Multi-level Decompositions of Electronic Wave Functions

Harry Yserentant

Institut für Mathematik, Technische Universität Berlin, 10623 Berlin, Germany
yserentant@math.tu-berlin.de

1 Introduction

The approximation of high-dimensional functions, whether they be given explicitly or implicitly as solutions of differential equations, represents one of the grand challenges of applied mathematics. High-dimensional problems arise in many fields of application such as data analysis and statistics, but first of all in the sciences. One of the most notorious and complicated problems of this type is the Schrödinger equation. The Schrödinger equation forms the basis of quantum mechanics and is of fundamental importance for our understanding of atoms and molecules. It links chemistry to physics and describes a system of electrons and nuclei that interact by Coulomb attraction and repulsion forces. As proposed by Born and Oppenheimer in the nascency of quantum mechanics, the slower motion of the nuclei is mostly separated from that of the electrons. This results in the electronic Schrödinger equation, the problem to find the eigenvalues and eigenfunctions of the Hamilton operator

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|\mathbf{x}_i-\mathbf{a}_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|}. \tag{1}$$

It acts on functions with arguments $\mathbf{x}_1,\dots,\mathbf{x}_N \in \mathbb{R}^3$, which are associated with the positions of the considered electrons. The $\mathbf{a}_\nu$ are the fixed positions of the nuclei and the values Z_ν the charges of the nuclei in multiples of the absolute electron charge.

The high dimensionality of the equation immediately rules out classical discretization methods for partial differential equations as numerical analysts are familiar with. To overcome this curse of dimensionality, procedures like the Hartree-Fock method and its many variants and successors or density functional theory based methods have been developed over the decades. They are used with much success and form the basis of a steadily expanding branch of chemistry. See [6] for an overview on the present state of the art in quantum chemistry, and [3, 10], and [11] for mathematically oriented expositions. All these methods suffer, however, either from a priori modeling errors or from the fact that it is not clear how the accuracy can be systematically improved without the effort truly exploding for larger numbers of electrons.

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It is therefore rather surprising that simple sparse grid-like multi-level expansions of the electronic wave functions can be constructed whose convergence rate, measured in terms of the number of basis functions involved, is independent of the number of electrons and does not much differ from that for a two- or even one-electron system. The purpose of this note is to explain these results and the effects behind them. For details we refer to the references.

2 Regularity and Decay of the Wave Functions

The at least asymptotically, in relation to the high space dimension rapid convergence of these expansions is based on very particular properties of the solutions of the electronic Schrödinger equation: their regularity, that surprisingly increases with the number of electrons, the decay behavior of their mixed derivatives, and their antisymmetry enforced by the Pauli principle.

The solution space of the electronic Schrödinger equation is first the Hilbert space H^1 that consists of the square integrable functions

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : (\mathbf{x}_1, \ldots, \mathbf{x}_N) \to u(\mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{2}$$

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 and the L_2-norm of the gradient. In the language of physics, 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. It can be shown that the second-order differential operator (1) induces a bounded bilinear form on H^1 that satisfies a Garding inequality. The mathematically precise formulation of the eigenvalue problem is therefore the corresponding weak form of the equation on the space H^1, the same kind of weak form that one knows from the finite element method. The physically admissible solutions are components $u(\mathbf{x}) = \psi(\mathbf{x}, \boldsymbol{\sigma})$ of a full, spin-dependent wave function. By the Pauli principle, they are therefore antisymmetric with respect to the exchange of the positions $\mathbf{x}_i$ of electrons of the same spin $\sigma_i = \pm 1/2$.

To describe the regularity properties of the eigenfunctions, we need to introduce a scale of norms that are defined in terms of Fourier transforms. We first introduce the polynomials

$$P_{\mathrm{iso}}(\boldsymbol{\omega}) = 1 + \sum_{i=1}^{N} |\boldsymbol{\omega}_i|^2, \quad P_{\mathrm{mix}}(\boldsymbol{\omega}) = \prod_{i=1}^{N} \big(1 + |\boldsymbol{\omega}_i|^2\big). \tag{3}$$

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

$$|||u|||^2_{\vartheta,m} = \int P_{\mathrm{iso}}(\boldsymbol{\omega})^m P_{\mathrm{mix}}(\boldsymbol{\omega})^{\vartheta} \, |\widehat{u}(\boldsymbol{\omega})|^2 \, \mathrm{d}\boldsymbol{\omega}. \tag{4}$$

They are defined on the Hilbert spaces $H^{\vartheta,m}_{\mathrm{mix}}$ that consist of the square integrable functions (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 parameter m measures the isotropic smoothness that does not distinguish between different directions, and the parameter ϑ the mixed smoothness in direction of the three-dimensional coordinate spaces of the electrons. The spaces L_2 and H^1 are special cases of such spaces.

It has been proved in [12] and [13] that the physically admissible eigenfunctions u of the electronic Schrödinger operator (1) are at least contained in $H^{\vartheta,1}_{\mathrm{mix}}$ for $\vartheta = 1/2$. Recently we were able to improve this result substantially. We have shown in [9] that the eigenfunctions u of the electronic Schrödinger operator are, independent of their symmetry properties, contained in

$$H^{1,0}_{\mathrm{mix}} \cap \bigcap_{\vartheta<3/4} H^{\vartheta,1}_{\mathrm{mix}}. \tag{5}$$

The bound $3/4$ is optimal and can, except for special cases, neither be reached nor improved further. The proof is based on a representation of the eigenfunctions that has been derived in [15] and for the two-electron case in [1]. It has been shown in [15] that the eigenfunctions can be written as products

$$u(\mathbf{x}) = \exp\left(\sum_{i<j} \phi(\mathbf{x}_i - \mathbf{x}_j)\right) v(\mathbf{x}) \tag{6}$$

of more regular functions $v \in H^{1,1}_{\mathrm{mix}}$ and a universal factor that covers their singularities. This kind of splitting can be traced back to the work of Hylleraas [8] in the early years of quantum mechanics. It has been used in [4] and [7] to study the Hölder regularity of the eigenfunctions. There is a lot of freedom in the choice of the function ϕ. It needs only to be of the form

$$\phi(\mathbf{x}) = \widetilde{\phi}(|\mathbf{x}|), \quad \widetilde{\phi}'(0) = \frac{1}{2}, \tag{7}$$

where $\widetilde{\phi} : [0,\infty) \to \mathbb{R}$ is an infinitely differentiable function behaving sufficiently well at infinity. The regularity is therefore determined by that of the explicitly known factor from (6) that describes the behavior of the solutions at the singular points of the electron-electron interaction potential.

The splitting (6) is of independent interest since it is obviously possible to obtain better convergence rates for the regular part of the solutions than for the solutions themselves. We will restrict ourselves, however, here to the direct approximation of the eigenfunctions. The domain of the eigenfunctions is infinitely extended. The eigenfunctions are, however, strongly localized. It is known for a long time that an eigenfunction u for an eigenvalue below the ionization threshold of the given atom or molecule decays exponentially in the L_2-sense. That means there is a constant $\gamma > 0$ such that the function

$$\mathbf{x} \to \exp\left(\gamma \sum_{i=1}^{N} |\mathbf{x}_i|\right) u(\mathbf{x}), \tag{8}$$

is square integrable. This constant 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 [14]. It has been shown in [15] that these exponentially weighted eigenfunctions admit the same kind of representation (6) as the eigenfunctions themselves. Thus they share with them the described regularity properties [9]. The convergence analysis is based on this observation.

3 Sparse Grids and Antisymmetry

To explain the meaning of these results for the approximation of the solutions of the Schrödinger equation, we consider a simple model problem, the approximation of functions u of the variables $x_1,\dots,x_d$ that are odd and 2π-periodic in every coordinate direction on the cube $Q=[0,\pi]^d$ by tensor products

$$\phi(\mathbf{k},\mathbf{x}) = \prod_{i=1}^{d} \phi_{k_i}(x_i) \tag{9}$$

of the one-dimensional trigonometric polynomials

$$\phi_{k_i}(\xi) = \sqrt{\frac{2}{\pi}}\,\sin(k_i\xi) \tag{10}$$

labeled by the components $k_i = 1,2,\dots$ of the multi-indices $\mathbf{k}$. Our presentation closely follows [14]. Functions of the given kind that are square integrable over Q can be expanded into a multivariate Fourier series

$$u(\mathbf{x}) = \sum_{\mathbf{k}} \widehat{u}(\mathbf{k})\phi(\mathbf{k},\mathbf{x}), \tag{11}$$

where the expansion coefficients are given by

$$\widehat{u}(\mathbf{k}) = \int_Q u(\mathbf{x})\phi(\mathbf{k},\mathbf{x})\,\mathrm{d}\mathbf{x}. \tag{12}$$

We measure the speed of convergence of this series in the sense of the L_2-norm which reads in terms of the expansion coefficients

$$\|u\|_0^2 = \sum_{\mathbf{k}} |\widehat{u}(\mathbf{k})|^2. \tag{13}$$

The speed of convergence of the series is therefore determined by the speed with which the expansion coefficients decay. Assume that all partial derivatives of u of order s exist and are square integrable. This implies that

$$|u|_s^2 = \sum_{\mathbf{k}} |\mathbf{k}|^{2s} |\widehat{u}(\mathbf{k})|^2 \tag{14}$$

remains finite, where $|\mathbf{k}|$ is defined by

$$|\mathbf{k}|^2 = \sum_{i=1}^{d} k_i^2. \tag{15}$$

Consider now the finite part u_ε of the series (11) that extends over the multi-indices $\mathbf{k}$ inside the ball of radius $1/\varepsilon$ around the origin, for which

$$|\mathbf{k}| < \frac{1}{\varepsilon}. \tag{16}$$

Due to the orthonormality of the functions (9), u_ε is the best approximation of u by a linear combination of the selected basis functions. It holds

$$\|u - u_\varepsilon\|_0^2 \leq \varepsilon^{2s} \sum_{\mathbf{k}} |\mathbf{k}|^{2s} |\widehat{u}(\mathbf{k})|^2 = \varepsilon^{2s} |u|_s^2. \tag{17}$$

The number n of these basis functions grows like

$$n \sim \frac{1}{\varepsilon^d} \tag{18}$$

as ε goes to zero. This is out of every reach for higher space dimensions d, the curse of dimensionality. It can only be broken if one restricts oneself to a class of functions whose smoothness increases sufficiently fast with the space dimension d. At this place the mixed regularity comes into play. Consider functions u that possess corresponding weak partial derivatives and set

$$|u|_{1,\text{mix}}^2 = \int_Q \left| \frac{\partial^d u}{\partial x_1 \dots \partial x_d} \right|^2 \mathrm{d}\mathbf{x} \tag{19}$$

or, in terms of the expansion coefficients,

$$|u|_{1,\text{mix}}^2 = \sum_{\mathbf{k}} \left(\prod_{i=1}^{d} k_i \right)^2 |\widehat{u}(\mathbf{k})|^2. \tag{20}$$

Let u_ε^* be the function represented by the finite part of the series (11) that extends over the multi-indices $\mathbf{k}$ inside the hyperboloid given by

$$\prod_{i=1}^{d} k_i < \frac{1}{\varepsilon}, \tag{21}$$

instead of the ball (16). The L_2-error can then be estimated as

$$\|u - u_\varepsilon^*\|_0 \leq \varepsilon\, |u|_{1,\text{mix}} \tag{22}$$

and tends like $\mathcal{O}(\varepsilon)$ to zero. The dimension n of the space spanned by the functions (9) for which (21) holds, now increases, however, only like

$$n \sim |\log \varepsilon|^{d-1} \varepsilon^{-1}. \tag{23}$$

This shows that a comparatively slow growth of the smoothness can help to reduce the complexity substantially, an observation that forms the basis of the sparse grid or hyperbolic cross techniques; see [2] for an overview. Due to the presence of the logarithmic term, the applicability of such methods is, however, still limited to moderate space dimensions.

The rescue comes from the symmetry properties of the wave functions enforced by the Pauli principle. They represent a possibility to escape from this dilemma without forcing up the smoothness requirements further, which has first been noted by Hackbusch [5]. Consider functions u that are antisymmetric with respect to the exchange of their variables, i.e., that

$$u(\mathbf{P}\mathbf{x}) = \operatorname{sign}(\mathbf{P})\,u(\mathbf{x}) \tag{24}$$

holds for all permutation matrices $\mathbf{P}$. It is not astonishing that such symmetry properties are immediately reflected in the expansion (11). Let

$$\widetilde{\phi}(\mathbf{k},\mathbf{x}) = \frac{1}{\sqrt{d!}} \sum_{\mathbf{P}} \operatorname{sign}(\mathbf{P})\,\phi(\mathbf{k},\mathbf{P}\mathbf{x}) \tag{25}$$

be the renormalized, antisymmetric parts of the functions (9), where the sums extend over the $d!$ permutation matrices $\mathbf{P}$ of order d. The antisymmetrized functions (25) can be written as determinants

$$\frac{1}{\sqrt{d!}} \begin{vmatrix} \phi_{k_1}(x_1) & \dots & \phi_{k_d}(x_1) \\ \vdots & \ddots & \vdots \\ \phi_{k_1}(x_d) & \dots & \phi_{k_d}(x_d) \end{vmatrix} \tag{26}$$

and evaluated in this way. For the functions u in the given symmetry class, many terms in the expansion (11) can be combined. It finally collapses into

$$u(\mathbf{x}) = \sum_{k_1>\ldots>k_d} \big(u, \widetilde{\phi}(\mathbf{k},\cdot)\big)\,\widetilde{\phi}(\mathbf{k},\mathbf{x}), \tag{27}$$

where the expansion coefficients are the L_2-inner products of u with the corresponding functions (25). The number of basis functions needed to reach a given accuracy is reduced by more than the factor $d!$, a very significant gain for larger dimensions d.

It remains to count the number of the sequences $k_1 > k_2 > \ldots > k_d$ of natural numbers that satisfy the condition (21) and with that also the number of basis function (25) needed to reach the accuracy $\mathcal{O}(\varepsilon)$. To study the asymptotic behavior of the number of these sequences in dependence of the dimension d and the accuracy ε, it suffices when we restrict ourselves to the case $\varepsilon = 1/2^L$, with positive integers L. That is, we have to give bounds for the number of sequences $k_1 > \ldots > k_d$ for which

$$\prod_{i=1}^{d} k_i \le 2^L. \tag{28}$$

The problem to estimate this number has to do with the prime factorization of integers. To simplify this problem, we group the numbers k_i into levels and decompose the space of the trigonometric polynomials correspondingly. Let

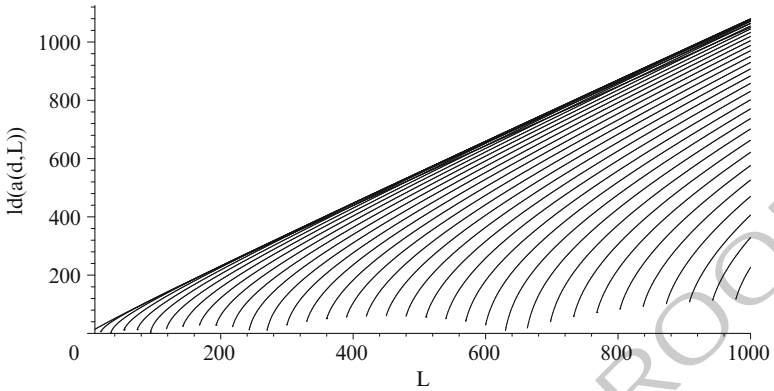

Fig. 1. The numbers $a^*(L)$ and $a(d,L)$ for $d = 10, 15, 20, \ldots, 175$

$$\ell(k_i) = \max\left\{ \ell \in \mathbb{Z} \,\middle|\, 2^\ell \le k_i \right\}. \tag{29}$$

An upper bound for the number of these sequences is then the number $a(d,L)$ of the sequences $k_1 > k_2 > \ldots > k_d$ of natural numbers for which

$$\prod_{i=1}^{d} 2^{\ell(k_i)} \le 2^L. \tag{30}$$

The numbers $a(d,L)$ can be calculated recursively; see [14] for details. A crude estimate yields $a(d,L) = 0$ if $L+1 < d$. Thus

$$a^*(L) := \max_{d \ge 1} a(d,L) = \max_{d \le L+1} a(d,L). \tag{31}$$

Figure 1 shows, in logarithmic scale, how the $a(d,L)$ behave compared to their joint least upper bound $a^*(L)$. It becomes obvious from this picture that this upper bound exceeds the actual dimensions for larger d by many orders of magnitude, the more the more the number d of variables increases. The joint least upper bound that is independent of d for the number of the sequences $k_1 > \ldots > k_d$ of natural numbers k_i for which (28) holds grows at least like $\sim 2^L$ since already for the case $d = 1$, there are 2^L such "sequences", namely those with values $k_1 = 1, \ldots, 2^L$. Figure 1 suggests conversely that the upper bound (31) for the number of these sequences does not grow much faster than $\sim 2^L$. This is in fact the case since the number of the decreasing infinite sequences $k_1 \ge k_2 \ge k_3 \ge \ldots$ of natural numbers for which

$$\prod_{i=1}^{\infty} 2^{\ell(k_i)} \le 2^L, \tag{32}$$

with L a given nonnegative integer, is bounded by

$$\sum_{\ell=0}^{L} p(\ell)\, 2^\ell, \tag{33}$$

where $p(\ell)$ denotes the partition number of ℓ, the number of possibilities of representing ℓ as sum of nonnegative integers without regard to the order. To show this, we observe that the number of these sequences is bounded by the number of sequences $k_1, k_2, k_3, \ldots$ of natural numbers for which at least their levels $\ell(k_1), \ell(k_2), \ldots$ decrease and that satisfy (32). We show that the expression (33) counts the number of these sequences. Let the integers $\ell_i = \ell(k_i)$ first be given. As there are 2^{ℓ_i} natural numbers k_i for which $\ell(k_i) = \ell_i$, namely $k_i = 2^{\ell_i}, \ldots, 2^{\ell_i+1} - 1$, there are

$$\prod_{i=1}^{\infty} 2^{\ell_i} = 2^{\ell}, \quad \ell = \sum_{i=1}^{\infty} \ell_i, \tag{34}$$

sequences $k_1, k_2, k_3, \ldots$ for which the $\ell(k_i)$ attain the prescribed values ℓ_i. The problem thus reduces to the question how many decreasing sequences of nonnegative integers ℓ_i exist that sum up to values $\ell \le L$, i.e., for which

$$\sum_{i=1}^{\infty} \ell_i = \ell. \tag{35}$$

This number is by definition the partition number $p(\ell)$ of the nonnegative integer ℓ. Every sequence $k_1 > k_2 > \ldots > k_d$ of natural numbers for which (28) holds can obviously be expanded to an infinite, decreasing sequence $k_1 \ge k_2 \ge k_3 \ge \ldots$ of natural numbers that satisfies the condition (32) by setting all $k_i = 1$ for $i > d$. The sum (33) represents therefore also an upper bound for the number of these sequences.

The partition number plays a big role in combinatorics. Hardy and Ramanujan have shown that it behaves asymptotically like

$$p(\ell) \sim \frac{\exp\left(\pi\sqrt{2\ell/3}\right)}{\ell} \tag{36}$$

as ℓ goes to infinity. We conclude that the upper bound (31) for the number of determinants needed to reach an error $\le 2^{-L}|u|_{1,\mathrm{mix}}$ behaves like

$$a^*(L) = (2^L)^{1+\delta(L)}, \quad 0 \le \delta(L) \le cL^{-1/2}, \tag{37}$$

where c is a constant that depends neither on L nor on the space dimension d or the function u. Using the representation of $a^*(L)$ from (31) and the recursively calculated values $a(d,L)$, the exponents $1 + \delta(L)$ can be calculated exactly. They decay for L ranging from 10 to 1,000 monotonely from 1.406 to 1.079. For $L = 100$, $1 + \delta(L) = 1.204$. In other words, the error tends faster to zero in the number n of determinants than

$$\sim \frac{1}{n^{1-\vartheta}} \tag{38}$$

for any given ϑ in the interval $0 < \vartheta < 1$. Not only does the convergence rate deteriorate neither with the dimension nor the number of variables, it behaves asymptotically almost as in the one-dimensional case. Similar results hold for partially antisymmetric functions as they occur in quantum mechanics.

4 Eigenfunction and Wavelet Expansions

The constructions sketched in the previous section transfer to the more complicated case of the expansion of the solutions of the electronic Schrödinger equation into correspondingly antisymmetrized tensor products of three-dimensional Hermite functions or other eigenfunctions of three-dimensional Schrödinger-like operators as in [14] or wavelets as in [16]. Indeed, it finally turns out that the convergence rate measured in terms of the number of basis functions involved does not deteriorate with the number of electrons and comes close to that for the two- or even one-particle case. We do not explicate the partly technical details here but explain how one can utilize the intermediate smoothness of the exponentially weighted solutions (8) to obtain optimal convergence rates.

Let e^{ψ} be exponential factor in (8). The argumentation starts from functions v whose exponentially weighted counterparts $e^{\psi}v$ are located in $H^{1,1}_{\mathrm{mix}}$, that is, have in contrast to the solutions of the Schrödinger equation full mixed regularity. The essential observation is that the norm $|||e^{\psi}v|||_{1,1}$ can be estimated by the sum of the weighted L_2-norms $\|e^{\psi}D^{\boldsymbol{\alpha}}v\|_0$ of the involved derivatives $D^{\boldsymbol{\alpha}}v$ of v and vice versa. This comes from the special structure of the function ψ. The norm $|||e^{\psi}v|||_{1,1}$ measures therefore the exponentially weighted L_2-norms of the involved derivatives of 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

$$\|v - T_n v\|_1 \lesssim n^{-q} \, |||e^{\psi}v|||_{1,1} \tag{39}$$

for all functions $v \in H^1$ for which $e^{\psi}v \in H^{1,1}_{\mathrm{mix}}$. 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 as those mentioned above modeled after the example from the last section. Another example is the expansion into tensor products of three-dimensional functions with given angular parts; see [14]. 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. The assumption (39) implies for the functions $u \in H^1$ for which $e^{\psi}u \in H^{\vartheta,1}_{\mathrm{mix}}$ for some $0 < \vartheta < 1$, the error estimate

$$\|u - T_n u\|_1 \lesssim n^{-\vartheta q} \, |||e^{\psi}u|||_{\vartheta,1}. \tag{40}$$

The proof utilizes that the spaces $H^{\vartheta,1}_{\mathrm{mix}}$, $0 < \vartheta < 1$, are interpolation spaces between the spaces $H^1 = H^{0,1}_{\mathrm{mix}}$ and $H^{1,1}_{\mathrm{mix}}$.

We conclude that for the case of the solutions u of the Schrödinger equation the H^1-error $\|u - T_n u\|_1$ tends faster to zero as $n^{-\vartheta q}$ for any $\vartheta < 3/4$. An estimate directly based on an estimate of their K-functional even shows that

$$\|u - T_n u\|_1 \lesssim \sqrt{\ln(n)}\, n^{-3/4q} \tag{41}$$

so that up to the logarithmic term only the factor $3/4$ gets lost compared to the case of full mixed regularity. The estimate is optimal, at least up to the logarithmic factor, and can in general not be improved further.

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