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The mixed regularity of electronic wave functions in fractional order and weighted Sobolev spaces

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Abstract We continue the study of the regularity of electronic wave functions in Hilbert spaces of mixed derivatives. It is shown that the eigenfunctions of electronic Schrödinger operators and their exponentially weighted counterparts possess, roughly speaking, square integrable mixed weak derivatives of fractional order ϑ for $\vartheta < 3/4$. The bound $3/4$ is best possible and can neither be reached nor surpassed. Such results are important for the study of sparse grid-like expansions of the wave functions and show that their asymptotic convergence rate measured in terms of the number of ansatz functions involved does not deteriorate with the number of electrons.

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1 Introduction

Quantum mechanics is the key to any deeper understanding of atomic and molecular systems. The basic problem is to find the solutions of the Schrödinger equation for a system of electrons and nuclei that interact by electrostatic attraction and repulsion forces. Due to the high-dimensionality of the problem, approximating these solutions is inordinately challenging and not possible with the standard methods of numerical mathematics. A further problem is the oscillatory character of the solutions and the many different time scales on which they vary and which can range

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over many orders of magnitude. Following Born and Oppenheimer the problem is therefore usually split into the electronic Schrödinger equation describing the motion of the electrons in the field of given clamped nuclei, and an equation for the motion of the nuclei in a potential field that is determined by solutions of the electronic equation. The present article is concerned with the mixed regularity of the solutions of the electronic Schrödinger equation, the eigenfunctions of the Hamilton operator

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

It extends the earlier work [14–17] of the second author. The mixed regularity of these solutions, the electronic wave functions, and of their correspondingly exponentially weighted counterparts can be used to expand them in sparse grid-like manner into tensor products for example of three-dimensional eigenfunctions of Schrödinger-like operators [16], orthogonal wavelets [18], or Gaussian frames [8,9]. Based on such regularity and decay properties and taking into account the partial antisymmetry of the wave functions enforced by the Pauli principle it has been shown that the convergence rates of such expansions measured in terms of the number of basis functions involved do not fall below that for systems of only two electrons [16]. The present results can be used to improve these estimates for the convergence rates further.

The solution space of the electronic Schrödinger equation is the Hilbert space H^1 that consists of the one times weakly differentiable, square integrable functions

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : (x_1, \ldots, x_N) \to u(x_1, \ldots, x_N) \tag{1.2}$$

with square integrable first-order weak derivatives; the dimension of their domain increases with the number N of electrons. The norm $\|\cdot\|_1$ on H^1 is composed of the L_2-norm $\|\cdot\|_0$ induced by the L_2-inner product $(\cdot,\cdot)$ and the L_2-norm of the gradient. The space H^1 is the space of the wave functions for which the total position probability remains finite and the expectation value of the kinetic energy can be given a meaning. To describe our results, we need to introduce a scale of norms that is defined in terms of Fourier transforms. We first introduce the polynomials

$$P_{\mathrm{iso}}(\omega) = 1 + \sum_{i=1}^{N}|\omega_i|^2, \quad P_{\mathrm{mix}}(\omega) = \prod_{i=1}^{N}\Big(1 + |\omega_i|^2\Big). \tag{1.3}$$

The $\omega_i \in \mathbb{R}^3$ forming together the variable $\omega \in (\mathbb{R}^3)^N$ can be associated with the momentums of the electrons. The expressions $|\omega_i|$ are their euclidean norms given by

$$|\omega_i|^2 = \sum_{\nu=1}^{3}\omega_{i,\nu}^2. \tag{1.4}$$

The norms describing the smoothness properties of the solutions are now given by

$$|||u|||_{\vartheta,m}^2 = \int P_{\text{iso}}(\omega)^m P_{\text{mix}}(\omega)^\vartheta \, |\widehat{u}(\omega)|^2 \, \mathrm{d}\omega. \tag{1.5}$$

They are defined on the Hilbert spaces $H_{\text{mix}}^{\vartheta,m}$ that consist of the square integrable functions (1.2) for which these expressions remain finite. For nonnegative integer values m and ϑ, the norms measure the L_2-norm of weak partial derivatives. The spaces L_2 and H^1 are special cases of such spaces. The rapidly decreasing functions (the functions in the Schwartz space) and even the infinitely differentiable functions with compact support form dense subsets of all these spaces. This can be seen first approximating the functions in these spaces by band-limited functions and these then, multiplying them by appropriately chosen cut-off functions, by infinitely differentiable functions with compact support. Our main result is that the eigenfunctions u of the electronic Schrödinger operator (1.1) are contained in the intersection of such spaces, in

$$H_{\text{mix}}^{1,0} \cap \bigcap_{\vartheta<3/4} H_{\text{mix}}^{\vartheta,1}. \tag{1.6}$$

In the general case, the bound $3/4$ can neither be completely reached nor improved further. An exception are systems of electrons of the same spin, for which the wave functions are completely antisymmetric under the exchange of the positions of the electrons and vanish therefore at the singular points of the electron-electron interaction potential. It has been shown in [14–16] that these wave functions are at least contained in the space $H_{\text{mix}}^{1,1}$. An alternative proof based on techniques as developed in the present paper is given in [12].

It is instructive to compare these regularity properties of multi-particle wave functions to those in the single-particle case, like to those of the solutions of the equation

$$-\frac{1}{2}\Delta u - \frac{1}{|x|}u = \lambda u \tag{1.7}$$

for the hydrogen atom. In the one-particle case, the spaces $H_{\text{mix}}^{\vartheta,1}$ coincide with the isotropic Sobolev spaces H^s, $s = 1 + \vartheta$. The regularity of the solutions of the equation (1.7) in this scale of spaces can be calculated directly [15] and increases with increasing angular momentum of the electron. The ground state eigenfunction

$$u(x) = \frac{1}{\sqrt{\pi}}\,\mathrm{e}^{-|x|}, \quad \widehat{u}(\omega) = \frac{\sqrt{2}}{\pi}\,\frac{2}{(1+|\omega|^2)^2} \tag{1.8}$$

is that of minimum regularity. It is contained in the spaces H^s, $s = 1+\vartheta$, for all values $\vartheta < 3/2$, but not for the value $\vartheta = 3/2$ itself. This transfers to Born-Oppenheimer atoms in which the electron-electron interaction is neglected. The eigenfunctions are then linear combinations of tensor products of such hydrogen-like eigenfunctions. They are contained in $H_{\text{mix}}^{\vartheta,1}$ for $\vartheta < 3/2$ and even in $H_{\text{mix}}^{s,0}$ for $s < 5/2$. The presence of the electron-electron interaction terms thus halves the order of mixed regularity.

Our proofs are based on a representation of the eigenfunctions u of the electronic Schrödinger operator (1.1) that has been derived in [17] and for the two-electron case in [1]. It has been shown in [17] that the eigenfunctions can be written as products

$$u(x) \;=\; \exp\left(\sum_{i<j}\phi(x_i - x_j)\right)v(x) \tag{1.9}$$

of more regular functions $v \in H^{1,1}_{\text{mix}}$ and a universal factor that covers their singularities. The same kind of splitting has been used in [6] and [10] to study the Hölder regularity of the eigenfunctions. Quantum chemists call regularizing factors as in (1.9) Jastrow factors. There is a lot of freedom in the choice of the function ϕ; only its behavior near the origin is fixed. It needs to be of the form

$$\phi(x) = \widetilde{\phi}(|x|), \quad \widetilde{\phi}'(0) = \frac{1}{2}, \tag{1.10}$$

where $\widetilde{\phi} : [0, \infty) \to \mathbb{R}$ is an infinitely differentiable function behaving sufficiently well at infinity. For the present purpose we can assume that this function vanishes for all r greater some bound. In fact, we will generally consider functions of the form (1.9), with v a function in $H^{1,1}_{\text{mix}}$, not only eigenfunctions of the operator (1.1). We will show that such functions are contained in the space (1.6) and will additionally prove optimal estimates for certain mixed weak derivatives of these functions in weighted L_2-spaces. The regularity of the functions (1.9) is therefore determined and limited by that of the explicitly known factor in front of their part v.

We are interested in eigenfunctions u of the Hamilton operator (1.1) for eigenvalues below the bottom of the essential spectrum, a value less than or equal to zero. Such eigenfunctions decay exponentially in the L_2-sense, as has first been shown in [13]. That means there is a constant $\gamma > 0$ such that the functions

$$x \;\to\; \exp\left(\gamma \sum_{i=1}^{N} |x_i|\right)u(x), \tag{1.11}$$

are square integrable. This constant γ depends on the distance of the eigenvalue under consideration to the bottom of the essential spectrum. More details and references to the literature can be found in [16]. It has been shown in [17] that these exponentially weighted eigenfunctions admit the same kind of representation (1.9) as the eigenfunctions themselves. Thus they share with them the described regularity properties. This observation is very important for the convergence analysis of sparse grid-like expansions [16,18]. We will come back to this point at the end of the paper.

2 Characterizations of the norms and function spaces

We begin our study with a closer inspection of the norms (1.5) and of the corresponding function spaces. The functions (1.2) that we examine depend on variables $x_1, \ldots, x_N$ in $\mathbb{R}^3$ that are associated with the positions of the electrons under consideration. The components of these vectors are the real numbers $x_{i,1}$, $x_{i,2}$, and $x_{i,3}$. Accordingly, we label partial derivatives doubly, that is, by multi-indices

$$\alpha = (\alpha_1, \ldots, \alpha_N) \in (\mathbb{Z}^3_{\geq 0})^N, \quad \alpha_i = (\alpha_{i,1}, \alpha_{i,2}, \alpha_{i,3}) \in \mathbb{Z}^3_{\geq 0}. \tag{2.1}$$

The differential operator D^α of order $|\alpha| = \sum_{i,k} \alpha_{i,k}$ is in this notation

$$\mathrm{D}^\alpha = \prod_{i=1}^{N} \prod_{k=1}^{3} \left(\frac{\partial}{\partial x_{i,k}} \right)^{\alpha_{i,k}}. \tag{2.2}$$

Multivariate polynomials x^α are defined correspondingly. We are particularly concerned with differential operators D^α with multi-indices α in the set

$$\mathscr{A} = \big\{ (\alpha_1, \ldots, \alpha_N) \,\big|\, \alpha_i \in \mathbb{Z}^3_{\geq 0},\ \alpha_{i,1} + \alpha_{i,2} + \alpha_{i,3} \leq 1 \big\}, \tag{2.3}$$

that is, that are of most first-order in each of the variables $x_i \in \mathbb{R}^3$ and of total order at most N. Introducing the differential operator

$$\mathscr{L} = \sum_{\alpha \in \mathscr{A}} (-1)^{|\alpha|} \mathrm{D}^{2\alpha} = \prod_{i=1}^{N} (\mathrm{I} - \Delta_i), \quad \Delta_i = \frac{\partial^2}{\partial x_{i,1}^2} + \frac{\partial^2}{\partial x_{i,2}^2} + \frac{\partial^2}{\partial x_{i,3}^2}, \tag{2.4}$$

and remembering that $(\mathrm{i}\omega)^\alpha \widehat{u}(\omega)$ is the Fourier transform of $\mathrm{D}^\alpha u$, one obtains

$$|\!|\!| u |\!|\!|_{1,0}^2 = (u, \mathscr{L} u), \quad |\!|\!| u |\!|\!|_{1,1}^2 = (u, (\mathrm{I} - \Delta) \mathscr{L} u) \tag{2.5}$$

for rapidly decreasing functions u. Integration by parts, possible at least for infinitely differentiable functions with compact support, yields

$$|\!|\!| u |\!|\!|_{1,0}^2 = \sum_{\alpha \in \mathscr{A}} \| \mathrm{D}^\alpha u \|_0^2, \quad |\!|\!| u |\!|\!|_{1,1}^2 = \sum_{\alpha \in \mathscr{A}} \| \mathrm{D}^\alpha u \|_1^2. \tag{2.6}$$

The representation (2.6) transfers to all functions in the spaces

$$X_0 = H^{1,0}_{\mathrm{mix}}, \quad X^1 = H^{1,1}_{\mathrm{mix}}, \tag{2.7}$$

since the infinitely differentiable functions with compact support are dense in these spaces. This shows that these spaces consist of square integrable functions with corresponding square integrable weak derivatives.

For values $0 < \vartheta < 1$, the spaces $H^{\vartheta,1}_{\mathrm{mix}}$ can be characterized as interpolation spaces between H^1 and X^1. To show this, we need to recall the notion of the K-functional. The K-functional of a function $u \in H^1$ in a version adapted to the given setting is

$$K(t, u) = \inf_{v \in X^1} \big\{ \| u - v \|_1^2 + t^2 \, |\!|\!| v |\!|\!|_{1,1}^2 \big\}^{1/2}. \tag{2.8}$$

The faster $K(t,u)$ tends to zero for $t \to 0+$ the smoother u is. The K-functional is needed to define the interpolation spaces

$$(H^1,\ X^1)_{\vartheta,2}, \quad 0 < \vartheta < 1, \tag{2.9}$$

the spaces for which the interpolation norm defined by

$$\|u\|^2 = \int_0^\infty [t^{-\vartheta} K(t,u)]^2 \, \frac{\mathrm{d}t}{t} \tag{2.10}$$

remains finite. This is a very general, far-reaching construction. More information on interpolation spaces can be found in [2] and [3]. In the present case, the interpolation norm given by (2.10) coincides, up to a known factor, with the norm (1.5). The interpolation spaces (2.9) are therefore the spaces $H^{\vartheta,1}_{\text{mix}}$.

Lemma 2.1 *The interpolation norm given by* (2.10) *of a function $u \in H^1$ remains finite if and only if u is contained in the space $H^{\vartheta,1}_{\text{mix}}$. In this case,*

$$\int_0^\infty [t^{-\vartheta} K(t,u)]^2 \, \frac{\mathrm{d}t}{t} \;=\; \int_0^\infty \frac{t^{1-2\vartheta}}{1+t^2} \, \mathrm{d}t \; |\!|\!| u |\!|\!|^2_{\vartheta,1}. \tag{2.11}$$

Proof For functions $u \in H^1$ and $v \in X^1$,

$$\|u - v\|_1^2 + t^2 \, |\!|\!| v |\!|\!|^2_{1,1} = \int P_{\text{iso}}(\omega) \big\{ |\widehat{u}(\omega) - \widehat{v}(\omega)|^2 + \; t^2 P_{\text{mix}}(\omega) \, |\widehat{v}(\omega)|^2 \big\} \, \mathrm{d}\omega.$$

The integrand is, for $\widehat{u}(\omega)$ a given value, minimized by the value

$$\widehat{v}(\omega) \;=\; \frac{\widehat{u}(\omega)}{1 + \, t^2 P_{\text{mix}}(\omega)}.$$

This expression defines, for $u \in H^1$ given, a function $v \in X^1$ at which the infimum in the definition of the K-functional is attained. Inserting this function above, we have found a closed representation of $K(t,u)$ in terms of the Fourier transform of u:

$$K(t,u)^2 = \int P_{\text{iso}}(\omega) \, \frac{t^2 P_{\text{mix}}(\omega)}{1 + \, t^2 P_{\text{mix}}(\omega)} \, |\widehat{u}(\omega)|^2 \, \mathrm{d}\omega.$$

The proposition follows from this representation with Fubini's theorem. □

The factor relating the two norms can be estimated as

$$\frac{1}{4\vartheta(1-\vartheta)} \;\le\; \int_0^\infty \frac{t^{1-2\vartheta}}{1+t^2} \, \mathrm{d}t \;\le\; \frac{1}{2\vartheta(1-\vartheta)} \tag{2.12}$$

as can be seen replacing the denominator $1 + t^2$ of the integrand on the right hand side of (2.11) by 1 for $t \leq 1$ and t^2 for $t > 1$. It tends to infinity when ϑ approaches the values 0 or 1 but remains uniformly bounded and uniformly bounded away from zero on every closed subinterval of the open interval $0 < \vartheta < 1$.

The mapping $u \to K(t, u)$ has, for $t > 0$ given, all properties of a norm. It defines a norm on H^1 that is equivalent to the original H^1-norm and satisfies the estimate

$$\frac{t}{\sqrt{1+t^2}}\, \|u\|_1 \leq K(t, u) \leq \|u\|_1. \tag{2.13}$$

This follows from the representation of the K-functional from the proof of the lemma and from $P_{\mathrm{mix}}(\omega) \geq 1$. The mapping is thus in particular continuous with respect to the H^1-norm. The mixed regularity of a function $u \in H^1$ is conversely almost characterized by the behavior of its K-functional $K(t, u)$ in the limit $t \to 0+$:

Lemma 2.2 *If u is contained in the space $H^{\vartheta,1}_{\mathrm{mix}}$ for a ϑ between* 0 *and* 1*,*

$$K(t, u) \leq t^{\vartheta}\, |||u|||_{\vartheta,1}. \tag{2.14}$$

If conversely $K(t, u) = \mathscr{O}(t^{\delta})$ in the limit $t \to 0+$ for a given positive $\delta \leq 1$, the function $u \in H^1$ is contained in the spaces $H^{\vartheta,1}_{\mathrm{mix}}$ for $\vartheta < \delta$.

Proof The first part immediately follows from the representation of the K-functional from the proof of Lemma 2.1 and the observation that for $0 \leq \vartheta \leq 1$

$$\left(\frac{t^2 P_{\mathrm{mix}}(\omega)}{1 + t^2 P_{\mathrm{mix}}(\omega)}\right)^{1-\vartheta} \left(\frac{t^2 P_{\mathrm{mix}}(\omega)}{1 + t^2 P_{\mathrm{mix}}(\omega)}\right)^{\vartheta} \leq t^{2\vartheta} P_{\mathrm{mix}}(\omega)^{\vartheta}.$$

The other direction follows from $K(t, u) \leq \|u\|_1$, the finiteness of the integrals

$$\int_0^1 \frac{t^{2\delta}}{t^{2\vartheta+1}}\, \mathrm{d}t, \qquad \int_1^{\infty} \frac{1}{t^{2\vartheta+1}}\, \mathrm{d}t$$

for the values $0 < \vartheta < \delta$, and the representation (2.11) of the norm on $H^{\vartheta,1}_{\mathrm{mix}}$. □

3 Hardy inequalities in three space dimensions

Hardy inequalities play a very important role in our argumentation. Our starting point is the classical Hardy inequality in three space dimensions that links a weighted L_2-norm of a function in H^1 to the L_2-norm of its gradient.

Lemma 3.1 *For all infinitely differentiable functions v in the variable $x \in \mathbb{R}^3$ that have a compact support,*

$$\int \frac{1}{|x|^2}\, v^2\, \mathrm{d}x \leq 4 \int |\nabla v|^2\, \mathrm{d}x. \tag{3.1}$$

A proof of this inequality can be found in [16]. The inequality (3.1) has to be supplemented by a further inequality that allows us to estimate more singular terms.

Lemma 3.2 *For all exponents s in the interval $1 < s < 3/2$ and all infinitely differentiable functions $v : \mathbb{R}^3 \to \mathbb{R}$ that have a compact support,*

$$\int \frac{1}{|x|^{2s}}\, v^2 \,\mathrm{d}x \;\le\; \frac{5}{3-2s} \sum_{|\alpha|\le 2} \int |\mathrm{D}^\alpha v|^2 \,\mathrm{d}x, \tag{3.2}$$

where the sum runs over all partial derivatives of order less than or equal two.

Proof Let $d(x) = |x|$ for convenience. To avoid any difficulty, we assume at first that the function v vanishes on a neighborhood of the origin. For the given exponents s,

$$\frac{1}{d^{2s}} \;=\; -\,\frac{1}{2s-1}\,\nabla\left(\frac{1}{d^{2s-1}}\right)\cdot\nabla d.$$

Integration by parts therefore yields

$$\int \frac{1}{d^{2s}}\, v^2 \,\mathrm{d}x \;=\; \frac{1}{2s-1}\int \frac{1}{d^{2s-1}}\,\nabla\cdot(v^2\nabla d)\,\mathrm{d}x$$

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

$$\int \frac{1}{d^{2s}}\, v^2 \,\mathrm{d}x \;=\; -\,\frac{2}{3-2s}\int \frac{1}{d^{2s-1}}\, v\,\nabla d\cdot\nabla v\;\mathrm{d}x$$

of the integral to be estimated. It transfers to arbitrary infinitely differentiable functions v with compact support as we show next. Let $\chi : \mathbb{R}^3 \to [0,1]$ be an infinitely differentiable function with $\chi(x) = 0$ for $|x| \le 1/2$ and $\chi(x) = 1$ for $|x| \ge 1$ and set

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

The representation then holds for the functions v_k as just proved. Using

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

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

$$x \;\to\; \frac{1}{|x|^{2s}}, \quad s < 3/2,$$

the representation follows from the dominated convergence theorem letting k go to infinity. Since $1/d^{\,2s-1} \le 1 + 1/d^2$ for the given exponents s, it leads to the estimate

$$\int \frac{1}{d^{2s}}\, v^2 \,\mathrm{d}x \;\le\; \frac{1}{3-2s}\int \left(1 + \frac{1}{d^2}\right)\left(v^2 + (\nabla d\cdot\nabla v)^2\right)\,\mathrm{d}x$$

of the integral on the left hand side of (3.2). The proposition follows using again that $|\nabla d| \leq 1$ and then applying the Hardy inequality (3.1) to the right hand side. □

An estimate of this kind cannot hold for exponents $s \geq 3/2$ as the singular part of the integrand on the left hand side of the inequality is not locally integrable for these s. If v does not vanish at the origin the integral on the left hand side of (3.2) grows like $1/(3-2s)$ when s approaches $3/2$, so that the estimate is in this sense optimal.

A similar estimate holds for the exponents $0 \leq s \leq 1$. It follows directly from the observation that $1/|x|^{2s} \leq 1 + 1/|x|^2$ for these s and the Hardy inequality (3.1).

Lemma 3.3 *For all exponents s in the interval $0 \leq s \leq 1$ and all infinitely differentiable functions $v : \mathbb{R}^3 \to \mathbb{R}$ that have a compact support,*

$$\int \frac{1}{|x|^{2s}} v^2 \,\mathrm{d}x \;\leq\; \int v^2 \,\mathrm{d}x \;+\; 4 \int |\nabla v|^2 \,\mathrm{d}x. \tag{3.3}$$

4 Estimates of mixed derivatives

We are now in the position to prove that a good deal of the smoothness of the regular part v of the wave functions (1.9) transfers to the wave functions themselves. The arguments are rather general and do not utilize that the functions under consideration solve the Schrödinger equation. We only assume that they are of the form

$$u(x) = \left\{ \prod_{i<j} F(x_i - x_j) \right\} v(x), \tag{4.1}$$

where $v : (\mathbb{R}^3)^N \to \mathbb{R}$ is a function in one of the spaces (2.7), i.e., possessing square integrable weak derivatives $\mathrm{D}^\alpha v$, $\alpha \in \mathscr{A}$, in L_2 respectively H^1. The product in front of v takes the role of the singular part of the wave function (1.9). We assume that

$$F : \mathbb{R}^3 \to \mathbb{R} : x \to f(r), \quad r = |x|, \tag{4.2}$$

is rotationally symmetric and takes the value $F(x) = 1$ for all x outside some ball around the origin and $f : [0, \infty) \to \mathbb{R}$ is infinitely differentiable.

Denoting by x_1, x_2, and x_3 for a moment the components of $x \in \mathbb{R}^3$, the first and second order partial derivatives of the function F are, for $x \neq 0$,

$$\frac{\partial}{\partial x_k} F(x) = \frac{x_k}{r} f'(r), \quad \frac{\partial^2}{\partial x_k \partial x_\ell} F(x) = \frac{x_k}{r}\frac{x_\ell}{r} f''(r) + \left(\delta_{k\ell} - \frac{x_k}{r}\frac{x_\ell}{r}\right) \frac{1}{r} f'(r) \tag{4.3}$$

and its third order partial derivatives can outside the origin be written as

$$\frac{\partial^3}{\partial x_k \partial x_\ell \partial x_m} F(x) = \frac{x_k}{r}\frac{x_\ell}{r}\frac{x_m}{r} f'''(r) + a_{k\ell m}(x) \left(\frac{1}{r} f''(r) - \frac{1}{r^2} f'(r) \right), \tag{4.4}$$

where we have utilized the abbreviation

$$a_{k\ell m}(x) = \delta_{\ell m}\frac{x_k}{r} + \delta_{km}\frac{x_\ell}{r} + \delta_{k\ell}\frac{x_m}{r} - 3\,\frac{x_k}{r}\frac{x_\ell}{r}\frac{x_m}{r}. \tag{4.5}$$

Since the derivatives of $r \to f(r)$ are bounded for $r \geq 0$ and vanish for all r greater than some $r_0 > 0$, we can deduce from that that their derivatives can be bounded via

$$\left|\frac{\partial}{\partial x_k}\,F(x)\right| \lesssim 1, \quad \left|\frac{\partial^2}{\partial x_k \partial x_\ell}\,F(x)\right| \lesssim \frac{1}{r}, \quad \left|\frac{\partial^3}{\partial x_k \partial x_\ell \partial x_m}\,F(x)\right| \lesssim \frac{1}{r^2} \tag{4.6}$$

and vanish outside the given ball. Here we have used the notation "$a \lesssim b$", which means that a can be estimated by b up to a positive constant that is independent of the parameters under consideration.

We will also need a regularized, smooth counterpart of the product function in front of v in (4.1). For this purpose, let $x \to B(r)$, $B(r) \geq r$, be an infinitely differentiable, radially symmetric function. Assume that $B(r) = r$ for $r > 1$ and set, for $\varepsilon > 0$,

$$F_\varepsilon(x) = f(B_\varepsilon(r)), \quad B_\varepsilon(r) \,=\, \varepsilon\, B\left(\frac{r}{\varepsilon}\right). \tag{4.7}$$

The infinitely differentiable function F_ε coincides outside the ball of radius ε around the origin with the function F. Inside this ball, its derivatives can be estimated as

$$\left|\frac{\partial}{\partial x_k}\,F_\varepsilon(x)\right| \lesssim 1, \quad \left|\frac{\partial^2}{\partial x_k \partial x_\ell}\,F_\varepsilon(x)\right| \lesssim \frac{1}{\varepsilon}, \quad \left|\frac{\partial^3}{\partial x_k \partial x_\ell \partial x_m}\,F_\varepsilon(x)\right| \lesssim \frac{1}{\varepsilon^2}, \tag{4.8}$$

with constants that are independent of the smoothing parameter $\varepsilon > 0$. These estimates follow from (4.3) and (4.4) replacing the function f by its smoothed counterparts $r \to f(B_\varepsilon(r))$ and using that $B\,'(0) = 0$. As follows from (4.6) and (4.8),

$$\left|\frac{\partial^3}{\partial x_k \partial x_\ell \partial x_m}\,F_\varepsilon(x)\right| \lesssim \varepsilon^{\,s-2}\,\frac{1}{r^{\,s}} \tag{4.9}$$

for all values $0 < s < 2$ and all $x \neq 0$, with a constant independent of ε. This estimate will later play a decisive role. Finally for all $x \in \mathbb{R}^3$,

$$|F(x) - F_\varepsilon(x)| \lesssim \varepsilon \tag{4.10}$$

so that the functions F_ε tend uniformly to F as ε goes to zero.

Theorem 4.1 *Let $v : (\mathbb{R}^3)^N \to \mathbb{R}$ be a function that possesses weak derivatives $\mathrm{D}^\alpha v$ in L_2 for all multi-indices α in the set $\mathscr{A}$ from (2.3). Thefunction (4.1) then possesses* *weak derivatives* $\mathrm{D}^\alpha u$, $\alpha \in \mathscr{A}$, *in* L_2 *as well, which can be estimated as*

$$|\!|\!| u |\!|\!|_{1,0} \lesssim |\!|\!| v |\!|\!|_{1,0} \tag{4.11}$$

by the corresponding derivatives of the function v.

Proof We first assume that v is an infinitely differentiable function with compact support and consider the regularized, themselves infinitely differentiable functions

$$u_\varepsilon(x) = \left\{ \prod_{i<j} F_\varepsilon(x_i - x_j) \right\} v(x). \tag{4.12}$$

Their partial derivatives $\mathrm{D}^\alpha u_\varepsilon$, $\alpha \in \mathscr{A}$, consist of sums of products of partial derivatives of the factors $F_\varepsilon(x_i - x_j)$ with respect to the components of x_i and x_j of orders up to two and of partial derivatives of v. We consider the single products in the following separately. According to (4.6) and (4.8), the partial derivatives of the factors $F_\varepsilon(x_i - x_j)$ of orders up to one are uniformly bounded in $\varepsilon > 0$ and thus do not require special attention. Their second order derivatives can be bounded via

$$\left| \frac{\partial^2}{\partial x_{i,k} \partial x_{j,\ell}} F_\varepsilon(x_i - x_j) \right| \lesssim \frac{1}{|x_i - x_j|} \tag{4.13}$$

uniformly in the smoothing parameter ε. If such a second order derivative appears in the product under consideration neither the variable x_i nor the variable x_j can appear in another such singular factor. Letting ε tend to zero, one therefore recognizes, with the help of the dominated convergence theorem and the definition of weak derivatives, that the weak derivatives $\mathrm{D}^\alpha u$, $\alpha \in \mathscr{A}$, exist and can formally be obtained by the product rule. The derivatives of the factors $F(x_i - x_j)$ have here to be interpreted pointwise outside the singular set and the derivatives of v still classically.

The estimate (4.11) follows from Fubini's theorem and the Hardy inequality (3.1), where one has to take into account that with the appearance of a second order derivative as in (4.13) the function v is not differentiated with respect to the components of x_i and x_j, and again that neither x_i nor x_j can appear in another such singular factor. With that we have proven the proposition for infinitely differentiable functions v with compact support. The rest follows from the density of these functions in X_0. Let $v_1, v_2, v_3, \ldots$ be such functions tending to v in X_0. The assigned u_k form then a Cauchy sequence in X_0 and tend with that to a limit function u both in X_0 and L_2. This limit function then necessarily coincides with the corresponding function (4.1) which is therefore itself contained in X_0 and satisfies the estimate (4.11). □

The theorem implies that, for every function v with the given properties, the assigned function $u = \mathsf{F}v$, with F the prefactor from (4.1), is contained in H^1. We keep in mind that its weak gradient and with that its first order weak derivatives are given by

$$\nabla u = \mathsf{F}\, \nabla v + v\, \nabla \mathsf{F}, \tag{4.14}$$

where the gradient of v is understood in the weak sense and that of F pointwise.

If the weak derivatives $\mathrm{D}^\alpha v$, $\alpha \in \mathscr{A}$, of the regular part of the function (4.1) are in H^1, the corresponding derivatives of the function (4.1) itself, however, do not need to be located in H^1 as the singularities arising in front of the derivatives of v are too strong. To cover the behavior of these derivatives of the wave functions near the singular set where two or more electrons meet, we introduce the weight function

$$\Omega(x) = \min\Big\{ \min_{i<j} |x_i - x_j|,\ 1\Big\}. \tag{4.15}$$

Theorem 4.2 *Let $v : (\mathbb{R}^3)^N \to \mathbb{R}$ be a square integrable function that possesses weak derivatives $\mathrm{D}^\alpha v$ in H^1 for all multi-indices α in the set $\mathscr{A}$ from (2.3). The weak derivatives $\mathrm{D}^\alpha u$, $\alpha \in \mathscr{A}$, of the function (4.1) are then themselves one times weakly differentiable outside the singular set Γ where two or more components x_i coincide. Their first order weak derivatives defined outside this singular set satisfy an estimate*

$$\|\Omega^\mu \nabla \mathrm{D}^\alpha u\|_0 \lesssim \frac{1}{\sqrt{2\mu - 1}}\, |\!|\!| v |\!|\!|_{1,1} \tag{4.16}$$

for all exponents $1/2 < \mu < 1$, with a constant that is independent of μ.

Proof The arguments are similar to those in the proof of the previous theorem and are based on the estimates (4.6) for the derivatives of the function F. We start again with an infinitely differentiable function v with compact support. The corresponding derivatives of u on the complement of the singular set Γ split into sums of products of partial derivatives of the factors $F(x_i - x_j)$ and derivatives of v. These products are again estimated separately. In addition to the products considered in the proof of the previous theorem also their first order partial derivatives have to be estimated here.

The first order derivatives of the factors $F(x_i - x_j)$ are bounded and do not require special attention. The situation is different with the second and the now arising third-order derivatives of these factors that are bounded, according to (4.6), by

$$\lesssim \frac{1}{|x_i - x_j|}, \quad \lesssim \frac{1}{|x_i - x_j|^2}.$$

In addition to the situation in the proof of the previous theorem, a pair of singular terms of the first kind with associated index pairs (i, j) and (i, k) can now appear. In this case, v is not differentiated with respect to a component of x_i, x_j, or x_k. A factor involving a third-order derivative of F can appear at most once in each of the products under consideration. The function v is in this case not differentiated with respect to the components of the corresponding parts x_i and x_j of x. As, with $1 < s = 2 - \mu < 3/2$,

$$\Omega(x)^{2\mu} \frac{1}{|x_i - x_j|^4} \le \frac{1}{|x_i - x_j|^{2s}},$$

the estimate (4.16) thus follows with the help of Fubini's theorem from the classical Hardy inequality (3.1) and the inequality from Lemma 3.2.

A limit process as in the proof of the previous theorem shows that the estimate transfers from the infinitely differentiable functions v with compact support to arbitrary functions v in X^1. Let v_k, $k = 1, 2, \ldots$, be a sequence of infinitely differentiable functions with compact support that tends in X^1 to a given function v in X^1. The assigned functions u_k tend then in L_2 to u and the functions

$$\Omega^\mu \frac{\partial}{\partial x_{i,\nu}} \mathrm{D}^\alpha u_k, \quad k = 1, 2, \ldots,$$

with α a multi-index in the set $\mathscr{A}$, on the complement of Γ in the L_2-sense to limit functions $w_{i\nu}$. Let φ now be an infinitely differentiable function with support in the complement of Γ. Since $\Omega^{-\mu}$ is bounded on the support of φ, the equation

$$\int \frac{\partial}{\partial x_{i,\nu}} \mathrm{D}^\alpha u_k \, \varphi \, \mathrm{d}x \;=\; (-1)^{|\alpha|+1} \int u_k \frac{\partial}{\partial x_{i,\nu}} \mathrm{D}^\alpha \varphi \, \mathrm{d}x$$

becomes in the limit of k tending to infinity

$$\int \Omega^{-\mu} w_{i\nu} \, \varphi \, \mathrm{d}x \;=\; (-1)^{|\alpha|+1} \int u \, \frac{\partial}{\partial x_{i,\nu}} \mathrm{D}^\alpha \varphi \, \mathrm{d}x.$$

This proves that $\Omega^{-\mu} w_{i\nu}$ is the corresponding weak derivative of u on the complement of Γ and that this weak derivative can be estimated as stated above. □

An estimate like (4.16) cannot hold for exponents $\mu \leq 1/2$. This follows from the fact that the function $x \to 1/r^{4-2\mu}$ is locally integrable in three space dimensions if and only if $\mu > 1/2$. The lower bound $\mu > 1/2$ can therefore not be improved further.

The results of this section can be summarized in the estimate

$$\sum_{\alpha \in \mathscr{A}} \Big\{ \|\mathrm{D}^\alpha u\|_0^2 + \|\Omega^\mu \nabla \mathrm{D}^\alpha u\|_0^2 \Big\} \lesssim \frac{1}{2\mu - 1} \sum_{\alpha \in \mathscr{A}} \|\mathrm{D}^\alpha v\|_1^2 \tag{4.17}$$

that holds for $1/2 < \mu < 1$ with a constant independent of μ and reflects the behavior of the mixed derivatives of the function (4.1) in the neighborhood of the singular set. The eigenfunctions u of the electronic Schrödinger operator (1.1) for eigenvalues below the bottom of the essential spectrum possess therefore square integrable weak derivatives $\mathrm{D}^\alpha u$ for all multi-indices $\alpha \in \mathscr{A}$, that is, are contained in $H^{1,0}_{\mathrm{mix}}$. Their weighted weak derivatives $\Omega^\mu \nabla \mathrm{D}^\alpha u$, $\alpha \in \mathscr{A}$, exist outside the singular set where two ore more electrons meet and are square integrable for all exponents $\mu > 1/2$.

5 The K-functional and estimates in fractional order spaces

The next theorem shows, in combination with the results from [17], that the solutions of the electronic Schrödinger equation are contained in the spaces $H^{\vartheta,1}_{\mathrm{mix}}$ for all ϑ below $3/4$. It is based on an estimate of the K-functional (2.8) of the function under consideration, from the perspective of approximation theory the decisive quantity.

Theorem 5.1 *Let* $v : (\mathbb{R}^3)^N \to \mathbb{R}$ *be a square integrable function that possesses weak derivatives* $\mathrm{D}^\alpha v$ *in* H^1 *for all multi-indices* α *in the set* $\mathscr{A}$ *from* (2.3). *The function* (4.1) *is then contained in the spaces* $H^{\vartheta,1}_{\mathrm{mix}}$ *for all values* $\vartheta < 3/4$. *Moreover,*

$$K(t,u) \lesssim |\ln(t)|^{1/2}\, t^{3/4}\, |||v|||_{1,1}, \quad t \to 0+, \tag{5.1}$$

which means that $K(t,u)$ *tends to zero faster than any power* t^ϑ, $\vartheta < 3/4$.

Proof We assume first that the given function v is an infinitely differentiable function with compact support. The idea is to estimate the K-functional by the expression

$$K(t,u) \le \left\{\|u-u_\varepsilon\|_1^2 + t^2\, |||u_\varepsilon|||_{1,1}^2\right\}^{1/2},$$

where $\varepsilon > 0$ will later be coupled to t and $u_\varepsilon = \mathsf{F}_\varepsilon v$ is the smoothed variant (4.12) in the space X^1 of the function $u = \mathsf{F}v$ from (4.1) in the space H^1. We recall that the weak gradient of u can be formally calculated by means of the product rule (4.14).

The function $u - u_\varepsilon$ vanishes outside the union of the sets Γ_{ij} that consist of those x for which $|x_i - x_j| \le \varepsilon$. The H^1-distance of u and u_ε over Γ_{ij} can be estimated as

$$\|u-u_\varepsilon\|_{1,\Gamma_{ij}} \le \|(\mathsf{F}-\mathsf{F}_\varepsilon)\nabla v\|_{0,\Gamma_{ij}} + \|(\nabla\mathsf{F}-\nabla\mathsf{F}_\varepsilon)\,v\|_{0,\Gamma_{ij}} + \|(\mathsf{F}-\mathsf{F}_\varepsilon)\,v\|_{0,\Gamma_{ij}}.$$

As $|(\mathsf{F}-\mathsf{F}_\varepsilon)(x)| \lesssim \varepsilon$ and $|(\nabla\mathsf{F}-\nabla\mathsf{F}_\varepsilon)(x)| \lesssim 1$, the squares of the first two terms on the right hand side can, for arbitrary s in the interval $1 < s < 3/2$, be estimated by

$$\varepsilon^{2s}\int_{\Gamma_{ij}} \frac{1}{|x_i-x_j|^{2s-2}}\,|\nabla v|^2\,\mathrm{d}x, \quad \varepsilon^{2s}\int_{\Gamma_{ij}} \frac{1}{|x_i-x_j|^{2s}}\,v^2\,\mathrm{d}x,$$

and the square of the last term correspondingly by the expression

$$\varepsilon^{2s}\int_{\Gamma_{ij}} \frac{1}{|x_i-x_j|^{2s-2}}\,v^2\,\mathrm{d}x.$$

These expressions can be further estimated by means of (3.2) and (3.3). This yields

$$\|u-u_\varepsilon\|_1^2 \lesssim \frac{1}{3-2s}\,\varepsilon^{2s}\,|||v|||_{1,1}^2,$$

with a constant that depends neither on ε nor on the choice of s.

Estimating the norm $|||u_\varepsilon|||_{1,1}$ means estimating partial derivatives of u_ε. These partial derivatives split again into sums of products of partial derivatives of the factors $F_\varepsilon(x_i - x_j)$ with respect to the components of x_i and x_j of orders up to three and of partial derivatives of v. One proceeds as in the proof of Theorem 4.2, where the estimate (4.9) for the third order derivatives of F_ε enters into the estimates of the terms involving a third order derivative of one of the factors $F_\varepsilon(x_i - x_j)$. One obtains, with the help of Fubini's theorem and the estimates from Sect. 3, the estimate

$$|||u_\varepsilon|||_{1,1}^2 \lesssim \frac{1}{3-2s}\,\varepsilon^{2s-4}\,|||v|||_{1,1}^2,$$

where the constant depends as before neither on $1 < s < 3/2$ nor on ε.

The estimates for the two single parts can now be combined to an estimate for the K-functional. Choosing for both the same s and setting $\varepsilon = \sqrt{t}$, one obtains

$$K(t,u) \lesssim \frac{1}{\sqrt{3-2s}}\,t^{s/2}\,|||v|||_{1,1},$$

with a constant independent of $1 < s < 3/2$. The estimate (5.1) now follows choosing

$$s = \frac{3}{2} + \frac{1}{\ln t};$$

for $t < \mathrm{e}^{-2}$ this s is located in the admissible interval and minimizes the right hand side of the inequality above. That the estimate (5.1) holds for all functions $v \in X^1$, not only for the infinitely differentiable functions v with compact support as just proved, follows from the density of these functions in X^1, the continuity of the mapping $v \to u$ as a mapping from X^1 to H^1, and the continuity of the mapping $u \to K(t,u)$ from H^1 to the real numbers. The rest of the proposition follows from Lemma 2.2. □

The estimate (5.1) for the K-functional implies the norm estimate

$$|||u|||_{\vartheta,1} \lesssim \frac{1}{3-4\vartheta}\,|||v|||_{1,1} \tag{5.2}$$

for the function (4.1) that holds for $0 \le \vartheta < 3/4$, with a constant independent of ϑ. It suffices to prove the estimate for $\vartheta \ge 1/2$ as the norm on the left hand side of the equation increases with ϑ. This can be done using the representation (2.11) of this norm in terms of the K-functional and an argument as in the proof of Lemma 2.2.

6 A counterexample

The upper bound $\vartheta < 3/4$ from Theorem 5.1 is optimal and can neither be reached nor surpassed. This shows the example of the function

$$u(x) = \left(1 + \frac{1}{2}\,|x_1 - x_2|\right) \exp\left(-\frac{1}{4}\,|x_1|^2 - \frac{1}{4}\,|x_2|^2\right) \tag{6.1}$$

that falls into the considered category as can be seen splitting up the first factor into a product of a factor as in (4.1) and a smooth function. It often serves as a model for electronic wave functions. Its singular behavior at the diagonal $x_1 = x_2$ is the same as that of the solutions of the electronic Schrödinger equation at the positions where two electrons of distinct spin meet [7]. The function represents at the same time the ground state of the so-called hookium or harmonium atom [11], an artificial two-electron system with the Hamiltonian

$$-\frac{1}{2}\,\Delta + \frac{1}{8}\,|\,x\,|^2 + \frac{1}{|x_1 - x_2|} \tag{6.2}$$

in which the potential of the nucleus is replaced by that of a harmonic oscillator.

To show that the function (6.1) cannot be contained in $H^{\vartheta,1}_{\mathrm{mix}}$ for $\vartheta \geq 3/4$, we first rotate the coordinate system by the matrix

$$Q = \frac{1}{\sqrt{2}}\begin{pmatrix} I & -I \\ I & I \end{pmatrix} \tag{6.3}$$

built up from the (3×3)-identity matrix and write u in the form $u(x) = w(Qx)$, where

$$w(x) = \left(1 + \frac{1}{\sqrt{2}}\,|\,x_1|\right)\exp\left(-\frac{1}{4}\,|x_1|^2 - \frac{1}{4}\,|x_2|^2\right). \tag{6.4}$$

As Q is orthogonal the Fourier transform of u is then $\widehat{u}(\omega) = \widehat{w}(Q\omega)$. Therefore

$$\int P(\omega)|\widehat{u}(\omega)|^2\,\mathrm{d}\omega = \int P(Q^T\omega)|\widehat{w}(\omega)|^2\,\mathrm{d}\omega \tag{6.5}$$

for every polynomial $P(\omega)$. Since $|Q^T\omega| = |\omega|$ thus we have to show that the function

$$\omega \;\to\; (1 + |\omega|^2)\,P_{\mathrm{mix}}(Q^T\omega)^{\vartheta}\,|\widehat{w}(\omega)|^2 \tag{6.6}$$

cannot be integrable for exponents $\vartheta \geq 3/4$, where

$$P_{\mathrm{mix}}(Q^T\omega) = \left(1 + \frac{1}{2}\,|\omega_1 - \omega_2|^2\right)\left(1 + \frac{1}{2}\,|\omega_1 + \omega_2|^2\right). \tag{6.7}$$

To proceed, we need to know the asymptotic behavior of the Fourier transform of the function w. We rewrite w first in the form

$$w(x) = \phi(x_1)\,\mathrm{e}^{-|x_2|^2/4} = \widetilde{\phi}(|x_1|)\,\mathrm{e}^{-|x_2|^2/4} \tag{6.8}$$

with the univariate function

$$\widetilde{\phi}(r) = \left(1 + \frac{1}{\sqrt{2}}\,r\right)\,\mathrm{e}^{-r^2/4}. \tag{6.9}$$

The Fourier transform of w is in this notation

$$\widehat{w}(\omega) = \widehat{\phi}(\omega_1)\,(\sqrt{2})^3\,\mathrm{e}^{-|\omega_2|^2}. \tag{6.10}$$

The asymptotic behavior of the Fourier transform of ϕ is given by the following lemma that is of general nature and into which only the decay properties of $\widetilde{\phi}$ enter.

Lemma 6.1 *The Fourier transform of* ϕ *behaves for* $|\omega|$ *tending to infinity like*

$$\widehat{\phi}(\omega) = -2\sqrt{\frac{2}{\pi}}\,\frac{\widetilde{\phi}'(0)}{|\omega|^4} + \mathscr{O}\left(\frac{1}{|\omega|^6}\right). \tag{6.11}$$

Proof As ϕ is a rotationally symmetric function, $\widehat{\phi}(\omega) = \widehat{\phi}(Q\omega)$ for all orthogonal (3×3)-matrices Q. Particularly $\widehat{\phi}(\omega) = \widehat{\phi}(|\omega|e_3)$. Therefore

$$\widehat{\phi}(\omega) = \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int \widetilde{\phi}(|x|)\,\mathrm{e}^{-\mathrm{i}\,|\omega|\,x_3}\,\mathrm{d}x.$$

Transforming the integral to polar coordinates, the representation

$$\widehat{\phi}(\omega) = \sqrt{\frac{2}{\pi}}\,\frac{1}{|\omega|}\int_0^\infty r\,\widetilde{\phi}(r)\sin(|\omega|r)\,\mathrm{d}r$$

of the Fourier transform of a rotationally symmetric function $\phi(x) = \widetilde{\phi}(|x|)$ in three space dimensions follows. If $r \to a(r)$ is an infinitely differentiable function with integrable derivatives tending to zero as r goes to infinity, integration by parts yields

$$\int_0^\infty a(r)\sin(|\omega|r)\,\mathrm{d}r = \frac{1}{|\omega|}\,a(0) - \frac{1}{|\omega|^2}\int_0^\infty a''(r)\sin(|\omega|r)\,\mathrm{d}r.$$

Applying this relation a second and third time, one obtains

$$\int_0^\infty a(r)\sin(|\omega|r)\,\mathrm{d}r = \frac{1}{|\omega|}\,a(0) - \frac{1}{|\omega|^3}\,a''(0) + \mathscr{O}\left(\frac{1}{|\omega|^5}\right)$$

as $|\omega|$ goes to infinity and therefore, inserting $a(r) = r\,\widetilde{\phi}(r)$, the statement. □

We can now complete the proof and are ready to show that the function (6.6) cannot be integrable for $\vartheta \geq 3/4$. For that it suffices to show that it cannot be integrable over the cylinder $|\omega_2| \leq 1$ for these values of ϑ. For $|\omega_2| \leq 1$,

$$\left(1 + \frac{1}{2}|\omega_1 - \omega_2|^2\right)\left(1 + \frac{1}{2}|\omega_1 + \omega_2|^2\right) \geq 1 + \frac{1}{4}|\omega_1|^4. \tag{6.12}$$

In our case $\widetilde{\phi}'(0) \neq 0$. With the help of Lemma 6.1 one gets therefore, for ω in the given cylinder and sufficiently large $|\omega_1|$, the desired lower bound

$$(1 + |\omega|^2)\,P_{\mathrm{mix}}(Q^T\omega)^\vartheta\,|\widehat{w}(\omega)|^2 \gtrsim |\omega_1|^{4\vartheta-6} \tag{6.13}$$

for the function (6.6). If $\vartheta \geq 3/4$, the function (6.6) thus cannot be integrable over the cylinder $|\omega_2| \leq 1$ and even less over the full space. This proves that the function (6.1) is indeed contained in none of the spaces $H^{\vartheta,1}_{\mathrm{mix}}$ for $\vartheta \geq 3/4$. Moreover, for this u,

$$K(t,u) \gtrsim t^{3/4}, \tag{6.14}$$

as can be shown in the same way, by means of the representation of the K-functional from the proof of Lemma 2.1 and the asymptotic behavior of the Fourier transform of the function w on the cylinder $|\omega_2| \leq 1$. This shows that the estimate (5.1) from Theorem 5.1 is almost optimal and that at most the logarithmic factor got lost there.

7 Exponential decay, approximability, and approximation order

We mentioned in the introduction that the eigenfunctions u of the operator (1.1) decay exponentially in the L_2-sense, which means that the functions (1.11) here denoted as

$$x \;\to\; \mathrm{e}^{\psi(x)}u(x), \quad \psi(x) = \gamma \sum_{i=1}^{N} |x_i|, \tag{7.1}$$

are square integrable for values $\gamma > 0$ below some bound that depends on the distance of the eigenvalue under consideration to the bottom of the essential spectrum. It has been shown in [17] that these exponentially weighted eigenfunctions admit the same kind of representation (1.9) as the eigenfunctions themselves. They are therefore like these contained in the spaces $H^{\vartheta,1}_{\mathrm{mix}}$ for $\vartheta < 3/4$. We outline in this section how this can be used to study the convergence behavior of approximation processes.

Lemma 7.1 *For all functions v for which $\mathrm{e}^{\psi} v$ is located in $H^{1,1}_{\mathrm{mix}}$, that is, in X^1,*

$$|||\mathrm{e}^{\psi} v|||^2_{1,1} \lesssim \sum_{\alpha\in\mathscr{A}} \|\mathrm{e}^{\psi}\mathrm{D}^{\alpha} v\|_1^2 \lesssim |||\mathrm{e}^{\psi} v|||^2_{1,1}, \tag{7.2}$$

with constants that depend on the decay rate γ.

Proof This follows from the observation that for all multi-indices $\alpha \in \mathscr{A}$

$$\mathrm{D}^{\alpha}(\mathrm{e}^{\psi} v) = \sum_{\beta\leq\alpha} \gamma^{|\beta|} a_{\beta}\, \mathrm{e}^{\psi}\, \mathrm{D}^{\alpha-\beta} v,$$

where the bounded coefficient functions a_β are given by

$$a_{\beta}(x) = \prod_{i=1}^{N} \left(\frac{x_i}{|x_i|}\right)^{\beta_i}$$

and the relation $\beta \leq \alpha$ has to be understood componentwise. The reason is that the function $\mathrm{e}^{\psi} v$ is differentiated only once with respect to the components of every single x_i. Formally, the relation is obtained from the product rule, which can be justified in the sense of globally defined weak derivatives with an approximation argument as in the proof of Theorem 4.1. Differentiating the relation above once more, the proposition follows with the help of the Hardy inequality (3.1), taking into account that $a_\beta = 1$ for $\beta = 0$, $\nabla_i a_\beta = 0$ if $\beta_i = 0$, and $|\nabla_i a_\beta| \le 1/|x_i|$ otherwise. □

The norm $|||\mathrm{e}^\psi v|||_{1,1}$ measures therefore the exponentially weighted L_2-norms of the involved derivatives of the function v. It is therefore reasonable to start from a sequence $T_n : H^1 \to H^1$, $n = 1, 2, \ldots$, of linear approximation operators that are uniformly H^1-bounded and to require that

$$\|v - T_n v\|_1 \lesssim n^{-q}\, |||\mathrm{e}^\psi v|||_{1,1} \tag{7.3}$$

for all functions $v \in H^1$ for which $\mathrm{e}^\psi v \in H^{1,1}_{\mathrm{mix}}$. The constant $q > 0$ is an unspecified convergence rate also depending on what n means. These assumptions form a proper framework for sparse grid-like approximation methods, for example for the wavelet approximations studied in [18] or expansions into tensor products of Gaussians or other eigenfunctions of three-dimensional Schrödinger-like operators [16]. Another example is the expansion into tensor products of three-dimensional functions with given angular parts [16]. The range of the T_n is in this case infinite dimensional. The exponential factor is the tribute paid to the infinite extension of the domain.

Our assumptions imply the following error estimate for functions of reduced smoothness and in particular for the eigenfunctions of the operator (1.1).

Theorem 7.1 *For all functions $u \in H^1$ for which $\mathrm{e}^\psi u \in H^{\vartheta,1}_{\mathrm{mix}}$ for some $0 < \vartheta < 1$,*

$$\|u - T_n u\|_1 \lesssim n^{-\vartheta q}\, |||\mathrm{e}^\psi u|||_{\vartheta,1}. \tag{7.4}$$

Proof We use that $\|u\|_1 \lesssim \|\mathrm{e}^\psi u\|_1$ for functions u for which $\mathrm{e}^\psi u \in H^1$. The linearity of the T_n, their uniform boundedness, and (7.3) imply therefore the estimate

$$\|u - T_n u\|_1 \lesssim \|u - \mathrm{e}^{-\psi} v\|_1 + \|\mathrm{e}^{-\psi} v - T_n(\mathrm{e}^{-\psi} v)\|_1 \lesssim \|\mathrm{e}^\psi u - v\|_1 + n^{-q}\, |||v|||_{1,1}$$

for arbitrary such u and all $v \in X^1$. With that we can bound the approximation error

$$\|u - T_n u\|_1 \lesssim K(n^{-q}, \mathrm{e}^\psi u)$$

in terms of the K-functional of $\mathrm{e}^\psi u$. The estimate thus follows from (2.14). □

The scheme thus exploits the smoothness of the functions even if the convergence rate decreases unsurprisingly with decreasing smoothness. In the case of the solutions u of the electronic Schrödinger equation studied in this paper, we can apply the estimate for the K-functional of $\mathrm{e}^\psi u$ from Theorem 5.1 directly. It leads to an estimate

$$\|u - T_n u\|_1 \lesssim \sqrt{\ln(n)}\, n^{-3/4\, q} \tag{7.5}$$

for the approximation error: the convergence rate comes arbitrarily close to $3/4\, q$. Essentially only the factor $3/4$ gets lost compared to the case of full mixed regularity.

8 From approximation order back to regularity

Under some additional assumptions one can show that this convergence order cannot be improved further. We start from an orthogonal or biorthogonal expansion

$$v = \sum_{\lambda} (v, \phi'_\lambda)\, \phi_\lambda \tag{8.1}$$

of the square integrable functions into a series of functions $\phi_\lambda \in H^1$, where λ runs over a countable set of indices. The example that we have in mind is the expansion into wavelets from [18]. We introduce a new scale of discrete norms given by

$$\|[v]\|_{\vartheta,m}^2 = \sum_{\lambda} \kappa_0(\lambda)^m \kappa(\lambda)^\vartheta (v, \phi'_\lambda)^2, \tag{8.2}$$

where $\kappa_0(\lambda)$ and $\kappa(\lambda)$ are weight factors. The first one basically serves to measure the first order derivatives. The second one splits in Zeiser's construction into a part that is associated with the mixed derivatives and another one that is position dependent and associated with the decay of the functions under consideration. We assume in the sequel that, for the functions v for which $\mathrm{e}^{\psi} v$ is contained in the space $H^{1,1}_{\text{mix}}$,

$$|||v|||_{1,1} \lesssim \|[v]\|_{1,1} \lesssim |||\mathrm{e}^{\psi} v|||_{1,1}, \tag{8.3}$$

and that for $\vartheta = 0$ and $m = 1$ the new norm is equivalent to the H^1-norm, that is, that

$$\|v\|_1 \lesssim \|[v]\|_{0,1} \lesssim \|v\|_1 \tag{8.4}$$

holds for all functions $v \in H^1$. The wavelet expansions from [18] fulfill these assumptions. Our approximation operators T_n are now defined by

$$T_n v = \sum\nolimits'_{\lambda} (v, \phi'_\lambda)\, \phi_\lambda, \tag{8.5}$$

where the dash indicates that the sum runs here only over the indices λ for which $\kappa(\lambda)$ is less than a bound that is monotonically increasing with n and tending to infinity as n goes to infinity, say less than n^{2q} to adapt the notation to that in the previous section. The T_n are then bounded as operators from H^1 to H^1. Furthermore,

$$\|v - T_n v\|_1 \lesssim n^{-q}\, |||\mathrm{e}^{\psi} v|||_{1,1} \tag{8.6}$$

for the functions v for which $\mathrm{e}^{\psi} v$ is contained in $H^{1,1}_{\text{mix}}$. The operators thus fit into the framework considered before; in particular the error estimates (7.4) and (7.5) hold. The rest follows by means of a standard argument [3] from approximation theory:

Lemma 8.1 *Let u be a function in H^1 for which the error behaves like*

$$\|u - T_n u\|_1 = \mathscr{O}(n^{-\delta q}) \tag{8.7}$$

for n tending to infinity, where $0 < \delta < 1$. Then $u \in H^{\vartheta,1}_{\text{mix}}$ for $\vartheta < \delta$.

Proof Let $\widetilde{T}_\ell = T_{2^\ell}$ for abbreviation. Then

$$\|[\widetilde{T}_n u]\|_{\vartheta,1} \le \|[\widetilde{T}_1 u]\|_{\vartheta,1} + \sum_{\ell=1}^{n-1} (2^{\ell+1})^{\vartheta q} \, \|[\widetilde{T}_{\ell+1} u - \widetilde{T}_\ell u]\|_{0,1},$$

as follows from the triangle inequality and the inverse inequality

$$\|[v]\|_{\vartheta,1} \le (2^{\ell+1})^{\vartheta q} \|[v]\|_{0,1}$$

for the functions v in the range of $\widetilde{T}_{\ell+1}$. By the given assumptions,

$$\|[\widetilde{T}_{\ell+1} u - \widetilde{T}_\ell u]\|_{0,1} \lesssim \|\widetilde{T}_{\ell+1} - u\|_1 + \|u - \widetilde{T}_\ell u\|_1 \lesssim (2^{\ell+1})^{-\delta q}.$$

That means that the discrete norm

$$\|[u]\|_{\vartheta,1} = \lim_{n \to \infty} \|[\widetilde{T}_n u]\|_{\vartheta,1}$$

of u remains finite for $0 < \vartheta < \delta$. This implies $u \in H^{\vartheta,1}_{\mathrm{mix}}$ since

$$|||v|||_{\vartheta,1} \lesssim \|[v]\|_{\vartheta,1},$$

which follows by means of interpolation from (8.3) and (8.4), expressing both norms as in Lemma 2.1 in terms of the corresponding K-functionals. □

We conclude that for the functions considered in the previous sections, and in particular for electronic wave functions, a convergence rate ϑq, $\vartheta > 3/4$, is in general not possible. The estimate (7.5) is thus optimal, at least up to the logarithmic factor. Nonlinear, adaptive methods might shift this bound but also encounter hard limits due to the location of the singularities on the diagonals [4,5].

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