TETRAHEDRAL DISCRETIZATIONS OF THE SCHRÖDINGER OPERATOR FOR THE PURPOSES OF QUANTUM CHEMISTRY

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Abstract. Tetrahedral discretizations of the multielectron Schrödinger operator are suggested. They is based on tetrahedral triangulations of domains in $\mathbb{R}^3$. Theoretical results proving that these discretizations are able to approximate energy levels of electrons in atoms and molecules are obtained.

1. Introduction.

Let's consider a molecule. It is a quantum system composed by several positively charged atomic nuclei each of which brings the appropriate number of negatively charged electrons so that the system is electrically neutral as a whole. The ground state and excited states of any molecule are described by wave-functions which are eigenfunctions of the energy operator

$$H\,\Psi = E\,\Psi. \tag{1.1}$$

The energy operator H in (1.1) is called the Hamilton operator or the Hamiltonian. The equation (1.1) itself is called the Schrödinger equation.

Atomic nuclei are composed by protons and neutrons which are approximately 1840 times as heavier than electrons. They constitute the heavy and slow subsystem of a molecule. Electrons constitute the light and fast subsystem. The Born-Oppenheimer approximation is based on this subdivision of a molecule into a fast and a slow subsystem (see [1]). In this approximation

$$\Psi = \Psi_{\text{nuc}}\cdot\Psi_{\text{elec}}, \qquad\qquad H = H_{\text{nuc}} + H_{\text{elec}}. \tag{1.2}$$

The electron wave function Ψ_{elec} obeys its own Schrödinger equation:

$$H_{\text{elec}}\,\Psi_{\text{elec}} = E_{\text{elec}}\,\Psi_{\text{elec}}. \tag{1.3}$$

Assume that we have n nuclei in a molecule and let's denote through $\mathbf{R}_1,\,\ldots\,,\,\mathbf{R}_n$ their radius-vectors determining their spacial positions. The nuclei radius-vectors $\mathbf{R}_1,\,\ldots\,,\,\mathbf{R}_n$ play the role of parameters in the equation (1.3). This means that Ψ_{elec} and E_{elec} depend on $\mathbf{R}_1,\,\ldots\,,\,\mathbf{R}_n$. The operator H_{elec} also depend on $\mathbf{R}_1,\,\ldots\,,\,\mathbf{R}_n$. However it does not comprise any differentiation with respect to $\mathbf{R}_1,\,\ldots\,,\,\mathbf{R}_n$.

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The equation for Ψ_{nuc} is derived by substituting (1.2) into (1.1), taking into account (1.3), and omitting those terms where Ψ_{elec} is differentiated with respect to $\mathbf{R}_1, \ldots, \mathbf{R}_n$. This equation looks like

$$H_{\text{nuc}}\,\Psi_{\text{nuc}} + E_{\text{elec}}\,\Psi_{\text{nuc}} = E\,\Psi_{\text{nuc}}. \tag{1.4}$$

The operator H_{nuc} in (1.4) presents the kinetic energy of the nuclear subsystem of a molecule and the Coulomb repulsion of its nuclei. It is given by the formula

$$H_{\text{nuc}} = -\sum_{i=1}^{n} \frac{\hbar^2\,\triangle_{\mathbf{R}_i}}{2\,M_i} + \sum_{i\neq j}^{n} \frac{Q_i\,Q_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \tag{1.5}$$

where $M_1, \ldots, M_n$ are masses of the nuclei, $Q_1, \ldots, Q_n$ are their charges, and $\hbar$ is the Planck constant. Its value, according to Wikipedia [2], is

$$\hbar \approx 1.05457180013 \cdot 10^{-27}\ \text{erg} \cdot \text{sec}. \tag{1.6}$$

The triangle $\triangle_{\mathbf{R}_i}$ in the operator (1.5) stands for the Laplace operator with respect to the coordinates of the i-th nucleus:

$$\triangle_{\mathbf{R}_i} = \frac{\partial^2}{\partial {R_i^1}^2} + \frac{\partial^2}{\partial {R_i^2}^2} + \frac{\partial^2}{\partial {R_i^3}^2}. \tag{1.7}$$

In (1.7) and in what follows we use upper indices for the coordinates of vectors relying on the convention which is known as the Einstein's tensorial notation (see § 20 of Chapter I in [3]).

The term with E_{elec} in (1.4) is very important. The energy

$$E_{\text{elec}} = E_{\text{elec}}(\mathbf{R}_1, \ldots, \mathbf{R}_n) \tag{1.8}$$

in it should be negative in order to produce attractive forces that withstand Coulomb repulsion in (1.5), form chemical bonding and thus hold nuclei together in a molecule. Computing the energy (1.8) is the **main problem of quantum chemistry**. It is solved by solving the eigenvalue problem (1.3). The Hamilton operator H_{elec} in (1.3) is given by the formula

$$H_{\text{elec}} = -\sum_{i=1}^{N} \frac{\hbar^2\,\triangle_{\mathbf{r}_i}}{2\,m_e} - \sum_{i=1}^{N}\sum_{j=1}^{n} \frac{e\,Q_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i\neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1.9}$$

where m_e is the mass of electron and e is the absolute value of its charge. According to Wikipedia [4], the values of these two constants are

$$\begin{aligned} m_e &\approx 9.1093835611 \cdot 10^{-28}\ \text{g}, \\ e &\approx 4.8032045110 \cdot 10^{-10}\ \text{esu}. \end{aligned} \tag{1.10}$$

Let's denote through $\nu_1, \ldots, \nu_n$ the atomic numbers of the nuclei in our molecule. Then $Q_1, \ldots, Q_n$ are expressed through e in (1.10) as follows:

$$Q_i = \nu_i\,e, \quad \text{where} \quad i = 1, \ldots, n. \tag{1.11}$$

Substituting (1.11) into (1.9) we derive

$$H_{\rm elec} = -\sum_{i=1}^{N} \frac{\hbar^2 \triangle_{\mathbf{r}_i}}{2\, m_e} - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\nu_j\, e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i \neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1.12}$$

The atomic numbers $\nu_1, \ldots, \nu_n$ in (1.12) are integers. Therefore in (1.12) we have exactly three fundamental physical constants $\hbar$, e, and m_e. Their values are given in (1.6) and (1.10) above.

The equation (1.3) with the operator (1.12) is the basic equation of quantum chemistry. By its form it is a Schrödinger equation. The Hamilton operator $H_{\rm elec}$ of the form (1.12) in it is often called the Schrödinger operator. It can be further specified by adding terms responsible for spin-spin and spin-orbital interactions. Building a certain tetrahedral discretization for the Schrödinger operator (1.12) is the main goal of the present paper.

2. Conversion to atomic units.

Atomic units are especially designed for describing atoms and molecules. They are based on the fundamental physical constants (1.6) and (1.10):

$$1 \text{ au of charge} = e, \qquad 1 \text{ au of mass} = m_e, \qquad 1 \text{ au of action} = \hbar. \tag{2.1}$$

In the equation (1.3) we need the atomic units for length and energy. From (2.1) we derive the following relationships:

$$\begin{aligned} &1 \text{ au of velocity} = \frac{e^2}{\hbar}, && 1 \text{ au of energy} = \frac{m_e\, e^4}{\hbar^2}, \\ &1 \text{ au of time} = \frac{\hbar^3}{m_e\, e^4}, && 1 \text{ au of length} = \frac{\hbar^2}{m_e\, e^2}. \end{aligned} \tag{2.2}$$

Applying the relationships (2.2) to the Schrödinger equation (1.3), we find that the Schrödinger operator (1.12) in atomic units is written as

$$H_{\rm elec} = -\sum_{i=1}^{N} \frac{\triangle_{\mathbf{r}_i}}{2} - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\nu_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2.3}$$

The Schrödinger equation (1.3) itself is transformed to

$$H_{\rm elec}\, \Psi = \mathcal{E}\, \Psi, \tag{2.4}$$

where $H_{\rm elec}$ is given by the formula (2.3). Like $E_{\rm elec}$ in (1.8), the eigenvalue $\mathcal{E}$ in (2.4) depends on the radius-vectors of the nuclei $\mathbf{R}_1, \ldots, \mathbf{R}_n$:

$$\mathcal{E} = \mathcal{E}(\mathbf{R}_1, \ldots, \mathbf{R}_n). \tag{2.5}$$

The values of the functions (1.8) and (2.5) are related to each other as follows:

$$E_{\rm elec} = \frac{m_e\, e^4}{\hbar^2}\, \mathcal{E}. \tag{2.6}$$

However the arguments of the functions E_{elec} and $\mathcal{E}$ in (2.6) are different since they are given in different units.

The wave function Ψ in (2.4) depends on the electron radius-vectors $\mathbf{r}_1, \ldots, \mathbf{r}_N$ and on the radius-vectors of the nuclei $\mathbf{R}_1, \ldots, \mathbf{R}_n$ as well:

$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{R}_1, \ldots, \mathbf{R}_n). \tag{2.7}$$

Moreover, it can depend on spin states of both. However we shall not consider spins in this paper. The number of electrons N in (2.7) is calculated through the atomic numbers of the nuclei in the case of a neutral molecule:

$$N = \sum_{j=1}^{n} \nu_j. \tag{2.8}$$

The number N can be different from (2.8) if we deal with an ion.

The values of the wave function Ψ in (2.7) and the wave function Ψ_{elec} in (1.3) are related to each other by means of the formula

$$\Psi_{\text{elec}} = \Big(\frac{m_e\, e^2}{\hbar^2}\Big)^{3N/2} \Psi. \tag{2.9}$$

However, like in (2.6), the arguments of the functions in (2.9) are different since they are given in different units.

The wave function Ψ in (2.7) is normalized by the condition

$$\int |\Psi|^2\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N = 1. \tag{2.10}$$

Due to (2.10) we say that the Schrödinger operator (2.3) is an operator in the Hilbert space of square-integrable complex functions $L_2(\mathbb{C}, \mathbb{R}^{3N})$, see [5–7].

3. Closed and self adjoint operators.

The Schrödinger operator (2.3) is a differential operator. However a typical square-integrable function from $L_2(\mathbb{C}, \mathbb{R}^{3N})$ is not differentiable. This means that the domain of the operator (2.3) is smaller than $L_2(\mathbb{C}, \mathbb{R}^{3N})$. The Coulomb potentials of (2.3) are locally square integrable. Therefore initially H_{elec} is defined on the set of smooth functions with compact support $\mathcal{D}(\mathbb{C}, \mathbb{R}^{3N})$ (see [8]). The set $\mathcal{D}(\mathbb{C}, \mathbb{R}^{3N})$ is dense in $L_2(\mathbb{C}, \mathbb{R}^{3N})$, while H_{elec} is symmetric in $\mathcal{D}(\mathbb{C}, \mathbb{R}^{3N})$:

$$\langle \varphi | H_{\text{elec}} \psi \rangle = \langle H_{\text{elec}} \varphi | \psi \rangle \quad \text{for all} \quad \varphi, \psi \in \mathcal{D}(\mathbb{C}, \mathbb{R}^{3N}). \tag{3.1}$$

Therefore H_{elec} has a unique minimal closed extension (see [9]) with the domain $D(H_{\text{elec}})$. Below, referring to the Schrödinger operator (2.3) and writing H_{elec}, we shall implicitly assume this unique minimal closed extension of H_{elec}. Now let's recall some definitions from [9].

Definition 3.1. A linear operator F in a Hilbert space H is called a closed operator if its graph $\Gamma(F)$ is a closed subspace in the Cartesian product $H \times H$.

The domain $D(F)$ of an operator F is the projection of its graph $\Gamma(F)$ onto the first component of the Cartesian product $H \times H$. The minimal closed extension of

the Schrödinger operator (2.3) is constructed through the closure of its graph on smooth functions with compact support $\mathcal{D}(\mathbb{C}, \mathbb{R}^{3N})$:

$$\Gamma((H_{\rm elec}) = \overline{\Gamma((H_{\rm elec})}. \tag{3.2}$$

Due to (3.2) we have the following lemma which is immediate from (3.2).

Lemma 3.1. *A square integrable complex function $\Psi \in L_2(\mathbb{C}, \mathbb{R}^{3N})$ belongs to $D(H_{\rm elec})$ if and only if there is a sequence ψ_n of smooth complex functions with compact support in $\mathbb{R}^{3N}$ such that*

$$\lim_{n\to\infty} \psi_n = \Psi, \qquad\qquad \exists \lim_{n\to\infty} H_{\rm elec}\psi_n = \Phi. \tag{3.3}$$

Limits in (3.3) are understood in the sense of the strong convergence in the space $L_2(\mathbb{C}, \mathbb{R}^{3N})$, i. e. with respect to the norm of $L_2(\mathbb{C}, \mathbb{R}^{3N})$. The function Φ in (3.3) is taken for the value $H_{\rm elec}\Psi$ of the minimal closed extension $H_{\rm elec}$.

Definition 3.2. Let F be a linear operator with the dense domain $D(F)$ in a Hilbert space H. The operator F^* with the domain

$$D(F^*) = \{\Psi \in H\colon \exists\, \Theta \in H\colon \langle\Psi|F\Phi\rangle = \langle\Theta|\Phi\rangle \ \forall\, \Phi \in D(F)\} \tag{3.4}$$

defined by the formula $F^*\Psi = \Theta$, where a unique Θ is given by (3.4), is called the adjoint operator for F.

The following theorem is proved in [9] (see § 1 of Chapter VIII therein).

Theorem 3.1. *Let F be a linear operator with the dense domain $D(F)$ in a Hilbert space H. Then for this operator:*

(1) *the adjoint operator F^* is closed;*
(2) *the operator F admits a closed extension if and only if $D(F^*)$ is dense in H and in this case $\bar{F} = F^{**}$;*
(3) *if the operator F admits a closed extension then $(\bar{F})^* = F^*$.*

Definition 3.3. A linear operator F with the dense domain $D(F)$ in a Hilbert space H is called a symmetric operator if its adjoint operator F^* extends F, i. e. if $D(F) \subseteq D(F^*)$ and $F^*\Psi = F\Psi$ for all $\Psi \in D(F)$.

Actually an operator F is symmetric in the sense of Definition 3.3 if and only if

$$\langle\Phi|F\Psi\rangle = \langle F\Phi|\Psi\rangle \quad \text{for all} \quad \Phi, \Psi \in D(F). \tag{3.5}$$

It is easy to see that (3.1) is a version of the formula (3.5) specified to the case of the Schrödinger operator (2.3) in $\mathcal{D}(\mathbb{C}, \mathbb{R}^{3N})$.

Definition 3.4. A linear operator F with the dense domain $D(F)$ in a Hilbert space H is called self-adjoint if $F^* = F$, i. e. if F is symmetric and $D(F) = D(F^*)$.

Definition 3.5. A symmetric linear operator F in a Hilbert space H is called essentially self-adjoint if its closure $\bar{F}$ is self adjoint.

4. Sesquilinear forms and matrix elements.

For any two functions Ψ and Φ from the Hilbert space of square-integrable complex functions $L_2(\mathbb{C},\mathbb{R}^{3N})$ the sesquilinear form

$$\langle\Phi|\Psi\rangle = \int \overline{\Phi}\,\Psi\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \tag{4.1}$$

is defined. The form (4.1) is a basic scalar product of this Hilbert space. Overlined functions in (4.1) and in what follows mean complex conjugates. Norms of functions in the Hilbert space $L_2(\mathbb{C},\mathbb{R}^{3N})$ are defined through (4.1) as follows:

$$\|\Psi\| = \sqrt{\langle\Psi|\Psi\rangle}. \tag{4.2}$$

Lemma 4.1. *The domain $D(H_{\text{elec}})$ of the Schrödinger operator (2.3) is a dense subspace in the Hilbert space $L_2(\mathbb{C},\mathbb{R}^{3N})$.*

Indeed, applying Lemma 3.1, we find that $\mathcal{D}(\mathbb{C},\mathbb{R}^{3N}) \subset D(H_{\text{elec}})$, while the set of smooth functions with compact support $\mathcal{D}(\mathbb{C},\mathbb{R}^{3N})$ is dense in $L_2(\mathbb{C},\mathbb{R}^{3N})$.

In quantum mechanics the sesquilinear form (4.1) is used for defining other sesquilinear forms associated with linear operators (see [10] or [11]). In the case of the Schrödinger operator (2.3) we have

$$\langle\Phi|H_{\text{elec}}\Psi\rangle = \int \overline{\Phi}\, H_{\text{elec}}\Psi\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N. \tag{4.3}$$

The sesquilinear form (4.3) is known as the matrix element of the operator H_{elec} (see [10] or [11]).

Assume that $\Psi \in \mathcal{D}(\mathbb{C},\mathbb{R}^{3N})$ and $\Phi \in \mathcal{D}(\mathbb{C},\mathbb{R}^{3N})$. Then, applying integration by parts, we can derive the following expression for the matrix element (4.3):

$$\begin{aligned}\langle\Phi|H_{\text{elec}}\Psi\rangle = \int \sum_{i=1}^{N} \frac{(\nabla_{\mathbf{r}_i}\overline{\Phi}, \nabla_{\mathbf{r}_i}\Psi)}{2}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N - \\ - \int \sum_{i=1}^{N}\sum_{j=1}^{n} \frac{\nu_j\,\overline{\Phi}\,\Psi}{|\mathbf{r}_i - \mathbf{R}_j|}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N + \int \sum_{i\neq j}^{N} \frac{\overline{\Phi}\,\Psi}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N.\end{aligned} \tag{4.4}$$

From (4.4) one can easily derive that

$$\langle\Phi|H_{\text{elec}}\Psi\rangle = \overline{\langle\Psi|H_{\text{elec}}\Phi\rangle}. \tag{4.5}$$

Substituting $\Phi = \Psi$ into (4.4) we obtain a diagonal matrix element of H_{elec}:

$$\begin{aligned}\langle\Psi|H_{\text{elec}}\Psi\rangle = \int \sum_{i=1}^{N} \frac{|\nabla_{\mathbf{r}_i}\Psi|^2}{2}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N - \\ - \int \sum_{i=1}^{N}\sum_{j=1}^{n} \frac{\nu_j\,|\Psi|^2}{|\mathbf{r}_i - \mathbf{R}_j|}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N + \int \sum_{i\neq j}^{N} \frac{|\Psi|^2}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N.\end{aligned} \tag{4.6}$$

Due to (4.5) the diagonal matrix element (4.6) is a real number. In quantum mechanics diagonal matrix elements of operators are interpreted as probabilistic

expectation values of the corresponding physical observables (see [10], [11], and [12]). In particular, (4.6) is the expectation value of energy for the quantum state of a molecule given by the wave function Ψ.

Note that the equality (4.5) can be rewritten in the form of the equality (3.1). Applying Lemma 3.1 to the equality (3.1), we derive

$$\langle \Phi | H_{\text{elec}} \Psi \rangle = \langle H_{\text{elec}} \Phi | \Psi \rangle = \overline{\langle \Psi | H_{\text{elec}} \Phi \rangle} \quad \text{for all} \quad \Phi, \Psi \in D(H_{\text{elec}}). \tag{4.7}$$

The equality (4.7) is a particular case of the general theorem.

Theorem 4.1. *The closure $\bar{F}$ of a symmetric operator F in a Hilbert space is a symmetric operator.*

Definition 4.1. A symmetric operator F with the domain $D(F)$ in a Hilbert space H is called lower semi-definite if there is a real constant C such that

$$\langle \Psi | F \Psi \rangle \geqslant C \, \|\Psi\|^2 \quad \text{for all} \quad \Psi \in D(F), \tag{4.8}$$

where $\|\Psi\|$ is given by the formula (4.2). If $C = 0$ in (4.8), then the operator F is called semi-positive.

Relying on Definition 4.1, we subdivide the Schrödinger operator (2.3) into several parts the sum of which is equal to H_{elec}:

$$H^{[i]}_{\text{attr}} = -\frac{\triangle_{\mathbf{r}_i}}{2} - \sum_{j=1}^{n} \frac{\nu_j}{|\mathbf{r}_i - \mathbf{R}_j|}, \tag{4.9}$$

$$H_{\text{rep}} = \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{4.10}$$

$$H_{\text{elec}} = \sum_{i=1}^{N} H^{[i]}_{\text{attr}} + H_{\text{rep}}. \tag{4.11}$$

Note that the space $\mathbb{R}^{3N}$ is the direct sum of N copies of $\mathbb{R}^3$:

$$\mathbb{R}^{3N} = \mathbb{R}^3 \oplus \ldots \oplus \mathbb{R}^3. \tag{4.12}$$

The i-th operator $H^{[i]}_{\text{attr}}$ in (4.9), being restricted to i-th copy of $\mathbb{R}^3$ in (4.12), produces the following operator in $\mathbb{R}^3$:

$$H_{\text{attr}} = -\frac{\triangle_{\mathbf{r}}}{2} - \sum_{j=1}^{n} \frac{\nu_j}{|\mathbf{r} - \mathbf{R}_j|}. \tag{4.13}$$

Lemma 4.2. *The 3-dimensional Schrödinger operator (4.13) is a lower semi-definite operator in the Hilbert space $L_2(\mathbb{C}, \mathbb{R}^3)$.*

Lemma 4.2 is immediate from the results given in [13]. In the simplest case $n = 1$ the eigenvalues and eigenfunctions of the operator (4.13) are explicitly known (see [10] or [11]). Therefore in this case we can write the inequality

$$\langle \Psi | H_{\text{attr}} \Psi \rangle \geqslant -\nu_1^2 \, \|\Psi\|^2 / 2,$$

which is in agreement with Lemma 4.2 and Definition 4.1. The following lemma is a corollary of Lemma 4.2.

Lemma 4.3. *The $3N$-dimensional attractive Schrödinger operators (4.9) are lower semi-definite operators in the Hilbert space $L_2(\mathbb{C}, \mathbb{R}^{3N})$.*

The scalar repulsive operator H_{rep} in (4.10) is obviously semi-positive. As a result from Lemma 4.3 we derive the following lemma for the sum (4.11).

Lemma 4.4. *The $3N$-dimensional Schrödinger operator (2.3) represented as the sum (4.11) is a lower semi-definite operator in the Hilbert space $L_2(\mathbb{C}, \mathbb{R}^{3N})$.*

Theorem 4.2. *The closed Schrödinger operator (2.3) with the domain $D(H_{\text{elec}})$ described in Lemma 3.1 is a self-adjoint operator.*

Theorem 4.2 is proved in [14] starting with the Schrödinger operator defined on quasi-polynomials, i. e. functions of the form

$$p(\mathbf{r}) = P(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \exp(-|\mathbf{r}_1|^2 - \ldots - |\mathbf{r}_N|^2), \tag{4.14}$$

where $\mathbf{r} \in \mathbb{R}^{3N}$ and $P(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is a polynomial of the components of the three-dimensional radius vectors $\mathbf{r}_1, \ldots, \mathbf{r}_N$. Actually, if we set $\mu_0 = 0$ in [14], the self-adjoint Schrödinger operator defined in [14] through quasi-polynomials (4.14) coincides with the closed Schrödinger operator (2.3) whose domain $D(H_{\text{elec}})$ is described in Lemma 3.1. In order to prove this fact we need to show that

$$p(\mathbf{r}) \in D(H_{\text{elec}}). \tag{4.15}$$

Let's consider some smooth function $U(x)$ in $\mathbb{R}$ whose graph is shown in Fig. 4.1.

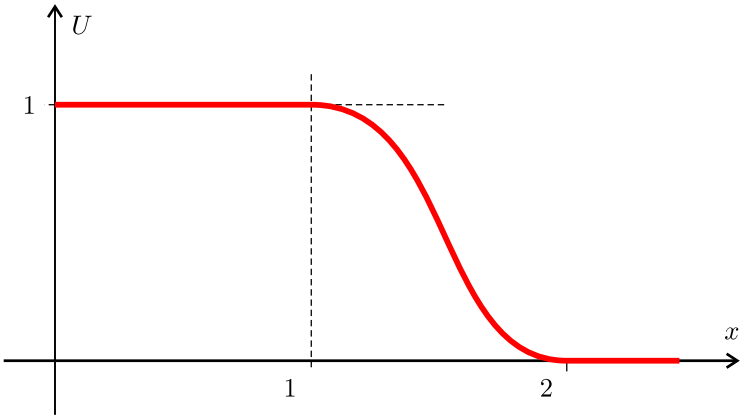

Fig. 4.1

Using the function $U(x)$ and the function (4.14), we define another function:

$$p_\theta(\mathbf{r}) = U(\theta\,|\mathbf{r}|)\, p(\mathbf{r}) \quad \text{where} \quad \theta > 0. \tag{4.16}$$

It is clear that the function (4.16) obeys the following relationship:

$$\lim_{\theta \to 0} p_\theta = p. \tag{4.17}$$

The function (4.16) belongs to $\mathcal{D}(\mathbb{C},\mathbb{R}^{3N})$, i. e. it is a smooth function with compact support. Applying the operator (2.3) to it, we derive

$$\begin{aligned} H_{\mathrm{elec}}p_\theta = U(\theta\,|\mathbf{r}|)\,H_{\mathrm{elec}}p - \sum_{i=1}^{N}\theta\,U'(\theta\,|\mathbf{r}|)\,\frac{(\mathbf{r}_i,\nabla_{\mathbf{r}_i}p)}{|\mathbf{r}|} - \\ - \sum_{i=1}^{N}\theta\,U'(\theta\,|\mathbf{r}|)\,\frac{(3\,N-1)\,p}{2\,|\mathbf{r}|} - \sum_{i=1}^{N}\frac{\theta^2\,U''(\theta\,|\mathbf{r}|)\,p}{2}. \end{aligned} \tag{4.18}$$

Through $(\bullet,\bullet)$ in the second term of the right hand side of (4.18) we denote the regular scalar product (dot product) in $\mathbb{R}^3$. From (4.18) we derive

$$\lim_{\theta\to 0}(H_{\mathrm{elec}}p_\theta) = H_{\mathrm{elec}}p. \tag{4.19}$$

Both limits in (4.17) and (4.19) are understood in the sense of strong convergence with respect to the norm in the Hilbert space $L_2(\mathbb{C},\mathbb{R}^{3N})$.

Applying Lemma 3.1 to (4.17) and (4.19) we derive the required relationship (4.15). This relationship means that Theorem 4.2 is proved.

5. Quadratic forms.

The left hand side of the formula (4.8) is the quadratic form of the operator F. It is produced from the sesquilinear form $\langle\Phi|F\Psi\rangle$ by setting $\Phi=\Psi$. General quadratic forms $q(\Psi)$ are also produced from the corresponding sesquilinear forms $q(\Phi,\Psi)$ by setting $\Phi=\Psi$, i. e. $q(\Psi)=q(\Psi,\Psi)$.

Definition 5.1. A sesquilinear form q in a Hilbert space H is complex-valued numeric function $q(\Phi,\Psi)$ with two vectorial arguments Φ and Ψ in some dense subspace $Q(q)$ of H obeying the relationships

(1) $q(\Phi,\Psi_1+\Psi_2)=q(\Phi,\Psi_1)+q(\Phi,\Psi_2)$ for all $\Phi,\Psi_1,\Psi_2\in Q(q)$;
(2) $q(\Phi,\alpha\,\Psi)=\alpha\,q(\Phi,\Psi)$ for all $\Phi,\Psi\in Q(q)$ and $\alpha\in\mathbb{C}$;
(3) $q(\Phi_1+\Phi_2,\Psi)=q(\Phi_1,\Psi)+q(\Phi_2,\Psi)$ for all $\Phi_1,\Phi_2,\Psi\in Q(q)$;
(4) $q(\alpha\,\Phi,\Psi)=\bar{\alpha}\,q(\Phi,\Psi)$ for all $\Phi,\Psi\in Q(q)$ and $\alpha\in\mathbb{C}$.

The subspace $Q(q)$ is called the domain of the sesquilinear form q.

Definition 5.2. A sesquilinear form q in a Hilbert space H is called symmetric if $q(\Psi,\Phi)=\overline{q(\Phi,\Psi)}$ for all $\Phi,\Psi\in Q(q)$.

Quadratic forms are in one-to-one correspondence with the corresponding sesquilinear forms due to the following formula:

$$q(\Phi,\Psi)=\frac{q(\Phi+\Psi)}{4}-\frac{q(\Phi-\Psi)}{4}+\frac{q(\Phi+\imath\,\Psi)}{4\,\imath}-\frac{q(\Phi-\imath\,\Psi)}{4\,\imath}. \tag{5.1}$$

Here $\imath=\sqrt{-1}$. The formula (5.1) is called the polarization formula or the recovery formula. It is used to recover the information lost by setting $\Phi=\Psi$ in $q(\Phi,\Psi)$.

Definition 5.3. A symmetric sesquilinear form q with the domain $Q(q)$ in a Hilbert space H is called lower semi-definite if there is a real constant C such that

$$q(\Psi,\Psi)\geqslant C\,\langle\Psi|\Psi\rangle \quad \text{for all} \quad \Psi\in Q(q). \tag{5.2}$$

If $C = 0$ in (5.2), then the form q is called semi-positive.

Let F be a self-adjoint linear operator with the dense domain $D(F)$ in a Hilbert space H. Then we have the sesquilinear form

$$q_F(\Phi, \Psi) = \langle \Phi | F\Psi \rangle, \quad \text{where} \quad \Phi, \Psi \in D(F). \tag{5.3}$$

The sesquilinear form (5.3) is symmetric in the sense of Definition 5.2 since F is self-adjoint and we have $\langle \Phi | F\Psi \rangle = \langle F\Phi | \Psi \rangle$. The quadratic form $q_F(\Psi) = q_F(\Psi, \Psi)$ associated with (5.3) is a real-valued function in $D(F)$.

It turns out that the form (5.3) can be extended to a larger domain $Q(F)$ such that $D(F) \subset Q(F)$. This domain is defined as follows:

$$Q(F) = D(\sqrt{|F|}\,). \tag{5.4}$$

The form (5.3) is extended from $D(F)$ to $Q(F)$ using the spectral theorem for self-adjoint operators (see § 6 of Chapter VIII in [9]).

Definition 5.4. For any self-adjoint operator F in a Hilbert space H the sesquilinear form (5.3) extended to the domain (5.4) is called the sesquilinear form associated with this operator.

The Schrödinger operator (2.3) is not only a self-adjoint operator, but also a semi-definite operator (see Definition 4.1). Therefore its form $\langle \Phi | H_{\text{elec}} \Psi \rangle$ is semi-definite in the sense of Definition 5.3. Relying on (5.2), we introduce the norm

$$\|\Psi\|_{+1} = \sqrt{\langle \Psi | H_{\text{elec}} \Psi \rangle + (1 - C)\, \|\Psi\|^2}. \tag{5.5}$$

The norm (5.5) is stronger than the standard norm (4.2) of the Hilbert space of square integrable functions $L_2(\mathbb{C}, \mathbb{R}^{3N})$. The domain $Q(H_{\text{elec}}) = D(\sqrt{|H_{\text{elec}}|}\,)$ is the closure of the domain $D(H_{\text{elec}})$ with respect to the norm (5.5) in the sense of the following theorem (see § 53 of Part XV in [15] and § 6 of Chapter VIII in [9]).

Theorem 5.1. *A function Ψ belongs to the domain $Q(H_{\text{elec}})$ if and only if there is a sequence of functions Ψ_n from the domain $D(H_{\text{elec}})$ such that*

(1) $\|\Psi_n - \Psi\| \to 0$ *as* $n \to \infty$;
(2) $\langle \Psi_n - \Psi_m | H_{\text{elec}}(\Psi_n - \Psi_m) \rangle \to 0$ *as* $n, m \to \infty$.

Combining Theorem 5.1 with Lemma 3.1 one can prove the following theorem.

Theorem 5.2. *A function Ψ belongs to the domain $Q(H_{\text{elec}})$ if and only if there is a sequence Ψ_n of smooth functions with compact support such that*

(1) $\|\Psi_n - \Psi\| \to 0$ *as* $n \to \infty$;
(2) $\langle \Psi_n - \Psi_m | H_{\text{elec}}(\Psi_n - \Psi_m) \rangle \to 0$ *as* $n, m \to \infty$.

Theorem 5.3. *Let Φ and Ψ be two functions from the domain $Q(H_{\text{elec}})$ and let Φ_n and Ψ_n be the approximating sequences for them in the sense of Theorem 5.1 or Theorem 5.2. Then the sesquilinear form of the operator H_{elec} for these two functions is given by the formula*

$$\langle \Phi | H_{\text{elec}} \Psi \rangle = \lim_{n \to \infty} \langle \Phi_n | H_{\text{elec}} \Psi_n \rangle. \tag{5.6}$$

Theorem 5.3 is immediate from the fact that (5.5) is a norm producing the structure of a Hilbert space in $Q(H_{\rm elec})$ (see § 53 of Part XV in [15] and § 6 of Chapter VIII in [9]).

6. Minimax principle.

In [16] one can find the following theorem (see § 1 of Chapter XIII therein).

Theorem 6.1. *Let F be a lower semi-definite self-adjoint operator with the domain $D(F)$ in a Hilbert space H. For some positive integer n denote*

$$\mu_n(F) = \sup_{\varphi_1,\,\ldots\,,\,\varphi_{n-1}} U_F(\varphi_1,\,\ldots\,,\,\varphi_{n-1}), \tag{6.1}$$

where

$$U_F(\phi_1,\,\ldots\,,\,\varphi_m) = \inf_{\substack{\psi\in D(F),\ \|\psi\|=1\\ \psi\perp\varphi_1,\,\ldots\,,\,\psi\perp\varphi_m}} \langle\psi|F\psi\rangle. \tag{6.2}$$

Then exactly one of the two options holds:

1. *there exist n eigenvalues of the operator F below the lower limit of its essential spectrum $\sigma_{\rm ess}(F)$, each being counted with its multiplicity, and $\lambda=\mu_n(F)$ is n-th eigenvalue of the operator F;*
2. *$\mu_n(F)$ coincides with the lower limit of the essential spectrum $\sigma_{\rm ess}(F)$ of the operator F. In this case there are at most $n-1$ eigenvalues below the lower limit of the essential spectrum $\sigma_{\rm ess}(F)$, each being counted with its multiplicity, and $\mu_m(F)=\mu_n(F)$ for all $m>n$.*

Theorem 6.1 presents the minimax principle for operators in Hilbert spacers. Note that $\varphi_1,\,\ldots\,,\,\varphi_{n-1}$ in Theorem 6.1 are arbitrary elements of the Hilbert space H. They need not be linearly independent.

The case $n=1$ in Theorem 6.1 is exceptional. In this case two formulas (6.1) and (6.2) reduce to one formula:

$$\mu_1(F) = \inf_{\psi\in D(F),\ \|\psi\|=1} \langle\psi|F\psi\rangle. \tag{6.3}$$

The following theorem is a corollary of Theorem 6.1.

Theorem 6.2. *If lower semi-definite self-adjoint operator F with the domain $D(F)$ in a Hilbert space H has the discrete spectrum, then the smallest eigenvalue of this operator $\lambda_{\rm min}=\mu_1(F)$ is given by the formula (6.3).*

In quantum chemistry the wave function Ψ in (2.4) associated with the smallest eigenvalue $\mathcal{E}_{\rm min}$ of the Schrödinger operator $H_{\rm elec}$ is called the ground state wave function. The smallest eigenvalue $\mathcal{E}_{\rm min}$ is called the ground state energy level.

Typically the domain $Q(F)$ of the form $\langle\Phi|F\Psi\rangle$ is larger than the domain $D(F)$ of the operator F itself. For this case in [16] we find the following theorem.

Theorem 6.3. *If F a lower semi-definite self-adjoint operator in a Hilbert space H, then $\mu_n(F)$ is given by the formula*

$$\mu_n(F) = \sup_{\varphi_1,\,\ldots\,,\,\varphi_{n-1}}\ \inf_{\substack{\psi\in Q(F),\ \|\psi\|=1\\ \psi\perp\varphi_1,\,\ldots\,,\,\psi\perp\varphi_{n-1}}} \langle\psi|F\psi\rangle, \tag{6.4}$$

where $Q(F)$ is the domain of the sesquilinear form $\langle\varphi|F\psi\rangle$.

The formula (6.4) looks like a combination of the formulas (6.1) and (6.2) except for $D(F)$ is replaced by $Q(F)$. For the case $n = 1$ it reduces to

$$\mu_1(F) = \inf_{\psi \in Q(F),\ \|\psi\|=1} \langle \psi | F\psi \rangle. \tag{6.5}$$

The next theorem is a corollary of Theorem 6.3.

Theorem 6.4. *If lower semi-definite self-adjoint operator F in a Hilbert space H has the discrete spectrum, then its smallest eigenvalue $\lambda_{\min} = \mu_1(F)$ is given by the formula (6.5), where $Q(F)$ is the domain of the sesquilinear form $\langle \varphi | F\psi \rangle$.*

7. Rayleigh-Ritz method.

In [16] one can find the following theorem (see § 2 of Chapter XIII therein).

Theorem 7.1. *Let F be a lower semi-definite self-adjoint operator with the domain $D(F)$ in a Hilbert space H, let $V \subset D(F)$ be an n-dimensional subspace in $D(F)$, and let P be the orthogonal projector onto V. The composite operator $P \circ F \circ P$ is lower semi-definite and self-adjoint. It has n eigenvalues $\hat{\mu}_1, \ldots, \hat{\mu}_n$ that can be enumerated in a non-decreasing order*

$$\hat{\mu}_1 \leqslant \ldots \leqslant \hat{\mu}_n. \tag{7.1}$$

Under these assumptions the following inequalities hold:

$$\mu_m(F) \leqslant \hat{\mu}_m, \quad \text{where} \quad m = 1, \ldots, n. \tag{7.2}$$

The quantities $\mu_m(F)$ in (7.2) coincide with those in (6.1) and (6.4). Note that V is an invariant space of the composite operator $P \circ F \circ P$ in Theorem 7.1. Therefore we can restrict the composite operator $P \circ F \circ P$ to V:

$$F_V = P \circ F \circ P \Big|_V \tag{7.3}$$

The eigenvalues (7.1) coincide with the eigenvalues of the linear operator (7.3) in the finite-dimensional space V.

Here is the next theorem from [16] (see § 2 of Chapter XIII therein).

Theorem 7.2. *Let F be a lower semi-definite self-adjoint operator with the domain $D(F)$ in a Hilbert space H such that its discrete spectrum is not empty and*

$$\lambda_{\min} = \mu_1(F) \tag{7.4}$$

is its smallest eigenvalue. Let Ψ be an eigenvector of F associated with the eigenvalue (7.4) and expanded in some orthonormal basis $\{h_i\}_{i=1,\ldots,\infty}$ of the space H:

$$\Psi = \lim_{n\to\infty} \Psi_n, \quad \text{where} \quad \Psi_n = \sum_{i=1}^{n} \psi^i h_i. \tag{7.5}$$

Assume that $h_i \in D(F)$ for all $i = 1, \ldots, \infty$ and assume that

$$\exists \lim_{n\to\infty} \langle \Psi_n | F\Psi_n \rangle = \lambda_{\min} \|\Psi\|^2. \tag{7.6}$$

Under these assumptions we have the equality

$$\lambda_{\min} = \lim_{n\to\infty} \hat{\mu}_1^{(n)}, \tag{7.7}$$

where $\hat{\mu}_1^{(n)}$ *is the smallest eigenvalue of the Hermitian* $n \times n$ *matrix* $\Phi^{(n)}$ *with the elements* $\Phi_{ij} = \langle h_i | F h_j \rangle$.

The equalities (7.5) in Theorem 7.2 express the convergence of the series

$$\Psi = \sum_{i=1}^{\infty} \psi^i \, h_i \tag{7.8}$$

with respect to the norm of the Hilbert space H. The coefficients ψ^i in (7.5) and (7.8) are designated according to Einstein's tensorial notation (see (1.7) and § 20 of Chapter I in [3]), i. e. using the upper index i for the coordinates of Ψ.

Actually, the matrix $\Phi^{(n)}$ in Theorem 7.2 does not depend on the eigenfunction Ψ. Indeed, let's consider the following subspace:

$$V_n = \mathrm{Span}(h_1, \ldots, h_n) \tag{7.9}$$

and denote through P_n the orthogonal projector onto it. Then $\Phi^{(n)}$ is the matrix of the composite operator similar to (7.3):

$$F_{V_n} = P_n \circ F \circ P_n \Big|_{V_n}, \tag{7.10}$$

$\Phi_{ij} = \langle h_i | F h_j \rangle = \langle h_i | F_{V_n} h_j \rangle$. The subspaces (7.9) constitute an infinite sequence of finite-dimensional subspaces of H enclosed in each other:

$$V_1 \subset V_2 \subset \ldots \subset V_n \subset \ldots . \tag{7.11}$$

Definition 7.1. A growing sequence $V_1 \subset V_2 \subset \ldots \subset V_n \subset \ldots$ of finite-dimensional subspaces of a Hilbert space H is called exhaustive if the closure of their union coincides with H.

The sequence of subspaces (7.11) is exhaustive in the sense of the definition 7.1. Each such sequence is backward associated with some (not unique) orthonormal basis in H so that V_n are spans of basis vectors. However, we cannot avoid the basis $\{h_i\}_{i=1,\ldots,\infty}$ and the eigenvector Ψ at all in Theorem 7.2 since (7.6) is an auxiliary condition for both of them.

Proof of Theorem 7.2. Applying Theorem 7.1 to the subspace (7.9), we get

$$\lambda_{\min} = \mu_1(F) \leqslant \hat{\mu}_1^{(n)}. \tag{7.12}$$

Then we apply Theorem 6.2 to the operator (7.10) in V_n and from (6.3) we derive

$$\hat{\mu}_1^{(n)} = \inf_{\psi\in V_n,\ \|\psi\|=1} \langle \psi | F_{V_n} \psi \rangle = \inf_{\psi\in V_n,\ \|\psi\|=1} \langle \psi | F \psi \rangle. \tag{7.13}$$

The approximate eigenvector Ψ_n in (7.5) is one of the elements of the space V_n. Therefore, taking into account that $\|\Psi_n\| \neq 1$, from (7.13) we obtain

$$\hat{\mu}_1^{(n)} \leqslant \frac{\langle \Psi_n | F\Psi_n \rangle}{\|\Psi_n\|^2} \tag{7.14}$$

Combining (7.14) with (7.12), we produce the inequalities

$$\lambda_{\min} \leqslant \hat{\mu}_1^{(n)} \leqslant \frac{\langle \Psi_n | F\Psi_n \rangle}{\|\Psi_n\|^2}. \tag{7.15}$$

Due to the convergence of the series (7.8) we have

$$\lim_{n\to\infty} \|\Psi_n\| = \|\Psi\|. \tag{7.16}$$

Now, applying (7.6) and (7.16) to (7.15), we derive the required result (7.7). Theorem 7.2 is proved. □

Remark. Like in Theorems 6.3 and 6.4, the domain $D(F)$ of the operator F in the above two Theorems 7.1 and 7.2 can be replaced by the domain $Q(F)$ of its sesquilinear form $\langle \varphi | F\psi \rangle$.

Theorems 7.1 and 7.2 constitute a base for the Rayleigh-Ritz method (see [17]). Its application to the experimental confirmation of the Lamb shift [18] is described in [16] (see § 3 of Chapter XIII therein). See also [19–26].

8. Minimum principle.

Note that the minimax principle for $\mu_1(F)$ expressed by the formulas (6.3) and (6.5) looks different from that of (6.1) and (6.4). In this reduced form it can be called the minimum principle. A similar minimum principle can be formulated for other $\mu_n(F)$ as well. It is expressed by the following theorem.

Theorem 8.1. *Let F be a lower semi-definite self-adjoint operator with the domain $D(F)$ in a Hilbert space H that has the discrete spectrum with at least n eigenvalues*

$$\lambda_{\min} = \lambda_1 \leqslant \ldots \leqslant \lambda_{n-1} \leqslant \lambda_n. \tag{8.1}$$

Let $\Psi_1, \ldots, \Psi_{n-1}$ be linearly independent eigenvectors associated with $n-1$ smallest eigenvalues $\lambda_1 \leqslant \ldots \leqslant \lambda_{n-1}$ in (8.1). Them $\lambda_n = \mu_n(F)$ is given by the formula

$$\lambda_n = \inf_{\substack{\psi\in D(F),\ \|\psi\|=1 \\ \psi\perp\Psi_1,\ldots,\psi\perp\Psi_{n-1}}} \langle \psi | F\psi \rangle. \tag{8.2}$$

Remark. Like in Theorems 6.3 and 6.4, the domain $D(F)$ of the operator F in Theorems 8.1 can be replaced by the domain $Q(F)$ of its sesquilinear form $\langle \varphi | F\psi \rangle$.

The minimum principle similar to Theorem 8.1 for symmetric operators in finite-dimensional Euclidean spaces can be found in [27]. For the Laplace operator it is formulated in [28].

Proof of Theorem 8.1. Since the eigenvectors $\Psi_1, \ldots, \Psi_{n-1}$ are fixed, let's consider the orthogonal complement of these vectors in H:

$$\tilde{H} = \{\psi \in H\colon\ \psi \perp \Psi_1, \ldots, \psi \perp \Psi_{n-1}\}. \tag{8.3}$$

The orthogonal complement (8.3) is a topologically closed linear subspace of the Hilbert space H. It can be treated as a separate Hilbert space with the induced sesquilinear form and norm. The restriction

$$\tilde{F} = F\Big|_{\tilde{H}} \tag{8.4}$$

of the operator F to $\tilde{H}$ is an operator in $\tilde{H}$ with the domain $D(\tilde{F}) = D(F) \cap \tilde{H}$. The operator (8.4) is a lower semi-definite self-adjoint operator in $\tilde{H}$ with the discrete spectrum that has at least one eigenvalue

$$\tilde{\lambda}_{\min} = \tilde{\lambda}_1 = \lambda_n. \tag{8.5}$$

Applying Theorem 6.2 to the operator (8.4) and taking into account (8.5), we get

$$\lambda_n = \inf_{\psi \in \tilde{D}(\tilde{F}),\ \|\psi\|=1} \langle \psi | \tilde{F} \psi \rangle = \inf_{\substack{\psi \in D(F),\ \|\psi\|=1 \\ \psi \perp \Psi_1, \ldots, \psi \perp \Psi_{n-1}}} \langle \psi | F \psi \rangle. \tag{8.6}$$

Comparing (8.6) with (8.2), we see that Theorem 8.1 is proved. □

9. Approximation of several eigenvalues at once

Theorem 9.1. *Let F be a lower semi-definite self-adjoint operator with the domain $D(F)$ in a Hilbert space H. Assume that the discrete spectrum of the operator F is not empty and has at least m eigenvalues*

$$\lambda_{\min} = \lambda_1 \leqslant \ldots \leqslant \lambda_m. \tag{9.1}$$

Let $\Psi_1, \ldots, \Psi_m$ be linearly independent eigenvectors associated with m smallest eigenvalues $\lambda_1 \leqslant \ldots \leqslant \lambda_m$ in (9.1) each of which is expanded in some orthonormal basis $\{h_i\}_{i=1,\ldots,\infty}$ of the Hilbert space H:

$$\Psi_k = \lim_{n\to\infty} \Psi_{kn}, \quad \text{where} \quad \Psi_{kn} = \sum_{i=1}^{n} \psi_k^i \, h_i \quad \text{and} \quad k = 1, \ldots, m. \tag{9.2}$$

Assume that $h_i \in D(F)$ for all $i = 1, \ldots, \infty$ and assume that

$$\exists \lim_{n\to\infty} \langle \Psi_{kn} | F \Psi_{qn} \rangle = \langle \Psi_k | F \Psi_q \rangle \quad \text{for} \quad 1 \leqslant k, q \leqslant m. \tag{9.3}$$

Under these assumptions we have the equalities

$$\lambda_k = \lim_{n\to\infty} \hat{\mu}_k^{(n)} \quad \text{for} \quad k = 1, \ldots, m, \tag{9.4}$$

where $\hat{\mu}_1^{(n)} \leqslant \ldots \leqslant \hat{\mu}_m^{(n)}$ are the first m smallest eigenvalues of the Hermitian $n \times n$ matrix $\Phi^{(n)}$ with the elements $\Phi_{ij} = \langle h_i | F h_j \rangle$.

The equalities (9.2) in Theorem 9.1 express the convergence of the series

$$\Psi_k = \sum_{i=1}^{\infty} \psi_k^i \, h_i \quad \text{for} \quad k = 1, \ldots, m \tag{9.5}$$

with respect to the norm of the Hilbert space H. The coefficients ψ_k^i in (9.2) and (9.5) are the coordinates of the vectors Ψ_k in the basis $\{h_i\}_{i=1,\dots,\infty}$. They are designated according to Einstein's tensorial notation (see (1.7), (7.8), and § 20 of Chapter I in [3]), i. e. using the upper index i.

The matrix $\Phi^{(n)}$ in Theorem 9.1 is the same as in Theorem 7.2. It is associated with the subspace V_n in (7.9) and with the composite operator F_{V_n} in (7.10). Apart from $\Phi^{(n)}$ there are several other matrices that are implicitly present in Theorem 9.1. The first of them is the diagonal matrix

$$\mathcal{F} = \begin{Vmatrix} \lambda_1 & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \lambda_m \end{Vmatrix}. \tag{9.6}$$

The matrix (9.6) is associated with the subspace

$$\mathcal{V} = \operatorname{Span}(\Psi_1, \dots, \Psi_m). \tag{9.7}$$

Since the eigenvectors $\Psi_1, \dots, \Psi_m$ are linearly independent, the dimension of the subspace (9.7) is m, i. e. $\dim \mathcal{V} = m$. If we denote trough $\mathcal{P}$ the orthogonal projector onto the subspace (9.7) and define the composite operator

$$F_{\mathcal{V}} = \mathcal{P} \circ F \circ \mathcal{P}\Big|_{\mathcal{V}}, \tag{9.8}$$

then $\mathcal{F}$ is the matrix of the operator (9.8) in the basis $\Psi_1, \dots, \Psi_m$ of the subspace $\mathcal{V}$. This fact is expressed by the relationships

$$F_{\mathcal{V}}\Psi_k = F\Psi_k = \lambda_k \Psi_k = \sum_{q=1}^{m} \mathcal{F}_k^q \, \Psi_q, \tag{9.9}$$

where $\mathcal{F}_k^q$ are the components of the matrix (9.6).

Along with (9.6), we have two Hermitian matrices $\mathcal{H}$ and G associated with the subspace (9.7) and the basis $\Psi_1, \dots, \Psi_m$ in it. Their components are

$$\mathcal{H}_{sk} = \langle \Psi_s | F_{\mathcal{V}} \Psi_k \rangle, \qquad\qquad g_{sq} = \langle \Psi_s | \Psi_q \rangle. \tag{9.10}$$

The matrix G with the components g_{sk} in (9.10) is known as the Gram matrix of the basis $\Psi_1, \dots, \Psi_m$ (see § 29 of Chapter I in [3]), while $\mathcal{H}$ is the matrix of the sesquilinear form $\langle \varphi | F_{\mathcal{V}} \psi \rangle$ in this basis. It is easy to derive that the matrices $\mathcal{F}$, $\mathcal{H}$, and G are related to each other as follows:

$$\mathcal{H} = G\,\mathcal{F}, \qquad\qquad \mathcal{F} = G^{-1}\,\mathcal{H}. \tag{9.11}$$

The Gram matrix of a basis is always non-degenerate (see § 1 of Chapter V in [27]), which agrees with (9.11).

The vectors $\Psi_{1n}, \dots, \Psi_{mn}$ in (9.2) are similar to $\Psi_1, \dots, \Psi_m$. We shall call them the approximate eigenvectors. Their span

$$\mathcal{V}_n = \operatorname{Span}(\Psi_{1n}, \dots, \Psi_{mn}) \tag{9.12}$$

is a subspace of H. We denote through $\mathcal{P}_n$ the orthogonal projector onto the subspace (9.12) and consider the composite operator

$$F_{\mathcal{V}_n} = \mathcal{P}_n \circ F \circ \mathcal{P}_n \Big|_{\mathcal{V}_n}. \tag{9.13}$$

Then we define two Hermitian matrices $\mathcal{H}^{(n)}$ and $G^{(n)}$ similar to the matrices $\mathcal{H}$ and G in (9.10). Their components are

$$\mathcal{H}[n]_{sk} = \langle \Psi_{sn} | F_{\mathcal{V}_n} \Psi_{kn} \rangle, \qquad g[n]_{sq} = \langle \Psi_{sn} | \Psi_{qn} \rangle. \tag{9.14}$$

Applying (9.2) to (9.14) and taking into account (9.10), we derive

$$\lim_{n\to\infty} g[n]_{sq} = g_{sq}, \qquad \lim_{n\to\infty} \det G^{(n)} = \det G. \tag{9.15}$$

Since $\det G \neq 0$, the second equality (9.15) means that the Gram matrix $G^{(n)}$ is non-degenerate for sufficiently large n. Hence in this case the vectors $\Psi_{1n}, \ldots, \Psi_{mn}$ are linearly independent and constitute a basis of the subspace (9.12). The $m \times m$ matrix $\mathcal{F}^{(n)}$ with the components $\mathcal{F}^q_k[n]$ is defined through the formula

$$F_{\mathcal{V}_n} \Psi_{kn} = \sum_{q=1}^{m} \mathcal{F}^q_k[n]\, \Psi_{qn}\,. \tag{9.16}$$

Due to (9.16) the matrix $\mathcal{F}^{(n)}$ is the matrix of the operator (9.13) in the basis $\Psi_{1n}, \ldots, \Psi_{mn}$. The formula (9.16) is similar to (9.9). However, unlike the matrix $\mathcal{F}$ in (9.6), typically the matrix $\mathcal{F}^{(n)}$ is non-diagonal.

Applying the formula (9.16) to (9.14) one can easily derive the following relationships for the matrices $\mathcal{F}^{(n)}$, $\mathcal{H}^{(n)}$, and $G^{(n)}$:

$$\mathcal{H}^{(n)} = G^{(n)}\, \mathcal{F}^{(n)}, \qquad \mathcal{F}^{(n)} = (G^{(n)})^{-1}\, \mathcal{H}^{(n)}. \tag{9.17}$$

The relationships (9.17) are analogous to the relationships (9.11).

Now let's return to the relationships (9.10) and (9.14). The vectors $\Psi_1, \ldots, \Psi_m$ belong to the subspace (9.7). Therefore

$$\mathcal{P}\Psi_k = \Psi_k \quad \text{for all} \quad k = 1, \ldots, m. \tag{9.18}$$

Similarly, the vectors $\Psi_{1n}, \ldots, \Psi_{mn}$ belong to the subspace (9.12). Therefore

$$\mathcal{P}_n \Psi_{kn} = \Psi_{kn} \quad \text{for all} \quad k = 1, \ldots, m. \tag{9.19}$$

Applying (9.8) and (9.18) to (9.10), we get

$$\mathcal{H}_{sk} = \langle \Psi_s | (\mathcal{P} \circ F \circ \mathcal{P}) \Psi_k \rangle = \langle \mathcal{P}\Psi_s | F \mathcal{P} \Psi_k \rangle = \langle \Psi_s | F \Psi_k \rangle. \tag{9.20}$$

Similarly, applying (9.13) and (9.19) to (9.14), we obtain

$$\mathcal{H}[n]_{sk} = \langle \Psi_{sn} | (\mathcal{P}_n \circ F \circ \mathcal{P}_n) \Psi_{kn} \rangle = \langle \mathcal{P}_n \Psi_{sn} | F \mathcal{P}_n \Psi_{kn} \rangle = \langle \Psi_{sn} | F \Psi_{kn} \rangle. \tag{9.21}$$

Let's compare the right hand sides of the formulas (9.20) and (9.21) with (9.3). As a result we derive the following relationships:

$$\lim_{n\to\infty} \mathcal{H}[n]_{sk} = \mathcal{H}_{sk}, \qquad \lim_{n\to\infty} \mathcal{H}^{(n)} = \mathcal{H}. \tag{9.22}$$

Combining (9.22) with (9.15) and taking into account (9.17) with (9.11), we get

$$\lim_{n\to\infty} \mathcal{F}[n]^q_k = \mathcal{F}^q_k, \qquad \lim_{n\to\infty} \mathcal{F}^{(n)} = \mathcal{F}. \tag{9.23}$$

For sufficiently large n the operator (9.13) is lower semi-definite self-adjoint operator in the m-dimensional space (9.12). It has exactly m real eigenvalues

$$\hat{\lambda}^{(n)}_1 \leqslant \ldots \leqslant \hat{\lambda}^{(n)}_m. \tag{9.24}$$

They coincide with the eigenvalues of the matrix $\mathcal{F}^{(n)}$ in (9.23) since $\mathcal{F}^{(n)}$ is the matrix of the operator (9.13) in the basis $\Psi_{1n}, \ldots, \Psi_{mn}$. The matrix $\mathcal{F}$ is given explicitly in (9.6). Its eigenvalues

$$\lambda_1 \leqslant \ldots \leqslant \lambda_m. \tag{9.25}$$

coincide with the eigenvalues of the operator (9.8) since $\mathcal{F}$ is the matrix of this operator in the basis $\Psi_1, \ldots, \Psi_m$. As we remember, they do coincide with the eigenvalues (9.1) of the operator F in Theorem 9.1.

It is well-known that eigenvalues of a matrix are continuous functions of its components (see [29]). Therefore for the eigenvalues (9.24) and (9.25) from (9.23) we derive the following relationships:

$$\lim_{n\to\infty} \hat{\lambda}^{(n)}_k = \lambda_k \quad \text{for} \quad k = 1, \ldots, m. \tag{9.26}$$

Proof of Theorem 9.1. The relationships (9.26) is a very important result. However, they do not prove Theorem 9.1 yet. In Theorem 9.1, i. e. in in the formula (9.4), we deal with the much larger $n \times n$ Hermitian matrix $\Phi^{(n)}$, where $n \to \infty$. The initial part of its eigenvalues is denoted trough

$$\hat{\mu}^{(n)}_1 \leqslant \ldots \leqslant \hat{\mu}^{(n)}_m \tag{9.27}$$

in (9.4). So the numbers (9.27) are different from (9.24).

Let's recall that the matrix $\Phi^{(n)}$ is associated with the subspace (7.9) and the operator (7.10) in it. Theorem 7.1 applied to the subspace (7.9) yields

$$\lambda_k = \mu_k(F) \leqslant \hat{\mu}^{(n)}_k, \quad \text{where} \quad k = 1, \ldots, m. \tag{9.28}$$

Looking at (9.2), we see that the vectors $\Psi_{1n}, \ldots, \Psi_{mn}$ belong to the subspace (7.9). Therefore the subspace (9.12) is enclosed in the subspace (7.9):

$$\mathcal{V}_n \subset V_n. \tag{9.29}$$

Applying (9.29) to the orthogonal projectors $\mathcal{P}_n$ and P_n, we derive

$$\mathcal{P}_n \circ P_n = P_n \circ \mathcal{P}_n = \mathcal{P}_n. \tag{9.30}$$

Due to (9.30) the operators (7.10) and (9.13) are related as follows:

$$F_{\mathcal{V}_n} = \mathcal{P}_n \circ F_{V_n} \circ \mathcal{P}_n \Big|_{\mathcal{V}_n}. \tag{9.31}$$

The subspace V_n in (9.29) is equipped with the sesquilinear scalar product $\langle\varphi|\psi\rangle$ inherited from the Hilbert space H. Hence V_n can be treated as a finite-dimensional Hilbert space[1] with the lower semi-definite self-adjoint operator F_{V_n} in it. Applying Theorem 7.1 to the operator F_{V_n} and the subspace $\mathcal{V}_n$ in (9.29) and taking into account (9.31), we derive the following inequalities:

$$\hat{\mu}_k^{(n)} \leqslant \hat{\lambda}_k^{(n)}, \quad \text{where} \quad k = 1, \ldots, m. \tag{9.32}$$

The inequalities (9.28) and (9.32) combined with (9.26) yield the required result

$$\lim_{n\to\infty} \hat{\mu}_k^{(n)} = \lambda_k \quad \text{for} \quad k = 1, \ldots, m. \tag{9.33}$$

Since (9.33) coincides with (9.4), the proof of Theorem 9.1 is over. □

Remark. Theorem 9.1 generalizes Theorem 7.2. Like in Theorems 6.3 and 6.4, the domain $D(F)$ of the operator F in Theorem 9.1 can be replaced by the domain $Q(F)$ of its sesquilinear form $\langle\varphi|F\psi\rangle$.

10. Triangulated domains and polylinear splines.

Definition 10.1. A planar polygonal domain is called triangulated if it is presented as a union of triangles so that any two triangles, if they do intersect, have a common side or a common vertex.

An example of planar triangulated domain is shown in Fig. 10.1. Three-dimensional analogs of triangles are tetrahedrons. Therefore we have the following definitions.

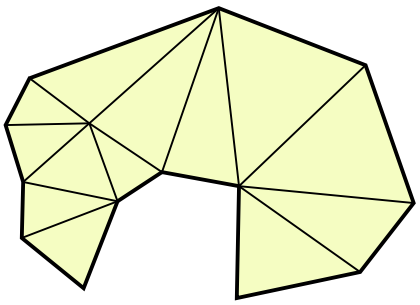

Fig. 10.1

Definition 10.2. A polyhedral domain in $\mathbb{R}^3$ is called triangulated if it is presented as a union of a finite number of tetrahedrons so that any two tetrahedrons, if their intersection is not empty, have a common face, a common edge, or a common vertex.

Definition 10.3. Let G be a triangulated polyhedral domain in $\mathbb{R}^3$. The maximal size (edge length) of tetrahedrons constituting the triangulation of G is called the granularity of G. We denote this numeric parameter through $\mathrm{gran}(G)$.

In some cases the term "mesh" is used instead of granularity, e. g. in partitioning intervals when defining the Riemann integral (see [30]). We say that the triangulation of a domain G is refined if it is replaced by a more dense network of tetrahedrons so that the total granularity $\mathrm{gran}(G)$ of the domain decreases.

[1] Finite-dimensional Hilbert spaces are called Hermitian spaces.

Definition 10.4. Let G be a triangulated polyhedral domain in $\mathbb{R}^3$. A complex-valued function $f(\mathbf{r})$ in G is called a linear spline function if it is continuous in G and if it is a linear function within each particular tetrahedron of the given triangulation of G.

Linear spline functions are simplest ones. Mote complicated spline functions are considered in [31]. A linear spline function f can take arbitrary values at nodes of the triangulation network of its domain G. Once these values are given, its values at other points of G are uniquely defined.

Definition 10.5. A spline function f that vanishes at the boundary of its domain G and is extended with zero values to the exterior of G is called a spline function with the compact support G.

Complex-valued linear spline function with the compact support G are uniquely defined by its values at interior nodes of their triangulation networks, i. e. those nodes which are in the interior of G. Therefore they constitute a finite-dimensional complex linear space which is denoted through $\mathrm{LSpline}(\mathbb{C}, G)$:

$$\dim(\mathrm{LSpline}(\mathbb{C}, G)) < \infty.$$

Remark. Linear spline function with compact support are square integrable in $\mathbb{R}^3$. They are differentiable in the sense of distributions (see [8]) and their first order partial derivatives are also square integrable in $\mathbb{R}^3$. These derivatives are discontinuous step functions with compact support that take constant values within the interior of tetrahedrons of their triangulation.

Note that wave functions associated with the Schrödinger operator (2.3) are multivariate functions with N arguments each representing a point in $\mathbb{R}^3$:

$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N). \tag{10.1}$$

Unlike (2.7), in (10.1) we did not write the dependence of Ψ on the radius-vectors of nuclei $\mathbf{R}_1, \ldots, \mathbf{R}_n$ since they are treated as constant parameters in the Born-Oppenheimer approximation. Spline versions of the functions (10.1) should also be multivariate. Therefore we introduce the concept of polylinear splines. Let

$$\underbrace{G \times \ldots \times G}_{N} \subset \mathbb{R}^{3N} \tag{10.2}$$

be the Cartesian product of N copies of a triangulated domain $G \subset \mathbb{R}^3$. Then we have the following definitions.

Definition 10.6. A multivariate complex-valued function $f(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ with the triangulated domain (10.2) in $\mathbb{R}^{3N}$ is called a polylinear spline function if it is a linear spline function in each of its arguments.

Definition 10.7. A multivariate spline function $f(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ that vanishes at the boundary of its domain $G \times \ldots \times G$ and is extended with zero values to the exterior of $G \times \ldots \times G$ is called a spline function with the compact support $G \times \ldots \times G$.

Complex-valued polylinear spline function with the compact support (10.2) constitute a finite-dimensional complex linear space. This complex linear space is

denoted through $\mathrm{PLSpline}(\mathbb{C}, G^N)$. Its dimension is given by the formula

$$\dim(\mathrm{PLSpline}(\mathbb{C}, G^N)) = \dim(\mathrm{LSpline}(\mathbb{C}, G))^N. \tag{10.3}$$

Remark. Polylinear spline function with compact support are square integrable in $\mathbb{R}^{3N}$. Their first order partial derivatives are step functions which are also square integrable in $\mathbb{R}^{3N}$. Therefore the formulas (4.4) and (4.6) are applicable to them. More formally, we have the following theorem.

Theorem 10.1. *Any polylinear spline function with compact support in* $\mathbb{R}^{3N}$ *belong to the domain* $Q(H_{\mathrm{elec}})$ *of the sesquilinear form* $\langle\Phi|H_{\mathrm{elec}}\Psi\rangle$ *associated with the Schrödinger operator* (2.3).

Proof. The proof is based on Theorem 5.2. Let Ψ be a polylinear spline function with the compact support $G \times \ldots \times G$ in $\mathbb{R}^{3N}$. Then

$$\sup_{\mathbb{R}^{3N}} |\Psi| < \infty, \qquad\qquad \sup_{\mathbb{R}^{3N}} |\nabla_{\mathbf{r}_i}\Psi| < \infty \tag{10.4}$$

for all $i = 1, \ldots, N$. Since $G \times \ldots \times G$ is a compact subset of $\mathbb{R}^{3N}$ from (10.4) we derive that Ψ and all its first order derivatives are square integrable:

$$\Psi \in L_2(\mathbb{C}, \mathbb{R}^{3N}), \qquad\qquad \nabla_{\mathbf{r}_i}\Psi \in L_2(\mathbb{C}, \mathbb{R}^{3N}) \tag{10.5}$$

for all $i = 1, \ldots, N$. The relationships (10.5) mean that Ψ belongs to the Sobolev space $W_2^1(\mathbb{C}, \mathbb{R}^{3N}) = H^1(\mathbb{C}, \mathbb{R}^{3N})$. The space $H^1(\mathbb{C}, \mathbb{R}^{3N})$ is a Hilbert space with its own norm and its own sesquilinear scalar product (see [32–34]).

In order to approximate the function Ψ in the sense of Theorem 5.2 we should remember the Meyers-Serrin theorem (see [35]). In our case it says that each function $\Psi \in W_2^1(\mathbb{C}, \mathbb{R}^{3N})$ can be approximated by smooth functions in the norm of the space $W_2^1(\mathbb{C}, \mathbb{R}^{3N})$. When proving the Meyers-Serrin theorem the approximating function is usually constructed with the use of the following integral:

$$\Psi_\delta(\mathbf{r}) = \int J_\delta(\mathbf{r} - \tilde{\mathbf{r}})\, \Psi(\tilde{\mathbf{r}})\, d^{3N}\tilde{\mathbf{r}}. \tag{10.6}$$

Through J_δ in (10.6) we denote the function

$$J_\delta(\mathbf{r}) = \frac{J(\mathbf{r}/\delta)}{\delta^{3N}}, \tag{10.7}$$

where $J(\mathbf{r})$ is some fixed positive smooth function whose support is enclosed in the unit ball centered at the origin and such that

$$\int J(\mathbf{r})\, d^{3N}\mathbf{r} = 1. \tag{10.8}$$

It is well-known that the function (10.7) obeying the condition (10.8) converges to Dirack's delta-function as $\delta \to 0$ in the sense of distributions (see [8]). As for the function (10.6), it converges to Ψ in $W_2^1(\mathbb{C}, \mathbb{R}^{3N})$, i. e.

$$\|\Psi_\delta - \Psi\| \to 0 \qquad\qquad \|\nabla_{\mathbf{r}_i}\Psi_\delta - \nabla_{\mathbf{r}_i}\Psi\| \to 0 \tag{10.9}$$

in the sense of norms in $L_2(\mathbb{C},\mathbb{R}^{3N})$ as $\delta\to 0$ for all $i=1,\ldots,N$. Moreover, using (10.4), from (10.6), (10.7), and (10.8) one can easily derive

$$\sup_{\mathbb{R}^{3N}}|\Psi_\delta|\leqslant\sup_{\mathbb{R}^{3N}}|\Psi|,\qquad\qquad \sup_{\mathbb{R}^{3N}}|\nabla_{\mathbf{r}_i}\Psi_\delta|\leqslant\sup_{\mathbb{R}^{3N}}|\nabla_{\mathbf{r}_i}\Psi|. \tag{10.10}$$

When deriving the second inequality (10.10) the integration by parts is applied.

In the next step we use (10.4), (10.10), and (10.9) in order to derive that

$$\exists\lim_{\delta\to 0}\langle\Psi_\delta|H_{\text{elec}}\Psi_\delta\rangle=\langle\Psi|H_{\text{elec}}\Psi\rangle\neq\infty. \tag{10.11}$$

The left hand side of (10.11) can be calculated using either (4.3) or (4.6). However the right hand side of (10.11) can be calculated using the formula (4.6) only since $H_{\text{elec}}\Psi$ is defined as a distribution (see [8]). It is not a square integrable function from the space $L_2(\mathbb{C},\mathbb{R}^{3N})$. Let's set

$$\delta=\delta(n)=\frac{1}{n},\ \text{ where }\ n\in\mathbb{N}\ \text{ and }\ n\to\infty.$$

Then $\Psi_n=\Psi_{\delta(n)}$ is a sequence of smooth functions with compact support such that $\|\Psi_n-\Psi\|\to 0$ as $n\to\infty$ (see (10.9)). From (10.11) we derive

$$\exists\lim_{n\to\infty}\langle\Psi_n|H_{\text{elec}}\Psi_n\rangle=\langle\Psi|H_{\text{elec}}\Psi\rangle\neq\infty. \tag{10.12}$$

It's elementary calculus that a numeric sequence converging to a finite limit is a Cauchy sequence. Therefore from (10.12) we derive

$$\langle\Psi_n-\Psi_m|H_{\text{elec}}(\Psi_n-\Psi_m)\rangle\to 0\ \text{ as }\ n,m\to\infty.$$

Now both premises of Theorem 5.2 are established. Applying this theorem, we derive the required inclusion $\Psi\in Q(H_{\text{elec}})$. Thus Theorem 10.1 is proved □

Theorem 10.2. *Polylinear spline functions with compact support are dense in the domain $Q(H_{\text{elec}})$ of the sesquilinear form $\langle\Phi|H_{\text{elec}}\Psi\rangle$ associated with the Schrödinger operator (2.3) so that for any two functions $\Phi,\Psi\in Q(H_{\text{elec}})$ there are two sequences of polylinear spline function with compact support in $\mathbb{R}^{3N}$ such that $\|\Phi_n-\Phi\|\to 0$, $\|\Psi_n-\Psi\|\to 0$ and $\langle\Phi_n|H_{\text{elec}}\Psi_n\rangle\to\langle\Phi|H_{\text{elec}}\Psi\rangle$ as $n\to\infty$.*

Remark. Theorems 5.2 and 5.3 (due to the formula (5.6)) mean that it is sufficient to prove Theorem 10.2 for two arbitrary smooth functions Φ and Ψ with compact support.

Theorem 10.2 extends the previous theorem. However, the proof of Theorem 10.2 is absolutely different from the proof of Theorem 10.1. Its idea is illustrated in Fig. 10.2 below in one-dimensional case. In Fig. 10.2 we see the graphs of two functions $f(x)$ and $\varphi(x)$. Both of them are functions with compact support. Their support is the segment $[a,b]$ of the real line R. The function $f(x)$ is smooth, while the second function $\varphi(x)$ is a linear spline function for a certain partition of the segment $[a,b]$. These functions share their values at the nodes of this partition. Therefore we can say that the second function is a trapezoidal approximation for the first one (see [36]).

Looking at Fig. 10.2, one can easily prove that if we gradually refine the partition of the segment $[a, b]$ so that its granularity will tend to zero, we shall get a sequence $\varphi_n(x)$ of trapezoidal approximations of $f(x)$ such that

$$\|\varphi_n - f\| \to 0 \quad \text{and} \quad \|\nabla_x \varphi_n - \nabla_x f\| \to 0 \quad \text{as} \quad n \to \infty \tag{10.13}$$

with respect to $L_2(\mathbb{C}, \mathbb{R})$ norm. Apart from (10.13) the same sequence $\varphi_n(x)$ will provide the C_0^∞ approximation for $f(x)$:

$$\sup_{\mathbb{R}} |\varphi_n - f| \to 0 \quad \text{as} \quad n \to \infty.$$

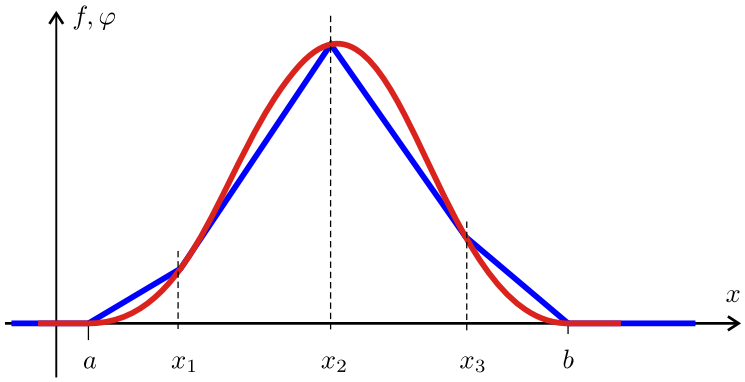

Fig. 10.2

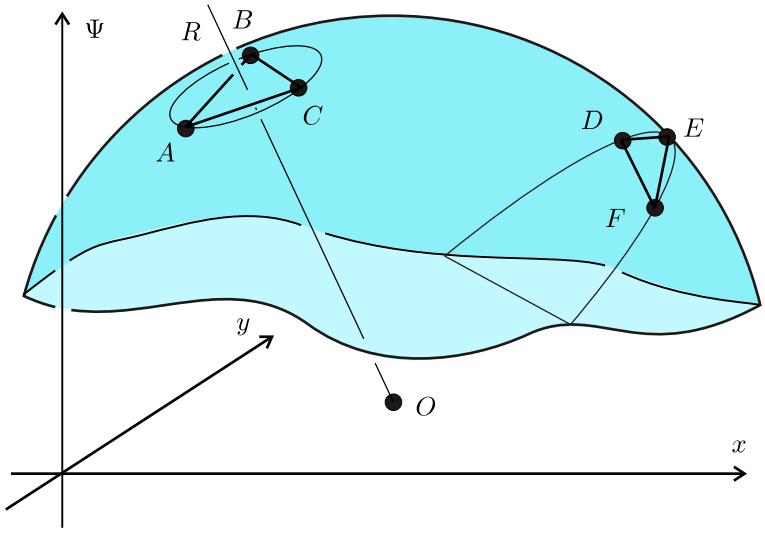

Fig. 10.3

Definition 10.8. Let Ψ be a smooth function with compact support in $\mathbb{R}^{3N}$. A polylinear spline function Φ with the compact support $G \times \ldots \times G$ is called a

trapezoidal approximation of Ψ if $\operatorname{supp}(\Psi) \subseteq G \times \ldots \times G$ and if Ψ and Φ share their values at the nodes of the triangulation grid induced from G to $G \times \ldots \times G$.

Trapezoidal approximations can be used in two-dimensional and in higher dimensional cases. However, unlike the one-dimensional case, here there are some obstacles that should be avoided. These obstacles are explained in Fig. 10.3. As an example we consider a function $\Psi(x, y)$ whose graph in $\mathbb{R}^3$ has a spherical fragment. The triangle ABC is in the plane perpendicular to the radial ray OR of the sphere. Therefore the smaller the triangle ABC is, the better its plane approximates the tangent plane of the sphere which is perpendicular to this ray.

The triangle DEF is different. It is in the plane passing through the center O of the sphere. Therefore its plane never approximates any tangent plane of the sphere even if the points D and F move toward the point E making the triangle smaller and smaller.

Despite the crucial difference of two triangles ABC and DEF in Fig. 10.3, both of them are produced by triples of points on the sphere and their projections onto the xy-plane are regular triangles therein. They can become a part of some triangulation in the xy-plane.

Conclusion. Dealing with trapezoidal approximations by polylinear spline functions in $\mathbb{R}^{3N}$, in order to avoid the obstacles observed we should control not only the granularity of the tetrahedral networks, but also the quality of tetrahedrons.

The quality problems for triangular networks are considered in [37]. Taking into account the results of [37], below in this paper we elaborate some quality criteria for tetrahedral networks.

Definition 10.9. Let $f(\mathbf{r})$ be a smooth function with compact support in $\mathbb{R}^3$. A linear spline function $\varphi(\mathbf{r})$ with the compact support G is called a trapezoidal approximation of $f(\mathbf{r})$ if $\operatorname{supp}(f) \subseteq G$ and if $f(\mathbf{r})$ and $\varphi(\mathbf{r})$ share their values at the nodes of the triangulation grid in G.

Definition 10.9 is a reduction of Definition 10.8 from $\mathbb{R}^{3N}$ back to $\mathbb{R}^3$.

Theorem 10.3. *Let $f(\mathbf{r})$ be a smooth function with compact support in $\mathbb{R}^3$ and let $\varphi(\mathbf{r})$ be a trapezoidal approximation of $f(\mathbf{r})$ with the support G. Then*

$$\sup_{\mathbf{r}\in\mathbb{R}^3} |f - \varphi| \leqslant C \operatorname{gran}(G), \quad \text{where} \quad C = 2 \sup_{\mathbf{r}\in\mathbb{R}^3} |\nabla_{\mathbf{r}} f|. \tag{10.14}$$

Proof. Note that the inequality (10.14) depends only on the granularity of the triangulation in the domain G. No auxiliary quality parameters of tetrahedrons are required yet in Theorem 10.3. The main tool for proving this theorem is the Taylor's formula (see [38]).

Since $\operatorname{supp}(f) \subseteq G$, in the exterior of G both functions f and φ do vanish. Therefore it is sufficient to prove the inequality (10.14) in G. Let T be one of the tetrahedrons of the triangulation in G and let $\mathbf{r}_0$, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ be radius-vectors of its vertices. Since φ is a linear function in T, for $\mathbf{r} \in T$ we have

$$|\varphi(\mathbf{r}) - \varphi(\mathbf{r}_0)| \leqslant \max_{i=1,2,3} |\varphi(\mathbf{r}_i) - \varphi(\mathbf{r}_0)| \tag{10.15}$$

The function φ is trapezoidal approximation of f. Therefore the values of these two functions f and φ at the vertices of the tetrahedron T do coincide:

$$\varphi(\mathbf{r}_i) = f(\mathbf{r}_i) \quad \text{for} \quad i = 0, 1, 2, 3. \tag{10.16}$$

Applying (10.16) to (10.15), we derive the following inequality:

$$|\varphi(\mathbf{r}) - f(\mathbf{r}_0)| \leqslant \max_{i=1,2,3} |f(\mathbf{r}_i) - f(\mathbf{r}_0)|. \tag{10.17}$$

Now let's proceed to the function $f(\mathbf{r})$. In this case we apply the Taylor's formula with the remainder term in the Lagrange form:

$$f(\mathbf{r}) = f(\mathbf{r}_0) + (\nabla_{\mathbf{r}} f(\boldsymbol{\xi}), \mathbf{r} - \mathbf{r}_0). \tag{10.18}$$

Through $(\bullet, \bullet)$ in the second term of the right hand side of (10.18) we denote the regular scalar product (dot product) in $\mathbb{R}^3$.

Typically the radius-vector $\boldsymbol{\xi}$ corresponds to some point on the segment $[\mathbf{r}_0, \mathbf{r}]$. Since we deal with the complex-valued function, generally speaking, $\boldsymbol{\xi}$ stands for two different points for the real and the imaginary parts of $f(\mathbf{r})$, both belonging to the segment $[\mathbf{r}_0, \mathbf{r}] \subset T$. From (10.18) we derive the estimate

$$|f(\mathbf{r}) - f(\mathbf{r}_0)| \leqslant \Big(\sup_{\mathbf{r} \in \mathbb{R}^3} |\nabla_{\mathbf{r}} f| \Big) |\mathbf{r} - \mathbf{r}_0|. \tag{10.19}$$

The radius-vectors $\mathbf{r}_i$ in (10.17) are special instances of the general radius-vector r in (10.19). Applying (10.19) to them, we derive

$$|f(\mathbf{r}_i) - f(\mathbf{r}_0)| \leqslant \Big(\sup_{\mathbf{r} \in \mathbb{R}^3} |\nabla_{\mathbf{r}} f| \Big) |\mathbf{r}_i - \mathbf{r}_0| \quad \text{for} \quad i = 0, 1, 2, 3. \tag{10.20}$$

For the deflection value $|f(\mathbf{r}) - \varphi(\mathbf{r})|$ we have the estimate

$$|f(\mathbf{r}) - \varphi(\mathbf{r})| \leqslant |f(\mathbf{r}) - f(\mathbf{r}_0)| + |\varphi(\mathbf{r}) - f(\mathbf{r}_0)|. \tag{10.21}$$

Since the radius-vectors $\mathbf{r}$, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_0$ correspond to the points within the tetrahedron T, their mutual distances $|\mathbf{r} - \mathbf{r}_0|$ and $|\mathbf{r}_i - \mathbf{r}_0|$ are estimated by the granularity of the triangulation in G:

$$|\mathbf{r} - \mathbf{r}_0| \leqslant \operatorname{gran}(G), \qquad |\mathbf{r}_i - \mathbf{r}_0| \leqslant \operatorname{gran}(G) \quad \text{for} \quad i = 0, 1, 2, 3. \tag{10.22}$$

The rest is to apply (10.19) and (10.17) to (10.21), then take into account (10.20) and (10.22) and derive the required inequality (10.14). Theorem 10.3 is proved. □

The next theorem generalizes Theorem 10.3 from $\mathbb{R}^3$ to $\mathbb{R}^{3N}$. Its proof is more technical, but is based on the same ideas. It is left for forthcoming papers.

Theorem 10.4. *Let $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be a smooth function with compact support in $\mathbb{R}^{3N}$ and let $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be a trapezoidal polylinear spline approximation of $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ with the support $G \times \ldots \times G$. Then there is a constant C depending on the function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ such that*

$$\sup_{\mathbb{R}^{3N}} |\Psi - \Phi| \leqslant C \operatorname{gran}(G). \tag{10.23}$$

Let's return again from $\mathbb{R}^{3N}$ to $\mathbb{R}^3$. Let $f(\mathbf{r})$ be a smooth function with compact support in $\mathbb{R}^3$ and let $\varphi(\mathbf{r})$ be its linear trapezoidal approximation with the

compact support G (see Definition 10.9). The gradient of $\varphi(\mathbf{r})$ is a step function which is constant within each tetrahedron of the triangulation in G. Let's choose one of such tetrahedrons and denote it through T. The radius vectors of its vertices are denoted through $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_0$ in Fig. 10.4. Then

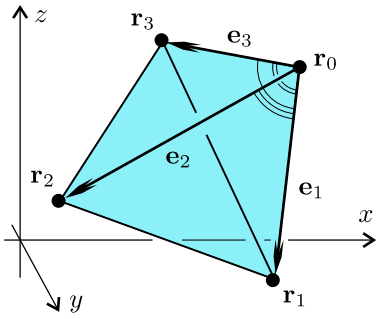

Fig. 10.4

$$\begin{aligned} \mathbf{e}_1 &= \mathbf{r}_1 - \mathbf{r}_0, \\ \mathbf{e}_2 &= \mathbf{r}_2 - \mathbf{r}_0, \\ \mathbf{e}_3 &= \mathbf{r}_3 - \mathbf{r}_0. \end{aligned} \tag{10.24}$$

Three vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ defined in (10.24) constitute a basis in $\mathbb{R}^3$. Typically it is a skew-angular basis. The angles between vectors of this basis are shown by small arcs in Fig. 10.4. Let's denote them α_1, α_2, α_3 in the following way: α_1 is the angle between $\mathbf{e}_2$ and $\mathbf{e}_3$, α_2 is the angle between $\mathbf{e}_3$ and $\mathbf{e}_1$, α_3 is the angle between $\mathbf{e}_1$ and $\mathbf{e}_2$:

$$\alpha_1 = \widehat{\mathbf{e}_2, \mathbf{e}_3}, \qquad \alpha_2 = \widehat{\mathbf{e}_3, \mathbf{e}_1}, \qquad \alpha_3 = \widehat{\mathbf{e}_1, \mathbf{e}_2}. \tag{10.25}$$

The gradients $\nabla_{\mathbf{r}} f$ and $\nabla_{\mathbf{r}} \varphi$ can be expanded in the basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$:

$$\begin{aligned} \nabla_{\mathbf{r}} f(\mathbf{r}_0) = \mathbf{a} &= a^1\,\mathbf{e}_1 + a^2\,\mathbf{e}_2 + a^3\,\mathbf{e}_3, \\ \nabla_{\mathbf{r}} \varphi = \mathbf{b} &= b^1\,\mathbf{e}_1 + b^2\,\mathbf{e}_2 + b^3\,\mathbf{e}_3. \end{aligned} \tag{10.26}$$

The quantities a^1, a^2, a^3 and b^1, b^2, b^3 in (10.26) are their coordinates. The function $\varphi(\mathbf{r})$ is a linear function within the tetrahedron T in Fig. 10.4. Therefore its gradient $\mathbf{b} = \nabla_{\mathbf{r}} \varphi$ is a constant vector. Taylor's formula for this function is written without any remainder term:

$$\varphi(\mathbf{r}) = \varphi(\mathbf{r}_0) + (\mathbf{b}, \mathbf{r} - \mathbf{r}_0). \tag{10.27}$$

Applying (10.16) and (10.24) to (10.27), we derive the following equations:

$$\begin{aligned} (\mathbf{b}, \mathbf{e}_1) &= f(\mathbf{r}_1) - f(\mathbf{r}_0), \\ (\mathbf{b}, \mathbf{e}_2) &= f(\mathbf{r}_2) - f(\mathbf{r}_0), \\ (\mathbf{b}, \mathbf{e}_3) &= f(\mathbf{r}_3) - f(\mathbf{r}_0). \end{aligned} \tag{10.28}$$

The equations (10.28) are used in order to express the vector $\mathbf{b}$ through the values of $f(\mathbf{r})$ at the vertices of the tetrahedron T. In (10.27) and in (10.28), like in (10.18), we use $(\bullet, \bullet)$ to denote the regular scalar product in $\mathbb{R}^3$ (the dot product).

The function $f(\mathbf{r})$ is not linear in T. Therefore Taylor's formulas for $f(\mathbf{r})$ and $\nabla_{\mathbf{r}} f(\mathbf{r})$ are written with remainder terms:

$$f(\mathbf{r}) = f(\mathbf{r}_0) + (\nabla_{\mathbf{r}} f(\mathbf{r}_0), \mathbf{r} - \mathbf{r}_0) + h_1(\mathbf{r}), \tag{10.29}$$

$$\nabla_{\mathbf{r}} f(\mathbf{r}) = \nabla_{\mathbf{r}} f(\mathbf{r}_0) + \mathbf{h}_0(\mathbf{r}). \tag{10.30}$$

Both remainder terms in (10.29) and (10.30) are estimated through second order partial derivatives of $f(\mathbf{r})$ using Legendre presentation for them (see [38]):

$$|h_1(\mathbf{r})| \leqslant \frac{9}{2}\, C\, |\mathbf{r}-\mathbf{r}_0|^2, \quad \text{where} \quad C = \max_{i,j=1,2,3} \sup_{\mathbf{r}\in\mathbb{R}^3} \Big|\frac{\partial^2 f(\mathbf{r})}{\partial x^i \partial x^j}\Big|, \tag{10.31}$$

$$|\mathbf{h}_0(\mathbf{r})| \leqslant 9\, C\, |\mathbf{r}-\mathbf{r}_0|, \quad \text{where} \quad C = \max_{i,j=1,2,3} \sup_{\mathbf{r}\in\mathbb{R}^3} \Big|\frac{\partial^2 f(\mathbf{r})}{\partial x^i \partial x^j}\Big|. \tag{10.32}$$

The difference of gradients in T is calculated using (10.30) and (10.26) as follows

$$\nabla_{\mathbf{r}} f(\mathbf{r}) - \nabla_{\mathbf{r}} \varphi(\mathbf{r}) = \mathbf{a} - \mathbf{b} + \mathbf{h}_0(\mathbf{r}). \tag{10.33}$$

The formula (10.33) provides an inequality for the deflection $|\nabla_{\mathbf{r}} f - \nabla_{\mathbf{r}} \varphi|$:

$$|\nabla_{\mathbf{r}} f - \nabla_{\mathbf{r}} \varphi| \leqslant |\mathbf{a}-\mathbf{b}| + |\mathbf{h}_0(\mathbf{r})|. \tag{10.34}$$

For $|\mathbf{h}_0(\mathbf{r})|$ in (10.34) we already have the estimate (10.32). The main issue now is to find a similar estimate for $|\mathbf{a}-\mathbf{b}|$.

If we recall that $\varphi(\mathbf{r}_0) = f(\mathbf{r}_0)$ (see (10.16)), then substituting $\mathbf{r} = \mathbf{r}_1$, $\mathbf{r} = \mathbf{r}_2$, and $\mathbf{r} = \mathbf{r}_3$ into (10.29) and taking into account (10.26) and (10.24), we derive

$$\begin{aligned} (\mathbf{a}, \mathbf{e}_1) &= f(\mathbf{r}_1) - f(\mathbf{r}_0) - h_1(\mathbf{r}_1), \\ (\mathbf{a}, \mathbf{e}_2) &= f(\mathbf{r}_2) - f(\mathbf{r}_0) - h_1(\mathbf{r}_2), \\ (\mathbf{a}, \mathbf{e}_3) &= f(\mathbf{r}_3) - f(\mathbf{r}_0) - h_1(\mathbf{r}_3). \end{aligned} \tag{10.35}$$

These are the equations for the vector $\mathbf{a}$. Note that the equations (10.35) are very similar to the equations (10.28). Let's denote

$$\mathbf{c} = \mathbf{b} - \mathbf{a} \tag{10.36}$$

Then from (10.35) and (10.28) we derive the following equations for $\mathbf{c}$:

$$\begin{aligned} (\mathbf{c}, \mathbf{e}_1) &= h_1(\mathbf{r}_1), \\ (\mathbf{c}, \mathbf{e}_2) &= h_1(\mathbf{r}_2), \\ (\mathbf{c}, \mathbf{e}_3) &= h_1(\mathbf{r}_3). \end{aligned} \tag{10.37}$$

Note that $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ in (10.36) are constant vectors and (10.37) are linear equations for them. Using (10.26) we derive the expansion for $\mathbf{c}$:

$$\mathbf{c} = c^1\, \mathbf{e}_1 + c^2\, \mathbf{e}_2 + c^3\, \mathbf{e}_3, \tag{10.38}$$

where $c^1 = b^1 - a^1$, $c^2 = b^2 - a^2$, and $c^3 = b^3 - a^3$. Let's substitute (10.38) into (10.37). As a result we derive linear equations for the coordinates c^1, c^2, c^3 of the vector $\mathbf{c}$ in the expansion (10.38):

$$\begin{aligned} g_{11}\, c^1 + g_{12}\, c^2 + g_{13}\, c^3 &= h_1(\mathbf{r}_1), \\ g_{21}\, c^1 + g_{22}\, c^2 + g_{23}\, c^3 &= h_1(\mathbf{r}_2), \\ g_{31}\, c^1 + g_{32}\, c^2 + g_{33}\, c^3 &= h_1(\mathbf{r}_3). \end{aligned} \tag{10.39}$$

The coefficients g_{ij} of the linear equations (10.39) are given by the formulas

$$g_{ij} = (\mathbf{e}_i, \mathbf{e}_j) = (\mathbf{e}_j, \mathbf{e}_i). \tag{10.40}$$

The symmetric 3×3 square matrix G with the components g_{ij} given by scalar products (10.40) is known as the Gram matrix of the basis (10.24) (see § 29 of Chapter I in [3]). The determinant of G is given by the formula

$$\det G = V^2, \tag{10.41}$$

where V is the volume of the tetrahedron T in Fig. 10.4 (see § 51 and § 56 of Chapter I in [3]). Due to (10.41) the determinant $\det G$ is positive and G is a non-degenerate matrix. Hence the system of linear equations (10.39) has a unique solution given by the formulas

$$\begin{aligned} c^1 &= g^{11}\, h_1(\mathbf{r}_1) + g^{12}\, h_1(\mathbf{r}_2) + g^{13}\, h_1(\mathbf{r}_3), \\ c^2 &= g^{21}\, h_1(\mathbf{r}_1) + g^{22}\, h_1(\mathbf{r}_2) + g^{23}\, h_1(\mathbf{r}_3), \\ c^2 &= g^{31}\, h_1(\mathbf{r}_1) + g^{32}\, h_1(\mathbf{r}_2) + g^{33}\, h_1(\mathbf{r}_3). \end{aligned} \tag{10.42}$$

The coefficients g^{ij} with upper indices in (10.42) are components of the inverse matrix G^{-1}. Using (10.42), one can calculate the length of the vector $\mathbf{c}$:

$$|\mathbf{c}| = \sqrt{(\mathbf{c}, \mathbf{c})} = \sqrt{\sum_{i=1}^{3} \sum_{j=1}^{3} g^{ij}\, h_1(\mathbf{r}_i)\, h_1(\mathbf{r}_j)} \tag{10.43}$$

Since $|\mathbf{c}| = |\mathbf{a} - \mathbf{b}|$ is used in the estimate (10.34), we shall carefully examine the formula (10.43). Note that the components (10.40) of the Gram matrix G can be expressed through the angles (10.25). As a result we get

$$G = \begin{Vmatrix} \rho_1^2 & \rho_1\, \rho_2\, \cos\alpha_3 & \rho_1\, \rho_3\, \cos\alpha_2 \\ \rho_2\, \rho_1\, \cos\alpha_3 & \rho_2^2 & \rho_2\, \rho_3\, \cos\alpha_1 \\ \rho_3\, \rho_1\, \cos\alpha_2 & \rho_3\, \rho_2\, \cos\alpha_1 & \rho_3^2 \end{Vmatrix}, \tag{10.44}$$

where $\rho_1 = |\mathbf{e}_1|$, $\rho_2 = |\mathbf{e}_2|$, $\rho_3 = |\mathbf{e}_3|$. Actually the matrix (10.44) is the following product of three symmrytic 3×3 matrices:

$$G = R\, \tilde{G}\, R, \tag{10.45}$$

where

$$R = \begin{Vmatrix} \rho_1 & 0 & 0 \\ 0 & \rho_2 & 0 \\ 0 & 0 & \rho_3 \end{Vmatrix}, \qquad \tilde{G} = \begin{Vmatrix} 1 & \cos\alpha_3 & \cos\alpha_2 \\ \cos\alpha_3 & 1 & \cos\alpha_1 \\ \cos\alpha_2 & \cos\alpha_1 & 1 \end{Vmatrix}. \tag{10.46}$$

The matrix R in (10.46) is responsible for the lengths of the vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, while $\tilde{G}$ is responsible for the angles between them. From $\det G > 0$ we derive

$$\det \tilde{G} > 0. \tag{10.47}$$

The inequality (10.47) is immediate from (10.41) and (10.45).

In order to proceed with the formula (10.43) we need some auxiliary notations. Let's denote through $\tilde{g}_{ij}$ the components of the matrix $\tilde{G}$ and through $\tilde{g}^{ij}$ the components of the inverse matrix $\tilde{G}^{-1}$. Additionally, let's denote

$$h_1 = \frac{h_1(\mathbf{r}_1)}{\rho_1}, \qquad h_2 = \frac{h_1(\mathbf{r}_2)}{\rho_2}, \qquad h_3 = \frac{h_1(\mathbf{r}_3)}{\rho_3}. \tag{10.48}$$

Using (10.48), the formula (10.43) is transformed as follows:

$$|\mathbf{c}| = \sqrt{\sum_{i=1}^{3}\sum_{j=1}^{3} \tilde{g}^{ij}\, h_i\, h_j}\,. \tag{10.49}$$

Let's apply the estimate (10.31) to the quantities (10.48) and take into account that $|\mathbf{r}_i - \mathbf{r}_0| = \rho_i$ for $i = 1, 2, 3$. As a result we get

$$|h_i| \leqslant \frac{9\,C\,\rho_i}{2}, \quad \text{where} \quad i = 1, 2, 3. \tag{10.50}$$

In order to get upper estimates for $|\mathbf{c}|$ in (10.49) we need upper estimates for $|\tilde{g}^{ij}|$. Looking at (10.46), one can see that

$$|\tilde{g}_{ij}| \leqslant 1. \tag{10.51}$$

The components of the inverse matrix $\tilde{G}^{-1}$ can be calculated through $\tilde{g}_{ij}$ using minors and cofactors (algebraic complements) of the matrix $\tilde{G}$ (see [39]). This yields the following estimates for $\tilde{g}^{ij}$ in (10.49) derived from (10.51):

$$|\tilde{g}^{ij}| \leqslant \frac{4}{\det \tilde{G}}. \tag{10.52}$$

The determinant $\det \tilde{G}$ in (10.52) can be calculated explicitly:

$$\begin{aligned} \det \tilde{G} = 1 + 2\,\cos\alpha_1\,\cos\alpha_2\,\cos\alpha_3 - \\ - \cos^2\alpha_1 - \cos^2\alpha_3 - \cos^2\alpha_3. \end{aligned} \tag{10.53}$$

The inequality (10.47) says that $\det \tilde{G}$ in (10.53) is always positive. However it can be very close to zero unless otherwise is explicitly stated.

Definition 10.10. Any tetrahedron T with one marked vertex $\mathbf{r}_0$ is characterized by the following numeric parameter associated with this vertex:

$$\begin{aligned} \mathrm{AQual}(T, \mathbf{r}_0) = 1 + 2\,\cos\alpha_1\,\cos\alpha_2\,\cos\alpha_3 - \\ - \cos^2\alpha_1 - \cos^2\alpha_3 - \cos^2\alpha_3. \end{aligned} \tag{10.54}$$

Here α_1, α_2, α_3 are three planar angles between three edges of T connected to the vertex $\mathbf{r}_0$. The parameter (10.54) is called the angular quality of the tetrahedron T at its vertex $\mathbf{r}_0$.

We can extend the concept of angular quality to a tetrahedron as whole and further to tetrahedral triangulations of domains in $\mathbb{R}^3$.

Definition 10.11. The angular quality of a tetrahedron T as whole is the maximum of angular qualities at all of its four vertices:

$$\mathrm{AQual}(T) = \max_{i=0,1,2,3} \mathrm{AQual}(T, \mathbf{r}_i). \tag{10.55}$$

Definition 10.12. The angular quality of a tetrahedral triangulation in a triangulated domain $G \subset R^3$ is the minimum of angular qualities of tetrahedrons composing this tetrahedral triangulation:

$$\mathrm{AQual}(G) = \min_{T \subset G} \mathrm{AQual}(T). \tag{10.56}$$

Let's apply the estimates (10.50) and (10.52) to (10.49) and take into account Definition 10.10. As a result we get

$$|\mathbf{c}| \leqslant 9\,C \sqrt{\sum_{i=1}^{3}\sum_{j=1}^{3} \frac{\rho_i\,\rho_j}{\mathrm{AQual}(T, \mathbf{r}_0)}}\,. \tag{10.57}$$

When passing from a single tetrahedron to the tetrahedral network in G we use (10.55) and (10.56) and we estimate ρ_i and ρ_j through the granularity of the network. Then the formula (10.57) reduces to

$$|\mathbf{c}| \leqslant \frac{27\,C\ \mathrm{gran}(G)}{\sqrt{\mathrm{AQual}(G)}}. \tag{10.58}$$

Since $|\mathbf{a} - \mathbf{b}| = |\mathbf{c}|$ in (10.34), we can apply (10.58) and (10.32) to (10.34). As a result we get the following theorem.

Theorem 10.5. *Let $f(\mathbf{r})$ be a smooth function with compact support in $\mathbb{R}^3$ and let $\varphi(\mathbf{r})$ be a trapezoidal approximation of $f(\mathbf{r})$ with the support G. Then*

$$\sup_{\mathbf{r}\in\mathbb{R}^3} |\nabla_{\mathbf{r}} f - \nabla_{\mathbf{r}}\varphi| \leqslant 9\,C \left(1 + \frac{3}{\sqrt{\mathrm{AQual}(G)}}\right) \mathrm{gran}(G), \tag{10.59}$$

where

$$C = \max_{i,j=1,2,3} \sup_{\mathbf{r}\in\mathbb{R}^3} \left|\frac{\partial^2 f(\mathbf{r})}{\partial x^i \partial x^j}\right|. \tag{10.60}$$

Theorem 10.6. *Let $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be a smooth function with compact support in $\mathbb{R}^{3N}$ and let $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be a trapezoidal polylinear spline approximation of $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ with the support $G \times \ldots \times G$. Then there are two constants C_1 and C_2 depending on the function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ such that*

$$\max_{i=1,\ldots,N} \sup_{\mathbb{R}^{3N}} |\nabla_{\mathbf{r}_i}\Psi - \nabla_{\mathbf{r}_i}\Phi| \leqslant \left(C_1 + \frac{C_2}{\sqrt{\mathrm{AQual}(G)}}\right) \mathrm{gran}(G). \tag{10.61}$$

Theorem 10.6 and the formula (10.61) generalizes Theorem 10.5 and the formulas (10.59) and (10.60). Its proof is more technical, but is based on the same ideas.

Like the proof of Theorem 10.4, it is left for forthcoming papers. A demanding and incredulous reader can take both of these two theorems for conjectures.

Proof of Theorem 10.2. As it was noted in Remark to this theorem, it is sufficient to prove it for two smooth functions Ψ and Φ with compact support in $\mathbb{R}^{3N}$. Let's choose some triangulated domain G such that $G \times \ldots \times G$ comprises the supports of both functions Ψ and Φ. Subdividing large tetrahedrons into smaller ones, we can construct a sequence of triangulations of G with decreasing granularity:

$$\operatorname{gran}(G) \to 0.$$

Definition 10.13. A sequence of triangulations of a domain G is called a sequence with nonvanishing quality if there is a constant $\varepsilon > 0$ such that $\operatorname{AQual}(G) > \varepsilon$ for all triangulations in the sequence.

Sequences of triangulations with nonvanishing quality do exist and are easily constructed since all similar tetrahedrons T (i. e. produced by scaling from each other) have the same angular quality $\operatorname{AQual}(T)$.

Assuming that we have constructed a sequence of triangulations of G with nonvanishing quality and with the granularity $\operatorname{gran}(G) \to 0$, we build trapezoidal polylinear spline approximations of the functions Ψ and Φ for them. As a result we get two sequences of approximating functions Ψ_n and Φ_n. The inequality (10.23) from Theorem 10.4 means that

$$\sup_{\mathbb{R}^{3N}} |\Psi - \Psi_n| \to 0 \quad \text{and} \quad \sup_{\mathbb{R}^{3N}} |\Phi - \Phi_n| \to 0 \quad \text{as} \quad n \to \infty. \tag{10.62}$$

Similarly the inequality (10.61) from Theorem 10.6 yields

$$\sup_{\mathbb{R}^{3N}} |\nabla_{\mathbf{r}_i}\Psi - \nabla_{\mathbf{r}_i}\Psi_n| \to 0 \quad \text{and} \quad \sup_{\mathbb{R}^{3N}} |\nabla_{\mathbf{r}_i}\Phi - \nabla_{\mathbf{r}_i}\Phi_n| \to 0 \quad \text{as} \quad n \to \infty \tag{10.63}$$

for all $i = 1, \ldots, N$. The supports of all functions Ψ_n, Φ_n, Ψ, and Φ_n are enclosed in the compact set $G \times \ldots \times G$. Therefore from (10.62) and (10.63) we derive the convergence in $L_2(\mathbb{C}, \mathbb{R}^{3N})$ for our approximating sequences:

$$\begin{gathered} \|\Psi - \Psi_n\| \to 0 \quad \text{and} \quad \|\Phi - \Phi_n\| \to 0 \quad \text{as} \quad n \to \infty, \\ \|\nabla_{\mathbf{r}_i}\Psi - \nabla_{\mathbf{r}_i}\Psi_n\| \to 0 \quad \text{and} \quad \|\nabla_{\mathbf{r}_i}\Phi - \nabla_{\mathbf{r}_i}\Phi_n\| \to 0 \quad \text{as} \quad n \to \infty \end{gathered} \tag{10.64}$$

for all $i = 1, \ldots, N$. Now, applying (10.62) and (10.64) to (4.4), we derive the required convergence $\langle \Phi_n | H_{\text{elec}} \Psi_n \rangle \to \langle \Phi | H_{\text{elec}} \Psi \rangle$ as $n \to \infty$. The proof of Theorem 10.2 is over. □

11. Application to quantum chemistry.

Computing energy states of electrons in atoms, molecules, and ions and thus finding configurations of their chemical bonds is one of the important problems in quantum chemistry. Polylinear spline functions are applied to this problem through a slightly modified version of Theorem 9.1. Let $\Psi_1, \ldots, \Psi_m$ be linear independent eigenfunctions of the Schrödinger operator (2.3) associated with its eigenvalues

$$\mathcal{E}_{\min} = \mathcal{E}_1 \leqslant \ldots \leqslant \mathcal{E}_m. \tag{11.1}$$

Actually we do not know $\Psi_1, \ldots, \Psi_m$. But we know that they belong to the domain $D(H_{\text{elec}})$ of the operator H_{elec}. The domain $D(H_{\text{elec}})$ is enclosed in the domain $Q(H_{\text{elec}})$ of the sesquilinear form (4.4). Hence, applying Theorem 10.2, we conclude that the eigenfunctions $\Psi_1, \ldots, \Psi_m$ can be approximated by polylinear spline functions Ψ_{kn} in the sense of the relationships

$$\Psi_k = \lim_{n\to\infty} \Psi_{kn} \quad \text{and} \quad \exists \lim_{n\to\infty} \langle \Psi_{kn} | H_{\text{elec}} \Psi_{qn} \rangle = \langle \Psi_k | H_{\text{elec}} \Psi_q \rangle, \tag{11.2}$$

where $1 \leqslant k, q \leqslant m$. Without loss of generality we can assume that for each particular $n \in \mathbb{N}$ the functions $\Psi_{1n}, \ldots, \Psi_{mn}$ are associated with the same triangulated domain G_n and do vanish in the exterior of $G_n \times \ldots \times G_n$. Again without loss of generality we can assume that $G_n \subseteq G_{n+1}$ and that the triangulation of G_{n+1} inherits and partitions the triangulation of G_n. Under these assumptions we have the chain of complex finite-dimensional linear spaces (see (10.3))

$$\ldots \subseteq \text{PLSpline}(\mathbb{C}, G_n^N) \subseteq \text{PLSpline}(\mathbb{C}, G_{n+1}^N) \subseteq \ldots \tag{11.3}$$

such that

$$\Psi_{kn} \in \text{PLSpline}(\mathbb{C}, G_n^N) \quad \text{for} \quad k = 1, \ldots, m. \tag{11.4}$$

The relationships (11.2) are analogous to the relationships of (9.2) and (9.3) in Theorem 9.1. However, the analogy is incomplete. In this case we have no orthonormal basis $\{h_i\}_{i=1,\ldots,\infty}$ at all. Fortunately it is inessential. When proving Theorem 9.1 the basis vectors $h_1, \ldots, h_n$ were used in order to define the finite-dimensional space V_n in (7.9). In the present case we use (11.3) and set

$$V_n = \text{PLSpline}(\mathbb{C}, G_n^N). \tag{11.5}$$

The space $\mathcal{V}_n$ is defined by the formula

$$\mathcal{V}_n = \text{Span}(\Psi_{1n}, \ldots, \Psi_{mn}), \tag{11.6}$$

which formally coincides with (9.12). Due to (11.4) we have the embedding of the space (11.6) into the space (11.5):

$$\mathcal{V}_n \subset V_n. \tag{11.7}$$

None of the spaces (11.7) is enclosed in the domain $D(H_{\text{elec}})$ of the Schrödinger operator (2.3), but both of them are enclosed in the domain $Q(H_{\text{elec}})$ of its sesquilinear form $q(\Phi, \Psi) = \langle \Phi | H_{\text{elec}} \Psi \rangle$. Therefore we cannot restrict the operator H_{elec} to the spaces V_n and $\mathcal{V}_n$ directly, but we can define the unique operators F_{V_n} and $F_{\mathcal{V}_n}$ in V_n and $\mathcal{V}_n$ respectively by means of the following relationships:

$$q(\Phi, \Psi) = \langle \Phi | F_{V_n} \Psi \rangle \quad \text{for all} \quad \Phi, \Psi \in V_n, \tag{11.8}$$

$$q(\Phi, \Psi) = \langle \Phi | F_{\mathcal{V}_n} \Psi \rangle \quad \text{for all} \quad \Phi, \Psi \in \mathcal{V}_n. \tag{11.9}$$

The embedding (11.7) is analogous to (9.29). If we denote through P_n and $\mathcal{P}_n$ the orthogonal projectors onto the subspaces (11.5) and (11.6) respectively, then due to (11.7) we can write the relationship (9.30) for them. Moreover, we can write the relationship (9.31) for the operators F_{V_n} and $F_{\mathcal{V}_n}$, which are introduced through

(11.8) and (11.9) in the present case. Repeating the arguments from the proof of Theorem 9.1 we can write the inequalities

$$\hat{\mu}_k^{(n)} \leqslant \hat{\lambda}_k^{(n)}, \quad \text{where} \quad k = 1, \ldots, m, \tag{11.10}$$

which formally coincide with (9.32). Through $\hat{\lambda}_1^{(n)} \leqslant \ldots \leqslant \hat{\lambda}_m^{(n)}$ in (11.10) we denote the eigenvalues of the operator $F_{\mathcal{V}_n}$, while $\hat{\mu}_1^{(n)} \leqslant \ldots \leqslant \hat{\mu}_m^{(n)}$ represent the initial part of eigenvalues of the operator F_{V_n}.

In the present case we cannot apply Theorem 7.1 to the space V_n since V_n is not enclosed in $D(H_{\text{elec}})$, but we can apply its version where $D(F)$ is replaced by $Q(F)$ (see Remark to Theorems 7.1 and 7.2 on page 14). As a result we get

$$\mathcal{E}_k = \mu_k(H_{\text{elec}}) \leqslant \hat{\mu}_k^{(n)}, \quad \text{where} \quad k = 1, \ldots, m. \tag{11.11}$$

The inequalities (11.11) are analogous to the inequalities (9.28).

The third space $\mathcal{V}$ is introduced as the span of the eigenfunctions $\Psi_1, \ldots, \Psi_m$:

$$\mathcal{V} = \text{Span}(\Psi_1, \ldots, \Psi_m) \tag{11.12}$$

(compare with (9.7)). Unlike V_n and $\mathcal{V}_n$, the space (11.12) is enclosed in $D(H_{\text{elec}})$. The Schrödinger operator (2.3) restricted to $\mathcal{V}$ is denoted through F_V. In the basis $\Psi_1, \ldots, \Psi_m$ it is presented by the diagonal matrix

$$\mathcal{F} = \begin{Vmatrix} \mathcal{E}_1 & \ldots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \ldots & \mathcal{E}_m \end{Vmatrix}. \tag{11.13}$$

with the eigenvalues (11.1) in its diagonal. The matrix (11.13) is analogous to the matrix (9.6). Repeating the arguments from Section 9, from (11.2) we derive

$$\lim_{n\to\infty} \hat{\lambda}_k^{(n)} = \mathcal{E}_k \quad \text{for} \quad k = 1, \ldots, m \tag{11.14}$$

(compare with (9.26)). Then, combining (11.14) with the inequalities (11.10) and (11.11), we derive the following result:

$$\lim_{n\to\infty} \hat{\mu}_k^{(n)} = \mathcal{E}_k \quad \text{for} \quad k = 1, \ldots, m. \tag{11.15}$$

The result expressed by the relationships (11.15) is formulated as follows.

Theorem 11.1. *Assume that for a given configuration of the nuclei the discrete spectrum of the Schrödinger operator (2.3) is not empty and comprises at least m eigenvalues* $\mathcal{E}_{\min} = \mathcal{E}_1 \leqslant \ldots \leqslant \mathcal{E}_m$. *Then there is a chain of triangulated domains*

$$G_1 \subseteq \ldots \subseteq G_n \subseteq G_{n+1} \subseteq \ldots$$

in $\mathbb{R}^3$ *and the chain of polylinear spline spaces associated with them*

$$\text{PLSpline}(\mathbb{C}, G_1^N) \subseteq \ldots \subseteq \text{PLSpline}(\mathbb{C}, G_n^N) \subseteq \text{PLSpline}(\mathbb{C}, G_{n+1}^N) \subseteq \ldots$$

such that the initial eigenvalues $\hat{\mu}^{(n)}_{\min} = \hat{\mu}^{(n)}_1 \leqslant \ldots \leqslant \hat{\mu}^{(n)}_m$ *of the operator* F_{V_n} *produced in the space* $V_n = \mathrm{PLSpline}(\mathbb{C}, G^N_n)$ *by the sesquilinear form* (4.4) *approximate the eigenvalues* $\mathcal{E}_1 \leqslant \ldots \leqslant \mathcal{E}_m$ *in the sense of the relationships*

$$\lim_{n\to\infty} \hat{\mu}^{(n)}_k = \mathcal{E}_k, \quad \textit{where} \quad k = 1, \ldots, m.$$

The eigenfunctions $\Psi_1, \ldots, \Psi_m$ and spline approximations Ψ_{kn} of them are not explicitly present in Theorem 11.1. Their existence and their convergence properties (11.2) are provided by other theorems.

12. Conclusions and acknowledgments.

Note that the polylinear spline spaces $V_n = \mathrm{PLSpline}(\mathbb{C}, G^N_n)$ in Theorem 11.1 are finite-dimensional. The operators F_{V_n} in these spaces are discrete operators presented by matrices upon choosing some bases in them. These operators are called tetrahedral discretizations of the Schrödinger operator in the title of the paper. The spectra of their matrix presentations can be computed using powerful linear algebra tools in various computational packages.

Theorems 9.1 and 11.1 are the main results of this paper. They show that tetrahedral discretizations of the Schrödinger operator using polylinear spline functions are able to approximate spectra of electrons in atoms, molecules, and ions. The angular quality measure and the quality criterion for tetrahedral networks formulated in Definitions 10.10, 10.11, 10.12, and 10.13 can be applied for building faster computational algorithms. Practical computations exploiting the methods of this paper will be presented in forthcoming papers.

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13. Acknowledgments

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