REGULARITY PROPERTIES OF WAVEFUNCTIONS AND THE COMPLEXITY OF THE QUANTUM-MECHANICAL N-BODY PROBLEM

HARRY YSERENTANT *

Abstract. This paper considers the electronic Schrödinger equation of quantum chemistry that 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. Here we indicate why 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, dependent on the spin configuration.

Key words. Schrödinger equation, N-body problem, regularity, computational complexity

AMS subject classifications. 35Q40, 35B65, 81V70, 68Q17

1. Introduction. The approximation of high-dimensional functions, might 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 or machine learning and computational finance, but first of all in the sciences. A high-dimensional function, of a big number of variables, carries a lot of information. Imagine a cubic grid with 10 grid points in each coordinate direction, which is a simple object for $d = 1, 2$, or 3 space dimensions and is fixed there by $10^d = 10, 100$, or 1000 values. The situation dramatically changes for high space dimensions d. For $d = 60$, to give an example, the number of values already exceeds the number of atoms of which the earth is composed by orders of magnitude. This exponential growth is often denoted as curse of dimensionality. Such an amount of data can neither be generated nor administrated nor interpreted. Fortunately, the true content of information that is encoded in high-dimensional functions coming from applications is normally much smaller. The task of mathematics is to provide techniques and tools that allow to extract this information. The principle is as simple as obvious. One has to restrict the class of possible solutions on the basis of the properties of the considered system, so far that methods tailored to their structure no longer suffer from an exponential growth of work and storage when increasing the accuracy demands. It is shown in the present paper that one of the most notorious and probably most complicated problems of this type, the electronic Schrödinger equation, can at least in theory be tackled in this manner.

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. The much slower motion of the nuclei is usually separated from that of the electrons. This results in the electronic Schrödinger equation,

* Institut für Mathematik, TU Berlin, 10623 Berlin, Germany (yserentant@math.tu-berlin.de)
The author was partially supported by *Deutsche Forschungsgemeinschaft* through the DFG Research Center MATHEON *Mathematics for Key Technologies* in Berlin

the problem to find the eigenvalues and eigenfunctions of the Hamilton operator

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

written here in dimensionless form or atomic units. It acts on functions with arguments $x_1, \ldots, x_N \in \mathbb{R}^3$, the coordinates of given N electrons; the positions $a_\nu \in \mathbb{R}^3$ of the nuclei are kept fixed. The positive values Z_ν are the charges of the nuclei. For an introduction to quantum mechanics, see textbooks like [3], [47], or [57] and [58].

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 [35] 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 [53] set up his equation and Born and Oppenheimer [6] simplified it, treating the motion of the nuclei and electrons separately. An important breakthrough was the Hunziker-van Winter-Zhislin theorem [33], [63], [71], 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 are in the given context the regularity properties of the eigenfunctions, whose study began with [36]. For newer developments in this direction, see [21], [32], and the literature cited therein. Surveys on the development of the mathematical theory of Schrödinger operators and the quantum N-body problem in particular are given in [34] and [55].

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 this in [15] 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 did not much change during the last seventy 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 last decades a whole raft of such methods of steadily increasing sophistication. The most prominent are presumably the Hartree-Fock method, that came up 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 [44] proved the existence of a Hartree-Fock ground state and Lions [46] 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 [22] and Lewin [43]. 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 [20]. See [30] and the Nobel lectures [37] of Kohn and [50] of Pople for an overview on the present state of the art in quantum chemistry, and [8] and [40], [41], and [42] for more mathematically oriented expositions.

The present methods are highly successful and are routinely applied in practice, so that the goals Dirac formulated almost seventy years ago are widely reached. But from the point of view of a mathematician they have a decisive drawback. In the end they represent simplified models and do not allow for a systematic improvement of the approximate solutions. In other words, they are no true, unbiased discretizations of the electronic Schrödinger equation in the sense of numerical analysis. This is the reason 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. A promising approach is developed by Beylkin and Mohlenkamp [5] and at the Max Planck Institute in Leipzig in Wolfgang Hackbusch's group, see [9], for example. The idea is to approximate the wavefunctions, the high-dimensional solutions of the Schrödinger equation, similarly as in the multiconfiguration Hartree-Fock method by sums of tensor products of three-dimensional functions. These tensor product approximations are, however, not derived from a variational principle as in Hartree-Fock methods, but from a reformulation of the electronic Schrödinger equation as an integral equation. The central observation on which these approaches rely is that the kernels of the corresponding integral operators can themselves be approximated by finite sums of separable functions.

A second line starts from ideas that emerged from the Russian school of numerical analysis and approximation theory [4], [38], [39], [56] and have since then been reinvented several times [13], [14], [70], the idea of hyperbolic-cross or sparse-grid approximation. Since the work of Zenger [70], approaches of this kind have become increasingly popular in the numerical solution of partial differential equations. For a comprehensive survey of such techniques, see [7] and, as it regards their application to truly high-dimensional problems, [25]. Among the first papers in which such ideas have been applied to the Schrödinger equation are [23], [28], and [31]. More recent attempts are [16] and [17] and first of all [26] and [27]. Although the order of convergence that can be reached with such methods is limited since the involved basis functions do not align with the singularities caused by the electron-electron interaction [18], [19], they have a high potential as our considerations will show.

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

$$\psi(k, x) \;=\; \prod_{i=1}^{d} \phi_{k_i}(x_i) \tag{1.2}$$

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

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

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

$$u(x) \;=\; \sum_{k} \widehat{u}(k)\psi(k, x), \quad \widehat{u}(k) \;=\; \int_Q u(x)\psi(k, x)\, dx, \tag{1.4}$$

where the sum extends over the multi-indices $k = (k_1, \ldots, k_d) \in \mathbb{N}^d$ and its convergence has to be understood in the L_2-sense. The speed of convergence of this series

depends on the velocity with which the expansion coefficients $\widehat{u}(k)$ decay. Assume, for example, that u is continuously differentiable, which implies that

$$|\,u\,|_1^2 \;=\; \sum_{i=1}^{d} \int_Q \Big|\frac{\partial u}{\partial x_i}\Big|^2 dx \;=\; \sum_k \Big(\sum_{i=1}^{d} k_i^2\Big)|\widehat{u}(k)|^2 \tag{1.5}$$

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

$$\sum_{i=1}^{d} k_i^2 \;<\; \frac{1}{\varepsilon^2}. \tag{1.6}$$

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 L_2-error estimate

$$\|u - u_\varepsilon\|_0^2 \;\le\; \varepsilon^2 \sum_k \Big(\sum_{i=1}^{d} k_i^2\Big)|\widehat{u}(k)|^2 \;=\; \varepsilon^2 |\,u\,|_1^2. \tag{1.7}$$

Unfortunately, the number of these basis functions grows like

$$\sim \frac{1}{\varepsilon^d} \tag{1.8}$$

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 the corresponding partial derivatives and that these are continuous and set

$$|\,u\,|_{1,\mathrm{mix}}^2 \;=\; \int_Q \Big|\frac{\partial^d u}{\partial x_1 \ldots \partial x_d}\Big|^2 dx \;=\; \sum_k \Big(\prod_{i=1}^{d} k_i\Big)^2 |\widehat{u}(k)|^2. \tag{1.9}$$

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

$$\prod_{i=1}^{d} k_i \;<\; \frac{1}{\varepsilon}. \tag{1.10}$$

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

$$\|u - u_\varepsilon^*\|_0^2 \;\le\; \varepsilon^2 \sum_k \Big(\prod_{i=1}^{d} k_i\Big)^2 |\widehat{u}(k)|^2 \;=\; \varepsilon^2 |\,u\,|_{1,\mathrm{mix}}^2 \tag{1.11}$$

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

$$\sim\; |\log \varepsilon\,|^{d-1}\, \varepsilon^{-1}. \tag{1.12}$$

This shows that already a comparatively slow growth of the smoothness can help to reduce the complexity substantially, an observation that forms the basis of sparse grid- or hyperbolic cross space 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 wavefunctions have typical symmetry properties, as they will be discussed below 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 [28] 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

$$u(Px) \;=\; \mathrm{sign}(P)u(x) \tag{1.13}$$

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

$$\widetilde{\psi}(k,x) \;=\; \frac{1}{\sqrt{d\,!}} \sum_{P} \mathrm{sign}(P)\psi(k,Px) \tag{1.14}$$

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

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

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

$$u(x) \;=\; \sum_{k_1>\ldots>k_d} \big(u, \widetilde{\psi}(k,\,\cdot\,)\big)\, \widetilde{\psi}(k,x), \tag{1.16}$$

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 section 12) that the number of ordered sequences $k_1 > k_2 > \ldots > k_d$ 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

$$\sim\; \frac{1}{\varepsilon^{1+\vartheta}}, \tag{1.17}$$

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 article 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 approximation methods that are based on such or similar ideas. One may wonder that this can work remembering 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 and do not affect the other variables essentially. This and the Pauli principle discussed below, that restricts the class of the physically admissible wavefunctions substantially, suffice to show that the admissible solutions of the electronic Schrödinger equation fit into the indicated framework and to break the curse of dimensionality at least in the sense of complexity theory.

The long chain of arguments that will finally lead to these results is organized as follows. In section 2, the eigenvalue problem for the electronic Schrödinger operator is precisely formulated and put into a variational framework such as in the L_2-theory of second-order linear elliptic differential equations. This approach is not as common as the operator theoretic approach, but is very natural from a physical point of view since it starts from a quadratic form representing the total energy of the system. The solution space naturally associated with this quadratic or the associated bilinear form is the Sobolev space H^1, which is the largest subspace of L_2 for which the expectation value of the kinetic energy can be given a meaning. The main technical tool in this section (and in some sense for the rest of this paper as well) is the classical Hardy inequality in three space dimensions, for which a proof is given.

Section 3 deals with the Pauli principle that fixes the symmetry properties of the wavefunctions under the exchange of the electrons and is closely linked to an internal property of the electrons, the spin. The Pauli principle is a basic physical principle that is independent of the Schrödinger equation and of fundamental importance for the structure of matter. The Pauli principle excludes wavefunctions that are not antisymmetric in a specific sense. Remembering our model problem analysis, it represents a basic building block for the construction of approximation methods of low complexity. Since wavefunctions that obey the Pauli principle vanish at many of the singular points of the electron-electron interaction potential, it enforces a higher regularity of the eigenfunctions than could otherwise be expected, a fact that we utilize essentially. Based on symmetry considerations the overall spin-dependent problem is decomposed in section 3 into a small number of subproblems that are adapted to the regularity properties of the eigenfunctions.

Section 4 is centered around the exponential decay of the eigenfunctions, that makes bound states what they are, and that has been thoroughly studied during the seventies and eighties of the last century. One of the first results of this type is due to O'Connor [48], who showed that the solutions of the electronic Schrödinger equation decay exponentially in the L_2-sense. Since this kind of exponential decay is a basic building block for the further discussion, and because of the survey character of this article, we give a short, comparatively elementary proof of O'Connor's theorem that follows the lines given in [1] and takes the Pauli principle into consideration. Theorem 4.3 of this section, in which a differential equation for the appropriately exponentially weighted eigenfunctions is set up, is central to the further argumentation. In some sense, the present paper focuses on a regularity theory for this modified eigenvalue problem in spaces involving high-order mixed weak derivatives. The corresponding framework is fixed in section 5. Particularly the norms and functions spaces on which our regularity theory relies are introduced in this section.

Sections 6 and 7 are of purely technical character, but form the key to our argumentation. They deal with the singular low-order parts in the differential operators that are estimated in terms of the norms introduced in section 5 involving high-order mixed derivatives. In section 6, the one-particle terms are treated, which is the easy part for which the classical Hardy inequality essentially suffices. The estimates in this section are independent of the Pauli principle. This is no longer the case in section 7, that deals with the terms resulting from the electron-electron interaction. The much harder singularities occurring there can only be mastered with help of properties of the wavefunctions that are enforced by the Pauli principle.

The estimates from section 6 and section 7 for the singular low-order parts form the basis for the proof of our central regularity results (Theorem 8.7 and Theorem 8.9)

in section 8. These results state that the unweighted and exponentially weighted eigenfunctions for eigenvalues below the ionization threshold indeed possess the desired square integrable high-order mixed weak derivatives. They show moreover that these solutions of the electronic Schrödinger equation can be controlled by their low-frequency parts. Rather explicit estimates for the norms of the mixed derivatives in terms of an intrinsic length scale that describes the oscillatory behavior of the solutions are given. The given solutions are therefore supported essentially only on small, hyperboloid-like subregions of the frequency- or momentum space. They behave in this respect very much like products of three-dimensional orbitals, which roughly justifies the picture that we have of atoms and molecules. The discussion in the sections 6, 7, and 8 is in part based on two former papers [67], [69] of the author, in which the case of the unweighted eigenfunctions has been treated. The idea behind the proofs is to show that the solutions of the given second-order problem and a corresponding high-order problem coincide, a technique that works in this form only for problems that are formulated on the whole space.

In section 9, the sharpness of these estimates is discussed by the example of atoms. The main tool in this section is the virial theorem that establishes a correspondence between the expectation values of the kinetic and the total energy, that is, between between the L_2-norm of the gradient of a normed solution and the corresponding eigenvalue, and fixes in this way the length scale on which this solution varies.

In section 10, we approach our goal to transfer the technique just discussed for the model problem to the Schrödinger equation. The idea is to expand the wavefunctions in terms of tensor products of the eigenfunctions of three-dimensional Schrödinger operators with potentials that tend to infinity for the argument tending to infinity, so-called confinement potentials in the language of physics. The central result of this section is Theorem 10.7, which actually imitates the effects that we observed for the model problem. Its proof is fundamentally based on the regularity theorems from section 8 for the exponentially weighted eigenfunctions. An interesting point is that the right hand side of the corresponding estimate in Theorem 10.7 no longer depends on the derivatives of the solutions, but only on their decay behavior.

The speed of convergence of the expansions from section 10 is in the end determined by the speed with which the eigenvalues of the three-dimensional operators, on which the construction is based, tend to infinity. The eigenvalue distribution of second-order elliptic differential operators such as they enter here has been examined for a long time, beginning with the work of Weyl [66] and of Courant and Hilbert [11]. A standard reference is [59]. It is well-known that the growth rate of these eigenvalues is bounded from above by the rate for the case of the Laplace operator on three-dimensional bounded domains. One cannot completely reach this bound, but can come arbitrarily close to it. This is briefly proven in section 11.

In section 12, finally the complexity of the N-particle electronic Schrödinger equation is discussed on the basis of the regularity theory developed in this article, or more precisely on the basis of Theorem 10.7 and the growth behavior of the eigenvalues of the given three-dimensional operators. The result is surprising. The rate of convergence in terms of the number of correspondingly antisymmetrized products of the three-dimensional eigenfunctions does not deteriorate with an increasing number of electrons. The complexity of the quantum-mechanical N-body problem is almost the same as that for a one-electron problem for the case that all particles 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.

2. The variational formulation of the eigenvalue problem. Before we can examine the regularity of the eigenfunctions, we have to give the eigenvalue problem a precise mathematical meaning. In particular, we have to fix, explicitly or implicitly, the behavior of the eigenfunctions at the singularities of the interaction potentials and at infinity. We start from two properties that are intimately linked to the physical interpretation of the wavefunctions. First, a physically meaningful wavefunction

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : (x_1, \dots, x_N) \to u(x_1, \dots, x_N) \tag{2.1}$$

needs to be square integrable. Its L_2-norm given by

$$\|u\|_0^2 \;=\; \int |u(x)|^2 \, dx \tag{2.2}$$

is usually normalized to one; the integral of the function $x \to |u(x)|^2$ over a subdomain of the $\mathbb{R}^{3N}$ then represents the probability that the electrons are located in this part of the configuration space. Secondly, the expectation value

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

of the kinetic energy, that is, the H^1-seminorm given by

$$|\,u\,|_1^2 \;=\; \int |(\nabla u)(x)|^2 \, dx \tag{2.4}$$

must attain a finite value. The natural solution space of the eigenvalue problem is therefore the Hilbert space $H^1(\mathbb{R}^{3N})$, that consists of the square integrable functions (2.1) with square integrable first-order weak partial derivatives and that is equipped with the H^1-norm given by the expression

$$\|u\|_1^2 \;=\; \|u\|_0^2 + |\,u\,|_1^2. \tag{2.5}$$

Much easier to handle than the functions in $H^1(\mathbb{R}^{3N})$ or shortly H^1 are the infinitely differentiable functions (2.1) that have a compact support. We denote the space of these functions by $\mathcal{D}$. The functions in $\mathcal{D}$ form a dense subset of H^1. Alternatively, H^1 can therefore be considered as completion of $\mathcal{D}$ under the norm (2.5).

The rest of this section is based on a classical inequality, the Hardy inequality for functions defined on the $\mathbb{R}^3$. Hardy-type inequalities play a central role in this work.

LEMMA 2.1. *For all infinitely differentiable functions v in the variable $x \in \mathbb{R}^3$ that have a compact support,*

$$\int \frac{1}{|x|^2}\, v^2 \, dx \;\le\; 4 \int |\nabla v|^2 \, dx\,. \tag{2.6}$$

Proof. Let $d(x) = |x|$ for abbreviation. To avoid any difficulty, we assume at first that v vanishes on a neighborhood of the origin. Using the relation

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

integration by parts then yields

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

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

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

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

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

or, using $|\nabla d| = 1$, the estimate (2.6) for functions v vanishing near the origin. To complete the proof, let $\omega : \mathbb{R}^3 \to [0,1]$ be an infinitely differentiable cut-off function with $\omega(x) = 0$ for $|x| \le 1/2$ and with $\omega(x) = 1$ for $|x| \ge 1$. Set

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

The estimate (2.6) then holds for the functions v_k as just proved. Using

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

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

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

the proposition follows with help of the dominated convergence theorem. □

Both sides of (2.6) scale in the same way under a change of units, that is, under a dilation $x \to \alpha x$. This resonance phenomenon is responsible for the fact that the constant in (2.6) does not depend on the size of the support of the considered functions.

The Hardy inequality (2.6) first serves to estimate terms involving the potential

$$V(x) \;=\; -\sum_{i=1}^{N} \sum_{\nu=1}^{K} \frac{Z_\nu}{|x_i - a_\nu|} \;+\; \frac{1}{2} \sum_{\substack{i,j=1 \\ i \ne j}}^{N} \frac{1}{|x_i - x_j|} \tag{2.7}$$

in the Hamilton operator (1.1) that is composed of the nucleus-electron interaction potential, the first term in (2.7), and the electron-electron interaction potential. Let Z denote the total charge of the nuclei, the sum of the charges Z_ν, and set

$$\theta(N,Z) = \sqrt{N}\, \max(N,Z). \tag{2.8}$$

A simple calculation on the basis of the Hardy inequality (2.6), Fubini's theorem, and the Cauchy-Schwarz inequality then yields our first important estimate:

THEOREM 2.2. *The functions u and v in $\mathcal{D}$ satisfy the estimate*

$$\int V\, u\, v\, dx \;\le\; 3\, \theta(N,Z)\, \|u\|_0 |\, v\,|_1. \tag{2.9}$$

Next we write the Hamilton operator (1.1) in the form

$$H \;=\; -\,\frac{1}{2}\,\Delta + V \tag{2.10}$$

and introduce the bilinear form

$$a(u,v) \;=\; (Hu,v) \tag{2.11}$$

on $\mathcal{D}$, where $(\ ,\ )$ denotes the L_2-inner product. Since

$$(-\Delta u,v) \;=\; \int \nabla u\cdot\nabla v\,dx, \tag{2.12}$$

there exists, by Theorem 2.2, a constant M depending on N and on Z with

$$a(u,v) \;\le\; M\,\|u\|_1\|v\|_1 \tag{2.13}$$

for all $u,v\in\mathcal{D}$. The bilinear form (2.11) can therefore be extended to a bounded, symmetric bilinear form on H^1. Furthermore, for $\mu\ge 9\,\theta^2+1/4$ and all $u,v\in H^1$,

$$a(u,u)+\mu\,(u,u) \;\ge\; \frac{1}{4}\,\|u\|_1^2. \tag{2.14}$$

The value $a(u,u)$ is the expectation value of the total energy in the state described by the normed wavefunction $u\in H^1$. A function $u\ne 0$ in H^1 is an eigenfunction of the Hamilton operator (1.1) or (2.10) and λ the associated eigenvalue, if the relation

$$a(u,\chi)=\lambda\,(u,\chi) \tag{2.15}$$

holds for all $\chi\in H^1$, that is, u is a weak solution of the eigenvalue equation

$$Hu=\lambda u, \tag{2.16}$$

in the same way as one defines weak solutions of boundary value problems. The relation (2.14) shows that the set of eigenvalues or energies λ is bounded from below.

3. Spin and the Pauli principle. Electrons have an internal property called spin that behaves similar to angular momentum. Although spin does not explicitly appear in the electronic Schrödinger equation, it influences the structure of atoms and molecules decisively. The purpose of this section is to explain how spin can be incorporated into the variational framework. The spin of an electron can attain the two half-integer values $\pm 1/2$. Correspondingly, the true wavefunctions are of the form

$$\psi : (\mathbb{R}^3)^N\times\{-1/2,\,1/2\}^N\to\ \mathbb{R} : (x,\sigma)\to\psi(x,\sigma), \tag{3.1}$$

that is, depend not only on the positions $x_i\in\mathbb{R}^3$, but also on the spins $\sigma_i=\pm 1/2$ of the electrons. The Pauli principle, one of the fundamental principles of quantum mechanics, states that only those eigenfunctions 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, that is, are antisymmetric in the sense that

$$\psi(Px,P\sigma) \;=\; \mathrm{sign}(P)\psi(x,\sigma) \tag{3.2}$$

holds for arbitrary simultaneous permutations $x\to Px$ and $\sigma\to P\sigma$ of the electron positions and spins. The Pauli principle forces the admissible wavefunctions to vanish where $x_i=x_j$ and $\sigma_i=\sigma_j$ for $i\ne j$, that is, that the probability that two electrons i and j with the same spin meet is zero. The admissible solutions of the scalar Schrödinger equation (2.15) are those that are components

$$u : (\mathbb{R}^3)^N\to\ \mathbb{R} : x\to\psi(x,\sigma) \tag{3.3}$$

of an antisymmetric wavefunction (3.1). To clarify these relations and deduce (2.15) from the full equation incorporating spin, we introduce the bilinear forms

$$B(\psi,\psi') \;=\; \sum_\sigma a\big(\psi(\,\cdot\,,\sigma),\psi'(\,\cdot\,,\sigma)\big), \tag{3.4}$$

$$(\psi,\psi') \;=\; \sum_\sigma \big(\psi(\,\cdot\,,\sigma),\psi'(\,\cdot\,,\sigma)\big) \tag{3.5}$$

on the spaces of functions (3.1) with components in H^1, respectively, L_2 where the sums extend over the 2^N possible spin vectors σ. The quantity $B(\psi,\psi)$ represents the expectation value of the total energy for normed ψ and B is thus the bilinear form that is induced by the complete Hamilton operator of the system, the operator whose eigenvalues and eigenfunctions are sought. An antisymmetric function ψ with components in H^1 is a solution of the full problem if and only if

$$B(\psi,\psi') = \lambda\,(\psi,\psi') \tag{3.6}$$

for all test functions ψ' of this kind. This eigenvalue problem decouples into eigenvalue problems for the components of the eigenfunctions ψ due to the fact that the bilinear form (2.11) is invariant under permutations of the electron positions x_i, i.e., that

$$a\big(u(P\,\cdot\,),v(P\,\cdot\,)\big) \;=\; a(u,v) \tag{3.7}$$

holds for all such permutations P and all functions $u,v\in H^1$.

Our argumentation is based on the antisymmetrization operator $\mathcal{A}$ given by

$$(\mathcal{A}\psi)(x,\sigma) \;=\; \frac{1}{N!}\sum_P \mathrm{sign}(P)\psi(Px,P\sigma) \tag{3.8}$$

where the sum extends over the $N!$ possible permutations of the electrons. It maps an arbitrary function (3.1) into an antisymmetric function and reproduces antisymmetric functions. For all functions (3.1) with components in H^1 respectively L_2,

$$B(\psi,\mathcal{A}\psi') = B(\mathcal{A}\psi,\psi'),\quad (\psi,\mathcal{A}\psi') = (\mathcal{A}\psi,\psi'). \tag{3.9}$$

THEOREM 3.1. *An antisymmetric function ψ with components in H^1 satisfies the eigenvalue equation* (3.6) *if and only if its components solve the equations*

$$a\big(\psi(\,\cdot\,,\sigma),\,v\,\big) \;=\; \lambda\,\big(\psi(\,\cdot\,,\sigma),\,v\,\big),\quad v\in H^1. \tag{3.10}$$

Proof. Let $\delta(\eta,\sigma)=1$ if $\eta=\sigma$ and $\delta(\eta,\sigma)=0$ otherwise. Every function (3.1) with components in H^1 can then be written as

$$\psi(x,\eta) \;=\; \sum_\sigma \psi(x,\sigma)\delta(\eta,\sigma),$$

that is, as a linear combination of functions of the form

$$\psi'(x,\eta) = v(x)\delta(\eta,\sigma)$$

with $v\in H^1$ and some given σ, and every antisymmetric function therefore as a linear combination of antisymmetrized functions of this form. It suffices therefore to restrict

oneself to test functions $\mathcal{A}\psi'$ where ψ' is a function of the given form. Let ψ now be an arbitrary antisymmetric function with components in H^1. Then

$$B(\psi,\mathcal{A}\psi') = B(\mathcal{A}\psi,\psi') = B(\psi,\psi') = a(\psi(\,\cdot\,,\sigma),v),$$
$$(\psi,\mathcal{A}\psi') = (\mathcal{A}\psi,\psi') = (\psi,\psi') = (\psi(\,\cdot\,,\sigma),v),$$

from which the proposition follows. □

The components of the solutions ψ of the full equation (3.6) are therefore indeed solutions of the scalar equation (2.15). To characterize these components, let $\mathcal{D}(\sigma)$ denote the space of all functions $u \in \mathcal{D}$ with

$$u(Px) = \operatorname{sign}(P)u(x) \tag{3.11}$$

for all permutations P that leave σ invariant and let $L_2(\sigma)$ and $H^1(\sigma)$ be the closure of $\mathcal{D}(\sigma)$ in the corresponding spaces.

THEOREM 3.2. *A function in $\mathcal{D}$ is the component* (3.3) *of an antisymmetric function* (3.1) *with components in $\mathcal{D}$ if and only if it belongs to $\mathcal{D}(\sigma)$. The corresponding statement holds for functions in L_2 and H^1, respectively.*

Proof. If ψ is antisymmetric, $u(x) = \psi(x,\sigma)$, and $P\sigma = \sigma$, then

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

so that the components (3.3) of an antisymmetric function are of the form (3.11). A function u satisfying (3.11) is conversely the component $u(x) = \psi(x,\sigma)$ of

$$\psi(x,\eta) \;=\; \frac{\sum_P \operatorname{sign}(P)u(Px)\delta(P\eta,\sigma)}{\sum_P \delta(P\sigma,\sigma)},$$

and can thus be recovered from an antisymmetric function. □

The components $u = \psi(\cdot,\sigma)$ in $H^1(\sigma)$ of the full, spin-dependent eigenfunctions ψ solve, by Theorem 3.1, particularly the reduced eigenvalue equation

$$a(u,v) = \lambda\,(u,v), \quad v \in H^1(\sigma), \tag{3.12}$$

that results from (3.10) replacing the test space H^1 by its subspace $H^1(\sigma)$, the solution space. From the solutions of these equations, one can conversely recover the solutions of the full equation (3.6) for all 2^N components of the spin-dependent eigenfunctions ψ.

THEOREM 3.3. *If the function $u \neq 0$ in $H^1(\sigma)$ solves the eigenvalue equation* (3.12) *reduced to the space $H^1(\sigma)$, the antisymmetric function $\psi \neq 0$ defined by*

$$\psi(x,\eta) \;=\; \frac{1}{N!}\sum_P \operatorname{sign}(P)u(Px)\delta(P\eta,\sigma) \tag{3.13}$$

solves the full equation (3.6) *and the function u itself again the original equation*

$$a(u,v) = \lambda\,(u,v), \quad v \in H^1. \tag{3.14}$$

Proof. Let ψ' be an antisymmetric function with components in H^1. Its component $x \to \psi'(x,\sigma)$ then belongs to $H^1(\sigma)$. Since, as in the proof of Theorem 3.1,

$$B(\psi,\psi') = B(\psi',\psi) = a(\psi'(\,\cdot\,,\sigma),u) = a(u,\psi'(\,\cdot\,,\sigma)),$$
$$(\psi,\psi') = (\psi',\psi) = (\psi'(\,\cdot\,,\sigma),u) = (u,\psi'(\,\cdot\,,\sigma)),$$

the function (3.13) therefore solves the equation (3.6) for the complete, spin-dependent wavefunctions. As $u(x) = \mathrm{sign}(P)u(Px)$ whenever P fixes σ, u is a constant multiple of the function $\psi(\,\cdot\,,\sigma)$. The rest of the proposition follows from Theorem 3.1. □

With that the circle is closed. Since the functions $u \in H^1(\sigma)$ and $\widetilde{u}(x) = u(Q^{-1}x)$ in $H^1(Q\sigma)$ generate, up to a possible change of sign, for arbitrary permutations Q of the electrons the same function (3.13), one can restrict oneself to the reduced equations (3.12) on the $\lfloor N/2 \rfloor$ essentially different spaces $H^1(\sigma)$ instead of solving the system (3.6) for the 2^N components of a wavefunction (3.1) directly. Every solution of such a reduced equation also solves the eigenvalue problem (2.15) on the bigger space H^1.

4. Spectrum and exponential decay. A real number λ belongs to the resolvent of the bilinear form (2.11) restricted to $H^1(\sigma)$, if and only if the equation

$$a(u,v) - \lambda\,(u,v) \;=\; (f,v), \quad v \in H^1(\sigma), \tag{4.1}$$

possesses a unique solution $u \in H^1(\sigma)$ for all given $f \in L_2(\sigma)$ and if the linear mapping $f \to u$ from $L_2(\sigma)$ to $H^1(\sigma)$ is bounded as a mapping from $L_2(\sigma)$ to $H^1(\sigma)$ or, because of (2.14), equivalently from $L_2(\sigma)$ to $L_2(\sigma)$. The real numbers λ which do not belong to the resolvent form the spectrum of the bilinear form. The spectrum splits into the isolated eigenvalues of finite multiplicity and the essential spectrum. By (2.14), the bilinear form on the left hand side of (4.1) is coercive for all $\lambda \le -(9\,\theta^2 + 1/4)$. By the Lax-Milgram theorem, these λ therefore belong to the resolvent. The spectrum is thus bounded from below, and so is the essential spectrum. We are interested in the eigenfunctions for eigenvalues below the essential spectrum. For the spectral theory of Schrödinger-type operators we refer to textbooks on mathematical physics. A standard reference is [52]. Much information can also be found in [34] and [55].

Our starting point is a characterization of the bottom of the essential spectrum that is due to Persson [49]; see also [24] and particularly [1]. The symmetry properties enforced by the Pauli principle are easily built in into Persson's characterization. Let

$$\Sigma(R,\sigma) = \inf\big\{a(u,u)\,\big|\,u \in \mathcal{D}(\sigma),\ \|u\|_0 = 1,\ u(x) = 0 \text{ for } |x| \le R\,\big\}. \tag{4.2}$$

Transferred to the present situation, Persson showed that the essential spectrum of a bilinear form (2.11) on $H^1(\sigma)$ induced by an operator of the form (2.10) is non-empty if and only if the $\Sigma(R,\sigma)$ remain uniformly bounded in $R > 0$, that is, if the quantity

$$\Sigma^*(\sigma) = \lim_{R\to\infty} \Sigma(R,\sigma) \tag{4.3}$$

remains finite, which then also represents the bottom of the essential spectrum. This characterization can be regarded as counterpart to the variational characterization

$$\lambda_0(\sigma) = \inf\big\{a(u,u)\,\big|\,u \in \mathcal{D}(\sigma),\ \|u\|_0 = 1\big\} \tag{4.4}$$

of the minimum eigenvalue, the ground state energy of the system. The constant (4.3) has a nice physical interpretation as the energy that is needed to shift at least one electron to infinity and is therefore denoted as ionization threshold.

THEOREM 4.1. *The essential spectrum of the electronic Schrödinger operator* (1.1) *is non-empty and its greatest lower bound* (4.3) *is less than or equal zero.*

Proof. Let $u \ne 0$ in $\mathcal{D}(\sigma)$ be a normed infinitely differentiable function that vanishes on the ball of radius 1 around the origin of the $\mathbb{R}^{3N}$. The rescaled functions

$$u_R(x) \;=\; \frac{1}{R^{3N/2}}\,u\Big(\frac{x}{R}\Big)$$

then have L_2-norm 1, too, and vanish on the ball of radius R around the origin. Therefore, by the definition (4.2) of the constant $\Sigma(R,\sigma)$,

$$\Sigma(R,\sigma) \,\leq\, a(u_R,u_R).$$

At this place, the particular properties of the given potential V enter. By Theorem 2.2,

$$a(u_R,u_R) \,\leq\, \frac{1}{2}\,|u_R|_1^2 \,+\, 3\,\theta(N,Z)\,\|u_R\|_0|u_R|_1.$$

This estimate can be rewritten in terms of the original function u using the relations

$$\|u_R\|_0 = \|u\|_0, \quad |u_R|_1 = \frac{1}{R}\,|\,u\,|_1.$$

For arbitrarily given $\varepsilon > 0$ and R chosen sufficiently large, therefore $\Sigma(R,\sigma) \leq \varepsilon$. Since the $\Sigma(R,\sigma)$ are monotonely increasing in R, thus $\Sigma(R,\sigma) \leq 0$ for all $R > 0$. □

The spectral properties of Schrödinger operators are strongly intertwined with the exponential decay of their eigenfunctions for eigenvalues below the essential spectrum. The first results of this type for more than three electrons are due to Ahlrichs [2] for the case of a single nucleus, that is, an atom, and to O'Connor [48], who treated the general case and derived an in a certain sense optimal isotropic L_2-bound. O'Connor's result was a short time after improved by Combes and Thomas [10]. Simon [54] found a pointwise isotropic bound. The actual decay behavior of the eigenfunctions is complicated and in general highly anisotropic. A first result in this direction was proven by Deift, Hunziker, Simon, and Vock [12]. The in some sense final study is Agmon's monograph [1]. Agmon introduced the Agmon distance named by him with the help of which the decay of the eigenfunctions can be described rather precisely.

The isotropic L_2-decay of the eigenfunctions plays a central role for this work because we want to show, on the basis of this result, that also many of the high-order mixed derivatives of the eigenfunctions decay exponentially. For this reason, and to keep the presentation as self-contained as possible, we give a short proof of O'Connor's theorem that closely follows Agmon's argumentation [1]. It starts directly from the definition (4.3) of the ionization threshold and does not utilize the fact that it represents the infimum of the essential spectrum.

THEOREM 4.2. *Let $\lambda < \Sigma^*(\sigma)$ be an eigenvalue below the ionization threshold (4.3) and $u \in H^1(\sigma)$ be an assigned eigenfunction. For $\lambda < \Sigma < \Sigma^*(\sigma)$, the functions*

$$x \;\to\; \exp\Big(\sqrt{2\,(\Sigma-\lambda)}\,|\,x\,|\,\Big)\,u(x), \;\; \exp\Big(\sqrt{2\,(\Sigma-\lambda)}\,|\,x\,|\,\Big)\,(\nabla u)(x) \tag{4.5}$$

are then square integrable, that is, u and ∇u decay exponentially in the L_2-sense.

Proof. We begin choosing a radius R such that

$$\Sigma(R,\sigma) - \Sigma \,=:\, \alpha > 0. \tag{4.6}$$

We further introduce the bounded functions

$$\delta(x) \,=\, \sqrt{2\,(\Sigma-\lambda)}\,\frac{|x|}{1+\varepsilon\,|x|}$$

with $\varepsilon > 0$ given arbitrarily and observe that

$$|(\nabla\delta)(x)|^2 \,\leq\, 2\,(\Sigma-\lambda)$$

for all $x \neq 0$ independent of the choice of ε. Since

$$\nabla(e^{-\delta}v)\cdot\nabla(e^{\,\delta}v) \;=\; \nabla v\cdot\nabla v \;-|\nabla\delta|^2v^2,$$

this leads to the estimate

$$a(e^{-\delta}v, e^{\,\delta}v) \;\geq\; a(v,v) - (\Sigma-\lambda)\|v\|_0^2 \tag{4.7}$$

for all infinitely differentiable functions v that have a compact support and that vanish on a neighborhood of the origin. In particular, the estimate holds for the functions $v \in \mathcal{D}(\sigma)$ that attain the value 0 on the ball of radius R around the origin. For these v,

$$a(v,v) \;\geq\; \Sigma(R,\sigma)\|v\|_0^2.$$

In combination with (4.6) and (4.7), this yields

$$\alpha\,\|v\|_0^2 \;\leq\; a(e^{-\delta}v, e^{\,\delta}v) - \lambda\,\|v\|_0^2. \tag{4.8}$$

Next, we fix a rotationally symmetric, infinitely differentiable function χ that vanishes on the ball of radius R around the origin and attains the value $\chi(x) = 1$ for $|x| \geq R+1$. Let u be an arbitrary function in $\mathcal{D}(\sigma)$. Setting $v = \chi e^{\,\delta}u$, (4.8) becomes

$$\alpha\,\|\chi e^{\,\delta}u\|_0^2 \;\leq\; a(\chi u, \chi e^{2\delta}u) - \lambda\,(\chi u, \chi e^{2\delta}u). \tag{4.9}$$

To shift the factor χ to the right hand side, we introduce the function

$$\eta \;=\; \frac{2\,\chi\nabla\chi\cdot\nabla\delta + |\nabla\chi|^2}{2}$$

that attains the value $\eta(x) = 0$ for $|x| \leq R$ and $|x| \geq R+1$. With help of the relation

$$\nabla(\chi u)\cdot\nabla(\chi e^{2\delta}u) = \nabla u\cdot\nabla(\chi^2 e^{2\delta}u) + 2\eta e^{2\delta}u^2,$$

the estimate (4.9) for the functions $u \in \mathcal{D}(\sigma)$ can then be rewritten as

$$\alpha\,\|\chi e^{\,\delta}u\|_0^2 \;\leq\; a(u, \chi^2 e^{2\delta}u) - \lambda\,(u, \chi^2 e^{2\delta}u) \;+\; (u, \eta e^{2\delta}u). \tag{4.10}$$

As $\chi e^{2\delta}$, $\chi^2 e^{2\delta}$, and $\eta e^{2\delta}$ are bounded functions with bounded first-order derivatives and $\mathcal{D}(\sigma)$ is dense in $H^1(\sigma)$, the estimate transfers to arbitrary functions $u \in H^1(\sigma)$.

Since $\chi^2 e^{2\delta}u \in H^1(\sigma)$, the first two terms on the right hand side of (4.10) cancel for the given eigenfunction u for the eigenvalue λ. The estimate thus reduces to

$$\alpha\,\|\chi e^{\,\delta}u\|_0^2 \;\leq\; (u, \eta e^{2\delta}u). \tag{4.11}$$

for this u. To estimate the H^1-norm of $\chi e^{\,\delta}u$, we recall that, by (2.14) and (4.7),

$$\frac{1}{4}\,\|v\|_1^2 \;\leq\; a(v,v) + \mu\,\|v\|_0^2 \;\leq\; a(e^{-\delta}v, e^{\,\delta}v) + (\Sigma-\lambda+\mu)\|v\|_0^2$$

for all infinitely differentiable functions v that have a compact support and that vanish on a neighborhood of the origin, where the constant $\mu > 0$ was more precisely specified in section 2. From that one obtains, in the same way as above, the estimate

$$\frac{1}{4}\,\|\chi e^{\,\delta}u\|_1^2 \;\leq\; (u, \eta e^{2\delta}u) + (\Sigma+\mu)\|\chi e^{\,\delta}u\|_0^2$$

for the given eigenfunction u and, with (4.11), finally the estimate

$$\|\chi e^{\,\delta} u\|_1^2 \,\le\, \Big(4 + 4\,\frac{\Sigma+\mu}{\alpha}\,\Big)(u, \eta e^{2\delta} u).$$

Since the functions $\eta e^{2\delta}$ and $\nabla\delta$ are uniformly bounded in ε, the L_2-norms of the functions $e^{\,\delta} u$ and $e^{\delta}\nabla u$ therefore remain bounded uniformly in ε. The proposition follows with the monotone convergence theorem letting ε tend to zero. □

The given decay rates cannot be improved without further assumptions on the considered system. This can already be recognized by the case of a single electron that moves in the field of a nucleus of charge Z, that is, by the Hamilton operator

$$H \,=\, -\,\frac{1}{2}\,\Delta \,-\, \frac{Z}{|x|}. \tag{4.12}$$

In this case, the bottom of the essential spectrum is $\Sigma^* = 0$ as follows from Persson's characterization. The ground state wavefunction and the associated eigenvalue are

$$u(x) \,=\, e^{-Z|x|}, \quad \lambda \,=\, -\,\frac{1}{2}\,Z^2, \tag{4.13}$$

up to normalization of u. For this example,

$$\exp\Big(\sqrt{2\,(\Sigma^* - \lambda)}\,|\,x\,|\,\Big)\,u(x) \,=\, 1 \tag{4.14}$$

so that the functions (4.5) cannot be square integrable for $\Sigma \ge \Sigma^*$.

Next we replace the rotationally symmetric exponential weight functions in front of the wavefunctions by products of weight functions that depend only on the coordinates of a single electron. Such weights are easier to analyze and fit into the framework that we will develop in the following sections. Let $u \in H^1(\sigma)$ be an eigenfunction for the eigenvalue $\lambda < \Sigma^*(\sigma)$. Let $\theta_1, \ldots, \theta_N \ge 0$ be given weight factors and

$$\psi(x) \,=\, \sum_{i=1}^{N} \theta_i |x_i|, \quad \sum_{i=1}^{N} \theta_i^2 \,=\, 1. \tag{4.15}$$

Let α be a decay rate as in Theorem 4.2, that is,

$$\alpha \,<\, \sqrt{2\,\big(\Sigma^*(\sigma) - \lambda\big)}, \tag{4.16}$$

and define the correspondingly exponentially weighted eigenfunction as

$$\widetilde{u}(x) \,=\, \exp\big(\alpha\,\psi(x)\big)\,u(x). \tag{4.17}$$

This exponentially weighted eigenfunction solves then an eigenvalue equation that is similar to the original one, but contains an additional skew-symmetric term.

THEOREM 4.3. *Let $u \in H^1(\sigma)$ be an eigenfunction for the eigenvalue $\lambda < \Sigma^*(\sigma)$. The function $\widetilde{u}$ defined as in* (4.17) *is then also contained in H^1 and solves the equation*

$$a(\widetilde{u}, v) \,+\, \alpha\, s(\widetilde{u}, v) \,=\, \widetilde{\lambda}\,(\widetilde{u}, v), \quad v \in H^1, \tag{4.18}$$

where s denotes the skew-symmetric bilinear form

$$s(u, v) \,=\, \frac{1}{2}\,\big((\nabla\psi\cdot\nabla u,\, v) - (u,\, \nabla\psi\cdot\nabla v)\big) \tag{4.19}$$

and the real number $\widetilde{\lambda} < 0$ *is given by*

$$\widetilde{\lambda} \,=\, \lambda + \frac{1}{2}\,\alpha^2. \tag{4.20}$$

Proof. We show first that, for all $v \in H^1$, the exponentially weighted functions $\widetilde{v}$ defined by $\widetilde{v} = e^{\,\alpha\psi} v$ have the locally integrable first-order weak partial derivatives

$$D_k \widetilde{v} \,=\, \alpha\, e^{\,\alpha\psi} D_k \psi\, v \,+\, e^{\,\alpha\psi} D_k v,$$

which formally results from the product rule; the operator D_k here denotes (weak) partial differentiation with respect to the component k. To prove this relation, let

$$\psi_\varepsilon(x) = \sum_{i=1}^{N} \theta_i \sqrt{|x_i|^2 + \varepsilon^2}$$

be a smoothed variant of ψ and assume first that $v \in \mathcal{D}$. Integration by parts then yields, for all infinitely differentiable test functions φ with compact support,

$$\int \Big(\alpha\, e^{\,\alpha\psi_\varepsilon} D_k \psi_\varepsilon\, v + e^{\,\alpha\psi_\varepsilon} D_k v \Big)\, \varphi \, dx \,=\, \int D_k \big(e^{\,\alpha\psi_\varepsilon} v \big)\, \varphi \, dx \,=\, -\int e^{\,\alpha\psi_\varepsilon} v\, D_k \varphi \, dx.$$

Letting ε tend to zero, one obtains, from the dominated convergence theorem,

$$\int \Big(\alpha\, e^{\,\alpha\psi} D_k \psi\, v + e^{\,\alpha\psi} D_k v \Big)\, \varphi \, dx \,=\, -\int e^{\,\alpha\psi} v\, D_k \varphi \, dx.$$

Since ψ and its first-order partial derivatives are bounded on the support of φ and $\mathcal{D}$ is a dense subspace of H^1, this relation transfers to all functions $v \in H^1$, which proves the differentiation formula above.

Hence, the exponentially weighted eigenfunction $\widetilde{u}$ is indeed weakly differentiable and has first-order weak derivatives as given above. Since $\psi(x) \le |x|$ and the first-order derivatives of ψ are bounded, these weak derivatives are, by Theorem 4.2, square integrable. Therefore $\widetilde{u}$ is contained in H^1. For all $v \in \mathcal{D}$, by the formula above,

$$\nabla \widetilde{u} \cdot \nabla v \,+\, \alpha \left(v\, \nabla\psi \cdot \nabla \widetilde{u} - \widetilde{u}\, \nabla\psi \cdot \nabla v \right) \,=\, \nabla u \cdot \nabla \widetilde{v} \,+\, \alpha^2\, |\nabla\psi|^2\, \widetilde{u} v,$$

where $\widetilde{v} = e^{\,\alpha\psi} v$ is again in H^1. From that and $|\nabla\psi|^2 = 1$, one deduces

$$a(\widetilde{u}, v) \,+\, \alpha\, s(\widetilde{u}, v) \,=\, a(u, \widetilde{v}) \,+\, \frac{1}{2}\,\alpha^2\, (\widetilde{u}, v).$$

Since u is an eigenfunction for the eigenvalue λ,

$$a(u, \widetilde{v}) = \lambda\, (u, \widetilde{v}) = \lambda\, (\widetilde{u}, v).$$

This shows that (4.18) holds for all infinitely differentiable test functions v with compact support and hence also for all functions v in the space H^1. By definition of α,

$$\lambda + \frac{1}{2}\,\alpha^2 \,=\, \Sigma \,<\, \Sigma^*(\sigma).$$

Since $\Sigma^*(\sigma) \le 0$ by Theorem 4.1, the constant (4.20) is therefore negative. □

5. The modified eigenvalue problem. The next sections are devoted to the study of the modified eigenvalue problem (4.18) that the exponentially weighted eigenfunctions (4.17) satisfy. Hereby we take up a slightly more general position and relax the symmetry properties prescribed by the Pauli principle a little bit. Let $\mathcal{I}$ be a nonempty subset of the set of the electron indices $1,\dots,N$. Let $\mathcal{D}_\mathcal{I}$ denote the subspace of $\mathcal{D}$ that consists of those functions in $\mathcal{D}$ that change their sign under the exchange of the electron positions x_i and x_j in $\mathbb{R}^3$ for indices $i \neq j$ in $\mathcal{I}$. The closed hull of $\mathcal{D}_\mathcal{I}$ in H^1 is the Hilbert space $H^1_\mathcal{I}$. Our modified eigenvalue problem then consists in finding functions $u \neq 0$ in $H^1_\mathcal{I}$ and values $\lambda < 0$ that satisfy the condition

$$a(u,v) \,+\, \alpha\, s(u,v) \,=\, \lambda\,(u,v), \quad v \in H^1_\mathcal{I}. \tag{5.1}$$

Our aim is to study the regularity of the solutions of this eigenvalue problem in Hilbert spaces of mixed derivatives. Conditions on the parameter α enter only implicitly since, with u a solution of (5.1) and with that also of equation (5.4) below, $\widetilde{u} = e^{-\alpha\psi}u$ is conversely a solution of the original eigenvalue equation (2.15) for which $e^{\alpha\psi}\widetilde{u}$ is then a square integrable function. We assume $\alpha \geq 0$ in the sequel. The expression

$$s(u,v) \,=\, \frac{1}{2}\,\big((\nabla\psi\cdot\nabla u,\, v) - (u,\, \nabla\psi\cdot\nabla v)\big) \tag{5.2}$$

is the skew-symmetric, bounded bilinear form on H^1 from the previous section, where

$$\psi(x) \,=\, \sum_{i=1}^N \theta_i|x_i|, \quad \sum_{i=1}^N \theta_i^2 \,=\, 1, \tag{5.3}$$

is assumed to be symmetric with respect to the given permutations of the electrons with indices $i \in \mathcal{I}$, which is the case if and only if all θ_i for i in $\mathcal{I}$ are equal.

THEOREM 5.1. *A function $u \in H^1_\mathcal{I}$ that solves* (5.1) *also solves the full equation*

$$a(u,v) \,+\, \alpha\, s(u,v) \,=\, \lambda\,(u,v), \quad v \in H^1, \tag{5.4}$$

that is, (5.1) *does not only hold for test functions $v \in H^1_\mathcal{I}$, but for all $v \in H^1$.*

Proof. The proof is based on the observation that the affected bilinear forms are invariant under the considered permutations of the electrons, that is, on the fact that

$$a(u(P\,\cdot\,), v(P\,\cdot\,)) = a(u,v), \quad s(u(P\,\cdot\,), v(P\,\cdot\,)) = s(u,v)$$

for these permutations P, which follows from the invariance of the potential (2.7) and the function (5.3) under these permutations. Let G denote the group of these permutations and define the partial antisymmetrization operator

$$(\mathcal{A}v)(x) \,=\, \frac{1}{|G|}\sum_{P\in G} \operatorname{sign}(P) v(Px),$$

that reproduces functions in $\mathcal{D}_\mathcal{I}$ and $H^1_\mathcal{I}$, respectively, and maps functions in H^1 to partially antisymmetric functions in $H^1_\mathcal{I}$. Since, for arbitrary functions $u, v \in H^1$,

$$a(\mathcal{A}u, v) = a(u, \mathcal{A}v), \quad s(\mathcal{A}u, v) = s(u, \mathcal{A}v), \quad (\mathcal{A}u, v) = (u, \mathcal{A}v),$$

a solution $u \in H^1_\mathcal{I}$ of (5.1) satisfies the equation

$$\begin{aligned} a(u,v) + \alpha\, s(u,v) \,&=\, a(\mathcal{A}u, v) + \alpha\, s(\mathcal{A}u, v) \\ &=\, a(u, \mathcal{A}v) + \alpha\, s(u, \mathcal{A}v) \,=\, \lambda\,(u, \mathcal{A}v) \,=\, \lambda\,(\mathcal{A}u, v) \,=\, \lambda\,(u,v) \end{aligned}$$

for all $v \in H^1$, that is, solves the full equation (5.4). ∎

In the limit case $\alpha = 0$, the modified eigenvalue problem therefore transfers again into the original eigenvalue equation (2.15) from which our discussion started. We remark that (5.4) is the weak form of the differential equation

$$\widetilde{H}u \,:=\, Hu \,+\, \alpha \left(\nabla\psi \cdot \nabla u \,+\, \sum_{i=1}^{N} \theta_i \, \frac{1}{|x_i|} \, u \right) \,=\, \lambda u, \tag{5.5}$$

as can be shown with help of the representation (6.2) and integration by parts as in the proof of Lemma 6.2 from the following section. Since we do not utilize the strong form (5.5) of the modified eigenvalue problem, we refrain from a detailed proof.

We attempt to prove that the solutions of the equation (5.1) possess, regardless of their origin, high-order mixed derivatives and that it is possible to estimate the L_2-norms of these derivatives by the L_2-norm of the solutions themselves. Let

$$\Delta_i \,=\, \sum_{k=1}^{3} \frac{\partial^2}{\partial x_{i,k}^2} \tag{5.6}$$

denote the Laplacian that acts upon the spatial coordinates $x_{i,1}$, $x_{i,2}$, and $x_{i,3}$ of the electron i and let the differential operator $\mathcal{L}$ of order $2|\mathcal{I}|$ be the product

$$\mathcal{L} \,=\, (-1)^{|\mathcal{I}|} \prod_{i \in \mathcal{I}} \Delta_i \tag{5.7}$$

of the second-order operators $-\Delta_i$. The seminorms $|\cdot|_{\mathcal{I},0}$ and $|\cdot|_{\mathcal{I},1}$ on the space $\mathcal{D}$ of the infinitely differentiable functions with compact support are then defined by

$$|\,u\,|_{\mathcal{I},0}^2 = (u, \mathcal{L}u), \quad |\,u\,|_{\mathcal{I},1}^2 = -\,(u, \Delta\mathcal{L}u). \tag{5.8}$$

Correspondingly, we introduce, for $s = 0, 1$, the norms given by

$$\|u\|_{\mathcal{I},s}^2 \,=\, \|u\|_s^2 + |\,u\,|_{\mathcal{I},s}^2. \tag{5.9}$$

Let $\mathcal{I}^*$ be the set of all mappings $\alpha : \mathcal{I} \to \{1, 2, 3\}$. The operator $\mathcal{L}$ and with that the given seminorms can then be written in terms of the products

$$L_\alpha = \prod_{i \in \mathcal{I}} \frac{\partial}{\partial x_{i,\alpha(i)}}, \quad \alpha \in \mathcal{I}^*, \tag{5.10}$$

of first-order differential operators, more precisely as the sum

$$\mathcal{L} \,=\, (-1)^{|\mathcal{I}|} \sum_{\alpha \in \mathcal{I}^*} L_\alpha^2. \tag{5.11}$$

Correspondingly, since all partial derivatives of a function in $\mathcal{D}$ commute,

$$|\,u\,|_{\mathcal{I},0}^2 \,=\, \sum_{\alpha \in \mathcal{I}^*} \|L_\alpha u\|_0^2, \quad |\,u\,|_{\mathcal{I},1}^2 \,=\, \sum_{\alpha \in \mathcal{I}^*} |L_\alpha u|_1^2. \tag{5.12}$$

The completions of $\mathcal{D}_\mathcal{I}$ under the norms given by (5.9) are the spaces $X_\mathcal{I}^s$. They consist of functions that possess, for big $|\mathcal{I}|$, very high order weak partial derivatives. We will show in section 8 that the solutions of the equation (5.1) are contained in $X_\mathcal{I}^1$.

The structure of the proof is in the end very simple; it relies on the Lax-Milgram theorem, some Fourier analysis, and a tricky perturbation argument. Expressed naively, we transform the second-order equation (5.5) into the high-order equation

$$(\varepsilon I + \mathcal{L})\,\widetilde{H} u = \lambda\,(\varepsilon I + \mathcal{L})\,u \tag{5.13}$$

with weak solutions in $X^1_{\mathcal{I}}$. Since the operator $\varepsilon I + \mathcal{L}$ is invertible for $\varepsilon > 0$, both equations are equivalent and our regularity theorem is proved. Of course, this does not work in this simple way, one reason being all the singularities of the coefficient functions of the differential operator $\widetilde{H}$. However, we can switch to the weak form

$$a(u, \varepsilon v + \mathcal{L}v) \,+\, \alpha\, s(u, \varepsilon v + \mathcal{L}v) \,=\, \lambda\,(u, \varepsilon v + \mathcal{L}v), \quad v \in \mathcal{D}_{\mathcal{I}}, \tag{5.14}$$

of this equation, that is formally obtained from (5.13) if one multiplies both sides of the equation with a test function v of the given form, integrates, and then transforms the resulting integrals integrating by parts, or simply by replacing the test functions v in (5.1) by test functions $\varepsilon v + \mathcal{L}v$. The solutions of equation (5.1) obviously satisfy the equation (5.14). The idea is to interpret this equation as an equation on $X^1_{\mathcal{I}}$ and to show that its solutions are conversely solutions of the original equation (5.1). Before we can realize this idea, we have, however, to show that the bilinear form

$$\widetilde{a}(u, v) \,=\, a(u, \varepsilon v + \mathcal{L}v) \,+\, \alpha\, s(u, \varepsilon v + \mathcal{L}v) \tag{5.15}$$

on $\mathcal{D}_{\mathcal{I}} \times \mathcal{D}_{\mathcal{I}}$ can be extended to a bounded bilinear form on $X^1_{\mathcal{I}} \times X^1_{\mathcal{I}}$. This is trivial for its leading part. The problem is to estimate its singular low-order terms appropriately. The resulting estimates can be written down in a few lines, but their proof is rather tedious because the single parts have to be analyzed and estimated very carefully. The next two sections exclusively deal with this task. We will then come back to the eigenvalue problem itself in section 8.

6. Estimates for the low-order terms I. As stated, the key to our regularity theory are estimates for the low-order terms in the bilinear form (5.15), that is, for the terms involving the nucleus-electron and the electron-electron interaction potential

$$V_{ne}(x) \,=\, -\sum_{i=1}^{N}\sum_{\nu=1}^{K} \frac{Z_\nu}{|x_i - a_\nu|}, \quad V_{ee}(x) \,=\, \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} \frac{1}{|x_i - x_j|}, \tag{6.1}$$

and for its part arising from the bilinear form (5.2). This bilinear form can, if one splits the coefficient function ψ into the functions $\psi_i(x) = |x_i|$, be represented as sum

$$s(u, v) \,=\, \frac{1}{2}\sum_{i=1}^{N} \theta_i \left\{ \int \nabla\psi_i \cdot \nabla u\; v\, dx \,-\, \int u\; \nabla\psi_i \cdot \nabla v\, dx \right\}, \tag{6.2}$$

that is, because the products of the gradients are of the form

$$\nabla\psi_i \cdot \nabla u \,=\, \frac{x_i}{|x_i|} \cdot \nabla_i u, \quad \nabla\psi_i \cdot \nabla v \,=\, \frac{x_i}{|x_i|} \cdot \nabla_i v, \tag{6.3}$$

like the nucleus-electron interaction potential as a sum of one-electron terms. These terms involving only one single electron represent the simple part. The corresponding estimates are in the end based on the Hardy inequality from Lemma 2.1. They do

not rely on symmetry properties of the wavefunctions. The situation is different for the terms of which the electron-electron interaction potential is composed. These estimates are therefore treated in a separate section.

The first of the estimates we need to study the regularity properties, namely the estimate (2.9) from Theorem 2.2, has already been stated in section 2 and formed the basis of the variational formulation of the eigenvalue problem. The aim of the present section is to complement this estimate by estimates for the expressions

$$(V_{ne}u, \mathcal{L}v), \quad s(u, \mathcal{L}v), \quad s(u, v). \tag{6.4}$$

in the modified bilinear form (5.15) respectively in (5.1). The crucial observation is that most of the partial derivatives of which the differential operator $\mathcal{L}$ is composed commute with the single parts of the interaction potentials (6.1) and can be shifted from one to the other side in the single parts of the bilinear form (6.2), up to those few that act upon a component of the position vector of the just considered electron.

THEOREM 6.1. *For all infinitely differentiable functions u and v in the space $\mathcal{D}$,*

$$(V_{ne}u, \mathcal{L}v) \;\leq\; 2\, N^{1/2} Z \,|\, u \,|_{\mathcal{I},0} \,|\, v \,|_{\mathcal{I},1}. \tag{6.5}$$

Proof. We first consider a single electron i and have then to distinguish the cases $i \notin \mathcal{I}$ and $i \in \mathcal{I}$. The first case is the easier one. We start from the representation (5.11) of $\mathcal{L}$. Since the partial derivatives of which the L_α are composed do in this case not act upon the components of x_i, the Fubini theorem and integration by parts yield

$$\begin{aligned}\int \frac{1}{|x_i - a_\nu|}\, u\, \mathcal{L}v\, dx \;&=\; (-1)^{|\mathcal{I}|} \sum_{\alpha \in \mathcal{I}^*} \int \frac{1}{|x_i - a_\nu|} \left(\int u\, L_\alpha^2 v\, d\widetilde{x} \right) dx_i \\ &=\; \sum_{\alpha \in \mathcal{I}^*} \int \left(\int \frac{1}{|x_i - a_\nu|}\, L_\alpha u\, L_\alpha v\, dx_i \right) d\widetilde{x},\end{aligned}$$

where we have split x into x_i and $\widetilde{x}$. By the Cauchy-Schwarz and the Hardy inequality, the inner integrals on the right hand side can be estimated by the expressions

$$\left(\int \left| L_\alpha u \right|^2 dx_i \right)^{1/2} \left(4 \sum_{\ell=1}^{3} \int \left| \frac{\partial}{\partial x_{i,\ell}}\, L_\alpha v \right|^2 dx_i \right)^{1/2}.$$

With help of the Cauchy-Schwarz inequality, now first applied to the resulting outer integrals and then to the sum over the single $\alpha \in \mathcal{I}^*$, the estimate

$$\begin{aligned}&\int \frac{1}{|x_i - a_\nu|}\, u\, \mathcal{L}v\, dx \\ &\qquad \leq\; 2 \left(\sum_{\alpha \in \mathcal{I}^*} \int \left| L_\alpha u \right|^2 dx \right)^{1/2} \left(\sum_{\alpha \in \mathcal{I}^*} \sum_{\ell=1}^{3} \int \left| \frac{\partial}{\partial x_{i,\ell}}\, L_\alpha v \right|^2 dx \right)^{1/2}\end{aligned}$$

follows. In more compact notion, this estimate reads

$$\int \frac{1}{|x_i - a_\nu|}\, u\, \mathcal{L}v\, dx \;\leq\; 2 \,|\, u \,|_{\mathcal{I},0} \,|\nabla_i v|_{\mathcal{I},0}. \tag{6.6}$$

It transfers without change to the case of indices $i \in \mathcal{I}$, but the proof is somewhat more complicated then. In this case, we decompose the operator $\mathcal{L}$ into the sum

$$\mathcal{L} \;=\; (-1)^{|\mathcal{I}|} \sum_{\alpha \in \mathcal{I}^*} L_\alpha^2 \;=\; (-1)^{|\mathcal{I}|} \sum_{\beta \in \mathcal{I}_i^*} L_\beta \Delta_i L_\beta, \quad L_\beta \;=\; \prod_{j \in \mathcal{I}_i} \frac{\partial}{\partial x_{j,\beta(j)}},$$

where $\mathcal{I}_i = \mathcal{I} \setminus \{i\}$ and $\mathcal{I}_i^*$ denotes the set of the mappings β that assign one of the components 1, 2, or 3 to the electron indices j in $\mathcal{I}_i$. Since the L_β do not act upon the components of x_i, integration by parts and the Fubini theorem lead as above to

$$\begin{aligned}\int \frac{1}{|x_i - a_\nu|}\, u\, \mathcal{L}v\, dx \;&=\; (-1)^{|\mathcal{I}|} \sum_{\beta\in\mathcal{I}_i^*} \int \frac{1}{|x_i - a_\nu|} \Big(\int u\, L_\beta \Delta_i L_\beta v\, d\widetilde{x} \Big)\, dx_i \\ &=\; -\sum_{\beta\in\mathcal{I}_i^*} \int \Big(\int \frac{1}{|x_i - a_\nu|}\, L_\beta u\, \Delta_i L_\beta v\, dx_i \Big)\, d\widetilde{x}.\end{aligned}$$

By the Cauchy-Schwarz and the Hardy inequality, the inner integrals on the right hand side can, up to the factor 2, be estimated by the expressions

$$\Big(\int |\nabla_i L_\beta u|^2\, dx_i \Big)^{1/2} \Big(\int |\Delta_i L_\beta v|^2\, dx_i \Big)^{1/2}.$$

These expressions can be rewritten as

$$\Big(\sum_{k=1}^{3} \int \Big| \frac{\partial L_\beta u}{\partial x_{i,k}} \Big|^2\, dx_i \Big)^{1/2} \Big(\sum_{k=1}^{3} \sum_{\ell=1}^{3} \int \Big| \frac{\partial}{\partial x_{i,\ell}} \frac{\partial L_\beta v}{\partial x_{i,k}} \Big|^2\, dx_i \Big)^{1/2},$$

where we have applied the relation

$$\sum_{k=1}^{3} \sum_{\ell=1}^{3} \int \frac{\partial^2 w}{\partial x_{i,k}^2}\, \frac{\partial^2 w}{\partial x_{i,\ell}^2}\, dx_i \;=\; \sum_{k=1}^{3} \sum_{\ell=1}^{3} \int \Big| \frac{\partial^2 w}{\partial x_{i,\ell} \partial x_{i,k}} \Big|^2\, dx_i$$

to the functions $w = L_\beta v$. This relation is proved integrating by parts. Since the set of the differential operators L_α, $\alpha \in \mathcal{I}^*$, coincides with the set of the operators

$$\frac{\partial}{\partial x_{i,k}}\, L_\beta, \quad k = 1, 2, 3, \;\; \beta \in \mathcal{I}_i^*,$$

summation over all β, the Cauchy-Schwarz inequality (applied twice, first to the outer integrals and then to the sum over the β), and Fubini's theorem lead again to (6.6).

Summation over the single contributions in the potential finally yields

$$(V_{ne} u, \mathcal{L}v) \;\le\; 2\, Z\, |\, u\, |_{\mathcal{I},0} \sum_{i=1}^{N} |\nabla_i v|_{\mathcal{I},0},$$

from which the proposition follows with the elementary estimate

$$\sum_{i=1}^{N} |\nabla_i v|_{\mathcal{I},0} \;\le\; N^{1/2} \Big(\sum_{i=1}^{N} |\nabla_i v|_{\mathcal{I},0}^2 \Big)^{1/2} \;=\; N^{1/2}\, |\, v\, |_{\mathcal{I},1},$$

that is responsible for the factor $N^{1/2}$. □

The proof of the estimates for the expression $s(u, \mathcal{L}v)$ resembles that of Theorem 6.1. It is prepared by the following lemma for functions of three real variables.

LEMMA 6.2. *For all infinitely differentiable functions $u, v : \mathbb{R}^3 \to \mathbb{R}$ that vanish outside a bounded subset,*

$$\int \frac{x}{|x|} \cdot \nabla u\; v\, dx \;-\; \int u\; \frac{x}{|x|} \cdot \nabla v\, dx \;\le\; 6 \Big(\int |\nabla u|^2\, dx \Big)^{1/2} \Big(\int |\, v\, |^2\, dx \Big)^{1/2}. \tag{6.7}$$

Proof. The difficulty is that the derivatives of v have to be shifted to u. We first assume that v vanishes on a neighborhood of the origin. Integration by parts then yields

$$-\int u\,\frac{x}{|x|}\cdot\nabla v\,dx \;=\; 2\int\frac{1}{|x|}\,u\,v\,dx+\int\frac{x}{|x|}\cdot\nabla u\,v\,dx.$$

This relation remains true for the general case, as one can show by an argument as in the proof of Lemma 2.1, that is, by multiplying v with a sequence of cut-off functions and applying the dominated convergence theorem. The proposition then follows again from the Cauchy-Schwarz inequality and the Hardy inequality. □

THEOREM 6.3. *For all infinitely differentiable functions u and v in the space $\mathcal{D}$,*

$$s(u,\mathcal{L}v)\;\le\;3\,|\,u\,|_{\mathcal{I},0}\,|\,v\,|_{\mathcal{I},1}. \tag{6.8}$$

Proof. We consider again a single electron i and have, as in the proof of Theorem 6.1, to distinguish the cases $i\in\mathcal{I}$ and $i\notin\mathcal{I}$. For indices $i\in\mathcal{I}$, one obtains, by the representation (6.3) of the $\nabla\psi_i$, the Fubini theorem, and integration by parts,

$$\begin{aligned}\int\nabla\psi_i\cdot\nabla u\;\mathcal{L}v\,dx\;-\int u\;\nabla\psi_i\cdot\nabla\mathcal{L}v\,dx\\ =\;-\sum_{\beta\in\mathcal{I}_i^*}\int\Big\{\int\nabla\psi_i\cdot\nabla L_\beta u\;\Delta_i L_\beta v\,dx_i\;-\int L_\beta u\;\nabla\psi_i\cdot\nabla\Delta_i L_\beta v\,dx_i\Big\}\,d\widetilde{x}.\end{aligned}$$

By the representation (6.3) of the gradients of the ψ_i and Lemma 6.2, the inner integrals on the right hand side can, up to the factor 6, be estimated by the expressions

$$\Big(\int|\nabla_i L_\beta u|^2\,dx_i\Big)^{1/2}\Big(\int|\Delta_i L_\beta v|^2\,dx_i\Big)^{1/2}.$$

Rewriting these expressions as in the proof of Theorem 6.1, from this the estimate

$$\int\nabla\psi_i\cdot\nabla u\;\mathcal{L}v\,dx\;-\int u\;\nabla\psi_i\cdot\nabla\mathcal{L}v\,dx\;\le\;6\,|\,u\,|_{\mathcal{I},0}\,|\nabla_i v|_{\mathcal{I},0}$$

follows. This estimate also holds if $i\notin\mathcal{I}$, as is shown starting directly from the representation of $\mathcal{L}$ as the sum of the differential operators L_α^2, that is, from

$$\begin{aligned}\int\nabla\psi_i\cdot\nabla u\;\mathcal{L}v\,dx\;-\int u\;\nabla\psi_i\cdot\nabla\mathcal{L}v\,dx\\ =\;\sum_{\alpha\in\mathcal{I}^*}\int\Big\{\int\nabla\psi_i\cdot\nabla L_\alpha u\;L_\alpha v\,dx_i\;-\int L_\alpha u\;\nabla\psi_i\cdot\nabla L_\alpha v\,dx_i\Big\}\,d\widetilde{x}.\end{aligned}$$

The inner integrals are now, with Lemma 6.2, up to the factor 6 estimated as

$$\Big(\int|L_\alpha u|^2\,dx_i\Big)^{1/2}\Big(\int|\nabla_i L_\alpha v|^2\,dx_i\Big)^{1/2},$$

where the role of the two functions has been exchanged here. From that then again the estimate above follows. Summation over the indices i, the Cauchy-Schwarz inequality, and the fact that the θ_i^2 sum up to 1 complete the proof. □

The group of estimates for the one-electron parts in the bilinear form (5.15) is completed by the following estimate for the expression $s(u,v)$ itself:

THEOREM 6.4. *For all infinitely differentiable functions u and v in the space $\mathcal{D}$,*

$$s(u,v) \;\le\; 3\,\|u\|_0\,|\,v\,|_1. \tag{6.9}$$

Proof. With help of Lemma 6.2, the single parts can again be estimated as

$$\int \nabla\psi_i\cdot\nabla u\;v\,dx \;-\; \int u\;\nabla\psi_i\cdot\nabla v\,dx \;\le\; 6\;\|u\|_0\,\|\nabla_i v\|_0.$$

The proposition follows from that in the known way. □

7. Estimates for the low-order terms II. The part in the bilinear form resulting from the electron-electron interaction potential is estimated basically in the same way as the terms considered in the previous section. The central observation is again that most of the derivatives of which the differential operators L_α are composed commute with the single parts of the potential. However, there is one important difference. In the already studied cases only first-order derivatives remained, in contrast to the second-order derivatives we have to face here. This causes an additional problem since the second-order partial derivatives of a Coulomb potential are no longer locally integrable in three space dimensions. Therefore the Pauli principle has to brought into play here. A wavefunction that is compatible with the Pauli principle vanishes where two electrons with the same spin meet, a fact which counterbalances the singular behavior of the second-order derivatives of the interaction potential and enables it to estimate the terms under consideration.

To master the most singular terms, the Hardy estimate from Lemma 2.1 has to be complemented by a second, closely related estimate for functions of three variables.

LEMMA 7.1. *For all infinitely differentiable functions v in the variable $x\in\mathbb{R}^3$ that have a compact support and that vanish at the origin,*

$$\int \frac{1}{|x|^4}\,v^2\,dx \;\le\; 4\int \frac{1}{|x|^2}\,|\nabla v|^2\,dx\,. \tag{7.1}$$

Proof. The estimate is proved in the same way as the Hardy inequality (2.6). Setting temporarily $d(x)=|x|$, it starts from the relation

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

with the help of which (7.1) is proved for functions v that vanish on a neighborhood of the origin. To transfer this estimate to functions v that vanish only at the origin itself, one has to utilize that there exists a constant K with

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

and can then complete the proof in the same way as that of (2.6) with help of the dominated convergence theorem, multiplying v with a sequence of cut-off functions. □

It should be noted that the estimate (7.1) does not hold for functions not vanishing at the origin since the function $x\to 1/|x|^4$ is not locally integrable in three space dimensions, which is the source of our problems.

The single parts of which the electron-electron interaction potential is composed involve only two electrons so that the estimates that we have to prove are essentially two-electron estimates. To simplify the notation, we restrict ourselves for a while to the two-electron case and denote the three-dimensional coordinate vectors of these electrons by x and y. Correspondingly, the real numbers x_1, x_2, and x_3 and y_1, y_2, and y_3 denote the components of these vectors. For abbreviation, let

$$\phi(x,y) = \frac{1}{|x-y|}, \quad d(x,y) = |x-y|. \tag{7.2}$$

In this notation, our task is essentially to estimate the integrals like

$$\int \phi u \sum_{k,\ell=1}^{3} \frac{\partial^4 v}{\partial x_k^2 \, \partial y_\ell^2} \, d(x,y) \tag{7.3}$$

for infinitely differentiable functions u and v that have a compact support and that are antisymmetric under the exchange of x and y.

The first step is to combine the inequality (7.1) and the Hardy inequality (2.6) to the estimate for antisymmetric functions on which our argumentation is founded.

LEMMA 7.2. *For all infinitely differentiable functions u in the variables $x, y \in \mathbb{R}^3$ that have a compact support and are antisymmetric under the exchange of x and y,*

$$\int \frac{1}{|x-y|^4} \, u^2 \, d(x,y) \;\le\; 16 \sum_{k,\ell=1}^{3} \int \Big(\frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big)^2 \, d(x,y). \tag{7.4}$$

Proof. Since such functions v vanish where $y = x$, Lemma 7.1 yields

$$\int \Big(\int \frac{1}{|x-y|^4} \, u^2 \, dy \Big) \, dx \;\le\; \int \Big(4 \sum_{\ell} \int \frac{1}{|x-y|^2} \Big(\frac{\partial u}{\partial y_\ell} \Big)^2 \, dy \Big) \, dx.$$

By the Hardy inequality from Lemma 2.1,

$$\int \Big(\int \frac{1}{|x-y|^2} \Big(\frac{\partial u}{\partial y_\ell} \Big)^2 \, dx \Big) \, dy \;\le\; \int \Big(4 \sum_{k} \int \Big(\frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big)^2 \, dx \Big) \, dy.$$

The proposition follows with Fubini's theorem. □

The counterparts to this estimate are the following variants

$$\int \frac{1}{|x-y|^2} \, v^2 \, d(x,y) \;\le\; 4 \sum_{k=1}^{3} \int \Big(\frac{\partial v}{\partial x_k} \Big)^2 \, d(x,y), \tag{7.5}$$

$$\int \frac{1}{|x-y|^2} \, v^2 \, d(x,y) \;\le\; 4 \sum_{\ell=1}^{3} \int \Big(\frac{\partial v}{\partial y_\ell} \Big)^2 \, d(x,y) \tag{7.6}$$

of the Hardy inequality (2.6) that, in contrast to (7.4), do not rely on the antisymmetry of the considered function. They are proved in the same way as (7.4). The argumentation in this section centers in the estimates (7.4), (7.5), and (7.6).

Now we can begin to estimate the integrals (7.3). In the first step we shift half of the partial derivatives from the function v to the function u.

LEMMA 7.3. *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support, and let u be antisymmetric with respect to the exchange of x and y. Then, for all indices k and ℓ,*

$$\int \phi u \, \frac{\partial^4 v}{\partial x_k^2 \, \partial y_\ell^2} \, d(x,y) \;=\; \int \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi u) \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \, d(x,y). \tag{7.7}$$

Proof. The problem are the singularities of ϕ that do not allow to integrate by parts directly, and in particular the strong singularities of the second-order partial derivatives of the interaction potential ϕ. To overcome this difficulty, let $\varphi(r)$ be a twice continuously differentiable function of the real variable $r \geq 0$ that coincides with the function $1/r$ for $r \geq 1$ and is constant for $r \leq 1/2$. Let

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

The ϕ_ν are then itself twice continously differentiable functions and coincide with the original function ϕ for all x, y of distance $|x-y| \geq 1/\nu$. Integration by parts leads to

$$\int \phi_\nu u \, \frac{\partial^4 v}{\partial x_k^2 \, \partial y_\ell^2} \, d(x,y) \;=\; \int \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi_\nu u) \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \, d(x,y).$$

The integral on the right hand side of this equation splits, because of

$$\frac{\partial^2}{\partial x_k \partial y_\ell}(\phi_\nu u) \;=\; \frac{\partial^2 \phi_\nu}{\partial x_k \partial y_\ell} \, u + \frac{\partial \phi_\nu}{\partial x_k} \frac{\partial u}{\partial y_\ell} + \frac{\partial \phi_\nu}{\partial y_\ell} \frac{\partial u}{\partial x_k} + \phi_\nu \, \frac{\partial^2 u}{\partial x_k \partial y_\ell},$$

into four parts. We claim that there is a constant M, independent of ν, such that

$$\Big| \, \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi_\nu u) \, \Big| \;\leq\; \frac{M}{|x-y|^2}.$$

This is because, for the first and second-order derivatives of the ϕ_ν, the estimates

$$\Big| \frac{\partial^2 \phi_\nu}{\partial x_k \partial y_\ell} \Big| \leq \frac{c}{|x-y|^3}, \quad \Big| \frac{\partial \phi_\nu}{\partial x_k} \Big| \leq \frac{c}{|x-y|^2}, \quad \Big| \frac{\partial \phi_\nu}{\partial y_\ell} \Big| \leq \frac{c}{|x-y|^2}$$

hold, and for function ϕ_ν itself the estimate

$$|\phi_\nu| \;\leq\; \frac{c}{|x-y|},$$

where c is a constant independent of ν, and finally because u can be estimated as

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

since $u(x,y) = 0$ for $x = y$ and its first order derivatives are bounded.

Since u vanishes outside a bounded set, the given second-order partial derivatives of the $\phi_\nu u$ are thus uniformly bounded by an integrable function. Since the ϕ_ν and their first and second-order partial derivatives converge to ϕ and its respective derivatives outside the diagonal $x = y$, a set of measure zero, and as the derivatives of v are bounded, the dominated convergence theorem yields

$$\lim_{\nu \to \infty} \int \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi_\nu u) \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \, d(x,y) \;=\; \int \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi u) \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \, d(x,y).$$

For the other side of the equation, one can argue correspondingly and obtains

$$\lim_{\nu\to\infty} \int \phi_\nu u \, \frac{\partial^4 v}{\partial x_k^2 \, \partial y_\ell^2} \, d(x,y) \;=\; \int \phi u \, \frac{\partial^4 v}{\partial x_k^2 \, \partial y_\ell^2} \, d(x,y),$$

which then completes the proof of (7.7). □

We continue estimating the integrals on the right hand side of (7.7). Lemma 7.3 in particular guarantees that these integrals exist despite the singularities of the second-order partial derivatives of ϕ. Here, as with the following estimate, the fact that u is antisymmetric and therefore vanishes on the diagonal $x = y$ substantially enters.

LEMMA 7.4. *Let u and v be infinitely differentiable functions in the variables $x, y \in \mathbb{R}^3$ that have a compact support and let the function u be antisymmetric with respect to the exchange of x and y. Then the estimate*

$$\begin{aligned} (7.8) \qquad \sum_{k,\ell=1}^{3} \int \frac{\partial^2}{\partial x_k \partial y_\ell}(\phi u) \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \, d(x,y) \\ \leq\; C \Big\{ \sum_{k,\ell=1}^{3} \Big\| \frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big\|_0^2 \Big\}^{1/2} \Big\{ \sum_{k,\ell=1}^{3} \Big| \frac{\partial^2 v}{\partial x_k \partial y_\ell} \Big|_1^2 \Big\}^{1/2} \end{aligned}$$

holds, where the constant C is specified in the proof.

Proof. First we decompose the given derivatives of the function ϕu into the parts

$$\frac{\partial^2}{\partial x_k \partial y_\ell}(\phi u) \;=\; \frac{\partial^2 \phi}{\partial x_k \partial y_\ell} \, u + \frac{\partial \phi}{\partial x_k} \frac{\partial u}{\partial y_\ell} + \frac{\partial \phi}{\partial y_\ell} \frac{\partial u}{\partial x_k} + \phi \, \frac{\partial^2 u}{\partial x_k \partial y_\ell}.$$

and estimate the expression on the left hand side of (7.8) by a corresponding sum

$$X_1 Y \;+\; X_2 Y \;+\; X_3 Y \;+\; X_4 Y,$$

with the quantities $X_i, Y \geq 0$ defined as follows. The most critical part X_1, that can only be estimated for functions u for which $u(x,y) = 0$ for $x = y$, is given by

$$X_1^2 \;=\; \sum_{k,\ell=1}^{3} \Big\| \frac{1}{\phi} \, \frac{\partial^2 \phi}{\partial x_k \partial y_\ell} \, u \Big\|_0^2 \;=\; 6 \, \Big\| \frac{1}{d^2} \, u \Big\|_0^2$$

and contains the second-order derivatives of ϕ. The squares of X_2 and X_3 are

$$\begin{aligned} X_2^2 \;&=\; \sum_{k,\ell=1}^{3} \Big\| \frac{1}{\phi} \, \frac{\partial \phi}{\partial x_k} \frac{\partial u}{\partial y_\ell} \Big\|_0^2 = \sum_{\ell=1}^{3} \Big\| \frac{1}{d} \, \frac{\partial u}{\partial y_\ell} \Big\|_0^2, \\ X_3^2 \;&=\; \sum_{k,\ell=1}^{3} \Big\| \frac{1}{\phi} \, \frac{\partial \phi}{\partial y_\ell} \frac{\partial u}{\partial x_k} \Big\|_0^2 = \sum_{k=1}^{3} \Big\| \frac{1}{d} \, \frac{\partial u}{\partial x_k} \Big\|_0^2, \end{aligned}$$

and X_4 is the remaining term that is given by the expression

$$X_4^2 \;=\; \sum_{k,\ell=1}^{3} \Big\| \frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big\|_0^2.$$

Because of the factor $1/\phi$ in the norms defining the X_i, the part Y given by

$$Y^2 = \sum_{k,\ell=1}^{3} \Big\| \phi \, \frac{\partial^2 v}{\partial x_k \partial y_\ell} \Big\|_0^2$$

contains conversely the factor $\phi = 1/d$. The quantities X_1, X_2, X_3 can, by Lemma 7.2 and (7.5) and (7.6), respectively, be estimated by X_4. More precisely, the estimates

$$X_1^2 \le 6 \cdot 16\, X_4^2, \quad X_2^2 \le 4\, X_4^2, \quad X_3^2 \le 4\, X_4^2$$

hold. Since, again by the variants (7.5) and (7.6) of the Hardy inequality, finally

$$Y^2 \le 2 \sum_{k,\ell=1}^{3} \Big| \frac{\partial^2 v}{\partial x_k \partial y_\ell} \Big|_1^2,$$

the proposition is proved with $C = (5+4\sqrt{6})\sqrt{2}$, a still rather small constant. □

By Lemmas 7.3 and 7.4, we can conclude that, for all infinitely differentiable functions u that are antisymmetric under the exchange of x and y and have a compact support, and all infinitely differentiable functions v that have a compact support,

$$\sum_{k,\ell=1}^{3} \int \phi u\, \frac{\partial^4 v}{\partial x_k^2\, \partial y_\ell^2}\, d(x,y) \;\le\; C \Big\{ \sum_{k,\ell=1}^{3} \Big\| \frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big\|_0^2 \Big\}^{1/2} \Big\{ \sum_{k,\ell=1}^{3} \Big| \frac{\partial^2 v}{\partial x_k \partial y_\ell} \Big|_1^2 \Big\}^{1/2}, \tag{7.9}$$

where $C = (5+4\sqrt{6})\sqrt{2}$. Correspondingly one can prove the estimate

$$\sum_{k=1}^{3} \int \phi u\, \frac{\partial^2 v}{\partial x_k^2}\, d(x,y) \;\le\; C \Big\{ \sum_{k=1}^{3} \Big\| \frac{\partial u}{\partial x_k} \Big\|_0^2 \Big\}^{1/2} \Big\{ \sum_{k=1}^{3} \Big| \frac{\partial v}{\partial x_k} \Big|_1^2 \Big\}^{1/2}, \tag{7.10}$$

with C now the constant $C = 3\sqrt{2}$, and finally the estimate

$$\int \phi u\, v\, d(x,y) \;\le\; \sqrt{2}\, \|u\|_0 |\, v\,|_1 \tag{7.11}$$

for all infinitely differentiable functions u and v that have a compact support, regardless their antisymmetry with respect to the exchange of x and y.

We can now return to the full set of the electron coordinate vectors $x_1, x_2, \ldots, x_N$ in $\mathbb{R}^3$ and the old notation. The estimates (7.9) to (7.11) are now merged into:

THEOREM 7.5. *For all infinitely differentiable functions $u \in \mathcal{D}_\mathcal{I}$ and $v \in \mathcal{D}$,*

$$(V_{ee} u, \mathcal{L} v) \;\le\; C N^{3/2}\, |\, u\,|_{\mathcal{I},0}\, |\, v\,|_{\mathcal{I},1}, \tag{7.12}$$

where the constant $C \le 5+4\sqrt{6}$ is independent of the number N of electrons.

Proof. We first turn our attention to the interaction potential

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

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

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

The strategy is the same as in the previous section. We split the operators L_α into the product of operators L_β that do not act upon the components of x_i and x_j and a remaining part. Here we have to distinguish three cases, namely that both indices i and j belong to the index set $\mathcal{I}$, that only one of these indices belongs to $\mathcal{I}$, and that none of these indices is contained in $\mathcal{I}$.

The first case is the most critical one because of the strong singularities of the second-order derivatives of the given interaction potential and is therefore considered first. Let $\mathcal{I}_{ij} = \mathcal{I} \setminus \{i,j\} \neq \emptyset$ and let $\mathcal{I}_{ij}^*$ again denote the set of the mappings β that assign one of the components 1, 2, or 3 to an electron index in $\mathcal{I}_{ij}$. The set of the differential operators L_α, $\alpha \in \mathcal{I}^*$, coincides then with the set of the operators

$$\frac{\partial}{\partial x_{i,k}} \frac{\partial}{\partial x_{i,\ell}} L_\beta, \quad k,\ell = 1,2,3, \;\; \beta \in \mathcal{I}_{ij}^*,$$

and the integral to be estimated can, as in the previous section, be written as sum

$$(-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \int \phi_{ij} u \, L_\alpha^2 v \, dx \;=\; \sum_{\beta\in\mathcal{I}_{ij}^*} \int \Big(\sum_{k,l=1}^{3} \iint \phi_{ij} L_\beta u \, \frac{\partial^4 L_\beta v}{\partial x_{i,k}^2 \partial x_{j,\ell}^2} \, dx_i dx_j \Big) \, d\widetilde{x},$$

where x is split into x_i, x_j, and the remaining components $\widetilde{x}$. Like u itself, its partial derivatives $L_\beta u$, $\beta \in \mathcal{I}_{ij}^*$, are antisymmetric under the exchange of x_i and x_j. This is due to the fact that the operators L_β do not act upon the components of x_i and x_j and can be seen as follows. Let w be an arbitrary function that changes its sign under the permutation P that exchanges x_i for x_j and let $e \neq 0$ be a vector that is invariant under P. Let $\widetilde{w}(x) = w(Px)$. Since $\widetilde{w}(x) = -w(x)$, then

$$(\nabla w)(Px) \cdot e = P^T (\nabla w)(Px) \cdot e = (\nabla \widetilde{w})(x) \cdot e = \; - (\nabla w)(x) \cdot e,$$

so that the directional derivative of w in direction e inherits the antisymmetry of w. The proposition follows from that by induction on the order of L_β. The inner integrals on the right hand side of the equation above can therefore be estimated with the help of (7.9). In the same fashion as in the previous section, finally the estimate

$$(-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \int \phi_{ij} u \, L_\alpha^2 v \, dx \;\leq\; C \,|\, u \,|_{\mathcal{I},0} \Big\{ \,|\nabla_i v|_{\mathcal{I},0}^2 + |\nabla_j v|_{\mathcal{I},0}^2 \Big\}^{1/2} \tag{7.13}$$

follows, where $C \leq (5{+}4\sqrt{6})\sqrt{2}$ is the same constant as in (7.9). The case that $\mathcal{I}_{ij}$ is empty, that is, $\mathcal{I}$ consists only of the indices i and j, is treated in the same way.

In the case that $i \in \mathcal{I}$, but $j \notin \mathcal{I}$, we set $\mathcal{I}_i = \mathcal{I} \setminus \{i\}$ and denote by $\mathcal{I}_i^*$ again the set of the mappings β from $\mathcal{I}_i$ to the set of the indices 1, 2, and 3. The set of the differential operators L_α, $\alpha \in \mathcal{I}^*$, then coincides with the set of the operators

$$\frac{\partial}{\partial x_{i,k}} L_\beta, \quad k = 1,2,3, \;\; \beta \in \mathcal{I}_i^*,$$

and the integral to be estimated splits into the sum

$$(-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \int \phi_{ij} u \, L_\alpha^2 v \, dx \;=\; - \sum_{\beta\in\mathcal{I}_i^*} \int \Big(\sum_{k=1}^{3} \iint \phi_{ij} L_\beta u \, \frac{\partial^2 L_\beta v}{\partial x_{i,k}^2} \, dx_i dx_j \Big) \, d\widetilde{x}.$$

The inner sum on the right hand side can be estimated with help of (7.10), which then finally again results in the estimate (7.13), where $C \leq 3\sqrt{2}$ is now the constant from (7.10). The same estimate holds, of course, for the case that $i \notin \mathcal{I}$ and $j \in \mathcal{I}$.

If neither i nor j are contained in $\mathcal{I}$, one simply starts from

$$(-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \int \phi_{ij} u \, L_\alpha^2 v \, dx \;=\; \sum_{\alpha\in\mathcal{I}^*} \int \Big(\iint \phi_{ij} L_\alpha u \, L_\alpha v \, dx_i dx_j \Big) \, d\widetilde{x},$$

from which one obtains, with the help of (7.11), again the estimate (7.13), now with the constant $C = \sqrt{2}$. Independent of whether two, one, or none of the indices i and j is contained in $\mathcal{I}$, the estimate (7.13) holds with a constant $C \leq (5+4\sqrt{6})\sqrt{2}$.

The proposition finally follows from the elementary estimate

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

summing over all particle pairs. □

8. The regularity theorems. We are now in the position to prove that the solutions $u \in H^1_{\mathcal{I}}$ of the modified eigenvalue equation (5.1) are located in the space $X^1_{\mathcal{I}}$ from section 5, the completion of the space $\mathcal{D}_{\mathcal{I}}$ of the infinitely differentiable functions (2.1) with compact support that are invariant under the exchange of arguments x_i and x_j in $\mathbb{R}^3$ for all indices $i \neq j$ in the given subset $\mathcal{I}$ of the set of indices $1, \ldots, N$ under a norm measuring high-order mixed derivatives. The key to our results are the estimates for the low-order terms from the preceding two sections, that can be summarized as follows. For all functions u in $\mathcal{D}_{\mathcal{I}}$ and v in $\mathcal{D}$, first the estimates

$$(Vu, \mathcal{L}v) \leq C\,\theta(N,Z)\,|\,u\,|_{\mathcal{I},0}\,|\,v\,|_{\mathcal{I},1}, \quad s(u,\mathcal{L}v) \leq 3\,|\,u\,|_{\mathcal{I},0}\,|\,v\,|_{\mathcal{I},1} \tag{8.1}$$

in terms of the seminorms (5.8) hold, where the first one for the term with the interaction potential (2.7) represents a combination of the estimates (6.5) from Theorem 6.1 and (7.12) from Theorem 7.5, and the second one is the estimate (6.8) from Theorem 6.3. The constant C is independent of the number N of electrons, of the considered index set $\mathcal{I}$, of the number, the position, and the charge of the nuclei, and particularly of their total charge Z. The proofs yielded the upper bound $C = 7+4\sqrt{6}$ for C. The quantity $\theta(N,Z)$ has been defined in (2.8) and covers the growth of the bound in N and Z. The antisymmetry of the functions u with respect to the exchange of the corresponding electron coordinates substantially enters into the proof of the first estimate, since without this property it is not possible to get a handle on the electron-electron interaction terms. The estimates (8.1) potentially involving very high-order derivatives are complemented by the estimates

$$(Vu, v) \leq 3\,\theta(N,Z)\,\|u\|_0\,|\,v\,|_1, \quad s(u,v) \leq 3\,\|u\|_0\,|\,v\,|_1 \tag{8.2}$$

from Theorem 2.2 and Theorem 6.4 for functions u and v in $\mathcal{D}$, that generally hold and do not rely on the given antisymmetry properties. The estimates (8.1) and (8.2) show that the bilinear forms $(Vu, \mathcal{L}v)$ and $s(u, \mathcal{L}v)$ can be uniquely extended from $\mathcal{D}_{\mathcal{I}} \times \mathcal{D}_{\mathcal{I}}$ to bounded bilinear forms on $X^0_{\mathcal{I}} \times X^1_{\mathcal{I}}$, and that particularly the bilinear form

$$\widetilde{a}(u,v) \;=\; a(u, \varepsilon v + \mathcal{L}v) \;+\; \alpha\, s(u, \varepsilon v + \mathcal{L}v) \tag{8.3}$$

from section 5 can be uniquely extended from $\mathcal{D}_{\mathcal{I}}$ to a bounded bilinear form on $X^1_{\mathcal{I}}$. For the ease of presentation, we will keep the notation $(Vu, \mathcal{L}v)$ and $s(u, \mathcal{L}v)$ for arguments $u \in X^0_{\mathcal{I}}$ and $v \in X^1_{\mathcal{I}}$ and mean the extended forms then, where, of course, some care has to be taken to avoid misinterpretations and fallacies.

The second ingredient of the proof of the regularity theorems is Fourier analysis. Recall that a rapidly decreasing function is an infinitely differentiable function that tends, together with all its derivatives, faster to zero for $|x|$ tending to infinity than any polynomial grows. The space $\mathcal{D}$ of the infinitely differentiable functions with bounded support is a subspace of the Schwartz space $\mathcal{S}$ of the rapidly decreasing functions. The

advantage of $\mathcal{S}$ over $\mathcal{D}$ is that the Fourier transform of a rapidly decreasing function is again a rapidly decreasing function. As with $\mathcal{D}_\mathcal{I}$, let $\mathcal{S}_\mathcal{I}$ denotes the space of the rapidly decreasing functions of corresponding antisymmetry. The seminorms (5.8) of a rapidly decreasing function read in terms of its Fourier transform

$$|\,u\,|^2_{\mathcal{I},s} = \int \Big(\sum_{i=1}^N |\omega_i|^2 \Big)^s \Big(\prod_{i\in\mathcal{I}} |\omega_i|^2 \Big)\, |\widehat{u}(\omega)|^2\, d\omega. \tag{8.4}$$

Correspondingly, the H^1-seminorm $|\,u\,|_1$ and the L_2-norm $\|u\|_0 = |\,u\,|_0$ are given by

$$|\,u\,|^2_s = \int \Big(\sum_{i=1}^N |\omega_i|^2 \Big)^s\, |\widehat{u}(\omega)|^2\, d\omega. \tag{8.5}$$

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

$$\mathcal{S}_{\mathcal{I},H} = \{\, v \in \mathcal{S}_\mathcal{I} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \le \Omega \,\} \tag{8.6}$$

of rapidly decreasing functions with the given symmetry properties in $H^1_\mathcal{I}$ and $X^1_\mathcal{I}$, respectively, are the Hilbert spaces $H^1_{\mathcal{I},H}$ and $X^1_{\mathcal{I},H}$. The closures of the space

$$\mathcal{S}_{\mathcal{I},L} = \{\, v \in \mathcal{S}_\mathcal{I} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \ge \Omega \,\} \tag{8.7}$$

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

$$H^1_\mathcal{I} = H^1_{\mathcal{I},L} \oplus H^1_{\mathcal{I},H}, \quad X^1_\mathcal{I} = X^1_{\mathcal{I},L} \oplus X^1_{\mathcal{I},H} \tag{8.8}$$

into orthogonal parts. By the Fourier representation (8.4) and (8.5) of the norms,

$$|u_L|_{\mathcal{I},s} \;\le\; \Omega^s \left(\frac{\Omega}{\sqrt{|\,\mathcal{I}\,|}} \right)^{|\,\mathcal{I}\,|} \|u_L\|_0 \tag{8.9}$$

for the low-frequency functions $u_L \in \mathcal{S}_{\mathcal{I},L}$. The space $H^1_{\mathcal{I},L}$ and its subspace $X^1_{\mathcal{I},L}$ therefore coincide. The relation (8.9) transfers to all functions in these spaces. In fact, the functions in $H^1_{\mathcal{I},L}$ are infinitely differentiable and all their derivatives are square integrable. Fourier analysis also shows that

$$\|u_H\|_0 \le \Omega^{-1} |u_H|_1, \quad |u_H|_{\mathcal{I},0} \le \Omega^{-1} |u_H|_{\mathcal{I},1} \tag{8.10}$$

for all high-frequency functions in u_H in $H^1_{\mathcal{I},H}$ and $X^1_{\mathcal{I},H}$ respectively. On $H^1_{\mathcal{I},H}$, the seminorm $|\cdot|_1$ and the norm $\|\cdot\|_1$ thus are equivalent. For $u_L \in H^1_{\mathcal{I},L}$, conversely

$$|u_L|_1 \le \Omega\, \|u_L\|_0, \quad |u_L|_{\mathcal{I},1} \le \Omega\, |u_L|_{\mathcal{I},0}. \tag{8.11}$$

The central observation, on which the proof of our regularity theorem is based, is that the low-order terms in the bilinear form in the second-order equation (5.1), as well as in the high-order bilinear form (8.3), behave like small perturbations on the corresponding spaces of high-frequency functions. More precisely, by (8.1) and (8.10),

$$(V u_H, \mathcal{L} v_H) \le C\, \theta(N,Z)\, \Omega^{-1} |u_H|_{\mathcal{I},1}\, |v_H|_{\mathcal{I},1}, \tag{8.12}$$

$$s(u_H, \mathcal{L} v_H) \le 3\,\Omega^{-1} |u_H|_{\mathcal{I},1}\, |v_H|_{\mathcal{I},1} \tag{8.13}$$

for all $u_H, v_H \in \mathcal{S}_{\mathcal{I},H}$. Correspondingly, by (8.2) and (8.10), for these u_H and v_H

$$(V u_H, v_H) \le 3\,\theta(N,Z)\,\Omega^{-1} |u_H|_1\, |v_H|_1, \tag{8.14}$$

$$s(u_H, v_H) \le 3\,\Omega^{-1} |u_H|_1\, |v_H|_1. \tag{8.15}$$

This implies that the two bilinear forms become coercive on the corresponding spaces of high-frequency functions, provided that the bound Ω separating the low from the high frequencies is chosen sufficiently large. If we assume $C \ge 3$ and choose

$$\Omega \;\ge\; 4\,C\,\theta(N,Z) + 12\,\alpha, \tag{8.16}$$

for all high-frequency functions $u_H \in H^1_{\mathcal{I},H}$

$$a(u_H, u_H) + \alpha\, s(u_H, u_H) \;\ge\; \frac{1}{4}\, |u_H|_1^2 \tag{8.17}$$

and correspondingly, for the functions $u_H \in X^1_{\mathcal{I},H}$,

$$\widetilde{a}(u_H, u_H) \;\ge\; \frac{1}{4}\, \big(\varepsilon\, |u_H|_1^2 + |u_H|_{\mathcal{I},1}^2\big). \tag{8.18}$$

The claimed coercivity follows from that by the equivalence of the seminorm $|\cdot|_1$ and the norm $\|\cdot\|_1$ on the given spaces of high-frequency functions. We still combine the low-order terms in $\widetilde{a}(u,v)$ respectively $a(u,v)$ in the bilinear forms

$$\widetilde{b}(\varphi, v) = (V\varphi, \varepsilon v + \mathcal{L} v) + \alpha\, s(\varphi, \varepsilon v + \mathcal{L} v), \tag{8.19}$$

$$b(\varphi, \chi) \;= (V\varphi, \chi) + \alpha\, s(\varphi, \chi) \tag{8.20}$$

on $X^0_{\mathcal{I}} \times X^1_{\mathcal{I}}$ and $L_2 \times H^1$, respectively. They satisfy, for Ω as in (8.16), the estimates

$$\widetilde{b}(\varphi, v) \;\le\; \frac{1}{4}\,\Omega\, \big(\varepsilon\, \|\varphi\|_0^2 + |\,\varphi\,|_{\mathcal{I},0}^2\big)^{1/2} \big(\varepsilon\, |\,v\,|_1^2 + |\,v\,|_{\mathcal{I},1}^2\big)^{1/2}, \tag{8.21}$$

$$b(\varphi, \chi) \;\le\; \frac{1}{4}\,\Omega\, \|\varphi\|_0\, |\,\chi\,|_1 \tag{8.22}$$

for functions φ, v, and χ in the corresponding spaces.

Due to the orthogonality properties of the low- and the high-frequency functions, the low- and the high-frequency part of a solution of the eigenvalue equation (5.1)

$$a(u, \chi) + \alpha\, s(u, \chi) \;=\; \lambda\, (u, \chi), \quad \chi \in H^1_{\mathcal{I}}, \tag{8.23}$$

interact only by the low-order part in the bilinear form on the left hand side. The aim is to control the high-frequency part and its mixed derivatives by the low-frequency part of the given solution. The first step to reach this goal is the following lemma that immediately results from the orthogonality of the low- and the high-frequency functions both with respect to the L_2- and the H^1-inner product.

LEMMA 8.1. *Let $u = u_L + u_H$ be the decomposition of a solution in $u \in H^1_{\mathcal{I}}$ of the equation* (5.1), (8.23) *into its low-frequency and its high-frequency part. Then*

$$a(u_H, \chi_H) + \alpha\, s(u_H, \chi_H) - \lambda\, (u_H, \chi_H) \;=\; -\, b(u_L, \chi_H), \quad \chi_H \in H^1_{\mathcal{I},H}. \tag{8.24}$$

We will keep the low-frequency part u_L fixed for a while and will consider (8.24) as an equation for the high-frequency part u_H. We will show that such equations are uniquely solvable for frequency bounds (8.16) and that the regularity of the right hand side transfers to the regularity of the solution.

LEMMA 8.2. *For frequency bounds Ω as in* (8.16)*, the equation*

$$a(u_H, \chi_H) + \alpha\, s(u_H, \chi_H) + \mu\,(u_H, \chi_H) \;=\; b(\varphi, \chi_H), \quad \chi_H \in H^1_{\mathcal{I},H}, \tag{8.25}$$

possesses a unique solution $u_H \in H^1_{\mathcal{I},H}$ for all given functions $\varphi \in L_2$ and arbitrary nonnegative parameters μ. This solution satisfies the estimates

$$\|u_H\|_0 \le \|\varphi\|_0, \quad |u_H|_1 \le \Omega\, \|\varphi\|_0. \tag{8.26}$$

Proof. As $\mu \ge 0$, the additional term does not alter the coercivity (8.17) of the bilinear form on the left hand side of the equation (8.25). The Lax-Milgram theorem hence guarantees the existence and uniqueness of a solution. The estimate for the H^1-seminorm of the solution follows directly from (8.17) and (8.22) inserting $\chi_H = u_H$. The L_2-norm of the solution can be estimated by its H^1-seminorm utilizing the property (8.10) of high-frequency functions, from which the other estimate follows. □

A corresponding result holds for the high-order counterpart of the equation (8.25), that formally results from this equation replacing the test function χ_H by test functions $\varepsilon v_H + \mathcal{L} v_H$, with all the care that has to be taken with this type of arguments.

LEMMA 8.3. *For frequency bounds Ω as in* (8.16)*, the equation*

$$\widetilde{a}(u_H, v_H) + \mu\,(u_H, \varepsilon v_H + \mathcal{L} v_H) \;=\; \widetilde{b}(\varphi, v_H), \quad v_H \in X^1_{\mathcal{I},H}, \tag{8.27}$$

possesses a unique solution $u_H \in X^1_{\mathcal{I},H}$ for all given functions $\varphi \in X^0_{\mathcal{I}}$ and arbitrary nonnegative parameters μ. This solution satisfies the estimate

$$|u_H|_{\mathcal{I},1} \;\le\; \Omega\, \big(\varepsilon\, \|\varphi\|_0^2 + |\,\varphi\,|^2_{\mathcal{I},0}\big)^{1/2}. \tag{8.28}$$

Proof. As $\mu \ge 0$ and $(u, \varepsilon u + \mathcal{L} u) \ge 0$ for $u \in X^1_{\mathcal{I}}$, the proposition again follows from the coercivity (8.18) of the bilinear form $\widetilde{a}(u_H, v_H)$, from the bound (8.21) for the bilinear form $\widetilde{b}(\varphi, v)$ on the right hand side, and the Lax-Milgram theorem. □

We want to show that the solutions of the equations (8.25) and (8.27) coincide for $\varphi \in X^0_{\mathcal{I}}$. For that we need the following, at first sight seemingly obvious lemma:

LEMMA 8.4. *The solution $u_H \in X^1_{\mathcal{I},H}$ of the equation* (8.27) *satisfies the equation* (8.25) *for all rapidly decreasing functions χ_H of the particular form*

$$\chi_H \;=\; \varepsilon v_H + \mathcal{L} v_H, \quad v_H \in \mathcal{S}_{\mathcal{I},H}. \tag{8.29}$$

Proof. It suffices to show that the representation (8.3) holds not only for functions u and v in $\mathcal{D}_{\mathcal{I}}$ but for all functions $u \in X^1_{\mathcal{I}}$ and $v \in \mathcal{S}_{\mathcal{I}}$, and to prove a corresponding relation for the bilinear form (8.19), that, in a strict sense, is defined by (8.19) only for functions φ and v in $\mathcal{D}_{\mathcal{I}}$ and then continously extended to $X^0_{\mathcal{I}} \times X^1_{\mathcal{I}}$. We begin with the case that $u \in \mathcal{D}_{\mathcal{I}}$ and approximate $v \in \mathcal{S}_{\mathcal{I}}$ by the functions

$$v_R(x) = \phi\Big(\frac{x}{R}\Big)\, v(x), \quad R > 0,$$

in $\mathcal{D}_\mathcal{I}$, where ϕ is an infinitely differentiable cut-off function with values $\phi(x) = 1$ for $|x| \le 1$ and $\phi(x) = 0$ for $|x| \ge 2$. For sufficiently large R, v_R and v coincide on the support of u. Since v_R tends to v in the $X^1_\mathcal{I}$-norm, by the definition of $\widetilde{a}(u,v)$ on $\mathcal{D}_\mathcal{I}$

$$\widetilde{a}(u,v) \;=\; \lim_{R\to\infty} \widetilde{a}(u,v_R) \;=\; a(u,\varepsilon v + \mathcal{L}v) \;+\; \alpha\, s(u,\varepsilon v + \mathcal{L}v)$$

for all $u \in \mathcal{D}_\mathcal{I}$ and $v \in \mathcal{S}_\mathcal{I}$. Since the left and the right hand sides of this equation represent bounded linear functionals in $u \in X^1_\mathcal{I}$ for $v \in \mathcal{S}_\mathcal{I}$ given, and since $\mathcal{D}_\mathcal{I}$ is a dense subset of $X^1_\mathcal{I}$, the equation transfers to all $u \in X^1_\mathcal{I}$ and $v \in \mathcal{S}_\mathcal{I}$. Correspondingly,

$$\widetilde{b}(\varphi, v) = b(\varphi, \varepsilon v + \mathcal{L}v)$$

for all $\varphi \in X^0_\mathcal{I}$ and $v \in \mathcal{S}_\mathcal{I}$, from which the proposition then follows. □

The argument that closes the gap between the equations (8.25) and (8.27) is the observation that every function in $\chi_H \in \mathcal{S}_{\mathcal{I},H}$ can be represented in the form (8.29). The proof requires that the parameter ε is strictly positive and breaks down for $\varepsilon = 0$.

LEMMA 8.5. *For all rapidly decreasing high-frequency functions $\chi_H \in \mathcal{S}_{\mathcal{I},H}$ there is a rapidly decreasing high-frequency function $v_H \in \mathcal{S}_{\mathcal{I},H}$ that solves the equation*

$$\varepsilon\, v_H + \mathcal{L}v_H = \chi_H. \tag{8.30}$$

Proof. The antisymmetry of a function with respect to the given permutations transfers to its Fourier transform and vice versa. The function $v_H \in \mathcal{S}_{\mathcal{I},H}$ given by

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

has by this reason the required symmetry properties and solves the equation. □

The solution of the modified equation (8.27) therefore satisfies the equation (8.25) for all $\chi_H \in \mathcal{S}_{\mathcal{I},H}$ and, as $\mathcal{S}_{\mathcal{I},H}$ is dense in $H^1_{\mathcal{I},H}$, for all $\chi_H \in H^1_{\mathcal{I},H}$. Since the equation (8.25) possesses only one solution, the solutions of both equations coincide for $\varphi \in X^0_\mathcal{I}$ given. Since $\varepsilon > 0$ was arbitrary, this observation and (8.10) prove:

LEMMA 8.6. *If the bound Ω separating the high from the low frequencies is chosen according to* (8.16) *and $\varphi \in X^0_\mathcal{I}$, the solution $u_H \in H^1_{\mathcal{I},H}$ of the equation* (8.25) *is contained in the space $X^1_{\mathcal{I},H}$ and satisfies the estimates*

$$|u_H|_{\mathcal{I},0} \le |\,\varphi\,|_{\mathcal{I},0}, \quad |u_H|_{\mathcal{I},1} \le \Omega\,|\,\varphi\,|_{\mathcal{I},0}. \tag{8.31}$$

Since the low-frequency part u_L of the solution u of the equation (5.1), (8.23) is contained in $X^0_\mathcal{I}$ and even in $X^1_\mathcal{I}$, we can apply the result just proved to the equation (8.24), from which it follows that also the high-frequency part u_H of u and with that u itself are contained in $X^1_\mathcal{I}$. The quantitative version of this result reads:

THEOREM 8.7. *The solutions $u \in H^1_\mathcal{I}$ of the modified eigenvalue problem* (5.1) *for negative values λ are contained in $X^1_\mathcal{I}$. For frequency bounds* (8.16) *and the u_L their corresponding low-frequency parts, their seminorms* (5.8), (5.12) *satisfy the estimates*

$$|\,u\,|_{\mathcal{I},0} \le \sqrt{2}\,|u_L|_{\mathcal{I},0}, \quad |\,u\,|_{\mathcal{I},1} \le \sqrt{2}\,\Omega\,|u_L|_{\mathcal{I},0}. \tag{8.32}$$

Proof. By Lemma 8.6, the high frequency parts u_H of these u satisfy the estimates

$$|u_H|_{\mathcal{I},0} \le |u_L|_{\mathcal{I},0}, \quad |u_H|_{\mathcal{I},1} \le \Omega\, |u_L|_{\mathcal{I},0}.$$

They can thus be controlled by the corresponding low-frequency parts u_L independent of the given $\lambda<0$. The proposition follows from the orthogonality of the decomposition of the functions into the two parts u_L and u_H and the inverse estimate in (8.11). □

The estimates (8.32) for the mixed derivatives of the solutions have a counterpart for the solutions themselves that follows in the same way directly from Lemma 8.2.

THEOREM 8.8. *Under the same assumptions as in Theorem* 8.7*, the solutions of the modified eigenvalue problem* (5.1) *satisfy the two estimates*

$$\|u\|_0 \le \sqrt{2}\, \|u_L\|_0, \quad |\, u\,|_1 \le \sqrt{2}\, \Omega\, \|u_L\|_0. \tag{8.33}$$

A solution $u \in H^1_{\mathcal{I}}$ of the equation (5.1), (8.23) is trivially contained in $H^1_{\mathcal{I}'}$ for all nonempty subsets $\mathcal{I}'$ of $\mathcal{I}$. As $s(u,v)$ is obviously invariant under the exchange of all electrons i in the subset $\mathcal{I}'$ of $\mathcal{I}$, Theorem 5.1 ensures that u solves the equations

$$a(u,\chi) + \alpha\, s(u,\chi) \;=\; \lambda\, (u,\chi), \quad \chi \in H^1_{\mathcal{I}'}, \tag{8.34}$$

on all of these spaces $H^1_{\mathcal{I}'}$ and thus satisfies, by Theorem 8.7, the estimates

$$|\, u\,|_{\mathcal{I}',0} \le \sqrt{2}\, |u_L|_{\mathcal{I}',0}, \quad |\, u\,|_{\mathcal{I}',1} \le \sqrt{2}\, \Omega\, |u_L|_{\mathcal{I}',0} \tag{8.35}$$

for all nonempty subsets $\mathcal{I}'$ of the given index set $\mathcal{I}$. Therefore the norms given by

$$|\!|\!| u |\!|\!|^2_{\mathcal{I},1} \;=\; \int \Big(\sum_{i=1}^{N} \Big|\frac{\omega_i}{\Omega}\Big|^2 \Big) \prod_{i\in\mathcal{I}} \Big(1 + \Big|\frac{\omega_i}{\Omega}\Big|^2 \Big)\, |\widehat{u}(\omega)|^2\, d\omega, \tag{8.36}$$

$$|\!|\!| u |\!|\!|^2_{\mathcal{I},0} \;=\; \int \prod_{i\in\mathcal{I}} \Big(1 + \Big|\frac{\omega_i}{\Omega}\Big|^2 \Big)\, |\widehat{u}(\omega)|^2\, d\omega. \tag{8.37}$$

of these functions, that combine the H^1-norm and H^1-norms of the corresponding mixed derivatives, remain finite. The frequency bound Ω fixes a length scale here. Such length scales naturally appear in every estimate that relates derivatives of distinct order to each other. They have to be incorporated in the definition of the corresponding norms to compensate the different scaling behavior of the derivatives and to obtain physically meaningful estimates that are independent of the choice of units.

With these notations, we can now formulate and prove our final and conclusive regularity theorem for the solutions of the modified eigenvalue problem (5.1):

THEOREM 8.9. *The solutions $u \in H^1_{\mathcal{I}}$ of the modified eigenvalue problem* (5.1) *for negative values λ satisfy, for frequency bounds* (8.16)*, the estimates*

$$|\!|\!| u |\!|\!|_{\mathcal{I},0} \le \sqrt{2e}\, \|u\|_0, \quad |\!|\!| u |\!|\!|_{\mathcal{I},1} \le \sqrt{2e}\, \|u\|_0. \tag{8.38}$$

Proof. By the estimates (8.33) for the L_2-norm of the solution itself, respectively the estimates (8.35) for the L_2-norms of its corresponding mixed derivatives,

$$\int \prod_{i\in\mathcal{I}'} \Big|\frac{\omega_i}{\Omega}\Big|^2\, |\widehat{u}(\omega)|^2\, d\omega \;\le\; 2 \int_{|\omega|\le\Omega} \prod_{i\in\mathcal{I}'} \Big|\frac{\omega_i}{\Omega}\Big|^2\, |\widehat{u}(\omega)|^2\, d\omega \tag{8.39}$$

for all subsets $\mathcal{I}'$ of $\mathcal{I}$, where the empty product is by definition 1. As

$$\sum_{\mathcal{I}'\subseteq\mathcal{I}} \prod_{i\in\mathcal{I}'} \Big|\frac{\omega_i}{\Omega}\Big|^2 = \prod_{i\in\mathcal{I}} \Big(1+\Big|\frac{\omega_i}{\Omega}\Big|^2\Big), \tag{8.40}$$

one obtains from (8.39) first the estimate

$$\|\!|u|\!\|_{\mathcal{I},0}^2 \;\le\; 2\int_{|\omega|\le\Omega} \prod_{i\in\mathcal{I}} \Big(1+\Big|\frac{\omega_i}{\Omega}\Big|^2\Big)\,|\widehat{u}(\omega)|^2\,d\omega. \tag{8.41}$$

The product on the right hand side of (8.40) is, because of

$$\prod_{i\in\mathcal{I}} \Big(1+\Big|\frac{\omega_i}{\Omega}\Big|^2\Big) \le\; \exp\Big(\sum_{i\in\mathcal{I}} \Big|\frac{\omega_i}{\Omega}\Big|^2\Big), \tag{8.42}$$

bounded by the constant e for all ω in the ball of radius Ω around the origin. This proves the first of the two estimates (8.38). The second is treated in the same way. □

Theorem 8.9 can be easily translated back from a statement about the solutions of the modified eigenvalue problems (5.1), that have only an auxiliary function, into a statement about the original eigenvalue problems (3.12), in which we are actually interested and on which this work centers. The index set $\mathcal{I}$ is then either a subset of the set $\mathcal{I}_-$ of the indices of the electrons with spin $-1/2$ or of the set $\mathcal{I}_+$ of the indices of the electrons with spin $+1/2$. The theorem states that the true solutions of the electronic Schrödinger equation in some sense behave like products

$$u(x) \;=\; \prod_{i=1}^{N} \phi_i(x_i) \tag{8.43}$$

of orbitals, that is, exponentially decaying functions in H^1, a fact that roughly justifies the picture of atoms and molecules that we have in our minds.

Only small portions of the frequency domain substantially contribute to the wavefunctions. This remark can be quantified with help of the notion of hyperbolic crosses, hyperboloid-like regions in the frequency space that consist of those ω for which

$$\prod_{i\in\mathcal{I}_-} \Big(1+\Big|\frac{\omega_i}{\Omega}\Big|^2\Big) \;+\; \prod_{i\in\mathcal{I}_+} \Big(1+\Big|\frac{\omega_i}{\Omega}\Big|^2\Big) \;\le\; \frac{1}{\varepsilon^2}, \tag{8.44}$$

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

$$\|u-u_\varepsilon\|_1 = \;\mathcal{O}(\varepsilon) \tag{8.45}$$

tends to zero like $\mathcal{O}(\varepsilon)$ with increasing size of the crosses. This observation might also serve as a basis for the construction of approximation methods, for example utilizing the fact that functions like the projections u_ε with Fourier transforms vanishing outside such hyperbolic crosses can be sampled on sparse grids [68].

It is remarkable that Theorem 8.9 not only ensures that the given high-order mixed derivatives of the correspondingly exponentially weighted or unweighted eigenfunctions exist and are square integrable, but also gives a rather explicit estimate for

their norms in terms of the L_2-norm of the weighted or unweighted eigenfunctions themselves. Taking into account the upper bound

$$\alpha \;<\; \sqrt{2\,(\Sigma^*(\sigma)-\lambda_0(\sigma))} \tag{8.46}$$

for the possible decay rates α, that has been studied in section 4, the theorem tells us that the estimates (8.38) hold at least for the scaling parameters

$$\Omega \;\geq\; 4\,C\,\sqrt{N}\,\max(N,Z) + 12\,\sqrt{2\,(\Sigma^*(\sigma)-\lambda_0(\sigma))} \tag{8.47}$$

independent of the considered eigenvalue $\lambda < \Sigma^*(\sigma)$, and in particular for the Ω that is equal to the right hand side of this inequality. Hence there is conversely a minimum

$$\Omega \;\leq\; 4\,C\,\sqrt{N}\,\max(N,Z) + 12\,\sqrt{2\,(\Sigma^*(\sigma)-\lambda_0(\sigma))} \tag{8.48}$$

independent of the choice of the coefficients θ_i in the definition of the exponential weight (provided that the choice of the θ_i maintains the given antisymmetry, of course) such that these estimates hold for all eigenfunctions for these eigenvalues. This minimum Ω can principally be much smaller than the given upper bound and fixes an intrinsic length scale of the considered atomic or molecular system.

9. Atoms as model systems. The scaling parameter Ω limits the local variation of the wavefunctions quantitatively. It can be assumed that (8.48) considerably overestimates the optimum Ω for spatially extended molecules that are composed of a big number of light atoms. The question is how sharp this bound is for compact systems with many electrons tightly bound to the nuclei, like heavier atoms. Atoms are, in the given Born-Oppenheimer approximation, described by the Hamilton operator

$$H \;=\; \sum_{i=1}^{N} \left\{ -\,\frac{1}{2}\,\Delta_i \,-\, \frac{Z}{|x_i|} \right\} \,+\, \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|x_i - x_j|}. \tag{9.1}$$

The first term covers the attraction of the electrons by the nucleus and the second their interaction with each other. The crucial property that we utilize here is that the potential in this operator is homogeneous of degree minus one, i.e., that

$$V(\vartheta x) = \vartheta^{-1} V(x) \tag{9.2}$$

for all $\vartheta > 0$. The H^1-seminorm and the L_2-norm of eigenfunctions of such operators are linked to each other by the famous virial theorem, a proof of which we include for the sake of completeness. This proof is essentially a reformulation of that in [65] in terms of weak solutions of the eigenvalue problem.

THEOREM 9.1. *The H^1-seminorm and the L_2-norm of an eigenfunction $u \in H^1$ for the eigenvalue λ of the atomic Hamilton operator* (9.1) *are linked via the relation*

$$|\,u\,|_1^2 \;=\; -\,2\lambda\,\|u\|_0^2. \tag{9.3}$$

Proof. Let $u_\vartheta(x) = u(\vartheta x)$ for $\vartheta > 0$. A short calculation only utilizing the fact that u is an eigenfunction for the eigenvalue λ then shows that

$$\int \nabla u_\vartheta \cdot \nabla v \, dx \;=\; 2\vartheta^2 \lambda \int u_\vartheta v \, dx \;-\; 2\vartheta^2 \int V(\vartheta x)\, u_\vartheta v \, dx$$

for arbitrary test functions $v \in H^1$. Because of $V(\vartheta x) = \vartheta^{-1} V(x)$, this reduces to

$$\int \nabla u_\vartheta \cdot \nabla v \, dx \;=\; 2\vartheta^2 \lambda \int u_\vartheta v \, dx \;-\; 2\vartheta \int V u_\vartheta v \, dx.$$

On the other hand, for all test functions $v \in H^1$,

$$\int \nabla u \cdot \nabla v \, dx \;=\; 2\lambda \int uv \, dx \;-\; 2 \int V u \, v \, dx.$$

Setting $v = u$ in the first and $v = u_\vartheta$ in the second case, for $\vartheta \neq 1$ it follows that

$$(\vartheta + 1)\, \lambda \int u u_\vartheta \, dx \;= \int V u \, u_\vartheta \, dx.$$

Since for all square integrable functions u and v

$$\lim_{\vartheta \to 1} \int v(x)\, u(\vartheta x)\, dx \;= \int v(x) u(x)\, dx,$$

and since for $u \in H^1$ the product Vu is square integrable, too, this yields

$$2\lambda \int u^2 \, dx \;= \int V u \, u \, dx.$$

Using once more that u is an eigenfunction, one finally gets the proposition. □

The virial theorem relates the expectation values of the kinetic energy, the potential energy, and the total energy to each other, but also determines, through the different scaling behavior of both sides of the equation, the length scale on which the considered eigenfunction varies. Hence it is no surprise that a lower bound for the optimal scaling parameter Ω can be derived in terms of the eigenvalues.

THEOREM 9.2. *If the estimates from Theorem* 8.9 *hold for the eigenfunction* $u \in H^1(\sigma)$ *for the eigenvalue* λ *of the atomic Hamilton operator* (9.1)*, necessarily*

$$\Omega \;\geq\; \sqrt{\frac{|\lambda|}{e}}\,. \tag{9.4}$$

Proof. From the just proved virial theorem, from the Fourier representation (8.5) of the H^1-seminorm and of the norm given by (8.36), and from Theorem 8.9 one gets

$$-\,2\lambda\, \|u\|_0^2 \;=\; |\,u\,|_1^2 \;\leq\; \Omega^2\, |||u|||_{\mathcal{I},1}^2 \;\leq\; 2e\,\Omega^2\, \|u\|_0^2.$$

Because $u \neq 0$, one can divide by the L_2-norm of u and obtains the proposition. □

Since the ionization threshold $\Sigma^*(\sigma)$ is less than or equal to zero by Theorem 4.1, the upper estimate (8.48) and the lower estimate (9.4) prove the inclusion

$$\sqrt{|\lambda_0(\sigma)|} \;\lesssim\; \Omega \;\lesssim\; \sqrt{N}\, \max(N, Z) + \sqrt{|\lambda_0(\sigma)|} \tag{9.5}$$

for the optimum Ω that is independent of the considered eigenvalue $\lambda < \Sigma^*(\sigma)$. The second term on the right hand side of (8.48) or (9.5), that comes from the skew-symmetric part in the equation (4.18) for the exponentially weighted eigenfunctions, will therefore never dominate the asymptotic behavior of the optimum Ω in N and Z.

The problem therefore reduces to the question how well the bound (8.48) reflects the growth of the optimum scaling parameter Ω in N and Z for the case of unweighted eigenfunctions, in which the second term on the right hand side of (8.48) can be omitted. To answer this question at least partially, we first consider the operator

$$H \;=\; \sum_{i=1}^{N} \left\{ -\frac{1}{2}\,\Delta_i \;-\; \frac{Z}{|x_i|} \right\} \tag{9.6}$$

in which the electron-electron interaction is completely neglected and to which Theorem 9.2 can be literally transfered. Due to the absence of the electron-electron interaction potential, the estimates (8.38) hold then regardless of any symmetry property. The eigenfunctions of this operator are linear combinations of the products

$$u(x) \;=\; \prod_{i=1}^{N} \phi_i(x_i) \tag{9.7}$$

of hydrogen-like wavefunctions, solutions of the Schrödinger equation

$$-\frac{1}{2}\,\Delta\phi \;-\; \frac{Z}{|x|}\,\phi \;=\; \lambda\,\phi \tag{9.8}$$

for a single electron in the field of a nucleus of charge Z. The hydrogen-like wavefunctions are explicitly known and are calculated in almost every textbook on quantum mechanics; see for instance [58]. The corresponding eigenvalues

$$\lambda_n = -\frac{1}{2}\,\frac{Z^2}{n^2}, \quad n = 1, 2, \ldots, \tag{9.9}$$

are highly degenerate and tend to the infimum of the essential spectrum. The associated eigenspaces are spanned by the eigenfunctions with the given principal quantum number n, the angular momentum quantum numbers $l = 0, \ldots, n-1$, and the magnetic quantum numbers $m = -l, \ldots, l$ and have dimension n^2. The knowledge about these eigenfunctions forms the basis of our understanding of the periodic table.

If we neglect the Pauli principle completely, every product (9.7) becomes an admissible eigenfunction. The ground state energy of the corresponding system is then N times the minimum eigenvalue (9.9), i.e., $\lambda = -NZ^2/2$, from which the lower bound

$$\Omega \;\gtrsim\; N^{1/2} Z \tag{9.10}$$

follows, which behaves like the upper bound (8.48) in the number N of electrons and the nuclear charge Z for the case of neutral atoms or positively charged ions. Thus neither the upper bound (8.48) nor the lower bound (9.4) can be improved without bringing the Pauli principle or the electron-electron interaction into play.

If the Pauli principle is taken into account, the orbitals ϕ_i in (9.7) have to be partitioned into two groups associated with the electrons with spin up and spin down. The orbitals in each group have to be linearly independent of each other since the product otherwise vanishes under the corresponding antisymmetrization. The ground state energy increases and the lower bound for the scaling parameter decreases by that. Unlike a real atom, the system attains its minimum energy λ in states in which the numbers of electrons with spin up and spin down differs at most by one, that is, with at most one unpaired electron. Consider, for example, the case that the electrons

can be distributed to M doubly occupied shells $n = 1, 2, \ldots, M$ with $2n^2$ electrons in the shell n, n^2 with spin up and n^2 with spin down. Then $\lambda = -MZ^2$. Because $N \sim 2M^3/3$, the minimum eigenvalue hence behaves in the described situation like $\lambda \sim N^{1/3}Z^2$ and the scaling parameter needs therefore to grow at least like

$$\Omega \gtrsim N^{1/6}Z. \tag{9.11}$$

There remains some gap between this lower bound and the upper bound (8.48), but the estimate shows at least that the actual growth of the optimal scaling parameter in N and Z is not substantially overestimated by the right hand side of (8.48) for systems like the ones considered here.

In fact, the observed behavior is not restricted to the model Hamiltonian (9.6). Lieb and Simon [45] proved that the minimum eigenvalue of the full operator (9.1) grows like $\gtrsim Z^{7/3}$ with the total nuclear charge Z in the case $Z = N$, i.e., of neutral systems, which confirms the lower estimate (9.11). A more detailed study [69] of the product eigenfunctions (9.7) moreover shows that the optimum Ω behaves in this case indeed like the square root of the ground state energy, which can be explained from the behavior of the orbitals. One may conjecture that this generally holds.

10. Eigenfunction expansions. The results from section 8 may pave the way for the construction of very different approximation schemes for the solutions of the electronic Schrödinger equation. In this section, we follow a classical approach and approximate the solutions by products of three-dimensional, globally defined orbitals. Our aim is to imitate the expansion of functions on d-dimensional cubes into trigonometric polynomials, such as it has been described in the introduction, and to break in this way the curse of dimensionality. The problem is that the solutions of the electronic Schrödinger equation are defined on the infinitely extended space so that not only their regularity properties, but also their decay behavior has to be utilized. The foundations for that have been laid in the previous sections. The idea is to replace the trigonometric polynomials by the eigenfunctions of three-dimensional operators

$$H \,=\, -\,\Delta \,+\, V^2 \tag{10.1}$$

with infinitely differentiable functions $V > 0$ for which

$$\lim_{|x|\to\infty} V(x) \,=\, +\infty. \tag{10.2}$$

By Persson's characterization [49] already applied in section 4, the essential spectrum of such operators is empty so that they possess an L_2-complete orthonormal system of eigenfunctions $\phi_1, \phi_2, \phi_3, \ldots$ for eigenvalues $0 < \lambda_1 \le \lambda_2 \le \ldots$. Every square integrable function $u : \mathbb{R}^{3N} \to \mathbb{R}$ can therefore be represented as L_2-convergent series

$$u(x) \,=\, \sum_{k\in\mathbb{N}^N} \widehat{u}(k) \prod_{i=1}^{N} \phi_{k_i}(x_i), \quad \widehat{u}(k) \,=\, \Big(u,\, \prod_{i=1}^{N} \phi_{k_i}\Big), \tag{10.3}$$

where the sum runs over the products of the three-dimensional eigenfunctions ϕ_{k_i}, that together form an L_2-complete orthonormal system in $L_2(\mathbb{R}^{3N})$. We will examine in this section the convergence properties of this series in H^1 for the eigenfunctions u of the Schrödinger operator (1.1) that obey the Pauli principle. Hereby we fix the symmetry class of the wavefunctions being considered again by the sets $\mathcal{I}_-$ and $\mathcal{I}_+$ of the indices of the electrons with spin $-1/2$ respectively $+1/2$.

Our analysis is based on the study of the corresponding two bilinear forms

$$B_{\pm}(u,v) \;=\; \Big(\Big(\sum_{i=1}^{N} H_i\Big)\Big(\prod_{i\in\mathcal{I}_{\pm}} H_i\Big)\,u,\; v\Big) \tag{10.4}$$

associated with the index sets $\mathcal{I}_-$ and $\mathcal{I}_+$, that are first only defined for functions $u, v \in \mathcal{D}$, that is, for infinitely differentiable functions with compact support. The

$$H_i \;=\; -\,\Delta_i \,+\, V_i^2, \quad V_i(x) = V(x_i), \tag{10.5}$$

are the three-dimensional operators (10.1) acting upon the electrons i.

LEMMA 10.1. *For all functions $u, v \in \mathcal{D}$,*

$$B_{\pm}(u,v) \;=\; \sum_{k}\Big(\sum_{i=1}^{N}\lambda_{k_i}\Big)\Big(\prod_{i\in\mathcal{I}_{\pm}}\lambda_{k_i}\Big)\,\widehat{u}(k)\,\widehat{v}(k), \tag{10.6}$$

where the outer sum runs over all multi-indices $k = (k_1, \ldots, k_N)$, with k_i in $\mathbb{N}$.

Proof. The proof utilizes the fact that, for $u \in \mathcal{D}$ and all i, also $H_i u \in \mathcal{D}$, so that we always remain on safe ground. Expanding v, we first obtain the representation

$$B_{\pm}(u,v) \;=\; \sum_{k}\Big(\Big(\sum_{i=1}^{N} H_i\Big)\Big(\prod_{i\in\mathcal{I}_{\pm}} H_i\Big)\,u,\; \prod_{i=1}^{N}\phi_{k_i}\Big)\,\widehat{v}(k).$$

Since the ϕ_{k_i} are themselves infinitely differentiable by elliptic regularity theory, we can consecutively shift the H_i to the right hand side and so get the proposition. □

One recognizes from (10.6) that the $B_{\pm}(u,v)$ represent symmetric and positive definite bilinear forms on $\mathcal{D}$. They therefore induce norms on $\mathcal{D}$. We want to show that the considered eigenfunctions u of the Schrödinger operator (1.1) are in the completions of $\mathcal{D}$ under these norms or, in other words, that the expressions

$$\sum_{k}\Big(\sum_{i=1}^{N}\lambda_{k_i}\Big)\Big(\prod_{i\in\mathcal{I}_{\pm}}\lambda_{k_i}\Big)\,|\widehat{u}(k)|^2. \tag{10.7}$$

remain bounded for these eigenfunctions for properly adapted operators (10.1). The task to bound these expressions is substantially complicated by the presence of the sum over the eigenvalues in (10.6) respectively (10.7), or equivalently by the sum over the operators H_i in (10.4). Without these parts the argumentation would be much simpler because all arising three-dimensional operators commute then. On the other hand, we cannot exclude these parts since we are interested in the H^1- and not only the L_2-error. The H^1-error needs, for example, to be estimated to obtain error bounds for the Ritz procedure to compute eigenvalues and eigenfunctions.

Due to these complications, our goal cannot be reached in one go. We first estimate the bilinear forms (10.4) in terms of intermediate norms on $\mathcal{D}$, which are formed with help of the functions V_i in the operators H_i. These norms are given by

$$\|u\|_{\pm}^2 \;=\; \sum_{\mathcal{I}\subseteq\mathcal{I}_{\pm}}\Big\{\,\Big|\Big(\prod_{i\in\mathcal{I}'} V_i\Big)u\Big|_{\mathcal{I}}^2 + \sum_{k\notin\mathcal{I}}\Big|\Big(V_k\prod_{i\in\mathcal{I}'} V_i\Big)u\Big|_{\mathcal{I},0}^2\Big\}, \tag{10.8}$$

where we have utilized the abbreviating notation

$$|\,v\,|_{\mathcal{I}}^2 \;=\; R^{-2}|\,v\,|_{\mathcal{I},0}^2 + |\,v\,|_{\mathcal{I},1}^2. \tag{10.9}$$

The index sets $\mathcal{I}'$ are the complements of the index sets $\mathcal{I}$, over which the outer sum runs, in $\mathcal{I}_-$ and $\mathcal{I}_+$, respectively. The empty product is the identity. We recall that for the empty index set $\mathcal{I}$, the two seminorms $|\cdot|_{\mathcal{I},0}$ and $|\cdot|_{\mathcal{I},1}$ turn into the L_2-norm and the H^1-seminorm, respectively. The quantity R is a length scale, to be fixed later, that serves to make the estimates independent of the choice of units. Correspondingly, we replace the norms on $H^1(\mathbb{R}^{3N})$ and $H^1(\mathbb{R}^3)$ by their scaled counterparts given by

$$\|v\|_1^2 \,=\, R^{-2}\|v\|_0^2 + |\,v\,|_1^2. \tag{10.10}$$

To proceed, we need a further assumption on the functions V_i, that is, on the three-dimensional function V with which we started, to keep control of the arising commutators. We require that there is a constant K such that for all $x \in \mathbb{R}^3$

$$\big|(V^{-1}\nabla V)(x)\big| \,\le\, K\left(\frac{1}{R} + \frac{1}{|x|}\right), \quad \big|(V^{-1}\Delta V)(x)\big| \,\le\, K\left(\frac{1}{R^2} + \frac{1}{|x|^2}\right). \tag{10.11}$$

Some examples of functions V that fulfill these conditions will be given below. Starting point of our considerations are the following two estimates for functions of three variables in terms of the rescaled H^1-norm that directly result from this assumption.

LEMMA 10.2. *For all infinitely differentiable $u, v : \mathbb{R}^3 \to \mathbb{R}$ with compact support,*

$$\int V^{-1}\Delta(Vu)\,v\,dx \,\le\, C_1\,\|u\|_1\|v\|_1, \tag{10.12}$$

$$\int V\Delta(V^{-1}u)\,v\,dx \,\le\, C_2\,\|u\|_1\|v\|_1, \tag{10.13}$$

with constants C_1 and C_2 that depend only on the constant K from (10.11).

Proof. The first estimate follows with help of the Cauchy-Schwarz and the Hardy inequality from the relation

$$V^{-1}\Delta(Vu) \,=\, \Delta u \,+\, 2\,V^{-1}\nabla V\cdot\nabla u \,+\, V^{-1}(\Delta V)\,u.$$

For the proof of the second estimate, let $W = V^{-1}$. Since then

$$W^{-1}\nabla W = \,-\,V^{-1}\nabla V, \quad W^{-1}\Delta W = \,2\,|V^{-1}\nabla V|^2 - V^{-1}\Delta V,$$

the function W satisfies an estimate as in (10.11) with another constant K so that the second estimate is a direct consequence of the first one. □

LEMMA 10.3. *For all $u, v \in \mathcal{D}$, the bilinear forms* (10.4) *satisfy the estimates*

$$B_\pm(u,v) \le\, CN\,\|u\|_\pm\,\|v\|_\pm, \tag{10.14}$$

where the constant C exclusively depends on the constant K from (10.11).

Proof. The main difficulty in the proof is that the Laplacian Δ_k does unfortunately not commute with the multiplication operator V_k and one has therefore to keep track of a lot of different terms. The proof starts from the representation

$$\Big(\sum_{k=1}^N H_k\Big)\Big(\prod_{i\in\mathcal{J}} H_i\Big) = \sum_{\mathcal{I}\subseteq\mathcal{J}} (-1)^{|\mathcal{I}|}\sum_{k=1}^N \Big(-\Delta_k + V_k^2\Big)\Big(\prod_{i\in\mathcal{I}'} V_i\Big)\Big(\prod_{i\in\mathcal{I}}\Delta_i\Big)\Big(\prod_{i\in\mathcal{I}'} V_i\Big)$$

that follows from the fact that Δ_i and V_j commute for $i \ne j$, where $\mathcal{J}$ stands for one of the two sets $\mathcal{I}_-$ or $\mathcal{I}_+$. Accordingly $\mathcal{I}' = \mathcal{J}\setminus\mathcal{I}$. Taking into account the fact that the operators V_k and Δ_k do not commute, one sees that the expressions

$$\Big(\Big(\sum_{k=1}^N H_k\Big)\Big(\prod_{i\in\mathcal{J}} H_i\Big)\,u,\,v\Big) \,=\, -\,Q_1^1 \,-\, Q_1^2 \,+\, Q_2^1 \,+\, Q_2^2$$

to be estimated expand, in operator notation, as follows

$$
\begin{aligned}
Q_1^1 &= \sum_{\mathcal{I}\subseteq\mathcal{J}} (-1)^{|\mathcal{I}|} \sum_{k\in\mathcal{I}'} \Big(\Big(V_k^{-1}\Delta_k V_k\Big) \Big(\prod_{i\in\mathcal{I}} \Delta_i\Big) \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, u, \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, v\Big),\\
Q_1^2 &= \sum_{\mathcal{I}\subseteq\mathcal{J}} (-1)^{|\mathcal{I}|} \sum_{k\notin\mathcal{I}'} \Big(\Big(\Delta_k \prod_{i\in\mathcal{I}} \Delta_i\Big) \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, u, \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, v\Big),\\
Q_2^1 &= \sum_{\mathcal{I}\subseteq\mathcal{J}} (-1)^{|\mathcal{I}|} \sum_{k\in\mathcal{I}} \Big(\Big(V_k\Delta_k V_k^{-1}\Big) \Big(\prod_{i\in\mathcal{I}_k} \Delta_i\Big) \Big(V_k \prod_{i\in\mathcal{I}'} V_i\Big)\, u, \Big(V_k \prod_{i\in\mathcal{I}'} V_i\Big)\, v\Big),\\
Q_2^2 &= \sum_{\mathcal{I}\subseteq\mathcal{J}} (-1)^{|\mathcal{I}|} \sum_{k\notin\mathcal{I}} \Big(\Big(\prod_{i\in\mathcal{I}} \Delta_i\Big) \Big(V_k \prod_{i\in\mathcal{I}'} V_i\Big)\, u, \Big(V_k \prod_{i\in\mathcal{I}'} V_i\Big)\, v\Big),
\end{aligned}
$$

where, for the index set $\mathcal{I}$ and $k\in\mathcal{I}$ given, we have written $\mathcal{I}_k = \mathcal{I}\setminus\{k\}$. Going back to the definition of the norms, the terms Q_1^2 and Q_2^2 can immediately be estimated as

$$
|Q_1^2| \,\le\, \|u\|\,\|v\|, \quad |Q_2^2| \,\le\, \|u\|\,\|v\|,
$$

in terms of the norm (10.8) corresponding to the given choice of the index set $\mathcal{J}$.

The two other terms are more difficult to handle because of the non-commutativity of the operators Δ_k and V_k. They can only be estimated under the additional assumption (10.11) which leads to the estimates (10.12) and (10.13). We begin with Q_1^1 and fix an index set $\mathcal{I}$ and an index k in $\mathcal{I}' = \mathcal{J}\setminus\mathcal{I}$. Let

$$
\widetilde{u} \,=\, \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, u, \quad \widetilde{v} \,=\, \Big(\prod_{i\in\mathcal{I}'} V_i\Big)\, v.
$$

If $\mathcal{I}$ is empty, by Fubini's theorem, Lemma 10.2, and the Cauchy-Schwarz inequality,

$$
\Big(\Big(V_k^{-1}\Delta_k V_k\Big) \Big(\prod_{i\in\mathcal{I}} \Delta_i\Big)\, \widetilde{u}, \widetilde{v}\Big) \,\le\, C_1\, \|\widetilde{u}\|_1 \|\widetilde{v}\|_1,
$$

with C_1 the constant from (10.12), where in fact only the derivatives associated with the index k are involved. If $\mathcal{I}\neq\emptyset$, we rewrite the product of the Δ_i as in (5.7), (5.11) as sum of the corresponding differential operators L_α^2. Integration by parts leads to

$$
\Big(\Big(V_k^{-1}\Delta_k V_k\Big) \Big(\prod_{i\in\mathcal{I}} \Delta_i\Big)\, \widetilde{u}, \widetilde{v}\Big) \,=\, (-1)^{|\mathcal{I}|} \sum_{\alpha\in\mathcal{I}^*} \Big(\big(V_k^{-1}\Delta_k V_k\big) L_\alpha \widetilde{u},\, L_\alpha \widetilde{v}\Big),
$$

where it has been used that the L_α do not act upon the electron $k\in\mathcal{I}'$ under consideration and therefore commute with V_k and V_k^{-1}. As above, Lemma 10.2 then yields

$$
\Big(\Big(V_k^{-1}\Delta_k V_k\Big) \Big(\prod_{i\in\mathcal{I}} \Delta_i\Big)\, \widetilde{u}, \widetilde{v}\Big) \,\le\, C_1 \sum_{\alpha\in\mathcal{I}^*} \|L_\alpha\widetilde{u}\|_1 \|L_\alpha\widetilde{v}\|_1,
$$

or, with help of the Cauchy-Schwarz inequality and the definitions (5.12) and (10.9),

$$
\Big(\Big(V_k^{-1}\Delta_k V_k\Big) \Big(\prod_{i\in\mathcal{I}} \Delta_i\Big)\, \widetilde{u}, \widetilde{v}\Big) \,\le\, C_1\, |\,\widetilde{u}\,|_{\mathcal{I}}\, |\,\widetilde{v}\,|_{\mathcal{I}}.
$$

Since the estimate for the case $\mathcal{I}=\emptyset$ can formally be written in the same way,

$$
|Q_1^1| \,\le\, C_1 N\, \|u\|\,\|v\|
$$

follows, if one inserts the definitions of $\widetilde{u}$ and $\widetilde{v}$, adds up the different terms, and estimates the number of the indices in the sets $\mathcal{I}'$ by the number N of the electrons.

The remaining term Q_2^1 is basically treated in the same way, distinguishing the cases $\mathcal{I}_k = \emptyset$ and $\mathcal{I}_k \neq \emptyset$. One obtains, using (10.13), first

$$|Q_2^1| \;\leq\; C_2 \sum_{\mathcal{I}\subseteq\mathcal{J}} \sum_{k\in\mathcal{I}} \left| \Big(V_k \prod_{i\in\mathcal{I}'} V_i \Big) u \right|_{\mathcal{I}_k} \left| \Big(V_k \prod_{i\in\mathcal{I}'} V_i \Big) v \right|_{\mathcal{I}_k} .$$

As $k \notin \mathcal{I}'$ for $k \in \mathcal{I}$ by definition, the right hand side can again be subsumed under the terms of which the corresponding norm (10.8) is composed. As, for a given index set $\mathcal{I}$, there are at most N index sets $\widetilde{\mathcal{I}}$ with $\widetilde{\mathcal{I}}_k = \mathcal{I}$ for some k, thus

$$|Q_2^1| \;\leq\; C_2 N \, \|u\| \, \|v\|.$$

This completes the proof of the estimate (10.14) and with that of the lemma. □

In the next step of our analysis we replace the norms given by (10.8) in the estimates (10.14) of the bilinear forms (10.4) by their counterparts given by

$$\|u\|_{\pm}^{*\,2} \;=\; \sum_{\mathcal{I}\subseteq\mathcal{I}_\pm} \left\{ \left| \Big(\prod_{i\in\mathcal{I}'} V_i^* \Big) u \right|_{\mathcal{I}}^2 + \sum_{k\notin\mathcal{I}} \left| \Big(V_k^* \prod_{i\in\mathcal{I}'} V_i^* \Big) u \right|_{\mathcal{I},0}^2 \right\}, \tag{10.15}$$

in which the functions V_i are replaced by the exponential functions

$$V_i^*(x) \;=\; \frac{\Lambda_0}{R} \, \exp\Big(\Big| \frac{x_i}{R} \Big| \Big), \tag{10.16}$$

with Λ_0 a constant and R the scaling parameter introduced above. We assume that

$$V_i(x) \;\leq\; V_i^*(x) \tag{10.17}$$

holds for all $x \in \mathbb{R}^{3N}$, that is, that the reference functions V_i^* dominate the original V_i.

Lemma 10.4. *For all functions $u \in \mathcal{D}$,*

$$\|u\|_\pm \;\leq\; C \sqrt{N} \, \|u\|_\pm^*, \tag{10.18}$$

where the constant C depends again only on the constant K from (10.11).

Proof. We first fix a subset $\mathcal{I} \neq \emptyset$ of $\mathcal{I}_-$ or $\mathcal{I}_+$, respectively, and set

$$W = \prod_{i\in\mathcal{I}'} V_i, \quad W^* = \prod_{i\in\mathcal{I}'} V_i^*$$

for abbreviation. Since the differential operators L_α, $\alpha \in \mathcal{I}^*$, do not act upon the variables on which W and the V_k, $k \notin \mathcal{I}$, depend, for these k,

$$|Wu|_{\mathcal{I},0}^2 = \sum_{\alpha\in\mathcal{I}^*} \|WL_\alpha u\|_0^2, \quad |V_k W u|_{\mathcal{I},0}^2 = \sum_{\alpha\in\mathcal{I}^*} \|V_k W L_\alpha u\|_0^2.$$

From (10.17) one immediately deduces

$$\|V_k W L_\alpha u\|_0^2 \;\leq\; \|V_k^* W^* L_\alpha u\|_0^2 \;=\; \|L_\alpha \{V_k^* W^* u\}\|_0^2,$$

and likewise the estimate

$$\|W L_\alpha u\|_0^2 \;\leq\; \|W^* L_\alpha u\|_0^2 \;=\; \|L_\alpha \{W^* u\}\|_0^2.$$

From this one obtains, for the indices k not in $\mathcal{I}$,

$$|Wu|_{\mathcal{I},0} \leq |W^*u|_{\mathcal{I},0}, \quad |V_kWu|_{\mathcal{I},0} \leq |V_k^*W^*u|_{\mathcal{I},0},$$

so that these parts represent no problem at all. To treat the remaining parts, we fix an $\alpha \in \mathcal{I}^*$, set $v = L_\alpha u$, and decompose the H^1-seminorm of $L_\alpha Wu = Wv$ into

$$|Wv|_1^2 \;=\; \sum_{k=1}^{N} \|\nabla_k\{Wv\}\|_0^2.$$

The single terms on the right hand side of this expression are treated separately, depending on whether the given k belongs to the index set $\mathcal{I}'$ or not. For $k \in \mathcal{I}'$, which is the critical case, we further decompose the gradient into the sum

$$\nabla_k\{Wv\} \;=\; (V_k^{-1}\nabla_k V_k)Wv \;+\; W\nabla_k v$$

and estimate it, with help of assumption (10.11), as

$$\|\nabla_k\{Wv\}\|_0 \;\leq\; K\,\Big\|\Big(\frac{1}{R} + \frac{1}{|x_k|}\Big)Wv\,\Big\|_0 \;+\; \|W\nabla_k v\|_0.$$

As only L_2-norms appear on the right hand side, we can replace the V_i by the V_i^* there and obtain, with help of the Hardy inequality, the estimate

$$\|\nabla_k\{Wv\}\|_0 \;\leq\; KR^{-1}\|W^*v\|_0 + 2K\,\|\nabla_k\{W^*v\}\|_0 + \|W^*\nabla_k v\|_0.$$

The argument in the third norm on the right hand side can be expanded as

$$W^*\nabla_k v \;=\; \nabla_k\{W^*v\} - (V_k^{*-1}\nabla_k V_k^*)W^*v.$$

One can now simply reverse the argumentation. In the present case, the estimate

$$\big|(V_k^{*-1}\nabla_k V_k^*)(x_k)\big| \;\leq\; \frac{1}{R}$$

holds, which takes the role of the first of the estimates (10.11) for the V_k. Hence

$$\|\nabla_k\{Wv\}\|_0 \;\leq\; (K+1)\,R^{-1}\|W^*v\|_0 + (2K+1)\,\|\nabla_k\{W^*v\}\|_0$$

for those indices k that belong to $\mathcal{I}'$. For the other indices k, simply

$$\|\nabla_k\{Wv\}\|_0 \;\leq\; \|\nabla_k\{W^*v\}\|_0,$$

because ∇_k commutes with the corresponding V_i and V_i^*. Therefore

$$|Wv|_1 \;\leq\; C\sqrt{N}\,\|W^*v\|_1$$

in terms of the rescaled H^1-norm (10.10), where C depends only on the constant K from (10.11), but not on R. Since the expressions

$$\|Wu\|_0, \quad |Wu|_1, \quad \|V_kWu\|_0$$

arising for $\mathcal{I} = \emptyset$ can be estimated in the same way, this completes the proof. □

The estimates from Lemma 10.3 and Lemma 10.4 can be combined to the following result that relates the eigenfunction expansion (10.3) to the regularity theory that has been developed in the previous sections.

LEMMA 10.5. *If the condition* (10.17) *is satisfied, the bilinear forms* (10.6) *can be extended to the completions of the space $\mathcal{D}$ of infinitely differentiable functions with compact support under the norms given by* (10.15)*, and satisfy the estimate*

$$B_\pm(u,v) \,\le\, CN^2\,\|u\|_\pm^*\,\|v\|_\pm^* \tag{10.19}$$

for all functions u and v in these Hilbert spaces, where the constant C depends only on the constant K in the condition (10.11) *needed to control the arising commutators.*

The final step is to transfer the estimate (10.19) to the classes of functions to which the solutions of the electronic Schrödinger equation belong.

LEMMA 10.6. *An integrable function $u : \mathbb{R}^{3N} \to \mathbb{R}$ that possesses weak derivatives of corresponding order and for which the expressions*

$$\left|\Big(\prod_{i\in\mathcal{I}'} V_i^*\Big)u\right|_{\mathcal{J}}, \quad \left|\Big(V_k^*\prod_{i\in\mathcal{I}'} V_i^*\Big)u\right|_{\mathcal{J},0}^2 \tag{10.20}$$

remain finite for all disjoint index sets $\mathcal{I}', \mathcal{J} \subseteq \mathcal{I}_\pm$ and all indices $k \notin \mathcal{J}$ can, in the sense of the norms (10.15)*, be approximated arbitrarily well by functions in $\mathcal{D}$ and is thus contained in the completion of $\mathcal{D}$ under these norms.*

Proof. Let χ be an infinitely differentiable cut-off function with values $\chi(x) = 1$ for $|x| \le 1$ and $\chi(x) = 0$ for $|x| \ge 2$ and set $\chi_\vartheta(x) = \chi(x/\vartheta)$. The functions $u_\vartheta = \chi_\vartheta u$ then possess weak derivatives of all considered orders. Moreover,

$$\lim_{\vartheta\to\infty} \|u - u_\vartheta\|_\pm^* \,=\, 0$$

by the dominated convergence theorem, because the functions χ_ϑ tend uniformly to one and their derivatives uniformly to zero for ϑ tending to infinity. Thus it suffices to approximate the functions u_ϑ. But this is possible without difficulties since the V_i^* and their involved derivatives remain bounded on bounded sets. □

At long last we can now devote our attention again to the solutions of the electronic Schrödinger equation, the eigenfunctions of the operator (1.1). The crucial observation is that the factors in front of u in the norms (10.15) do not depend on the positions x_i for the indices i in the index sets $\mathcal{I}$ under consideration. Hence the functions

$$\Big(\prod_{i\in\mathcal{I}'} V_i^*\Big)u, \quad \Big(V_k^*\prod_{i\in\mathcal{I}'} V_i^*\Big)u \tag{10.21}$$

inherit the antisymmetry of u under the exchange of the electrons i in these index sets. In the following, we consider eigenfunctions u in the given symmetry class for eigenvalues λ below the corresponding ionization threshold $\Sigma^*(\sigma)$, and assume that

$$\frac{1}{R^2} \,<\, 2\,\frac{\Sigma^*(\sigma) - \lambda}{N_\pm + 3}, \tag{10.22}$$

where N_- and N_+ are the numbers of indices in $\mathcal{I}_-$ respectively $\mathcal{I}_+$. By Theorem 4.3, the corresponding weighted versions (10.21) of these eigenfunctions are then square integrable and belong to the given space $H^1(\sigma)$. The regularity theory of section 8 applies to them and guarantees that the terms (10.20) from Lemma 10.6 remain

individually bounded. This observation essentially already proves the central result of this section and, after Theorem 8.9, our second main theorem:

THEOREM 10.7. *Provided the functions V_i we started from satisfy the estimate* (10.17) *with R chosen as in* (10.22)*, the norms defined by the expression*

$$\|\!|u|\!\|^2 \;=\; \sum_k \Big(\sum_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \Big) \Big(\prod_{i \in \mathcal{I}_-} \frac{\lambda_{k_i}}{\Omega^2} \;+\; \prod_{i \in \mathcal{I}_+} \frac{\lambda_{k_i}}{\Omega^2} \Big)\, |\widehat{u}(k)|^2, \tag{10.23}$$

with Ω chosen as in section 8, of the given eigenfunctions u can be bounded via

$$\|\!|u|\!\|^2 \;\leq\; C \Big(1 + \frac{1}{\Omega R}\Big)^2 N^2\, (u, Wu), \tag{10.24}$$

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

$$W_\pm \;=\; \Big(1 + \sum_{i=1}^N \Big| \frac{V_i^*}{\Omega} \Big|^2 \Big) \prod_{i \in \mathcal{I}_\pm} \Big(1 + \Big| \frac{V_i^*}{\Omega} \Big|^2 \Big) \tag{10.25}$$

and the constant C exclusively depends on the constant K from (10.11)*, but not on the number N of the electrons and the other parameters that determine the system.*

Proof. We treat the two parts corresponding to the index sets $\mathcal{I}_-$ and $\mathcal{I}_+$ as before separately. Then it has still to be shown that the weighted norms (10.15), when the corresponding powers of $1/\Omega$ are included, can be estimated by the respective parts of which the right hand side of (10.24) is composed. Consider, for example, the term

$$\Big(\frac{1}{\Omega}\Big)^{|\mathcal{I}_\pm|+1} \frac{1}{R} \Big| \Big(\prod_{i \in \mathcal{I}'} V_i^* \Big) u \Big|_{\mathcal{I},0} \;=\; \frac{1}{\Omega R} \Big(\frac{1}{\Omega}\Big)^{|\mathcal{I}|} \Big| \Big(\prod_{i \in \mathcal{I}'} \frac{V_i^*}{\Omega} \Big) u \Big|_{\mathcal{I},0}.$$

As the seminorm on the right hand side can, by Theorems 8.7 and 8.8 respectively, be estimated by its low-frequency part and that trivially again by the L_2-norm,

$$\Big(\frac{1}{\Omega}\Big)^{|\mathcal{I}_\pm|+1} \frac{1}{R} \Big| \Big(\prod_{i \in \mathcal{I}'} V_i^* \Big) u \Big|_{\mathcal{I},0} \leq\; \frac{1}{\Omega R}\, \sqrt{2}\, \Big\| \Big(\prod_{i \in \mathcal{I}'} \frac{V_i^*}{\Omega} \Big) u \Big\|_0 .$$

Corresponding estimates hold for the remaining parts, without the factor $1/\Omega R$. Since the sum over the squares of all the products can be combined to

$$\sum_{\mathcal{I} \subseteq \mathcal{I}_\pm} \Big(\prod_{i \in \mathcal{I}'} \frac{V_i^*}{\Omega} \Big)^2 \;=\; \prod_{i \in \mathcal{I}_\pm} \Big(1 + \Big| \frac{V_i^*}{\Omega} \Big|^2 \Big),$$

the proposition follows from Lemmas 10.5, 10.6, and the choice (10.22) of R. □

It is important to note that the right hand side of (10.24) no longer contains derivatives. The weights (10.25) are of the same structure as the weights in the norms (8.36) and (8.37) that have been considered in section 8, but here in the position space and not in the Fourier space. Theorem 10.7 shows that the question whether the expressions (10.23) are bounded or not basically depends on the decay behavior of the considered solutions of the Schrödinger equation. The size of their derivatives enters only indirectly via the constant Ω that measures their variation. The decay rate again depends, via the relation (10.22), on the gap between the considered eigenvalues of the Schrödinger operator and the ionization threshold. This gap determines, via the

relation (10.17), the admissible operators (10.1) and with that their eigenfunctions ϕ_k, into the products of which the solutions are expanded, and their eigenvalues λ_k, that finally determine the speed of convergence of the expansion. We remark that the comparatively harmless factor in front of the inner product on the right hand side of (10.24) comes from the inner sum over the indices $i = 1, \dots, N$ in (10.23) and the need to bound the arising commutators. The norm given by the expression

$$\|\!|u|\!\|_0^2 \,=\, \sum_k \Big(\prod_{i\in\mathcal{I}_-} \frac{\lambda_{k_i}}{\Omega^2} \,+\, \prod_{i\in\mathcal{I}_+} \frac{\lambda_{k_i}}{\Omega^2} \Big)\, |\widehat{u}(k)|^2 \tag{10.26}$$

of an eigenfunction u can, in a much simpler manner, be directly estimated as

$$\|\!|u|\!\|_0^2 \,\le\, 2\,(u, Wu). \tag{10.27}$$

We also remark that, remembering the estimate (10.14) from Lemma 10.3, the requirements on the decay of the eigenfunctions lessen the slower the potential V^2 tends to infinity, which unfortunately also means that the eigenvalues λ_k increase slower.

Theorem 10.7 offers a lot of freedom in the choice of the potentials V^2 in the three-dimensional operator (10.1) on which the whole construction is based. The most obvious possibility is to start from a reference function $V_0(x) \le \Lambda_0 \exp(|x|)$ that is independent of the considered solutions of the Schrödinger equation, and to set

$$V(x) \,=\, \frac{1}{R}\, V_0\Big(\frac{x}{R}\Big). \tag{10.28}$$

The requirement (10.11) turns in this case into the conditions

$$|(V_0^{-1}\nabla V_0)(x)| \,\le\, K\,\big(1 + |x|^{-1}\big), \quad |(V_0^{-1}\Delta V_0)(x)| \,\le\, K\,\big(1 + |x|^{-2}\big), \tag{10.29}$$

and the eigenfunctions and eigenvalues of the operator (10.1) are linked to the eigenfunctions $\phi_k^{(0)}$ and eigenvalues $\lambda_k^{(0)}$ of the reference operator $-\Delta + V_0^2$ by the relation

$$\phi_k(x) \,=\, \frac{1}{R^{3/2}}\, \phi_k^{(0)}\Big(\frac{x}{R}\Big), \quad \lambda_k \,=\, \frac{\lambda_k^{(0)}}{R^2}, \tag{10.30}$$

that is, by a rescaling. The product ΩR that then appears on both sides of the estimate (10.24) relates the length scale R, that measures the extension of the system, to the length scale $1/\Omega$, on which the considered solutions vary. As, after renormalization of u, both the norm (10.23) and (u, Wu) are then invariant under a change

$$R \to \vartheta R, \quad \Omega \to \vartheta^{-1}\Omega, \tag{10.31}$$

or correspondingly $x \to \vartheta^{-1}x$ and $\omega \to \vartheta\,\omega$, of units, the estimate (10.24) becomes itself invariant under such a change of units and depends only on the ratio of the length scales R and $1/\Omega$ measuring the oscillatory behavior of the considered solutions u of the Schrödinger equation, but not on these quantities themselves.

There are many infinitely differentiable, strictly positive functions V_0 that fit into the given framework and fulfill the conditions (10.29), for example those given by

$$V_0(x)^2 \,=\, \kappa\,|x|^\beta + \varepsilon^2, \quad \beta \,=\, 2m, \tag{10.32}$$

where m is a natural number and κ and ε are positive constants. The constant K is independent of κ and ε in this case. An even more rapidly increasing such function is

$$V_0(x) \,=\, \exp\Big(\sqrt{|x|^2 + 1}\,\Big). \tag{10.33}$$

The fact that the expressions (10.23) remain bounded leads exactly to the effects that have been described in the introduction. Let $\varepsilon > 0$ be given and consider the finite dimensional space that is spanned by the correspondingly antisymmetrized products

$$x \;\to\; \prod_{i=1}^{N} \phi_{k_i}(x_i) \tag{10.34}$$

for which the associated eigenvalues λ_{k_i} satisfy the estimate

$$\prod_{i \in \mathcal{I}_-} \frac{\lambda_{k_i}}{\Omega^2} \;+\; \prod_{i \in \mathcal{I}_+} \frac{\lambda_{k_i}}{\Omega^2} \;<\; \frac{1}{\varepsilon^2}. \tag{10.35}$$

Let u_ε be the L_2-orthogonal projection of one of the given solutions u of the electronic Schrödinger equation onto this space. Moreover, let

$$\|u\|^2 \;=\; \sum_k \left(\sum_{i=1}^{N} \frac{\lambda_{k_i}}{\Omega^2} \right) |\widehat{u}(k)|^2. \tag{10.36}$$

Since u_ε is the part of the expansion (10.3) of u associated with the selected product functions (10.34), respectively the eigenvalues λ_{k_i} for which (10.35) holds,

$$\|u - u_\varepsilon\| \;\le\; \varepsilon \,|\!|\!| u - u_\varepsilon |\!|\!| \;\le\; \varepsilon \,|\!|\!| u |\!|\!|. \tag{10.37}$$

As the norm given by (10.36) 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 (10.35). Therefore only a very small portion of the product eigenfunctions substantially contributes to the considered wavefunctions and a surprisingly high rate of convergence, related to the space dimension $3N$, can be achieved.

11. The growth of the eigenvalues in the 3d-case. The speed of convergence of the eigenfunction expansion (10.3) of the electronic wavefunctions is determined by the speed with which the eigenvalues of the three-dimensional operator (10.1) tend to infinity. The study of the growth of the eigenvalues of second-order elliptic differential operators is a classical topic. It has a long history that began with the work of Weyl [66] and Courant and Hilbert [11] in the first third of the last century. The growth of the eigenvalues of three-dimensional Schrödinger operators like (10.1) is, for example, examined in [59] and, for the case of rotationally symmetric potentials, in great detail in [60], [61], and [62]. In this section, we derive by elementary means some simple, but for our purposes sufficient estimates for the growth of the eigenvalues of operators of the form (10.1), (10.2) with continuous potentials.

We begin with the example of the three-dimensional harmonic oscillator

$$H\phi \;=\; -\,\Delta\phi \,+\, \omega^2 |x|^2 \phi. \tag{11.1}$$

The eigenfunctions and eigenvalues of this operator are explicitly known and are calculated in almost every textbook of quantum mechanics; see [57], for example. As the operator splits into the sum of three one-dimensional operators, the solution of this eigenvalue problem reduces to the solution of its one-dimensional counterpart. The eigenfunctions are products of rescaled Hermite polynomials (or linear combinations of such products) with a fixed Gaussian and the eigenvalues read

$$\lambda_k \;=\; (2n+3)\,\omega, \quad n = 0, 1, 2, \ldots. \tag{11.2}$$

The eigenspaces for these eigenvalues are highly degenerate and have the dimension

$$\frac{(n+1)(n+2)}{2}, \tag{11.3}$$

which is the number of the possible representations of n as a sum $n = n_1 + n_2 + n_3$ of three nonnegative integers n_1, n_2, and n_3 in given order. From this we obtain:

LEMMA 11.1. *The ascendingly ordered eigenvalues* (11.2) *of the three-dimensional harmonic oscillator counted with their multiplicity satisfy the lower estimate*

$$\lambda_k \,\geq\, 3\,\omega\,k^{1/3} \tag{11.4}$$

and behave asymptotically like $\lambda_k \sim (48k)^{1/3}\omega$ *for* k *tending to infinity.*

Proof. By (11.2) and (11.3), $\lambda_k = (2n+3)\,\omega$ for $n \geq 1$ if and only if

$$\sum_{\ell=0}^{n-1} \frac{(\ell+1)(\ell+2)}{2} \;<\; k \;\leq\; \sum_{\ell=0}^{n} \frac{(\ell+1)(\ell+2)}{2}.$$

The estimate (11.4) therefore holds for all $k \geq 2$ because, for all $n \geq 1$,

$$\Big(\frac{2n+3}{3}\Big)^3 \;\geq\; \sum_{\ell=0}^{n} \frac{(\ell+1)(\ell+2)}{2},$$

and this remains true for $k = 1$. The asymptotic representation of the eigenvalues follows from the fact that both sums behave like $\sim n^3/6$ for n tending to infinity. □

That this growth is not the best possible is suggested by the example of the eigenvalues of the Laplace operator on a cube, that is, by the eigenvalue problem

$$-\Delta\phi \;=\; \lambda\phi, \quad \phi|\partial Q \;=\; 0, \tag{11.5}$$

on the region $Q = (0, \pi R)^3$. The solutions of this eigenvalue problem are, of course, also explicitly known and can be easily calculated. The eigenvalues are in this case

$$\lambda_k \;=\; \frac{n_2^2 + n_2^2 + n_3^2}{R^2}, \tag{11.6}$$

where n_1, n_2, and n_3 are now natural numbers. As one can again associate exactly one eigenfunction to every such ordered triple of natural numbers, one gets:

LEMMA 11.2. *The ascendingly ordered eigenvalues* (11.6) *of the Laplace operator, again counted with their multiplicity, can be estimated from above as*

$$\lambda_k \;\leq\; 12\,R^{-2}k^{2/3}. \tag{11.7}$$

Proof. We assign to the triples (n_1, n_2, n_3) the axiparallel cubes of sidelength 1 with these triples as upper right corners. The number of the triples for which

$$n_1^2 + n_2^2 + n_3^2 \;\leq\; 3L^2$$

is then equal to the total volume of the assigned cubes. Since these cubes cover a cube of sidelength $\lfloor L \rfloor$, their total volume and with that the number of these triples is at least $(L-1)^3$. The proposition follows choosing $(L-1)^3 = k$. □

A somewhat more careful reasoning shows that the given eigenvalues of the negative Laplace operator indeed behave like $\sim k^{2/3}$. Not much surprisingly, the eigenvalues of operators of the form (10.1) cannot grow faster than those. Even worse:

THEOREM 11.3. *The eigenvalues $\lambda_1 \le \lambda_2 \le \dots$ of an operator of the given form tend toward infinity slower than $\sim k^{2/3}$ in the sense that always*

$$\lim_{k\to\infty} \frac{\lambda_k}{k^{2/3}} \;=\; 0. \tag{11.8}$$

Proof. Let $\phi_1, \phi_2, \dots \in H_0^1(Q)$ be the eigenfunctions with zero boundary conditions of the negative Laplace operator on the three-dimensional cube $Q = (0, \pi R)^3$ and $\lambda_1' \le \lambda_2' \le \dots$ the corresponding eigenvalues (11.6) in ascending order. Let $\mathcal{V}_k$ be the k-dimensional subspace of $H_0^1(Q) \subset H^1(\mathbb{R}^3)$ that is spanned by $\phi_1, \dots, \phi_k$. Then

$$(\phi, H\phi) \;\le\; -(\phi, \Delta\phi) + M(R)(\phi,\phi) \;\le\; \lambda_k' + M(R)$$

for all functions $\phi \in \mathcal{V}_k$ with L_2-norm one, where $M(R)$ denotes the maximum of the function V^2 on Q. By the min-max characterization of the eigenvalues of H therefore

$$\lambda_k \;\le\; \lambda_k' + M(R),$$

or, if we insert the upper estimate from Lemma 11.2,

$$\lambda_k \;\le\; 12\, R^{-2} k^{2/3} + M(R)$$

for $R > 0$ arbitrary. Since $R \to R^2 M(R)$ is a continuous function that increases monotonely from zero to infinity, there is a minimum $R = R(k)$ for which it attains the value $R^2 M(R) = k^{2/3}$. If we insert this particular R into our estimate, we obtain

$$\lambda_k \;\le\; 13\, R(k)^{-2} k^{2/3}.$$

Every computable lower bound for the $R(k)$, and particularly every strictly monotone increasing function $M^* \ge M$ for which the solution of the equation $R^2 M^*(R) = k^{2/3}$ can be given, thus leads to an upper bound for the eigenvalues. Since $R(k)$ tends in any case to infinity for k tending to infinity, the estimate proves the proposition. □

This fact limits the order of convergence that one can reach with the considered expansions of the wavefunctions into products of three-dimensional eigenfunctions. It is, however, possible to approach the growth $\sim k^{2/3}$ arbitrarily with potentials that increase sufficiently fast and approximate vertical walls increasingly well.

THEOREM 11.4. *If the potential V^2 can be estimated from below as*

$$V(x)^2 \;\ge\; \kappa\, |x|^\beta \tag{11.9}$$

with $\kappa > 0$ and $\beta \ge 2$, the eigenvalues grow like

$$\lambda_k \;\ge\; c\, k^{\alpha/3}, \quad \alpha \;=\; \frac{2\beta}{\beta+2}, \tag{11.10}$$

where c is a positive constant that depends only on κ and β.

Proof. We first assume $\beta > 2$. An simple calculation shows then that there is a constant $a > 0$ that depends on κ and β, but is independent of ω, such that

$$\kappa\, r^\beta \;\ge\; \omega^2 r^2 - a\, \omega^p, \quad p \;=\; \frac{2\beta}{\beta-2},$$

holds for all $r \geq 0$. If we denote by $\lambda'_1 \leq \lambda'_2 \leq \ldots$ the eigenvalues of the harmonic oscillator (11.1), the min-max characterization of the eigenvalues yields

$$\lambda_k \;\geq\; \lambda'_k \;-\; a\,\omega^p$$

or, with the lower estimate from Lemma 11.1 for these eigenvalues,

$$\lambda_k \;\geq\; 3\,\omega\,k^{1/3} - \,a\,\omega^p.$$

If one maximizes the right hand side with respect to ω, one obtains (11.10). The case $\beta = 2$ can, with help of the min-max characterization of the eigenvalues and Lemma 11.1, be directly reduced to the case of the harmonic oscillator. □

We remark that one can, with the technique from the proof of Theorem 11.3, easily show that from the reverse estimate

$$V(x)^2 \;\leq\; \kappa'\,|x|^\beta \tag{11.11}$$

for the potential in (10.1) conversely a lower bound

$$\lambda_k \;\leq\; c'k^{\alpha/3} \tag{11.12}$$

with the same exponent α as in (11.10) follows. Theorem 11.4 therefore yields the correct exponent for the case that the potential can be enclosed between two such bounds.

One can even go further and consider exponentially growing potentials. Such potentials fully exhaust the possible growth, as follows directly from Theorem 11.4:

THEOREM 11.5. *If the potential V^2 grows faster than any polynomial in the sense that there exists, for every $\beta \geq 2$, a constant $\kappa = \kappa(\beta) > 0$ such that* (11.9) *holds,*

$$\lim_{k\to\infty} \frac{k^{\alpha/3}}{\lambda_k} \;=\; 0 \tag{11.13}$$

for all exponents α in the interval $0 < \alpha < 2$.

There are many potentials that both satisfy the assumptions made in the previous section and for which the eigenvalues grow as in Theorem 11.5, for example that given by (10.33). Hence one can come arbitrarily close to the upper bound for the growth of the eigenvalues in the class of the operators to which Theorem 10.7 applies.

12. Complexity bounds. Most codes in quantum chemistry are based in some or the other way on Gaussian-type ansatz functions, i.e., on correspondingly antisymmetrized products of the eigenfunctions of the three-dimensional harmonic oscillator

$$H\phi \;=\; -\,\Delta\phi \,+\, \omega^2|x|^2\phi. \tag{12.1}$$

The main reason for that is that the complicated three- and six-dimensional integrals that arise in such methods can for this type of functions be reduced to one-dimensional integrals. We will show in this section that, even with such simple basis functions, it is in some sense possible to break the curse of dimensionality. To achieve optimal convergence rates, it is however necessary to replace the eigenfunctions of the harmonic oscillator by eigenfunctions of other three-dimensional operators (10.1) with faster growing potentials and with that also faster growing eigenvalues.

The idea is to apply the technique indicated in the introduction and described at the end of section 10 to the expansions (10.3) of the wavefunctions into the products of the eigenfunctions ϕ_{k_i} of the three-dimensional operator (10.1). To simplify the

notation a little bit, we will restrict ourselves in this section mainly to solutions u that are antisymmetric with respect to the exchange of all electrons, that is, to the case that all electrons have the same spin; the general case can be treated similarly. Under the conditions that are precisely stated in Theorem 10.7, the expression

$$\|\!|u|\!\|^2 \;=\; \sum_k \Big(\sum_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \Big) \Big(\prod_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \Big) \, |\widehat{u}(k)|^2 \tag{12.2}$$

remains bounded for such solutions. The problem is then to estimate the dimension of the ansatz space spanned by the antisymmetrized and renormalized products

$$\frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \operatorname{sign}(\pi) \prod_{i=1}^N \phi_{k_i}(x_{\pi(i)}) \tag{12.3}$$

of the eigenfunctions ϕ_{k_i} with indices $k_1 > k_2 > \ldots > k_N$ for which the product of the associated eigenvalues λ_{k_i} satisfies a condition of the form

$$\prod_{i=1}^N \frac{\lambda_{k_i}}{\Omega^2} \;<\; \frac{1}{\varepsilon^2}, \tag{12.4}$$

to which the condition (10.35) here transfers and which fixes the size of the error.

The dimensions of these spaces are at least asymptotically determined by the growth properties of the eigenvalues $\lambda_1 \le \lambda_2 \le \ldots$ of the three-dimensional operator (10.1) from which the whole construction starts. Suppose that

$$\lambda_k \;\ge\; c(u)\, k^{\alpha/3}, \tag{12.5}$$

with a constant $c(u) > 0$ that is independent of the indices k, but will generally depend on the other problem parameters and particularly on the decay rate of the considered solution u that determines the admissible operators (10.1) and their eigenfunctions and eigenvalues. The condition (12.4) to the choice of the basis functions (12.3) is then surely fulfilled if the indices $k_1 > k_2 > \ldots > k_N$ satisfy the estimate

$$\Big(\frac{c(u)}{\Omega^2} \Big)^N \Big(\prod_{i=1}^N k_i \Big)^{\alpha/3} \;<\; \frac{1}{\varepsilon^2}. \tag{12.6}$$

Thus it remains to estimate the number of the finite sequences $k_1 > k_2 > \ldots > k_N$ of natural numbers for which the product on the left hand side of this inequality does not exceed the bound given by (12.6). The minimum value that this product can attain is $N!$, so that its size at least partly counterbalances the size of the other quantities for bigger N. The central observation in the given context, however, is that the rate with which the number of these sequences grows with decreasing ε, that is, increasing accuracy, remains bounded independent of the number N of electrons.

This follows from a crude estimate that can be proven rather easily. The idea is to relax the condition that the numbers k_i are strictly decreasing and to group them into levels, which seems to be a minor modification, but is not at all.

LEMMA 12.1. *The number of the infinite, monotonely decreasing sequences*

$$k_1 \;\ge\; k_2 \;\ge\; k_3 \;\ge\; \ldots \tag{12.7}$$

of natural numbers for which

$$\prod_{i=1}^{\infty} k_i \;\leq\; 2^L, \tag{12.8}$$

with L a given nonnegative integer, is bounded by the quantity

$$\sum_{\ell=0}^{L} p(\ell)\, 2^\ell \;\leq\; p(L)\, 2^{L+1}, \tag{12.9}$$

where $p(\ell)$ denotes the partition number of ℓ, the number of possibilities to represent the nonnegative integer ℓ as sum of nonnegative integers without regard to the order.

Proof. For $k \in \mathbb{N}$, let $\ell(k)$ denote the maximum integer for which $2^{\ell(k)} \leq k$. The number of sequences (12.7) for which (12.8) holds is then bounded from above by the number of sequences $k_1, k_2, k_3, \ldots$ of natural numbers for which at least their levels $\ell(k_i)$ decrease monotonely and that satisfy the relaxed condition

$$\prod_{i=1}^{\infty} 2^{\ell(k_i)} \;\leq\; 2^L. \tag{12.10}$$

We show that the expression on the left hand side of (12.9) counts the number of these sequences. Let the integers $\ell_i = \ell(k_i)$ be given for that. Since 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 precisely

$$\prod_{i=1}^{\infty} 2^{\ell_i}$$

sequences for which the $\ell(k_i)$ attain the prescribed values ℓ_i. The problem therefore reduces to the question how many monotonely decreasing sequences of nonnegative integers ℓ_i exist that sum up to values $\ell \leq L$, that is, for which

$$\sum_{\ell=1}^{\infty} \ell_i \;=\; \ell$$

for an $\ell \leq L$. This number is the partition number $p(\ell)$ of ℓ. Since $p(\ell) \leq p(L)$ for $\ell \leq L$, the rest follows from the summation formula for finite geometric series. ∎

The partition number plays a big role in combinatorics and there exist a vast amount of literature on its properties. Hardy and Ramanujan [29] proved that the partition number behaves asymptotically, for ℓ tending to infinity, like

$$p(\ell) \;=\; \left(\frac{1}{4\sqrt{3}} + o(1)\right) \frac{\exp\left(\pi\,\sqrt{2\ell/3}\,\right)}{\ell}. \tag{12.11}$$

This result has later been improved by Rademacher [51], who has shown that (12.11) is the first term in an infinite series that represents $p(\ell)$ exactly. For all $\vartheta > 0$ thus

$$\lim_{\ell\to\infty} 2^{-\vartheta\ell} p(\ell) \;=\; 0, \tag{12.12}$$

so that $p(\ell)$ tends asymptotically slower to infinity than any power of 2^ℓ. Particularly,

$$\lim_{L\to\infty} 2^{-(1+\vartheta)L} \sum_{\ell=0}^{L} p(\ell)\, 2^\ell \;=\; 0. \tag{12.13}$$

The number of monotonely decreasing sequences (12.7) for which (12.8) holds hence does not increase substantially faster than $\mathcal{O}(2^L)$ for L tending to infinity.

It is clear that every sequence $k_1 > k_2 > \ldots > k_N$ of natural numbers for which

$$\prod_{i=1}^{N} k_i \;\leq\; 2^L \tag{12.14}$$

can be expanded to an infinite, monotonely decreasing sequence for which (12.8) holds by setting all $k_i = 1$ for $i > N$, and that (12.9) therefore also represents an upper bound for the number of these sequences. Conversely, there are 2^L such "sequences" in the case $N = 1$ of a single electron, with values $k_1 = 1, \ldots, 2^L$. Hence it is not possible to give a significantly better bound for the rate with which the number of these sequences grows that is independent of the number N of electrons.

These estimates demonstrate that the number of basis functions (12.3) that are needed to reach an H^1-error of order $\mathcal{O}(\varepsilon)$ does not increase much faster than $\mathcal{O}(\varepsilon^{-6/\alpha})$ for ε tending to zero, where, of course, nothing is said about the constant and its dependence on the different problem parameters. That is, the rate of convergence expressed in terms of the number of basis functions astonishingly does not deteriorate with the space dimension $3N$ or the number N of electrons! It behaves almost as with the expansion of a one-electron wavefunction into eigenfunctions of the given type. In the case of the expansion into Gaussians, the eigenfunctions of the harmonic oscillator (12.1), the constant α attains the value $\alpha = 1$, as follows from Lemma 11.1. The results from the previous section and particularly Theorem 11.5 show that one can come arbitrarily close to $\alpha = 2$, but cannot completely reach or even surpass this value. The rate with which the dimension of the corresponding spaces grows with increasing accuracy then behaves asymptotically almost like that of a first-order method in three space dimensions. In the general case of electrons of distinct spin, the order of convergence halves due to the singularities of the wavefunctions at the places at which electrons with opposite spin meet, which is reflected in the presence of two products instead of only one in (10.23) and (10.35). The rate of convergence remains, however, independent of the number of electrons and comes arbitrarily close to that for the two-electron case. Our considerations thus show that the complexity of the quantum-mechanical N-body problem is much lower than generally believed.

REFERENCES

[1] S. Agmon, *Lectures on the Exponential Decay of Solutions of Second-Order Elliptic Operators*, Princeton University Press, Princeton, 1981.

[2] R. Ahlrichs, *Asymptotic behavior of atomic bound state wavefunctions*, J. Math. Phys., 14 (1973), pp. 1860–1863.

[3] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics*, Oxford University Press, Oxford, 1997.

[4] K. I. Babenko, *Approximation by trigonometric polynomials in a certain class of periodic functions of several variables*, Sov. Math., Dokl., 1 (1960), pp. 672–675.

[5] G. Beylkin, M. J. Mohlenkamp, and F. Perez, *Approximating a wavefunction as an unconstrained sum of Slater determinants*, Preprint, 2007.

[6] M. Born and R. J. Oppenheimer, *Zur Quantentheorie der Molekeln*, Ann. d. Phys., 84 (1927), pp. 457–484.

[7] H.-J. Bungartz and M. Griebel, *Sparse Grids*, in Acta Numerica 2004, Cambridge University Press, Cambridge, 2004, pp. 1–123.

[8] E. Cancès, C. Le Bris, and Y. Maday, *Méthodes Mathématiques en Chimie Quantique*, Springer-Verlag, Berlin Heidelberg New York, 2006.

[9] S. R. Chinnamsetty, M. Espig, B. N. Khoromskij, W. Hackbusch, and H.-J. Flad, *Tensor product approximation with optimal rank in quantum chemistry*, J. Chem. Phys., 127 (2007), 084110.
[10] J. M. Combes and L. Thomas, *Asymptotic behavior of eigenfunctions for multiparticle Schrödinger operators*, Commun. Math. Phys., 34 (1973), pp. 251–270.
[11] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik I*, Springer-Verlag, Berlin, 1924.
[12] P. Deift, W. Hunziker, B. Simon, and E. Vock, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum systems IV*, Commun. Math. Phys., 64 (1978), pp. 1–34.
[13] F. Delvos, *d-variate Boolean interpolation*, J. Approximation Theory, 34 (1982), pp. 99–114.
[14] F. Delvos and W. Schempp, *Boolean methods in Interpolation and Approximation*, Pitman Research Notes in Mathematics, vol. 230, John Wiley and Sons, New York, 1989.
[15] P. A. M. Dirac, *Quantum mechanics of many electron systems*, Proc. R. Soc. Lond., Ser. A, 123 (1929), pp. 714–733.
[16] H.-J. Flad, W. Hackbusch, D. Kolb, and R. Schneider, *Wavelet approximation of correlated wave functions. I. Basics*, J. Chem. Phys., 116 (2002), pp. 9461–9657.
[17] H.-J. Flad, W. Hackbusch, D. Kolb, and T. Koprucki, *Wavelet approximation of correlated wave functions. II. Hyperbolic wavelets and adaptive approximation schemes*, J. Chem. Phys., 117 (2002), pp. 3625–3638.
[18] H.-J. Flad, W. Hackbusch, and R. Schneider, *Best N-term approximation in electronic structure calculations. I. One-electron reduced density matrix*, M2AN, 40 (2006), pp. 49–61.
[19] H.-J. Flad, W. Hackbusch, and R. Schneider, *Best N-term approximation in electronic structure calculations. II. Jastrow factors*, M2AN, 41 (2007), pp. 261–279.
[20] H.-J. Flad, R. Schneider, and B.-W. Schulze, *Asymptotic regularity of solutions of Hartree-Fock equations with Coulomb potential*, Preprint, 2007.
[21] S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and T. Østergard Sørensen, *Sharp regularity estimates for Coulombic many-electron wave functions*, Commun. Math. Phys., 255 (2005), pp. 183–227.
[22] G. Friesecke, *The multiconfiguration equations for atoms and molecules: charge quantization and existence of solutions*, Arch. Ration. Mech. Anal., 169 (2003), pp. 35–71.
[23] J. Garcke and M. Griebel, *On the computation of the eigenproblems of hydrogen and helium in strong magnetic and electric fields with the sparse grid combination technique*, J. Comput. Phys., 165 (2000), pp. 694–716.
[24] L. Gårding, *On the essential spectrum of Schrödinger operators*, J. Funct. Anal., 52 (1983), pp. 1–10.
[25] M. Griebel, *Sparse grids and related approximation schemes for higher dimensional problems*, in Foundations of Computational Mathematics, Santander 2005, London Math. Soc. Lecture Note Ser., vol. 331, Cambridge University Press, Cambridge, 2006, pp. 106–161.
[26] M. Griebel and J. Hamaekers, *Sparse grids for the Schrödinger equation*, M2AN, 41 (2007), pp. 215–247.
[27] M. Griebel and J. Hamaekers, *A wavelet based sparse grid method for the electronic Schrödinger equation*, in International Congress of Mathematicians, vol. III, Eur. Math. Soc., Zürich, 2006, pp. 1473–1506.
[28] W. Hackbusch, *The efficient computation of certain determinants arising in the treatment of Schrödinger's equation*, Computing, 67 (2000), pp. 35–56.
[29] G. H. Hardy and S. Ramanujan, *Asymptotic formulae in combinatory analysis*, Proc. Lond. Math. Soc., 17 (1918), pp. 75–115.
[30] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic Structure Theory*, John Wiley and Sons, New York, 2001.
[31] S. Hilgenfeldt, S. Balder, and C. Zenger, *Sparse grids: Applications to multi-dimensional Schrödinger problems*, SFB-Bericht 342/05/95, TU München, München, 1995.
[32] M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and H. Stremnitzer, *Local properties of Coulombic wave functions*, Commun. Math. Phys., 163 (1994), pp. 185–215.
[33] W. Hunziker, *On the spectra of Schrödinger multiparticle Hamiltonians*, Helv. Phys. Acta, 39 (1966), pp. 451–462.
[34] W. Hunziker and I. M. Sigal, *The quantum N-body problem*, J. Math. Phys., 41 (2000), pp. 3448–3510.
[35] T. Kato, *Fundamental properties of Hamiltonian operators of Schrödinger type*, Trans. Am. Math. Soc., 70 (1951), pp. 195–221.
[36] T. Kato, *On the eigenfunctions of many-particle systems in quantum mechanics*, Comm. Pure and Appl. Math., 10 (1957), pp. 151–177.

[37] W. Kohn, *Nobel lecture: Electronic structure of matter-wave functions and density functionals*, Rev. Mod. Phys., 71 (1999), pp. 1253–1266.
[38] N. M. Korobov, *Approximate calculation of repeated integrals by number-theoretical methods (Russian)*, Dokl. Akad. Nauk. SSSR, 115 (1957), pp. 1062–1065.
[39] N. M. Korobov, *Approximate calculation of repeated integrals (Russian)*, Dokl. Akad. Nauk. SSSR, 124 (1959), pp. 1207–1210.
[40] C. Le Bris, ed., *Handbook of Numerical Analysis, Vol. X: Computational Chemistry*, North Holland, Amsterdam, 2003.
[41] C. Le Bris, *Computational chemistry from the perspective of numerical analysis*, in Acta Numerica 2005, Cambridge University Press, Cambridge, 2005, pp. 363–444.
[42] C. Le Bris and P. L. Lions, *From atoms to crystals: a mathematical journey*, Bull. Am. Math. Soc., New Ser., 42 (2005), pp. 291–363.
[43] M. Lewin, *Solutions of the multiconfiguration equations in quantum chemistry*, Arch. Ration. Mech. Anal., 171 (2004), pp. 83–114.
[44] E. Lieb and B. Simon, *The Hartree-Fock theory for Coulomb systems*, Commun. Math. Phys., 53 (1977), pp. 185–194.
[45] E. Lieb and B. Simon, *The Thomas-Fermi theory of atoms, molecules, and solids*, Adv. Math., 23 (1977), pp. 22–116.
[46] P. L. Lions, *Solutions of Hartree-Fock equations for Coulomb systems*, Commun. Math. Phys., 109 (1987), pp. 33–97.
[47] A. Messiah, *Quantum Mechanics*, Dover Publications, New York, 2000.
[48] A. J. O' Connor, *Exponential decay of bound state wave functions*, Commun. Math. Phys., 32 (1973), pp. 319–340.
[49] A. Persson, *Bounds for the discrete part of the spectrum of a semi-bounded Schrödinger operator*, Math. Scand., 8 (1960), pp. 143–153.
[50] J. Pople, *Nobel lecture: Quantum chemical models*, Rev. Mod. Phys., 71 (1999), pp. 1267–1274.
[51] H. Rademacher, *On the partition function $p(n)$*, Proc. Lond. Math. Soc., 43 (1937), pp. 241–254.
[52] M. Reed and B. Simon, *Methods of Modern Mathematical Physics IV: Analysis of Operators*, Academic Press, San Diego, 1978.
[53] E. Schrödinger, *Quantisierung als Eigenwertproblem*, Ann. d. Phys., 79 (1926), pp. 361–376.
[54] B. Simon, *Pointwise bounds on eigenfunctions and wave packets in N-body quantum system I*, Proc. Am. Math. Soc., 208 (1975), pp. 317–329.
[55] B. Simon, *Schrödinger operators in the twentieth century*, J. Math. Phys., 41 (2000), pp. 3523–3555.
[56] S. A. Smolyak, *Quadrature and interpolation formulas for tensor products of certain classes of functions*, Dokl. Akad. Nauk SSSR, 4 (1963), pp. 240–243.
[57] B. Thaller, *Visual Quantum Mechanics*, Springer-Verlag, New York, 2000.
[58] B. Thaller, *Advanced Visual Quantum Mechanics*, Springer-Verlag, New York, 2004.
[59] E. C. Titchmarsh, *Eigenfunction Expansions, vols. I and II*, Oxford University Press, Oxford, 1953, 1958.
[60] E. C. Titchmarsh, *On the eigenvalues in problems with spherical symmetry*, Proc. R. Soc. Lond., Ser. A, 245 (1958), pp. 147–155.
[61] E. C. Titchmarsh, *On the eigenvalues in problems with spherical symmetry II*, Proc. R. Soc. Lond., Ser. A, 251 (1959), pp. 46–54.
[62] E. C. Titchmarsh, *On the eigenvalues in problems with spherical symmetry III*, Proc. R. Soc. Lond., Ser. A, 252 (1959), pp. 436–444.
[63] C. van Winter, *Theory of finite systems of particles*, Mat.-Fys. Skr. Danske Vid. Selsk., 1 (1964), 2 (1965).
[64] J. von Neumann, *Mathematische Grundlagen der Quantenmechanik*, Springer-Verlag, Berlin, 1932.
[65] J. Weidmann, *Linear Operators in Hilbert Spaces*, Springer-Verlag, New York Heidelberg Berlin, 1980.
[66] H. Weyl, *Das asymptotische Verteilungsgesetz der Eigenwerte linearer partieller Differentialgleichungen*, Math. Ann., 71 (1912), pp. 441–479.
[67] H. Yserentant, *On the regularity of the electronic Schrödinger equation in Hilbert spaces of mixed derivatives*, Numer. Math., 98 (2004), pp. 731–759.
[68] H. Yserentant, *Sparse grid spaces for the numerical solution of the electronic Schrödinger equation*, Numer. Math., 101 (2005), pp. 381–389.
[69] H. Yserentant, *The hyperbolic cross space approximation of electronic wavefunctions*, Numer. Math., 105 (2007), pp. 659–690.

[70] C. Zenger, *Sparse grids*, in Parallel Algorithms for Partial Differential Equations, Kiel 1990, W. Hackbusch, ed., Notes on Numerical Fluid Mechanics, vol. 31, Vieweg, Braunschweig, Wiesbaden, 1991, pp. 241–251.

[71] G. M. Zhislin, *A study of the spectrum of the Schrödinger operator for a system of several particles (Russian)*, Tr. Mosk. Mat. O.-va, 9 (1960), pp. 81–120.

Appendix. An estimate for the partition numbers. Our estimate for the complexity of the quantum N-body problem depends on the estimate from section 12 for the number $c(N, L)$ of the sequences $k_1 > \ldots > k_N$ of natural numbers for which

$$\prod_{i=1}^{N} k_i \;\leq\; 2^L. \tag{1}$$

Since obviously $c(N, L) = 0$ for $N! > 2^L$, there is a finite least upper bound $c^*(L)$ for the $c(N, L)$ that is independent of N. For $N = 1$, $c(N, L) = 2^L$. Therefore

$$c^*(L) \;\geq\; 2^L. \tag{2}$$

The crucial point is that, for all $\vartheta > 0$, conversely

$$\lim_{L\to\infty} 2^{-(1+\vartheta)L} c^*(L) \;=\; 0, \tag{3}$$

which means that $c^*(L)$ essentially grows like 2^L for L tending to infinity.

We proved (3) with help of Lemma 12.1 and the asymptotic representation (12.11) of the partition numbers $p(n)$ due to Hardy and Ramanujan [29]. The proof of (12.11) is far from being elementary and is rather long and complicated. In the mentioned paper, Hardy and Ramanujan derived, however, also a somewhat weaker upper bound for the partition numbers that is accessible to a much more elementary reasoning and is sufficient to prove (3). We present this result and its proof in this appendix.

Hardy and Ramanujan start from three identities that go back to Euler [73–76]. Euler first observed that the $p(n)$ are the expansion coefficients of the infinite product

$$\sum_{n=0}^{\infty} p(n)\, z^n \;=\; \prod_{i=1}^{\infty} \frac{1}{1 - z^i}, \tag{4}$$

or that this infinite product is in today's terminology their generating function.

The partial products of this infinite product converge uniformly on the discs $|z| \leq R$ of all radii $R < 1$. The limit function is thus an analytic function that possesses a power series expansion converging for $|z| < 1$. Expanding the single factors as

$$\prod_{i=1}^{\infty} \frac{1}{1 - z^i} \;=\; \prod_{i=1}^{\infty} \Big(\sum_{k=0}^{\infty} z^{ki} \Big),$$

one further recognizes that the coefficient in front of z^n is the number of possibilities to represent the number n as a sum $n = k_1 \cdot 1 + \ldots + k_n \cdot n$ of nonnegative integer multiples of $i = 1, \ldots, n$, which is the partition number $p(n)$ of n. This proves (4).

Let $p(n; r)$ denote the number of possibilities to write the nonnegative integer n as an infinite sum $n = n_1 + n_2 + \ldots$ of nonnegative integers $n_1 \geq n_2 \geq \ldots$ with $n_i = 0$ for all indices i greater than r. In the same way one sees then that

$$\sum_{n=0}^{\infty} p(n; r)\, z^n \;=\; \prod_{i=1}^{r} \frac{1}{1 - z^i} \tag{5}$$

is the generating function of these restricted partition numbers $p(n; r)$ that play an important role in our argumentation too. The difficulties in describing the asymptotic behavior of $p(n)$ for n tending to infinity have a lot to do with the complicated behavior of the infinite product (4) when approaching the boundary of the unit circle.

The third identity is a little bit more tricky. Its proof is based on an elementary but ingenious argument from combinatorics. We refer to [72] for such techniques.

LEMMA 1. *For all complex numbers* $|z| < 1$,

$$\prod_{i=1}^{\infty} \frac{1}{1-z^i} \;=\; 1 + \sum_{r=1}^{\infty} z^{r^2} \prod_{i=1}^{r} \Big(\frac{1}{1-z^i}\Big)^2. \tag{6}$$

Proof. The proof is based on a classification of the partitions of natural numbers. The idea is to assign to each finite partition $n = n_1 + n_2 + \ldots,\ n_1 \geq n_2 \geq \ldots \geq 1$, a so-called Ferrers diagram that consists of n dots which are arranged in rows and columns. The first row consists of n_1 dots, the second of n_2 dots, and so on. Figure 1 shows, as example, the Ferrers diagram assigned to the partition $7+5+4+3+2+1+1$ of the number 23. The Durfee square of a partition is the largest $r \times r$ square that can be drawn into the upper left corner of its Ferrers diagram. The Durfee square of the given partition of 23 is a 3×3 square and is shown in the right picture in Figure 1. The partitions of n are classified by the size $r \times r$ of their Durfee squares.

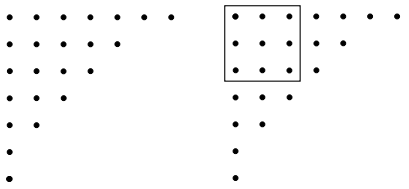

FIG. 1. *The Ferrers diagram of a partition and the associated Durfee square*

Assume that, additionally to the r^2 dots in the Durfee square of a given partition of the number n, there are $k + \ell = n - r^2$ dots in the upper right and the lower left corner of the corresponding Ferrers diagram, k in the upper right and ℓ in the lower left. The upper right corner has at most r rows and corresponds therefore, for $k \geq 1$, to a partition of k into a sum of at most r natural numbers. The number of such partitions is $p(k;r)$. The lower left corner corresponds, for $\ell \geq 1$, to a partition of ℓ whose Ferrers diagram has at most r columns. The number of these partitions is $p(\ell;r)$. The reason for that is that one can assign to every partition of the number ℓ a conjugate partition of ℓ interchanging the rows and columns of the associated Ferrers diagram. As $p(0;r) = 1$, the total number of partitions of a natural number n is thus

$$p(n) \;=\; \sum_{1 \,\leq\, r^2 \,\leq\, n} \;\; \sum_{k+\ell \,=\, n-r^2} p(k;r)\, p(\ell;r), \tag{7}$$

including those with no dot to the right or below the assigned Durfee square. The outer sum classifies the partitions of n by the size of their Durfee squares, and the inner sum is the number of partitions of n with an $r \times r$ Durfee square.

The proof of (6) is based on this identity. If one inserts (7) into the left hand side, splits z^n according to the partition $n = r^2 + k + \ell$, and rearranges the sums, one gets

$$\sum_{n=1}^{\infty} p(n)\, z^n \;=\; \sum_{r=1}^{\infty} z^{r^2} \Big(\sum_{k=0}^{\infty} p(k;r)\, z^k \Big) \Big(\sum_{\ell=0}^{\infty} p(\ell;r)\, z^\ell \Big).$$

If one inserts the generating function (5) for the inner sums on the right hand side and adds the value 1 to both sides, the proposition follows from (4). □

Equation (6) can be translated into a set of formulas that can be used to calculate the partition numbers, but also form the basis for our subsequent estimates.

LEMMA 2. *Let $q_1(n) = n+1$ and define $q_r(n)$ for $n \geq 0$ and $r > 1$ recursively by*

$$q_{r+1}(n) \;=\; \sum_{(r+1)\,\ell \,\leq\, n} (\ell+1)\, q_r\big(n-(r+1)\,\ell\,\big). \tag{8}$$

Then the partition numbers $p(n)$ for all natural numbers n are given by

$$p(n) \;=\; \sum_{1 \,\leq\, r^2 \,\leq\, n} q_r\big(n-r^2\big). \tag{9}$$

Proof. The $q_r(n)$ are the expansion coefficients of the product

$$\prod_{i=1}^{r} \Big(\frac{1}{1-z^i}\Big)^2 \;=\; \sum_{n=0}^{\infty} q_r(n)\, z^n,$$

as can be shown by induction on r. If one inserts this relation and (4) into Euler's formula (6), the relation (9) follows equating the expansion coefficients. □

The following estimate, from which Hardy and Ramanujan derived their bound for the partition numbers, is based on the representation from Lemma 2.

LEMMA 3. *For all natural numbers n,*

$$p(n) \;\leq\; \sum_{r=1}^{\infty} \frac{n^{2r-1}}{(2r-1)!\,(r!)^2}. \tag{10}$$

Proof. Following Hardy and Ramanujan, we show first that

$$q_r(n) \;\leq\; \frac{(n+r^2)^{2r-1}}{(2r-1)!\,(r!)^2}. \tag{11}$$

As $q_1(n) = n+1$, this is true for $r = 1$. Provided (11) holds for r given, (8) yields

$$q_{r+1}(n) \;\leq \sum_{(r+1)\,\ell \,\leq\, n} (l+1)\; \frac{(n-(r+1)\,\ell + r^2)^{2r-1}}{(2r-1)!\,(r!)^2}. \tag{12}$$

For $a, b \geq 0$ and all integers $m \geq 2$,

$$m\,(m-1)\,a^{m-2}\,b^2 \;\leq\; (a+b)^m - 2\,a^m + (a-b)^m.$$

Inserting the values $m = 2r+1$, $a = n-(r+1)\,l + r^2$, and $b = r+1$ and utilizing the abbreviation $\alpha(\ell) = (n-(r+1)\,\ell + r^2)^{2r+1}$, one obtains from this inequality

$$(2r+1)\,2r\,(r+1)^2\,(n-(r+1)\,\ell + r^2)^{2r-1} \leq\; \alpha(\ell-1) - 2\,\alpha(\ell) + \alpha(\ell+1).$$

If we denote by L the maximum integer ℓ for which $(r+1)\,\ell \,\leq\, n$, (12) yields

$$(2r+1)!\,((r+1)!)^2\; q_{r+1}(n) \;\leq\; \sum_{\ell=0}^{L} (\ell+1)\big(\alpha(\ell-1) - 2\,\alpha(\ell) + \alpha(\ell+1)\big)$$

and, evaluating the sum on the right hand side,

$$(2r+1)!\,((r+1)!)^2\,q_{r+1}(n)\;\le\;\alpha(-1)+(L+1)\,\alpha(L+1)-(L+2)\,\alpha(L).$$

If $n-(r+1)\,(L+1)+r^2\ge 0$, one has $0\le\alpha(L+1)\le\alpha(L)$. Otherwise $\alpha(L+1)<0$. Since $\alpha(L)\ge 0$ by the definition of L, one obtains in each of the two cases

$$(2r+1)!\,((r+1)!)^2\,q_{r+1}(n)\;\le\;\alpha(-1)\;\le\;(n+(r+1)^2)^{2r+1},$$

which finishes the proof of (11). From (9) and (11) we get

$$p(n)\;\le\sum_{1\le r^2\le n}\frac{n^{2r-1}}{(2r-1)!\,(r!)^2},$$

which proves the asserted estimate (10) for the partition numbers. □

The rest follows from Stirling's formula that relates factorials to powers. It reads

$$\lim_{n\to\infty}\frac{n^{n+1/2}}{n!\,e^n}\;=\;\frac{1}{\sqrt{2\pi}},\tag{13}$$

and is proven in many introductory analysis textbooks; see for instance [77].

LEMMA 4. *There is a constant K independent of n such that*

$$p(n)\;\le\;\frac{K}{n}\,e^{2\sqrt{2n}}\tag{14}$$

holds for all natural numbers n.

Proof. Stirling's formula yields in the limit of r tending to infinity

$$\lim_{r\to\infty}\frac{1}{(2r-1)!\,(r!)^2}\,\frac{(4r)!}{2^{6r}}\;=\;\frac{\sqrt{2}}{\pi}.$$

Hence there exists, by Lemma 3, a constant K such that

$$p(n)\;\le\;K\sum_{r=1}^{\infty}\frac{2^{6r}n^{2r-1}}{(4r)!}\;=\;\frac{K}{n}\sum_{r=1}^{\infty}\frac{\big(2\sqrt{2n}\,\big)^{4r}}{(4r)!}.$$

The proposition follows from the power series expansion of the exponential function. □

Particularly, we can conclude from this lemma that

$$\sum_{\ell=0}^{L}p(\ell)\,2^{\ell}\;=\;(2^L)^{1+\varepsilon(L)},\tag{15}$$

where the exponent can, because of $p(\ell)\le p(L)$ for $\ell\le L$, be estimated in the form

$$1\;\le\;1+\varepsilon(L)\;\le\;1+\alpha L^{-1/2}+\beta L^{-1}\tag{16}$$

with constants $\alpha>0$ and β that are independent of L. For all $\vartheta>0$ therefore

$$\lim_{L\to\infty}2^{-(1+\vartheta)L}\sum_{\ell=0}^{L}p(\ell)\,2^{\ell}\;=\;0.\tag{17}$$

This completes the proof of our complexity bounds for the quantum N-body problem.

REFERENCES

[72] M. Aigner, *A Course in Enumeration*, Springer-Verlag, Berlin Heidelberg New York, 2007.
[73] L. Euler, *Introductio in analysin infinitorum*, vol. 1, Bousquet, Lausanne, 1748, reprinted in *Opera omnia*, Series I, vol. 8, English translation by J. D. Blanton, Springer-Verlag, Berlin Heidelberg New York, 1988.
[74] L. Euler, *Observationes analyticae variae de combinationibus*, Commentarii academiae scientarium Petropolitanae, 13 (1751), pp. 64–93, reprinted in *Opera omnia* Series I, vol. 2, pp. 163–193.
[75] L. Euler, *De partitione numerorum*, Novi commentarii academiae scientarium Petropolitanae, 3 (1753), pp. 125–169, reprinted in *Opera omnia* Series I, vol. 2, pp. 254–294.
[76] L. Euler, *De partitione numerorum in partes tam numero quam specie datas*, Novi commentarii academiae scientarium Petropolitanae, 14 (1770), pp. 168–187, reprinted in *Opera omnia* Series I, vol. 3, pp. 131–147.
[77] K. Königsberger, *Analysis 1*, Springer-Verlag, Berlin Heidelberg New York, 2004.