

# Introduction to First-Principle Simulation of Molecular Systems

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**Abstract** First-principle molecular simulation aims at computing the physical and chemical properties of a molecule, or more generally of a material system, from the fundamental laws of quantum mechanics. It is widely used in various application fields ranging from quantum chemistry to materials science and molecular biology, and is the source of many very interesting and challenging mathematical and numerical problems. This chapter is an elementary introduction to this field, covering some modeling, mathematical, and numerical aspects.

## 1 Introduction

This chapter contains lecture notes of a 4 h introductory course to first-principle molecular simulation, delivered in June 2016 in Gijón, on the occasion of the XVII Jacques-Louis Lions Spanish-French School on Numerical Simulation in Physics and Engineering. First-principle molecular simulation aims at computing the physical and chemical properties of a molecule, or more generally of a material system, from the fundamental laws of quantum mechanics. Its power is that it can be used in principle to compute *any* property of *any* molecule or materials from its chemical formula. Its limitations are on the one hand that approximations are required to deal with the curse of dimensionality (see Sect. 5), and on the other hand that the computational costs of the approximate models increase fast with the size and complexity of the simulated system.

First-principle molecular simulation is used by thousands of physicists, chemists, biologists, materials scientists, and nanoscientists on a daily basis. Such simulations are reported in over 20,000 scientific articles published in 2015, and are the matter of about 15% of the high-performance computing (HPC) projects funded by PRACE (Partnership for Advanced Computing in Europe) in 2016. The importance of

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molecular simulation for the applications was acknowledged by the 1998 and 2013 Nobel prizes in Chemistry [43, 45, 50, 64, 77].

From a mathematical point of view, first-principle molecular simulation is an extremely rich field, which gives rise to a variety of interesting modeling, mathematical analysis, and numerical problems of different natures, ranging from easy to extremely difficult. The many mathematical models encountered in this field involve linear and nonlinear partial differential equations (PDEs), optimization problems, spectral theory, stochastic processes, high-performance computing, machine learning, as well as some tools of differential geometry (Berry curvature), non-commutative geometry ( $C^*$ -algebras), or algebraic topology (Chern classes). This is therefore a fantastic playground for mathematicians.

This chapter is organized as follows. In Sects. 2 and 3, we briefly present two fundamental mathematical tools, namely optimization in Hilbert spaces, and the spectral theory of self-adjoint operators, which are useful in many fields of mathematics, and are heavily relied upon in Sects. 4–7. The reader familiar with these tools can directly proceed to Sect. 4. In the latter, we introduce the (non-relativistic) quantum many-problem and the  $N$ -body Schrödinger equation, and we then apply this formalism to the special case of a molecular system in Sect. 5. In Sect. 6, we present the Hartree-Fock model, which is the simplest variational approximation of the central equation in first-principle molecular simulation, that is the  $N$ -electron Schrödinger equation. As will be seen throughout these notes, (linear and nonlinear) elliptic eigenvalue problems play a key role in this field. Section 7 is devoted to the numerical approximation of the eigenvalues of (linear) elliptic eigenvalue problems.

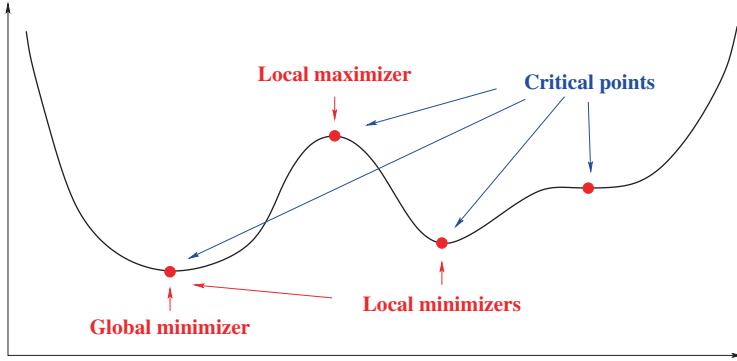
## 2 Optimization in Hilbert Spaces

It is well-known that if  $J : \mathbb{R} \rightarrow \mathbb{R}$  is differentiable, the set of the local minimizers of  $J$  is included in the set  $\mathcal{C} = \{x \in \mathbb{R} \mid J'(x) = 0\}$  of the critical points of  $J$ . The latter set contains all the local minimizers and maximizers of  $J$ , as well as points which are neither minimizers nor maximizers (see Fig. 1).

The purpose of this section is to extend this elementary result to unconstrained and constrained optimization problems in finite or infinite dimensional Hilbert spaces. Let us first recall some basic definitions.

In this section,  $V$  and  $W$  are two real Hilbert spaces. We denote by  $(\cdot, \cdot)_V$  and  $(\cdot, \cdot)_W$  the scalar products on  $V$  and  $W$  respectively, by  $\|\cdot\|_V$  and  $\|\cdot\|_W$  the associated norms, and by  $\mathcal{B}(V, W)$  the vector space of the continuous (also called bounded) linear maps from  $V$  to  $W$ . Recall that  $\mathcal{B}(V, W)$ , endowed with the norm defined by

$$\|A\|_{\mathcal{B}(V, W)} := \sup_{v \in V \setminus \{0\}} \frac{\|Av\|_W}{\|v\|_V},$$



**Fig. 1** Critical points of a simple differentiable function  $J : \mathbb{R} \rightarrow \mathbb{R}$

is a Banach space. The adjoint of a continuous linear map  $A \in \mathcal{B}(V, W)$  is the continuous linear map  $A^* \in \mathcal{B}(W, V)$  characterized by

$$\forall (v, w) \in V \times W, \quad (A^*w, v)_V = (w, Av)_W.$$

The above definition makes sense by virtue of Riesz representation theorem [69, Theorem II.4].

**Definition 1** Let  $U$  be an open subset of  $V$ ,  $F : U \rightarrow W$ , and  $v \in U$ . The function  $F$  is called differentiable at  $v$ , if there exists  $d_v F \in \mathcal{B}(V, W)$  such that in the vicinity of  $v$ ,

$$F(v + h) = F(v) + d_v F(h) + o(h),$$

which means

$$\forall \varepsilon > 0, \exists \eta > 0 \text{ s.t. } \forall h \in V \text{ s.t. } \|h\|_V \leq \eta, \text{ we have } v + h \in U \text{ and}$$

$$\|F(v + h) - F(v) - d_v F(h)\|_W \leq \varepsilon \|h\|_V.$$

If such a linear map  $d_v F$  exists, it is unique. It is called the derivative of  $F$  at  $v$ .

**Definition 2** The function  $F$  is called differentiable on  $U$  if  $F$  is differentiable at each point of  $U$ . In this case, the mapping

$$\begin{aligned} dF : U &\rightarrow \mathcal{B}(V, W) \\ v &\mapsto d_v F \end{aligned}$$

is called the derivative of  $F$ . The function  $F$  is called of class  $C^1$  on  $U$  if  $dF$  is continuous.

**Definition 3** Let  $U$  be an open subset of  $V$  and  $J : U \rightarrow \mathbb{R}$  a function differentiable at  $v \in U$ . The unique vector of  $V$  denoted by  $\nabla J(v)$  and uniquely defined<sup>1</sup> by

$$\forall h \in V, \quad d_v J(h) = (\nabla J(v), h)_V,$$

is called the gradient of  $J$  at  $v$ .

Note that the above abstract definition of the gradient agrees with the usual one when  $V$  is the space  $\mathbb{R}^d$  endowed with the Euclidean scalar product:

$$\forall h \in \mathbb{R}^d, \quad J(x+h) = J(x) + \sum_{i=1}^d \frac{\partial J}{\partial x_i}(x) h_i + o(h) = J(x) + \nabla J(x) \cdot h + o(h),$$

where

$$\nabla J(x) = \begin{pmatrix} \frac{\partial J}{\partial x_1}(x) \\ \vdots \\ \frac{\partial J}{\partial x_d}(x) \end{pmatrix}.$$

It is important to keep in mind the geometric interpretation of the gradient. Let  $J : V \rightarrow \mathbb{R}$  be a function of class  $C^1$ ,  $v \in V$  and  $\alpha = J(v)$ . If  $\nabla J(v) \neq 0$ , then

- in the vicinity of  $v$ , the level set

$$\mathcal{C}_\alpha := \{w \in V \mid J(w) = \alpha\}$$

is a  $C^1$  hypersurface (a codimension one  $C^1$  manifold);

- the vector  $\nabla J(v)$  is orthogonal to the affine hyperplane tangent to  $\mathcal{C}_\alpha$  at  $v$  and points toward the steepest ascent direction.

The first-order optimality condition for smooth unconstrained optimization problems in Hilbert spaces, that is for problems consisting in minimizing some differentiable real-valued function on an open subset of a Hilbert space, is a direct extension of the basic result for the one-dimensional case recalled at the beginning of the present section.

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<sup>1</sup>Again by Riesz representation theorem.

**Theorem 4 (Optimality Condition for Unconstrained Optimization Problems)**

Let  $J : V \rightarrow \mathbb{R}$  be a differentiable function. The set of the local minima of  $J$  is included in the set

$$\mathcal{C} = \{v \in V \mid d_v J = 0\} = \{v \in V \mid \nabla J(v) = 0\}$$

of the critical points of  $J$ .

The proof of this result is elementary and is left to the reader.

As a first example, consider  $V = \mathbb{R}^2$ , endowed with the Euclidean scalar product, and  $J : \mathbb{R}^2 \rightarrow \mathbb{R}$  defined by

$$\forall \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \in \mathbb{R}^2, \quad J(\mathbf{x}) = (x_1^3 + x_2^2) e^{-(x_1^2 + x_2^2)}. \quad (1)$$

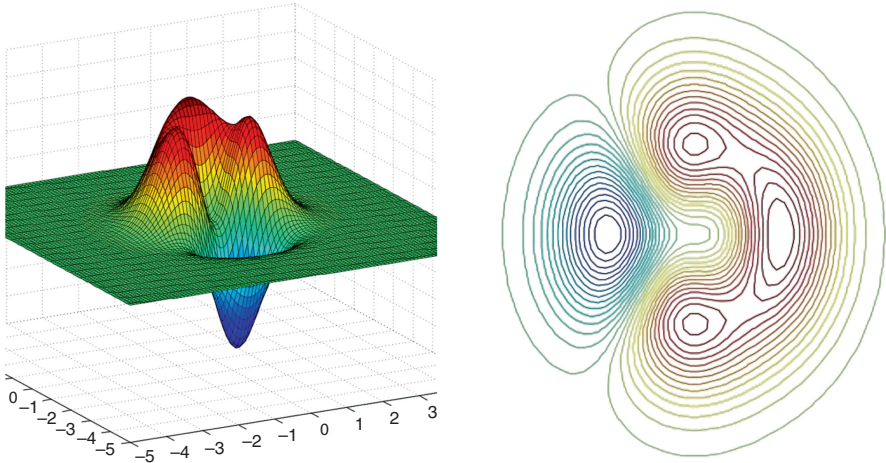
We have

$$\nabla J(\mathbf{x}) = \begin{pmatrix} x_1 (3x_1 - 2x_1^3 - 2x_2^2) e^{-(x_1^2 + x_2^2)} \\ 2x_2 (1 - x_1^3 - x_2^2) e^{-(x_1^2 + x_2^2)} \end{pmatrix} = 0 \quad \Leftrightarrow \quad (x_1, x_2) = \begin{cases} (0, 0), \\ (\pm\sqrt{3/2}, 0), \\ (0, \pm 1), \\ (2/3, \pm\sqrt{19/27}). \end{cases}$$

We can clearly see the positions of these seven critical points on the level set representation of the function  $J$  plotted on Fig. 2.

The second example is concerned with an infinite dimensional optimization problem in the Sobolev space

$$V = H^1(\mathbb{R}^d) = \{v \in L^2(\mathbb{R}^d) \mid \nabla v \in (L^2(\mathbb{R}^d))^d\},$$



**Fig. 2** Graphical representations of the function  $J$  defined by (1): 3D plot (*left*) and level sets (*right*)

endowed with its usual scalar product

$$(u, v)_{H^1} = \int_{\mathbb{R}^d} uv + \int_{\mathbb{R}^d} \nabla u \cdot \nabla v,$$

and the quadratic functional  $J : H^1(\mathbb{R}^d) \rightarrow \mathbb{R}$  defined by

$$\forall v \in H^1(\mathbb{R}^d), \quad J(v) = \frac{1}{2} \int_{\mathbb{R}^d} |\nabla v|^2 + \frac{1}{2} \int_{\mathbb{R}^d} v^2 - \int_{\mathbb{R}^d} f v,$$

where  $f$  is a given function of  $L^2(\mathbb{R}^d)$ . To compute the derivative of  $J$ , we proceed as follows. For  $v \in V$  and  $h \in V$ , we have

$$\begin{aligned} J(v+h) &= \frac{1}{2} \int_{\mathbb{R}^d} |\nabla(v+h)|^2 + \frac{1}{2} \int_{\mathbb{R}^d} (v+h)^2 - \int_{\mathbb{R}^d} f(v+h) \\ &= \frac{1}{2} \int_{\mathbb{R}^d} |\nabla v|^2 + \int_{\mathbb{R}^d} \nabla v \cdot \nabla h + \frac{1}{2} \int_{\mathbb{R}^d} |\nabla h|^2 + \frac{1}{2} \int_{\mathbb{R}^d} v^2 + \int_{\mathbb{R}^d} v h + \frac{1}{2} \int_{\mathbb{R}^d} h^2 \\ &\quad - \int_{\mathbb{R}^d} f v - \int_{\mathbb{R}^d} f h \\ &= J(v) + \int_{\mathbb{R}^d} \nabla v \cdot \nabla h + \int_{\mathbb{R}^d} v h - \int_{\mathbb{R}^d} f h + \frac{1}{2} \int_{\mathbb{R}^d} |\nabla h|^2 + \frac{1}{2} \int_{\mathbb{R}^d} h^2, \end{aligned}$$

with

$$\left| \int_{\mathbb{R}^d} \nabla v \cdot \nabla h + \int_{\mathbb{R}^d} v h - \int_{\mathbb{R}^d} f h \right| \leq C_{v,f} \|h\|_{H^1},$$

and

$$\left| \frac{1}{2} \int_{\mathbb{R}^d} |\nabla h|^2 + \frac{1}{2} \int_{\mathbb{R}^d} h^2 \right| = \frac{1}{2} \|h\|_{H^1}^2 = o(h).$$

This allows one to conclude that  $J$  is differentiable at  $v$  and that

$$\forall h \in V, \quad d_v J(h) = \int_{\mathbb{R}^d} \nabla v \cdot \nabla h + \int_{\mathbb{R}^d} v h - \int_{\mathbb{R}^d} f h.$$

By definition, the gradient of  $J$  at  $v$  is the function  $w \in H^1(\mathbb{R}^d)$  characterized by

$$\forall h \in V = H^1(\mathbb{R}^3), \quad (w, h)_{H^1} = d_v J(h) = \int_{\mathbb{R}^3} \nabla v \cdot \nabla h + \int_{\mathbb{R}^3} v h - \int_{\mathbb{R}^3} f h.$$

To compute  $w = \nabla J(v)$ , we therefore have to solve the linear elliptic problem

$$\begin{cases} \text{seek } w \in V \text{ such that} \\ \forall h \in V, \quad a(w, h) = L(h), \end{cases}$$

where

$$a(w, h) = \int_{\mathbb{R}^3} \nabla w \cdot \nabla h + \int_{\mathbb{R}^3} wh \quad \text{and} \quad L(h) = \int_{\mathbb{R}^3} \nabla v \cdot \nabla h + \int_{\mathbb{R}^3} vh - \int_{\mathbb{R}^3} fh,$$

or equivalently the PDE

$$\text{seek } w \in H^1(\mathbb{R}^3) \text{ such that } -\Delta w + w = -\Delta v + v - f \text{ in } \mathcal{D}'(\mathbb{R}^3),$$

where  $\mathcal{D}'(\mathbb{R}^3)$  is the space of distributions in  $\mathbb{R}^3$ . The integral kernel of the operator  $(-\Delta + 1)^{-1}$  being the Green function  $G(x, y) = \frac{e^{-|x-y|}}{4\pi|x-y|}$ , we therefore have

$$\nabla_v J(x) = v(x) - \int_{\mathbb{R}^3} \frac{e^{-|x-y|}}{4\pi|x-y|} f(y) dy.$$

Let us now turn to the more interesting case of equality constrained optimization problems. Let  $V$  and  $W$  be real Hilbert spaces such that  $\dim(W) < \infty$ ,  $J : V \rightarrow \mathbb{R}$ , and  $F : V \rightarrow W$ . We consider the optimization problem

$$\inf_{v \in K} J(v) \quad \text{where} \quad K = \{v \in V \mid F(v) = 0\}.$$

The first-order optimality conditions for the above problem are easy to state when the constraints  $F = 0$  are qualified in the following sense.

**Definition 5 (Qualification of the Constraints)** The equality constraints  $F = 0$  are called qualified at  $u \in K$  if  $d_u F : V \rightarrow W$  is surjective.

We are now in position to write down the central result of this section.

**Theorem 6** Let  $V$  and  $W$  be real Hilbert spaces such that  $\dim(W) < \infty$ ,  $J : V \rightarrow \mathbb{R}$ , and  $F : V \rightarrow W$ . Let  $u \in K$  be a local minimum of  $J$  on

$$K = \{v \in V \mid F(v) = 0\}.$$

Assume that

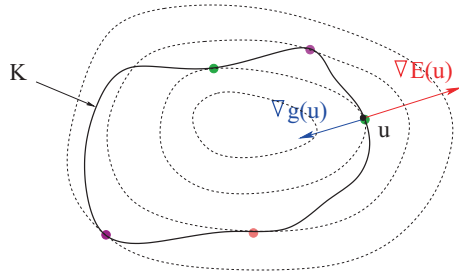
1.  $J$  is differentiable at  $u$  and  $F$  is  $C^1$  in the vicinity of  $u$ ;
2. the equality constraint  $F = 0$  is qualified at  $u$ .

Then, there exists a unique  $\lambda \in W$  such that

$$\forall h \in V, \quad d_u J(h) + (\lambda, d_u F(h))_W = 0 \quad \text{or equivalently} \quad \nabla J(u) + d_u F^*(\lambda) = 0,$$

where  $d_u F^*$  is the adjoint of  $d_u F$ . The vector  $\lambda \in W$  is called the Lagrange multiplier of the constraint  $F = 0$ .

**Fig. 3** Graphical illustration of Theorem 6 for  $V = \mathbb{R}^2$  and  $W = \mathbb{R}$ . Some level sets of  $J$  are represented in dashed closed curves, while  $K = F^{-1}(0)$  is represented by a solid closed curve. The five critical points of  $J$  on  $K$  are represented by bullets



Assume that the constraints are qualified at any point of  $K$ . The solutions of the Euler-Lagrange equations

$$\begin{cases} \text{seek } (u, \lambda) \in V \times W \text{ such that} \\ \nabla J(u) + d_u F^*(\lambda) = 0, \\ F(u) = 0, \end{cases} \quad (2)$$

are called the critical points of  $J$  on  $K$ . The set of critical points contains in particular the local minimizers and the local maximizers of  $J$  on  $K$ .

*Remark 7* If  $\dim(V) = d < \infty$  and  $\dim(W) = m < \infty$ , then the above problem consists of  $(d + m)$  scalar equations with  $(d + m)$  scalar unknowns.

A simple case when  $V = \mathbb{R}^2$  and  $W = \mathbb{R}$  is depicted on Fig. 3. On  $K = F^{-1}(0) = \{v \in V \mid F(v) = 0\}$ , the function  $J$  possesses

- two local minimizers, both global
- two local maximizers, among which the global maximizer
- one critical point which is neither a local minimizer nor a local maximizer.

*Sketch of the Proof of Theorem 6* Let  $u$  be a local minimizer of  $J$  on  $K = F^{-1}(0) = \{v \in V \mid F(v) = 0\}$  and  $\alpha = J(u)$ . If the constraint  $F = 0$  is qualified at  $u$  (i.e. if  $d_u F : \mathcal{H} \rightarrow \mathcal{K}$  is surjective), then, in the vicinity of  $u$ ,  $K$  is a  $C^1$  manifold and its affine tangent subspace at  $u$  is

$$u + T_u K = u + \{h \in V \mid d_u F(h) = 0\} = u + \text{Ker}(d_u F).$$

Since  $u$  is a minimizer of  $J$  on  $K$ , the vector  $\nabla J(u)$  must be orthogonal to  $T_u K$ . Indeed, for any  $h \in T_u K$ , there exists a  $C^1$  curve  $\phi : [-1, 1] \rightarrow V$  drawn on  $K$  such that  $\phi(0) = u$  and  $\phi'(0) = h$ , and we have

$$0 \leq J(\phi(t)) - J(u) = J(u + th + o(t)) - J(u) = t \nabla J(u) \cdot h + o(t).$$

Therefore,  $\nabla J(u) \cdot h = 0$ . In addition, it holds

$$\nabla J(u) \in (T_u K)^\perp = (\text{Ker}(d_u F))^\perp = \overline{\text{Ran}(d_u F^*)} = \text{Ran}(d_u F^*) \text{ since } \dim(W) < \infty.$$



Therefore, there exists  $\lambda \in W$  such that  $\nabla J(u) + d_u F^*(\lambda) = 0$ .  $\square$

Most often, Lagrange multipliers have a “physical” interpretation:

- in statistical mechanics [9], the equilibrium state of a chemical system interacting with its environment is obtained by maximizing the entropy (which is equivalent to minimizing minus the entropy) under the constraints that the energy, the volume and the concentration of chemical species are given on average: the corresponding Lagrange multipliers are respectively  $1/T$ ,  $P/T$  and  $\mu_i/T$ , where  $T$  is the temperature,  $P$  the pressure, and  $\mu_i$  the chemical potential of species  $i$ ;
- in fluid mechanics [25], the admissible dynamics of an incompressible fluid are the critical points of some action under the constraint that the density of the fluid remains constant ( $\text{div}(u) = 0$ ). The Lagrange multiplier of the incompressibility constraint is the pressure field;
- in microeconomics [66], prices are Lagrange multipliers arising in the optimization of utility functions under the constraints that some goods have limited availability.

Let us conclude this section with a result on the differentiability of functions defined by equality constrained optimization problems. Such a situation is encountered in many fields of science and engineering, and is very useful in first-principle molecular simulation to compute atomic forces (see Sects. 5 and 6) or molecular properties such as polarizabilities or hyperpolarizabilities [40]. Consider the function  $W : \mathbb{R}^d \rightarrow \mathbb{R}$  defined as

$$\forall \mathbf{x} \in \mathbb{R}^d, \quad W(\mathbf{x}) = \inf \{E(\mathbf{x}, v), v \in V, F(\mathbf{x}, v) = 0\}, \quad (3)$$

where  $E : \mathbb{R}^d \times V \rightarrow \mathbb{R}$ ,  $F : \mathbb{R}^d \times V \rightarrow W$ ,  $V$  and  $W$  being real Hilbert spaces such that  $\dim(W) < \infty$ .

Assume that for each  $x \in \mathbb{R}^d$ , problem (3) has a unique minimizer  $v(\mathbf{x})$ , and that the function  $\mathbf{x} \mapsto v(\mathbf{x})$  is regular. Then,

$$W(\mathbf{x}) = E(\mathbf{x}, v(\mathbf{x})) \quad \Rightarrow \quad \frac{\partial W}{\partial x_i}(\mathbf{x}) = \frac{\partial E}{\partial x_i}(\mathbf{x}, v(\mathbf{x})) + \frac{\partial E}{\partial v}(\mathbf{x}, v(\mathbf{x})) \left( \frac{\partial v}{\partial x_i}(\mathbf{x}) \right),$$

$$F(\mathbf{x}, v(\mathbf{x})) = 0 \quad \Rightarrow \quad \frac{\partial F}{\partial x_i}(\mathbf{x}, v(\mathbf{x})) + \frac{\partial F}{\partial v}(\mathbf{x}, v(\mathbf{x})) \left( \frac{\partial v}{\partial x_i}(\mathbf{x}) \right) = 0.$$

On the other hand, the Euler-Lagrange equations associated with the constrained optimization problem (3) give

$$\forall h \in V, \quad \frac{\partial E}{\partial v}(\mathbf{x}, v(\mathbf{x}))(h) + \left( \frac{\partial F}{\partial v}(\mathbf{x}, v(\mathbf{x}))(h), \lambda(\mathbf{x}) \right)_W = 0.$$

Therefore

$$\frac{\partial W}{\partial x_i}(\mathbf{x}) = \frac{\partial E}{\partial x_i}(\mathbf{x}, v(\mathbf{x})) + \left( \frac{\partial F}{\partial x_i}(\mathbf{x}, v(\mathbf{x})), \lambda(\mathbf{x}) \right). \quad (4)$$

This formula is very important for practical purposes: it implies that it is possible to compute the derivatives of  $W$  at  $\mathbf{x}$  without computing the derivatives of the minimizer  $v(\mathbf{x})$ . Only the state itself  $v(\mathbf{x})$  and the Lagrange multiplier  $\lambda(\mathbf{x})$  are necessary, and those quantities can be obtained by solving the Euler-Lagrange equations.

### 3 Introduction to the Spectral Theory of Self-adjoint Operators

The purpose of this section is to transpose to the case of self-adjoint operators on infinite-dimensional separable complex Hilbert spaces, the following well-known results on Hermitian<sup>2</sup> matrices:

1. the spectrum  $\sigma(A) = \{z \in \mathbb{C} \mid (z - A) \in \mathbb{C}^{d \times d} \text{ non-invertible}\}$  of a Hermitian matrix  $A \in \mathbb{C}^{d \times d}$  consists of the set

$$\begin{aligned} \sigma_p(A) &= \{z \in \mathbb{C} \mid (z - A) \in \mathbb{C}^{d \times d} \text{ non-injective}\} \\ &= \{z \in \mathbb{C} \mid \exists \mathbf{x} \in \mathbb{C}^d \setminus \{0\} \text{ s.t. } A\mathbf{x} = z\mathbf{x}\} \end{aligned}$$

of the eigenvalues of  $A$ , and  $\sigma(A) \subset \mathbb{R}$ ;

2. any Hermitian matrix  $A \in \mathbb{C}^{d \times d}$  can be diagonalized in an orthonormal basis:

$$A = \sum_{i=1}^d \lambda_i \mathbf{x}_i \mathbf{x}_i^*, \quad \lambda_i \in \sigma(A) \subset \mathbb{R}, \quad \mathbf{x}_i \in \mathbb{C}^d, \quad \mathbf{x}_i^* \mathbf{x}_j = \delta_{ij}, \quad A\mathbf{x}_i = \lambda_i \mathbf{x}_i. \quad (5)$$

Here  $\lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_d$  denote the  $d$  eigenvalues of  $A$  (counting multiplicities), and  $(\mathbf{x}_1, \dots, \mathbf{x}_d)$  an orthonormal basis of associated eigenvectors;

3. there exists a functional calculus for Hermitian matrices: for any Hermitian matrix  $A$ , and any  $f : \mathbb{R} \rightarrow \mathbb{C}$ , the matrix

$$f(A) := \sum_{i=1}^d f(\lambda_i) \mathbf{x}_i \mathbf{x}_i^* \quad (6)$$

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<sup>2</sup>Recall that a matrix  $A \in \mathbb{C}^{d \times d}$  is called Hermitian if  $A^* = A$  (i.e.  $\overline{A_{ij}} = A_{ji}$ ,  $\forall 1 \leq i, j \leq d$ ). If  $z \in \mathbb{C}$  and  $A \in \mathbb{C}^{d \times d}$ , we use the shorthand notation  $z - A$  to denote the matrix  $zI_d - A$ , where  $I_d$  is the rank- $d$  identity matrix. We proceed similarly with linear operators on complex Hilbert spaces.

is independent of the choice of the spectral decomposition of  $A$ , that is on the choice of the basis  $(\mathbf{x}_1, \dots, \mathbf{x}_d)$  of eigenvectors. This definition agrees with the usual definition of  $f(A)$  for polynomial functions  $f$ . Indeed, if  $f(\lambda) = \sum_{k=0}^n \alpha_k \lambda^k$ , then

$$f(A) = \sum_{i=1}^d f(\lambda_i) \mathbf{x}_i \mathbf{x}_i^* = \sum_{i=1}^d \left( \sum_{k=0}^n \alpha_k \lambda_i^k \right) x_i x_i^* = \sum_{k=0}^n \alpha_k \left( \sum_{i=1}^d \lambda_i^k x_i x_i^* \right) = \sum_{k=0}^n \alpha_k A^k.$$

The strength of formula (6) is that it makes sense for any function  $f : \mathbb{R} \rightarrow \mathbb{C}$ , while the definition based on a polynomial expansion of  $f$  only works for polynomial functions, and in the limit, for continuous functions by virtue of Weierstrass approximation theorem.

In this section,  $\mathcal{H}$  denotes a separable complex Hilbert space,  $\langle \cdot | \cdot \rangle$  its scalar product, and  $\| \cdot \|$  the associated norm.

### 3.1 Linear Operators on Hilbert Spaces

Let us first review some basic properties of *bounded* linear operators on Hilbert spaces.

**Definition 8 (Bounded Linear Operator)** A bounded operator on  $\mathcal{H}$  is a linear map  $A : \mathcal{H} \rightarrow \mathcal{H}$  such that

$$\|A\| := \sup_{u \in \mathcal{H} \setminus \{0\}} \frac{\|Au\|}{\|u\|} < \infty.$$

In other words, a bounded operator on  $\mathcal{H}$  is an element of  $\mathcal{B}(\mathcal{H}) := \mathcal{B}(\mathcal{H}, \mathcal{H})$ .

**Theorem 9** The set  $\mathcal{B}(\mathcal{H})$  of bounded operators on  $\mathcal{H}$  is a non-commutative algebra and  $\| \cdot \|$  is a norm on the algebra  $\mathcal{B}(\mathcal{H})$ :

$$\forall (A, B) \in \mathcal{B}(\mathcal{H}) \times \mathcal{B}(\mathcal{H}), \quad \|AB\| \leq \|A\| \|B\|. \quad (7)$$

Endowed with the norm  $\| \cdot \|$ ,  $\mathcal{B}(\mathcal{H})$  is a Banach algebra.

The proof that  $\| \cdot \|$  is a norm on  $\mathcal{B}(\mathcal{H})$  is elementary, as well as the one of (7). Regarding the completeness of  $\mathcal{B}(\mathcal{H})$  for the resulting topology, we refer e.g. to [69, Theorem III.2].

Note that, in view of Riesz representation theorem, a bounded linear operator  $B$  is uniquely defined by the values of the sesquilinear form  $\mathcal{H} \times \mathcal{H} \ni (u, v) \mapsto \langle u | Bv \rangle \in \mathbb{C}$ . This is the reason why the following definition makes sense.

**Definition 10 (Adjoint of a Bounded Linear Operator)** Let  $A \in \mathcal{B}(\mathcal{H})$ . The operator  $A^* \in \mathcal{B}(\mathcal{H})$  defined by

$$\forall (u, v) \in \mathcal{H} \times \mathcal{H}, \quad \langle u | A^* v \rangle = \langle Au | v \rangle, \quad (8)$$

is called the adjoint of  $A$ . The operator  $A$  is called self-adjoint if  $A^* = A$ .

Endowed with its norm  $\| \cdot \|$  and the  $*$  operation,  $\mathcal{B}(\mathcal{H})$  is in fact a  $C^*$ -algebra [5]:

$$(A^*)^* = A, \quad \|A^*\| = \|A\|, \quad \text{and} \quad \|A^* A\| = \|A\|^2.$$

Many linear operators arising in quantum mechanics are not bounded operators on some Hilbert space. This is the case for instance of the kinetic energy operator, formally defined as  $T = -\frac{\hbar^2}{2m}\Delta$ . We therefore have to introduce the concept of (non-necessarily bounded) linear operators on Hilbert spaces.

**Definition 11 (Linear Operator)** A linear operator on  $\mathcal{H}$  is a linear map  $A : D(A) \rightarrow \mathcal{H}$ , where  $D(A)$  is a subspace of  $\mathcal{H}$  called the domain of  $A$ .

Note that bounded linear operators are special linear operators, for which  $D(A) = \mathcal{H}$  and  $A : \mathcal{H} \rightarrow \mathcal{H}$  is continuous.

**Definition 12 (Extensions of Operators)** Let  $A_1$  and  $A_2$  be operators on  $\mathcal{H}$ .  $A_2$  is called an extension of  $A_1$  if  $D(A_1) \subset D(A_2)$  and if  $\forall u \in D(A_1), A_2 u = A_1 u$ .

**Definition 13 (Unbounded Linear Operator)** An operator  $A$  on  $\mathcal{H}$  which does not possess a bounded extension is called an unbounded operator on  $\mathcal{H}$ .

A possible way to extend the notion of bounded self-adjoint operator to the case of unbounded operators is the following.

**Definition 14 (Symmetric Operator)** A linear operator  $A$  on  $\mathcal{H}$  with dense domain  $D(A)$  is called symmetric if

$$\forall (u, v) \in D(A) \times D(A), \quad \langle Au | v \rangle = \langle u | Av \rangle. \quad (9)$$

Criterion (9) is simple and usually quite easy to check, but, unfortunately, symmetric operators are not very interesting. Only self-adjoint operators—which we are going to introduce—represent physical observables and have nice mathematical properties reminiscent of those of Hermitian matrices (real spectrum, spectral decomposition, functional calculus).

**Definition 15 (Adjoint of a Linear Operator with Dense Domain)** Let  $A$  be a linear operator on  $\mathcal{H}$  with dense domain  $D(A)$ , and  $D(A^*)$  the vector space defined as

$$D(A^*) = \{v \in \mathcal{H} \mid \exists w_v \in \mathcal{H} \text{ s.t. } \forall u \in D(A), \langle Au | v \rangle = \langle u | w_v \rangle\}.$$

The linear operator  $A^*$  on  $\mathcal{H}$ , with domain  $D(A^*)$ , defined by

$$\forall v \in D(A^*), \quad A^*v = w_v,$$

(if  $w_v$  exists, it is unique since  $D(A)$  is dense) is called the adjoint of  $A$ .

Note that this definition agrees with definition (8) for bounded operators.

**Definition 16 (Self-adjoint Operator)** A linear operator  $A$  with dense domain is called self-adjoint if  $A^* = A$  (that is if  $A$  symmetric and  $D(A^*) = D(A)$ ).

Any self-adjoint operator is symmetric, but the converse is not true. As mentioned previously, only self-adjoint operators have interesting mathematical properties. While it is usually easy to check that a given operator is symmetric, proving self-adjointness is not trivial and often relies on deep theorems of linear operator theory. We will not elaborate on these technicalities in these lectures notes and refer the reader to the literature [67]. We will only provide a short list of self-adjoint operators commonly encountered in first-principle molecular simulation:

- free-particle Hamiltonian (or kinetic energy operator)

$$\mathcal{H} = L^2(\mathbb{R}^d), \quad D(T) = H^2(\mathbb{R}^d), \quad \forall u \in D(T), \quad Tu = -\frac{\hbar^2}{2m}\Delta u,$$

where  $m > 0$  is the mass of the particle, and  $\hbar$  the reduced Planck constant;

- Schrödinger operators with confining potential  $V \in C^0(\mathbb{R}^d)$  s.t.  $V(x) \xrightarrow{|x| \rightarrow +\infty} +\infty$

$$\mathcal{H} = L^2(\mathbb{R}^d), \quad D(H) = \left\{ u \in L^2(\mathbb{R}^d) \mid -\frac{\hbar^2}{2m}\Delta u + Vu \in L^2(\mathbb{R}^d) \right\}$$

$$\forall u \in D(H), \quad Hu = -\frac{\hbar^2}{2m}\Delta u + Vu;$$

- Schrödinger operators with uniformly locally  $L^2$  potentials in dimension 3, i.e.

$$V \in L^2_{\text{unif}}(\mathbb{R}^3) := \left\{ u \in L^2_{\text{loc}}(\mathbb{R}^3) \mid \sup_{x \in \mathbb{R}^3} \int_{x+[0,1]^3} |u|^2 < \infty \right\},$$

$$\mathcal{H} = L^2(\mathbb{R}^d), \quad D(H) = H^2(\mathbb{R}^3), \quad \forall u \in D(H), \quad Hu = -\frac{\hbar^2}{2m}\Delta u + Vu.$$

### 3.2 Spectrum

The following definition is a natural extension of the definition of the spectrum of a square matrix  $A \in \mathbb{C}^{d \times d}$ .

**Definition 17 (Spectrum of a Linear Operator)** Let  $A$  be a closed<sup>3</sup> linear operator on  $\mathcal{H}$ . Then

- the set  $\rho(A) = \{z \in \mathbb{C} \mid (z - A) : D(A) \rightarrow \mathcal{H} \text{ invertible}\}$  is called the resolvent set of  $A$ ;
- the set  $\sigma(A) = \mathbb{C} \setminus \rho(A)$  is called the spectrum of  $A$ .

As for Hermitian matrices, the spectrum of a self-adjoint operator  $A$  is always a subset of  $\mathbb{R}$ . On the other hand, it does not only contains the set of the eigenvalues of  $A$ , that is the set of the complex numbers  $z$  such that  $(z - A) : D(A) \rightarrow \mathcal{H}$  is *injective*. Indeed, even in the case when  $D(A) = \mathcal{H}$ , the linear map  $(z - A)$  can be injective and not surjective since  $\mathcal{H}$  is infinite dimensional.

**Theorem 18 (Spectrum and Resolvent)** Let  $A$  be a closed linear operator on  $\mathcal{H}$ . Then

- the resolvent set  $\rho(A)$  is an open subset of  $\mathbb{C}$  and the function

$$\rho(A) \ni z \mapsto R_z(A) := (z - A)^{-1} \in \mathcal{B}(\mathcal{H})$$

is analytic. It is called the resolvent of  $A$ . It holds

$$\forall (z, z') \in \rho(A) \times \rho(A), \quad R_z(A) - R_{z'}(A) = (z' - z)R_z(A)R_{z'}(A).$$

The above equality is called the resolvent identity;

- the spectrum  $\sigma(A)$  of  $A$  is a closed subset of  $\mathbb{C}$ .

**Theorem 19 (Spectrum of a Self-adjoint Operator)** Let  $A$  be a self-adjoint operator on  $\mathcal{H}$ . Then  $A$  is closed,  $\sigma(A) \subset \mathbb{R}$ , and it holds

$$\sigma(A) = \sigma_p(A) \cup \sigma_c(A),$$

where  $\sigma_p(A)$  and  $\sigma_c(A)$  are respectively

- the point spectrum of  $A$

$$\sigma_p(A) = \{z \in \mathbb{C} \mid (z - A) : D(A) \rightarrow \mathcal{H} \text{ non-injective}\} = \{\text{eigenvalues of } A\};$$

- the continuous spectrum of  $A$

$$\sigma_c(A) = \overline{\{z \in \mathbb{C} \mid (z - A) : D(A) \rightarrow \mathcal{H} \text{ injective but non surjective}\}}.$$

The mathematical decomposition of the spectrum of a self-adjoint operator into point and continuous spectra has an interesting physical counterpart, which will

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<sup>3</sup>The operator  $A$  is called closed if its graph  $\Gamma(A) := \{(u, Au), u \in D(A)\}$  is a closed subspace of  $\mathcal{H} \times \mathcal{H}$ .

be presented in the next section. The following alternative decomposition of the spectrum is fundamental both for theoretical and numerical purposes, as will be seen in Sect. 7.

**Definition 20** Let  $A$  be a closed linear operator on  $\mathcal{H}$ . Then  $\sigma(A) = \sigma_d(A) \cup \sigma_{\text{ess}}(A)$  where

$$\begin{aligned}\sigma_d(A) &= \{\text{isolated eigenvalues of } A \text{ with finite multiplicities}\} \quad (\text{discrete spectrum}); \\ \sigma_{\text{ess}}(A) &= \sigma(A) \setminus \sigma_d(A) \quad (\text{essential spectrum}).\end{aligned}$$

The essential spectrum therefore consists of

- the continuous spectrum;
- the eigenvalues of infinite multiplicities;
- the eigenvalues embedded in the continuous spectrum.

**Theorem 21 (Weyl)** Let  $A$  be a self-adjoint operator on  $\mathcal{H}$  and  $B$  a symmetric operator on  $\mathcal{H}$  with domain  $D(A)$  such that  $B(A + i)^{-1} \in \mathcal{L}(\mathcal{H})$  is compact. Then  $A + B$ , with  $D(A + B) = D(A)$  is self-adjoint and  $\sigma_{\text{ess}}(A + B) = \sigma_{\text{ess}}(A)$ .

Weyl theorem allows in particular to prove the following result, which covers many interesting cases arising in first-principle molecular simulation.

**Corollary 22** Let  $\alpha > 0$  and  $V \in L^2(\mathbb{R}^3) + L^\infty_\varepsilon(\mathbb{R}^3)$ , where

$$\begin{aligned}L^2(\mathbb{R}^3) + L^\infty_\varepsilon(\mathbb{R}^3) &:= \{V \in L^2_{\text{loc}}(\mathbb{R}^3) \mid \forall \varepsilon > 0, \exists (V_2, V_\infty) \in L^2(\mathbb{R}^3) \times L^\infty(\mathbb{R}^3) \\ &\text{such that } V = V_2 + V_\infty, \|V_\infty\|_{L^\infty} \leq \varepsilon\}.\end{aligned}$$

Then the operator  $H = -\alpha\Delta + V$  is self-adjoint on  $L^2(\mathbb{R}^3)$  with domain  $H^2(\mathbb{R}^3)$  and  $\sigma_{\text{ess}}(H) = [0, +\infty)$ .

We conclude this brief introduction to spectral theory, with the famous min-max principle, which gives a variational characterization of the discrete eigenvalues (with their multiplicities) located below the bottom of the essential spectrum of a bounded below self-adjoint operator.

**Theorem 23 (Min-Max Principle, Courant-Fisher Formula)** Let  $A$  be a bounded below self-adjoint operator on  $\mathcal{H}$ ,  $Q(A)$  its form domain,<sup>4</sup> and  $a$  its associated quadratic form. For each  $j \in \mathbb{N}^*$ , we define

$$\lambda_j(A) = \inf_{w_j \in \mathcal{E}_j} \sup_{w \in W_j \setminus \{0\}} \frac{a(w, w)}{\|w\|^2},$$

<sup>4</sup>Since  $A$  is bounded below, there exists  $C \in \mathbb{R}$  s.t.  $(u, v)_{Q(A)} := \langle u|Av \rangle + C\langle u|v \rangle$  is a scalar product on  $D(A)$ . The Cauchy closure of  $D(A)$  for the associated norm is a Hilbert space, independent of  $C$ , called the form domain of  $A$ . The quadratic form associated with  $A$  is the unique continuous extension of  $(u, v) \mapsto \langle u|Av \rangle$  to  $Q(A)$ .

where  $\mathcal{E}_j$  is the set of the  $j$ -dimensional subspaces of  $Q(A)$ . Then,

- if  $A$  has at least  $j$  eigenvalues lower than  $\min \sigma_{\text{ess}}(A)$  (taking multiplicities into account), then  $\lambda_j(A)$  is the smallest  $j$ th eigenvalue of  $A$ ;
- otherwise,  $\lambda_j(A) = \min \sigma_{\text{ess}}(A)$ .

## 4 The Quantum Many-Body Problem

According to the first principles of quantum mechanics, an isolated quantum system is described by

- a state space  $\mathcal{H}$  (a complex Hilbert space);
- a Hamiltonian  $H$  (a self-adjoint operator on  $\mathcal{H}$ );
- other observables (i.e. self-adjoint operators on  $\mathcal{H}$ ) allowing one to connect theory and experiments.

The state<sup>5</sup> of the system at time  $t$  is completely characterized by a wavefunction  $\Psi(t) \in \mathcal{H}$  such that  $\|\Psi(t)\|_{\mathcal{H}} = 1$ . Its dynamics is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi}{dt}(t) = H\Psi(t), \quad (10)$$

where we recall that  $\hbar$  is the reduced Planck constant. The steady states are by definition states of the form  $\Psi(t) = f(t)\psi$ , where  $f(t) \in \mathbb{C}$  and  $\psi \in \mathcal{H}$ . Inserting the Ansatz  $\Psi(t) = f(t)\psi$  in (10) and separating the variables, we obtain that the function  $f$  is just a physically irrelevant phase factor<sup>6</sup>:  $f(t) = e^{-iEt/\hbar}$ , with  $E \in \mathbb{R}$  is homogenous to an energy. The function  $\psi$  satisfies the time-independent Schrödinger equation

$$H\psi = E\psi, \quad \|\psi\|_{\mathcal{H}} = 1.$$

The energy  $E$  is therefore an eigenvalue of the Hamiltonian  $H$  and  $\psi$  an associated normalized eigenvector.

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<sup>5</sup>We limit ourselves to pure states in these lectures notes.

<sup>6</sup>It may seem weird that steady states explicitly depend on time. This apparent paradox is due to the fact that a state is in fact an element of the projective space  $(\mathcal{H} \setminus \{0\})/\mathbb{C}^*$ , so that  $f(t)\psi$  and  $\psi$  actually represent the exact same state.



## 4.1 One-Particle Systems

The above formalism is completely general, and valid for any isolated quantum system. Let us now deal with specific systems of physical interest, starting with a very simple one: a spinless particle of mass  $m$  subjected to an external potential  $V_{\text{ext}}$ . In this case, the state space is  $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C})$  and the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\Delta + V_{\text{ext}},$$

which, under assumptions on  $V_{\text{ext}}$  (see some examples in Sect. 3.1), is a self-adjoint operator on  $\mathcal{H}$ . In the so-called position representation, the wavefunction has a clear physical meaning:  $|\Psi(t, \mathbf{r})|^2$  is the probability density of observing the particle at point  $\mathbf{r}$  at time  $t$ . Note that it follows from the normalization condition that

$$\int_{\mathbb{R}^3} |\Psi(t, \mathbf{r})|^2 d\mathbf{r} = \|\Psi(t)\|_{\mathcal{H}}^2 = 1.$$

The time-dependent Schrödinger equation then takes the form of a partial differential equation (PDE):

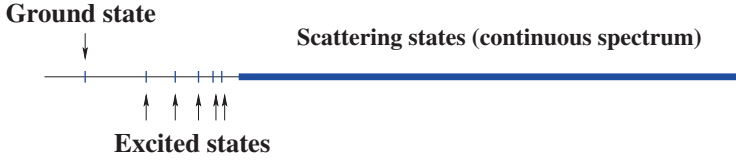
$$i\hbar \frac{\partial \Psi}{\partial t}(t, \mathbf{r}) = -\frac{\hbar^2}{2m}\Delta \Psi(t, \mathbf{r}) + V_{\text{ext}}(\mathbf{r})\Psi(t, \mathbf{r}).$$

Likewise, the time-independent Schrödinger equation reads in this case as an elliptic linear eigenvalue problem:

$$-\frac{\hbar^2}{2m}\Delta \psi(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

The spectrum of  $H$  strongly depends on  $V_{\text{ext}}$  (see Sect. 3.2). The spectrum of the free Hamiltonian ( $V_{\text{ext}} = 0$ ) is purely continuous and equal to  $\mathbb{R}_+$ . For confining potentials, the spectrum of  $H$  is purely discrete and consists of an increasing sequence of real eigenvalues of finite multiplicities going to  $+\infty$ . For one-particle or mean-field Hamiltonians usually encountered in first-principle models of finite molecular systems, the potential  $V_{\text{ext}}$  vanishes at infinity,  $\sigma_{\text{ess}}(H) = \mathbb{R}_+$ , and  $\sigma_{\text{d}}(H)$  can be either empty (no bound states), or consist of a finite or infinite increasing sequence of negative eigenvalues of finite multiplicities. If  $H$  has negative eigenvalues, the lowest one is called the ground state energy. If  $V_{\text{ext}}$  is not too singular (see [68, Theorem XIII.46] for details), it is non-degenerate. The higher eigenvalues are called excited state energies. If  $H$  has infinitely many negative eigenvalues, then they necessarily accumulate at 0, the bottom of the essential spectrum. This is the case for instance for the Hamiltonian of the hydrogen atom: the discrete spectrum of the Hamiltonian

$$H = -\frac{\hbar^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}$$



**Fig. 4** Typical spectrum of one-particle Hamiltonians encountered in first-principle simulation of finite molecular systems



**Fig. 5** Emission spectrum of atomic hydrogen in the visible range

on  $L^2(\mathbb{R}^3)$  is the Rydberg series  $(E_n)_{n \in \mathbb{N}^*}$ , where  $E_n = -\frac{E_{\text{Ryd}}}{n^2}$ , and where

$$E_{\text{Ryd}} := \frac{m_e}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2$$

is the Rydberg energy. Here  $m_e$  is the electron mass,  $e$  the elementary charge, and  $\epsilon_0$  the dielectric permittivity of the vacuum (Fig. 4).

When this model is coupled to a quantized electromagnetic field, transitions between electronic energy levels may occur. The electron of the hydrogen atom may jump from a higher energy level  $E_m$  to a lower one  $E_n$  ( $m > n$ ) by emitting a photon of energy  $h\nu_{m \rightarrow n} = E_m - E_n$  ( $h = 2\pi\hbar$  is the Planck constant and  $\nu_{m \rightarrow n}$  the frequency of the photon), or, conversely, absorb a photon of energy  $h\nu_{m \rightarrow n}$  and jump from the energy level  $E_n$  to the energy level  $E_m$ . As a consequence, the transitions between electronic levels are quantized. This is the reason why the emission and absorption spectra of molecular gases consist of rays (see Fig. 5). In the case of the hydrogen atom, four rays lay in the visible spectrum (wavelengths between 400 and 700 nm). They are part of the Balmer series (transitions between  $E_m$  and  $E_2$ ) and can be easily measured experimentally:

$$\lambda_{6 \rightarrow 2}^{\text{exp}} = 410.17 \text{ nm}, \lambda_{5 \rightarrow 2}^{\text{exp}} = 434.05 \text{ nm}, \lambda_{4 \rightarrow 2}^{\text{exp}} = 486.13 \text{ nm}, \lambda_{3 \rightarrow 2}^{\text{exp}} = 656.28 \text{ nm}.$$

Using the relation  $\lambda_{m \rightarrow n} = c/\nu_{m \rightarrow n}$ , where  $c$  is the speed of light, the wavelengths of the electronic transitions are given by

$$\lambda_{m \rightarrow n} = \frac{8\pi\hbar c}{E_{\text{Ryd}}} \left( \frac{1}{n^2} - \frac{1}{m^2} \right)^{-1},$$

which leads to the following numerical results

$$\lambda_{6 \rightarrow 2} = 410.07 \text{ nm}, \lambda_{5 \rightarrow 2} = 433.94 \text{ nm}, \lambda_{4 \rightarrow 2} = 486.01 \text{ nm}, \lambda_{3 \rightarrow 2} = 656.11 \text{ nm}.$$

The slight discrepancies between these results and the experimental ones are due to the fact that the motion of the nucleus and the relativistic effects have not been taken into account. Replacing the electron mass  $m_e$  with the reduced mass  $m_e m_p / (m_e + m_p)$ , where  $m_p$  is the proton mass, and adding to the non-relativistic Hamiltonian the so-called Breit terms [30], experimental values can be recovered with a very high relative accuracy of the order of  $10^{-8}$ .

The above discussion provides a physical interpretation of the discrete spectrum of the Hamiltonian of the hydrogen atom. Let us now turn to the continuous spectrum.

**Theorem 24 (RAGE Theorem, Ruelle [70], Amrein and Georgescu [3], Enss [33])** *Let  $H$  be a locally compact<sup>7</sup> self-adjoint operator on  $L^2(\mathbb{R}^d)$ . Let*

$$\mathcal{H}_p = \overline{\text{Span}\{\text{eigenvectors of } H\}} \quad \text{and} \quad \mathcal{H}_c = \mathcal{H}_p^\perp.$$

*Let  $\chi_{B_R}$  be the characteristic function of the ball  $B_R = \{\mathbf{r} \in \mathbb{R}^d \mid |\mathbf{r}| < R\}$ . Then,*

$$(\phi_0 \in \mathcal{H}_p) \Leftrightarrow \forall \varepsilon > 0, \exists R > 0, \forall t \geq 0, \left\| (1 - \chi_{B_R}) e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 \leq \varepsilon;$$

$$(\phi_0 \in \mathcal{H}_c) \Leftrightarrow \forall R > 0, \lim_{T \rightarrow +\infty} \frac{1}{T} \int_0^T \left\| \chi_{B_R} e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 dt = 0.$$

The physical meaning of this result is the following: if the particle is in the quantum state  $\phi_0$  at  $t = 0$ , then its state at time  $t$  is the solution at time  $t$  of the time-dependent Schrödinger equation (10) with initial datum  $\phi_0$ , that is  $\psi(t) = e^{-itH/\hbar} \phi_0$ . In view of the physical interpretation of the wavefunction in the position representation,

$$\left\| \chi_{B_R} e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 = \int_{B_R} |\psi(t, \mathbf{r})|^2 d\mathbf{r}$$

<sup>7</sup>An operator  $A$  on  $L^2(\mathbb{R}^d)$  such that  $\rho(A) \neq \emptyset$  is called locally compact if for any bounded set  $B$ , the operator  $\chi_B(z - A)^{-1}$  is a compact operator on  $L^2(\mathbb{R}^d)$  for some (and then all by virtue of the resolvent formula)  $z \in \rho(A)$ . Here,  $\chi_B$  is the characteristic function of  $B$ ; in the expression  $\chi_B(z - A)^{-1}$ ,  $\chi_B$  should be understood as the multiplication operator by the bounded function  $\chi_B$ , which is a bounded self-adjoint operator on  $\mathcal{H}$ . The Hamiltonian of the hydrogen atom is a locally compact self-adjoint operator on  $L^2(\mathbb{R}^3)$ , and for this operator,  $\dim(\mathcal{H}_p) = \dim(\mathcal{H}_c) = \infty$ .

is the probability that the particle lays inside the ball  $B_R$  at time  $t$ , while

$$\left\| (1 - \chi_{B_R}) e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 = \int_{\mathbb{R}^3 \setminus B_R} |\psi(t, \mathbf{r})|^2 d\mathbf{r}$$

is the probability that the particle lays outside the ball  $B_R$  at time  $t$ .

The subspace  $\mathcal{H}_p$  can therefore be seen as a set of bound states, and the subspace  $\mathcal{H}_c$  as a set of scattering states:

- if  $\phi_0 \in \mathcal{H}_p$ , then the particle essentially remains in the vicinity of the nucleus at all times;
- if  $\phi_0 \in \mathcal{H}_c$ , then the particle scatters away from the nucleus. Note that in the case of the hydrogen atom, which has no singular continuous spectrum [68, Section XIII.10], the convergence is stronger:  $\left\| \chi_{B_R} e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2$  goes to zero when  $t$  goes to infinity.

## 4.2 Many-Particle Systems

The state space  $\mathcal{H}$  of a quantum system consisting of two spinless particles is always a closed subspace of  $L^2(\mathbb{R}^3, \mathbb{C}) \otimes L^2(\mathbb{R}^3, \mathbb{C}) \equiv L^2(\mathbb{R}^6, \mathbb{C})$ , and, in the position representation, if the system is in the pure state  $\Psi(t)$  at time  $t$ , then  $|\Psi(t, \mathbf{r}_1, \mathbf{r}_2)|^2$  is the probability density of observing at time  $t$  particle 1 at  $\mathbf{r}_1$  and particle 2 at  $\mathbf{r}_2$ . The precise structure of  $\mathcal{H}$  depends of the natures of the two particles<sup>8</sup>:

- for two different particles:  $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \otimes L^2(\mathbb{R}^3, \mathbb{C})$ ;
- for two identical bosons (e.g. two carbon 12 nuclei),  $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \vee L^2(\mathbb{R}^3, \mathbb{C})$ , where  $\vee$  denotes the symmetrized tensor product. Otherwise stated, the wavefunction  $\Psi$  must satisfy the symmetry condition

$$\Psi(t, \mathbf{r}_2, \mathbf{r}_1) = \Psi(t, \mathbf{r}_1, \mathbf{r}_2);$$

- for two identical fermions (e.g. two electrons),  $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \wedge L^2(\mathbb{R}^3, \mathbb{C})$ , where  $\wedge$  denotes the antisymmetrized tensor product. In other words, the wavefunction  $\Psi$  must satisfy the antisymmetry condition, also called Pauli principle,

$$\Psi(t, \mathbf{r}_2, \mathbf{r}_1) = -\Psi(t, \mathbf{r}_1, \mathbf{r}_2).$$

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<sup>8</sup>For simplicity, we omit the spin variables. See Remark 25 below for more details.

Note that for two identical particles, whatever they are bosons or fermions, the particle density is given by

$$\rho(t, \mathbf{r}) = \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}, \mathbf{r}_2)|^2 d\mathbf{r}_2 + \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}_1, \mathbf{r})|^2 d\mathbf{r}_1 = 2 \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}, \mathbf{r}_2)|^2 d\mathbf{r}_2.$$

Consider now  $N$  quantum particles of masses  $m_1, \dots, m_N$  subjected to an external potential  $V_{\text{ext}}(\mathbf{r})$  and pair-interaction potentials  $W_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ . The state space  $\mathcal{H}$  then is a closed subspace of  $L^2(\mathbb{R}^3, \mathbb{C}) \otimes \dots \otimes L^2(\mathbb{R}^3, \mathbb{C}) \equiv L^2(\mathbb{R}^{3N}, \mathbb{C})$ , whose precise structure depends on the natures of the  $N$  particles. In the case of  $N$  identical bosons,  $\mathcal{H} = \vee^N L^2(\mathbb{R}^3, \mathbb{C})$ , while in the case of  $N$  identical fermions,  $\mathcal{H} = \wedge^N L^2(\mathbb{R}^3, \mathbb{C})$ . Likewise, if the state of the system at time  $t$  is characterized by the wavefunction  $\Psi(t) \in \mathcal{H}$  in the position representation, then  $|\Psi(t, \mathbf{r}_1, \dots, \mathbf{r}_N)|^2$  is the probability density of observing at time  $t$  particle 1 at  $\mathbf{r}_1$ , particle 2 at  $\mathbf{r}_2$ , etc. The time-independent Schrödinger equation of such a system reads

$$\left( -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} W_{ij}(\mathbf{r}_i, \mathbf{r}_j) \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

and therefore has the structure of a  $3N$ -dimensional linear elliptic eigenvalue problem.

In general, such an equation is extremely difficult to solve. However, in the special case of  $N$  *non-interacting* identical particles of mass  $m$  subjected to an external potential  $V_{\text{ext}}(\mathbf{r})$ , the Hamiltonian becomes separable

$$H = -\sum_{i=1}^N \frac{\hbar^2}{2m} \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) = \sum_{i=1}^N \mathfrak{h}_{\mathbf{r}_i}$$

and all the bound states of  $H$  can be easily computed from the bound states of the three-dimensional Schrödinger operator  $\mathfrak{h}$ :

$$\begin{cases} \mathfrak{h} \phi_i = \varepsilon_i \phi_i, & \varepsilon_1 \leq \varepsilon_2 \leq \dots, \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \\ \mathfrak{h} = -\frac{\hbar^2}{2m} \Delta + V_{\text{ext}}. \end{cases}$$

In particular, if  $\mathfrak{h}$  is bounded below and has at least one (for bosons) or  $N$  (for fermions) eigenvalues below the bottom of the essential spectrum, then  $H$  has a ground state:

- the bosonic ground state energy is  $E_0 = N\varepsilon_1$  and the ground state wavefunction and density are given by

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi_1(\mathbf{r}_i) \quad \text{and} \quad \rho(\mathbf{r}) = N|\phi_1(\mathbf{r})|^2;$$

- the fermionic ground state energy is  $E_0 = \sum_{i=1}^N \varepsilon_i$ , a ground state wavefunction is the Slater determinant

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det(\phi_i(\mathbf{r}_j)) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \cdots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix},$$

and the corresponding density is  $\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$ .

## 5 First-Principle Molecular Simulation

First-principle molecular simulation is based on a simple observation:

- any molecule is a set of  $M$  nuclei and  $N$  electrons in Coulomb interaction;
- the state space  $\mathcal{H}$  is the subset of  $L^2(\mathbb{R}^{3(M+N)}, \mathbb{C})$  defined by the suitable symmetry and antisymmetry constraints for identical bosons and fermions;
- the Hamiltonian of the molecule is

$$H = - \sum_{k=1}^M \frac{1}{2m_k} \Delta_{\mathbf{R}_k} - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (11)$$

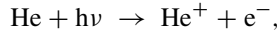
Here, we have used atomic units, that is the set of units such that

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\epsilon_0 = 1.$$

Remarkably, the Hamiltonian (11) is free of empirical parameters specific to the molecular system, and it can be deduced from the mere chemical formula of the latter. Likewise, any physical observable associated with the system and can be written down from the first-principles of quantum mechanics. Quoting Dirac [28],

*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved.*

The model described above is extremely accurate, at least for light atoms, for which relativistic effects can be neglected. As a matter of example, let us consider the computation of the ionization energy of the helium atom. The ionization process is the reaction



in which a helium atom absorbs a photon; if the energy of the photon is larger than a threshold value  $\Delta E = h\Delta\nu$ , one of the two electrons of the atom is kicked out of its bound state and escapes to infinity. The threshold frequency  $\Delta\nu$  can be measured experimentally with high accuracy. Two different experiments on helium 4 (the most common isotope of helium, whose nucleus contains four nucleons: two protons and two neutrons) performed in 1997 and 1998 respectively lead to the following results:

$$\Delta\nu^{\text{exp.1}} \simeq 5,945,204,238 \text{ MHz [32]} \quad \text{and} \quad \Delta\nu^{\text{exp.2}} \simeq 5,945,204,356 \text{ MHz [11]}.$$

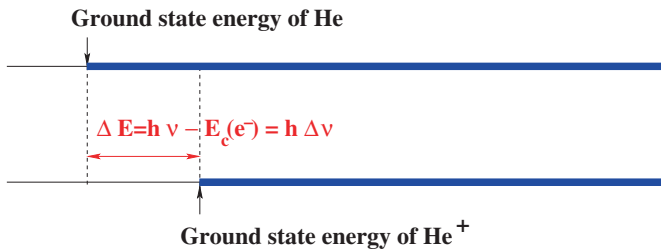
From a theoretical point of view,  $\Delta\nu$  can be computed as  $\Delta\nu = \Delta E/h$ , where  $\Delta E = \min(\sigma(H_{\text{He}^+})) - \min(\sigma(H_{\text{He}}))$ , where  $\sigma(H_{\text{He}^+})$  and  $\sigma(H_{\text{He}})$  are the spectra of the operators

$$H_{\text{He}} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

and

$$H_{\text{He}^+} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|},$$

respectively (see Fig. 6), where  $m$  denotes the mass of the Helium 4 nucleus. It can be shown that  $\min(\sigma(H_{\text{He}^+})) = -2$ . Using translational and rotational invariance, the quantity  $\min(\sigma(H_{\text{He}}))$  can be obtained by solving a three-dimensional linear elliptic eigenvalue problem. A careful calculation reported in [47] gives:  $\Delta E^{\text{calc.1}} = 5,945,262,288 \text{ MHz}$ . Taking relativistic corrections (Breit terms) into account gives  $\Delta E^{\text{calc.2}} = 5,945,204,223 \text{ MHz}$ , to be compared with the experimental



**Fig. 6** Spectra of the Hamiltonians  $H_{\text{He}}$  and  $H_{\text{He}^+}$

values reported above. The agreement between theory and experiment is therefore exceptionally good.

Let us now turn to the more complicated case of a polyatomic system. As a matter of example, we will deal with a water molecule  $\text{H}_2\text{O}$ , which consists of  $M = 3$  atomic nuclei (1 oxygen 16 nucleus, and 2 hydrogen 1 nuclei<sup>9</sup>) and  $N = 10$  electrons in Coulomb interaction. Such a system can be fully described by the laws of quantum mechanics (many-body Schrödinger equation) and statistical physics. The only parameters of these models are

- a few fundamental constants of physics

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad \varepsilon_0 = (4\pi)^{-1},$$

$$c \simeq 137.0359996287515 \dots, \quad k_B = 3.16681537 \dots \times 10^{-6},$$

where  $c$  is the speed of light and  $k_B$  the Boltzmann constant (all the values are in atomic units);

- the charges and masses of the hydrogen 1 and oxygen 16 nuclei

$$z_H = 1, \quad z_O = 8, \quad m_H = 1836.152701 \dots, \quad m_O = 29156.944123 \dots$$

We then observe that the ratio  $m_e/m_n$  (electron mass/nucleus mass) is very small, even for the lightest nucleus (hydrogen 1). Following Born and Oppenheimer, this suggests to use this ratio as a small parameter to approximate the many-body Schrödinger equation. The procedure described in the sequel can be justified to some point with mathematically rigorous arguments; we refer the interested reader to the literature cited below. The so-called Born-Oppenheimer method can be decomposed in two steps:

- step 1: definition of the potential energy surfaces;
- step 2: analysis of the potential energy surfaces.

Let us first detail the first step. Assuming that the  $M$  nuclei are clamped point-like particles located at positions  $\mathbf{R}_1, \dots, \mathbf{R}_M$ ,  $\mathbf{R}_k \in \mathbb{R}^3$ , the electronic problem for the nuclear configuration  $\{\mathbf{R}_k\}_{1 \leq k \leq M}$  consists in computing the bound states of the  $N$  electrons in the electrostatic potential

$$V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

---

<sup>9</sup>These are the most common isotopes of oxygen and hydrogen.



generated by the nuclei. For the water molecule, we have:  $M = 3$ ,  $N = 10$ ,  $z_1 = 8$ ,  $z_2 = 1$ ,  $z_3 = 1$ . The electronic bound states are obtained by solving the time-independent Schrödinger equation

$$\left( -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \psi(\mathbf{r}_1, \dots, \mathbf{r}_N).$$

Since electrons are fermions, the wavefunction  $\psi$  must satisfy the antisymmetry condition

$$\forall p \in \mathfrak{S}_N, \quad \psi(\mathbf{r}_{p(1)}, \dots, \mathbf{r}_{p(N)}) = \varepsilon(p) \psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (\text{Pauli principle}).$$

The electronic density associated with  $\psi$  is

$$\rho_\psi(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N, \quad (12)$$

and the normalization condition  $\|\psi\|_{L^2} = 1$  ensures that

$$\int_{\mathbb{R}^3} \rho_\psi(\mathbf{r}) d\mathbf{r} = N.$$

*Remark 25* For simplicity, we omit here the spin variables. In fact, electrons are particles of spin  $s = 1/2$ , so that the one-electron state space is not  $L^2(\mathbb{R}^3, \mathbb{C})$  but

$$L^2(\mathbb{R}^3, \mathbb{C}^{2s+1}) = L^2(\mathbb{R}^3, \mathbb{C}^2) \equiv L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C}),$$

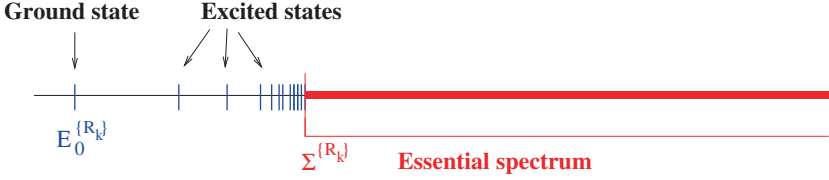
where  $|\uparrow\rangle$  and  $|\downarrow\rangle$  respectively denote the spin-up and spin-down states. An  $N$ -electron wavefunction therefore is a vector of  $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C})$ , that is a complex-valued function of the variables  $(\mathbf{r}_1, \sigma_1; \dots, \mathbf{r}_N, \sigma_N) \in (\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\})^N$  satisfying the antisymmetry condition

$$\forall p \in \mathfrak{S}_N, \quad \psi(\mathbf{r}_{p(1)}, \sigma_{p(1)}; \dots; \mathbf{r}_{p(N)}, \sigma_{p(N)}) = \varepsilon(p) \psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N).$$

In this framework,  $|\psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)|^2$  represents the probability density of observing electron 1 at  $\mathbf{r}_1$  in the spin state  $\sigma_1$ , electron 2 at  $\mathbf{r}_2$  in the spin state  $\sigma_2$ , etc.

The structure of the spectrum of the electronic Hamiltonian

$$H_N^{\{\mathbf{R}_k\}} = -\sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



**Fig. 7** Graphical illustration of Zhislin's theorem

on  $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C})$  with domain  $\mathcal{H}_N \cap H^2(\mathbb{R}^{3N})$ , which can be proved to be self-adjoint, is given by Zhislin's theorem (illustrated by Fig. 7).

**Theorem 26 (Zhislin [79])** *If  $N \leq \sum_{k=1}^M z_k$  (neutral or positively charged system), then*

$$\sigma_d(H_N^{\{\mathbf{R}_k\}}) = \{E_n^{\{\mathbf{R}_k\}}\}_{n \in \mathbb{N}} \quad \text{and} \quad \sigma_{\text{ess}}(H_N^{\{\mathbf{R}_k\}}) = [\Sigma_N^{\{\mathbf{R}_k\}}, +\infty),$$

where  $(E_n^{\{\mathbf{R}_k\}})_{n \in \mathbb{N}}$  is a nondecreasing sequence of negative eigenvalues<sup>10</sup> converging to  $\Sigma^{\{\mathbf{R}_k\}}$ , the bottom of the essential spectrum of  $H_N^{\{\mathbf{R}_k\}}$ . Besides  $\Sigma_N^{\{\mathbf{R}_k\}} = 0$  if  $N = 1$  and  $\Sigma^{\{\mathbf{R}_k\}} < 0$  if  $N \geq 1$ .

It can also be shown (HVZ theorem [42, 76, 78]) that  $\Sigma_N^{\{\mathbf{R}_k\}} = \min \sigma(H_{N-1}^{\{\mathbf{R}_k\}})$ .

The lowest eigenvalue  $E_0^{\{\mathbf{R}_k\}}$  is called the ground state energy of  $H_N^{\{\mathbf{R}_k\}}$ , while the eigenvalues  $E_n^{\{\mathbf{R}_k\}} > E_0^{\{\mathbf{R}_k\}}$  are called the excited state energies of  $H_N^{\{\mathbf{R}_k\}}$ . For each  $n \in \mathbb{N}$ , the function  $\mathbb{R}^{3M} \ni (\mathbf{R}_1, \dots, \mathbf{R}_M) \mapsto E_n^{\{\mathbf{R}_k\}} \in \mathbb{R}$  is continuous. This can be proved using e.g. the minmax principle (Theorem 23), or Kato's perturbation theory of self-adjoint operators [44]. Using the latter approach, it can be shown in addition that this function is  $C^1$  at  $(\mathbf{R}_1, \dots, \mathbf{R}_M)$  whenever  $E_n^{\{\mathbf{R}_k\}}$  is a nondegenerate eigenvalue of  $H_N^{\{\mathbf{R}_k\}}$ .

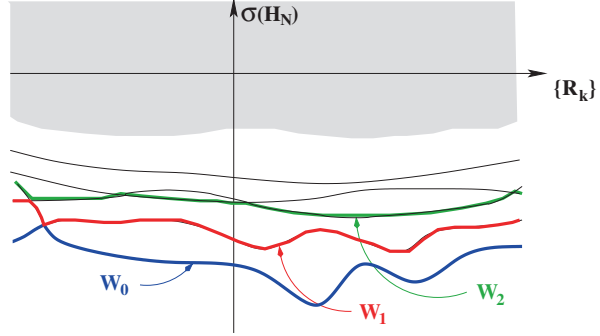
The potential energy surfaces are then defined as the real-valued functions  $W_n$  on  $\mathbb{R}^{3M}$ ,  $n \in \mathbb{N}$ , defined by

$$W_n(\mathbf{R}_1, \dots, \mathbf{R}_M) = E_n^{\{\mathbf{R}_k\}} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (13)$$

The function  $W_0$  is called the ground state potential energy surface (PES), the function  $W_1$  the first excited state PES, etc. (Fig. 8).

<sup>10</sup>Eigenvalues are counted with their multiplicities, so that  $E_0^{\{\mathbf{R}_k\}} \leq E_1^{\{\mathbf{R}_k\}} \leq E_2^{\{\mathbf{R}_k\}} \dots$ , with a priori large inequalities.

**Fig. 8** Sketch of the potential energy surfaces  $W_n$



Let us now turn to the second step, that is the analysis of the potential energy surfaces. Usually,<sup>11</sup> the Born-Oppenheimer approximation is invoked at this point. This approximation is based on the fact that

1. the ratio  $m_e/m_n$  (electron mass/nucleus mass) is small, which allows one to somehow decouple the electronic and nuclear dynamics by means of an adiabatic limit [61]. At low enough temperature (usually from 0 K to room temperature or more), it can be considered for most systems that the wave function of the molecular system at time  $t$  can be approximated by a wave function of the form

$$\psi^{\text{BO}}(t; \mathbf{R}_1, \dots, \mathbf{R}_M; \mathbf{r}_1, \dots, \mathbf{r}_N) = \Phi(t; \mathbf{R}_1, \dots, \mathbf{R}_M) \psi^{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

where  $\psi^{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is a normalized ground state of  $H_N^{\{\mathbf{R}_k\}}$ , that is a  $L^2$ -normalized eigenfunction of the electronic Hamiltonian  $H_N^{\{\mathbf{R}_k\}}$  associated with the ground state eigenvalue  $E_0^{\{\mathbf{R}_k\}}$ , assumed here to be non-degenerate;

2. nuclei are heavy particles, so that their dynamics can be well-approximated by the classical Newton equation

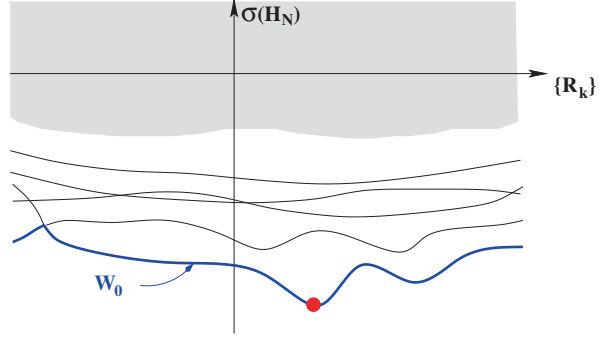
$$m_k \frac{d^2 \mathbf{R}_k}{dt^2}(t) = -\nabla_{\mathbf{R}_k} W_0(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t)), \quad 1 \leq k \leq M. \quad (14)$$

This equation is obtained from the Schrödinger equation on  $\Phi(t; \mathbf{R}_1, \dots, \mathbf{R}_M)$  resulting from the adiabatic approximation, by letting the reduced Planck constant  $\hbar$  go to zero (semiclassical limit, see [1, 2] and references therein).

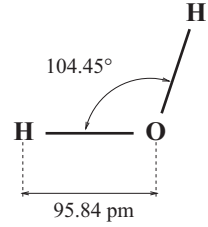
Equation (14), together with the definition (13) for  $n = 0$  of the ground state PES, are the fundamental equations of first-principle molecular dynamics. According to this model, the nuclei behave as point-like classical particles interacting via the effective  $M$ -body potential  $W_0$ .

<sup>11</sup>Breakdowns of the adiabatic approximation are studied in [14, 22, 35].

**Fig. 9** Within the Born-Oppenheimer approximation, the global minimizers of  $W_0$  correspond to the most stable configurations of the system



**Fig. 10** Equilibrium configuration of the water molecule (experimental values)

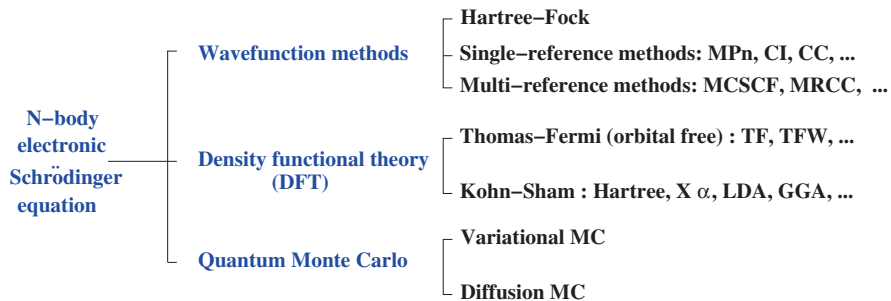


It follows from (14) that the local minima of  $W_0$  correspond to equilibrium configurations of the system. In particular, global minima of  $W_0$  correspond to the most stable configurations of the molecular system under consideration (Fig. 9). The water molecule has a single global minimum (up to translations and rotations), corresponding to the configuration depicted on Fig. 10.

The limiting step for integrating numerically the first-principle molecular dynamics Eq. (14) is the computation of the effective forces  $-\nabla_{\mathbf{R}_k} W_0(\mathbf{R}_1, \dots, \mathbf{R}_M)$  experienced by the nuclei. The nucleus-nucleus interaction is explicit and easy to deal with. The main issue is the computation of  $-\nabla_{\mathbf{R}_k} E_0^{\{\mathbf{R}_1, \dots, \mathbf{R}_M\}}$ . Since  $E_0^{\{\mathbf{R}_1, \dots, \mathbf{R}_M\}}$  is the ground state eigenvalue of  $H_N^{\{\mathbf{R}_k\}}$ , it can be obtained by solving the constrained optimization problem

$$E_0^{\{\mathbf{R}_1, \dots, \mathbf{R}_M\}} = \inf \left\{ \langle \psi | H_N^{\{\mathbf{R}_k\}} | \psi \rangle, \psi \in \bigwedge^N L^2(\mathbb{R}^3) \cap H^1(\mathbb{R}^{3N}), \|\psi\|_{L^2} = 1 \right\}. \quad (15)$$

This problem has the same structure as problem (3), which implies that it is not necessary to compute the first derivatives of the minimizers with respect to the  $\mathbf{R}_k$ 's to compute  $-\nabla_{\mathbf{R}_k} E_0^{\{\mathbf{R}_1, \dots, \mathbf{R}_M\}}$ . In addition, since the constraint  $\|\psi\|_{L^2} = 1$  does



**Fig. 11** Classification of the main electronic structure methods

not depend explicitly on the  $\mathbf{R}_k$ 's, the gradients  $-\nabla_{\mathbf{R}_k} E_0^{\{\mathbf{R}_1, \dots, \mathbf{R}_M\}}$  can be computed explicitly from the minimizer  $\psi_0^{\{\mathbf{R}_k\}}$ . A simple calculation shows that

$$-\nabla_{\mathbf{R}_k} W_0(\mathbf{R}_1, \dots, \mathbf{R}_M) = z_k \int_{\mathbb{R}^3} \rho_0^{\{\mathbf{R}_k\}}(\mathbf{r}) \frac{\mathbf{r} - \mathbf{R}_k}{|\mathbf{r} - \mathbf{R}_k|^3} d\mathbf{r} + \sum_{l \neq k} z_k z_l \frac{\mathbf{R}_k - \mathbf{R}_l}{|\mathbf{R}_k - \mathbf{R}_l|^3},$$

where the ground state density

$$\rho_0^{\{\mathbf{R}_k\}}(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\psi_0^{\{\mathbf{R}_k\}}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N,$$

is the electronic density associated with the ground state wavefunction  $\psi_0^{\{\mathbf{R}_k\}}$ . Since the electronic Schrödinger equation is a  $3N$ -dimensional PDE, it is not possible to solve it accurately for systems containing more than a couple of electrons. Several approximations have been proposed along the past 80 years, which can be classified in three main groups (see Fig. 11). Describing all these methods is out of the scope of this introductory lecture notes. We will only focus on the simplest of them, namely the Hartree-Fock method, which will be presented in the next section. We refer the reader to [40] for a comprehensive monograph on wavefunction methods, to [29, 34] for reference textbooks on DFT, to [7] for a several relevant contributions, including a mathematical introduction to quantum Monte Carlo methods, and to [4, 17–19, 24, 26, 37–39, 48, 51, 53–60, 71, 74] and reference therein for various mathematical and numerical works on these models.

Let us mention that the various avatars of the Kohn-Sham model [10, 46, 62, 63, 73, 75] are the most widely used models in the present time, since it is generally considered as the best compromise between computational efficiency and accuracy. The mathematical structure of the Kohn-Sham LDA model is quite similar to the one of the Hartree-Fock model we are now going to discuss.

## 6 Hartree-Fock Approximation

In this section, we assume that the nuclear configuration  $\{\mathbf{R}_k\}$  is given, and we focus on the calculation of the electronic ground state energy  $E_0^{\{\mathbf{R}_k\}}$  and of the electronic components  $-\nabla_{\mathbf{R}_k} E_0^{\{\mathbf{R}_k\}}$  of the atomic forces. In order to simplify the notation, we set  $E_0 := E_0^{\{\mathbf{R}_k\}}$ ,  $\rho_0 := \rho_0^{\{\mathbf{R}_k\}}$ ,

$$H_N := -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{and} \quad V^{\text{ne}}(\mathbf{r}) := -\sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}.$$

Recall that the operator  $H_N$  is self-adjoint on  $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3)$  with domain  $D(H_N) = \mathcal{H}_N \cap H^2(\mathbb{R}^{3N})$  and form domain  $Q(H_N) = \mathcal{H}_N \cap H^1(\mathbb{R}^{3N})$ , and that the ground state energy can be obtained as

$$E_0 = \inf \{ \langle \psi | H_N | \psi \rangle, \psi \in \mathcal{W}_N \},$$

where

$$\mathcal{W}_N = \left\{ \psi \in \bigwedge^N L^2(\mathbb{R}^3) \cap H^1(\mathbb{R}^{3N}), \|\psi\|_{L^2} = 1 \right\}.$$

The Hartree-Fock approximation is a variational approximation consisting in minimizing the exact energy functional  $\langle \psi | H_N | \psi \rangle$  on the subset of  $\mathcal{W}_N$  defined as

$$\left\{ \psi_\Phi, \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

where

$$\psi_\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) := \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

is the Slater determinant constructed with the functions  $\phi_1, \dots, \phi_N$ .

Rewriting  $\langle \psi_\Phi | H_N | \psi_\Phi \rangle$  as a function of  $\Phi = (\phi_1, \dots, \phi_N)$ , we obtain after some technical manipulations that the Hartree-Fock ground state energy is

$$E_0^{\text{HF}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\},$$

where the Hartree-Fock energy functional is defined by

$$E^{\text{HF}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V^{\text{ne}} \\ + \underbrace{\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{Coulomb term}} - \underbrace{\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{exchange term}},$$

with

$$V^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}, \quad \gamma_{\Phi}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r}) \phi_i(\mathbf{r}'), \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2.$$

Since the Hartree-Fock approximation is variational, we have  $E_0 \leq E_0^{\text{HF}}$ . The function  $\rho_{\Phi}$  is the electronic density associated with  $\Phi$ . It is easy to check that  $\rho_{\Phi} = \rho_{\psi_{\Phi}}$ , where  $\rho_{\psi_{\Phi}}$  is the density associated with the  $N$ -body wavefunction  $\psi_{\Phi}$  by (12). The function  $\gamma_{\Phi}$  is called the (one-electron) density matrix associated with  $\Phi$ . It holds

$$\gamma_{\Phi}(\mathbf{r}, \mathbf{r}') = N \int_{\mathbb{R}^{3(N-1)}} \psi_{\Phi}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi_{\Phi}(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N.$$

The Hartree-Fock model enjoys a gauge invariance property: if  $\Phi \in (H^1(\mathbb{R}^3))^N$  satisfies the  $L^2$ -orthonormality constraints, then so does  $\Phi U$  for all  $U \in O(N)$  and  $E(\Phi U) = E(\Phi)$ . This is due to the fact that  $\psi_{\Phi U} = \det(U) \psi_{\Phi}$ . This property is used in the proof of the fifth statement of the following theorem.

**Theorem 27** Assume that  $N \leq Z := \sum_{k=1}^M z_k$  (neutral or positively charged molecular system). Then

1. the Hartree-Fock model has a ground state  $\Phi^0 = (\phi_1^0, \dots, \phi_N^0)$  [56];
2. Euler-Lagrange equations: there exists  $\lambda \in \mathbb{R}^{N \times N}$  symmetric such that

$$\left\{ \begin{array}{l} \Phi^0 = (\phi_1^0, \dots, \phi_N^0) \in (H^1(\mathbb{R}^3))^N \\ -\frac{1}{2} \Delta \phi_i^0 + V^{\text{ne}} \phi_i^0 + (\rho_{\Phi^0} \star |\cdot|^{-1}) \phi_i^0 - \int_{\mathbb{R}^3} \frac{\gamma_{\Phi^0}(\cdot, \mathbf{r}')}{|\cdot - \mathbf{r}'|} \phi_i^0(\mathbf{r}') d\mathbf{r}' = \sum_{j=1}^N \lambda_{ij} \phi_j^0 \\ \int_{\mathbb{R}^3} \phi_i^0 \phi_j^0 = \delta_{ij}; \end{array} \right.$$

3. elliptic regularity:  $\phi_i^0 \in H^2(\mathbb{R}^3) \cap C^{0,1}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{\mathbf{R}_k\})$ ;

4. *Fock operator:*

$$\mathcal{F}_{\Phi^0} := -\frac{1}{2}\Delta + V^{\text{nc}} + \rho_{\Phi^0} \star |\cdot|^{-1} + \mathcal{K}_{\Phi^0},$$

where

$$(\mathcal{K}_{\Phi^0}\phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{\gamma_{\Phi^0}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}',$$

defines a self-adjoint operator on  $L^2(\mathbb{R}^3)$  with domain  $H^2(\mathbb{R}^3)$  and form domain  $H^1(\mathbb{R}^3)$ . It is bounded below and  $\sigma_{\text{ess}}(H_0) = [0, +\infty)$ ;

5. *Hartree-Fock equations:* up to replacing  $\Phi^0$  by  $\Phi^0 U$  for some  $U \in O(N)$ , it holds

$$\mathcal{F}_{\Phi^0}\phi_i^0 = \varepsilon_i\phi_i^0, \quad \int_{\mathbb{R}^3} \phi_i^0 \phi_j^0 = \delta_{ij}, \quad \varepsilon_1 \leq \dots \leq \varepsilon_N < 0;$$

6. *Aufbau principle:*  $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$  are the lowest  $N$  eigenvalues of  $\mathcal{F}_{\Phi^0}$ , counting multiplicities;
7. *no unfilled-shell property* [8]:  $\varepsilon_N < \varepsilon_{N+1}$  where  $\varepsilon_{N+1} = \lambda_{N+1}(\mathcal{F}_{\Phi^0})$  is the  $(N+1)^{\text{st}}$  eigenvalue of  $\mathcal{F}_{\Phi^0}$  (counting multiplicities) if  $\mathcal{F}_{\Phi^0}$  has at least  $(N+1)$  negative eigenvalues and 0 otherwise.

The Hartree-Fock model can be solved numerically by means of a Galerkin approximation. Let  $\mathcal{X} = \text{Span}(\chi_1, \dots, \chi_{N_b})$  be a subspace of  $H^1(\mathbb{R}^3)$  of finite dimension  $N_b$ . An upper bound  $E_{0,\mathcal{X}}^{\text{HF}}$  of the exact Hartree-Fock ground state energy  $E_0^{\text{HF}}$ , which is itself an upper bound of the exact ground state energy  $E_0$  of the electronic Hamiltonian, is obtained by minimizing the Hartree-Fock energy functional on the sets of orbitals in  $\mathcal{X} = \text{Span}(\chi_1, \dots, \chi_{N_b})$  satisfying the  $L^2$  orthonormality conditions:

$$E_0 \leq E_0^{\text{HF}} \leq E_{0,\mathcal{X}}^{\text{HF}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}.$$

Denoting by  $C = [C_{\mu i}]_{1 \leq \mu \leq N_b, 1 \leq i \leq N}$  the matrix collecting the coefficients of the orbitals  $\phi_1, \dots, \phi_N$  in the basis  $(\chi_1, \dots, \chi_{N_b})$ ,

$$\phi_i(\mathbf{r}) = \sum_{\mu=1}^{N_b} C_{\mu i} \chi_{\mu}(\mathbf{r}),$$

the discretized Hartree-Fock model can be written as

$$E_{0,\mathcal{X}}^{\text{HF}} = \inf \{ E^{\text{HF}}(CC^T), C \in \mathbb{R}^{N_b \times N}, C^T SC = I_N \},$$



where

$$E^{\text{HF}}(D) = \text{Tr}(hD) + \frac{1}{2} \text{Tr}(G(D)D), \quad [G(D)]_{\mu\nu} = \sum_{\kappa\lambda} [(\mu\nu|\kappa\lambda) - (\mu\lambda|\kappa\nu)] D_{\kappa\lambda},$$

and where the entries of the overlap matrix  $S$ , the core Hamiltonian matrix  $h$ , and the two-electron integrals  $(\mu\lambda|\kappa\nu)$  are defined as

$$S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu, \quad h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu - \sum_{k=1}^M z_k \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r}, \quad (16)$$

and

$$(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\kappa(\mathbf{r}') \chi_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (17)$$

A fundamental observation made by Boys in the 1950s [15] is that if the  $\chi_\mu$ 's are gaussian-polynomial functions, i.e. functions of the form

$$\chi_\mu(\mathbf{r}) = p(\mathbf{r}) \exp(-\alpha|\mathbf{r}|^2),$$

where  $p$  is a polynomial function and  $\alpha$  a positive real number, then all the integrals in (16) and (17) can be computed analytically.

In practice, most calculations in quantum chemistry are performed using gaussian atomic orbital basis sets, which are built as follows:

1. a collection  $\{\xi_\mu^A\}_{1 \leq \mu \leq n_A}$  of  $n_A$  linearly independent linear combinations of gaussian polynomials are associated with each chemical element  $A$  of the periodic table: these are the atomic orbitals of  $A$ ;
2. to perform a calculation on a given chemical system, one builds a basis  $\{\chi_\mu\}$  by putting together all the atomic orbitals related to all the atoms of the system.

This approach is reminiscent of the reduced basis method used in other fields of science and engineering (see e.g. [41, 65] and references therein). For instance, still in the case of a water molecule  $\text{H}_2\text{O}$ , we have

$$\{\chi_\mu\} = \{\xi_1^H(\mathbf{r} - \mathbf{R}_{H_1}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_1}); \xi_1^H(\mathbf{r} - \mathbf{R}_{H_2}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_2}); \xi_1^O(\mathbf{r} - \mathbf{R}_O), \dots, \xi_{n_O}^O(\mathbf{r} - \mathbf{R}_O)\},$$

where  $\mathbf{R}_{H_1}$ ,  $\mathbf{R}_{H_2}$  and  $\mathbf{R}_O$  denote the positions in  $\mathbb{R}^3$  of the hydrogen nuclei and of the oxygen nucleus respectively.

To better understand the geometric nature of the discretized Hartree-Fock model, let us assume that the family  $(\chi_\mu)_{1 \leq \mu \leq N_b}$  is orthonormal. The discretized Hartree-Fock model can be written in two different ways:

- molecular orbital formulation

$$E_{0,\mathcal{C}}^{\text{HF}} = \inf \{E^{\text{HF}}(CC^T), C \in \mathcal{C}\}, \quad (18)$$

where

$$E^{\text{HF}}(D) = \text{Tr}(hD) + \frac{1}{2}\text{Tr}(G(D)D),$$

and where

$$\mathcal{C} = \{C \in \mathbb{R}^{N_b \times N}, C^T C = I_N\}$$

is a so-called Stiefel manifold;

- density matrix formulation

$$E_{0,\mathcal{D}}^{\text{HF}} = \inf \{E^{\text{HF}}(D), D \in \mathcal{D}\}, \quad (19)$$

where

$$\mathcal{D} = \{D \in \mathbb{R}^{N_b \times N_b}, D = D^T, \text{Tr}(D) = N, D^2 = D\}$$

is the set of rank- $N$  orthogonal projectors of  $\mathbb{R}^{N_b \times N_b}$  and is called a Grassmann manifold.

The equivalence between (18) and (19) comes from the fact that when  $C$  varies in the set  $\mathcal{C}$ ,  $D = CC^T$  spans  $\mathcal{D}$ .

The Euler-Lagrange equations associated with (18) can be transformed as in the fifth statement of Theorem 27 by a unitary transform to diagonalize the Lagrange multiplier  $\lambda$  of the orthonormality constraints ( $\lambda$  is an  $N \times N$  real symmetric matrix). We thus obtain the discretized Hartree-Fock equations (for the general case of a non-orthogonal basis)

$$\begin{cases} D = \sum_{i=1}^N \Phi_i \Phi_i^T, \\ F = h + G(D), \\ F\Phi_i = \varepsilon_i S\Phi_i, \quad \varepsilon_1 \leq \dots \leq \varepsilon_N, \quad \Phi_i^T \Phi_j = \delta_{ij}. \end{cases} \quad (20)$$

where  $\varepsilon_1 \leq \dots \leq \varepsilon_N$  are the lowest  $N$  generalized eigenvalues (counting multiplicities) of the generalized eigenvalue problem

$$F\Phi = \varepsilon S\Phi,$$

and where

$$D \in \mathbb{R}_{\text{sym}}^{N_b \times N_b}, \quad F \in \mathbb{R}_{\text{sym}}^{N_b \times N_b}, \quad \Phi_i \in \mathbb{R}^{N_b},$$

respectively denote the discretizations of the density matrix, of the Fock operator, of the Hartree-Fock orbitals in the discretization basis  $(\chi_1, \dots, \chi_{N_b})$ .

Solutions to the discretized Hartree-Fock problem can be obtained

- either by solving a constrained optimization problem (on a Stiefel or a Grassmann manifold [31, 49]);
- or by solving the above equations by means of a self-consistent field (SCF) algorithm (see [16] and references therein).

The design of more efficient methods, in particular for very large molecular systems, is still an active field of research.

Since the Hartree-Fock ground state energy for the nuclear configuration  $\{\mathbf{R}_k\}$  is obtained by solving a constrained optimization problem depending parametrically on the  $\{\mathbf{R}_k\}$ , it also falls into the scope of formulas (3) and (4). A simple calculation shows that the effective forces in the discretized Hartree-Fock model are given by

$$-\nabla_{\mathbf{R}_k} W_0^{\text{HF}}(\mathbf{R}_1, \dots, \mathbf{R}_M) = -\text{Tr}(\nabla_{\mathbf{R}_k} hD) - \text{Tr}(\nabla_{\mathbf{R}_k} SD_E) + \sum_{l \neq k} z_k z_l \frac{\mathbf{R}_k - \mathbf{R}_l}{|\mathbf{R}_k - \mathbf{R}_l|^3},$$

where  $D$  is the ground state density of the discretized Hartree-Fock model for the nuclear configuration  $\{\mathbf{R}_k\}$  obtained by solving (20) and  $D_E$  is the energy weighted ground state density matrix defined by

$$D_E = \sum_{i=1}^N \varepsilon_i \Phi_i \Phi_i^T,$$

where the  $\varepsilon_i$ 's and the  $\Phi_i$ 's are solutions to (20).

## 7 Numerical Approximation of Eigenvalues of Self-adjoint Operators

Let  $A$  be a self-adjoint operator on a Hilbert space  $\mathcal{H}$  with domain  $D(A)$  and form domain  $Q(A)$ , and  $a$  the associated quadratic form. The typical example we have in mind is the three-dimensional Schrödinger operator

$$\mathcal{H} = L^2(\mathbb{R}^3), \quad D(A) = H^2(\mathbb{R}^3), \quad A = -\frac{1}{2}\Delta + V, \quad V \in L^2_{\text{unif}}(\mathbb{R}^3).$$

The quadratic form associated with  $A$  is defined on the form domain  $Q(A) = H^1(\mathbb{R}^3)$  by

$$\forall (u, v) \in Q(A) \times Q(A), \quad a(u, v) = \frac{1}{2} \int_{\mathbb{R}^3} \nabla u \cdot \nabla v + \int_{\mathbb{R}^3} Vuv.$$

Let  $(V_n)_{n \in \mathbb{N}}$  be a sequence of finite-dimensional subspaces of  $Q(A)$  such that

$$\forall v \in Q(A), \quad \inf_{v_n \in V_n} \|v - v_n\|_{Q(A)} \xrightarrow{n \rightarrow \infty} 0.$$

For each  $n$ , we denote by  $A|_{V_n}$  the self-adjoint operator on  $V_n$  defined by

$$\forall (u_n, v_n) \in V_n \times V_n, \quad (A|_{V_n} u_n, v_n)_{\mathcal{H}} = a(u_n, v_n).$$

The spectrum of  $A|_{V_n}$  is obtained by solving the variational problem

$$\begin{cases} \text{search } (u_n, \lambda_n) \in V_n \times \mathbb{R} \text{ such that} \\ \forall v_n \in V_n, \quad a(u_n, v_n) = \lambda_n (u_n, v_n)_{\mathcal{H}} \\ \|u_n\|_{\mathcal{H}} = 1 \end{cases}$$

The question we would like to investigate in this section is the following: does  $\sigma(A|_{V_n})$ , the spectrum of  $A|_{V_n}$ , converge to  $\sigma(A)$ , the spectrum of  $A$ ? Quite surprisingly, the answer to this question is no, in general.

Recall that, according to Theorem 23, if  $A$  is bounded below, then the real number

$$\lambda_j(A) = \inf_{W_j \in \mathcal{E}_j} \sup_{w \in W_j \setminus \{0\}} \frac{a(w, w)}{\|w\|^2},$$

where  $\mathcal{E}_j$  is the set of the  $d$ -dimensional subspaces of  $Q(A)$ , is equal to

- the smallest  $j$ th eigenvalue of  $A$  if  $A$  has at least  $j$  eigenvalues lower than  $\min \sigma_{\text{ess}}(A)$  (taking multiplicities into account);
- $\min \sigma_{\text{ess}}(A)$  otherwise.

From this result, we can infer the following classical results (see e.g. [6, 23]).

**Theorem 28** *Let  $A$  be a bounded below self-adjoint operator on  $\mathcal{H}$ . Then*

$$\forall j \in \mathbb{N}^*, \quad \lambda_j(A|_{V_n}) \downarrow_{n \rightarrow \infty} \lambda_j(A).$$

**Theorem 29** *Let  $A$  be a bounded below self-adjoint operator on  $\mathcal{H}$ ,  $\lambda < \min \sigma_{\text{ess}}(A)$  a discrete eigenvalue of  $A$  of multiplicity  $m$ , and  $\varepsilon > 0$  such that*

$$[\lambda - \varepsilon, \lambda + \varepsilon] \cap \sigma(A) = \{\lambda\}.$$

Let  $P := \mathbb{1}_{\{\lambda\}}(A)$  and  $P_n := \mathbb{1}_{[\lambda-\varepsilon/2, \lambda+\varepsilon/2]}(A|_{V_n})$ . Then, for  $n$  large enough,  $\text{Rank}(P_n) = m$  and there exists  $C \in \mathbb{R}_+$  such that

$$\|(P - P_n)P\|_{\mathcal{B}(\mathcal{H}, Q(A))} \leq C\|(1 - \Pi_{V_n}^{Q(A)})P\|_{\mathcal{B}(\mathcal{H}, Q(A))},$$

$$\|(P - P_n)P_n\|_{\mathcal{B}(\mathcal{H}, Q(A))} \leq C\|(1 - \Pi_{V_n}^{Q(A)})P\|_{\mathcal{B}(\mathcal{H}, Q(A))},$$

$$\max_{\lambda_n \in \sigma(A|_{V_n}) \cap [\lambda - \varepsilon, \lambda + \varepsilon]} |\lambda_n - \lambda| \leq C\|(1 - \Pi_{V_n}^{Q(A)})P\|_{\mathcal{B}(\mathcal{H}, Q(A))}^2,$$

where  $\Pi_{V_n}^{Q(A)}$  is the orthogonal projection of  $Q(A)$  on  $V_n$  for the  $Q(A)$ -scalar product.

As previously mentioned, the spectrum of the discretized operator  $A|_{V_n}$  does not, in general, converge to the spectrum of the original operator  $A$ . However, everything goes well if  $A$  is a bounded operator with compact resolvent.<sup>12</sup>

**Theorem 30** Assume that  $A$  is bounded below with compact resolvent. Then

$$\lim_{n \rightarrow \infty} \sigma(A|_{V_n}) = \sigma(A).$$

More precisely,

- the spectrum of  $A$  is purely discrete and the sequence  $(\lambda_j)_{j \in \mathbb{N}^*}$  of the eigenvalues of  $A$  (counted with their multiplicities) forms a non-decreasing sequence going to  $+\infty$ ;
- let  $\lambda_1^n \leq \lambda_2^n \leq \dots \leq \lambda_{N_n}^n$  denote the eigenvalues of  $A|_{V_n}$  (counted with their multiplicities). Then

$$\forall j \in \mathbb{N}^*, \quad \lambda_j^n \geq \lambda_j \text{ for all } n \in \mathbb{N} \text{ such that } N_n \geq j, \quad \text{and} \quad \lim_{n \rightarrow \infty} \lambda_j^n = \lambda_j.$$

*Example 31* Let  $\mathcal{H} = L^2(\mathbb{R}^d)$  and  $V \in C^0(\mathbb{R}^d)$  such that  $\lim_{|x| \rightarrow +\infty} V(x) = +\infty$  (confining potential). Consider the operator  $A$  defined as

$$D(A) = \left\{ u \in L^2(\mathbb{R}^d) \mid -\frac{1}{2}\Delta u + Vu \in L^2(\mathbb{R}^d) \right\},$$

and

$$\forall u \in D(A), \quad Au = -\frac{1}{2}\Delta u + Vu.$$

<sup>12</sup>The operator  $A$  has a compact resolvent if, for some  $z \in \rho(A)$  (and therefore for all  $z \in \rho(A)$  by virtue of the resolvent formula),  $z - A$ , considered as a bounded operator on  $\mathcal{H}$ , is compact.

Then  $A$  is bounded below and has a compact resolvent. The spectrum of  $A$  therefore is an increasing sequence of eigenvalues of finite multiplicities going to  $+\infty$ , and Theorem 23 can be applied.

If more general situations, two different problems may occur. First, it may happen that

$$\sigma(A) \not\subseteq \liminf_{n \rightarrow \infty} \sigma(A|_{V_n}).$$

This is referred to as the lack of approximation problem. It may also happen that

$$\limsup_{n \rightarrow \infty} \sigma(A|_{V_n}) \not\subseteq \sigma(A).$$

This is called the spectral pollution problem.

*Example 32 (Lack of Approximation Problem)* Let  $\mathcal{H} = L^2_{\text{per}}((0, 2\pi), \mathbb{C})$ ,  $D(A) = H^1_{\text{per}}((0, 2\pi), \mathbb{C})$  and  $A = -i\frac{d}{dx}$ . The operator  $A$  is the momentum operator in one-dimensional quantum mechanics. Let  $(e_k)_{k \in \mathbb{Z}}$  be the basis of the Fourier modes  $(e_k(x) = (2\pi)^{-1/2} e^{ikx})$ , and

$$V_n = \mathbb{C}e_{0,n} \oplus \mathbb{C}\tilde{e}_{0,n} \oplus \text{Span}\{e_k, 1 \leq |k| \leq n-1\},$$

where

$$e_{0,n} := \cos(1/n)e_0 + \frac{\sin(1/n)}{\sqrt{2}}e_n + \frac{\sin(1/n)}{\sqrt{2}}e_{-n}, \quad \tilde{e}_{0,n} = \frac{1}{\sqrt{2}}e_n - \frac{1}{\sqrt{2}}e_{-n}.$$

Then

$$\sigma(A) = \mathbb{Z} \quad \text{and} \quad \lim_{n \rightarrow \infty} \sigma(A|_{V_n}) = \mathbb{Z}^*,$$

which reveals a lack of approximation problem: the eigenvalue 0 of the operator  $A$  is missed by the numerical approximation.

The lack of approximation and spectral solutions problems are investigated from a mathematical point of view in the references [13, 27, 52, 72], from which we have extracted some important general results.

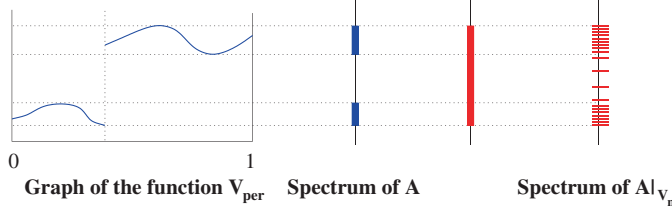
First, there is no risk of lack of approximation whenever the operator is semibounded, that is bounded from above, or bounded from below.

**Theorem 33** *If  $A$  is semibounded, then  $\sigma(A) \subset \liminf_{n \rightarrow \infty} \sigma(A|_{V_n})$ .*

The following nice example of spectral pollution is due to Szegő.

*Example 34* Let  $V_{\text{per}} \in L^\infty_{\text{per}}((0, 2\pi), \mathbb{R})$ ,  $\mathcal{H} = L^2_{\text{per}}((0, 2\pi), \mathbb{C})$ ,

$$(Au)(x) = V_{\text{per}}(x)u(x).$$



**Fig. 12** A case of spectral pollution (Example 34)

Let  $V_n = \text{Span} \{e_k, |k| \leq n\}$ , where  $(e_k)_{k \in \mathbb{Z}}$  is the Fourier basis. Then (see Fig. 12),

$$\sigma(A) = \text{ess-range}(V_{\text{per}}) \quad \text{and} \quad \lim_{n_0 \rightarrow \infty} \overline{\bigcup_{n \geq n_0} \sigma(A|_{V_n})} = \text{CH}(\sigma(A)),$$

where  $\text{CH}(B)$  denotes the convex hull of the set  $B$ .

**Definition 35** A real number  $\lambda \notin \sigma(A)$  such that there exists a sequence  $(V_n)_{n \in \mathbb{N}}$  of finite-dimensional subspaces of  $Q(A)$  such that

- $\forall v \in Q(A), \inf_{v_n \in V_n} \|v - v_n\|_{Q(A)} \xrightarrow{n \rightarrow \infty} 0$
- $\lambda \in \lim_{n \rightarrow \infty} \sigma(A|_{V_n})$

is called a spurious eigenvalue of  $A$ . The set of the spurious eigenvalues of  $A$  is denoted by  $\text{Spu}(A)$ .

**Theorem 36** *It holds*

$$\text{Spu}(A) = \text{CH} \left( \overline{\sigma(A)}^{\mathbb{R}} \setminus \sigma_d(A) \right) \setminus \sigma(A).$$

Let us illustrate the spectral pollution problem and the above theorem on the more physical case of a perturbed periodic Schrödinger operators on  $L^2(\mathbb{R}^d)$ . Such a situation notably arises in the modeling of crystals with point defects within density functional theory (DFT). Consider a periodic lattice  $\mathcal{R}$  of  $\mathbb{R}^d$ , and the operator

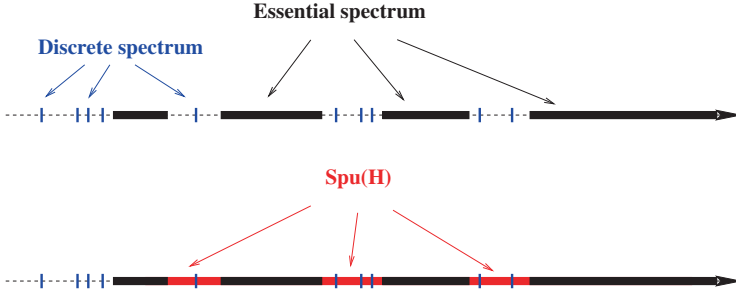
$$H = -\frac{1}{2}\Delta + V_{\text{per}} + W, \quad (21)$$

with

$$V_{\text{per}} \in L^\infty(\mathbb{R}^d) \text{ } \mathcal{R}\text{-periodic} \quad \text{and} \quad W \in L^\infty(\mathbb{R}^d), \quad \lim_{|x| \rightarrow \infty} W(x) = 0.$$

The operator  $H$  can be seen as a perturbation of the periodic Schrödinger operator

$$H_0 = -\frac{1}{2}\Delta + V_{\text{per}}.$$



**Fig. 13** Sketch of the spectrum of the perturbed periodic Schrödinger operator  $H$  defined by (21) (top) and of the set of the spurious eigenvalues of  $H$  (bottom) given by Theorem 36

It can be shown that the multiplication operator by the function  $W$  is  $H_0$ -compact. It therefore follows from Weyl's theorem (Theorem 21) that  $\sigma_{\text{ess}}(H) = \sigma_{\text{ess}}(H_0)$ . Besides, the spectrum of  $H_0$  can be studied using Bloch's theory (see e.g. [68, Section XIII.16]). It turns out that  $H_0$  is bounded below and that its spectrum is purely continuous (i.e.  $H_0$  has no eigenvalues), and consists of bands: it is a countable union of possibly overlapping closed bounded intervals of  $\mathbb{R}$ .

In view of the previous results, there is no risk of lack of approximation since  $H$  is bounded below (cf. Theorem 33), but spectral pollution may be a problem (Fig. 13).

Quoting Boulton and Levitin [12], *the natural approach of truncating  $\mathbb{R}^d$  to a large compact domain and applying the projection method to the corresponding Dirichlet problem is prone to spectral pollution*. Consider for instance the case when  $d = 2$ ,  $\mathcal{R} = 2\pi\mathbb{Z}^2$  (so that a unit cell is  $[-\pi, \pi)^2$ ),

$$\begin{aligned} V_{\text{per}}(x, y) &= \cos(x) + 3 \sin(2(x + y) + 1), \\ W(x, y) &= -(x + 2)^2(2y - 1)^2 \exp(-(x^2 + y^2)), \end{aligned}$$

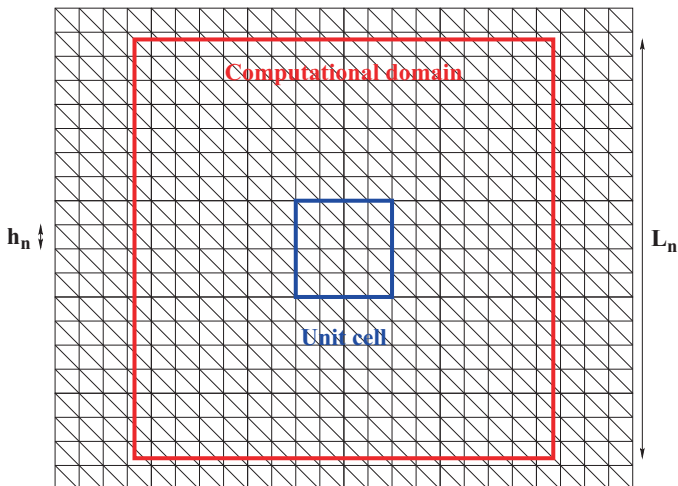
and the approximation spaces

$$V_n = \{v_n \in C^0(\mathbb{R}^2) \mid \text{Supp}(v_n) \subset \Omega_n, \forall K_n \in \mathcal{T}_n^\infty, v_n|_{K_n} \in \mathbb{P}_1\},$$

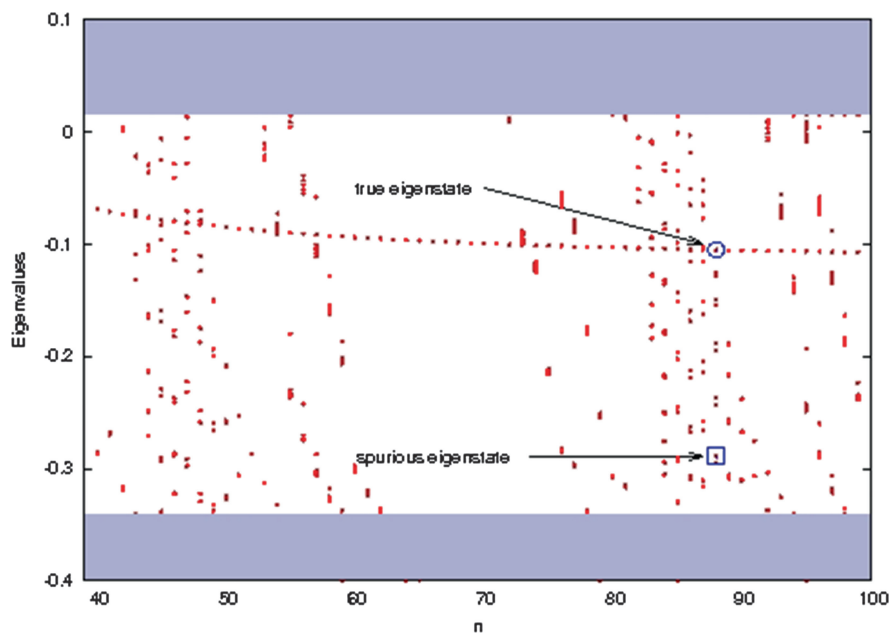
where the computational domain is defined as  $\Omega_n = [-L_n/2, L_n/2]$  with  $L_n \rightarrow \infty$ , and the mesh  $\mathcal{T}_n^\infty$  is a uniform  $\mathcal{R}$ -periodic mesh of  $\mathbb{R}^2$  with  $2n^2$  triangles per unit cell (see Fig. 14).

Numerical simulations using Bloch theory show that there is a gap  $(-0.341, 0.016)$  between the first and second bands of the unperturbed operator  $H_{\text{per}}^0 = -\Delta + V_{\text{per}}$ , and that  $H = H_{\text{per}}^0 + W$  has exactly one eigenvalue  $\lambda \simeq -0.105$  in this gap. The spectral pollution problem can be clearly observed on Fig. 15. The eigenfunction associated with the approximation of the eigenvalue  $\lambda$  in the circle on Fig. 15 is plotted on Fig. 16. The one associated with the spurious approximation in the square on Fig. 15 is plotted on Fig. 17. We can see that the spurious eigenfunction



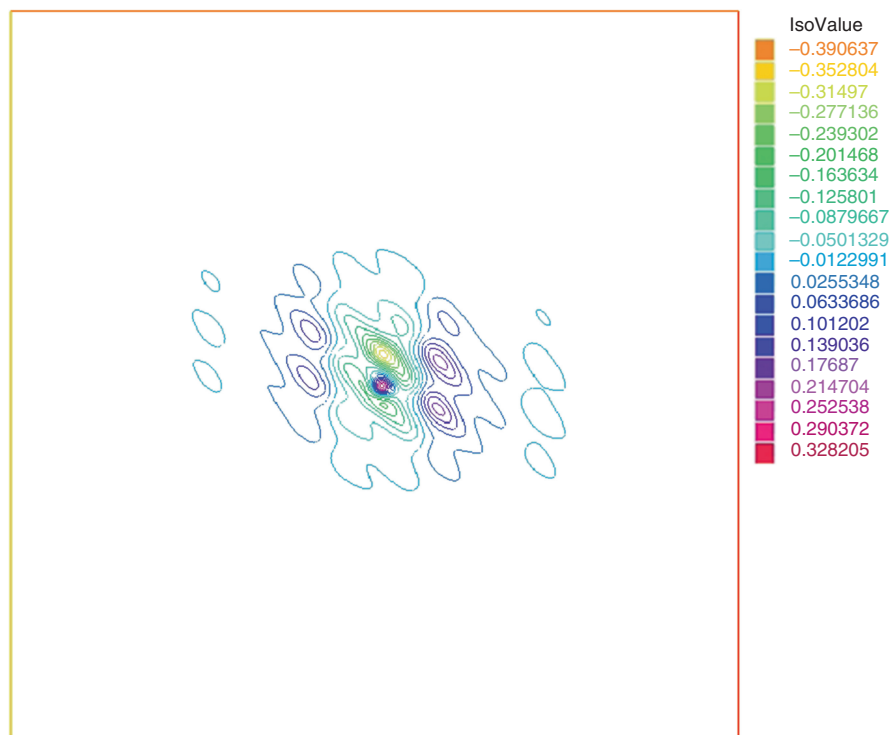


**Fig. 14** Computation domain  $\Omega_n$  and mesh  $\mathcal{T}_n^\infty$



**Fig. 15** Spectrum of  $H|_{V_n}$  in the gap for  $40 \leq n \leq 100$

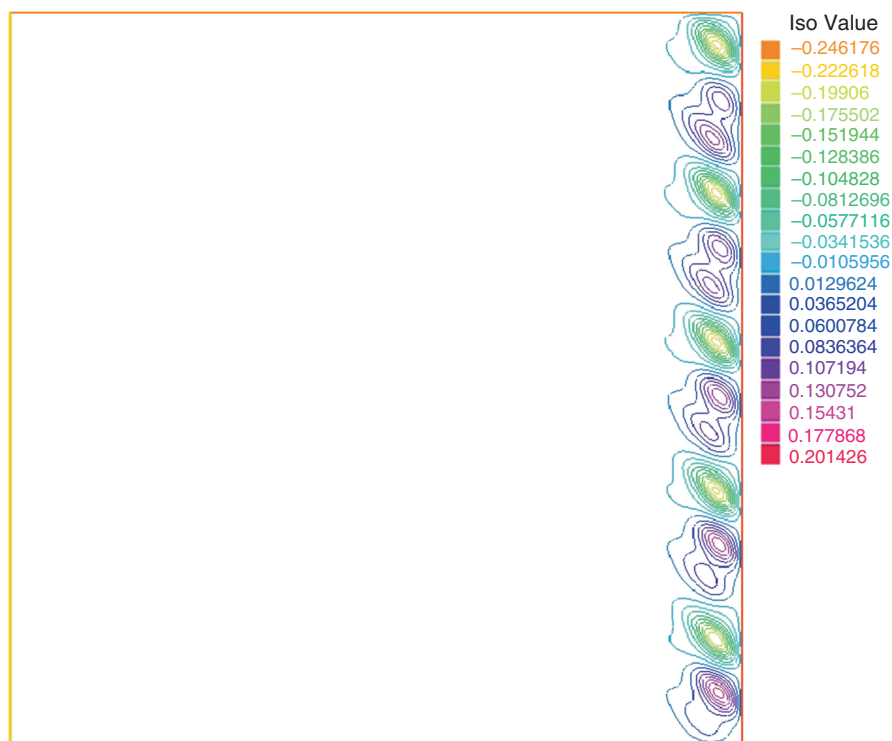
seems to concentrate on the boundary of the simulation domain. A mathematical explanation of this phenomenon is given in [21] (see also [20]). These calculations were performed with FreeFEM++ [36].



**Fig. 16** Profile of a “true” eigenvector

Let us summarize the main messages of this section:

- variational approximations work well if the operator  $A$  is bounded below and has a purely discrete spectrum;
- if the operator is bounded below (resp. bounded above), variational approximations allow one to approximate the eigenvalues which are below the bottom (resp. above the top) of the essential spectrum;
- if the operator is bounded neither from below nor from above, variational approximations can lead to lack of approximation (some eigenvalues can be missed);
- variational approximation can give rise to spectral pollution in the “gaps” of the essential spectrum;
- in the latter two cases, the approximation spaces must be chosen very carefully.



**Fig. 17** Profile of a “spurious” eigenvector

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