

Mathematical models and numerical methods for electronic structure calculation

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Abstract. This contribution provides a pedagogical introduction for mathematicians to the field of electronic structure calculation. The N -body electronic Schrödinger equation and the main methods to approximate the solutions to this equation (wavefunction methods, density functional theory, quantum Monte Carlo) are presented. The numerical simulation of the resulting models, the construction of electronic structure models for systems with infinitely many electrons (perfect crystals, crystals with local defects, disordered materials) by means of thermodynamic limits, and the modeling and simulation of molecules interacting with complex environments, are discussed.

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1. Introduction

Electronic structure calculation has become an essential tool in chemistry, condensed matter physics, molecular biology, materials science, and nanosciences. Over 10,000 research articles containing electronic structure calculations were published in 2013, and the field utilizes about 15% of the CPU time available in scientific computing centers worldwide. Its importance in contemporary research was acknowledged by the 1998 Nobel Prize in Chemistry shared by Kohn and Pople for their contributions to density functional theory and wavefunction methods for electronic structure calculation. The 2013 Nobel Prize in Chemistry was then awarded to Karplus, Levitt and Warshel for the development of multiscale models for complex chemical systems, the finer scale being dealt with electronic structure models.

The field is also an inexhaustible source of exciting mathematical and numerical problems. In this contribution, we explain how to model and simulate a sample of matter at the molecular scale from the first principles of quantum mechanics. The central object is the time-independent N -body Schrödinger equation allowing one to compute the possible electronic states of the system for a given configuration of the nuclei. This equation is a linear elliptic eigenvalue problem on \mathbb{R}^{3N} where N is the number of electrons in the system. The construction of mathematical approximations of this equation and the design of efficient numerical methods

to directly simulate the 3N-dimensional linear Schrödinger equation and its various lower-dimensional but nonlinear approximations (such as the Hartree-Fock and Kohn-Sham models) is a very active field of interdisciplinary research. After introducing the electronic Schrödinger equation and the main three approaches to approximate and simulate it (wavefunction methods, density functional theory, and quantum Monte Carlo methods), we present recent advances in the mathematical understanding of electronic structure models and in the methods to solve them numerically, as well as open questions and future research directions. In order to make this contribution self-contained, we first recall the fundamental principles of quantum mechanics and briefly discuss the Born-Oppenheimer approximation allowing one (in most cases) to decouple electronic and nuclear degrees of freedom.

2. Basics of (non-relativistic) quantum mechanics

An autonomous quantum system is described by a separable complex Hilbert space \mathcal{H} called the state space, and a self-adjoint operator H on the state space called the Hamiltonian. The (pure) states of the system are in one-to-one correspondence with the projective space \mathcal{H}/\mathbb{C} , which means that the state of the system at time t is completely characterized by a normalized vector $\psi(t) \in \mathcal{H}$, called the wave function, $\psi(t)$ and $e^{i\alpha}\psi(t)$ describing the same state for all $\alpha \in \mathbb{R}$. The dynamics of the system is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi}{dt}(t) = H\Psi(t), \quad (1)$$

where \hbar is the reduced Planck constant. Of particular importance are the stationary states, namely the states of the form $\Psi(t) = e^{i\alpha(t)}\psi$, where $\|\psi\|_{\mathcal{H}} = 1$ and where $e^{i\alpha(t)}$ is an irrelevant global phase factor. Inserting this Ansatz in the time-dependent Schrödinger equation (1), we obtain that there exists a real number E such that ψ satisfies the time-independent Schrödinger equation

$$H\psi = E\psi$$

and $\alpha(t) = -iEt/\hbar$. In other words, ψ is an eigenvector of the self-adjoint operator H associated with the eigenvalue E . From a physical viewpoint, E is the energy of the stationary state ψ .

The formalism presented above is completely general and valid for any isolated quantum system. For a simple system consisting of a single particle of mass m and spin s subjected to a stationary external potential V_{ext} (take for instance $V_{\text{ext}} \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ to avoid technical problems), the state space is the Hilbert space $L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C}) \equiv L^2(\mathbb{R}^3, \mathbb{C}^{2s+1})$, where Σ is a finite set of cardinality $2s + 1$. In the so-called position representation, the integrable function $x \mapsto |\Psi(t; x, \sigma)|^2$ is the probability density of observing at time t the particle at point x with spin σ . The Hamiltonian is the self-adjoint operator on $L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C})$ defined by

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

where Δ is the Laplace operator with respect to the variable x , and V_{ext} the operator of multiplication by the real-valued function V_{ext} . The first term of the Hamiltonian models the kinetic energy of the particle, and the second term its potential energy. In the absence of external magnetic field, an assumption we make here, both terms are independent of the spin variable, so that it is not necessary for our purpose to specify the physical meaning of the spin variable. Lastly, the time-evolution of the particle is driven by the linear time-dependent Schrödinger equation in the three dimensional space:

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

Likewise, the stationary states are obtained by solving a linear elliptic eigenvalue problem in the three dimensional space:

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

The spectrum of the Hamiltonian H obviously depends on the external potential V_{ext} . For typical potentials encountered in electronic structure calculation, it has the structure displayed on Fig. 1. The lowest energy eigenmode is called the ground state; the higher energy eigenmodes are called excited states.

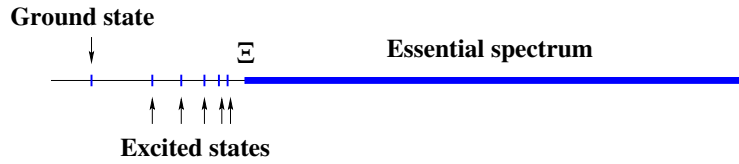


Figure 1. Typical spectra of the Hamiltonians encountered in (non-relativistic) electronic structure calculation of atoms and molecules: the essential spectrum is a half-line $[\Xi, +\infty)$; the discrete spectrum (bound states) can be empty, or consist of a finite or countable sequence of isolated eigenvalues of finite multiplicities. In the case when the number of discrete eigenvalues is infinite, they accumulate at Ξ . The essential spectrum coincides with the continuous spectrum (diffusion states) but can also contain eigenvalues embedded in the continuous spectrum.

Let us now consider a quantum system consisting of two particles of spins s_1 and s_2 respectively. The state space then is a subspace of the tensor product of the one-particle state spaces of the two particles. In other words, the wavefunction $\Psi(t)$ is a function of $L^2(\mathbb{R}^3 \times \Sigma_1, \mathbb{C}) \otimes L^2(\mathbb{R}^3 \times \Sigma_2, \mathbb{C}) \equiv L^2(\mathbb{R}^6, \mathbb{C}^{(2s_1+1)(2s_2+1)})$. In the position representation, the wavefunction Ψ is a function of the time variable t and of the position and spin variables $(x_i, \sigma_i) \in \mathbb{R}^3 \times \Sigma_i$ of each particle (where Σ_i is a set of cardinality $2s_i + 1$; for electrons, which are particles of spin $s = 1/2$, this set is usually denoted by $\{|\uparrow\rangle, |\downarrow\rangle\}$ and the spin states $|\uparrow\rangle$ and $|\downarrow\rangle$ are respectively called spin-up and spin-down). The function $|\Psi(t; x_1, \sigma_1; x_2, \sigma_2)|^2$ is interpreted as the probability density of observing at time t the particle 1 at point x_1 with spin σ_1 and the particle 2 at point x_2 with spin σ_2 . If the two particles are

different in nature (for instance an electron and a positron), the state space is equal to the tensor product $L^2(\mathbb{R}^3 \times \Sigma_1, \mathbb{C}) \otimes L^2(\mathbb{R}^3 \times \Sigma_2, \mathbb{C})$. If the two particles are identical bosons, the state space is the *symmetrized* tensor product $\mathcal{H} \vee \mathcal{H}$ of the one-particle state space $\mathcal{H} = L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C})$, while if they are identical fermions, it is the *antisymmetrized* tensor product $\mathcal{H} \wedge \mathcal{H}$, so that the wavefunction Ψ must satisfy the symmetry properties

$$\begin{aligned}\Psi(t; x_2, \sigma_2; x_1, \sigma_1) &= \Psi(t; x_1, \sigma_1; x_2, \sigma_2) && \text{(for two identical bosons),} \\ \Psi(t; x_2, \sigma_2; x_1, \sigma_1) &= -\Psi(t; x_1, \sigma_1; x_2, \sigma_2) && \text{(for two identical fermions).}\end{aligned}$$

According to the spin-statistics theorem, particles with integer spins are bosons, while particles with half-integer spins are fermions. *In order to simplify the formalism, we will omit the spin variable in the sequel.*

Finally, for a quantum system consisting of N particles, the state space is a subspace of the tensor product of the one-particle state spaces and, in the position representation, $|\Psi(t; x_1, \dots, x_N)|^2$ is the probability density of observing at time t the first particle at x_1 , the second particle at x_2 , etc. If all the N particles are identical, the state space is $\vee^N \mathcal{H}$ for bosons and $\wedge^N \mathcal{H}$ for fermions, and an important physical observable is the particle density

$$\rho_\Psi(t, x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(t; x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N.$$

The time-independent Schrödinger equation is then a 3N-dimensional elliptic eigenvalue problem. In the case of N identical particles with mass m , subjected to a stationary external potential V_{ext} , and interacting through a two-body potential W , we have

$$\left(- \sum_{i=1}^N \frac{\hbar^2}{2m} \Delta_{x_i} + \sum_{i=1}^N V_{\text{ext}}(x_i) + \sum_{1 \leq i < j \leq N} W(x_i, x_j) \right) \Psi(x_1, \dots, x_N) = E \Psi(x_1, \dots, x_N).$$

At first sight, it seems impossible to solve such an equation numerically for N greater than one or two. There is however one case, and this is key for electronic structure calculation, when this equation can be solved relatively easily. It is when the particles are identical and do not interact. In this case indeed, the Hamiltonian is separable (it is the sum of one-body operators)

$$H_{\text{NI}} = - \sum_{i=1}^N \frac{\hbar^2}{2m} \Delta_{x_i} + \sum_{i=1}^N V_{\text{ext}}(x_i) = \sum_{i=1}^N \mathfrak{h}_{x_i}$$

and the bound states of the N particle system can be easily obtained from the bound states ϕ_1, ϕ_2, \dots of the one-particle system, the latter being solutions to

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

where $\varepsilon_1 \leq \varepsilon_2 \leq \dots$ are the discrete eigenvalues of \mathfrak{h} (counting multiplicities). In particular, the ground state of a system of N non-interacting bosons is given by

$$\Psi(x_1, \dots, x_N) = \prod_{i=1}^N \phi_1(x_i), \quad \rho_\Psi(x) = N|\phi_1(x)|^2 \quad (\text{non-interacting bosons}),$$

where ϕ_1 is the ground state eigenfunction of the one-body Hamiltonian \mathfrak{h} . For a system of N non-interacting fermions, the shape of the ground state wavefunction is more complex due to the antisymmetry constraint:

$$\Psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)), \quad \rho_\Psi(x) = \sum_{i=1}^N |\phi_i(x)|^2 \quad (\text{non-int. fermions}),$$

where (ϕ_1, \dots, ϕ_N) is a family of L^2 -orthonormal eigenfunctions of \mathfrak{h} associated with the lowest N eigenvalues (counting multiplicities). Note that, as the Hamiltonian H_{NI} is real-valued, it is sufficient to consider real-valued wavefunctions.

3. First-principle molecular simulation

First principle molecular simulation is based on the simple observation that a given sample of matter is nothing but a collection of atomic nuclei and electrons in Coulomb interaction, and that we can specify the state space and the Hamiltonian of such a system provided we know its chemical formula (that is the chemical nature of the nuclei, and the number of electrons). Thus, the Hamiltonian of a molecular system composed of M nuclei with masses m_1, \dots, m_M and charges z_1, \dots, z_M , and N electrons is

$$\begin{aligned} H_{\text{mol}} = & - \sum_{k=1}^M \frac{1}{2m_k} \Delta_{\mathbf{R}_k} - \sum_{i=1}^N \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \mathbf{R}_k|} \\ & + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}. \end{aligned}$$

The first term of H_{mol} models the kinetic energy of the nuclei, the second term, the kinetic energy of the electrons, and the last three terms the Coulomb interactions between nuclei and electrons, electrons and electrons, and nuclei and nuclei, respectively. Here and in the sequel, we adopt the system of atomic units obtained by setting to 1 the values of the reduced Planck constant \hbar , of the electron mass m_e , of the elementary charge e and of $4\pi\epsilon_0$, where ϵ_0 is the dielectric permittivity of the vacuum:

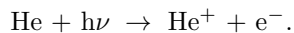
$$\text{atomic units: } \hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\epsilon_0 = 1.$$

A remarkable feature of this model is that it does not involve any empirical parameters specific to the system under consideration. It only depends on a few fundamental constants of physics, on the charges of the nuclei (1 for hydrogen, 2 for helium,

3 for lithium, ...), and on their masses, which have been measured experimentally with very high accuracy. This implies that the properties of the molecular system under consideration can be, *in principle*, computed from its chemical formula. The problem is that to do so, we need to solve the corresponding Schrödinger equation, that is a partial differential equation in dimension $3(N+M)$:

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. (Dirac, 1929 [31])

Solving N -body Schrödinger equations for interacting particles was obviously not possible in Dirac's time, but it is doable nowadays, at least to some point. Before devoting a lot of effort to try and solve this equation for molecular systems, it is interesting to get some insights on the quality of the model. For this purpose, we first consider a very simple molecular system for which both extremely accurate calculations and experiments can be performed: a helium atom consisting of one nucleus of charge $z = 2$ and two electrons. If a laser with frequency ν is shone on a helium atom, and if ν is large enough, a photon with energy $h\nu$ is absorbed by the helium atom ($h = 2\pi\hbar$ is the Planck constant) and causing an electron to escape to infinity (where it does not feel anymore the Coulomb potential generated by the nucleus and the other electron) with kinetic energy E_k :



The difference $\Delta E = h\nu - E_k = h\Delta\nu$ between the energy of the photon and the kinetic energy of the electron at infinity, which can be measured very accurately, is equal to the difference between the ground state energy of the helium atom and the ground state energy of the He^+ ion (see Fig. 2), whose respective Hamiltonians are

$$H_{\text{He}} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{x_1} - \frac{1}{2}\Delta_{x_2} - \frac{2}{|x_1 - \mathbf{R}|} - \frac{2}{|x_2 - \mathbf{R}|} + \frac{1}{|x_1 - x_2|},$$

and

$$H_{\text{He}^+} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{x_1} - \frac{2}{|x_1 - \mathbf{R}|},$$

with $m \simeq 7294.29953$ a.u. The ground state energy of He^+ can be computed analytically, and, using translational and rotational symmetries, the ground state energy of He can be obtained by solving numerically a 3-dimensional Schrödinger equation [55]. The agreement between theory ($\Delta\nu \simeq 5,945,262,288$ MHz) and experiment (two independent experiments gave $\Delta\nu \simeq 5,945,204,238$ MHz and $\Delta\nu \simeq 5,945,204,356$ MHz) is very good, and even extremely good if the so-obtained solution is post-treated to include relativistic corrections by means of perturbation theory ($\Delta\nu \simeq 5,945,204,223$ MHz). Note that relativistic effect cannot be dealt with perturbatively for heavy nuclei (see e.g. [35] for a mathematical analysis of fully relativistic quantum models).

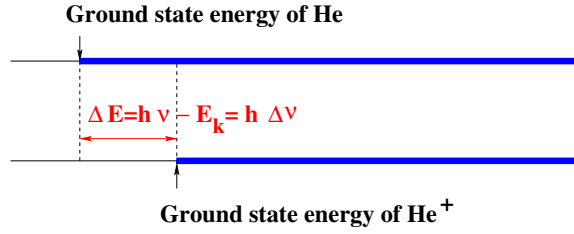


Figure 2. Spectra of He (top) and He^+ (bottom). The corresponding Hamiltonians being translation invariant, their discrete spectrum is empty.

3.1. Born-Oppenheimer approximation. Of course, the helium atom is a simple three body system. For more complex systems with dozens of nuclei and hundreds of electrons, approximations must be used. The first one is the so-called Born-Oppenheimer approximation. It relies on the fact that nuclei are much heavier than electrons. Using the mass ratio as a small parameter, it is possible to decouple the nuclear and electronic degrees of freedom by means of an adiabatic limit [77]. Using in a second stage a semiclassical approximation on the nuclear dynamics [1, 2], it is shown that, in most cases, nuclei behave as classical point-like particles interacting through an effective potential energy function $W : \mathbb{R}^{3M} \rightarrow \mathbb{R}$ (see [12, 39] and references therein for mathematical studies of cases when the Born-Oppenheimer approximation breaks down). The state of the nuclei at time t is then described by the positions $\mathbf{R} = (\mathbf{R}_k(t))_{1 \leq k \leq M} \in \mathbb{R}^{3M}$ and the momenta $\mathbf{P} = (\mathbf{P}_k(t))_{1 \leq k \leq M} \in \mathbb{R}^{3M}$ of the M nuclei, and the classical nuclear Hamiltonian reads

$$H_{\text{BO}}(\mathbf{P}, \mathbf{R}) = \sum_{k=1}^M \frac{|\mathbf{P}_k|^2}{2m_k} + W(\mathbf{R}_1, \dots, \mathbf{R}_M).$$

The global minima of W are the equilibrium configurations of the molecular system. Loosely speaking, the local, non-global, minima correspond to metastable states and the critical points of W of Morse index 1 can be seen as the transition states of all the different possible chemical reactions or the conformational changes involving the atoms of the system. Sampling the nuclear configuration space according to suitable probability measures (note that the Gibbs measure $Z^{-1}e^{-\beta W}$ where β is an inverse temperature for instance and Z a normalization constant is not well-defined for a molecule free to move in the whole space \mathbb{R}^3) allows one to compute the thermodynamical properties of the system [59]. The various dynamics which can be inferred from H_{BO} (classical Hamiltonian dynamics, Langevin dynamics, overdamped Langevin dynamics, ...) provide information on the kinetics of the reactions or conformational changes at thermodynamic equilibrium, as well as on non-equilibrium processes. The quantum counterpart of H_{BO} (obtained from H_{mol} by an adiabatic limit, not followed by a semiclassical limit) is also useful to compute properties such as the infrared spectra of molecules, proton tunneling in biological systems, or the superfluidity of helium 4 [28]. We will not further discuss the nuclear dynamics and focus on the electrons, which seem to have disappeared from

the picture. They are in fact hidden in the definition of the effective potential W , the expression of which is given by

$$W(\mathbf{R}_1, \dots, \mathbf{R}_M) = E_0^{\{\mathbf{R}_k\}} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}, \quad (3)$$

where $E_0^{\{\mathbf{R}_k\}}$ is the ground state eigenvalue of

$$H_{\text{elec}}^{\{\mathbf{R}_k\}} = -\frac{1}{2} \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}.$$

The electronic Hamiltonian $H_{\text{elec}}^{\{\mathbf{R}_k\}}$ is a self-adjoint operator on $\mathcal{H}_N := \wedge^N L^2(\mathbb{R}^3, \mathbb{C})$ (recall that we omit the spin variable) with domain $\mathcal{D}_N := \wedge^N H^2(\mathbb{R}^3, \mathbb{C})$ and form domain $\mathcal{Q}_N := \wedge^N H^1(\mathbb{R}^3, \mathbb{C})$.

3.2. Solving the electronic ground state problem. In the sequel, we focus on the computation of the ground state of the electronic Hamiltonian $H_{\text{elec}}^{\{\mathbf{R}_k\}}$ for a given nuclear configuration $\{\mathbf{R}_k\}$. In order to simplify the notation, we will denote by $E_0 := E_0^{\{\mathbf{R}_k\}}$ and $H_N := H_{\text{elec}}^{\{\mathbf{R}_k\}}$ (recall that N is the number of electrons in the system), so that

$$H_N = -\frac{1}{2} \sum_{i=1}^N \Delta_{x_i} + \sum_{i=1}^N V_{\text{ne}}(x_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \quad \text{with} \quad V_{\text{ne}}(x) = -\sum_{k=1}^M \frac{z_k}{|x - \mathbf{R}_k|}.$$

If the molecular system is neutral or positively charged, the spectrum of H_N has the structure sketched on Fig. 1, the number of discrete eigenvalues being infinite, and the bottom Ξ of the essential spectrum being the ground state of H_{N-1} [95]. In particular, $\Xi = 0$ for one electron systems, and $\Xi < 0$ if $N \geq 2$. The electronic ground state can be obtained by solving the minimization problem

$$E_0 = \inf \{ \langle \Psi | H_N | \Psi \rangle, \Psi \in \mathcal{Q}_N, \|\Psi\|_{\mathcal{H}_N} = 1 \}, \quad (4)$$

where $\langle \psi | A | \psi \rangle$ denotes the quadratic form associated with the self-adjoint operator A (Dirac's bra-ket notation). Note that as $H_N \Psi$ is real-valued whenever Ψ is real-valued, it suffices to minimize over real-valued test functions Ψ .

Many approaches have been developed in the past 70 years to approximate electronic ground states, which can be classified into several families, the main ones being wavefunction methods [49], density functional theory [32] and quantum Monte Carlo methods (Fig. 3). All these methods have advantages and drawbacks. Some are more accurate than others, but require much higher computational effort, and their use is therefore limited to smaller systems. Some methods allow to correctly predict some properties (equilibrium geometry, infrared spectrum, polarizability, ...) but fail to predict other properties (reaction rates, magnetic shielding, ...). We refer e.g. to [49] for more details on these aspects.

The detailed description of all these methods goes beyond the scope of this pedagogical introduction. We will only explain the basic ideas underlying each

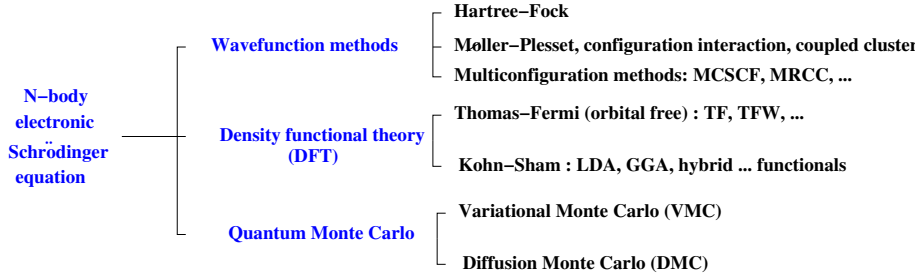


Figure 3. Classification of the main approximation methods for electronic ground state calculations.

of them. Beforehand, we report a numerical example illustrating the fact that electronic structure calculation can provide quantitatively correct results for polyatomic molecules. A water molecule H_2O consists of 3 nuclei and 10 electrons. The equilibrium geometry of the molecule (see Fig. 4) corresponds to the global minimizers of the interatomic potential W defined by (3). The results obtained with the Hartree-Fock model (93.96 pm, 106.33°) are reasonably close to experimental data. Better results are obtained with, for instance the Kohn-Sham LDA model [54] (96.86 pm, 105.00°), the Kohn-Sham GGA model with PBE functional [78] (96.90 pm, 104.75°), or the coupled cluster CCSD(T) method [49] (95.89 pm, 104.16°).

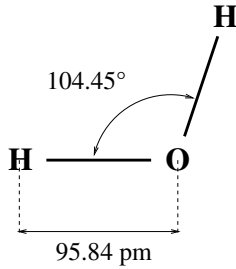


Figure 4. Geometry of the water molecule (experimental data).

3.2.1. Wavefunction methods. A natural way to approximate problem (4) is to minimize the energy functional $\langle \psi | H_N | \psi \rangle$ upon less general wavefunctions ψ . This leads to the variational problem

$$E_0^{\mathcal{X}} = \inf \{ \langle \psi | H_N | \psi \rangle, \psi \in \mathcal{X}, \|\psi\|_{\mathcal{H}} = 1 \}, \quad (5)$$

where \mathcal{X} is a properly chosen subset of \mathcal{Q}_N . Obviously, $E_0^{\mathcal{X}}$ is an upper bound of the target value E_0 . The Hartree-Fock (HF) approximation consists in minimizing over the set \mathcal{X} of the L^2 -normalized N -electron wavefunctions that can be written

as an antisymmetrized product of single electron molecular orbitals ϕ_i :

$$\psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)). \quad (6)$$

Such functions are called *Slater determinants*. Recall that the ground state of a system of non-interacting fermions is a Slater determinant (see Section 2). Since the determinant is an alternate multilinear map, one can, without loss of generality, impose that the functions ϕ_i satisfy the orthonormality constraints

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}.$$

When \mathcal{X} is the set of Slater determinants, problem (5) can be rewritten, once the computation of $\langle \psi | H_N | \psi \rangle$ is explicitly performed, as

$$E_0^{\text{HF}} = \inf \left\{ \mathcal{E}^{\text{HF}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}, \quad (7)$$

where

$$\begin{aligned} \mathcal{E}^{\text{HF}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V_{\text{ne}} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(x) \rho_{\Phi}(y)}{|x-y|} dx dy \\ &\quad - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(x, y)|^2}{|x-y|} dx dy, \end{aligned} \quad (8)$$

where the density matrix γ_{Φ} and the density ρ_{Φ} associated with the N -tuple $\Phi = (\phi_1, \dots, \phi_N)$ are defined as

$$\gamma_{\Phi}(x, y) = \sum_{i=1}^N \phi_i(x) \phi_i(y), \quad \rho_{\Phi}(x) = \gamma_{\Phi}(x, x) = \sum_{i=1}^N |\phi_i(x)|^2. \quad (9)$$

Note that the density ρ_{Φ} is in fact the density ρ_{ψ} of the N -body wavefunction ψ defined by (6). The last term in the HF energy functional (8) is called the exchange term. It has a purely quantum nature (it arises from the antisymmetry of the electronic wavefunction) and has no classical counterpart. The first-order optimality conditions associated with the constrained optimization problem (7) read, after some algebraic manipulation (see e.g. [68] for details), as

$$\left\{ \begin{array}{l} \Phi^0 = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \\ \mathfrak{h}_{\Phi^0}^{\text{HF}} \phi_i = \varepsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \\ \mathfrak{h}_{\Phi^0}^{\text{HF}} \phi = -\frac{1}{2} \Delta \phi + V_{\text{ne}} \phi + (\rho_{\Phi^0} \star |\cdot|^{-1}) \phi - \int_{\mathbb{R}^3} \frac{\gamma_{\Phi^0}(\cdot, x')}{|\cdot - x'|} \phi(x') dx'. \end{array} \right. \quad (10)$$

If Φ^0 is a minimizer of (7), then $\varepsilon_1, \dots, \varepsilon_N$ are in fact the lowest N eigenvalues of the Hartree-Fock operator $\mathfrak{h}_{\Phi^0}^{\text{HF}}$ (a stronger property is shown in [5]). These equations look somewhat similar to the equations (2) we obtained for non-interacting

electrons. The big difference is that, this time, the mean-field Hamiltonian $\mathfrak{h}_{\Phi^0}^{\text{HF}}$ depends on the ground state Φ^0 . The Hartree-Fock equations (10) are therefore a *nonlinear* elliptic eigenvalue problem. The Hartree-Fock model has been thoroughly studied in the mathematical literature. The existence of a Hartree-Fock ground state for neutral molecules and positive ions was established by Lieb and Simon [68], and the set of solutions to the Hartree-Fock equations was studied by Lions [73]. Uniqueness is a difficult question [46]. Numerical algorithms are analyzed in [16, 22, 23, 60].

For polyatomic systems, the Hartree-Fock method is often not accurate enough to reach the requested accuracy. A natural way to improve the HF wavefunction is to consider finite sums of Slater determinants and search for an approximation of the ground state wavefunction of the form

$$\Psi(x_1, \dots, x_N) = c_0 \Psi^{\text{HF}}(x_1, \dots, x_N) + \text{finite sum of Slater determinants},$$

where c_0 is a normalization coefficient. Several ways to generate such improved wavefunctions have been proposed [49]: the Møller-Plesset perturbation method (mathematically based on Kato perturbation theory [51]), the configuration interaction method, and the coupled cluster method (see [82] for a mathematical analysis). The CCSD(T) method (the acronym stands for Coupled Cluster Single Double (Triple)) is considered as the gold standard of quantum chemistry. It however suffers from two major limitations:

- first, the required computational effort scales as N^7 , instead of N^3 for the Hartree-Fock model, where N is the number of electrons in the system, so that its use is limited to relatively small molecular systems (a dozen of atoms); the construction of coupled cluster methods with better scaling is an active field of research;
- second, the coupled cluster method fails when the Hartree-Fock wavefunction is not the dominant component of the ground state wavefunction, that is when several Slater determinants are necessary to get a decent estimate of the ground state wavefunction.

To address the second problem, one has to resort to multi-configuration methods. These methods include the multi-configuration self-consistent field (MCSCF) method [49], which was mathematically analyzed by Le Bris [57], Friesecke [41] and Lewin [62], as well as the recently developed multi-reference coupled cluster (MRCC) method [83]. The MCSCF method can be interpreted as a low rank tensor method based on Tucker format [7, 37].

3.2.2. Density Functional Theory (DFT). It has been shown by Hohenberg and Kohn [50] that the electronic ground state energy and density can be obtained by minimizing a functional of the electronic density. To establish this fact, we report here the simple argument proposed later by Levy [61] (see also [64]). Splitting

the electronic Hamiltonian as

$$H_N = H_N^1 + \sum_{i=1}^N V(x_i) \quad \text{with} \quad H_N^\lambda = -\frac{1}{2} \sum_{i=1}^N \Delta_{x_i} + \sum_{1 \leq i < j \leq N} \frac{\lambda}{|x_i - x_j|},$$

and observing that, due to the antisymmetry property, we have for all $\Psi \in \mathcal{Q}_N$,

$$\langle \Psi | \sum_{i=1}^N V(x_i) | \Psi \rangle = \sum_{i=1}^N \int_{\mathbb{R}^{3N}} V(x_i) |\Psi(x_1, \dots, x_N)|^2 dx_1 \cdots dx_N = \int_{\mathbb{R}^3} \rho_\Psi V,$$

the electronic ground state problem (4) also reads

$$\begin{aligned} E_0 &= \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_\Psi V, \Psi \in \mathcal{Q}_N, \|\Psi\|_{\mathcal{H}_N} = 1 \right\} \\ &= \inf \left\{ F_N(\rho) + \int_{\mathbb{R}^3} \rho V, \rho \in \mathcal{R}_N \right\}, \end{aligned}$$

where

$$\mathcal{R}_N = \{\rho \mid \exists \Psi \in \mathcal{Q}_N \text{ s.t. } \|\Psi\|_{\mathcal{H}_N} = 1 \text{ and } \rho_\Psi = \rho\}$$

is the set of admissible electronic densities and where

$$F_N(\rho) = \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle, \Psi \in \mathcal{Q}_N, \|\Psi\|_{\mathcal{H}_N} = 1, \rho_\Psi = \rho \right\} \quad (11)$$

is a *universal* density functional, in the sense that it only depends on the number of electrons in the system, not on the number, chemical natures, and positions of the nuclei. The set \mathcal{R}_N can be easily characterized:

$$\mathcal{R}_N = \left\{ \rho \geq 0 \mid \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}.$$

On the other hand, there is no simple way to evaluate $F_N(\rho)$ for a given $\rho \in \mathcal{R}_N$.

Although introduced decades before the works by Hohenberg and Kohn, Thomas-Fermi type models fall in the framework of DFT. They consist in approximating $F_N(\rho)$ by explicit functionals of the density ρ . Examples of such models include the original Thomas-Fermi (TF) model

$$F_{\text{TF}}(\rho) = C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy,$$

where $C_{\text{TF}} = \frac{10}{3}(3\pi^2)^{2/3}$ is the Thomas-Fermi constant, and the Thomas-Fermi-von Weizsäcker (TFW) model

$$F_{\text{TFW}}(\rho) = C_{\text{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy,$$

where the constant C_{W} takes different values depending on how the TFW model is derived [32]. The first term in $F_{\text{TF}}(\rho)$ models the kinetic energy of the electrons

$(C_{\text{TF}}\rho_0^{5/3}$ is the kinetic energy density of a homogeneous gas of non-interacting electrons of uniform density ρ_0 [32]). The second component of $F_{\text{TF}}(\rho)$ is the electrostatic energy of a *classical* charge distribution of density ρ . The first term in $F_{\text{TFW}}(\rho)$ is a correction to the Thomas-Fermi approximation of the kinetic energy of the electrons taking into account the fact that, in molecular systems, the electronic density is not uniform. The above Thomas-Fermi type models provide crude approximations of $F_N(\rho)$ (according to the TF model, any molecule is unstable! [89]), and are no longer used in quantum chemistry and materials science. On the other hand, some improvements of the TFW model, the so-called *orbital-free models* [94], are used for the simulation of specific materials (aluminum crystals with defects for example [80]). The main reason why we mention Thomas-Fermi like models is that they are very useful in the mathematical analysis of electronic structure models [63, 67, 76]. They are indeed toy models upon which new mathematical techniques can be developed before being applied to the more sophisticated models actually used in quantum chemistry and materials science.

The Kohn-Sham method [54] is to date the most popular electronic structure method as it provides the best compromise between computational efficiency and accuracy. It proceeds from the density functional theory remarking that on the one hand,

$$T_{\text{KS}}(\rho) = \inf \left\{ \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \Phi = (\phi_i) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \rho_\Phi = \rho \right\},$$

where the density ρ_Φ is defined by (9), is an excellent approximation (exact for pure state non-interacting V -representable densities [64]) of the density functional for non-interacting electrons, that is of the density functional obtained by replacing H_N^1 with H_N^0 in (11), and that, on the other hand, the classical Coulomb energy

$$J(\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy$$

is a reasonable first-order approximation of the electronic interaction. The functional $F_N(\rho)$ can therefore be decomposed as

$$F(\rho) = T_{\text{KS}}(\rho) + J(\rho) + E_{\text{xc}}(\rho), \quad (12)$$

where the exchange-correlation energy functional $E_{\text{xc}}(\rho)$ is expected to be a small correction of the first two terms of the decomposition (12). Numerical simulations confirm that the exchange-correlation energy is about 10% of the total energy for ground states of molecular systems. The Kohn-Sham model then reads

$$E_0^{\text{KS}} = \inf \left\{ \mathcal{E}^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}, \quad (13)$$

with

$$\mathcal{E}^{\text{KS}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{ne}} + J(\rho_\Phi) + E_{\text{xc}}(\rho_\Phi).$$

The Kohn-Sham approach is *in principle* exact in the sense that if (12) is exactly satisfied, then $E_0^{\text{KS}} = E_0$ for all molecular systems. On the other hand, as the exact exchange-correlation functional is not known explicitly, it must be approximated in practice to perform numerical calculations. For this reason, there is not one, but a whole zoology of Kohn-Sham models, corresponding to different approximations of $E_{\text{xc}}(\rho)$. The simplest Kohn-Sham model actually used in practice is obtained using the *Local Density Approximation* (LDA) introduced by Kohn and Sham [54] (see also [79]). The resulting model is mathematically very similar to the so-called $X\alpha$ model [84] where the exchange-correlation functional is approximated by the Dirac local exchange term:

$$E_{\text{xc}}^{X\alpha}(\rho) = -C_D \int_{\mathbb{R}^3} \rho^{4/3},$$

where $C_D = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$ is the Dirac constant. Other more refined exchange-correlation functionals have been developed in the past 30 years, leading to the *Generalized Gradient Approximation* (GGA) [78], meta-GGA functionals [88], hybrid functionals [6], range-separated functionals [92] ... The Kohn-Sham ground state energy and density can be obtained by solving the Kohn-Sham equations (deduced from the Euler-Lagrange equations associated with (13) by a simple algebraic manipulation)

$$\left\{ \begin{array}{l} \rho^0(x) = \sum_{i=1}^N |\phi_i(x)|^2 \\ \mathfrak{h}_{\rho^0} \phi_i = \varepsilon_i \phi_i, \quad \varepsilon_1 < \varepsilon_2 \leq \varepsilon_3 \leq \dots \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \\ \mathfrak{h}_{\rho^0} = -\frac{1}{2} \Delta + V_{\rho^0}^{\text{H}} + V_{\rho^0}^{\text{xc}} \\ -\Delta V_{\rho^0}^{\text{H}} = 4\pi \left(\rho^0 - \sum_{k=1}^M z_k \delta_{\mathbf{R}_k} \right), \end{array} \right. \quad (14)$$

where the Kohn-Sham potential $V_{\rho^0}^{\text{KS}} = V_{\rho^0}^{\text{H}} + V_{\rho^0}^{\text{xc}}$ is the sum of the Hartree potential $V_{\rho^0}^{\text{H}} = \rho_0 \star |\cdot|^{-1}$ and of the exchange-correlation potential $V_{\rho^0}^{\text{xc}} = \frac{\partial E_{\text{xc}}}{\partial \rho}(\rho^0)$. The differences between the various Kohn-Sham models lay in the form of the exchange-correlation potential. For the so-called $X\alpha$ model, we have $V_{\rho^0}^{\text{xc}, X\alpha} = -\frac{4}{3} C_D \rho^{1/3}$. As for Hartree-Fock, the Kohn-Sham equations have the mathematical form of a nonlinear elliptic eigenvalue problem. The Kohn-Sham model, as well as its generalizations (extended Kohn-Sham model, spin-polarized Kohn-Sham model) and approximations (reduced Hartree-Fock model), have been studied mathematically in [3, 45, 58, 64, 85]. A interesting related topic concerning the construction of density functionals for the Coulomb interaction is addressed in [30].

3.2.3. Quantum Monte Carlo methods. Quantum Monte Carlo (QMC) methods (see e.g. [4] and references therein) aim at solving the N -body quantum problem by means of stochastic algorithms. The term QMC encompasses sev-

eral classes of methods including variational Monte Carlo (VMC), diffusion Monte Carlo (DMC), and path integral Monte Carlo. In the framework of electronic structure calculation, the most commonly used are VMC and DMC methods. For convenience, we use in this section the shorthand notation $\mathbf{x} = (x_1, \dots, x_N)$,

$$V(\mathbf{x}) = - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \quad \text{and} \quad H_N = -\frac{1}{2}\Delta + V,$$

where Δ is the Laplace operator in the $3N$ -dimensional space.

VMC methods allow one to efficiently compute the energy of a large class of (non necessarily normalized) electronic wavefunctions ψ . The name *Variational* Monte Carlo originates from the fact that this approach can be used, in the spirit of usual variational methods, to seek an approximation of the ground state energy E_0 (and of a ground state wavefunction ψ_0) by minimizing the Rayleigh quotient $\frac{\langle \psi | H_N | \psi \rangle}{\langle \psi | \psi \rangle}$ over a family $\{\psi^{\mathbf{p}}, \mathbf{p} \in \mathcal{P}\}$ of trial wave functions depending on a set of parameters \mathbf{p} . VMC methods are based on the observation that

$$\frac{\langle \psi | H_N | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int_{\mathbb{R}^{3N}} E_L^\psi(\mathbf{x}) |\psi(\mathbf{x})|^2 d\mathbf{x}}{\int_{\mathbb{R}^{3N}} |\psi(\mathbf{x})|^2 d\mathbf{x}},$$

where the scalar field $E_L^\psi(\mathbf{x}) = [H_N \psi](\mathbf{x})/\psi(\mathbf{x}) = -\frac{1}{2} \frac{\Delta \psi(\mathbf{x})}{\psi(\mathbf{x})} + V(\mathbf{x})$ is called the local energy. Hence,

$$\frac{\langle \psi | H_N | \psi \rangle}{\langle \psi | \psi \rangle} = \lim_{\mathcal{N} \rightarrow \infty} \frac{1}{\mathcal{N}} \sum_{n=1}^{\mathcal{N}} E_L^\psi(\mathbf{X}^n), \quad (15)$$

where $(\mathbf{X}^n)_{n \geq 1}$ are points of \mathbb{R}^{3N} sampling the probability distribution

$$d\mu_\psi(\mathbf{x}) = \frac{|\psi(\mathbf{x})|^2}{\int_{\mathbb{R}^{3N}} |\psi|^2} d\mathbf{x}.$$

The VMC method consists in approximating the right-side of (15) by a empirical mean for large, but finite values of \mathcal{N} . Note that if ψ is an eigenfunction of H_N associated with the eigenvalue E , $E_L^\psi(\mathbf{x}) = E$ almost everywhere, so that the variance of E_L^ψ vanishes. In this extreme case, the relation

$$\frac{\langle \psi | H_N | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{1}{\mathcal{N}} \sum_{n=1}^{\mathcal{N}} E_L^\psi(\mathbf{X}^n)$$

in fact holds true whatever \mathcal{N} and the realizations $(\mathbf{X}^n)_{1 \leq n \leq \mathcal{N}}$ of the random variable with law μ_ψ . Most often, VMC calculations are performed with trial wavefunctions ψ that are good approximations of a ground state wavefunction ψ_0 . Consequently, $E_L^\psi(\mathbf{x})$ usually is a function of low variance (with respect to the

probability distribution μ_ψ). This is the reason why, in practice, the empirical mean $\frac{1}{N} \sum_{n=1}^N E_L^\psi(\mathbf{X}^n)$ is a fairly accurate approximation of $\frac{\langle \psi | H_N | \psi \rangle}{\langle \psi | \psi \rangle}$, even for relatively “small” values of N .

Of course, the quality of this approximation depends on the way the points $(\mathbf{X}^n)_{n \geq 1}$ are generated. The standard sampling method currently used for VMC calculations is a Metropolis-Hastings algorithm based on a biased random walk in the configuration space \mathbb{R}^{3N} [4].

Let us now turn to the DMC method [4]. For the sake of simplicity, we assume that the ground state energy E_0 is a *simple* eigenvalue of H_N , considered as an operator on \mathcal{H}_N , and we denote by $g = E_1 - E_0$ the spectral gap between the ground state energy E_0 and the first excited state energy E_1 . The DMC method is based on the following observation. Let $\psi_I \in \mathcal{D}_N$. The unique solution $\psi(t, \mathbf{x})$ in $C^0(\mathbb{R}_+, \mathcal{D}_N) \cap C^1(\mathbb{R}_+, \mathcal{H}_N)$ of the parabolic problem

$$\begin{cases} \frac{\partial \psi}{\partial t}(t, \mathbf{x}) = -(H_N \psi(t, \cdot))(\mathbf{x}) = \frac{1}{2} \Delta \psi(t, \mathbf{x}) - V(\mathbf{x}) \psi(t, \mathbf{x}), \\ \psi(0, \mathbf{x}) = \psi_I(\mathbf{x}), \end{cases} \quad (16)$$

reads $\psi(t, \cdot) = e^{-tH_N} \psi_I$ and is such that

$$\|\exp(E_0 t) \psi(t) - \langle \psi_0 | \psi_I \rangle \psi_0\|_{L^2} \leq \|\psi_I - \langle \psi_0 | \psi_I \rangle \psi_0\|_{L^2} \exp(-gt),$$

where as above, ψ_0 denotes an L^2 -normalized ground state of H_N . If moreover $\langle \psi_0 | \psi_I \rangle \neq 0$, one also has

$$0 \leq E(t) - E_0 \leq \frac{\langle \psi_I | H | \psi_I \rangle - E_0}{|\langle \psi_0 | \psi_I \rangle|^2} e^{-gt}, \quad \text{where} \quad E(t) = \frac{\langle \psi_I | H_N | \psi(t) \rangle}{\langle \psi_I | \psi(t) \rangle}. \quad (17)$$

As equation (16) is posed on \mathbb{R}^{3N} , and as in addition, V has singularities, it seems difficult to numerically solve (16) with deterministic methods.

On the other hand, a stochastic representation formula of the solution to (16) is provided by the Feynman-Kac formula

$$\psi(t, \mathbf{x}) = \mathbb{E} \left(\psi_I(\mathbf{x} + \mathbf{W}_t) \exp \left(- \int_0^t V(\mathbf{x} + \mathbf{W}_s) ds \right) \right), \quad (18)$$

where the expectation \mathbb{E} is over the \mathbb{R}^{3N} -valued Wiener process $(\mathbf{W}_t)_{t \geq 0}$, and could *a priori* be used to estimate E_0 [74]. As such, (18) is however not adapted to numerical simulations: it has indeed been observed that for a given $\mathbf{x} \in \mathbb{R}^{3N}$, the variance of the random variable

$$Y_t^\mathbf{x} = \psi_I(\mathbf{x} + \mathbf{W}_t) \exp \left(- \int_0^t V(\mathbf{x} + \mathbf{W}_s) ds \right)$$

increases very quickly with time.

In practice, one makes use of an importance sampling technique. If the importance function ψ_I the DMC method is based upon is well-chosen, the ground state

energy is approximated with a very good accuracy. In most cases, taking for ψ_I a Hartree-Fock ground state is sufficient to recover 90% of the correlation energy (the correlation energy is defined as the difference between the exact ground state energy E_0 and the energy E_0^{HF} of the Hartree-Fock ground state); for molecular systems in which the main part of the correlation energy is non-dynamical, that is when the ground state ψ_0 is badly approximated by a single Slater determinant, but fairly well approximated by a linear combination of a few Slater determinants, it is however necessary to consider multi-configurational importance functions [47]. The DMC method works as follows. Assume that the importance function ψ_I is continuous and such that the fields

$$\mathbf{b}^{\psi_I}(\mathbf{x}) = \frac{\nabla \psi_I(\mathbf{x})}{\psi_I(\mathbf{x})} \quad \text{and} \quad E_L^{\psi_I}(\mathbf{x}) = \frac{(H_N \psi_I)(\mathbf{x})}{\psi_I(\mathbf{x})} = -\frac{1}{2} \frac{\Delta \psi_I(\mathbf{x})}{\psi_I(\mathbf{x})} + V(\mathbf{x})$$

exist for almost every $\mathbf{x} \in \mathbb{R}^{3N}$ and can be calculated with a reasonable computational cost (for instance, $\mathbf{b}^{\psi_I}(\mathbf{x})$ and $E_L^{\psi_I}(\mathbf{x})$ can be computed in $O(N^4)$ operations if ψ_I is a Slater determinant). Consider the function

$$f_1(t, \mathbf{x}) = \psi_I(\mathbf{x}) \psi(t, \mathbf{x}), \quad (19)$$

where ψ is the solution of (16). The energy $E(t)$ defined by (17) also reads

$$E(t) = \frac{\int_{\mathbb{R}^{3N}} E_L^{\psi_I}(\mathbf{x}) f_1(t, \mathbf{x}) d\mathbf{x}}{\int_{\mathbb{R}^{3N}} f_1(t, \mathbf{x}) d\mathbf{x}},$$

and an elementary calculation shows that f_1 is solution to the equation

$$\frac{\partial f}{\partial t} = \frac{1}{2} \Delta f - \text{div}(\mathbf{b}^{\psi_I} f) - E_L^{\psi_I} f, \quad f(0, \mathbf{x}) = |\psi_I(\mathbf{x})|^2. \quad (20)$$

The above partial differential equation can be interpreted as the Fokker-Planck equation of a drift-diffusion process with source term. This leads us to considering the stochastic process defined by the stochastic differential equation (SDE)

$$d\mathbf{X}_t^{\mathbf{x}} = \mathbf{b}^{\psi_I}(\mathbf{X}_t^{\mathbf{x}}) dt + d\mathbf{W}_t, \quad \mathbf{X}_0^{\mathbf{x}} = \mathbf{x}, \quad (21)$$

the function

$$f_2(t, \mathbf{x}) = |\psi_I(\mathbf{x})|^2 \mathbb{E} \left(\exp \left(- \int_0^t E_L^{\psi_I}(\mathbf{X}_s^{\mathbf{x}}) ds \right) \right), \quad (22)$$

and the real-valued function of time

$$E^{\text{DMC}}(t) = \frac{\mathbb{E} \left(E_L^{\psi_I}(\mathbf{X}_t) \exp \left(- \int_0^t E_L^{\psi_I}(\mathbf{X}_s) ds \right) \right)}{\mathbb{E} \left(\exp \left(- \int_0^t E_L^{\psi_I}(\mathbf{X}_s) ds \right) \right)}. \quad (23)$$

If the field \mathbf{b}^{ψ_I} were regular enough and well-behaved at infinity (globally Lipschitz for instance), the SDE (21) would be well-posed by classical results (see e.g. [87]).

Under the additional condition that the function $E_L^{\psi_I}$ is bounded below, the functions f_1 and f_2 respectively defined by (19) and (22), would coincide, as well as the two quantities of interest $E(t)$ and $E^{\text{DMC}}(t)$ defined by (17) and (23). This ideal scenario is encountered in the simulation of bosons, where the function ψ_I can be chosen positive everywhere, regular enough, and well-behaved at infinity. The situation is more delicate for fermions, as the field $\mathbf{b}^{\psi_I} = \frac{\nabla \psi_I}{\psi_I}$ is singular on the nodal surfaces of ψ_I . Under some technical assumptions we do not spell out in detail here, which are fulfilled for toy models (a system of non-interacting fermions confined in a harmonic potential), but should probably be refined to fully cover the case of electrons interacting with point nuclei, it is established in [20] that the SDE (21) has a unique solution, and that for all $\mathbf{x} \in U = \mathbb{R}^{3N} \setminus \psi_I^{-1}(0)$, the function $\mathbb{R}_+ \ni t \mapsto \mathbf{X}_t^{\mathbf{x}} \in \mathbb{R}^{3N}$ is in $C^0(\mathbb{R}_+, \mathcal{C}(\mathbf{x}))$, where $\mathcal{C}(\mathbf{x})$ is the connected component of U containing \mathbf{x} . In particular, the trajectories of (21) cannot cross the nodal surfaces $\psi_I^{-1}(0)$. This is due to the fact that close to the nodal surfaces, the random variable $\delta(t) = \text{dist}(\mathbf{X}_t^{\mathbf{x}}, \psi_I^{-1}(0))$ behaves as the solutions to the SDE

$$dx_t = x_t^{-1} dt + dB_t,$$

where $(B_t)_{t \geq 0}$ is a one-dimensional Wiener process, which are known to stay away from zero almost surely in finite times. On the other hand, and similar to the case when \mathbf{b}^{ψ_I} is globally Lipschitz, the random variable $\mathbf{X}_t^{\mathbf{x}}$ has a density $p(t, \mathbf{x}, \mathbf{y})$ and the function $(\mathbf{x}, \mathbf{y}) \mapsto \psi_I(\mathbf{x})^2 p(t, \mathbf{x}, \mathbf{y})$ is symmetric. In the fermionic setting, the function f_2 defined by (22) still is a solution to (20) in the distributional sense, but it is not equal to f_1 . More precisely, it holds

$$f_2(t, \mathbf{x}) = \psi_I(\mathbf{x}) \phi(t, \mathbf{x}),$$

where $\phi(t, \mathbf{x})$ is the unique solution in $C^0(\mathbb{R}_+, \mathcal{D}_N) \cap C^1(\mathbb{R}_+, \mathcal{H}_N)$ to

$$\begin{cases} \frac{\partial \phi}{\partial t}(t, \mathbf{x}) = \frac{1}{2} \Delta \phi(t, \mathbf{x}) - V(\mathbf{x}) \phi(t, \mathbf{x}), \\ \phi(0, \mathbf{x}) = \psi_I(\mathbf{x}), \\ \phi(t, \mathbf{x}) = 0 \text{ on } \psi_I^{-1}(0). \end{cases} \quad (24)$$

Problem (24) differs from problem (16) through the additional homogeneous Dirichlet condition that ϕ vanishes on the nodal surfaces of ψ_I . As a consequence, $E^{\text{DMC}}(t)$ differs from $E(t)$ and it holds [20]

$$\lim_{t \rightarrow +\infty} E^{\text{DMC}}(t) = E_0^{\text{DMC}},$$

where

$$E_0^{\text{DMC}} = \inf \{ \langle \psi | H_N | \psi \rangle, \psi \in \mathcal{Q}_N, \|\psi\|_{L^2} = 1, \psi = 0 \text{ on } \psi_I^{-1}(0) \}.$$

Obviously $E_0^{\text{DMC}} \geq E_0$, and the equality holds if and only if the nodal surfaces of ψ_I coincide with those of a ground state ψ_0 of H_N . The systematic bias introduced by the choice of a function ψ_I which does not have the same nodes as ψ_0 (which is the case in practice), is called the *fixed node error*. Getting rid of the fixed node error in quantum Monte Carlo simulations of fermions is one of the major challenges in computational physics.

4. Some recent advances and open questions

4.1. Towards certified numerical methods. As we have seen, the Hartree-Fock and Kohn-Sham models are infinite-dimensional constrained (non-convex) optimization problems, whose Euler-Lagrange equations are nonlinear elliptic eigenvalue problems. Computing numerically the Hartree-Fock or Kohn-Sham ground states therefore requires

1. a discretization method to transform the infinite-dimensional problem into a finite-dimensional one;
2. an iterative algorithm to solve the so-obtained finite-dimensional constrained optimization problem, or the associated Euler-Lagrange equations.

Theoretical chemists and computational physicists have devoted a lot of effort to the development of efficient discretization methods for electronic structure calculation. The most common discretization methods are Gaussian atomic orbitals [49] for molecules, and planewaves [36] for solid state physics and materials science. New approaches based on wavelets [43] or discontinuous Galerkin methods [71] have also been recently introduced. We refer to [13] for a recent review of the iterative algorithms for solving the discretized Hartree-Fock and Kohn-Sham problems. The development of fast numerical methods is an active field of research [8, 33, 34, 42, 52, 69, 70, 72]. Note that optimized black-box algorithms are not yet available, and that very few convergence results for existing algorithms [22, 23, 60] have been established so far.

One of the challenges for the next decade is to construct accurate and robust error estimators with respect to the various numerical parameters used to perform the calculation (truncation of the discretization basis in variational approximations, number of points in numerical quadratures, convergence thresholds for iterative algorithms, ...). These estimators could then be used to adapt in real time the numerical parameters to equilibrate the various sources of error. As a result, the maximal committed error could be certified and the simulation time strongly reduced in comparison with the current usual approach consisting in fixing *a priori* the numerical parameters and testing the quality of the chosen parameters by checking that the results hardly change when refining the discretization and reducing the convergence thresholds. Important progress in this direction has been made in the last few years; in particular, optimal *a priori* error bounds on nonlinear eigenvalue problems have recently been obtained [14], and these results have been applied to the analysis of Kohn-Sham models [15, 29]. The construction of *a posteriori* error estimators for Kohn-Sham is a current active field of research.

4.2. Multiscale models. An important, very challenging, mathematical and numerical problem is concerned with the coupling of quantum chemistry models with coarser models in view of simulating larger molecular systems. Such approaches include QM/MM models [90] (for the development of which Karplus, Levitt and Warshel were awarded the 2013 Nobel Prize in Chemistry), and implicit

solvation models [91]. QM/MM models consist in cutting the molecular system (say a drug interacting with a protein) into two subsystems (the drug and the active site of the protein on the one hand, the rest of the protein on the other hand) and in treating the first one (small but key) with quantum mechanics (QM) and the second one (large and playing the role of the “environment”) with classical molecular mechanics (MM). Understanding such coupling between quantum and classical models is an essentially open mathematical question.

So far, we assumed that the molecule under study could be considered as an isolated system, which is almost never the case in practice. In particular, most chemical reactions take place in the liquid phase. In principle, we could apply the models previously introduced to a “supermolecule” consisting of the solute molecule and a big number of solvent molecules. This is however not doable in practice for two reasons. First, this would dramatically increase the size of the system; second, we would need to properly sample and average over the configurations of the solvent molecules, which is very difficult and most often unfeasible in practice. Implicit solvation models, which date back to Born, Kirkwood and Onsager, consist in replacing all the solvent molecules but the few ones strongly interacting with the solute, with an effective continuous medium accounting for long-range electrostatics. This amounts to replacing the Poisson equation in (14) by the inhomogeneous elliptic equation

$$-\operatorname{div}(\epsilon \nabla V_{\rho^0}^H) = 4\pi \left(\rho^0 - \sum_{k=1}^M z_k \delta_{\mathbf{R}_k} \right), \quad (25)$$

with $\epsilon(x) = 1$ inside a cavity Ω containing the molecule (see Fig. 5) and $\epsilon(x) = \epsilon_s$ outside Ω , where ϵ_s is the macroscopic dielectric permittivity of the solvent (about 80 for water). A numerical method coupling Schwarz’s domain decomposition method with integral equations has recently been proposed to solve the so-called COSMO approximation of (25) in the framework of classical and quantum molecular models [75]. This allows one to perform geometry optimization on large molecules in solution with a limited extra-cost with respect to the same calculation *in vacuo*.

Implicit solvation models are widely used in chemistry and give satisfactory results in many cases. On the other hand, they fail in other cases, in particular in the presence of strong interactions between the solute and the solvent. Also, the definition of the molecular cavity Ω is a touchy business, and some physical properties may strongly depend on the chosen definition. For all these reasons, constructing better solvation models using mathematical tools such as model reduction techniques is an interesting problem of major importance for applications.

4.3. Thermodynamic limits and the crystal problem. In contrast with the contents of the previous two subsections, we now present a purely theoretical problem. Consider a cluster with L^3 identical atoms, put the L^3 nuclei on the sites of a cubic lattice (for simplicity) and compute the electronic ground state for this nuclear configuration (Fig. 5). Several questions are in order: when L goes to infinity,

- (i) does the ground state energy per atom converge?
- (ii) does the ground state electronic density converge?
- (iii) does it converge to a periodic density?
- (iv) can those quantities be obtained by solving a periodic problem on a unit cell?
- (v) if nuclei are allowed to relax to their equilibrium positions for finite L , do we obtain a periodic crystal in the limit?

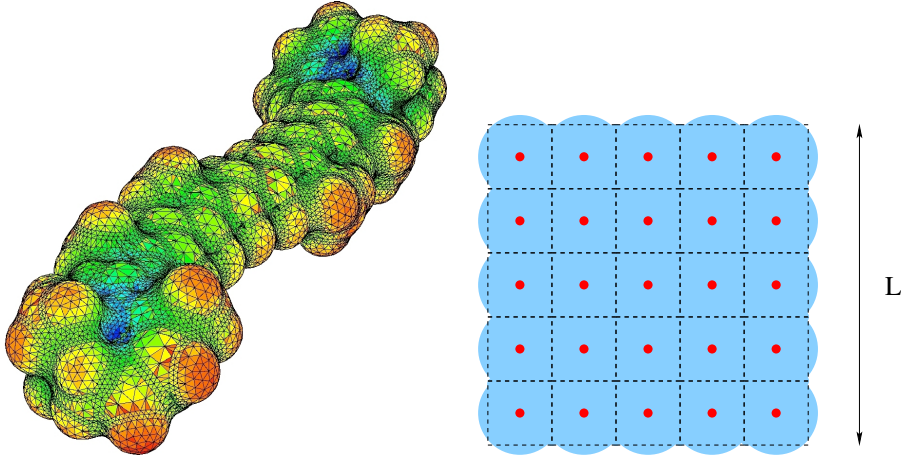


Figure 5. Left: a molecular cavity for the carotene molecule used in implicit salvation models (courtesy P. Laug, Inria). Right: a cubic cluster of size L . The thermodynamic limit problem consists in studying the limit of the electronic structure of the cluster when L goes to infinity.

The first four questions fall into the scope of thermodynamic limit problems. The fifth issue is called the crystal problem. The thermodynamic limit problems in the terms stated above have been the subject of many outstanding contributions in the context of various energy models and various physical systems [26, 38, 48, 65, 66, 81]. The thermodynamic limit problem is completely solved for the TF [67] and TFW [26] models. For Hartree-Fock and Kohn-Sham type models, the fundamental issues (ii)-(iii) remain open. The two key difficulties are first that the latter models are not convex (convexity plays a crucial role in the analysis of the TFW model) and second that the number of molecular orbitals ϕ_i to be dealt with, or equivalently the rank of the one-body density matrix $\gamma_\Phi = \sum_i |\phi_i\rangle\langle\phi_i|$, are also growing to infinity (in the TFW model, only the density ρ is relevant). For the HF model, partial results have been established [27, 44]. The results are partial in the sense that it is needed to *postulate*, in addition to the periodicity of the set of nuclei, the periodicity of the ground state density matrix in the limit. A simplified version of the HF model, namely the reduced Hartree-Fock model however allows for a complete proof [27].

4.4. Crystals with defects and disordered systems. In the previous section, we dealt with perfect crystals, while the really interesting systems for the applications are crystals with defects. The difficulty is that such systems contain infinitely many interacting electrons and have no symmetry allowing us to reduce the problem to a periodic cell, as is the case for perfect crystals. In the past few years, some progress has been made in the theoretical understanding of Kohn-Sham models for insulating and semiconducting crystals with local defects [17, 18, 24], but the cases of metals and extended defects is still open (see [40] for the case of a uniform electron gas and [19] for the TFW model). On the numerical side, very little is known: in particular, there is no completely satisfactory method to deal with charged defects in insulators and semi-conductors.

A huge amount of literature has been devoted to modeling electrons in random materials. In most cases, electrons are considered as non-interacting particles subjected to a stationary empirical potential $V(\omega, x)$ [25]. The analysis of the electronic properties of the material then reduces to the analysis of the spectral properties of the associated random Schrödinger operator $H(\omega) = -\frac{1}{2}\Delta + V(\omega, \cdot)$ acting on $L^2(\mathbb{R}^3)$. A remarkable property of random Schrödinger operators is that, under some ergodicity and integrability assumptions on V , the spectrum of $H(\omega)$ is deterministic: there exists a closed set $\Sigma \subset \mathbb{R}$ such that $\sigma(H(\omega)) = \Sigma$ almost surely. Similar results hold for the density of states (that is, loosely speaking, the number of quantum states per unit volume) of the Hamiltonian $H(\omega)$ [11]. Interesting questions are concerned with the nature of the spectrum (point spectrum, absolutely continuous spectrum, ...), which is related to the electronic transport properties of the material. We refer to [25, 86] and references therein for more details on the linear case.

Serious additional difficulties arise for models with interacting electrons. Recent results have been obtained on the thermodynamic limit of disordered quantum systems composed of interacting particles with short-range (Yukawa) interactions [9, 21, 93]. The case of long-range (Coulomb) interactions was investigated in [10]. The existence of a thermodynamic limit is proven, but the limit is not identified. An interesting open problem consists in studying the case of rare but possibly large random perturbations, which corresponds to the physical situation of doped semiconductors with low concentration of impurities. This question has been successfully addressed in [53] in the case of a linear model of non-interacting electrons. The case of interacting electrons with short-range interactions is dealt with in [56]. The problem is still open for electrons in Coulomb interactions.

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The bibliography mostly contains *mathematical* contributions to the field of electronic structure calculation. Due to the lack of space, very few of the hundreds of relevant references of the physics and chemistry literatures are cited.

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