Chapter 6
Existence and Decay of Mixed Derivatives

A primary aim of this work, and the decisive step to our analysis of the complexity of electronic wave functions, is to study the regularity of these functions. We want to show that they possess certain high-order square integrable weak derivatives and that these derivatives even decay exponentially, in the same way as the wave functions themselves. This goal is reached in the present chapter. A central idea of the proof is to examine instead of the solutions of the original Schrödinger equation the solutions of a modified equation for the correspondingly exponentially weighted wave functions. This equation is set up in the first section of this chapter and is based on the result on the exponential decay of the wave functions from Sect. 5.5. The study of the regularity in isotropic Hölder spaces in [32] is based on a similar idea. In Sect. 6.2 we introduce the high-order solution spaces and the corresponding norms. The actual proof relies on a mixture of variational techniques and Fourier analysis. The key is the estimates for the arising low-order terms, particularly for the nucleus-electron and the electron-electron interaction potential. These estimates are proven in Sect. 6.3 and Sect. 6.4. The estimates for the nucleus-electron interaction potential and an additional term coming from the exponential weights are in the end based on the Hardy inequality from Sect. 4.1, whose central role is reflected here again. In contrast to these estimates the estimates for the electron-electron interaction potential require that the considered functions satisfy the Pauli principle, that is, are antisymmetric with respect to the exchange of the positions of electrons with the same spin. The reason is that such functions vanish at the places where electrons with the same spin meet, which counterbalances the singularities of the electron-electron interaction potential. To derive these estimates and to master the arising singularities a further three-dimensional Hardy-type estimate is needed that holds only for functions vanishing at the origin. In Sect. 6.5 the regularity theorem for the exponentially weighted wave functions is stated and proven. This result serves then to derive bounds for the exponential decay of the mixed derivatives of the original wave functions. The present chapter is partly based on two former papers [92,94] of the author in which the existence of the mixed derivatives has been proven and estimates for their L_2-norms were given. The result on the exponential decay of these derivatives [95] was up to now only available on the author's website.

H. Yserentant, *Regularity and Approximability of Electronic Wave Functions*,
Lecture Notes in Mathematics 2000, DOI 10.1007/978-3-642-12248-4_6,

6.1 A Modified Eigenvalue Problem

First we replace the rotationally symmetric exponential weight functions in (5.56) by products of weight functions that depend only on the coordinates of one 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 $\theta_1, \ldots, \theta_N \geq 0$ be given weight factors and let

$$F(x) = \gamma \sum_{i=1}^{N} \theta_i \, |x_i|, \quad \sum_{i=1}^{N} \theta_i^2 = 1. \tag{6.1}$$

Let γ be a decay rate as in Theorem 5.17, that is,

$$\gamma < \sqrt{2\,(\Sigma(\sigma) - \lambda)}, \tag{6.2}$$

and define the correspondingly exponentially weighted eigenfunction as

$$\widetilde{u}(x) = \exp\big(F(x)\big)\, u(x). \tag{6.3}$$

This exponentially weighted eigenfunction solves then an eigenvalue equation that is similar to the original one. To derive it we start from the following two lemmata:

Lemma 6.1. *Let the function $u \in H^1$ and the constant $\gamma \in \mathbb{R}$ be first arbitrary. The function $\widetilde{u}$ defined as in (6.3) is then not only locally square integrable but has also locally square integrable first-order weak partial derivatives. They read*

$$D_k \widetilde{u} = \mathrm{e}^F D_k F \, u + \mathrm{e}^F D_k u, \tag{6.4}$$

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

Proof. We first consider functions $u \in \mathscr{D}$, that is, infinitely differentiable functions with bounded support, and replace the function (6.1) by its smooth counterparts

$$F_\varepsilon(x) = \gamma \sum_{i=1}^{N} \theta_i \sqrt{|x_i|^2 + \varepsilon^2}. \tag{6.5}$$

Integration by parts then yields, for all test functions φ of the same type,

$$\int \big(\mathrm{e}^{F_\varepsilon} D_k F_\varepsilon \, u + \mathrm{e}^{F_\varepsilon} D_k u\big)\varphi \,\mathrm{d}x = \int D_k\big(\mathrm{e}^{F_\varepsilon} u\big)\varphi \,\mathrm{d}x = -\int \mathrm{e}^{F_\varepsilon} u \, D_k \varphi \,\mathrm{d}x.$$

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

$$\int \big(\mathrm{e}^{F} D_k F \, u + \mathrm{e}^{F} D_k u\big)\varphi \,\mathrm{d}x = -\int \mathrm{e}^{F} u \, D_k \varphi \,\mathrm{d}x.$$

Since F and its first-order partial derivatives are bounded on the support of φ and $\mathscr{D}$ is a dense subspace of H^1, this relation transfers to all $u \in H^1$. This proves the differentiation formula above and transfers the product rule to the given case. □

Lemma 6.2. *For all functions $u \in H^1$ and all test functions $v \in \mathscr{D}$,*

$$a\big(u,\mathrm{e}^F v\big) - a\big(\mathrm{e}^F u,v\big) = c\big(\mathrm{e}^F u,v\big), \tag{6.6}$$

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

$$c(u,v) = \frac{1}{2}\int \big\{2\nabla F\cdot\nabla u + \big(\Delta F - |\nabla F|^2\big)\,u\big\}\,v\,\mathrm{d}x. \tag{6.7}$$

Proof. We consider again first only functions $u \in \mathscr{D}$ and replace F by its infinitely differentiable counterparts (6.5). A short calculation yields

$$\Delta\big(\mathrm{e}^{F_\varepsilon}u\big) - \mathrm{e}^{F_\varepsilon}\Delta u = 2\nabla F_\varepsilon\cdot\nabla\big(\mathrm{e}^{F_\varepsilon}u\big) + \big(\Delta F_\varepsilon - |\nabla F_\varepsilon|^2\big)\,\mathrm{e}^{F_\varepsilon}u.$$

If one multiplies this equation with a test function $v \in \mathscr{D}$ and integrates by parts

$$\int \nabla u\cdot\nabla\big(\mathrm{e}^{F_\varepsilon}v\big)\,\mathrm{d}x - \int \nabla\big(\mathrm{e}^{F_\varepsilon}u\big)\cdot\nabla v\,\mathrm{d}x$$
$$= \int\big\{2\nabla F_\varepsilon\cdot\nabla\big(\mathrm{e}^{F_\varepsilon}u\big) + \big(\Delta F_\varepsilon - |\nabla F_\varepsilon|^2\big)\,\mathrm{e}^{F_\varepsilon}u\big\}\,v\,\mathrm{d}x$$

follows. As F_ε and ∇F_ε are locally uniformly bounded in $\varepsilon \leq \varepsilon_0$ and $|\Delta_i F_\varepsilon| \lesssim 1/|x_i|$, one can let ε tend to zero in this expression and recognizes with help of the dominated convergence theorem that (6.6) holds for all functions u and v in $\mathscr{D}$. The H^1-boundedness of the bilinear form (6.7) follows from the Hardy inequality. As the functions in $\mathscr{D}$ have a bounded support, both sides of equation (6.6) thus represent, by Lemma 6.1, bounded linear functionals in $u \in H^1$ for $v \in \mathscr{D}$ given. The equation transfers therefore to all functions $u \in H^1$ and all test functions $v \in \mathscr{D}$. □

After these preparations we can now return to the initially introduced eigenfunction $u \in H^1(\sigma)$ for the eigenvalue λ and its exponentially weighted counterpart (6.3).

Theorem 6.1. *The exponentially weighted eigenfunction $\widetilde{u}$ defined by (6.3) is itself contained in the space H^1 and solves the eigenvalue equation*

$$a(\widetilde{u},v) + \gamma s(\widetilde{u},v) = \widetilde{\lambda}(\widetilde{u},v), \quad v \in H^1, \tag{6.8}$$

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

$$s(u,v) = \sum_{i=1}^{N}\theta_i\int\left\{\frac{x_i}{|x_i|}\cdot\nabla_i u + \frac{1}{|x_i|}\,u\right\}v\,\mathrm{d}x \tag{6.9}$$

and the real eigenvalue $\widetilde{\lambda} < \Sigma(\sigma) \leq 0$ *is given by*

$$\widetilde{\lambda} = \lambda + \frac{1}{2}\gamma^2. \tag{6.10}$$

Proof. The function (6.1) satisfies the estimate $F(x) \leq \gamma|x|$. Under the condition (6.2) the exponentially weighted eigenfunction (6.3) is therefore, by Theorem 5.17 and Lemma 6.1, contained in H^1. Setting $\widetilde{v} = \mathrm{e}^F v$, by Lemma 6.1 and Lemma 6.2

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

for all test functions $v \in \mathscr{D}$ and hence for all $v \in H^1$. The proposition follows calculating ∇F and ΔF explicitly and observing that $|\nabla F|^2 = \gamma^2$. □

The next sections are devoted to the study of the modified eigenvalue problem (6.8) that the exponentially weighted eigenfunctions (6.3) satisfy. Hereby we take up a slightly more general approach and relax the symmetry properties prescribed by the Pauli principle a little bit. Let I be a nonempty subset of the set of the electron indices $1,\ldots,N$. Let $\mathscr{D}_I$ denote the subspace of $\mathscr{D}$ that consists of those functions in $\mathscr{D}$ 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 I. The closure of the subspace $\mathscr{D}_I$ in H^1 is the Hilbert space H_I^1. Our modified eigenvalue problem then consists in finding functions $u \neq 0$ in H_I^1 and values $\lambda < 0$ that satisfy the condition

$$a(u,v) + \gamma s(u,v) = \lambda(u,v), \quad v \in H_I^1. \tag{6.11}$$

Our aim is to study the regularity of the solutions of this eigenvalue problem in Hilbert spaces of mixed derivatives. Conditions on the parameter γ enter only implicitly since, with u a solution of (6.11) and with that also of equation (6.12) below, $\widetilde{u} = \mathrm{e}^{-F}u$ is conversely a solution of the original eigenvalue equation (4.17) for which $\mathrm{e}^F\widetilde{u}$ is then a square integrable function. We assume $\gamma \geq 0$ in the sequel.

Theorem 6.2. *Provided that the function (6.1) is symmetric with respect to the permutations of the electrons with indices* $i \in I$*, which is the case if and only if all* θ_i *for* $i \in I$ *are equal, a function* $u \in H_I^1$ *that solves (6.11) also solves the full equation*

$$a(u,v) + \gamma s(u,v) = \lambda(u,v), \quad v \in H^1. \tag{6.12}$$

That is, (6.11) does not only hold for test functions $v \in H_I^1$*, 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 (4.9) and the function (6.1) under these permutations. Let G denote the group of permutations that fix the indices in the complement of I and define the operator

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

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

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

a solution $u \in H_I^1$ of (6.11) satisfies the equation

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

for all $v \in H^1$, that is, solves the full equation (6.12). □

In the limit case $\gamma = 0$, the modified eigenvalue problem therefore transfers again into the original eigenvalue equation (4.17) from which our discussion started.

6.2 Spaces of Functions with High-Order Mixed Derivatives

We attempt to prove that the solutions of the equation (6.11) 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

$$\Delta_i = \sum_{k=1}^{3}\frac{\partial^2}{\partial x_{i,k}^2} \tag{6.13}$$

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

$$\mathscr{L} = (-1)^{|I|}\prod_{i\in I}\Delta_i \tag{6.14}$$

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

$$|u|_{I,0}^2 = (u,\mathscr{L}u), \quad |u|_{I,1}^2 = -(u,\Delta\mathscr{L}u). \tag{6.15}$$

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

$$\|u\|_{I,s}^2 = \|u\|_s^2 + |u|_{I,s}^2. \tag{6.16}$$

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

$$L_\alpha = \prod_{i\in I} \frac{\partial}{\partial x_{i,\alpha(i)}}, \quad \alpha \in I^*, \tag{6.17}$$

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

$$\mathscr{L} = (-1)^{|I|} \sum_{\alpha\in I^*} L_\alpha^2. \tag{6.18}$$

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

$$|\,u\,|_{I,0}^2 = \sum_{\alpha\in I^*} \|L_\alpha u\|_0^2, \quad |\,u\,|_{I,1}^2 = \sum_{\alpha\in I^*} |L_\alpha u|_1^2. \tag{6.19}$$

The completions of $\mathscr{D}_I$ under the norms given by (6.16) are the spaces X_I^s. They consist of functions that possess, for big $|I|$, very high order weak partial derivatives. We will show in that the solutions of the equation (6.11) are contained in X_I^1.

The structure of the proof of our regularity theorems is in the end very simple. Expressed naively, we transform the strong form

$$\widetilde{H}u := Hu + \gamma \sum_{i=1}^N \theta_i \left\{ \frac{x_i}{|x_i|} \cdot \nabla_i u + \frac{1}{|x_i|}\, u \right\} = \lambda u, \tag{6.20}$$

of the second-order equation (6.12) into the high-order equation

$$(\varepsilon I + \mathscr{L})\widetilde{H}u = \lambda(\varepsilon I + \mathscr{L})u \tag{6.21}$$

with correspondingly smooth solutions. As the operator $\varepsilon I + \mathscr{L}$ 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 operator $\widetilde{H}$. However, we can switch to the weak form

$$a(u, \varepsilon v + \mathscr{L}v) + \gamma s(u, \varepsilon v + \mathscr{L}v) = \lambda(u, \varepsilon v + \mathscr{L}v), \quad v \in \mathscr{D}_I, \tag{6.22}$$

of this equation, that is formally obtained from (6.21) if one multiplies both sides of the equation with a test function $v \in \mathscr{D}_I$, integrates, and then transforms the resulting integrals integrating by parts, or simply by replacing the test functions v in (6.12) by test functions $\varepsilon v + \mathscr{L}v$. The solutions of equation (6.12) obviously satisfy the equation (6.22). The idea is to interpret this equation as an equation on X_I^1 and to show that its solutions are conversely solutions of the original equation (6.12). Before we can realize this idea, we have, however, to show that the bilinear form

$$\widetilde{a}(u,v) = a(u, \varepsilon v + \mathscr{L}v) + \gamma s(u, \varepsilon v + \mathscr{L}v) \tag{6.23}$$

on $\mathscr{D}_I \times \mathscr{D}_I$ can be extended to a bounded bilinear form on $X_I^1 \times X_I^1$. This is trivial for its leading part. The problem is to estimate its singular low-order terms correspondingly. The next two sections exclusively deal with this task.

6.3 Estimates for the Low-Order Terms, Part 1

As stated, the key to our regularity theory is estimates for the low-order terms in the bilinear form (6.23), that is, for the terms involving the interaction potentials

$$V_{ne}(x) = -\sum_{i=1}^{N}\sum_{\nu=1}^{K} \frac{Z_\nu}{|x_i - a_\nu|}, \quad V_{ee}(x) = \frac{1}{2}\sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|x_i - x_j|} \tag{6.24}$$

between the nuclei and the electrons and between the electron among each other, and estimates for the part arising from the bilinear form (6.9). This bilinear form consists, like the nucleus-electron interaction potential, of a sum of one-electron terms. The terms involving only one single electron represent the simple part. The corresponding estimates are in the end based on the Hardy inequality from Lemma 4.1. They do not rely on symmetry properties of the wave functions. 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 (4.11) from Theorem 4.1, has already been stated in Chap. 4 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

$$(V_{ne}u, \mathscr{L}v), \;\; s(u, \mathscr{L}v), \;\; s(u,v). \tag{6.25}$$

in the bilinear form (6.23) respectively in (6.11). The crucial observation is that most of the partial derivatives of which the differential operator $\mathscr{L}$ is composed commute with the single parts of the interaction potentials (6.24) and can be shifted from one to the other side in the single parts of the bilinear form (6.9), up to those few that act on a component of the position vectors of the electrons under consideration.

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

$$(V_{ne}u, \mathscr{L}v) \leq 2N^{1/2} Z\,|u|_{I,0}\,|v|_{I,1}. \tag{6.26}$$

Proof. We first consider a single electron i and have then to distinguish the cases $i \notin I$ and $i \in I$. The first case is the easier one. We start from the representation (6.18) of $\mathscr{L}$. Since the partial derivatives of which the L_α are composed in this case do not act on the components of x_i, Fubini's theorem and integration by parts yield

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

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

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

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

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

follows. In more compact notion, this estimate reads

$$\int \frac{1}{|x_i - a_\nu|}\, u\mathscr{L}v\,\mathrm{d}x \;\leq\; 2\,|u|_{I,0}\,|\nabla_i v|_{I,0}. \tag{6.27}$$

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

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

where $I_i = I \setminus \{i\}$ and 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 I_i. Since the L_β do not act upon the components of x_i, integration by parts and Fubini's theorem lead as above to

$$\begin{aligned}\int \frac{1}{|x_i - a_\nu|}\, u\mathscr{L}v\,\mathrm{d}x \;&=\; (-1)^{|I|} \sum_{\beta\in I_i^*} \int \frac{1}{|x_i - a_\nu|} \left(\int u L_\beta \Delta_i L_\beta v\,\mathrm{d}\widetilde{x}\right) \mathrm{d}x_i \\ &= -\sum_{\beta\in I_i^*} \int \left(\int \frac{1}{|x_i - a_\nu|} L_\beta u\, \Delta_i L_\beta v\,\mathrm{d}x_i \right) \mathrm{d}\widetilde{x}.\end{aligned}$$

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

$$\left(\int |\nabla_i L_\beta u|^2\,\mathrm{d}x_i \right)^{1/2} \left(\int |\Delta_i L_\beta v|^2\,\mathrm{d}x_i \right)^{1/2}.$$

These expressions can be rewritten as

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

where we have applied the relation

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

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

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

summation over all β, the Cauchy-Schwarz inequality (applied twice, to the outer integrals and then to the sum over the β), and Fubini's theorem lead again to (6.27).

Summation over the single contributions in the potential finally yields

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

from which the proposition follows with the elementary estimate

$$\sum_{i=1}^{N}|\nabla_i v|_{I,0} \leq N^{1/2}\bigg(\sum_{i=1}^{N}|\nabla_i v|_{I,0}^2\bigg)^{1/2} = N^{1/2}\,|v|_{I,1},$$

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

The proof of the estimates for the expression $s(u,\mathscr{L}v)$ resembles that of Theorem 6.3. It is prepared by the following lemma for functions of three real variables.

Lemma 6.3. *For all infinitely differentiable functions $u, v : \mathbb{R}^3 \to \mathbb{R}$ that vanish outside a bounded subset of their domain,*

$$\int\Big\{\frac{x}{|x|}\cdot\nabla u + \frac{1}{|x|}\,u\Big\}v\,\mathrm{d}x \;\leq\; 3\,\Big(\int|u|^2\,\mathrm{d}x\Big)^{1/2}\Big(\int|\nabla v|^2\,\mathrm{d}x\Big)^{1/2}. \qquad (6.28)$$

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

$$\int\Big\{\frac{x}{|x|}\cdot\nabla u + \frac{1}{|x|}\,u\Big\}v\,\mathrm{d}x = -\int u\,\frac{x}{|x|}\cdot\nabla v\,\mathrm{d}x - \int\frac{1}{|x|}\,u\,v\,\mathrm{d}x.$$

This relation remains true for the general case, as one can show by an argument as in the proof of Lemma 4.1, that is, by multiplying u 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 6.4. *For all infinitely differentiable functions u and v in the space $\mathscr{D}$,*

$$s(u,\mathscr{L}v) \leq 3\,|u|_{I,0}\,|v|_{I,1}. \tag{6.29}$$

Proof. We consider again a single electron i and have, as in the proof of Theorem 6.3, to distinguish the cases $i \in I$ and $i \notin I$. For indices $i \in I$, one obtains

$$\begin{aligned}\int \left\{ \frac{x_i}{|x_i|}\cdot \nabla_i u + \frac{1}{|x_i|}\,u \right\} \mathscr{L}v \,\mathrm{d}x \\ = \sum_{\beta\in I_i^*} \iint \left\{ \frac{x_i}{|x_i|}\cdot \nabla_i L_\beta u + \frac{1}{|x_i|}\,L_\beta u \right\} \Delta_i L_\beta v \,\mathrm{d}x_i\,\mathrm{d}\widetilde{x}.\end{aligned}$$

With help of the Cauchy-Schwarz and the Hardy inequality the inner integrals on the right hand side can, up to the factor 3, be estimated by the expressions

$$\left(\int |\nabla_i L_\beta u|^2 \,\mathrm{d}x_i\right)^{1/2} \left(\int |\Delta_i L_\beta v|^2 \,\mathrm{d}x_i\right)^{1/2}.$$

Rewriting these expressions as in the proof of Theorem 6.3, from this the estimate

$$\int \left\{ \frac{x_i}{|x_i|}\cdot \nabla_i u + \frac{1}{|x_i|}\,u \right\} \mathscr{L}v \,\mathrm{d}x \,\leq\, 3\,|u|_{I,0}\,|\nabla_i v|_{I,0}$$

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

$$\begin{aligned}\int \left\{ \frac{x_i}{|x_i|}\cdot \nabla_i u + \frac{1}{|x_i|}\,u \right\} \mathscr{L}v \,\mathrm{d}x \\ = \sum_{\alpha\in I^*} \iint \left\{ \frac{x_i}{|x_i|}\cdot \nabla_i L_\alpha u + \frac{1}{|x_i|}\,L_\alpha u \right\} L_\alpha v \,\mathrm{d}x_i\,\mathrm{d}\widetilde{x}.\end{aligned}$$

The inner integrals are now, with Lemma 6.3, up to the factor 3 estimated as

$$\left(\int |L_\alpha u|^2 \,\mathrm{d}x_i\right)^{1/2} \left(\int |\nabla_i L_\alpha v|^2 \,\mathrm{d}x_i\right)^{1/2}.$$

From that then again the estimate above follows. Summation over the 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 (6.23) is completed by the following estimate for the expression $s(u,v)$ itself:

Theorem 6.5. *For all infinitely differentiable functions u and v in the space $\mathscr{D}$,*

$$s(u,v) \,\leq\, 3\,\|u\|_0\,|\,v\,|_1. \tag{6.30}$$

Proof. With help of Lemma 6.3, the single parts can again be estimated as

$$\int \left\{ \frac{x_i}{|x_i|} \cdot \nabla_i u + \frac{1}{|x_i|}\, u \right\} v \,\mathrm{d}x \,\leq\, 3\,\|u\|_0\,\|\nabla_i v\|_0.$$

The proposition follows from that in the way already employed. □

6.4 Estimates for the Low-Order Terms, Part 2

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 cases already studied only one derivative remained, in contrast to the two derivatives we have to face here. One of these derivatives has to be shifted to the other side. This causes an additional problem since the partial derivatives of the interaction potential entering into the estimates are not locally square integrable in three space dimensions. Therefore the Pauli principle has to be brought into play. A wave function 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 derivatives of the interaction potential and enables us to estimate the terms under consideration.

To master the most singular terms, the Hardy estimate from Lemma 4.1 has to be complemented by a second, closely related estimate for functions of three variables.

Lemma 6.4. *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,*

$$\int \frac{1}{|x|^4}\, v^2 \,\mathrm{d}x \leq 4 \int \frac{1}{|x|^2}\, |\nabla v|^2 \,\mathrm{d}x. \tag{6.31}$$

Proof. The estimate is proved in the same way as the Hardy inequality (4.8). 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 (6.31) 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 in this case there exists a constant K with

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

and can then complete the proof in the same way as that of (4.8) with help of the dominated convergence theorem, multiplying v with cut-off functions. □

It should be noted that the estimate (6.31) 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 are the components of these vectors. For abbreviation, let

$$\phi(x,y) = \frac{1}{|x-y|}. \tag{6.32}$$

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

$$\int \phi u \sum_{k,\ell=1}^{3} \frac{\partial^4 v}{\partial x_k^2 \partial y_\ell^2} \, \mathrm{d}(x,y) \tag{6.33}$$

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 (6.31) and the Hardy inequality (4.8) to the estimate for antisymmetric functions on which our argumentation is founded.

Lemma 6.5. *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,*

$$\int \frac{1}{|x-y|^4} u^2 \, \mathrm{d}(x,y) \leq 16 \sum_{k,\ell=1}^{3} \int \Big(\frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big)^2 \mathrm{d}(x,y). \tag{6.34}$$

Proof. Since such functions vanish where $y = x$, Lemma 6.4 yields

$$\int \Big(\int \frac{1}{|x-y|^4} u^2 \, \mathrm{d}y \Big) \mathrm{d}x \leq \int \Big(4 \sum_\ell \int \frac{1}{|x-y|^2} \Big(\frac{\partial u}{\partial y_\ell} \Big)^2 \mathrm{d}y \Big) \mathrm{d}x.$$

By the Hardy inequality from Lemma 4.1,

$$\int \Big(\int \frac{1}{|x-y|^2} \Big(\frac{\partial u}{\partial y_\ell} \Big)^2 \mathrm{d}x \Big) \mathrm{d}y \leq \int \Big(4 \sum_k \int \Big(\frac{\partial^2 u}{\partial x_k \partial y_\ell} \Big)^2 \mathrm{d}x \Big) \mathrm{d}y.$$

The proposition follows with Fubini's theorem. □

The counterparts to this estimate are the following variants

$$\int \frac{1}{|x-y|^2}\, v^2 \,\mathrm{d}(x,y) \,\leq\, 4 \sum_{k=1}^{3} \int \Big(\frac{\partial v}{\partial x_k}\Big)^2 \mathrm{d}(x,y), \tag{6.35}$$

$$\int \frac{1}{|x-y|^2}\, v^2 \,\mathrm{d}(x,y) \,\leq\, 4 \sum_{\ell=1}^{3} \int \Big(\frac{\partial v}{\partial y_\ell}\Big)^2 \mathrm{d}(x,y) \tag{6.36}$$

of the Hardy inequality (4.8) that, in contrast to (6.34), do not rely on the antisymmetry of the considered function. They are proved in the same way as (6.34). The argumentation in this section centers in the estimates (6.34), (6.35), and (6.36).

Now we can begin to estimate the integrals (6.33). In the first step we shift one of the partial derivatives from the function v to the function u.

Lemma 6.6. *Let u and v be infinitely differentiable functions in the variables x and y in $\mathbb{R}^3$ that have a compact support. Then, for all indices k and ℓ,*

$$\int \phi u \,\frac{\partial^4 v}{\partial x_k^2\, \partial y_\ell^2}\, \mathrm{d}(x,y) \,=\, -\int \frac{\partial}{\partial x_k}(\phi u)\, \frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\, \mathrm{d}(x,y). \tag{6.37}$$

Proof. The problem is the singularity of ϕ that does not allow to integrate by parts directly. Let $\varphi(r)$ thus be a 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

$$\phi_n(x,y) \,=\, n\,\varphi(n\,|x-y|), \quad n \in \mathbb{N}.$$

The ϕ_n are then itself continuously differentiable and coincide with the original function ϕ for all x and y of distance $|x-y| \geq 1/n$. Integration by parts leads to

$$\int \phi_n u \,\frac{\partial^4 v}{\partial x_k^2\, \partial y_\ell^2}\, \mathrm{d}(x,y) \,=\, -\int \frac{\partial}{\partial x_k}(\phi_n u)\, \frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\, \mathrm{d}(x,y).$$

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

$$\frac{\partial}{\partial x_k}(\phi_n u) \,=\, \frac{\partial \phi_n}{\partial x_k}\, u + \phi_n \,\frac{\partial u}{\partial x_k},$$

into two parts. We claim that there is a constant M, independent of n, such that

$$\Big|\,\frac{\partial}{\partial x_k}(\phi_n u)\Big| \,\leq\, \frac{M}{|x-y|^2}.$$

This is because, for the function ϕ_n itself and its first-order derivatives, the estimates

$$|\phi_n| \,\leq\, \frac{c}{|x-y|}, \quad \Big|\frac{\partial \phi_n}{\partial x_k}\Big| \leq \frac{c}{|x-y|^2},$$

hold, where c is independent of n. As u vanishes outside a bounded set, the integrands are thus uniformly bounded by an integrable function. Since the ϕ_n and their first-order partial derivatives converge to ϕ and its respective derivatives outside the diagonal $x = y$, a set of measure zero, the dominated convergence theorem yields

$$\lim_{n\to\infty} \int \frac{\partial}{\partial x_k}(\phi_n u)\,\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\,\mathrm{d}(x,y) = \int \frac{\partial}{\partial x_k}(\phi u)\,\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\,\mathrm{d}(x,y).$$

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

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

which then completes the proof of (6.37). □

The next estimate is the place where the antisymmetry crucially enters. It depends on the fact that the corresponding functions u vanish on the diagonal $x = y$.

Lemma 6.7. *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*

$$\sum_{k,\ell=1}^{3} \int \phi u\,\frac{\partial^4 v}{\partial x_k^2 \partial y_\ell^2}\,\mathrm{d}(x,y) \le C\left\{\sum_{k,\ell=1}^{3}\left\|\frac{\partial^2 u}{\partial x_k \partial y_\ell}\right\|_0^2\right\}^{1/2}\left\{\sum_{k,\ell=1}^{3}\left|\frac{\partial^2 v}{\partial x_k \partial y_\ell}\right|_1^2\right\}^{1/2}, \tag{6.38}$$

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

Proof. We first rewrite the expression to be estimated with help of (6.37) and obtain

$$-\sum_{k,\ell=1}^{3} \int \frac{1}{|x-y|}\,\frac{\partial u}{\partial x_k}\,\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\,\mathrm{d}(x,y) + \sum_{k,\ell=1}^{3} \int \frac{1}{|x-y|^2}\,\frac{x_k - y_k}{|x-y|}\,u\,\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\,\mathrm{d}(x,y).$$

The first double sum is estimated by the expression

$$\left(3\sum_{k=1}^{3} \int \frac{1}{|x-y|^2}\left(\frac{\partial u}{\partial x_k}\right)^2 \mathrm{d}(x,y)\right)^{1/2}\left(\sum_{k,\ell=1}^{3} \int \left(\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\right)^2 \mathrm{d}(x,y)\right)^{1/2}.$$

As u vanishes on the diagonal $x = y$, there is a constant K with

$$|u(x,y)| \le K\,|x-y|.$$

The second double sum is thus bounded by the therefore finite expression

$$\left(3\int \frac{1}{|x-y|^4}\,u^2\,\mathrm{d}(x,y)\right)^{1/2}\left(\sum_{k,\ell=1}^{3} \int \left(\frac{\partial^3 v}{\partial x_k \partial y_\ell^2}\right)^2 \mathrm{d}(x,y)\right)^{1/2}.$$

The estimates (6.36), applied to the partial derivatives of u, and (6.34) show that the estimate (6.38) holds with $C = 6\sqrt{3}$. Since the role of x and y can be exchanged, the constant can be improved to $C = 3\sqrt{6}$, combining the two resulting estimates. □

Correspondingly one proves the estimate

$$\sum_{k=1}^{3} \int \phi u \frac{\partial^2 v}{\partial x_k^2} \,\mathrm{d}(x,y) \leq 2 \left\{ \sum_{k=1}^{3} \left\| \frac{\partial u}{\partial x_k} \right\|_0^2 \right\}^{1/2} \left\{ \sum_{k=1}^{3} \left| \frac{\partial v}{\partial x_k} \right|_1^2 \right\}^{1/2} \tag{6.39}$$

applying (6.35) to u, and finally, with help of (6.35) and (6.36), the estimate

$$\int \phi u v \,\mathrm{d}(x,y) \leq \sqrt{2}\, \|u\|_0 |v|_1 \tag{6.40}$$

for all infinitely differentiable functions u and v that have a compact support, in these cases 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 and merge the building blocks (6.38) to (6.40) into the last missing estimate for the interaction potentials.

Theorem 6.6. *For all infinitely differentiable functions $u \in \mathscr{D}_I$ and $v \in \mathscr{D}$,*

$$(V_{ee}u, \mathscr{L}v) \leq CN^{3/2} |u|_{I,0} |v|_{I,1}, \tag{6.41}$$

where the constant $C \leq 3\sqrt{3}$ 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 $i \neq j$ and estimate the expression

$$\int \phi_{ij} u \mathscr{L} v \,\mathrm{d}x = (-1)^{|I|} \sum_{\alpha \in I^*} \int \phi_{ij} u L_\alpha^2 v \,\mathrm{d}x.$$

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 I, that only one of these indices belongs to I, and that none of these indices is contained in I.

The first case is the most critical one because of the singularities of the derivatives of the interaction potential and the dependence on the antisymmetry. It is therefore considered first. Let $I_{ij} = I \setminus \{i, j\} \neq \emptyset$ and let 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 I_{ij}. The set of the differential operators L_α, $\alpha \in I^*$, coincides then with the set of the operators

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

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

$$(-1)^{|I|}\sum_{\alpha\in I^*}\int \phi_{ij}uL_\alpha^2 v\,\mathrm{d}x \;=\; \sum_{\beta\in I_{ij}^*}\int\bigg(\sum_{k,l=1}^{3}\iint \phi_{ij}L_\beta u\,\frac{\partial^4 L_\beta v}{\partial x_{i,k}^2\partial x_{j,\ell}^2}\,\mathrm{d}x_i\mathrm{d}x_j\bigg)\,\mathrm{d}\widetilde{x},$$

where x is split into x_i, x_j, and the remaining components $\widetilde{x}$. Like u itself, its partial derivatives $L_\beta u$, $\beta\in I_{ij}^*$, 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 $e=Pe$ and $\widetilde{w}(x)=-w(x)$, 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 (6.38). In the same fashion as in the previous section, finally the estimate

$$(-1)^{|I|}\sum_{\alpha\in I^*}\int \phi_{ij}uL_\alpha^2 v\,\mathrm{d}x \le C\,|\,u\,|_{I,0}\Big\{\,|\nabla_i v|_{I,0}^2+|\nabla_j v|_{I,0}^2\,\Big\}^{1/2} \tag{6.42}$$

follows, where $C\le 3\sqrt{6}$ is the same constant as in (6.38). The case that I_{ij} is empty, that is, I consists only of the indices i and j, is treated in the same way.

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

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

and the integral to be estimated splits into the sum

$$(-1)^{|I|}\sum_{\alpha\in I^*}\int \phi_{ij}uL_\alpha^2 v\,\mathrm{d}x \;=\; -\sum_{\beta\in I_i^*}\int\bigg(\sum_{k=1}^{3}\iint \phi_{ij}L_\beta u\,\frac{\partial^2 L_\beta v}{\partial x_{i,k}^2}\,\mathrm{d}x_i\mathrm{d}x_j\bigg)\,\mathrm{d}\widetilde{x}.$$

The inner sum on the right hand side can be estimated with help of (6.39), which then finally again results in the estimate (6.42), where $C\le 2$ is now the constant from (6.39). The same estimate holds, of course, for the case that $i\notin I$ and $j\in I$.

If neither i nor j are contained in I, one simply starts from

$$(-1)^{|I|}\sum_{\alpha\in I^*}\int \phi_{ij}uL_\alpha^2 v\,\mathrm{d}x \;=\; \sum_{\alpha\in I^*}\int\bigg(\iint \phi_{ij}L_\alpha uL_\alpha v\,\mathrm{d}x_i\mathrm{d}x_j\bigg)\,\mathrm{d}\widetilde{x},$$

from which one obtains, with the help of (6.40), again the estimate (6.42), now with a constant $C \leq \sqrt{2}$. Independent of whether two, one, or none of the indices i and j is contained in I, the estimate (6.42) holds with a constant $C \leq 3\sqrt{6}$.

The proposition finally follows from the elementary estimate

$$\frac{1}{2}\sum_{i,j}\left(\eta_i^2+\eta_j^2\right)^{1/2} \leq \frac{1}{\sqrt{2}}N^{3/2}\Big(\sum_i \eta_i^2\Big)^{1/2}, \tag{6.43}$$

summing over all particle pairs. □

Again, the dependence of the bound on the problem parameters, here the number N of electrons, enters only in the very last step, through the estimate (6.43).

6.5 The Regularity of the Weighted Eigenfunctions

We are now in the position to prove that the solutions $u \in H_I^1$ of the modified eigenvalue equation (6.11) are located in the space X_I^1 from Sect. 6.2, the completion of the space $\mathscr{D}_I$ of the infinitely differentiable functions (4.3) with compact support that are antisymmetric under the exchange of arguments x_i and x_j in $\mathbb{R}^3$ for all indices $i \neq j$ in the given subset I of the set of indices $1,\ldots,N$ under a norm measuring high-order mixed derivatives. The key to our results is the estimates for the low-order terms, those discussed in the preceding two sections, that can be summarized as follows. For all functions u in $\mathscr{D}_I$ and v in $\mathscr{D}$, first the estimates

$$(Vu,\mathscr{L}v) \leq C\,\theta(N,Z)\,|\,u\,|_{I,0}\,|\,v\,|_{I,1}, \quad s(u,\mathscr{L}v) \leq 3\,|\,u\,|_{I,0}\,|\,v\,|_{I,1} \tag{6.44}$$

in terms of the seminorms (6.15) hold, where the first one for the term with the interaction potential (4.9) represents a combination of the estimates (6.26) from Theorem 6.3 and (6.41) from Theorem 6.6, and the second one is the estimate (6.29) from Theorem 6.4. The constant C is independent of the number N of electrons, of the considered index set 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 $C = 2+3\sqrt{3}$ for C. The quantity $\theta(N,Z)$ has been defined in (4.10) 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 (6.44) potentially involving very high-order derivatives are complemented by the estimates

$$(Vu,v) \leq 3\,\theta(N,Z)\,\|u\|_0\,|\,v\,|_1, \quad s(u,v) \leq 3\,\|u\|_0\,|\,v\,|_1 \tag{6.45}$$

from Theorem 4.1 and Theorem 6.5 for functions u and v in $\mathscr{D}$, that generally hold and do not rely on the given antisymmetry properties. The estimates show that the bilinear forms $(Vu, \mathscr{L}v)$ and $s(u, \mathscr{L}v)$ can be uniquely extended from $\mathscr{D}_I \times \mathscr{D}_I$ to bounded bilinear forms on $X_I^0 \times X_I^1$, and that particularly the bilinear form

$$\widetilde{a}(u,v) = a(u, \varepsilon v + \mathscr{L}v) + \gamma s(u, \varepsilon v + \mathscr{L}v) \tag{6.46}$$

from Sect. 6.2 can be uniquely extended from $\mathscr{D}_I$ to a bounded bilinear form on X_I^1. For the ease of presentation, we will keep the notation $(Vu, \mathscr{L}v)$ and $s(u, \mathscr{L}v)$ for arguments $u \in X_I^0$ and $v \in X_I^1$ 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 from Chap. 2 the definition of the space $\mathscr{S}$ of the rapidly decreasing functions. As with $\mathscr{D}_I$, let $\mathscr{S}_I$ denotes the space of the rapidly decreasing functions of corresponding antisymmetry. The seminorms (6.15) of a rapidly decreasing function read in terms of its Fourier transform

$$|u|_{I,s}^2 = \int \left(\sum_{i=1}^N |\omega_i|^2 \right)^s \left(\prod_{i \in I} |\omega_i|^2 \right) |\widehat{u}(\omega)|^2 \,\mathrm{d}\omega. \tag{6.47}$$

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

$$|u|_s^2 = \int \left(\sum_{i=1}^N |\omega_i|^2 \right)^s |\widehat{u}(\omega)|^2 \,\mathrm{d}\omega. \tag{6.48}$$

We call a rapidly decreasing function a rapidly decreasing high-frequency function if its Fourier transform vanishes on a ball of radius Ω, to be fixed later, around the origin of the frequency space. The closures of the corresponding space

$$\mathscr{S}_{I,H} = \{ v \in \mathscr{S}_I \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \leq \Omega \} \tag{6.49}$$

of rapidly decreasing functions with the given symmetry properties in H_I^1 and X_I^1, respectively, are the Hilbert spaces $H_{I,H}^1$ and $X_{I,H}^1$. The closures of the space

$$\mathscr{S}_{I,L} = \{ v \in \mathscr{S}_I \mid \widehat{v}(\omega) = 0 \text{ for } |\omega| \geq \Omega \} \tag{6.50}$$

in H_I^1 and X_I^1 are the spaces $H_{I,L}^1$ and $X_{I,L}^1$, respectively, of low-frequency functions. The low-frequency and the high-frequency functions decompose the spaces

$$H_I^1 = H_{I,L}^1 \oplus H_{I,H}^1, \quad X_I^1 = X_{I,L}^1 \oplus X_{I,H}^1 \tag{6.51}$$

into orthogonal parts. By the Fourier representation (6.47) and (6.48) of the norms,

$$|u_L|_{I,s} \leq \Omega^s \left(\frac{\Omega}{\sqrt{|I|}} \right)^{|I|} \|u_L\|_0 \tag{6.52}$$

for the low-frequency functions $u_L \in \mathscr{S}_{I,L}$. The space $H^1_{I,L}$ and its subspace $X^1_{I,L}$ therefore coincide. The relation (6.52) transfers to all functions in these spaces. In fact, the functions in $H^1_{I,L}$ are infinitely differentiable and all their derivatives are square integrable. Fourier analysis also shows that

$$\|u_H\|_0 \leq \Omega^{-1}|u_H|_1, \quad |u_H|_{I,0} \leq \Omega^{-1}|u_H|_{I,1} \tag{6.53}$$

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

$$|u_L|_1 \leq \Omega\,\|u_L\|_0, \quad |u_L|_{I,1} \leq \Omega\,|u_L|_{I,0}. \tag{6.54}$$

The central observation, on which the proof of the regularity theorems is based, is that the low-order terms in the bilinear form in the second-order equation (6.11), as well as in the high-order bilinear form (6.23), behave like small perturbations on the corresponding spaces of high-frequency functions. The reason is that the norms of such functions themselves and that of their derivatives as well can be estimated by the norms of derivatives of higher order. By (6.44) and (6.53),

$$(Vu_H, \mathscr{L}v_H) \leq C\,\theta(N,Z)\,\Omega^{-1}|u_H|_{I,1}\,|v_H|_{I,1}, \tag{6.55}$$

$$s(u_H, \mathscr{L}v_H) \leq 3\,\Omega^{-1}|u_H|_{I,1}\,|v_H|_{I,1} \tag{6.56}$$

for all $u_H, v_H \in \mathscr{S}_{I,H}$. Correspondingly, by (6.45) and (6.53), for these u_H and v_H

$$(Vu_H, v_H) \leq 3\,\theta(N,Z)\,\Omega^{-1}|u_H|_1\,|v_H|_1, \tag{6.57}$$

$$s(u_H, v_H) \leq 3\,\Omega^{-1}|u_H|_1\,|v_H|_1. \tag{6.58}$$

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 large enough. If we assume $C \geq 3$ and choose

$$\Omega \;\geq\; 4C\,\theta(N,Z) + 12\,\gamma, \tag{6.59}$$

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

$$a(u_H,u_H) + \gamma s(u_H,u_H) \;\geq\; \frac{1}{4}\,|u_H|_1^2 \tag{6.60}$$

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

$$\widetilde{a}(u_H,u_H) \;\geq\; \frac{1}{4}\left(\varepsilon\,|u_H|_1^2 + |u_H|_{I,1}^2\right). \tag{6.61}$$

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

$$\widetilde{b}(\varphi,v) = (V\varphi,\varepsilon v+\mathscr{L}v)+\gamma s(\varphi,\varepsilon v+\mathscr{L}v), \tag{6.62}$$

$$b(\varphi,\chi) = (V\varphi,\chi)+\gamma s(\varphi,\chi) \tag{6.63}$$

on $X_I^0 \times X_I^1$ and $L_2 \times H^1$, respectively. They satisfy, for Ω as in (6.59), the estimates

$$\widetilde{b}(\varphi,v) \leq \frac{1}{4}\Omega\left(\varepsilon\,\|\varphi\|_0^2+|\,\varphi\,|_{I,0}^2\right)^{1/2}\left(\varepsilon\,|\,v\,|_1^2+|\,v\,|_{I,1}^2\right)^{1/2}, \tag{6.64}$$

$$b(\varphi,\chi) \leq \frac{1}{4}\Omega\,\|\varphi\|_0\,|\,\chi\,|_1 \tag{6.65}$$

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 (6.11)

$$a(u,\chi)+\gamma s(u,\chi) = \lambda(u,\chi), \quad \chi \in H_I^1, \tag{6.66}$$

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 6.8. *Let $u = u_L + u_H$ be the decomposition of a solution $u \in H_I^1$ of the equation (6.11), (6.66) into its low-frequency and its high-frequency part. Then*

$$a(u_H,\chi_H)+\gamma s(u_H,\chi_H)-\lambda(u_H,\chi_H) = -b(u_L,\chi_H), \quad \chi_H \in H_{I,H}^1. \tag{6.67}$$

We will keep the low-frequency part u_L fixed for a while and will consider (6.67) as an equation for the high-frequency part u_H. We will show that such equations are uniquely solvable for frequency bounds (6.59) and that the regularity of the right hand side transfers to the regularity of the solution.

Lemma 6.9. *For frequency bounds Ω as in (6.59), the equation*

$$a(u_H,\chi_H)+\gamma s(u_H,\chi_H)+\mu(u_H,\chi_H) = b(\varphi,\chi_H), \quad \chi_H \in H_{I,H}^1, \tag{6.68}$$

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

$$\|u_H\|_0 \leq \|\varphi\|_0, \quad |u_H|_1 \leq \Omega\,\|\varphi\|_0. \tag{6.69}$$

Proof. As $\mu \geq 0$, the additional term does not alter the coercivity (6.60) of the bilinear form on the left hand side of the equation (6.68). 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 (6.60) and (6.65) inserting

$\chi_H = u_H$. The L_2-norm of the solution can be estimated by its H^1-seminorm utilizing the property (6.53) of high-frequency functions. □

A corresponding result holds for the high-order counterpart of the equation (6.68), that formally results from this equation replacing the test function χ_H by test functions $\varepsilon v_H + \mathscr{L} v_H$, with all the care that has to be taken with this type of arguments.

Lemma 6.10. *For frequency bounds Ω as in (6.59), the equation*

$$\widetilde{a}(u_H, v_H) + \mu(u_H, \varepsilon v_H + \mathscr{L} v_H) = \widetilde{b}(\varphi, v_H), \quad v_H \in X^1_{I,H}, \tag{6.70}$$

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

$$|u_H|_{I,1} \leq \Omega \left(\varepsilon \|\varphi\|_0^2 + |\varphi|_{I,0}^2\right)^{1/2}. \tag{6.71}$$

Proof. As $\mu \geq 0$ and $(u, \varepsilon u + \mathscr{L} u) \geq 0$ for $u \in X_I^1$, the proposition again follows from the coercivity (6.61) of the bilinear form $\widetilde{a}(u_H, v_H)$, from the bound (6.64) 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 (6.68) and (6.70) coincide for $\varphi \in X_I^0$. For that we need the following, at first sight seemingly obvious lemma:

Lemma 6.11. *The solution $u_H \in X^1_{I,H}$ of the equation (6.70) satisfies the equation (6.68) for all rapidly decreasing functions $\chi_H \in \mathscr{S}_{I,H}$ of the particular form*

$$\chi_H = \varepsilon v_H + \mathscr{L} v_H, \quad v_H \in \mathscr{S}_{I,H}. \tag{6.72}$$

Proof. It suffices to show that the representation (6.46) holds not only for functions u and v in $\mathscr{D}_I$ but for all functions $u \in X_I^1$ and $v \in \mathscr{S}_I$, and to prove a corresponding relation for the bilinear form (6.62), that, in a strict sense, is defined by (6.62) only for functions φ and v in $\mathscr{D}_I$ and then continuously extended to $X_I^0 \times X_I^1$. We begin with the case that $u \in \mathscr{D}_I$ and approximate $v \in \mathscr{S}_I$ by the functions

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

in $\mathscr{D}_I$, where ϕ is an infinitely differentiable, rotationally symmetric function with values $\phi(x) = 1$ for $|x| \leq 1$ and $\phi(x) = 0$ for $|x| \geq 2$. For sufficiently large R, v_R and v coincide on the support of u. As v_R tends to v in the X_I^1-norm, by the definition (6.46) of the bilinear form $\widetilde{a}(u, v)$ for functions in $\mathscr{D}_I$

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

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

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

for all $\varphi \in X_I^0$ and $v \in \mathscr{S}_I$, from which the proposition then follows. □

The argument that closes the gap between the equations (6.68) and (6.70) is the observation that every function in $\chi_H \in \mathscr{S}_{I,H}$ can be represented in the form (6.72). The proof requires that the parameter ε is strictly positive and breaks down for $\varepsilon = 0$.

Lemma 6.12. *For all rapidly decreasing high-frequency functions $\chi_H \in \mathscr{S}_{I,H}$ there is a rapidly decreasing high-frequency function $v_H \in \mathscr{S}_{I,H}$ that solves the equation*

$$\varepsilon v_H + \mathscr{L} v_H = \chi_H. \tag{6.73}$$

Proof. The antisymmetry of a function with respect to the given permutations transfers to its Fourier transform and vice versa. The function $v_H \in \mathscr{S}_{I,H}$ 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 (6.70) therefore satisfies the equation (6.68) for all $\chi_H \in \mathscr{S}_{I,H}$ and, as $\mathscr{S}_{I,H}$ is dense in $H^1_{I,H}$, for all $\chi_H \in H^1_{I,H}$. Since the equation (6.68) possesses only one solution, the solutions of both equations coincide for φ in X_I^0 given. Since $\varepsilon > 0$ was arbitrary, this observation and (6.53) prove:

Lemma 6.13. *If the bound Ω separating the high from the low frequencies is chosen according to (6.59) and $\varphi \in X_I^0$, the solution $u_H \in H^1_{I,H}$ of the equation (6.68) is contained in the space $X^1_{I,H}$ and satisfies the estimates*

$$|u_H|_{I,0} \leq |\,\varphi\,|_{I,0}, \quad |u_H|_{I,1} \leq \Omega\,|\,\varphi\,|_{I,0}. \tag{6.74}$$

Since the low-frequency part u_L of the solution u of the equation (6.11), (6.66) is contained in X_I^0 and even in X_I^1, we can apply the result just proved to the equation (6.67), from which it follows that also the high-frequency part u_H of u and with that u itself are contained in X_I^1. The quantitative version of this result reads:

Theorem 6.7. *The solutions $u \in H_I^1$ of the modified eigenvalue problem (6.11) for negative λ are contained in X_I^1. For frequency bounds (6.59), their seminorms (6.15), (6.19) can be estimated as follows in terms of their low-frequency parts:*

$$|\,u\,|_{I,0} \leq \sqrt{2}\,|u_L|_{I,0}, \quad |\,u\,|_{I,1} \leq \sqrt{2}\,\Omega\,|u_L|_{I,0}. \tag{6.75}$$

Proof. By Lemma 6.13, the high frequency parts u_H of these u satisfy the estimates

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

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 into the two parts u_L and u_H and the inverse estimate in (6.54). □

The estimates (6.75) for the mixed derivatives of the solutions have a counterpart for the solutions themselves that follows in the same way directly from Lemma 6.9.

Theorem 6.8. *Under the same assumptions as in Theorem 6.7, the solutions of the modified eigenvalue problem (6.11) satisfy the two estimates*

$$\|u\|_0 \leq \sqrt{2}\, \|u_L\|_0, \quad |\, u\,|_1 \leq \sqrt{2}\,\Omega\, \|u_L\|_0. \tag{6.76}$$

A solution $u \in H^1_I$ of the equation (6.11), (6.66) is trivially contained in $H^1_{I'}$ for all nonempty subsets I' of I. As $s(u,v)$ is obviously invariant under the exchange of all electrons i in the subset I' of I, Theorem 6.2 ensures that u solves the equations

$$a(u,\chi) + \gamma s(u,\chi) \,=\, \lambda\,(u,\chi), \quad \chi \in H^1_{I'}, \tag{6.77}$$

on all of these spaces $H^1_{I'}$ and thus satisfies, by Theorem 6.7, the estimates

$$|\, u\,|_{I',0} \leq \sqrt{2}\, |u_L|_{I',0}, \quad |\, u\,|_{I',1} \leq \sqrt{2}\,\Omega\, |u_L|_{I',0} \tag{6.78}$$

for all nonempty subsets I' of the given index set I. Therefore the norms given by

$$|||u|||^2_{I,1} \,=\, \int \bigg(\sum_{i=1}^{N} \left|\frac{\omega_i}{\Omega}\right|^2 \bigg) \prod_{i \in I} \bigg(1 + \left|\frac{\omega_i}{\Omega}\right|^2 \bigg)\, |\widehat{u}(\omega)|^2\, \mathrm{d}\omega, \tag{6.79}$$

$$|||u|||^2_{I,0} \,=\, \int \prod_{i \in I} \bigg(1 + \left|\frac{\omega_i}{\Omega}\right|^2 \bigg)\, |\widehat{u}(\omega)|^2\, \mathrm{d}\omega. \tag{6.80}$$

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. 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 (6.11):

Theorem 6.9. *The solutions $u \in H^1_I$ of the modified eigenvalue problem (6.11) for negative values λ satisfy, for frequency bounds (6.59), the estimates*

$$|||u|||_{I,0} \,\leq\, \sqrt{2\mathrm{e}}\, \|u\|_0, \quad |||u|||_{I,1} \,\leq\, \sqrt{2\mathrm{e}}\, \|u\|_0. \tag{6.81}$$

Proof. By the estimates (6.76) for the L_2-norm of the solution itself, respectively the estimates (6.78) for the L_2-norms of its corresponding mixed derivatives,

$$\int \prod_{i\in I'} \left|\frac{\omega_i}{\Omega}\right|^2 |\widehat{u}(\omega)|^2 \,\mathrm{d}\omega \;\leq\; 2\int_{|\omega|\leq\Omega} \prod_{i\in I'} \left|\frac{\omega_i}{\Omega}\right|^2 |\widehat{u}(\omega)|^2 \,\mathrm{d}\omega \tag{6.82}$$

for all subsets I' of I, where the empty product is by definition 1. As

$$\sum_{I'\subseteq I} \prod_{i\in I'} \left|\frac{\omega_i}{\Omega}\right|^2 = \prod_{i\in I} \left(1+\left|\frac{\omega_i}{\Omega}\right|^2\right), \tag{6.83}$$

one obtains from (6.82) first the estimate

$$|||u|||_{I,0}^2 \;\leq\; 2\int_{|\omega|\leq\Omega} \prod_{i\in I} \left(1+\left|\frac{\omega_i}{\Omega}\right|^2\right) |\widehat{u}(\omega)|^2 \,\mathrm{d}\omega. \tag{6.84}$$

The product on the right hand side of (6.83) is, because of

$$\prod_{i\in I} \left(1+\left|\frac{\omega_i}{\Omega}\right|^2\right) \leq \exp\left(\sum_{i\in I}\left|\frac{\omega_i}{\Omega}\right|^2\right), \tag{6.85}$$

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. The second is treated in the same way. □

Theorem 6.9 particularly states that the solutions u of the electronic Schrödinger equation (4.30) itself possess high-order mixed derivatives. Only small portions of the frequency domain substantially contribute to the wave functions. This remark can be quantified with help of the notion of hyperbolic crosses, hyperboloid-like regions in the frequency or momentum-space that consist of those ω for which

$$\prod_{i\in I_-} \left(1+\left|\frac{\omega_i}{\Omega}\right|^2\right) + \prod_{i\in I_+} \left(1+\left|\frac{\omega_i}{\Omega}\right|^2\right) \;\leq\; \frac{1}{\varepsilon^2}, \tag{6.86}$$

where $\varepsilon > 0$ is a control parameter that determines their size, and I_- and I_+ are again the sets of the indices i of the electrons with spin $\sigma_i = -1/2$ and $\sigma_i = +1/2$ respectively. If u_ε denotes that part of the wave function whose Fourier transform coincides with that of u on this domain and vanishes outside of it, the H^1-error

$$\|u - u_\varepsilon\|_1 = \mathscr{O}(\varepsilon) \tag{6.87}$$

tends to zero like $\mathscr{O}(\varepsilon)$ with increasing size of the crosses. This observation might 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 [93]. The solutions of the electronic Schrödinger equation in some sense behave like products

$$u(x) = \prod_{i=1}^{N} \phi_i(x_i) \tag{6.88}$$

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.

It is remarkable that Theorem 6.9 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. The estimate (4.11) from Theorem 4.1 implies the lower bound $\lambda \geq -9\theta^2/2$ for the eigenvalues. As $\Sigma(\sigma) \leq 0$, this results in the upper bound

$$\gamma < \sqrt{2\,(\Sigma(\sigma) - \lambda)} \leq 3\theta(N,Z) \tag{6.89}$$

for the decay rates γ considered in Sect. 6.1. Theorem 6.9 tells us therefore that the estimates (6.81) hold at least for the scaling parameters

$$\Omega \geq (4C+36)\sqrt{N}\max(N,Z), \tag{6.90}$$

independent of the considered eigenvalue below the ionization threshold, and in particular for the Ω that is equal to the right hand side. There is conversely a minimum

$$\Omega \leq (4C+36)\sqrt{N}\max(N,Z) \tag{6.91}$$

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.

6.6 Atoms as Model Systems

The scaling parameter Ω limits the local variation of the wave functions quantitatively. It can be assumed that the right hand side of (6.91) 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

$$H = \sum_{i=1}^{N} \left\{ -\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right\} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|x_i - x_j|}. \tag{6.92}$$

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

$$V(\vartheta x) = \vartheta^{-1} V(x) \tag{6.93}$$

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 [86] in terms of weak solutions of the eigenvalue problem.

Theorem 6.10. *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 (6.92) are linked via the relation*

$$|u|_1^2 = -2\lambda \|u\|_0^2. \tag{6.94}$$

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

$$\int \nabla u_\vartheta \cdot \nabla v \,\mathrm{d}x = 2\vartheta^2 \lambda \int u_\vartheta v \,\mathrm{d}x - 2\vartheta^2 \int V(\vartheta x)\, u_\vartheta v \,\mathrm{d}x$$

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

$$\int \nabla u_\vartheta \cdot \nabla v \,\mathrm{d}x = 2\vartheta^2 \lambda \int u_\vartheta v \,\mathrm{d}x - 2\vartheta \int V u_\vartheta v \,\mathrm{d}x.$$

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

$$\int \nabla u \cdot \nabla v \,\mathrm{d}x = 2\lambda \int uv \,\mathrm{d}x - 2 \int V u v \,\mathrm{d}x.$$

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

$$(\vartheta + 1)\lambda \int u u_\vartheta \,\mathrm{d}x = \int V u u_\vartheta \,\mathrm{d}x.$$

For all square integrable functions u and v

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

as can be shown approximating u by continuous functions with bounded support. Since for $u \in H^1$ the product Vu is square integrable, too, this yields

$$2\lambda \int u^2 \,\mathrm{d}x = \int V u u \,\mathrm{d}x.$$

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 6.11. *If the estimates from Theorem 6.9 hold for the eigenfunction u in $H^1(\sigma)$ for the eigenvalue λ of the atomic Hamilton operator (6.92), necessarily*

$$\Omega \geq \sqrt{\frac{|\lambda|}{\mathrm{e}}}. \tag{6.95}$$

Proof. From the virial theorem, from the Fourier representation (6.48) of the H^1-seminorm and of the norm given by (6.79), and from Theorem 6.9 one gets

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

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

Since the ionization threshold $\Sigma(\sigma)$ is less than or equal to zero by Theorem 5.16, the upper estimate resulting from Theorem 6.9 and the lower estimate just derived resulting from the virial theorem lead to the bounds

$$\sqrt{|\Lambda(\sigma)|} \lesssim \Omega \lesssim \sqrt{N}\max(N,Z) + \sqrt{|\Lambda(\sigma)|} \tag{6.96}$$

for the optimum Ω that is independent of the considered eigenvalues $\lambda < \Sigma(\sigma)$. The second term on the right hand side of (6.96) that comes from the additional part (6.9) in the equation (6.8) for the exponentially weighted eigenfunctions will therefore never dominate the asymptotic behavior of the optimum Ω in N and Z.

The problem thus reduces to the question of how well the bound (6.91) reflects the growth of the optimum scaling parameter Ω in N and Z for unweighted eigenfunctions, in which case the second term on the right hand side of (6.91) can be omitted. To answer this question at least partially, we consider the operator

$$H = \sum_{i=1}^{N} \left\{ -\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right\} \tag{6.97}$$

in which the electron-electron interaction is completely neglected and to which Theorem 6.11 can be literally transferred. Due to the absence of the electron-electron interaction potential, the estimates (6.81) hold then regardless of any symmetry property. The eigenfunctions of this operator are linear combinations of the products

$$u(x) = \prod_{i=1}^{N} \phi_i(x_i) \tag{6.98}$$

of hydrogen-like wave functions, solutions of the Schrödinger equation

$$-\frac{1}{2}\Delta\phi - \frac{Z}{|x|}\phi = \lambda\phi \tag{6.99}$$

for a single electron in the field of a nucleus of charge Z. The hydrogen-like wave functions are explicitly known and are calculated in almost every textbook on quantum mechanics; see Chap. 9 for details. The corresponding eigenvalues

$$\lambda = -\frac{Z^2}{2n^2}, \quad n = 1, 2, \ldots, \tag{6.100}$$

are highly degenerate. 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 ignore the Pauli principle, every product (6.98) becomes an admissible eigenfunction. The ground state energy of the corresponding system is then N times the minimum eigenvalue (6.100), i.e., $\lambda = -NZ^2/2$, from which the lower bound

$$\Omega \gtrsim N^{1/2} Z \tag{6.101}$$

follows, which behaves like the upper bound (6.91) 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 (6.91) nor the lower bound (6.95) 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 (6.98) 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 as the product otherwise vanishes under the corresponding antisymmetrization. That increases the ground state energy and correspondingly decreases the lower bound for the scaling parameter. 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

$$\Omega \gtrsim N^{1/6} Z. \tag{6.102}$$

There remains some gap between this lower bound and the upper bound (6.91), 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 (6.91) for systems like the ones considered here.

In fact, the observed behavior is not restricted to the model Hamiltonian (6.97). Lieb and Simon [61] proved that the minimum eigenvalue of the full operator (6.92) grows like $\gtrsim Z^{7/3}$ with the nuclear charge Z in the case $Z = N$, i.e., of neutral systems, which confirms the lower estimate (6.102). A more detailed study [94] of the product eigenfunctions (6.98) 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.

6.7 The Exponential Decay of the Mixed Derivatives

In Sect. 6.5 we have proven that the eigenfunctions themselves as well as the correspondingly exponentially weighted eigenfunctions possess square integrable high-order mixed weak derivatives. In this short concluding section it is shown that the exponentially weighted mixed derivatives of the eigenfunctions are square integrable. This follows essentially from the fact that the corresponding partial derivatives of the exponential weight factors can be estimated by these factors themselves:

Theorem 6.12. *Let $D^\nu u = L_\alpha u$, L_α as in (6.17), be one of the weak partial derivatives of the eigenfunction u whose existence and square integrability follows from the results of Sect. 6.5, and let e^F be one of the associated weight factors for which $D^\nu(\mathrm{e}^F u)$ has been shown to be square integrable too. The weighted derivatives*

$$\mathrm{e}^F D^\nu u, \quad \mathrm{e}^F \frac{\partial}{\partial x_{i,k}} D^\nu u \tag{6.103}$$

are then square integrable as well.

Proof. The proof is based on the representation

$$D^\nu(\mathrm{e}^F u) \,=\, \sum_{\mu \leq \nu} \mathrm{e}^F F_\mu D^{\nu-\mu} u$$

of the corresponding weak derivatives of $\mathrm{e}^F u$, that is a generalization of the product rule from Lemma 6.1 and can be derived from it taking into account the special structure of the multi-indices ν considered. The coefficient functions are products

$$F_\mu(x) \,=\, \gamma^{|\mu|} \prod_i \theta_i \frac{x_{i,\alpha(i)}}{|x_i|}$$

that run over the components upon which D^μ acts. This representation allows us to express $\mathrm{e}^F D^\nu u$ in terms of $D^\nu(\mathrm{e}^F u)$ and the weighted lower order derivatives $\mathrm{e}^F D^{\nu-\mu} u$ of u. Since the F_μ are uniformly bounded, the square integrability of $\mathrm{e}^F D^\nu u$ 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 F_μ one needs again the Hardy inequality. □

The exponential functions $x \to \exp(F(x))$ dominate every polynomial, regardless the decay rate γ determined by the gap between the considered eigenvalue λ and the ionization threshold. This results in the following corollary of Theorem 6.12:

Theorem 6.13. *Let $D^\nu u = L_\alpha u$, L_α as in (6.17), be one of the weak partial derivatives of the eigenfunction u whose existence and square integrability follows from the results of Sect. 6.5, and let P be an arbitrary polynomial. Then*

$$P D^\nu u,\ P \frac{\partial}{\partial x_{i,k}} D^\nu u \ \in\ L_2. \tag{6.104}$$

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