

Lecture Notes in Mathematics

Harry Yserentant

Regularity and Approximability of Electronic Wave Functions

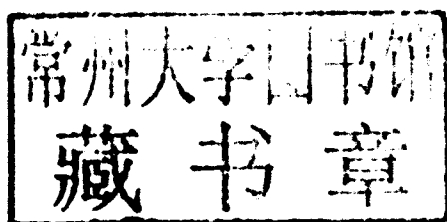
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Regularity and Approximability of Electronic Wave Functions



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Preface

The electronic Schrödinger equation describes the motion of N electrons under Coulomb interaction forces in a field of clamped nuclei. Solutions of this equation depend on $3N$ variables, three spatial dimensions for each electron. Approximating the solutions is thus inordinately challenging, and it is conventionally believed that a reduction to simplified models, such as those of the Hartree-Fock method or density functional theory, is the only tenable approach. This book seeks to convince the reader that this conventional wisdom need not be ironclad: the regularity of the solutions, which increases with the number of electrons, the decay behavior of their mixed derivatives, and the antisymmetry enforced by the Pauli principle contribute properties that allow these functions to be approximated with an order of complexity which comes arbitrarily close to that for a system of one or two electrons. The present notes arose from lectures that I gave in Berlin during the academic year 2008/09 to introduce beginning graduate students of mathematics into this subject. They are kept on an intermediate level that should be accessible to an audience of this kind as well as to physicists and theoretical chemists with a corresponding mathematical training. The text requires a good knowledge of analysis to the extent taught at German universities in the first two years of study, including Lebesgue integration and some basic facts on Banach and Hilbert spaces (completion, orthogonality, projection theorem, Lax-Milgram theorem, weak convergence), but no deeper knowledge of the theory of partial differential equations, of functional analysis, or quantum theory. I thank everybody with whom I had the opportunity to discuss the topic during the past years, my coworkers both from Tübingen and Berlin, above all Jerry Gagelman, who read this text very carefully, found many inconsistencies, and to whom I owe many hints to improve my English, and particularly my colleagues Hanns Ruder, who raised my awareness of the physical background, and Reinhold Schneider, who generously shared all his knowledge and insight into quantum-chemical approximation methods. The Deutsche Forschungsgemeinschaft supported my work through several projects, inside and outside the DFG-Research Center MATHEON. I dedicate this book to my sons Klaus and Max.

Berlin, September 2009

Harry Yserentant

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Chapter 1

Introduction and Outline

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

$$H = -\frac{1}{2} \sum_{i=1}^N \Delta_i - \sum_{i=1}^N \sum_{v=1}^K \frac{Z_v}{|x_i - a_v|} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|x_i - x_j|} \quad (1.1)$$

written down here in dimensionless form or atomic units. It acts on functions with arguments $x_1, \dots, x_N \in \mathbb{R}^3$, which are associated with the positions of the considered electrons. The a_v are the fixed positions of the nuclei and the positive values Z_v the charges of the nuclei in multiples of the absolute electron charge.

The mathematical theory of the Schrödinger equation for a system of charged particles is today a central, highly developed part of mathematical physics. Starting point was Kato's work [48] in which he showed that Hamilton operators of the given form fit into the abstract framework that was laid by von Neumann [64] a short time after Schrödinger [73] set up his equation and Born and Oppenheimer [11] simplified it. An important breakthrough was the Hunziker-van Winter-Zhislin theorem [46, 90, 98], which states that the spectrum of an atom or molecule consists of isolated eigenvalues $\lambda_0 \leq \lambda < \Sigma$ of finite multiplicity between a minimum eigenvalue λ_0 and a ionization bound Σ and an essential spectrum $\lambda \geq \Sigma$. The mathematical theory of the Schrödinger equation traditionally centers on spectral theory. Of at least equal importance in the given context are the regularity properties of the eigenfunctions, whose study began with [49]. For newer developments in this

direction, see [32] and [45]. Surveys on the mathematical theory of Schrödinger operators and the quantum N -body problem in particular are given in the articles [47, 75] and in the monograph [38].

Because of its high-dimensionality, it seems to be completely hopeless to attack the electronic Schrödinger equation directly. Dirac, one of the fathers of quantum theory, commented on this in [25] with the often quoted words, “the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” This situation has not changed much during the last eighty years, and depending on what one understands by soluble, it will never change. Dirac continued, “it therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.” Physicists and chemists followed Dirac’s advice and invented, during the previous decades, a whole raft of such methods of steadily increasing sophistication. The most prominent are the Hartree-Fock method that arose a short time after the advent of quantum mechanics, and its many variants, extensions, and successors, and the density functional based methods, that have been introduced in the sixties of the last century and are based on the observation that the ground state energy is completely determined by the electron density. These methods present themselves a challenge for mathematics. Lieb and Simon [60] proved the existence of a Hartree-Fock ground state and Lions [62] the existence of infinitely many solutions of the Hartree-Fock equations. The existence of solutions of the more general multiconfiguration Hartree-Fock equations was proven by Friesecke [33] and Lewin [59]. The singularities of the solutions of the Hartree-Fock equations at the positions of the nuclei have recently been studied by Flad, Schneider, and Schulze [31]. Schneider [72] gave an insightful interpretation and analysis of one of the most accurate methods of this type, the coupled cluster method. See [42] and the Nobel lectures of Kohn [51] and of Pople [66] for an overview on the present state of the art in quantum chemistry, and [16, 56–58] for more mathematically oriented expositions.

The current methods are highly successful and are routinely applied in practice, so that the goals Dirac formulated eighty years ago are today widely reached. Nevertheless the situation is not very satisfying from the point of view of a mathematician. This is because the success of many of these methods can only be explained by clever intuition. In the end, most of these methods resemble more simplified models than true, unbiased discretizations and, at least from the practical point of view, do not allow for a systematic improvement of the approximations. That is why mathematicians, encouraged by the progress in the approximation of high-dimensional functions, have recently tried to find points of attack to treat the electronic Schrödinger equation directly. Promising tools are tensor product techniques as they are developed on a broad basis in Wolfgang Hackbusch’s group at the Max Planck Institute in Leipzig. Beylkin and Mohlenkamp [10] apply such techniques to a reformulation of the electronic Schrödinger equation as an integral equation.

The present text intends to contribute to these developments. Aim is to identify structural properties of the electronic wave functions, the solutions of the electronic

Schrödinger equation, that will ideally enable breaking the curse of dimensionality. We start from ideas to the approximation of high-dimensional functions that emerged from the Russian school of numerical analysis and approximation theory [7, 53, 54, 76] and have since then been reinvented several times [23, 24, 97]. They are known under the name hyperbolic-cross or sparse-grid approximation. Since the work of Zenger [97], approaches of this kind have become increasingly popular in the numerical solution of partial differential equations. For a comprehensive survey of such techniques, see [15] and, as it regards their application to truly high-dimensional problems, [35]. Among the first papers in which direct application of such ideas has been tried for the Schrödinger equation are [34, 39, 43]. More recent attempts are [27, 28, 36, 37], and very recently the doctoral theses [40, 96]. The order of convergence that such methods can reach is limited since the involved basis functions do not align with the singularities caused by the electron-electron interaction [29, 30]. Nevertheless such methods have a high potential as our considerations will show, and be it only for the study of the complexity of electronic wave functions.

The principle behind these constructions can best be understood by means of a model problem, the L_2 -approximation of functions $u : \mathbb{R}^d \rightarrow \mathbb{R}$ that are odd and 2π -periodic in every coordinate direction on the cube $Q = [-\pi, \pi]^d$ by tensor products

$$\phi(k, x) = \prod_{i=1}^d \phi_{k_i}(x_i) \quad (1.2)$$

of the one-dimensional trigonometric polynomials $\phi_1, \phi_2, \phi_3, \dots$ given by

$$\phi_{k_i}(\xi) = \frac{1}{\sqrt{\pi}} \sin(k_i \xi). \quad (1.3)$$

Functions with the given properties that are square integrable over Q can be expanded into a multivariate Fourier series and possess therefore the representation

$$u(x) = \sum_k \hat{u}(k) \phi(k, x), \quad \hat{u}(k) = \int_Q u(x) \phi(k, x) dx, \quad (1.4)$$

where the sum extends over the multi-indices $k = (k_1, \dots, k_d) \in \mathbb{N}^d$ and its convergence has to be understood in the L_2 -sense. The speed of convergence of this series depends on that with which the expansion coefficients $\hat{u}(k)$ decay. Assume, for example, that u is continuously differentiable, which implies that

$$|u|_1^2 = \sum_{i=1}^d \int_Q \left| \frac{\partial u}{\partial x_i} \right|^2 dx = \sum_k \left(\sum_{i=1}^d k_i^2 \right) |\hat{u}(k)|^2 \quad (1.5)$$

remains bounded. Consider now the finite part u_ε of the series (1.4) that extends over the multi-indices k inside the ball of radius $1/\varepsilon$ around the origin, that is, for which

$$\sum_{i=1}^d k_i^2 < \frac{1}{\varepsilon^2}. \quad (1.6)$$

Due to the orthonormality of the functions (1.2), u_ε is the best approximation of u by a linear combination of the selected basis functions and satisfies the error estimate

$$\|u - u_\varepsilon\|_0^2 \leq \varepsilon^2 \sum_k \left(\sum_{i=1}^d k_i^2 \right) |\widehat{u}(k)|^2 = \varepsilon^2 \|u\|_1^2 \quad (1.7)$$

in the L_2 -norm. Unfortunately, the number of these basis functions grows like

$$\sim \frac{1}{\varepsilon^d} \quad (1.8)$$

for ε tending to zero, which is out of every reach for higher space dimensions d . The situation changes if one does not fix the smoothness of the functions to be approximated, but let it increase with the dimension. Assume, to avoid technicalities, that u possesses corresponding partial derivatives and that these are continuous and set

$$\|u\|_{1,\text{mix}}^2 = \int_Q \left| \frac{\partial^d u}{\partial x_1 \dots \partial x_d} \right|^2 dx = \sum_k \left(\prod_{i=1}^d k_i \right)^2 |\widehat{u}(k)|^2. \quad (1.9)$$

Let u_ε^* be the function represented by the finite part of the series (1.4) that extends over the multi-indices k now not inside a ball but inside the hyperboloid given by

$$\prod_{i=1}^d k_i < \frac{1}{\varepsilon}. \quad (1.10)$$

The L_2 -error can then, by the same reasons as above, be estimated as

$$\|u - u_\varepsilon^*\|_0^2 \leq \varepsilon^2 \sum_k \left(\prod_{i=1}^d k_i \right)^2 |\widehat{u}(k)|^2 = \varepsilon^2 \|u\|_{1,\text{mix}}^2 \quad (1.11)$$

and tends again like $\mathcal{O}(\varepsilon)$ to zero. The difference is that the dimension of the space spanned by the functions (1.2) for which (1.10) holds, now increases only like

$$\sim |\log \varepsilon|^{d-1} \varepsilon^{-1}. \quad (1.12)$$

This shows that a comparatively slow growth of the smoothness can help to reduce the complexity substantially, an observation that forms the basis of sparse grid techniques. Due to the presence of the logarithmic term, the applicability of such methods is, however, still limited to moderate space dimensions.

Because of the Pauli principle, physically admissible wave functions have typical symmetry properties that will later be discussed in detail. Such symmetry properties represent a possibility to escape from this dilemma without forcing up the smoothness requirements further, a fact that has first been noted by Hackbusch [39]

and is basic for the present work. Assume that the functions u to be approximated are antisymmetric with respect to the exchange of their variables, that is, that

$$u(Px) = \text{sign}(P)u(x) \quad (1.13)$$

holds for all permutation matrices P . It is not astonishing that symmetry properties such as the given one are immediately reflected in the expansion (1.4). Let

$$\tilde{\phi}(k, x) = \frac{1}{\sqrt{d!}} \sum_P \text{sign}(P) \phi(k, Px) \quad (1.14)$$

denote the renormalized, antisymmetric parts of the functions (1.2), where the sums extend over the $d!$ permutation matrices P of order d . By means of the corresponding permutations π of the indices $1, \dots, d$, they can be written as determinants

$$\frac{1}{\sqrt{d!}} \sum_{\pi} \text{sign}(\pi) \prod_{i=1}^d \phi_{k_i}(x_{\pi(i)}) \quad (1.15)$$

and easily evaluated in this way. For the functions u in the given symmetry class, many terms in the expansion (1.4) can be combined. It finally collapses into

$$u(x) = \sum_{k_1 > \dots > k_d} (u, \tilde{\phi}(k, \cdot)) \tilde{\phi}(k, x), \quad (1.16)$$

where the expansion coefficients are the L_2 -inner products of u with the corresponding functions (1.14). The number of basis functions needed to reach a given accuracy is reduced by more than the factor $d!$, a significant gain. It can be shown (see Chap. 8 for details) that the number of ordered sequences $k_1 > k_2 > \dots > k_d$ of natural numbers that satisfy the condition (1.10) and with that also the number of basis function (1.14) needed to reach the accuracy $\mathcal{O}(\varepsilon)$ does not increase faster than

$$\sim \frac{1}{\varepsilon^{1+\vartheta}}, \quad (1.17)$$

independent of d , where $\vartheta > 0$ is an arbitrarily chosen small number. In cases such as the given one the rate of convergence in terms of the number of basis functions needed to reach a given accuracy becomes independent of the space dimension.

The present work is motivated by these observations. It has the aim to transfer these techniques from our simple model problem to the electronic Schrödinger equation and to establish a mathematically sound basis for the development of numerical approximation methods. One may wonder that this can work considering all the singularities in the Schrödinger equation. The deeper reason for that is that the terms of which the interaction potentials are composed depend only on the coordinates of one or two electrons. This and the symmetry properties enforced by the Pauli principle suffice to show that the admissible solutions of the electronic Schrödinger equation fit into the indicated framework.

The Pauli principle is a basic physical principle that is associated with the indistinguishability of electrons and is independent of the Schrödinger equation. It is of fundamental importance for the structure of matter. Electrons have an internal property called spin that behaves in many respects like angular momentum. Although spin does not explicitly appear in the electronic Schrödinger equation, it influences the structure of atoms and molecules decisively. The spin σ_i of an electron can attain the two values $\pm 1/2$. Correspondingly, the true wave functions are of the form

$$\psi : (\mathbb{R}^3)^N \times \{-1/2, 1/2\}^N \rightarrow \mathbb{R} : (x, \sigma) \rightarrow \psi(x, \sigma), \quad (1.18)$$

that is, depend not only on the positions x_i , but also on the spins σ_i of the electrons. The Pauli principle states that only those wave functions ψ are admissible that change their sign under a simultaneous exchange of the positions x_i and x_j and the spins σ_i and σ_j of two electrons i and j , i.e., are antisymmetric in the sense that

$$\psi(Px, P\sigma) = \text{sign}(P)\psi(x, \sigma) \quad (1.19)$$

holds for arbitrary simultaneous permutations $x \rightarrow Px$ and $\sigma \rightarrow P\sigma$ of the electron positions and spins. The Pauli principle forces the admissible wave functions to vanish where $x_i = x_j$ and $\sigma_i = \sigma_j$ for $i \neq j$. Thus the probability that two electrons i and j with the same spin meet is zero, a purely quantum mechanical effect. The admissible solutions of the electronic Schrödinger equation are those that are components

$$u : (\mathbb{R}^3)^N \rightarrow \mathbb{R} : x \rightarrow \psi(x, \sigma) \quad (1.20)$$

of an antisymmetric wave function (1.18). They are classified by the spin vector σ , being antisymmetric with respect to every permutation of the electrons that keeps σ fixed. We will discuss these interrelations in Chap. 4 and will study the different components (1.20) separately. Let σ be a spin vector that remains fixed throughout, and let I_- and I_+ be the sets of the indices i of the electrons with spin $\sigma_i = -1/2$ and $\sigma_i = +1/2$. To both index sets we assign a norm that can best be expressed in terms of the Fourier transforms of the considered functions and is given by

$$\|u\|_{\pm}^2 = \int \left(1 + \sum_{i=1}^N \left|\frac{\omega_i}{\Omega}\right|^2\right) \prod_{i \in I_{\pm}} \left(1 + \left|\frac{\omega_i}{\Omega}\right|^2\right) |\hat{u}(\omega)|^2 d\omega. \quad (1.21)$$

These two norms are combined to a norm that is defined by

$$\|u\|^2 = \|u\|_-^2 + \|u\|_+^2. \quad (1.22)$$

The momentum vectors $\omega_i \in \mathbb{R}^3$ form together the vector $\omega \in (\mathbb{R}^3)^N$. Their euclidean length is $|\omega_i|$. The quantity Ω fixes a characteristic length scale that will be discussed below. The norm given by (1.22) is related to the norm (1.9) and measures mixed derivatives whose order increases with the number of the electrons. It is

first only defined for the functions in the space $\mathcal{D}(\sigma)$ of the infinitely differentiable functions u with compact support that are antisymmetric in the described sense but can be extended to the space $X^1(\sigma)$, the completion of $\mathcal{D}(\sigma)$ under this norm. The space $X^1(\sigma)$ is a subspace of the Sobolev space H^1 consisting of functions that possess high-order mixed weak derivatives.

Our first result, which originates in the papers [92, 94] of the author and will be proven in Chap. 6, is that the eigenfunctions u of the Schrödinger operator (1.1) of corresponding (anti-)symmetry for eigenvalues below the ionization threshold, i.e., the infimum of the essential spectrum, are contained in $X^1(\sigma)$. This means that they possess mixed weak derivatives whose order increases with the number of electrons. The norm (1.22) of these eigenfunctions can be explicitly estimated in terms of the L_2 -norm of the eigenfunctions. If $\Omega \geq C\sqrt{N}\max(N, Z)$ is chosen

$$\|u\| \leq 2\sqrt{c} \|u\|_0 \quad (1.23)$$

holds, where Z denotes the total charge of the nuclei and C is a generic constant depending neither on the number of the electrons nor on the number, the position, nor the charge of the nuclei. Conversely, there is a minimum $\Omega \leq C\sqrt{N}\max(N, Z)$ such that (1.23) holds for all these eigenfunctions independent of the associated eigenvalue. There are hints that this Ω behaves like the square root of the ground state energy. The estimate (1.23) depends on the partial antisymmetry of the eigenfunctions, particularly on the fact that the admissible wave functions vanish at many of the singular points of the electron-electron interaction potential, everywhere where electrons with the same spin meet. Only small portions of the frequency domain thus contribute substantially to the admissible eigenfunctions. This remark can be quantified with help of the notion of hyperbolic crosses, hyperboloid-like regions in the momentum space that consist of those ω for which

$$\prod_{i \in I_-} \left(1 + \left|\frac{\omega_i}{\Omega}\right|^2\right) + \prod_{i \in I_+} \left(1 + \left|\frac{\omega_i}{\Omega}\right|^2\right) \leq \frac{1}{\varepsilon^2}, \quad (1.24)$$

with $\varepsilon > 0$ given. If u_ε denotes that part of the wave function whose Fourier transform coincides with that of u on this domain and vanishes outside of it, the H^1 -error

$$\|u - u_\varepsilon\|_1 \leq \varepsilon \|u - u_\varepsilon\| \leq \varepsilon \|u\| \quad (1.25)$$

tends to zero like $\mathcal{O}(\varepsilon)$ with increasing size of the crosses. This estimate is a first counterpart to the estimate (1.11) in the analysis of our model problem.

These observations, however, do not suffice to break the curse of dimensionality. As is known from [20] and is proven in Chap. 5, the eigenfunctions u for eigenvalues λ below the infimum $\Sigma(\sigma)$ of the essential spectrum decay exponentially, the decay rate depending on the eigenfunction. Let $R > 0$ satisfy the estimate

$$\frac{1}{2R^2} < \frac{\Sigma(\sigma) - \lambda}{N}, \quad (1.26)$$

that is, let it be big enough compared to the size of the gap between λ and $\Sigma(\sigma)$, and define the correspondingly exponentially weighted eigenfunction as

$$\tilde{u}(x) = \exp\left(\sum_{i=1}^N \left|\frac{x_i}{R}\right|\right) u(x). \quad (1.27)$$

The weighted eigenfunction \tilde{u} is then not only square integrable, as follows from [20], it also belongs to the space $X^1(\sigma)$ and moreover satisfies the estimate

$$\|\tilde{u}\| \leq 2\sqrt{e} \|\tilde{u}\|_0. \quad (1.28)$$

This is shown in Chap. 6 along with the proof of (1.23). The parameter Ω scaling the frequencies is the same as before, common to all eigenfunctions for eigenvalues below the essential spectrum. In the limit of R tending to infinity (1.28) reduces to the estimate (1.23). With that the corresponding mixed derivatives of the given eigenfunctions decay exponentially in the L_2 -sense. The estimate relates the decay of the eigenfunctions in the position and the frequency space to one another, i.e., their spatial extension and the length scales on which they vary. Estimates like (1.23) and (1.28) are characteristic for products of three-dimensional orbitals. Our results show that the solutions of the full Schrödinger equation behave in the same way and justify in this sense the picture of atoms and molecules that we have in our minds.

Estimates like (1.28) have striking consequences for the approximability of electronic wave functions and limit the complexity of the quantum-mechanical N -body problem. The idea is to expand the eigenfunctions of the electronic Schrödinger operator (1.1) into products of the eigenfunctions of three-dimensional operators

$$-\Delta + V, \quad \lim_{|x| \rightarrow \infty} V(x) = +\infty, \quad (1.29)$$

like the Hamilton operator of the harmonic oscillator with a locally square integrable potential $V \geq 0$, tending to infinity for its argument tending to infinity. The essential spectrum of such operators is empty so that they possess a complete L_2 -orthonormal system of eigenfunctions $\phi_1, \phi_2, \phi_3, \dots$ for eigenvalues $0 < \lambda_1 \leq \lambda_2 \leq \dots$. Every L_2 -function $u : \mathbb{R}^{3N} \rightarrow \mathbb{R}$ can therefore be represented as L_2 -convergent series

$$u(x) = \sum_{k \in \mathbb{N}^N} \tilde{u}(k) \prod_{i=1}^N \phi_{k_i}(x_i), \quad \tilde{u}(k) = \left(u, \prod_{i=1}^N \phi_{k_i} \right). \quad (1.30)$$

The speed of convergence of this expansion is examined in Chaps. 7 and 8 for the given eigenfunctions u of the Schrödinger operator (1.1) under the condition

$$V(x_i) \leq V_i^*(x)^2, \quad V_i^*(x) = \frac{\Lambda_0}{R} \exp\left(\left|\frac{x_i}{R}\right|\right), \quad (1.31)$$

limiting the growth of the potential V , with R the length scale from (1.26) describing the decay of the considered eigenfunctions and Λ_0 a constant basically independent of R . The result can again be best described in terms of a kind of norm estimate

$$\sum_k \left(\sum_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \right) \left(\prod_{i \in I_-} \frac{\lambda_{k_i}}{\Omega^2} + \prod_{i \in I_+} \frac{\lambda_{k_i}}{\Omega^2} \right) |\widehat{u}(k)|^2 \leq 4(u, Wu), \quad (1.32)$$

where the weight function $W = W_- + W_+$ is composed of the two parts

$$W_{\pm} = \left(1 + \sum_{i=1}^N \left| \frac{V_i^*}{\Omega} \right|^2 \right) \prod_{i \in I_{\pm}} \left(1 + \left| \frac{V_i^*}{\Omega} \right|^2 \right) \quad (1.33)$$

and Ω chosen as in the estimates (1.23) or (1.28). Interestingly, the right hand side of this estimate solely depends on the decay behavior of the considered eigenfunction.

The crucial point is the appearance of the two products of the eigenvalues λ_k in the estimate (1.32). These products grow similar to factorials. The reason is that the eigenvalues λ_k of corresponding operators (1.29) increase polynomially like

$$\lambda_k \gtrsim k^{\alpha/3} \quad (1.34)$$

for potentials that grow sufficiently fast, at least as fast as polynomials. The three comes from the fact that we start from an expansion into products of three-dimensional eigenfunctions. The constant $\alpha < 2$ is related to the growth behavior of the potential V . It can come arbitrarily close to $\alpha = 2$ for correspondingly chosen potentials. Let $\varepsilon > 0$ be given and consider the finite dimensional space that is spanned by the correspondingly antisymmetrized tensor products of the three-dimensional eigenfunctions ϕ_{k_i} for which the associated eigenvalues λ_{k_i} satisfy the estimate

$$\prod_{i \in I_-} \frac{\lambda_{k_i}}{\Omega^2} + \prod_{i \in I_+} \frac{\lambda_{k_i}}{\Omega^2} < \frac{1}{\varepsilon^2}. \quad (1.35)$$

Let u_{ε} be the L_2 -orthogonal projection of one of the given solutions u of the Schrödinger equation onto this space. Moreover, let

$$\|u\|^2 = \sum_k \left(\sum_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \right) |\widehat{u}(k)|^2. \quad (1.36)$$

Since u_{ε} is the part of the expansion (1.30) of u associated with the selected product functions, respectively the eigenvalues λ_{k_i} for which (1.35) holds,

$$\|u - u_{\varepsilon}\| \leq \varepsilon \|u - u_{\varepsilon}\| \leq \varepsilon \|u\|. \quad (1.37)$$

As the norm given by (1.36) dominates the H^1 -norm up to a rather harmless constant, this means that u_{ε} approximates the solution with an H^1 -error of order ε if one

lets ε tend to zero. The parameter ε determines the size of the hyperbolic crosses (1.35). Therefore only a very small portion of the product eigenfunctions substantially contributes to the considered wave functions and a surprisingly high rate of convergence, related to the space dimension $3N$, can be achieved.

One can even go a step further. Assume that the potential V in the three-dimensional operator (1.29) is rotationally symmetric. The eigenfunctions, now labeled by integers $n, \ell \geq 0$ and $|m| \leq \ell$, are then of the form

$$\phi_{n\ell m}(x) = \frac{1}{r} f_{n\ell}(r) Y_{\ell}^m(x), \quad r = |x|, \quad (1.38)$$

where the radial parts $f_{n\ell}$ as well as the assigned eigenvalues $\lambda_{n\ell}$ do not depend on the index m and the Y_{ℓ}^m are the spherical harmonics, functions that are homogeneous of degree zero and thus depend only on the angular part x/r of x . The L_2 -orthogonal expansion (1.30) of a square integrable function $u : (\mathbb{R}^3)^N \rightarrow \mathbb{R}$ becomes then

$$u(x) = \sum_{n,\ell,m} \hat{u}(n,\ell,m) \prod_{i=1}^N \phi_{n_i\ell_i m_i}(x_i), \quad (1.39)$$

where n, ℓ , and m are multi-indices here. Define now the L_2 -orthogonal projections

$$(Q(\ell, m)u)(x) = \sum_n \hat{u}(n, \ell, m) \prod_{i=1}^N \phi_{n_i\ell_i m_i}(x_i) \quad (1.40)$$

in which the angular parts are kept fixed and the sum extends only over the corresponding radial parts. These projections are in fact independent of the chosen three-dimensional operator and can be defined without recourse to the given eigenfunction expansion. They map the Sobolev space H^1 into itself. For all functions in H^1

$$\|u\|_1^2 = \sum_{\ell, m} \|Q(\ell, m)u\|_1^2, \quad (1.41)$$

as is shown in Chap. 9. The point is that for the eigenfunctions u of the electronic Schrödinger operator (1.1) of corresponding antisymmetry the expression

$$\sum_{\ell} \sum_m \left\{ \prod_{i \in I_-} (1 + \ell_i(\ell_i + 1)) + \prod_{i \in I_+} (1 + \ell_i(\ell_i + 1)) \right\} \|Q(\ell, m)u\|_1^2 \quad (1.42)$$

remains finite. This is another important consequence from the regularity theory from Chap. 6. It states that only few of the projections contribute significantly to an admissible solution of the electronic Schrödinger equation and estimates the speed of convergence of the expansion (1.39) in terms of the angular momentum quantum numbers ℓ_i . To reach an H^1 -error of order $\mathcal{O}(\varepsilon)$ hence it suffices to restrict oneself to the contributions of the tensor products of eigenfunctions $\phi_{n_i\ell_i m_i}$ for which

$$\prod_{i \in I_-} (1 + \ell_i(\ell_i + 1)) + \prod_{i \in I_+} (1 + \ell_i(\ell_i + 1)) < \frac{1}{\varepsilon^2}, \quad (1.43)$$

$$\prod_{i \in I_-} \frac{\lambda_{n_i \ell_i}}{\Omega^2} + \prod_{i \in I_+} \frac{\lambda_{n_i \ell_i}}{\Omega^2} < \frac{1}{\varepsilon^2}, \quad (1.44)$$

provided the potential V is adapted as described to the considered eigenfunction. The condition (1.43) represents an additional selection principle that can help substantially reduce the number of the antisymmetrized tensor products of eigenfunctions that are needed to reach a given accuracy. The expansion into tensor products of Gauss functions forms an example for the efficacy of such measures.

The final result is truly surprising. Our estimates demonstrate that the rate of convergence expressed in terms of the number of correspondingly antisymmetrized tensor products of the three-dimensional eigenfunctions involved astonishingly does not deteriorate with the space dimension $3N$ or the number N of electrons. It is almost the same as that for a one-electron problem for the case that all electrons have the same spin, and almost the same as that for a problem with two electrons otherwise. What that means for the numerical solution of the Schrödinger equation is not clear so far, but our considerations show at least that the complexity of the quantum-mechanical N -body problem is much lower than generally believed.

Keeping the intended audience in mind, the exposition starts with a short chapter on Fourier analysis and spaces of weakly differentiable functions. The third chapter gives a short introduction to quantum mechanics that is tailored to the later needs. An interesting point for physicists and chemists might be that we start from the weak form of the Schrödinger equation, an approach that is common in the theory of partial differential equations but less in the given context. Chapter 4 deals with the electronic Schrödinger equation itself, formulates it precisely, and embeds it into a functional analytic framework. As indicated we consider the spin components of the eigenfunctions separately and do not exploit the symmetry properties of the problem to the maximum extent. This approach is enforced by the distinct regularity properties of the components. Chapter 5 contains a short introduction to some notions from spectral theory, that are rewritten here in terms of the bilinear forms underlying the weak form of the eigenvalue problem, and discusses the Rayleigh-Ritz method for the approximate calculation of the eigenvalues and eigenfunctions. We characterize the infimum of the essential spectrum in the spirit of Agmon [3] and Persson [65] and prove a simple but for us basic result on the exponential decay of the eigenfunctions. The Chaps. 6 to 9 form the core of this work. They contain a lot of unpublished material going far beyond [92] and [94]. The results we have just sketched are derived and proven there in detail.