the potential is needed.

Combining the electron-electron interaction potential (3.1) and the nucleus-electron interaction potential (3.2) to the total potential

$$V \;=\; V_{ne} + V_{ee}\,, \tag{3.27}$$

we thus result in an estimate

$$\sum_{\alpha\in\mathcal{I}^*} \int L_\alpha(Vu) L_\alpha v\, dx \;\leq\; C N^{3/2} |\, u\,|_{\mathcal{I},0} |\, v\,|_{\mathcal{I},1} \tag{3.28}$$

and in the partial integration formula

$$\sum_{\alpha\in\mathcal{I}^*} \int L_\alpha(Vu) L_\alpha v\, dx \;=\; (-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \int Vu\, L_\alpha^2 v\, dx \tag{3.29}$$

for the functions functions $u \in \mathcal{D}_\mathcal{I}$ and $v \in \mathcal{D}$, where the constant C is independent of the number N of electrons and the positions and charges of the nuclei. Using (2.11) and introducing the differential operator

$$\Delta^\mathcal{I} \;=\; \prod_{i\in\mathcal{I}} \Delta_i \tag{3.30}$$

of order $2|\mathcal{I}|$, (3.29) can be rewritten as

$$\sum_{\alpha\in\mathcal{I}^*} \int L_\alpha(Vu) L_\alpha v\, dx \;=\; (-1)^{|\mathcal{I}|} \int Vu\, \Delta^\mathcal{I} v\, dx\,. \tag{3.31}$$

The estimate (3.28) and the partial integration formula (3.31) form the essence of this section and the basis of the regularity proof.

The regularity theory developed in the sequel transfers to the case of all potentials V for which estimates like (3.24) and (3.28) hold and for which partial integration as in (3.29) or (3.31) is permitted. In particular, this is the

case when the nucleus-electron interaction potential (3.2) is replaced by a more general potential

$$V_{\mathit{eff}}(x) \;=\; \sum_{i=1}^{N} V_0(x_i) \tag{3.32}$$

composed of parts depending only on the single electron coordinates, provided that these parts satisfy three-dimensional estimates of the type

$$\int V_0 u\, v\, dx \;\lesssim\; \|u\|_0 |\, v\,|_1\,, \qquad \int \frac{\partial}{\partial x_k}(V_0 u)\, v\, dx \;\lesssim\; |\, u\,|_1 |\, v\,|_1 \tag{3.33}$$

for functions $u, v : \mathbb{R}^3 \to \mathbb{R}$ having a compact support (where the x_k again denote the components of the vector $x \in \mathbb{R}^3$) and that partial integration

$$\int \frac{\partial}{\partial x_k}(V_0 u)\, v\, dx \;=\; -\int V_0 u\, \frac{\partial v}{\partial x_k}\, dx \tag{3.34}$$

is allowed. Models of this type occur in quantum chemistry for example when only a wavefunction for the outermost electrons is sought and the other electrons are taken into account only via more or less sophisticated shielding potentials, or simply when a finite extension is given to the nuclei.

4 A first regularity theorem

We are now in the position to give the operator equation (2.4) a precise meaning and to study the regularity of its solutions. In the next section, these results will be transferred to the eigenvalue problem (2.5). We first write the Hamilton operator (1.1) in the form

$$H \;=\; -\frac{1}{2}\,\Delta + V \tag{4.1}$$

and introduce the bilinear form

$$a(u, v) \;=\; \big((H + \mu I)u, v\big) \tag{4.2}$$

on $\mathcal{D}$, where $(\ ,\ )$ again denotes the L_2-inner product and μ is a positive constant still to be specified. Since

$$(-\Delta u, v) \;=\; \int \nabla u \cdot \nabla v\, dx \tag{4.3}$$

and, by Theorem 3 and (3.26) respectively,

$$(Vu, v) \;\le\; C N^{3/2} \|u\|_0 |\, v\,|_1 \tag{4.4}$$

with the constant $C = 3$ independent of the number N of electrons and the positions and charges of the nuclei, there exists a constant M depending on N and on the shift parameter μ with

$$a(u, v) \leq M \|u\|_1 \|v\|_1 \tag{4.5}$$

for all $u, v \in \mathcal{D}$. Thus, the bilinear form (4.2) can be extended to a bounded, symmetric bilinear form on H^1.

A function $u \neq 0$ in H^1 now is called an eigenfunction of the Hamilton operator (1.1) or (4.1) and λ the associated eigenvalue, if the relation

$$a(u, \chi) = (\lambda + \mu)(u, \chi) \tag{4.6}$$

holds for all test functions $\chi \in H^1$. Correspondingly, for given $f \in H^{-1}$, a function $u \in H^1$ is a weak solution of the operator equation (2.4), if

$$a(u, \chi) = (f, \chi) \tag{4.7}$$

for all test functures $\chi \in H^1$. This section focuses on this formulation of the equation (2.4) and not on the eigenvalue problem.

By the relation (4.3) and the estimate (4.4),

$$a(u, u) \geq \frac{1}{2} |u|_1^2 - CN^{3/2} \|u\|_0 |u|_1 + \mu \|u\|_0^2 \tag{4.8}$$

holds for all $u \in H^1$. For $\mu \geq C^2 N^3 + 1/4$, therefore

$$a(u, u) \geq \frac{1}{4} \|u\|_1^2 \tag{4.9}$$

follows. For μ chosen sufficiently large in dependence of the number N of electrons, the bilinear form (4.2) thus is coercive. The Lax-Milgram theorem or already the Riesz representation theorem then states that the equation (4.7) possesses a unique solution $u \in H^1$ for all right-hand sides $f \in H^{-1}$. Since the Hamilton operator is invariant to the exchange of the electrons, this solution belongs to $H^1_{\mathcal{I}}$ for $f \in H^{-1}_{\mathcal{I}}$ and then is already fixed, if (4.7) only holds for the functions $\chi \in H^1_{\mathcal{I}}$.

In this case, the solution does not only inherit the symmetry properties of the right-handed side f, but also the regularity. To prove this, we introduce the augmented bilinear form

$$\widetilde{a}(u, v) = \big((H + \mu I)u, v\big) + \sum_{\alpha \in \mathcal{I}^*} \big(L_\alpha (H + \mu I)u, L_\alpha v\big) \tag{4.10}$$

on the space $\mathcal{D}_{\mathcal{I}}$. Because, by (3.28),

$$\sum_{\alpha \in \mathcal{I}^*} (L_\alpha V u, L_\alpha v) \leq \widetilde{C} N^{3/2} |u|_{\mathcal{I},0} |v|_{\mathcal{I},1} \tag{4.11}$$

with a constant $\widetilde{C}$ independent of the number N of electrons and the positions and charges of the nuclei and because of (4.4), there is a constant $\widetilde{M}$ dependent on N with

$$\widetilde{a}(u,v) \;\le\; \widetilde{M}\,\|u\|_{\mathcal{I},1}\|v\|_{\mathcal{I},1} \tag{4.12}$$

for all functions u and v in $\mathcal{D}_{\mathcal{I}}$, that is, for all infinitely differentiable functions that have a bounded support and that are antisymmetric under the exchange of two electron coordinates x_i and x_j for indices i and j in $\mathcal{I}$. Thus, the bilinear form (4.10) can be extended to a bounded bilinear form on the space $X^1_{\mathcal{I}}$ introduced in Sect. 2, the corresponding completion of $\mathcal{D}_{\mathcal{I}}$. Furthermore,

$$\begin{aligned}\widetilde{a}(u,u) \;\ge\; \frac{1}{2}\,|\,u\,|_1^2 \;-\; CN^{3/2}\|u\|_0|\,u\,|_1 \;+\; \mu\,\|u\|_0^2 \\ +\; \frac{1}{2}\,|\,u\,|_{\mathcal{I},1}^2 \;-\; \widetilde{C}N^{3/2}|\,u\,|_{\mathcal{I},0}|\,u\,|_{\mathcal{I},1} \;+\; \mu\,|\,u\,|_{\mathcal{I},0}^2\end{aligned} \tag{4.13}$$

for all u in $\mathcal{D}_{\mathcal{I}}$ or $X^1_{\mathcal{I}}$. Thus, for μ chosen sufficiently large in dependence of the number N of electrons, the estimate

$$\widetilde{a}(u,u) \;\ge\; \frac{1}{4}\,\|u\|_{\mathcal{I},1}^2 \tag{4.14}$$

holds for the functions $u \in X^1_{\mathcal{I}}$.

Contrary to the original bilinear form (4.2), the bilinear form (4.10) is no longer symmetric as the differential operators L_α and the multiplication with the potential V do not commute. Nevertheless, because of (4.12) and (4.14), the Lax-Milgram theorem guarantees that, for given $f \in X^{-1}_{\mathcal{I}}$, there exists a unique $u \in X^1_{\mathcal{I}}$ satisfying the relation

$$\widetilde{a}(u,v) \;=\; (f,v) \;+\; \sum_{\alpha\in\mathcal{I}^*}(L_\alpha f, L_\alpha v) \tag{4.15}$$

for all $v \in X^1_{\mathcal{I}}$. Because of (4.14), this u can be estimated as

$$\|u\|_{\mathcal{I},1} \;\le\; 4\,\|f\|_{\mathcal{I},-1}\,. \tag{4.16}$$

Our final aim in this section is to show that the solution of the modified problem (4.15) coincides with the solution of the original problem (4.7).

We prepare this by two lemmata. The first one crucially depends on the partial integration formula derived in Sect. 3. It cannot be extended to higher order mixed derivatives, the fact that finally limits the regularity.

Lemma 8 *The solution $u \in X^1_{\mathcal{I}}$ of the equation (4.15) satisfies the relation*

$$a\big(u, v + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}}v\big) \;=\; \big(f, v + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}}v\big) \tag{4.17}$$

for all rapidly decreasing functions $v \in \mathcal{S}_{\mathcal{I}}$.

Proof. We recall that, by (3.31), for all $u \in \mathcal{D}_{\mathcal{I}}$ and all $v \in \mathcal{D}$ the relation

$$\sum_{\alpha \in \mathcal{I}^*} (L_\alpha V u, L_\alpha v) \;=\; (-1)^{|\mathcal{I}|} (V u, \Delta^{\mathcal{I}} v)$$

holds, that is, one can integrate by parts despite the singularities of V. Here again the antisymmetry of the functions u under the exchange of the corresponding electron coordinates enters, and in particular the fact that these functions vanish at the corresponding singular points of the electron-electron interaction potential. As, by (2.11) and (3.30), obviously

$$\sum_{\alpha \in \mathcal{I}^*} \big(L_\alpha(-\Delta + 2\mu I)u, L_\alpha v\big) \;=\; (-1)^{|\mathcal{I}|} \big((-\Delta + 2\mu I)u, \Delta^{\mathcal{I}} v\big)$$

for all u and v in $\mathcal{D}$, the formula above implies that

$$\widetilde{a}(u, v) \;=\; a\big(u, v + (-1)^{|\mathcal{I}|} \Delta^{\mathcal{I}} v\big)$$

for all functions $u \in \mathcal{D}_{\mathcal{I}}$ and $v \in \mathcal{D}$. This relation remains true for pairs of functions $u \in \mathcal{D}_{\mathcal{I}}$ and $v \in \mathcal{S}$, because every such v coincides with a function in $\mathcal{D}$ on a given bounded region. Since, for a given $v \in \mathcal{S}$, also

$$\chi \;=\; v + (-1)^{|\mathcal{I}|} \Delta^{\mathcal{I}} v \tag{4.18}$$

belongs to $\mathcal{S}$ and therefore to H^1, both sides of the equation above represent bounded linear functionals in $u \in X^1_{\mathcal{I}}$ for $v \in \mathcal{S}$ kept fixed. The relation therefore transfers to pairs of functions $u \in X^1_{\mathcal{I}}$ and $v \in \mathcal{S}$. Analogously, integration by parts shows that

$$(f, v) + \sum_{\alpha \in \mathcal{I}^*} (L_\alpha f, L_\alpha v) \;=\; \big(f, v + (-1)^{|\mathcal{I}|} \Delta^{\mathcal{I}} v\big)$$

first for the functions $f \in \mathcal{D}_{\mathcal{I}}$ and $v \in \mathcal{S}$ and then, by completion, for all $f \in X^{-1}_{\mathcal{I}}$ and $v \in \mathcal{S}$. Together this proves (4.17). □

The missing link between the original equation (4.7) and the modified equation (4.15) now is that every rapidly decreasing function χ with corresponding symmetry properties can be written in the form (4.18).

Lemma 9 *For all rapidly decreasing functions $\chi \in \mathcal{S}_{\mathcal{I}}$, there is a rapidly decreasing function $v \in \mathcal{S}_{\mathcal{I}}$ that solves the equation*

$$v + (-1)^{|\mathcal{I}|} \Delta^{\mathcal{I}} v \;=\; \chi\,. \tag{4.19}$$

Proof. The equation (4.19) possesses a solution $v \in \mathcal{S}$ for an arbitrary rapidly decreasing function $\chi \in \mathcal{S}$. In terms of the Fourier transform $\widehat{\chi} \in \mathcal{S}$ of χ, the Fourier transform of this solution reads

$$\widehat{v}(\omega) \;=\; \frac{1}{1 + \prod_{i \in \mathcal{I}} |\omega_i|^2}\, \widehat{\chi}(\omega)$$

where $\omega \in \mathbb{R}^{3N}$ is, like the spatial coordinates x, composed of parts $\omega_i \in \mathbb{R}^3$ corresponding to the single electrons and $|\omega_i|$ again denotes the euclidean norm of ω_i.

A rapidly decreasing function χ is antisymmetric under the exchange of the coordinates x_i for $i \in \mathcal{I}$, if and only if its Fourier transform $\widehat{\chi}$ is antisymmetric under the exchange of the corresponding frequency components ω_i. Thus, for $\chi \in \mathcal{S}_\mathcal{I}$, the given solution v of the equation (4.19) inherits the antisymmetry of χ under the exchange of the corresponding variables and itself belongs to $\mathcal{S}_\mathcal{I}$. □

Combining the two lemmata, we see that, for given $f \in X_\mathcal{I}^{-1}$, the solution $u \in X_\mathcal{I}^1$ of the equation (4.15) satisfies the relation (4.7) for all functions $\chi \in \mathcal{S}_\mathcal{I}$. Since $\mathcal{S}_\mathcal{I}$ is a dense subspace of $H_\mathcal{I}^1$, u also solves the original equation, and since the solutions of both equations are unique, they coincide. This proves our final regularity theorem:

Theorem 4 *Provided that the constant μ in the bilinear form (4.2) is chosen sufficiently large in dependence of the number of electrons, the solution $u \in H_\mathcal{I}^1$ of the equation*

$$a(u, \chi) = (f, \chi), \quad \chi \in H_\mathcal{I}^1, \tag{4.20}$$

is contained in $X_\mathcal{I}^1$ for all $f \in X_\mathcal{I}^{-1}$ and then satisfies the estimate

$$\|u\|_{\mathcal{I},1} \;\le\; 4\, \|f\|_{\mathcal{I},-1}\,. \tag{4.21}$$

Thus, for corresponding right-hand sides f which are antisymmetric under the exchange of the given electron coordinates and sufficiently smooth, the solution u possesses the weak derivatives (2.10) of order $|\mathcal{I}|$ that then even themselves have first order square integrable weak derivatives.

5 The Ritz restriction to spaces of high-frequency functions

A straightforward regularity proof for the eigenfunctions would start from Theorem 4 and be based on an induction argument, but then the constants grow rapidly with the number of electrons, a highly undesirable effect. Therefore we proceed differently and will utilize a variant of Theorem 4 for the high-frequency part of the solution that is derived in this section.

A rapidly decreasing high-frequency function is a rapidly decreasing function with a Fourier transform that vanishes on a ball around the origin of a radius Ω to be fixed later. The closure of the corresponding space

$$\mathcal{S}_{\mathcal{I},H} = \{\, v \in \mathcal{S}_{\mathcal{I}} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \le \Omega \,\} \tag{5.1}$$

of rapidly decreasing functions with given symmetry properties in $H^1_{\mathcal{I}}$ and $X^1_{\mathcal{I}}$, respectively, then is denoted as $H^1_{\mathcal{I},H}$ and $X^1_{\mathcal{I},H}$. The closure of

$$\mathcal{S}_{\mathcal{I},L} = \{\, v \in \mathcal{S}_{\mathcal{I}} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \ge \Omega \,\} \tag{5.2}$$

in $H^1_{\mathcal{I}}$ and $X^1_{\mathcal{I}}$, respectively, are the spaces $H^1_{\mathcal{I},L}$ and $X^1_{\mathcal{I},L}$ of low-frequency functions. The low-frequency and the high-frequency functions decompose

$$H^1_{\mathcal{I}} = H^1_{\mathcal{I},L} \oplus H^1_{\mathcal{I},H}, \quad X^1_{\mathcal{I}} = X^1_{\mathcal{I},L} \oplus X^1_{\mathcal{I},H} \tag{5.3}$$

into orthogonal parts. As the corresponding norms are equivalent on $\mathcal{S}_{\mathcal{I},L}$,

$$H^1_{\mathcal{I},L} = X^1_{\mathcal{I},L}. \tag{5.4}$$

In fact, the functions in $H^1_{\mathcal{I},L}$ are infinitely differentiable and all their partial derivatives are square integrable. Fourier transformation also shows:

Lemma 10 *For functions in u_H in $H^1_{\mathcal{I},H}$ and $X^1_{\mathcal{I},H}$, respectively,*

$$\|u_H\|_0 \le \Omega^{-1}|u_H|_1, \quad |u_H|_{\mathcal{I},0} \le \Omega^{-1}|u_H|_{\mathcal{I},1}. \tag{5.5}$$

The estimates (5.5) are the decisive properties on which our argumentation is based in the following. They allow to consider the potential parts as perturbations in spaces of high-frequency functions such that the coercivity of the bilinear forms (4.2) and (4.10) can be controlled independent of the value of the shift parameter μ. If the constant Ω is chosen so large that

$$CN^{3/2}\Omega^{-1} \le \frac{1}{4}, \tag{5.6}$$

by (4.4) the interaction potentials can be estimated as

$$(Vu_H, v_H) \le \frac{1}{4}|u_H|_1|v_H|_1 \tag{5.7}$$

for all $u_H, v_H \in H^1_{\mathcal{I},H}$. Independent of the choice of $\mu \ge 0$, then

$$a(u_H, u_H) \ge \frac{1}{4}|u_H|_1^2 \tag{5.8}$$

for all $u_H \in H^1_{\mathcal{I},H}$. This guarantees that the Ritz restriction of the equation (4.7), (4.20) to the subspace of high-frequency functions possesses a unique solution for all given right-hand sides. The regularity of the right-hand side again transfers to this solution. The version of this result we need reads:

Theorem 5 *Provided that the frequency bound Ω is chosen sufficiently large in dependence of the number of electrons, the solution $u_H \in H^1_{\mathcal{I},H}$ of*

$$a(u_H, \chi_H) = (V\varphi, \chi_H), \quad \chi_H \in H^1_{\mathcal{I},H}, \tag{5.9}$$

is contained in $X^1_{\mathcal{I},H}$ for all given $\varphi \in X^0_{\mathcal{I}}$ and then satisfies the estimate

$$\|u_H\|_{\mathcal{I},1} \;\le\; 4\,\|V\varphi\|_{\mathcal{I},H,-1} \tag{5.10}$$

where the norm on the right-hand side can be estimated by the corresponding norms of $V\varphi$ or φ and is nearer specified in the proof.

Proof. To give the equation a precise meaning, we note that the expression

$$b(\varphi, \chi) = (V\varphi, \chi)$$

defines a bilinear form on $\mathcal{D} \times \mathcal{D}$ that, by (4.4), satisfies the estimate

$$b(\varphi, \chi) \le\; CN^{3/2}\|\varphi\|_0|\,\chi\,|_1$$

and thus can be extended to a bounded bilinear form on $L_2 \times H^1$. With given right-hand side φ, the equation (5.9) then can be reformulated as

$$a(u_H, \chi_H) = \; b(\varphi, \chi_H), \quad \chi_H \in H^1_{\mathcal{I},H}. \tag{5.11}$$

It possesses a unique solution $u_H \in H^1_{\mathcal{I},H}$, if Ω fulfills the condition (5.6). As follows from the estimates (4.4) and (4.11), the expression

$$\widetilde{b}(\varphi, v) \;=\; (V\varphi, v) \;+ \sum_{\alpha \in \mathcal{I}^*} (L_\alpha V\varphi, L_\alpha v)$$

defines a bilinear form on $\mathcal{D}_{\mathcal{I}} \times \mathcal{S}$ satisfying the estimate

$$\widetilde{b}(\varphi, v) \;\le\; C'N^{3/2}\|\varphi\|_{\mathcal{I},0}\|v\|_{\mathcal{I},1}$$

with C' the maximum of the constants C and $\widetilde{C}$ and can therefore be extended to a bounded bilinear form on $X^0_{\mathcal{I}} \times X^1_{\mathcal{I}}$. If Ω fulfills the condition

$$C'N^{3/2} \;\le\; \frac{1}{4}\,(\Omega - \Omega^{-1}), \tag{5.12}$$

by (4.11) and (4.13), respectively, and Lemma 10 the estimate

$$\widetilde{a}(u_H, u_H) \;\ge\; \frac{1}{4}\,\|u_H\|^2_{\mathcal{I},1}$$

holds for all $u_H \in X^1_{\mathcal{I},H}$, independent of how the shift parameter $\mu \ge 0$ is chosen. The modified equation

$$\widetilde{a}(u_H, v_H) = \; \widetilde{b}(\varphi, v_H), \quad v_H \in X^1_{\mathcal{I},H}, \tag{5.13}$$

therefore possesses a unique solution $u_H \in X^1_{\mathcal{I},H}$ for given $\varphi \in X^0_{\mathcal{I}}$. This solution satisfies the estimate (5.10) with the right-hand side defined by

$$\|V\varphi\|_{\mathcal{I},H,-1} = \sup\{\,\widetilde{b}(\varphi, v_H) \mid v_H \in X^1_{\mathcal{I},H},\ \|v_H\|_{\mathcal{I},1} = 1\,\} \tag{5.14}$$

and therefore in particular

$$\|u_H\|_{\mathcal{I},1} \le C' N^{3/2} \|\varphi\|_{\mathcal{I},0}.$$

We show that it coincides with the solution of the original problem (5.11). The argumentation is the same as in Sect. 4 and is based on the relations

$$\begin{aligned}\widetilde{a}(u, v) &= a\big(u, v + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}} v\big),\\ \widetilde{b}(\varphi, v) &= b\big(\varphi, v + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}} v\big)\end{aligned}$$

for $u \in X^1_{\mathcal{I}}$, $\varphi \in X^0_{\mathcal{I}}$, and $v \in \mathcal{S}$. The first of these relations has been shown in the proof of Lemma 8 and the second is proved in the same way. Therefore, the solution u_H of the modified equation (5.13) satisfies the relation

$$a\big(u_H, v_H + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}} v_H\big) = b\big(\varphi, v_H + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}} v_H\big)$$

for all rapidly decreasing functions v_H in the space (5.1). But because, as in Lemma 9, the equation

$$v_H + (-1)^{|\mathcal{I}|}\Delta^{\mathcal{I}} v_H = \chi_H$$

possesses a solution $v_H \in \mathcal{S}_{\mathcal{I},H}$ for all given $\chi_H \in \mathcal{S}_{\mathcal{I},H}$, (5.11) is fulfilled for all χ_H in a dense subset of $H^1_{\mathcal{I},H}$, which proves the proposition. □

Up to a negligible small constant, the estimate (5.10) is sharp: The reason for this is that, under the condition (5.12),

$$\widetilde{a}(u_H, v_H) \le \Big(\frac{3}{4} + \frac{\mu}{\Omega^2}\Big)\|u_H\|_{\mathcal{I},1}\|v_H\|_{\mathcal{I},1} \tag{5.15}$$

holds for $v_H \in X^1_{\mathcal{I},H}$, from which the inverse estimate

$$\|V\varphi\|_{\mathcal{I},H,-1} \le \Big(\frac{3}{4} + \frac{\mu}{\Omega^2}\Big)\|u_H\|_{\mathcal{I},1} \tag{5.16}$$

follows. It should be noted that Theorem 5 can even be extended to negative shift parameters μ. The condition (5.12) then has only to be replaced by

$$C' N^{3/2} \le \frac{1}{4}(\Omega - \Omega^{-1}) + \mu\Omega^{-1}. \tag{5.17}$$

The bound Ω separating the low from the high frequencies then is no longer independent of μ, but further independent of the positions of the nuclei.

6 The eigenfunctions and their approximation

Not operator equations like (2.4) or better (4.7) are of interest in quantum mechanics, but the corresponding eigenvalue problem (2.5) and its weak form (4.6), respectively, which fixes the steady states of the system under consideration. Here we start from a physically admissible eigenfunction $u \in H^1$ of the electronic Hamilton operator (1.1), that is, a function in the largest space in which the expectation value of the kinetic energy can still be given a meaning and which therefore represents the natural solution space. Let the electron indices split into two sets $\mathcal{I}_-$ and $\mathcal{I}_+$ such that the given eigenfunction is antisymmetric under the exchange of electron coordinates x_i and x_j with indices i and j in $\mathcal{I}_-$ and antisymmetric under the exchange of electron coordinates x_i and x_j with indices i and j in $\mathcal{I}_+$, as discussed in the introduction and as enforced by the Pauli principle. Let X^1_- and X^1_+ be the corresponding spaces $X^1_{\mathcal{I}}$ of smooth functions introduced in Sect. 2. Our expositions then culminate in the following result:

Theorem 6 *An eigenfunction $u \in H^1$ of the Hamilton operator (1.1) having the given symmetry properties is contained both in X^1_- and in X^1_+.*

The most straightforward way to prove Theorem 6 is based on Theorem 4. Starting from the fact that u belongs to L_2 or H^1, one can force up the degree of regularity of the eigenfunction step by step until the given derivatives are reached. Because, in every step, a new factor is introduced, the constants rapidly grow with the numbers of electrons so that only a purely qualitative result can be obtained with this method of proof.

Therefore we proceed differently. Let u be an eigenfunction to the eigenvalue λ and let the index set $\mathcal{I}$ be a subset of one of the two associated index sets $\mathcal{I}_-$ and $\mathcal{I}_+$ above. We split the eigenfunction into its low-frequency part u_L and its high-frequency part u_H. As follows from the orthogonality properties of the low-frequency and high-frequency functions, then

$$a(u_H, \chi_H) - (\lambda + \mu)(u_H, \chi_H) \;=\; -\,(V u_L, \chi_H) \tag{6.1}$$

for all high-frequency functions $\chi_H \in H^1_{\mathcal{I},H}$. With u_L kept fixed, this is an equation as considered in Theorem 5 with $\mu = -\lambda$ as shift parameter. Because the low-frequency part u_L of the eigenfunction belongs to $X^1_{\mathcal{I}}$ by (5.4), Theorem 5 therefore states that u_H belongs to $X^1_{\mathcal{I}}$, too, and that

$$\|u_H\|_{\mathcal{I},1} \;\le\; 4\,\|V u_L\|_{\mathcal{I},H,-1}, \tag{6.2}$$

provided the bound Ω separating the low frequencies and the high frequencies is chosen large enough. With that, we have not only proved the regularity of the eigenfunction, but have also shown that its high-frequency part can be controlled by its low-frequency part.

The eigenvalues below the essential spectrum, that represent the bound states and therefore are of main interest, are always negative in the case of the electronic Schrödinger equation.[1] Restricting oneself to such states, the bound Ω separating the high frequencies from the low frequencies therefore cannot only be chosen independent of the positions of the nuclei, but even independent of the considered state. Furthermore, by (5.16), then also

$$\|Vu_L\|_{\mathcal{I},H,-1} \leq \Big(\frac{3}{4} - \frac{\lambda}{\Omega^2}\Big)\|u_H\|_{\mathcal{I},1}\,. \tag{6.3}$$

The estimate (6.2) hence is sharp up to a small factor independent of the number of electrons; the influence of the problem parameters is completely hidden in the splitting of the solution space.

These observations express that large norms of the corresponding mixed derivatives of the eigenfunctions are reflected in the behavior of their low-frequency parts, but do not tell much about the actual size of the norms. However, the argumentation can be reversed and the size of the derivatives be related to the stability and the regularity properties of the equation (6.1). Therefore there is evidence that the norms of the given mixed derivatives of the eigenfunctions keep within reasonable limits.

To conclude: The weak partial derivatives of u of order $|\mathcal{I}_-|$ and $|\mathcal{I}_+|$, respectively, that act only onto the electron coordinates x_i with indices i that either all belong to $\mathcal{I}_-$ or all to $\mathcal{I}_+$ and that are of first order in every single such x_i, not only exist on the whole space including the singular points of the interaction potentials and are square-integrable, but themselves even have square-integrable first order weak derivatives. The solutions of the stationary Schrödinger equation that are compatible with the Pauli principle thus are surprisingly smooth and possess very high order mixed partial derivatives for large numbers of electrons. The maximum regularity is reached for purely antisymmetric spatial wavefunctions.

To give the regularity result a form which is independent of the particular decomposition of the indices $1, \ldots, N$ into the sets $\mathcal{I}_-$ and $\mathcal{I}_+$ and for which we do not need to refer to the symmetry properties of the eigenfunctions, we introduce a new scale of norms on $\mathcal{S}$ by

$$|||u|||_s^2 = \int \Big(1 + \sum_{i=1}^{N} |\omega_i|^2\Big)\Big(1 + \prod_{i=1}^{N} |\omega_i|^{2s}\Big)|\widehat{u}(\omega)|^2 d\omega \tag{6.4}$$

with $s \geq 0$ preliminarily arbitrary. The spaces Y_s then are defined as the completions of $\mathcal{S}$ under the norms given by this expression. The essential observation is that, independent of the index sets $\mathcal{I}_-$ and $\mathcal{I}_+$,

$$|||u|||_{1/2}^2 \leq \frac{1}{2}\|u\|_{\mathcal{I}_-,1}^2 + \frac{1}{2}\|u\|_{\mathcal{I}_+,1}^2 \tag{6.5}$$

[1] See [22] for an elementary exposition of such background material.

for all $u \in \mathcal{S}$. This follows immediately from the elementary inequality

$$\prod_{i=1}^{N} |\omega_i| \;\le\; \frac{1}{2}\Big(\prod_{i\in\mathcal{I}_-} |\omega_i|\Big)^2 + \frac{1}{2}\Big(\prod_{i\in\mathcal{I}_+} |\omega_i|\Big)^2 \tag{6.6}$$

and the Fourier representation of the norms. Thus, the intersection of the spaces X^1_- and X^1_+ introduced above is a subspace of $Y_{1/2}$. We obtain:

Theorem 7 *All admissible eigenfunctions $u \in H^1$ of the Hamilton operator (1.1), that is, all those which are compatible with the Pauli principle, are located in the space $Y_{1/2}$ and the fully antisymmetric even in Y_1.*

The intention of this paper was to lay a mathematical foundation for methods to solve the electronic Schrödinger equation that are based on the idea of sparse grids or hyperbolic cross spaces. One can model hyperbolic cross spaces by the ranges of the H^1-orthogonal projection operators

$$(P_l u)(x) \;=\; \Big(\frac{1}{\sqrt{2\pi}}\Big)^{3N} \int \chi_l(\omega)\widehat{u}(\omega)\exp(\mathrm{i}\,\omega\cdot x)\,d\omega \tag{6.7}$$

into corresponding spaces of band-limited functions where the

$$\chi_l(\omega) \;=\; \begin{cases} 1, & \text{if } \prod_{i=1}^{N}|\omega_i| < 2^l \\ 0, & \text{otherwise} \end{cases} \tag{6.8}$$

select the frequencies to be considered, which form, as the name indicates, a kind of hyperboloid in the frequency space. Obviously, the error estimate

$$\|u - P_l u\|_1 \;\le\; \Big(\frac{1}{\sqrt{2}}\Big)^l \,|||u|||_1 \tag{6.9}$$

then holds for the functions in $Y_{1/2}$ and, by Theorem 7, in particular for the admissible eigenfunctions of the Hamilton operator (1.1). The order of approximation doubles to $\sim 2^{-l}$ for purely antisymmetric eigenfunctions. The regularity theory developed in this article therefore raises hope that more efficient and accurate approximation methods for the electronic Schrödinger equation can be found than are in use today, and that in a sense it could even become possible to reduce the computational complexity of an N-electron problem (nearly) to that of a one-electron problem.

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