

# DFG-Schwerpunktprogramm 1324

„Extraktion quantifizierbarer Information aus komplexen Systemen“

## The Mixed Regularity of Electronic Wave Functions Multiplied by Explicit Correlation Factors

H. Yserentant

Preprint 49



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## THE MIXED REGULARITY OF ELECTRONIC WAVE FUNCTIONS MULTIPLIED BY EXPLICIT CORRELATION FACTORS \*

HARRY YSERENTANT<sup>1</sup>

**Abstract.** The electronic Schrödinger equation describes the motion of  $N$  electrons under Coulomb interaction forces in a field of clamped nuclei. The solutions of this equation, the electronic wave functions, depend on  $3N$  variables, three spatial dimensions for each electron. Approximating them is thus inordinately challenging. As is shown in the author's monograph [Lecture Notes in Mathematics, vol. 2000, Springer-Verlag (2010)], 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 two electrons. The present paper complements this work. It is shown that one can reach almost the same complexity as in the one-electron case adding a simple regularizing factor that depends explicitly on the interelectronic distances.

**1991 Mathematics Subject Classification.** 35J10, 35B65, 41A25, 41A63.

### 1. INTRODUCTION

Atoms, molecules, and ions are described by the Schrödinger equation for a system of charged particles that interact by Coulomb attraction and repulsion forces. As the nuclei are much heavier than the electrons, the electrons almost instantaneously follow their motion. Therefore it is usual in quantum chemistry and related fields to separate the motion of the nuclei from that of the electrons and to start from the electronic Schrödinger equation, the equation that describes the motion of a finite set of electrons in the field of a finite number of clamped nuclei, or in other words to look for the eigenvalues and eigenfunctions of the Hamilton operator

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

already written down here in dimensionless form or atomic units. It acts on functions with arguments  $x_1, \dots, x_N$  in  $\mathbb{R}^3$ , which are associated with the positions of the considered electrons. The  $a_1, \dots, a_K$  in  $\mathbb{R}^3$  are the fixed positions of the nuclei and the values  $Z_\nu > 0$  the charges of the nuclei in multiples of the electron charge. The problem with this equation is its high dimensionality which immediately rules out classical discretization methods like finite elements. To overcome this curse of dimensionality, procedures like the Hartree-Fock method and

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its many variants and successors and density functional theory based methods have been developed. They are used with much success and form the basis of a steadily expanding branch of chemistry. See the comprehensive monograph [5] and the Nobel lectures [7], [12] of Kohn and Pople for an overview on the present state of the art in quantum chemistry, and [1], [10], and [11] for mathematically oriented expositions.

From the point of view of a mathematician all these methods have a decisive drawback. In the end they represent simplified models and do not allow for a systematic improvement of the approximate solutions, at least not in a mathematically rigorous way. In other words, they are in the present form no true discretizations of the electronic Schrödinger equation in the sense of numerical analysis. There are a few points of attack that such discretizations could utilize, or which could help to improve existent methods in this sense and to develop them further. One is the surprisingly high regularity of the electronic wave functions, which increases with the number of electrons, and the decay behavior of their mixed derivatives. As shown in [14–16], the expression

$$\int \left\{ 1 + \sum_{i=1}^N |\omega_i|^2 \right\} \left\{ \prod_{i \in I_-} (1 + |\omega_i|^2) + \prod_{i \in I_+} (1 + |\omega_i|^2) \right\} |\widehat{u}(\omega)|^2 d\omega \quad (1.2)$$

remains finite for the physically admissible eigenfunctions  $u$  of the electronic Schrödinger operator (1.1). The frequency or momentum variable  $\omega \in (\mathbb{R}^3)^N$  is here decomposed into parts  $\omega_i \in \mathbb{R}^3$  associated with the momentums of the single electrons;  $|\omega_i|$  denotes the euclidean norm of  $\omega_i$ . The set of the electron indices  $1, 2, \dots, N$  is split into the set  $I_-$  of the indices of the electrons with spin  $-1/2$  and the set  $I_+$  of the indices of the electrons with spin  $+1/2$ . The reason why it is not possible to bound the expression

$$\int \left\{ 1 + \sum_{i=1}^N |\omega_i|^2 \right\} \left\{ \prod_{i=1}^N (1 + |\omega_i|^2) \right\} |\widehat{u}(\omega)|^2 d\omega \quad (1.3)$$

is the singularities of the wave functions at the places where electrons of distinct spin meet. Physically admissible wave functions are by the Pauli principle antisymmetric under the exchange of electrons with the same spin. Thus they vanish where such electrons meet, which counterbalances the singularities of the electron-electron interaction potential there. It has moreover been shown in [16] that the mixed weak derivatives of the wave functions, whose existence is guaranteed by this result, decay exponentially in the  $L_2$ -sense. Using these properties, the convergence rate of sparse-grid like expansions of the wave functions into correspondingly antisymmetrized tensor products of three-dimensional basis functions can be estimated [16]. The result is surprising in view of the high-dimensionality of the equation. The convergence rate of these expansions, measured in terms of the number of the antisymmetrized tensor products of basis functions involved, is essentially the same for the  $N$ -electron case as for the two-electron case and does not deteriorate with the number of the electrons.

The ultimate goal is to come down to the one-particle case. This is not possible without a refined regularity theory that exploits the behavior of the solutions at the singular points of the electron-electron interaction potential better. The aim of this paper is to develop such a theory. We start from an observation that goes back to the work of Hylleraas [6] in the nascency of quantum mechanics. Hylleraas calculated the ground state energy of the Helium atom approximately with remarkably high accuracy for the time. The results that he obtained marked a breakthrough and showed that quantum mechanics was able to predict the behavior of atoms and molecules beyond hydrogen. Hylleraas used an ansatz that takes the distance of the two electrons explicitly into account and that differs in this respect substantially from most other approaches in quantum chemistry. Only recently, probably beginning with the work [8] of Kutzelnigg and [9] of Kutzelnigg and Klopper, methods of this kind became again popular. They are denoted as  $r12$ -methods in quantum chemistry and deliver very accurate results. See [13] for a recent survey. Inspired by such approaches, we partition the solutions  $u$  of the electronic Schrödinger equation, the eigenfunctions of the differential operator (1.1), into a regular part

$$u_0(x) = \exp \left( - \sum_{i < j} \phi(x_i - x_j) \right) u(x) \quad (1.4)$$

and a universal factor that covers the electron cusps already to a large extent. The precise conditions on the function  $\phi$  will be given in Sect. 3. Possible examples for the choice of the function  $\phi$  are

$$\phi(x_i - x_j) = \frac{1}{2} |x_i - x_j|, \quad \phi(x_i - x_j) = \ln \left( 1 + \frac{1}{2} |x_i - x_j| \right). \quad (1.5)$$

If  $v_0$  is an approximation for the regular part  $u_0$ , the wave function  $u$  itself is conversely approximated by

$$\exp \left( \sum_{i < j} \phi(x_i - x_j) \right) v_0(x) \quad (1.6)$$

We will show that the norm defined according to (1.3) of the regular parts  $u_0$  remains finite and that the mixed weak derivatives of the regular parts, which therefore exist, decay exponentially in the  $L_2$ -sense. With the sparse grid techniques described in [16] it is thus possible to approximate the regular parts of the wave functions, and with that indirectly also the wave functions themselves, with an order of convergence that comes arbitrarily close to that for the one-electron case. The convergence rate becomes asymptotically the same as that of the solution of second-order elliptic boundary value problems in three space dimensions with linear finite elements.

The paper is organized as follows. In Sect. 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 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. In Sect. 3, we set up an equation for the modified wave functions (1.4) and their exponentially weighted counterparts and fix the conditions on the function  $\phi$ . The study of the regularity of the modified wave functions is based on this equation. The idea to start from such a modified equation is adapted from [3], an article, in which the regularity of the wave functions in isotropic Hölder spaces is analyzed and which marks the current state of the art in this part of the theory. Section 4 deals with the function spaces involved. Our technique of proof is described there in more detail. The core of this work, and the main technical challenge, are the a priori estimates for the low-order part of the modified equation in Sect. 5. They are used in Sect. 6 to prove the main theorem of this paper. The modifications that are actually needed are derived in Sect. 7. Sections 8 and 9 finally come back to the approximation of the wave functions.

The same kind of results as for the regular parts (1.4) of the eigenfunctions  $u$  also hold for their modifications

$$u_1(x) = \exp \left( 2 \sum_{i, \nu} Z_\nu \phi(x_i - a_\nu) - \sum_{i < j} \phi(x_i - x_j) \right) u(x) \quad (1.7)$$

that contain an additional term smoothing the singularities at the positions  $a_\nu$  of the nuclei. Our technique of proof can be directly extended to this situation. This observation might be helpful in the approximation of the wave functions in view of their analytic structure outside the coalescence points of more than two particles [4].

## 2. THE WEAK FORM OF THE EIGENVALUE PROBLEM

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

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

with square integrable first-order weak derivatives. The norm  $\|\cdot\|_1$  on  $H^1$  is composed of the  $L_2$ -norm  $\|\cdot\|_0$  and the  $H^1$ -seminorm  $|\cdot|_1$ , the  $L_2$ -norm of the gradient. The space  $H^1$  is the space of the wave functions for

which the total position probability remains finite and the expectation value of the kinetic energy can be given a meaning. By  $\mathcal{D}$  we denote the space of all infinitely differentiable functions (2.1) with bounded support. The functions in  $\mathcal{D}$  form a dense subset of  $H^1$ . Before we can state the problem, we have to study the potential

$$V(x) = - \sum_{i=1}^N \sum_{\nu=1}^K \frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|x_i - x_j|} \quad (2.2)$$

in the Schrödinger operator (1.1) that is composed of the nucleus-electron interaction potential, the first term in (2.2), and the electron-electron interaction potential. The basic observation is:

**Theorem 2.1.** *There is a  $\theta > 0$  such that for all infinitely differentiable functions  $u$  and  $v$  with compact support*

$$\int V u v \, dx \leq \theta \|u\|_0 \|\nabla v\|_0. \quad (2.3)$$

Theorem 2.1 is folklore and can be found in this or a similar form in many mathematical texts on the Schrödinger equation. Its proof is based on the three-dimensional Hardy inequality, the estimate

$$\int \frac{1}{|x|^2} v^2 \, dx \leq 4 \int |\nabla v|^2 \, dx \quad (2.4)$$

for infinitely differentiable functions  $v : \mathbb{R}^3 \rightarrow \mathbb{R}$  with compact support. See [16] for a proof. The Hardy inequality plays a central role in this work and represents a decisive tool in the proof of many of our estimates. By (2.3),

$$a(u, v) = (Hu, v) \quad (2.5)$$

is a  $H^1$ -bounded bilinear form on  $\mathcal{D}$ , where  $(\cdot, \cdot)$  denotes the  $L_2$ -inner product. It can be uniquely extended to a bounded bilinear form on  $H^1$ . In this setting, a function  $u \neq 0$  in  $H^1$  is an eigenfunction of the electronic Schrödinger operator (1.1) for the eigenvalue  $\lambda$  if

$$a(u, v) = \lambda(u, v), \quad v \in H^1. \quad (2.6)$$

The weak form (2.6) of the eigenvalue equation  $Hu = \lambda u$  in particular fixes the behavior of the eigenfunctions at the singularities of the interaction potential and at infinity. For normed  $u$ ,  $a(u, u)$  is the expectation value of the total energy. It should, however, be noted that only those solutions  $u \in H^1$  of the equation (2.6) are physically admissible that are antisymmetric with respect to the permutation of the positions  $x_i$  of electrons of the same spin. This is a consequence of the Pauli principle and is explained in more detail for example in [16]. In contrast to the estimates in [16], here we will not need this property to derive our regularity results.

We are interested in eigenfunctions  $u$  for eigenvalues below the bottom of the essential spectrum, a value less than or equal to zero. Such eigenfunctions and their first-order weak derivatives decay exponentially in the  $L_2$ -sense, as has first been shown by O'Connor [2]. That means there is a constant  $\gamma > 0$  such that the functions

$$x \rightarrow \exp\left(\gamma \sum_{i=1}^N |x_i|\right) u(x), \quad \exp\left(\gamma \sum_{i=1}^N |x_i|\right) (\nabla u)(x) \quad (2.7)$$

are square integrable. This constant depends on the distance of the eigenvalue under consideration to the bottom of the essential spectrum. More details and references to the literature can be found in [16].



### 3. A MODIFIED EIGENVALUE PROBLEM

In this section we set up the modified equation whose regularity properties will be studied later and fix the needed properties of the regularizing factor. This factor is first only defined on the open set

$$\mathcal{M} = \{(x_1, \dots, x_N) \in (\mathbb{R}^3)^N \mid x_i \neq 0, x_i \neq x_j \text{ for } i, j = 1, \dots, N\}, \quad (3.1)$$

in particular outside the singularities of the electron-electron interaction potential. We assume that  $F : \mathcal{M} \rightarrow \mathbb{R}$  is an infinitely differentiable, locally bounded function with bounded first-order derivatives and that an estimate

$$\int \Delta F uv \, dx \lesssim \|\nabla u\|_0 \|v\|_0 \quad (3.2)$$

holds for the functions  $u, v \in H^1$ . The notion  $a \lesssim b$  means  $a \leq b$  up to an unspecified constant. We will make extensive use of this notation in the rest of this paper. Our aim is to study the regularizing effect of the factor  $e^F$  onto eigenfunctions  $u$  of the Schrödinger operator (1.1), that is, the regularity of the products

$$\tilde{u}(x) = \exp(F(x))u(x). \quad (3.3)$$

The corresponding functions  $F$  will later be specified in more detail and conditions will be given under which (3.2) holds. To simplify our considerations, we introduce the space  $\mathcal{D}_0$  of the infinitely differentiable functions from  $(\mathbb{R}^3)^N$  to  $\mathbb{R}$  with compact support that vanish on a neighborhood of the singular set  $\Gamma = (\mathbb{R}^3)^N \setminus \mathcal{M}$ .

**Lemma 3.1.** *Every function  $u$  in the space  $\mathcal{D}$  of the infinitely differentiable functions with compact support can be approximated arbitrarily well in the  $H^1$ -sense by functions in  $\mathcal{D}_0$  that vanish outside the support of  $u$  itself.*

*Proof.* We proceed step by step multiplying  $u$  with cut-off functions. Let  $\chi : \mathbb{R}^3 \rightarrow [0, 1]$  be an infinitely differentiable function that takes the values  $\chi(x) = 0$  for  $|x| \leq 1$  and  $\chi(x) = 1$  for  $|x| \geq 2$ . Set  $\chi_\varepsilon(x) = \chi(x_1/\varepsilon)$ . The functions  $u_\varepsilon(x) = \chi_\varepsilon(x)u(x)$  vanish then on a neighborhood in  $(\mathbb{R}^3)^N$  of the hyperspace  $x_1 = 0$ . As

$$|(\nabla \chi_\varepsilon)(x)| \leq \frac{c}{|x_1|},$$

with  $c$  a constant independent of  $\varepsilon$ , and  $\chi_\varepsilon(x) \rightarrow 1$  and  $(\nabla \chi_\varepsilon)(x) \rightarrow 0$  for  $x_1 \neq 0$  as  $\varepsilon$  goes to zero, the dominated convergence theorem shows that the  $u_\varepsilon$  tend to  $u$  in the  $H^1$ -sense. The other sets  $x_i = 0$  and the diagonals  $x_i = x_j$  are successively treated in the same way until the approximating functions are found.  $\square$

Since  $\mathcal{D}$  is a dense subspace of  $H^1$ , the space  $\mathcal{D}_0$  is therefore a dense subspace of  $H^1$ , too.

**Lemma 3.2.** *Let  $u \in H^1$ . The function  $\tilde{u}$  defined as in (3.3) is then not only locally square integrable but also has locally square integrable first-order weak partial derivatives. They read*

$$D_k \tilde{u} = e^F D_k F u + e^F D_k u, \quad (3.4)$$

where the operator  $D_k$  denotes weak differentiation for  $u$  and pointwise for  $F$ .

*Proof.* We first consider functions  $u \in \mathcal{D}$  and test functions  $\varphi \in \mathcal{D}_0$ . Integration by parts then yields

$$\int (e^F D_k F u + e^F D_k u) \varphi \, dx = - \int e^F u D_k \varphi \, dx.$$

Since  $F$  and its first-order derivatives are by assumption locally bounded, both sides of this equation represent  $H^1$ -bounded linear functionals in  $\varphi$  for  $u$  fixed. The relation transfers therefore by Lemma 3.1 to all  $\varphi \in \mathcal{D}$ . If conversely  $\varphi \in \mathcal{D}$  is fixed, both sides represent  $H^1$ -bounded linear functionals in  $u$ . As  $\mathcal{D}$  is a dense subspace of  $H^1$ , the relation holds therefore for all  $u \in H^1$  and  $\varphi \in \mathcal{D}$ , which proves the proposition.  $\square$

**Lemma 3.3.** *For all functions  $u \in H^1$  and all test functions  $v \in \mathcal{D}_0$ ,*

$$a(e^F u, v) + c(e^F u, v) = a(u, e^F v), \quad (3.5)$$

where  $c(u, v)$  denotes the  $H^1$ -bounded bilinear form

$$c(u, v) = \frac{1}{2} \int \{2 \nabla F \cdot \nabla u + (\Delta F - |\nabla F|^2) u\} v \, dx \quad (3.6)$$

and the derivatives of  $F$  have again to be understood pointwise.

*Proof.* We consider again first only functions  $u \in \mathcal{D}$ . A short calculation yields

$$\Delta(e^F u) = e^F \Delta u + 2 \nabla F \cdot \nabla(e^F u) + (\Delta F - |\nabla F|^2) e^F u$$

outside the singular set  $\Gamma$ . If one multiplies this equation by a test function  $v \in \mathcal{D}_0$  and integrates by parts

$$- \int \nabla(e^F u) \cdot \nabla v \, dx = - \int \nabla u \cdot \nabla(e^F v) \, dx + 2c(e^F u, v)$$

follows. That is, (3.5) holds for all  $u \in \mathcal{D}$  and test functions  $v \in \mathcal{D}_0$ . For  $v \in \mathcal{D}_0$  fixed, the linear functionals

$$u \rightarrow a(e^F u, v), a(u, e^F v), c(e^F u, v)$$

can be continuously extended to  $H^1$ , as follows from the boundedness of  $F$ ,  $\nabla F$ , and  $\Delta F$  on the support of  $v$  and the density of  $\mathcal{D}$  in  $H^1$ . The equation (3.5) holds therefore for all  $u \in H^1$  and  $v \in \mathcal{D}_0$ . The  $H^1$ -boundedness of the bilinear form (3.6) follows from the assumed boundedness of  $\nabla F$  and the estimate (3.2).  $\square$

**Theorem 3.4.** *If  $u$  is an eigenfunction for the eigenvalue  $\lambda$  and  $F$  is chosen such that the function (3.3) and its first-order derivatives (3.4) are square integrable, the function (3.3) satisfies the eigenvalue equation*

$$a(\tilde{u}, v) + c(\tilde{u}, v) = \lambda(\tilde{u}, v), \quad v \in H^1. \quad (3.7)$$

*Proof.* If  $v \in \mathcal{D}_0$  the function  $e^F v$  is infinitely differentiable and has a compact support. Hence

$$a(u, e^F v) = \lambda(u, e^F v) = \lambda(e^F u, v)$$

For all functions  $v \in \mathcal{D}_0$ , by Lemma 3.3 therefore

$$a(e^F u, v) + c(e^F u, v) = \lambda(e^F u, v).$$

As by assumption  $e^F u \in H^1$ , both sides of this equation represent bounded linear functionals in  $v \in H^1$ . The proposition follows therefore from Lemma 3.1, which implies the density of  $\mathcal{D}_0$  in  $H^1$ .  $\square$

From now on we restrict ourselves to functions

$$F(x) = - \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \phi(x_i - x_j) + \gamma \sum_{i=1}^N |x_i|, \quad (3.8)$$

where  $\phi : \mathbb{R}^3 \setminus \{0\} \rightarrow \mathbb{R}$  is assumed to be an infinitely differentiable, locally bounded function with bounded first-order derivatives. We assume that  $\phi$  takes only values  $\geq 0$ , that  $\phi(-x) = \phi(x)$ , and that an estimate

$$|(\Delta \phi)(x)| \lesssim \frac{1}{|x|} \quad (3.9)$$

holds. The task of the interaction terms  $\phi(x_i - x_j)$  is to regularize the singularities of the wave functions at the places where electrons meet, particularly those with distinct spin. The second term is needed to prove that the mixed derivatives of the wave functions decay exponentially. The constant  $\gamma \geq 0$  is the same as in (2.7), or bounded from above by that constant, and has to be chosen such that the corresponding modified eigenfunction (3.3) and its first-order weak derivatives (3.4) remain square integrable.

**Lemma 3.5.** *The gradient of  $F$  with respect to the components of  $x_k$  is given by*

$$(\nabla_k F)(x) = \sum_{\substack{i=1 \\ i \neq k}}^N (\nabla \phi)(x_i - x_k) + \gamma \frac{x_k}{|x_k|}. \quad (3.10)$$

*The Laplacian of  $F$ , with respect to the complete set of variables, reads*

$$(\Delta F)(x) = - \sum_{\substack{i,j=1 \\ i \neq j}}^N (\Delta \phi)(x_i - x_j) + 2\gamma \sum_{i=1}^N \frac{1}{|x_i|}. \quad (3.11)$$

*Proof.* The symmetry of  $\phi$  implies that  $(D_\nu \phi)(-x) = -(D_\nu \phi)(x)$ . Hence

$$\frac{\partial}{\partial x_{k,\nu}} F(x) = - \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N (D_\nu \phi)(x_i - x_j) (\delta_{ik} - \delta_{jk}) + \gamma \frac{x_{k,\nu}}{|x_k|} = \sum_{\substack{i=1 \\ i \neq k}}^N (D_\nu \phi)(x_i - x_k) + \gamma \frac{x_{k,\nu}}{|x_k|},$$

which proves (3.10). Differentiating this equation once more one finds

$$\frac{\partial^2}{\partial x_{k,\nu}^2} F(x) = - \sum_{\substack{i=1 \\ i \neq k}}^N (D_\nu^2 \phi)(x_i - x_k) + \gamma \left(1 - \frac{x_{k,\nu}^2}{|x_k|^2}\right) \frac{1}{|x_k|}.$$

Summation first over the indices  $\nu = 1, 2, 3$  and then over  $k = 1, \dots, N$  yields (3.11).  $\square$

The assumptions on  $\phi$  imply that  $F$  is locally bounded and  $\nabla F$  bounded. The assumption (3.2) follows, via (3.9) and (3.11), from the Cauchy-Schwarz inequality, Fubini's theorem, and the Hardy inequality, that is, from

$$\int \frac{1}{|x_i - x_j|^2} u^2 dx \leq 2 \int \{|\nabla_i u|^2 + |\nabla_j u|^2\} dx, \quad (3.12)$$

$$\int \frac{1}{|x_i|^2} u^2 dx \leq 4 \int |\nabla_i u|^2 dx. \quad (3.13)$$

Inserting (3.10) and (3.11) into (3.6), we find the explicit representation

$$a(u, v) + c(u, v) = \frac{1}{2} \int \nabla u \cdot \nabla v dx + s(u, v) \quad (3.14)$$

of the bilinear form on  $H^1$  on the left hand side of (3.7), where the low-order part is composed of the terms

$$s(u, v) = - \sum_{i=1}^N \sum_{\nu=1}^K \int \frac{Z_\nu}{|x_i - a_\nu|} u v \, dx \quad (3.15)$$

$$+ \sum_{\substack{i,k=1 \\ i \neq k}}^N \int (\nabla \phi)(x_i - x_k) \cdot \nabla_k u v \, dx \quad (3.16)$$

$$+ \gamma \sum_{k=1}^N \int \frac{x_k}{|x_k|} \cdot \nabla_k u v \, dx \quad (3.17)$$

$$- \frac{1}{2} \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^N \int (\nabla \phi)(x_i - x_k) \cdot (\nabla \phi)(x_j - x_k) u v \, dx \quad (3.18)$$

$$- \frac{1}{2} \sum_{\substack{i,k=1 \\ i \neq k}}^N \int (\nabla \phi)(x_i - x_k) \cdot (\nabla \phi)(x_i - x_k) u v \, dx \quad (3.19)$$

$$- \gamma \sum_{\substack{i,k=1 \\ i \neq k}}^N \int \frac{x_k}{|x_k|} \cdot (\nabla \phi)(x_i - x_k) u v \, dx \quad (3.20)$$

$$- \frac{1}{2} N \gamma^2 \int u v \, dx \quad (3.21)$$

$$+ \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \int \left\{ \frac{1}{|x_i - x_j|} - (\Delta \phi)(x_i - x_j) \right\} u v \, dx \quad (3.22)$$

$$+ \gamma \sum_{i=1}^N \int \frac{1}{|x_i|} u v \, dx. \quad (3.23)$$

The term on the right hand side of (3.15) stems from the nucleus-electron interaction potential, (3.16) and (3.17) represent the terms coming from the expression  $\nabla F \cdot \nabla u$  in (3.6), and (3.18) to (3.21) the part with the coefficient function  $|\nabla F|^2$ . The sum in (3.18) runs over the indices  $i, j$ , and  $k$  that are all different from each other. The two remaining terms (3.22) and (3.23) combine the term resulting from  $\Delta F$  and the electron-electron interaction potential. The given assumptions imply:

**Theorem 3.6.** *The expressions (3.15) to (3.23) define a bilinear form on  $H^1 \times L_2$  that satisfies an estimate*

$$s(u, v) \leq \kappa \|u\|_1 \|v\|_0, \quad u \in H^1, v \in L_2. \quad (3.24)$$

The proof of Theorem 3.6 is based on the Cauchy-Schwarz inequality, Fubini's theorem, and the Hardy inequality. The crucial term giving the additional regularity is (3.22). With help of the function

$$W(x) = \frac{1}{|x|} - (\Delta \phi)(x) \quad (3.25)$$

from  $\mathbb{R}^3$  to  $\mathbb{R}$  it can, in short form, be rewritten as

$$\frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \int W(x_i - x_j) u v dx. \quad (3.26)$$

Choosing  $\phi(x) = |x|/2$ , the electron-electron interaction potential and the  $\phi$ -part of  $\Delta F$  cancel and the term (3.22) disappears completely. We assume in the sequel that  $\phi(x) = \tilde{\phi}(|x|)$ , where  $\tilde{\phi} : [0, \infty) \rightarrow \mathbb{R}$  is an infinitely differentiable function with values  $\tilde{\phi}(r) \geq 0$  whose first-order derivative remains bounded and whose second- and third-order derivatives decrease at least like  $\sim 1/r$  as  $r$  goes to infinity. Then

$$|(D_i \phi)(x)| \lesssim 1, \quad |(D_i D_j \phi)(x)| \lesssim \frac{1}{|x|}. \quad (3.27)$$

These estimates follow from the fact that, with  $r = |x|$  and  $x_1, x_2$ , and  $x_3$  here the components of  $x \in \mathbb{R}^3$ ,

$$(D_i \phi)(x) = \tilde{\phi}'(r) \frac{x_i}{r}, \quad (D_i D_j \phi)(x) = \tilde{\phi}''(r) \frac{x_i x_j}{r^2} + \frac{1}{r} \tilde{\phi}'(r) \left(1 - \frac{x_i x_j}{r^2}\right). \quad (3.28)$$

The representation of the function (3.25) in terms of the function  $\tilde{\phi}$  is

$$W(x) = \frac{1 - 2\tilde{\phi}'(r)}{r} - \tilde{\phi}''(r). \quad (3.29)$$

The condition that guarantees that the function (3.25) remains bounded and its gradient satisfies an estimate

$$|(\nabla W)(x)| \lesssim \frac{1}{|x|} \quad (3.30)$$

is thus  $\tilde{\phi}'(0) = 1/2$ . Examples of such functions are  $\tilde{\phi}(r) = r/2$  and  $\tilde{\phi}(r) = \ln(1 + r/2)$ . For approximation purposes it is more advantageous when  $\phi(x)$  itself remains bounded or even goes to zero as  $|x|$  goes to infinity.

#### 4. THE FUNCTION SPACES

In the previous sections we have decomposed the vectors  $x = (x_1, \dots, x_N) \in (\mathbb{R}^3)^N$  into parts  $x_i \in \mathbb{R}^3$  that are associated with the electron positions. The components of these vectors are the real numbers  $x_{i,1}, x_{i,2}$ , and  $x_{i,3}$ . Accordingly, we label partial derivatives doubly, that is, by multi-indices

$$\alpha = (\alpha_1, \dots, \alpha_N) \in (\mathbb{Z}_{\geq 0}^3)^N, \quad \alpha_i = (\alpha_{i,1}, \alpha_{i,2}, \alpha_{i,3}) \in \mathbb{Z}_{\geq 0}^3. \quad (4.1)$$

The differential operator  $D^\alpha$  and the monomial  $x^\alpha$  of order  $|\alpha| = \sum_{i,\nu} \alpha_{i,\nu}$  are in this notation

$$D^\alpha = \prod_{i=1}^N \prod_{\nu=1}^3 \left( \frac{\partial}{\partial x_{i,\nu}} \right)^{\alpha_{i,\nu}}, \quad x^\alpha = \prod_{i=1}^N \prod_{\nu=1}^3 x_{i,\nu}^{\alpha_{i,\nu}}. \quad (4.2)$$

We are particularly concerned with operators  $D^\alpha$  with multi-indices  $\alpha$  in the set

$$\mathcal{A} = \{(\alpha_1, \dots, \alpha_N) \mid \alpha_i \in \mathbb{Z}_{\geq 0}^3, \alpha_{i,1} + \alpha_{i,2} + \alpha_{i,3} \leq 1\}, \quad (4.3)$$

that is, that are of most first-order in each of the variables  $x_i \in \mathbb{R}^3$ . We introduce by

$$\|u\|_0^2 = \sum_{\alpha \in \mathcal{A}} \|D^\alpha u\|_0^2, \quad \|u\|_1^2 = \sum_{\alpha \in \mathcal{A}} \|D^\alpha u\|_1^2 \quad (4.4)$$

two norms on the space  $\mathcal{D}$  of the infinitely differentiable functions with compact support or, somewhat more generally, on the Schwartz space  $\mathcal{S}$  of the rapidly decreasing functions. Introducing the differential operator

$$\mathcal{L} = \sum_{\alpha \in \mathcal{A}} (-1)^{|\alpha|} D^{2\alpha} = \prod_{i=1}^N (I - \Delta_i), \quad \Delta_i = \frac{\partial^2}{\partial x_{i,1}^2} + \frac{\partial^2}{\partial x_{i,2}^2} + \frac{\partial^2}{\partial x_{i,3}^2}, \quad (4.5)$$

these norms can be rewritten in terms of the quadratic forms

$$\|u\|_0^2 = (u, \mathcal{L}u), \quad \|u\|_1^2 = (u, (I - \Delta)\mathcal{L}u). \quad (4.6)$$

Their Fourier representation is therefore given by expressions like those mentioned in the introduction:

$$\|u\|_1^2 = \int \left\{ 1 + \sum_{i=1}^N |\omega_i|^2 \right\} \left\{ \prod_{i=1}^N (1 + |\omega_i|^2) \right\} |\hat{u}(\omega)|^2 d\omega, \quad (4.7)$$

$$\|u\|_0^2 = \int \left\{ \prod_{i=1}^N (1 + |\omega_i|^2) \right\} |\hat{u}(\omega)|^2 d\omega, \quad (4.8)$$

where the frequency variable  $\omega \in (\mathbb{R}^3)^N$  is again decomposed into parts  $\omega_i \in \mathbb{R}^3$  and  $|\omega_i|$  denotes the euclidean norm of  $\omega_i$ . The completions of the space  $\mathcal{D}$  of the infinitely differentiable functions with compact support under these norms are the Hilbert spaces denoted as  $X_0$  and  $X^1$ . They consist of the functions from  $(\mathbb{R}^3)^N$  to the real numbers whose weak derivatives of corresponding order exist and are square integrable.

We have shown that the modified eigenfunction (3.3) for the eigenvalue  $\lambda$  satisfies the equation

$$a_0(\tilde{u}, \mathcal{L}v) + s(\tilde{u}, \mathcal{L}v) = \lambda(\tilde{u}, \mathcal{L}v), \quad v \in \mathcal{S}, \quad (4.9)$$

where  $a_0(u, v)$  is an abbreviation for the leading part of the bilinear form  $a(u, v)$ , the Dirichlet integral

$$a_0(u, v) = \frac{1}{2} \int \nabla u \cdot \nabla v dx. \quad (4.10)$$

Our strategy will be to reinterpret the equation (4.9) as an equation in the space  $X^1$  just defined and to show in this way that its solution possesses high-order mixed derivatives. This can only work if the bilinear form on the left hand side of (4.9) is bounded in the corresponding norm. This is easily shown for its main part since

$$a_0(u, \mathcal{L}v) = \frac{1}{2} \sum_{\alpha \in \mathcal{A}} \int D^\alpha \nabla u \cdot D^\alpha \nabla v dx \quad (4.11)$$

for all  $u \in \mathcal{D}$  and  $v \in \mathcal{S}$ . This representation implies that the bilinear form

$$\tilde{a}_0 : \mathcal{D} \times \mathcal{S} \rightarrow \mathbb{R} : (u, v) \rightarrow a_0(u, \mathcal{L}v) \quad (4.12)$$

can be extended to a bounded bilinear form from  $X^1 \times X^1$  to  $\mathbb{R}$  that satisfies the estimate

$$\tilde{a}_0(u, v) \leq \frac{1}{2} \|\nabla u\|_0 \|\nabla v\|_0 \quad (4.13)$$

for all  $u$  and  $v$  in  $X^1$ , and that is moreover coercive in the sense that

$$\tilde{a}_0(u, u) \geq \frac{1}{2} \|\nabla u\|_0^2 \quad (4.14)$$

holds for all  $u \in X^1$ . The defining relation

$$\tilde{a}_0(u, v) = a_0(u, \mathcal{L}v) \quad (4.15)$$

transfers to all  $u \in X^1$  and  $v \in \mathcal{S}$  as both sides of this equation represent bounded linear functionals in  $u \in X^1$  for  $v \in \mathcal{S}$  given. Similarly, the positive definite bilinear form given by

$$\tilde{m}(u, v) = \sum_{\alpha \in \mathcal{A}} \int \mathbb{D}^\alpha u \mathbb{D}^\alpha v \, dx = (u, \mathcal{L}v) \quad (4.16)$$

can be continuously extended from  $\mathcal{D} \times \mathcal{S}$  to  $X_0 \times X_0$ . For  $u \in X_0$  and  $v \in \mathcal{S}$ ,

$$\tilde{m}(u, v) = (u, \mathcal{L}v). \quad (4.17)$$

To show that estimates of similar type hold for the more complicatedly built low-order part

$$\tilde{s} : \mathcal{D} \times \mathcal{S} \rightarrow \mathbb{R} : (u, v) \rightarrow s(u, \mathcal{L}v) \quad (4.18)$$

of the bilinear form on the left hand side of (4.9) is a much harder task to which the next section is devoted.

## 5. A BOUND FOR THE LOW-ORDER PART

To show that the bilinear form (4.18) can be continuously extended to  $X_0 \times X^1$  we have to show that  $s(u, \mathcal{L}v)$  can be estimated by the corresponding norms (4.4) of  $u$  and  $v$  for  $u$  and  $v$  in the space  $\mathcal{D}$  of the infinitely differentiable functions with compact support. We consider for this the terms  $q(u, v)$  of which the sums (3.15) to (3.21) are composed to a large extent separately from each other and then have to estimate the expressions

$$(-1)^{|\alpha|} q(u, \mathbb{D}^{2\alpha} v) \quad (5.1)$$

for multi-indices  $\alpha$  in the set (4.3). The most simple case is that the coefficient functions in the integral defining the bilinear form  $q(u, v)$  do not depend on the variables on which the differential operator  $\mathbb{D}^\alpha$  acts. Then

$$(-1)^{|\alpha|} q(u, \mathbb{D}^{2\alpha} v) = q(\mathbb{D}^\alpha u, \mathbb{D}^\alpha v). \quad (5.2)$$

The proof is simple. The integral is first split with help of Fubini's theorem into an inner integral with respect to the variables on which  $\mathbb{D}^\alpha$  acts and a remaining outer integral. The inner integral is transformed by integration by parts and the result again recombined with help of Fubini's theorem. Since

$$q(u, v) \lesssim \|u\|_0 \|v\|_0 \quad \text{or} \quad q(u, v) \lesssim \|\nabla_i u\|_0 \|v\|_0 \quad (5.3)$$

for some index  $i$ , the relation (5.2) already proves the desired estimate

$$(-1)^{|\alpha|} q(u, \mathbb{D}^{2\alpha} v) \lesssim \|u\|_0 \|v\|_1, \quad (5.4)$$

where  $\alpha_i = 0$  has to be taken into account when the second estimate in (5.3) applies.

The case that  $D^\alpha$  acts on one (and only one) of the position vectors  $x_i$  on which the coefficient function in the defining integral depends is treated similarly. We split the differential operator  $D^\alpha = D^\sigma D^\beta$  then into a first-order operator  $D^\sigma$  acting upon one of the components of the relevant  $x_i$  and a rest  $D^\beta$ . As before then

$$(-1)^{|\alpha|} q(u, D^{2\alpha} v) = - q(D^\beta u, D^{2\sigma} D^\beta v). \quad (5.5)$$

The expression on the right-hand side is again estimated with help of the estimates in (5.3), where as in the previous case  $\beta_i = 0$  when the second estimate in (5.3) applies. Since in the expression on the right hand side only one second-order derivative acts on  $v$  and the derivatives with respect to the components of the other position vectors are at most first-order, one obtains again an estimate (5.4).

The critical case is when  $D^\alpha$  acts onto components of two or even three of the position vectors on which the coefficient function in the integral depends. Then one has to work harder. The first step is to again decompose the operator  $D^{2\alpha} = D^{2\sigma} D^{2\beta}$  into an uncritical part  $D^{2\beta}$  that can as before be distributed in equal parts to both sides and therefore be ignored in the sequel, and a fourth- or even sixth-order operator  $D^{2\sigma}$  that has to be considered separately and treated with more care. One or in the latter case even two of the remaining derivatives have to be shifted to the left hand side. This is essentially a two- or at most three-particle problem. In the general case, the arising integrals can again be split with help of Fubini's theorem and the estimate in this way be reduced to the two- or three-electron case. To simplify the presentation, we restrict ourselves for the rest of this section to the two- or three-electron case and denote the three-dimensional position vectors of the electrons temporarily by  $x$ ,  $y$ , and  $z$ . Their components are  $x_1, x_2$ , and  $x_3$ ,  $y_1, y_2$ , and  $y_3$ , and  $z_1, z_2$ , and  $z_3$ .

The first term for which this situation can occur is (3.16). The estimate that covers then this term reads:

**Lemma 5.1.** *For all infinitely differentiable functions  $u$  and  $v$  in the variables  $x, y \in \mathbb{R}^3$  with compact support,*

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int (\mathbf{D}_i \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} d(x, y) \\ & \lesssim \left( \sum_{i,k=1}^3 \int \left( \frac{\partial^2 u}{\partial x_i \partial y_k} \right)^2 d(x, y) \right)^{1/2} \left( \sum_{j,k=1}^3 \int \left( \frac{\partial^3 v}{\partial x_j^2 \partial y_k} \right)^2 d(x, y) \right)^{1/2}. \end{aligned} \quad (5.6)$$

*Proof.* The first problem is that one has to shift one of the derivatives with respect to  $y_k$  from  $v$  to the other parts. Because of the singularities of  $\phi$  it is not immediately clear whether one can integrate by parts. To solve this problem, let  $\chi : \mathbb{R}^3 \rightarrow [0, 1]$  be an infinitely differentiable function as in the proof of Lemma 3.1 that takes the values  $\chi(x) = 0$  for  $|x| \leq 1$  and  $\chi(x) = 1$  for  $|x| \geq 2$ . Set  $\chi_\varepsilon(x) = \chi(x/\varepsilon)$ . Integration by parts then yields

$$\begin{aligned} & \int \chi_\varepsilon(x-y) (\mathbf{D}_i \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} dy \\ & = \int (\mathbf{D}_k \chi_\varepsilon)(x-y) (\mathbf{D}_i \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \\ & \quad + \int \chi_\varepsilon(x-y) (\mathbf{D}_i \mathbf{D}_k \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \\ & \quad - \int \chi_\varepsilon(x-y) (\mathbf{D}_i \phi)(x-y) \frac{\partial^2 u}{\partial x_i \partial y_k} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy. \end{aligned}$$

The following inequalities hold uniformly in  $\varepsilon$ ,

$$|(\mathbf{D}_k \chi_\varepsilon)(x-y)| \lesssim \frac{1}{|x-y|}, \quad |(\mathbf{D}_i \mathbf{D}_k \phi)(x-y)| \lesssim \frac{1}{|x-y|},$$



by the assumptions on the function  $\phi$  and the construction of the cut-off function  $\chi_\varepsilon$ . As the remaining terms are uniformly bounded, and as  $u$  and  $v$  vanish outside a bounded set, the integrands are uniformly dominated by integrable functions, and the dominated convergence theorem yields

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} dy \\ &= \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \mathbb{D}_k \phi)(x-y) \frac{\partial u}{\partial x_i} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \\ & \quad - \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y) \frac{\partial^2 u}{\partial x_i \partial y_k} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \end{aligned}$$

for  $\varepsilon$  tending to zero, where the derivatives of  $\phi$  have to be understood pointwise. Integration by parts is thus allowed here. The first term is estimated with help of the Hardy inequality, that is, using (3.27) and

$$\int \frac{1}{|x-y|^2} \left( \frac{\partial u}{\partial x_i} \right)^2 dy \leq 4 \sum_{k=1}^3 \int \left( \frac{\partial^2 u}{\partial x_i \partial y_k} \right)^2 dy,$$

and the second, using the boundedness of  $\nabla \phi$ , simply applying the Cauchy-Schwarz inequality. Integrating the resulting estimate with respect to  $x$ , or in the general case with respect to all remaining variables, and applying the Cauchy-Schwarz inequality once more, now to the outer integral, the proposition follows.  $\square$

A similar situation arises with the terms in (3.19) and (3.20). They are covered by the following two estimates:

**Lemma 5.2.** *For all infinitely differentiable functions  $u$  and  $v$  in the variables  $x, y \in \mathbb{R}^3$  with compact support,*

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y)^2 u \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} d(x,y) \\ & \lesssim \left( \sum_{k=1}^3 \int \left( \frac{\partial u}{\partial y_k} \right)^2 d(x,y) \right)^{1/2} \left( \sum_{j,k=1}^3 \int \left( \frac{\partial^3 v}{\partial x_j^2 \partial y_k} \right)^2 d(x,y) \right)^{1/2}. \end{aligned} \quad (5.7)$$

*Proof.* The same type of arguments as above shows that integration by parts is possible here too and that

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y)^2 u \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} dy \\ &= 2 \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y) (\mathbb{D}_i \mathbb{D}_k \phi)(x-y) u \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \\ & \quad - \sum_{i,j,k=1}^3 \int (\mathbb{D}_i \phi)(x-y)^2 \frac{\partial u}{\partial y_k} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy. \end{aligned}$$

The estimate follows again with help of the Cauchy-Schwarz and the Hardy inequality and Fubini's theorem using the given bounds for the first- and the second-order derivatives of the function  $\phi$ .  $\square$

**Lemma 5.3.** *For all infinitely differentiable functions  $u$  and  $v$  in the variables  $x, y \in \mathbb{R}^3$  with compact support,*

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int \frac{x_i}{|x|} (\mathbb{D}_i \phi)(x-y) u \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} d(x, y) \\ & \lesssim \left( \sum_{k=1}^3 \int \left( \frac{\partial u}{\partial y_k} \right)^2 d(x, y) \right)^{1/2} \left( \sum_{j,k=1}^3 \int \left( \frac{\partial^3 v}{\partial x_j^2 \partial y_k} \right)^2 d(x, y) \right)^{1/2}. \end{aligned} \quad (5.8)$$

*Proof.* Integration by parts is again possible. Therefore

$$\begin{aligned} & \sum_{i,j,k=1}^3 \int \frac{x_i}{|x|} (\mathbb{D}_i \phi)(x-y) u \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} dy \\ & = \sum_{i,j,k=1}^3 \int \frac{x_i}{|x|} (\mathbb{D}_i \mathbb{D}_k \phi)(x-y) u \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy \\ & \quad - \sum_{i,j,k=1}^3 \int \frac{x_i}{|x|} (\mathbb{D}_i \phi)(x-y) \frac{\partial u}{\partial y_k} \frac{\partial^3 v}{\partial x_j^2 \partial y_k} dy. \end{aligned}$$

The proposition follows with help of the Cauchy-Schwarz and the Hardy inequality and Fubini's theorem, using the bounds for the first- and the second-order derivatives of  $\phi$ .  $\square$

Technically more challenging than the previous estimates are the estimates for the terms coming from (3.18) since the coefficient functions depend in this case on three electron positions. The task is to estimate integrals

$$\int (\mathbb{D}_i \phi)(x-z) (\mathbb{D}_i \phi)(y-z) u \frac{\partial^6 v}{\partial x_j^2 \partial y_k^2 \partial z_\ell^2} d(x, y, z), \quad (5.9)$$

$$\int (\mathbb{D}_i \phi)(x-z) (\mathbb{D}_i \phi)(y-z) u \frac{\partial^4 v}{\partial x_j^2 \partial y_k^2} d(x, y, z), \quad (5.10)$$

$$\int (\mathbb{D}_i \phi)(x-z) (\mathbb{D}_i \phi)(y-z) u \frac{\partial^4 v}{\partial x_j^2 \partial z_\ell^2} d(x, y, z), \quad (5.11)$$

$$\int (\mathbb{D}_i \phi)(x-z) (\mathbb{D}_i \phi)(y-z) u \frac{\partial^4 v}{\partial y_k^2 \partial z_\ell^2} d(x, y, z). \quad (5.12)$$

Equations (5.10), (5.11), and (5.12) indicate the case that derivatives with respect to components of two of the variables  $x$ ,  $y$ , and  $z$  arise. In these cases, one proceeds as in the proofs of the previous two lemmas and shifts one of the derivatives with respect to  $x_j$  respectively  $y_k$  to the other side and applies the Hardy inequality to estimate the term with the second-order derivative of  $\phi$ . Most delicate is the case indicated by equation (5.9) where two derivatives have to be brought to the other side. To master this situation, one needs:

**Lemma 5.4.** *For all infinitely differentiable functions  $u$  and  $v$  in the variables  $x, y, z \in \mathbb{R}^3$  with compact support,*

$$\begin{aligned} & \sum_{i,j,k,\ell=1}^3 \int (\mathbb{D}_i \phi)(x-z) (\mathbb{D}_i \phi)(y-z) u \frac{\partial^6 v}{\partial x_j^2 \partial y_k^2 \partial z_\ell^2} d(x, y, z) \\ & \lesssim \left( \sum_{j,k=1}^3 \int \left( \frac{\partial^2 u}{\partial x_j \partial y_k} \right)^2 d(x, y, z) \right)^{1/2} \left( \sum_{j,k,\ell=1}^3 \int \left( \frac{\partial^4 v}{\partial x_j \partial y_k \partial z_\ell^2} \right)^2 d(x, y, z) \right)^{1/2}. \end{aligned} \quad (5.13)$$

*Proof.* Splitting the integrals to be estimated with help of Fubini's theorem first into an inner integral with respect to  $x$  and an outer integral with respect to  $y$ , bringing the  $x$ -derivative in the inner integral to the other side as before, exchanging the order of integration, and once more integrating by parts, one obtains

$$\begin{aligned}
& \int (\mathbf{D}_i \phi)(x-z) (\mathbf{D}_i \phi)(y-z) u \frac{\partial^6 v}{\partial x_j^2 \partial y_k^2 \partial z_\ell^2} d(x, y) \\
&= \int (\mathbf{D}_i \mathbf{D}_j \phi)(x-z) (\mathbf{D}_i \mathbf{D}_k \phi)(y-z) u \frac{\partial^4 v}{\partial x_j \partial y_k \partial z_\ell^2} d(x, y) \\
&\quad + \int (\mathbf{D}_i \mathbf{D}_j \phi)(x-z) (\mathbf{D}_i \phi)(y-z) \frac{\partial u}{\partial y_k} \frac{\partial^4 v}{\partial x_j \partial y_k \partial z_\ell^2} d(x, y) \\
&\quad + \int (\mathbf{D}_i \phi)(x-z) (\mathbf{D}_i \mathbf{D}_k \phi)(y-z) \frac{\partial u}{\partial x_j} \frac{\partial^4 v}{\partial x_j \partial y_k \partial z_\ell^2} d(x, y) \\
&\quad + \int (\mathbf{D}_i \phi)(x-z) (\mathbf{D}_i \phi)(y-z) \frac{\partial^2 u}{\partial x_j \partial y_k} \frac{\partial^4 v}{\partial x_j \partial y_k \partial z_\ell^2} d(x, y).
\end{aligned}$$

The proposition follows estimating the single terms separately using again the Cauchy-Schwarz inequality, Fubini's theorem, and the Hardy inequality. To estimate the first term, that is, in the end to show that

$$\int \frac{1}{|x-z|^2} \frac{1}{|y-z|^2} u^2 d(x, y) \lesssim \sum_{j,k=1}^3 \int \left( \frac{\partial^2 u}{\partial x_j \partial y_k} \right)^2 d(x, y),$$

the Hardy inequality needs to be applied twice. The integral is first split into an inner integral with respect to the variable  $x$  and an outer integral with respect to  $y$ . The inner integral is estimated with help of the Hardy inequality, the order of integration is exchanged, and the Hardy inequality is applied a second time.  $\square$

What remains is the term (3.22) respectively (3.26). To estimate this term, the fact that the electron-electron interaction potential and the singular parts coming from  $\Delta \phi$  cancel enter decisively. Otherwise only a restricted version of the desired estimate could be proved bringing the Pauli principle into play, see [16]. One obtains:

**Lemma 5.5.** *For all infinitely differentiable functions  $u$  and  $v$  in the variables  $x, y \in \mathbb{R}^3$  with compact support,*

$$\begin{aligned}
& \sum_{i,j=1}^3 \int W(x-y) u \frac{\partial^4 v}{\partial x_i^2 \partial y_j^2} d(x, y) \\
& \lesssim \left( \sum_{j=1}^3 \int \left( \frac{\partial u}{\partial y_j} \right)^2 d(x, y) \right)^{1/2} \left( \sum_{i,j=1}^3 \int \left( \frac{\partial^3 v}{\partial x_i^2 \partial y_j} \right)^2 d(x, y) \right)^{1/2}.
\end{aligned} \tag{5.14}$$

*Proof.* Utilizing that  $W$  itself is bounded and the gradient of  $W$  satisfies an estimate (3.30), one can again integrate by parts and obtains the proposition in the same way as before.  $\square$

All terms of which the bilinear form (4.18) is composed can thus be estimated as desired. We remark that the differentiation orders are hereby heavily intermixed with each other. The essential point is that one gains, in comparison to the estimates (4.13), (4.14) for the main part, one differentiation order in  $u$ . We summarize:

**Theorem 5.6.** *There is a  $\tilde{\kappa} > 0$  such that for all infinitely differentiable functions  $u$  and  $v$  with compact support*

$$\tilde{s}(u, v) \leq \tilde{\kappa} \|u\|_0 \|v\|_1. \tag{5.15}$$

The estimate obviously remains true for functions  $u \in \mathcal{D}$  and  $v \in \mathcal{S}$ . The bilinear form (4.18) can thus be extended from its domain of definition  $\mathcal{D} \times \mathcal{S}$  to a bounded bilinear form on  $X_0 \times X^1$ . The defining relation

$$\tilde{s}(u, v) = s(u, \mathcal{L}v) \quad (5.16)$$

transfers to all  $u \in X_0$  and  $v \in \mathcal{S}$  as both sides of this equation represent bounded linear functionals in  $u \in X_0$  for  $v \in \mathcal{S}$  given. The estimate (5.15) transfers to all functions  $u$  and  $v$  in the full spaces  $X_0$  respectively  $X^1$ .

## 6. THE REGULARITY OF THE SOLUTIONS OF THE MODIFIED EQUATION

Besides the given a priori estimates, some Fourier analysis enters into the proof of our regularity theorem. The idea is to split the modified eigenfunctions into a high-frequency part and a low-frequency part and first to estimate the high-frequency part by the low frequency part. A rapidly decreasing high-frequency function is a rapidly decreasing function with a Fourier transform that vanishes on a ball of a radius  $\Omega \geq 1$ , still to be fixed, around the origin of the frequency space. The closure of the corresponding space

$$\mathcal{S}_H = \{v \in \mathcal{S} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \leq \Omega\} \quad (6.1)$$

of rapidly decreasing functions in  $H^1$  and  $X^1$ , respectively, is denoted as  $H_H^1$  and  $X_H^1$ . The closure of

$$\mathcal{S}_L = \{v \in \mathcal{S} \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \geq \Omega\} \quad (6.2)$$

in  $H^1$  and  $X^1$  are the spaces  $H_L^1$  and  $X_L^1$ , respectively, of low-frequency functions. The low-frequency and the high-frequency functions decompose the spaces

$$H^1 = H_L^1 \oplus H_H^1, \quad X^1 = X_L^1 \oplus X_H^1 \quad (6.3)$$

into orthogonal parts. The functions in  $H_L^1$  are infinitely differentiable and all their derivatives are square integrable. Of central importance for our further considerations are the inverse estimates

$$\|u_H\|_0 \leq \Omega^{-1} \|\nabla u_H\|_0, \quad \|u_H\|_0 \leq \Omega^{-1} \|\nabla u_H\|_0 \quad (6.4)$$

for the high-frequency functions  $u_H$  in  $H_H^1$  and  $X_H^1$  respectively, which follow from the Fourier representation of the norms. On  $H_H^1$ , the seminorm  $\|\nabla v\|_0$  and the norm  $\|v\|_1$  thus are equivalent. The same holds for the seminorm  $\|\nabla v\|_0$  and the norm  $\|v\|_1$  on  $X_H^1$ . The low-order parts  $s(u, v)$ , respectively  $\tilde{s}(u, v)$ , of the bilinear forms under consideration become small perturbations of the main part for large  $\Omega$ . We require in the sequel

$$\Omega \geq 4\sqrt{2} \max\{\kappa, \tilde{\kappa}\}, \quad (6.5)$$

with  $\kappa$  and  $\tilde{\kappa}$  the constants in (3.24) and (5.15). This implies the estimates

$$s(u_H, v_H) \leq \frac{1}{4} \|\nabla u_H\|_0 \|\nabla v_H\|_0, \quad \tilde{s}(u_H, v_H) \leq \frac{1}{4} \|\nabla u_H\|_0 \|\nabla v_H\|_0 \quad (6.6)$$

for the functions  $u_H$  and  $v_H$  in  $H_H^1$ , respectively in  $X_H^1$ , and therefore the lower estimates

$$\tilde{a}_0(u_H, u_H) + \tilde{s}(u_H, u_H) \geq \frac{1}{4} \|\nabla u_H\|_1^2, \quad u_H \in X_H^1, \quad (6.7)$$

$$a_0(u_H, u_H) + s(u_H, u_H) \geq \frac{1}{4} \|\nabla u_H\|_1^2, \quad u_H \in H_H^1, \quad (6.8)$$

establishing the coercivity of the bilinear forms on the corresponding spaces of high-frequency functions.

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 equation (3.7), here rewritten with help of (3.14) and (4.10) as

$$a_0(\tilde{u}, \chi) + s(\tilde{u}, \chi) = \lambda(\tilde{u}, \chi), \quad \chi \in H^1, \quad (6.9)$$

for the modified eigenfunction (3.3) 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 by the low-frequency part of the given solution. The first step to reach this goal is the following lemma that follows 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 6.1.** *Let  $\tilde{u} = u_L + u_H$  be the decomposition of a solution  $\tilde{u} \in H^1$  of the equation (6.9) into its low-frequency and its high-frequency part. Then*

$$a_0(u_H, \chi_H) + s(u_H, \chi_H) - \lambda(u_H, \chi_H) = -s(u_L, \chi_H), \quad \chi_H \in H_H^1. \quad (6.10)$$

We will keep the low-frequency part  $u_L$  fixed for a while and will consider (6.10) as an equation for the high-frequency part  $u_H$ . We will show that such equations are uniquely solvable for frequency bounds (6.5) and that the regularity of the right hand side transfers to the regularity of the solution. Before we start with the proof, we recall that the eigenvalues under consideration below the bottom of the essential spectrum are negative.

**Lemma 6.2.** *For frequency bounds  $\Omega$  as in (6.5), the equation*

$$a_0(u_H, \chi_H) + s(u_H, \chi_H) - \lambda(u_H, \chi_H) = s(\varphi, \chi_H), \quad \chi_H \in H_H^1, \quad (6.11)$$

*possesses a unique solution  $u_H \in H_H^1$  for all given functions  $\varphi \in H^1$ .*

*Proof.* As  $\lambda < 0$ , the additional term does not alter the coercivity (6.8) of the bilinear form on the left hand side of (6.11). The Lax-Milgram theorem hence guarantees the existence and uniqueness of a solution.  $\square$

A corresponding result holds for the high-order counterpart of the equation (6.11) that formally results from this equation after replacing the test functions  $\chi_H$  by test functions  $\mathcal{L}v_H$ .

**Lemma 6.3.** *For frequency bounds  $\Omega$  as in (6.5), the equation*

$$\tilde{a}_0(u_H, v_H) + \tilde{s}(u_H, v_H) - \lambda \tilde{m}(u_H, v_H) = \tilde{s}(\varphi, v_H), \quad v_H \in X_H^1, \quad (6.12)$$

*possesses a unique solution  $u_H \in X_H^1$  for all given functions  $\varphi \in X_0$ .*

*Proof.* This follows again from the Lax-Milgram theorem.  $\square$

As follows from the relations (4.15), (4.17), and (5.16), the equation (6.12) becomes

$$a_0(u_H, \mathcal{L}v_H) + s(u_H, \mathcal{L}v_H) - \lambda(u_H, \mathcal{L}v_H) = s(\varphi, \mathcal{L}v_H), \quad (6.13)$$

for test functions  $v_H \in \mathcal{S}_H$ . The argument that closes the gap between the equations (6.11) and (6.12) is therefore the observation that every function in  $\chi_H \in \mathcal{S}_H$  can be represented in the form  $\chi_H = \mathcal{L}v_H$ ,  $v_H \in \mathcal{S}_H$ .

**Lemma 6.4.** *For all rapidly decreasing high-frequency functions  $\chi_H \in \mathcal{S}_H$  there is a uniquely determined rapidly decreasing high-frequency function  $v_H \in \mathcal{S}_H$  that solves the equation  $\mathcal{L}v_H = \chi_H$ .*

*Proof.* The proof utilizes that the Fourier transform of a rapidly decreasing function is a rapidly decreasing function and vice versa. Because of the representation (4.5) of  $\mathcal{L}$ , the equation reads in Fourier representation

$$\left\{ \prod_{i=1}^N (1 + |\omega_i|^2) \right\} \hat{v}_H(\omega) = \hat{\chi}_H(\omega)$$

and determines the Fourier transform  $\hat{v}_H$  of the rapidly decreasing high-frequency function  $v_H$  uniquely.  $\square$

The solution of the equation (6.12) therefore satisfies the original equation (6.11) for all  $\chi_H \in \mathcal{S}_H$  and, as  $\mathcal{S}_H$  is dense in  $H_H^1$ , for all  $\chi_H \in H_H^1$ . Since the equation (6.11) possesses only one solution, the solutions of both equations coincide for  $\varphi$  in the subspace  $X_0$  of  $H^1$  given. This proves:

**Lemma 6.5.** *If the bound  $\Omega$  separating the high from the low frequencies is chosen according to (6.5) and  $\varphi \in X_0$ , the solution  $u_H \in H_H^1$  of the equation (6.11) is contained in the space  $X_H^1$ .*

Since the low-frequency part  $u_L$  of the solution  $\tilde{u}$  of the modified eigenvalue equation (6.9) is contained in  $X_0$ , we can apply the result just proved to the equation (6.10). From this it follows that the high-frequency part  $u_H$  of  $\tilde{u}$  can be controlled by the low-frequency part  $u_L$  and that  $\tilde{u}$  itself is contained in  $X^1$ .

**Theorem 6.6.** *The solutions  $\tilde{u} \in H^1$  of the modified eigenvalue problem (6.9) for negative eigenvalues  $\lambda$  are contained in  $X^1$ , that is, possess mixed weak derivatives  $D^\alpha \tilde{u} \in H^1$  for multi-indices  $\alpha$  in the set (4.3).*

## 7. EXISTENCE AND EXPONENTIAL DECAY OF THE MIXED DERIVATIVES

We have shown that, for every eigenfunction  $u \in H^1$  of the Schrödinger operator (1.1), the modified function

$$\tilde{u}(x) = \exp(\psi(x) - \psi_0(x))u(x) \quad (7.1)$$

is contained in the space  $X^1$ , that is, has mixed derivatives  $D^\alpha \tilde{u} \in H^1$  for multi-indices  $\alpha$  in the set (4.3), where we have split here the function (3.8) into the sum  $F = \psi - \psi_0$  of the functions

$$\psi_0(x) = \sum_{i < j} \phi(x_i - x_j), \quad \psi(x) = \gamma \sum_{i=1}^N |x_i|. \quad (7.2)$$

The universal factor  $e^{-\psi_0}$  attenuates the singular behavior of the eigenfunctions at the places where the electrons meet. The admissible constants  $\gamma > 0$  in the factor  $e^\psi$  are bounded from above, dependent on the decay behavior of the eigenfunction under consideration. In this section we will use these results to study the existence and the exponential decay of high-order mixed derivatives of the regular parts

$$u_0(x) = \exp(-\psi_0(x))u(x), \quad (7.3)$$

equipped only with the universal regularizing factor  $e^{-\psi_0}$  and without the exponentially increasing factor  $e^\psi$ .

**Theorem 7.1.** *Let  $D^\alpha u_0$ ,  $\alpha$  in the set (4.3), be one of the weak derivatives of the regular part (7.3) of the eigenfunction  $u$  whose existence and square integrability follows from Theorem 6.6, and let  $e^\psi$  be one of the associated weight factors for which  $D^\alpha(e^\psi u_0)$  has been shown to be square integrable too. The weighted derivatives*

$$e^\psi D^\alpha u_0, \quad e^\psi \frac{\partial}{\partial x_{i,k}} D^\alpha u_0 \quad (7.4)$$

are then square integrable as well.

*Proof.* The proof is based on the representation

$$D^\alpha(e^\psi u_0) = \sum_{\mu \leq \alpha} \gamma^{|\mu|} a_\mu e^\psi D^{\alpha-\mu} u_0$$

of the corresponding weak derivatives of  $e^\psi u_0$ , where the relation  $\mu \leq \alpha$  has to be understood componentwise. This representation is a generalization of the product rule from Lemma 3.1 and can be derived from it taking into account the special structure of the multi-indices  $\alpha$  considered. The coefficient functions are the products

$$a_\mu(x) = \prod_{\mu_i \neq 0} \frac{x_i^{\mu_i}}{|x_i|},$$

written down here in multi-index notation, where  $a_\mu(x) = 1$  for  $\mu = 0$ . This representation allows us to express  $e^\psi D^\alpha u_0$  in terms of the derivative  $D^\alpha(e^\psi u_0)$  of  $e^\psi u_0$  and the weighted lower order derivatives  $e^\psi D^{\alpha-\mu} u_0$  of  $u_0$ . Since the coefficient functions  $a_\mu$  are bounded, the square integrability of  $e^\psi D^\alpha u_0$  follows by induction on the order of differentiation. The square integrability of the second function is proven differentiating the representation above. To cover the resulting derivatives of the  $a_\mu$  one needs again the Hardy inequality.  $\square$

The exponential functions  $x \rightarrow \exp(\psi(x))$  dominate every polynomial, regardless of the decay rate  $\gamma > 0$  determined by the decay behavior of the eigenfunction under consideration. This yields the following corollary:

**Theorem 7.2.** *Let  $D^\alpha u_0$ ,  $\alpha$  in the set (4.3), be one of the weak derivatives of the regular part (7.3) of the eigenfunction  $u$  whose existence and square integrability has been shown, and let  $P$  be an arbitrary polynomial. Then*

$$P D^\alpha u_0, P \frac{\partial}{\partial x_{i,k}} D^\alpha u_0 \in L_2. \quad (7.5)$$

This statement can again be reversed. For every multi-index  $\mu$  the function  $D^\alpha(x^\mu u_0)$  and the weighted derivative  $\omega^\alpha D^\mu \hat{u}_0$  of its Fourier transform are in  $L_2$ . The  $\mu$  are not subject to restrictions, due to the exponential decay of the wave functions and their mixed derivatives, but the  $\alpha$  are, because of the restricted regularity.

## 8. THE RADIAL-ANGULAR DECOMPOSITION

An interesting consequence of Theorem 7.2 is the following. Consider a complete  $L_2$ -orthonormal system

$$\phi_{n\ell m}(x) = \frac{1}{r} f_{n\ell}(r) Y_\ell^m(x), \quad n, \ell = 0, 1, \dots, \quad m = -\ell, \dots, \ell, \quad (8.1)$$

of functions from  $\mathbb{R}^3$  to  $\mathbb{R}$ , where  $r = |x|$  has been set and the  $Y_\ell^m$  are the spherical harmonics. The joint eigenfunctions of the harmonic oscillator and the angular momentum operators  $L^2$  and  $L_3$  represent an example of such a system. Every square integrable function  $u : (\mathbb{R}^3)^N \rightarrow \mathbb{R}$  can then be expanded into an orthogonal series

$$u(x) = \sum_{n,\ell,m} \hat{u}(n,\ell,m) \prod_{i=1}^N \phi_{n_i \ell_i m_i}(x_i), \quad (8.2)$$

where  $n$ ,  $\ell$ , and  $m$  are multi-indices here with components  $n_i$ ,  $\ell_i$ , and  $m_i$ . Define the  $L_2$ -orthogonal projections

$$(Q(\ell, m)u)(x) = \sum_n \hat{u}(n, \ell, m) \prod_{i=1}^N \phi_{n_i \ell_i m_i}(x_i) \quad (8.3)$$

in which the angular parts are kept fixed and the sum extends only over the corresponding radial parts. These projections can in fact be defined without recourse to the given expansion. They are not only  $L_2$ -orthogonal but also orthogonal as projections of many other  $L_2$ -like Sobolev spaces into themselves. For functions in  $H^1$ ,

$$\|u\|_1^2 = \sum_{\ell, m} \|Q(\ell, m)u\|_1^2. \quad (8.4)$$

The point is that the weighted norm defined by the expression

$$\|u\|^2 = \sum_{\ell, m} \left\{ \prod_{i=1}^N (1 + \ell_i (\ell_i + 1)) \right\} \|Q(\ell, m)u\|_1^2 \quad (8.5)$$

of the regular parts (7.3) of the eigenfunctions remains finite. The proof uses that the functions (8.1) are eigenfunctions of the square of the angular momentum operator. Thus only very few of the projections make

a significant contribution to the regular parts  $u_0$  of the eigenfunctions. Their contributions essentially decrease with the product of the angular momentum quantum numbers  $\ell_i$ . To quantify this, let  $u_{0,\varepsilon}$  be that part of the expansion of  $u_0$  that is made up of the contributions assigned to the multi-indices  $\ell$  for which

$$\prod_{i=1}^N (1 + \ell_i (\ell_i + 1)) \leq \frac{1}{\varepsilon^2}. \quad (8.6)$$

Since the decomposition is orthogonal with respect to the  $H^1$ -norm,

$$\|u_0 - u_{0,\varepsilon}\|_1 \leq \varepsilon \|u_0 - u_{0,\varepsilon}\| \leq \varepsilon \|u_0\|. \quad (8.7)$$

For details we refer to [16] where a corresponding situation is analyzed.

## 9. APPROXIMATION AND COMPLEXITY OF THE EIGENFUNCTIONS

One reason to study the regularity of functions is to derive bounds for the speed of convergence of approximation procedures, or to construct such methods that are adapted to the regularity properties that these functions have. That is also the case here. The point is that it is much easier to approximate the regular parts

$$u_0(x) = \exp(-\psi_0(x))u(x), \quad \psi_0(x) = \sum_{i<j} \phi(x_i - x_j), \quad (9.1)$$

of the eigenfunctions than the eigenfunctions  $u$  themselves. The reason is that the singularities of the eigenfunctions, particularly at the places where electrons with opposite spin meet, are strongly damped by the exponential factor. We assume in this section, in addition to the assumptions made before, that the function  $\phi$  itself is bounded. Let  $v_0$  be a function that approximates  $u_0$ . The obvious idea is then to approximate  $u$  by

$$v(x) = \exp(\psi_0(x))v_0(x). \quad (9.2)$$

Since the total error  $d = u - v$  and its gradient can be expressed via

$$d = e^{\psi_0}d_0, \quad \nabla d = e^{\psi_0}\nabla d_0 - e^{\psi_0}d_0\nabla\psi_0 \quad (9.3)$$

in terms of the error  $d_0 = u_0 - v_0$  in the approximation of  $u_0$  and both  $\psi_0$  and  $\nabla\psi_0$  are bounded, the  $H^1$ -norm

$$\|u - v\|_1 \lesssim \|u_0 - v_0\|_1 \quad (9.4)$$

of the total error can be estimated in terms of the approximation error for the regular part. This observation can also be reinterpreted as follows. Every approximation space or manifold  $\mathcal{V}_0$  that is suitable for functions that are as smooth as the regular parts of the eigenfunctions induces, via

$$\mathcal{V} = \{v \mid v = e^{\psi_0}v_0, v_0 \in \mathcal{V}_0\}, \quad \mathcal{V}' = \{v \mid v = e^{\psi_0}v_0 + w_0, v_0, w_0 \in \mathcal{V}_0\}, \quad (9.5)$$

approximation spaces or manifolds of at least the same quality for the eigenfunctions themselves. One does not need to solve the complicated equation for the regular parts that has been used here to analyze them. It suffices to multiply the ansatz functions by the factor  $e^{\psi_0}$  to keep the approximation properties. The price to be paid is the necessity to evaluate more complicated integrals than for a pure tensor product construction.

Physically admissible solutions  $u$  of the electronic Schrödinger equation are antisymmetric with respect to the exchange of the positions  $x_i$  of electrons with the same spin. This is a consequence of the Pauli principle as has already been mentioned in Sect. 2. Since the function  $\psi_0$  is invariant to any permutation of the  $x_i$ , the function  $u_0$  shares these symmetry properties with  $u$  but possesses at the same time square integrable weak



partial derivatives  $D^\alpha u_0 \in H^1$  for multi-indices  $\alpha$  in the set (4.3). This is not the case for the eigenfunctions  $u$  themselves that have stronger singularities at the points where electrons of distinct spin meet. Moreover, all these derivatives decay exponentially in the  $L_2$ -sense. With help of the sparse grid techniques from [16] it is therefore possible to approximate the regular part  $u_0$  of the eigenfunction  $u$ , and with that indirectly the eigenfunction itself, up to an  $H^1$ -error of order  $\mathcal{O}(1/n)$  with linear combinations of no more than

$$\mathcal{O}(n^{3+\vartheta}), \quad \vartheta > 0 \text{ arbitrarily small}, \quad (9.6)$$

correspondingly antisymmetrized tensor products of given three-dimensional basis functions. This convergence rate is independent of the number  $N$  of electrons and comes arbitrarily close to that for the one-electron case.

## 10. REMOVING THE SINGULARITIES AT THE POSITIONS OF THE NUCLEI

If one replaces the regularized version (1.4) of the eigenfunctions by their counterparts (1.7), also paying regard to the singularities at the positions of the nuclei, the role of the term (3.15) is taken over by

$$- \sum_{i=1}^N \sum_{\nu=1}^K Z_\nu \int \left\{ \frac{1}{|x_i - a_\nu|} - (\Delta\phi)(x_i - a_\nu) \right\} u v \, dx, \quad (10.1)$$

that is, the nucleus-electron interaction potential is replaced by the less singular kernel (3.25), as with the electron interaction. The term coming from the expression  $\nabla F \cdot \nabla u$  in (3.6) splits now into (3.16), (3.17), and

$$2 \sum_{k=1}^N \sum_{\nu=1}^K Z_\nu \int (\nabla\phi)(x_k - a_\nu) \cdot \nabla_k u v \, dx. \quad (10.2)$$

The parts originating from the coefficient function  $|\nabla F|^2$  in (3.6) have to be complemented by the terms

$$- 2 \sum_{k=1}^N \sum_{\nu, \nu'=1}^K Z_\nu Z_{\nu'} \int (\nabla\phi)(x_k - a_\nu) \cdot (\nabla\phi)(x_k - a_{\nu'}) u v \, dx, \quad (10.3)$$

$$- 2 \sum_{\substack{i, k=1 \\ i \neq k}}^N \sum_{\nu=1}^K Z_\nu \int (\nabla\phi)(x_k - a_\nu) \cdot (\nabla\phi)(x_i - x_k) u v \, dx, \quad (10.4)$$

$$- \gamma \sum_{k=1}^N \sum_{\nu=1}^K Z_\nu \int \frac{x_k}{|x_k|} \cdot (\nabla\phi)(x_k - a_\nu) u v \, dx. \quad (10.5)$$

All these additional new terms can be estimated in the same way as before. Our results transfer therefore without any change to the present case, as asserted in the introduction.

The additional term does not improve the mixed regularity of the wave functions and from this point of view is of little value. The crucial observation is that the eigenfunctions can be locally represented in the form

$$u(x) = \exp \left( - 2 \sum_{i, \nu} Z_\nu \phi(x_i - a_\nu) + \sum_{i < j} \phi(x_i - x_j) \right) v(x) + w(x) \quad (10.6)$$

with real-analytic functions  $v$  and  $w$ . The condition is that  $\phi(x) = \tilde{\phi}(|x|)$  and  $\tilde{\phi}(r)$  is an analytic function. Locally means here on a neighborhood of every point at which no more than two electrons or nuclei meet. This

can be deduced without much effort from the results in [4]. The regularizing factor thus covers the singularities of the eigenfunctions in the neighborhood of such points completely. Approximation methods can clearly benefit from this property although it is difficult to quantify this effect.

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