# Chapter 4
# The Electronic Schrödinger Equation

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

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|x_i - x_j|} \tag{4.1}$$

written down here in dimensionless form or atomic units. It acts on functions with arguments $x_1, \ldots, x_N \in \mathbb{R}^3$, which are associated with the positions of the considered electrons. The $a_1, \ldots, a_K \in \mathbb{R}^3$ are the fixed positions of the nuclei and the positive values $Z_\nu$ the charges of the nuclei in multiples of the electron charge.

Like the Hamilton operator for a system of electrons moving in the potential of a harmonic oscillator, the Hamilton operator (4.1) is derived via the correspondence principle from its counterpart in classical physics, the Hamilton function or total energy of a system of point-like particles in a potential field. It is again composed of two parts, a first part representing the kinetic energy of the electrons, built up from the Laplacians $\Delta_i$ acting upon their position vectors $x_i$, and the potential part

$$V = -\sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|x_i - x_j|} \tag{4.2}$$

describing the interaction of the electrons among each other and with the nuclei. The difficulty is not only that these potentials are singular but that the electrons are coupled to each other so that the eigenfunctions are no longer products or linear combinations of products of three-dimensional one-electron eigenfunctions.

H. Yserentant, *Regularity and Approximability of Electronic Wave Functions*,
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The transition from the full, time-dependent Schrödinger equation taking also into account the motion of the nuclei to the electronic Schrödinger equation is a mathematically very subtle problem that is not addressed here; we refer to [78] and the literature cited therein. The present book is concerned with the study of the analytical properties of the eigenfunctions of the operator (4.1) with the aim to find points of attack to approximate them efficiently. This chapter is devoted to the precise mathematical formulation of the electronic Schrödinger equation. Our approach is based on the weak formulation of the problem outlined in Sect. 3.5.

## 4.1 The Hardy Inequality and the Interaction Energy

We first neglect the spin-dependence of the wave functions that will then be taken into account in the next section. Since the eigenvalues of a self-adjoint operator are always real, the electronic Schrödinger equation splits into two separate equations of the same form for the real and the imaginary part of the wave functions. We can therefore restrict ourselves in the sequel to real-valued wave functions

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : (x_1, \ldots, x_N) \to u(x_1, \ldots, x_N), \tag{4.3}$$

which, of course, need to be square integrable. Their $L_2$-norm given by

$$\|u\|_0^2 = \int |u(x)|^2 \, \mathrm{d}x \tag{4.4}$$

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

$$-\frac{1}{2} \sum_{i=1}^{N} \int u \Delta_i u \, \mathrm{d}x = \frac{1}{2} \sum_{i=1}^{N} \int |\nabla_i u|^2 \, \mathrm{d}x, \tag{4.5}$$

provided that it exists, the expectation value of the kinetic energy. That is, wave functions must possess first-order weak derivatives and the $H^1$-seminorm given by

$$|u|_1^2 = \int |(\nabla u)(x)|^2 \, \mathrm{d}x \tag{4.6}$$

must remain finite. The solution space of the eigenvalue problem must be a subspace of the Hilbert space $H^1(\mathbb{R}^{3N})$ or briefly $H^1$, the space that consists of the square integrable functions (4.3) with square integrable first-order weak partial derivatives and that is equipped with the $H^1$-norm given by the expression

$$\|u\|_1^2 = \|u\|_0^2 + |u|_1^2. \tag{4.7}$$

In Sect. 2.1 we introduced the space $\mathscr{D}$ of the infinitely differentiable functions with compact support. From Sect. 2.3 we know that the functions in $\mathscr{D}$ form a dense subset of $H^1$ and $H^1$ can thus be considered as completion of $\mathscr{D}$ under the norm (4.7).

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

**Lemma 4.1.** *For all infinitely differentiable functions $v$ in the variable $x \in \mathbb{R}^3$ that have a compact support,*

$$\int \frac{1}{|x|^2}\, v^2 \,\mathrm{d}x \le 4 \int |\nabla v|^2 \,\mathrm{d}x\,. \tag{4.8}$$

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

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

integration by parts then yields

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

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

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

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

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

or, using $|\nabla d| = 1$, the estimate (4.8) for functions $v$ vanishing near the origin. To complete the proof, let $\omega : \mathbb{R}^3 \to [0,1]$ be an infinitely differentiable cut-off function with $\omega(x) = 0$ for $|x| \le 1/2$ and with $\omega(x) = 1$ for $|x| \ge 1$. Set

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

The estimate (4.8) then holds for the functions $v_k$ as just proved. Using

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

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

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

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

The Hardy inequality (4.8) first serves to estimate terms involving the potential

$$V(x) = -\sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|x_i - x_j|} \tag{4.9}$$

in the Hamilton operator (4.1) that is composed of the nucleus-electron interaction potential, the first term in (4.9), and the electron-electron interaction potential. Let $Z$ denote the total charge of the nuclei, the sum of the charges $Z_\nu$, and set

$$\theta(N,Z) = \sqrt{N}\max(N,Z). \tag{4.10}$$

A simple calculation on the basis of the Hardy inequality (4.8), Fubini's theorem, and the Cauchy-Schwarz inequality then yields our first important estimate:

**Theorem 4.1.** *The functions $u$ and $v$ in $\mathscr{D}$ satisfy the estimate*

$$\int Vuv\,\mathrm{d}x \le 3\theta(N,Z)\,\|u\|_0\,|v|_1. \tag{4.11}$$

Next we write the Hamilton operator (4.1) in the form

$$H = -\frac{1}{2}\Delta + V \tag{4.12}$$

and introduce the bilinear form

$$a(u,v) = (Hu,v) \tag{4.13}$$

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

$$(-\Delta u,v) = \int \nabla u\cdot\nabla v\,\mathrm{d}x, \tag{4.14}$$

there exists, by Theorem 4.1, a constant $M$ depending on $N$ and on $Z$ with

$$a(u,v) \le M\,\|u\|_1\|v\|_1 \tag{4.15}$$

for all $u, v \in \mathscr{D}$. The bilinear form (4.13) can therefore be extended to a bounded, symmetric bilinear form on $H^1$. Furthermore, for $\mu \geq 9\theta^2 + 1/4$ and all $u, v \in H^1$,

$$a(u,u) + \mu(u,u) \geq \frac{1}{4}\|u\|_1^2. \tag{4.16}$$

Neglecting the spin, the Sobolev space $H^1$ would therefore be the proper Hilbert space associated with the given system of electrons and the value $a(u,u)$ the expectation value of the total energy in the state described by the normed wave function $u \in H^1$. A function $u \neq 0$ in $H^1$ is an eigenfunction of the Hamilton operator (4.1) or (4.12), and the real number $\lambda$ the associated eigenvalue, if the relation

$$a(u,\chi) = \lambda(u,\chi) \tag{4.17}$$

holds for all $\chi \in H^1$. That is, we consider weak solutions of the eigenvalue equation

$$Hu = \lambda u, \tag{4.18}$$

in the same way as this has been discussed in Sect. 3.5 in conjunction with the Friedrichs extension and as one defines weak solutions of boundary value problems. The relation (4.16) shows that the eigenvalues $\lambda$ are bounded from below.

## 4.2 Spin and the Pauli Principle

As described in Sect. 3.6, electrons have an internal property called spin that behaves similar to angular momentum. Although spin does not explicitly appear in the electronic Schrödinger equation, it influences the structure of atoms and molecules decisively. The purpose of this section is to explain how spin can be incorporated into the variational framework. The spin of an electron can attain the two half-integer values $\pm 1/2$. Correspondingly, the true wave functions are of the form

$$\psi : (\mathbb{R}^3)^N \times \{-1/2, 1/2\}^N \to \mathbb{R} : (x,\sigma) \to \psi(x,\sigma), \tag{4.19}$$

that is, depend not only on the positions $x_i \in \mathbb{R}^3$, but also on the spins $\sigma_i = \pm 1/2$ of the electrons. The Pauli principle, one of the fundamental principles of quantum mechanics, states that only those eigenfunctions are admissible that change their sign under a simultaneous exchange of the positions $x_i$ and $x_j$ and the spins $\sigma_i$ and $\sigma_j$ of two electrons $i$ and $j$, that is, are antisymmetric in the sense that

$$\psi(Px, P\sigma) = \operatorname{sign}(P)\psi(x,\sigma) \tag{4.20}$$

holds for arbitrary simultaneous permutations $x \to Px$ and $\sigma \to P\sigma$ of the electron positions and spins. The Pauli principle forces the admissible wave functions to vanish where $x_i = x_j$ and $\sigma_i = \sigma_j$ for $i \neq j$, that is, that the probability that two

electrons $i$ and $j$ with the same spin meet is zero. The admissible solutions of the scalar Schrödinger equation (4.17) are those that are components

$$u : (\mathbb{R}^3)^N \to \mathbb{R} : x \to \psi(x, \sigma) \tag{4.21}$$

of an antisymmetric wave function (4.19). To clarify these relations and deduce (4.17) from the full equation incorporating spin, we introduce the bilinear forms

$$B(\psi, \psi') = \sum_{\sigma} a\big(\psi(\cdot, \sigma), \psi'(\cdot, \sigma)\big), \tag{4.22}$$

$$(\psi, \psi') = \sum_{\sigma} \big(\psi(\cdot, \sigma), \psi'(\cdot, \sigma)\big) \tag{4.23}$$

on the spaces of functions (4.19) with components in $H^1$, respectively, $L_2$ where the sums extend over the $2^N$ possible spin vectors $\sigma$. The quantity $B(\psi, \psi)$ represents the expectation value of the total energy for normed $\psi$ and $B$ is thus the bilinear form that is induced by the complete Hamilton operator of the system, the operator whose eigenvalues and eigenfunctions are sought. An antisymmetric function $\psi$ with components in $H^1$ is a solution of the full problem if and only if

$$B(\psi, \psi') = \lambda(\psi, \psi') \tag{4.24}$$

for all test functions $\psi'$ of this kind. This eigenvalue problem decouples into eigenvalue problems for the components of the eigenfunctions $\psi$ due to the fact that the bilinear form (4.13) is invariant under permutations of the positions $x_i$, i.e., that

$$a\big(u(P\cdot), v(P\cdot)\big) = a(u, v) \tag{4.25}$$

holds for all such permutations $P$ and all functions $u, v \in H^1$. This property translates into a statement on the antisymmetrization operator $\mathscr{A}$ given by

$$(\mathscr{A}\psi)(x, \sigma) = \frac{1}{N!} \sum_{P} \operatorname{sign}(P)\, \psi(Px, P\sigma) \tag{4.26}$$

where the sum extends over the $N!$ possible permutations of the electrons. It maps an arbitrary function (4.19) into an antisymmetric function and reproduces antisymmetric functions. For all functions (4.19) with components in $H^1$ respectively $L_2$,

$$B(\psi, \mathscr{A}\psi') = B(\mathscr{A}\psi, \psi'), \quad (\psi, \mathscr{A}\psi') = (\mathscr{A}\psi, \psi'). \tag{4.27}$$

**Theorem 4.2.** *An antisymmetric function $\psi$ with components in $H^1$ satisfies the eigenvalue equation (4.24) if and only if its components solve the equations*

$$a\big(\psi(\cdot, \sigma), v\big) = \lambda\big(\psi(\cdot, \sigma), v\big), \quad v \in H^1. \tag{4.28}$$

*Proof.* Let $\delta(\eta,\sigma) = 1$ if $\eta = \sigma$ and $\delta(\eta,\sigma) = 0$ otherwise. Every function (4.19) with components in $H^1$ can then be written as

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

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

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

with $v \in H^1$ and some given $\sigma$, and every antisymmetric function therefore as a linear combination of antisymmetrized functions of this form. It suffices therefore to restrict oneself to test functions $\mathscr{A}\psi'$ where $\psi'$ is a function of the given form. Let $\psi$ now be an arbitrary antisymmetric function with components in $H^1$. Then

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

from which the proposition follows. □

The components of the solutions $\psi$ of the full equation (4.24) are therefore indeed solutions of the scalar equation (4.17). To characterize these components, let $\mathscr{D}(\sigma)$ denote the space of all functions $u \in \mathscr{D}$ with

$$u(Px) = \operatorname{sign}(P)u(x) \tag{4.29}$$

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

**Theorem 4.3.** *A function in $\mathscr{D}$ is the component (4.21) of an antisymmetric function (4.19) with components in $\mathscr{D}$ if and only if it belongs to $\mathscr{D}(\sigma)$. The corresponding statement holds for functions with components in $L_2$ and $H^1$, respectively.*

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

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

so that the components (4.21) of an antisymmetric function are of the form (4.29). A function $u$ satisfying (4.29) is conversely the component $u(x) = \psi(x,\sigma)$ of

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

and can thus be recovered from an antisymmetric function. □

The components $u = \psi(\cdot, \sigma)$ in $H^1(\sigma)$ of the full, spin-dependent eigenfunctions $\psi$ solve, by Theorem 4.2, particularly the reduced eigenvalue equation

$$a(u, v) = \lambda(u, v), \quad v \in H^1(\sigma), \tag{4.30}$$

that results from (4.28) replacing the test space $H^1$ by its subspace $H^1(\sigma)$. From the solutions of these equations, one can conversely recover solutions of the full equation (4.24) combining all $2^N$ components of the eigenfunctions $\psi$.

**Theorem 4.4.** *If the function $u \neq 0$ in $H^1(\sigma)$ solves the eigenvalue equation (4.30) reduced to the space $H^1(\sigma)$, the antisymmetric function $\psi \neq 0$ defined by*

$$\psi(x, \eta) = \frac{1}{N!} \sum_P \operatorname{sign}(P) u(Px) \delta(P\eta, \sigma) \tag{4.31}$$

*solves the full equation (4.24) and the function $u$ itself solves the original equation*

$$a(u, v) = \lambda(u, v), \quad v \in H^1. \tag{4.32}$$

*Proof.* Let $\psi'$ be an antisymmetric function with components in $H^1$. Its component $x \to \psi'(x, \sigma)$ then belongs to $H^1(\sigma)$. Since, as in the proof of Theorem 4.2,

$$\begin{aligned} B(\psi, \psi') = B(\psi', \psi) = a(\psi'(\cdot, \sigma), u) = a(u, \psi'(\cdot, \sigma)), \\ (\psi, \psi') = (\psi', \psi) = (\psi'(\cdot, \sigma), u) = (u, \psi'(\cdot, \sigma)), \end{aligned}$$

the function (4.31) therefore solves the equation (4.24) for the complete, spin-dependent wave functions. As $u(x) = \operatorname{sign}(P) u(Px)$ whenever $P$ fixes $\sigma$, $u$ is a constant multiple of the function $\psi(\cdot, \sigma)$. The rest follows from Theorem 4.2. □

With that the circle is closed. Since the functions $u \in H^1(\sigma)$ and $\widetilde{u}(x) = u(Q^{-1}x)$ in $H^1(Q\sigma)$ generate, up to a possible change of sign, the same function (4.31) for arbitrary permutations $Q$ of the electrons, and since $\widetilde{u} \in H^1(Q\sigma)$ solves the equation

$$a(\widetilde{u}, \widetilde{v}) = \lambda(\widetilde{u}, \widetilde{v}), \quad \widetilde{v} \in H^1(Q\sigma), \tag{4.33}$$

if and only if $u$ solves (4.30), one can restrict oneself to the reduced equations (4.30) on the $\lfloor N/2 \rfloor$ essentially different spaces $H^1(\sigma)$ instead of solving the system (4.24) for the $2^N$ components of a wave function (4.19) directly. Every solution of such a reduced equation also solves the eigenvalue problem (4.17) on the bigger space $H^1$.