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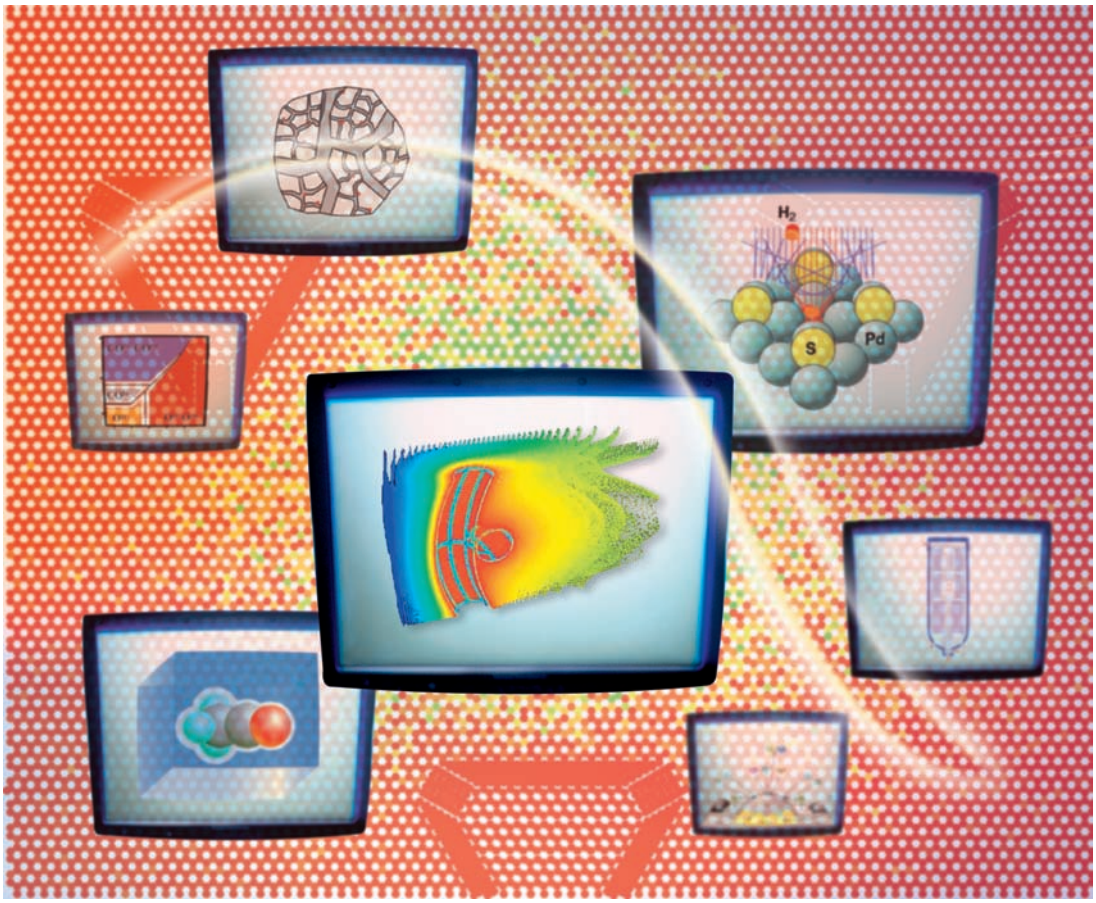
Modeling and Simulation of Heterogeneous Catalytic Reactions



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Modeling and Simulation of Heterogeneous Catalytic Reactions

From the Molecular Process to the Technical System

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Preface

The Nobel Prize in Chemistry 2007 awarded to Gerhard Ertl for his groundbreaking studies in surface chemistry highlighted the importance of heterogeneous catalysis not only for modern chemical industry but also for environmental protection. Today, heterogeneous catalysis is also expected to be the key technology to solve the challenges associated with the increasing diversification of raw materials and energy sources. Heterogeneous catalysis is the decisive step in most chemical industry processes, it is the major way to reduce pollutant emissions from mobile sources, and it is present in fuel cells to produce electricity and in many systems for the use of solar energy (photocatalysis).

With the increasing power of computers over the past decades and the development of numerical algorithms to solve highly coupled, nonlinear, and stiff equation systems, modeling and numerical simulation also have developed into valuable tools in heterogeneous catalysis. These tools were applied to study the molecular processes in very detail by quantum mechanical computations, density functional theory (DFT), molecular dynamics, and Monte Carlo simulations, but often neglecting the engineering aspects of catalytic reactors such as the interaction of chemistry and mass and heat transfer on one side. On the other side, mixing, flow structures, and heat transport in technical reactors and processes have been analyzed by computational fluid dynamics (CFD) in very detail, neglecting, however, the details of the microkinetics.

One objective of this book is to span bridges over the still existing gaps between both communities regarding modeling of heterogeneous catalytic reactions. In the past years, quite frequently, research proposal and programs on catalysis claim to work on bridging those gaps between surface science and industrial catalysis and indeed some progress has been made. Surface science studies, in experiment, theory, and simulation, more and more include technically relevant conditions. Reaction engineering of technical processes now often tries to understand the underlying molecular processes and even include quantum mechanical simulations in the search and development of new catalysts and catalytic reactors. However, convergence here is a slow process. One major reason is the gap between the high complexity of catalysts used in practice and the many approximations still to be made in molecular simulations. Furthermore, using kinetic data derived from numerical simulations in scale-up of technical systems might indeed become risky if the

engineer does not take into account the simplifying assumptions and the computational uncertainties of the numerical simulations. Actually, this warning holds for all simulations relevant for heterogeneous catalysis, from DFT to CFD. In many chapters of this book, the authors will lead the reader not only to the potentials but also to the limitations of the modeling approaches and show where the use of the models presented are beneficial and where they are rather risky.

In this book, the state of the art in modeling and simulations of heterogeneous catalytic reactions will be discussed on a molecular level and from an engineering perspective. Special attention is given to the potentials and – even more important – to the limitations of the approaches used. The reader will become familiar not only with the principal ideas of modeling in heterogeneous catalysis but also with the benefits, challenges, and still open issues. The book is organized as follows: from chapter to chapter, time- and length scales as well as complexity increase on the expense of details of the molecular processes bridging all the way from the surface science to the industrial view on modeling heterogeneous catalytic reactions (Figure 1).

The book starts with a chapter on density functional theory presenting the concept of theoretical calculations of surface reactions. The electrocatalytic oxygen reduction is used as an example, showing the potential of DFT to study different mechanistic aspects, also including environmental effects. On the basis of the energy diagram derived and the ambient conditions, the likelihood of the realization of a specific reaction pathway can be estimated. Chapter 2 focuses on the computation of the dynamics of reactions at surfaces from first principles.

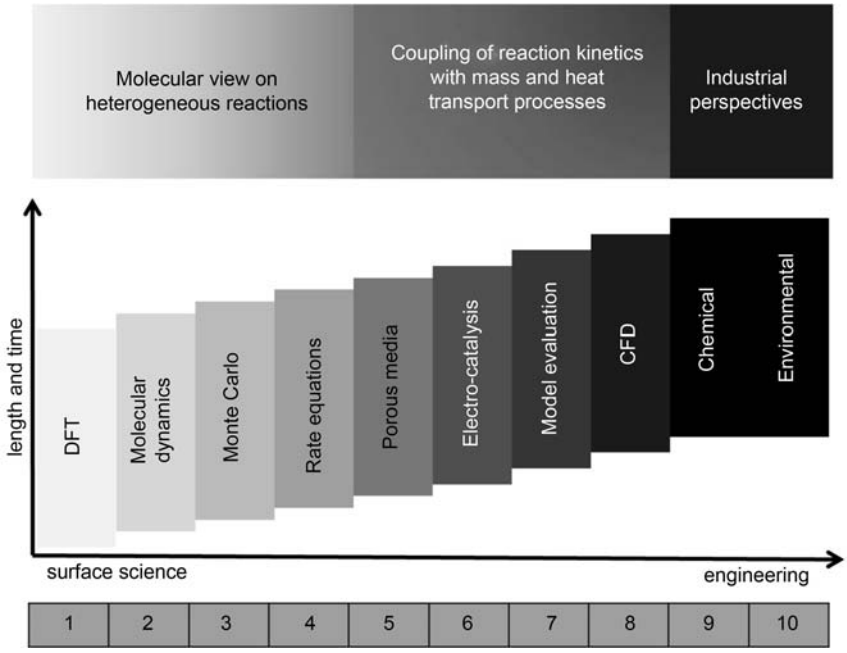

Figure 1 Organization of the book.

These dynamical simulations reveal the actual trajectory of the movement of a molecule on a catalytic surface but are in general restricted to the computation of this trajectory within few nanoseconds. If the interest is rather in the probability whether or not a certain process (adsorption, diffusion, or reaction) takes place, then Monte Carlos (MC) simulations are the model of choice, which are discussed in Chapter 3. Using information derived from DFT, first-principles kinetic Monte Carlo simulations lead directly to the surface reaction rate as function of ambient conditions and the state of the catalyst. They combine elementary kinetics with statistics to properly evaluate the kinetics of the catalytic particle. The diverse morphology of catalytic particles in technical systems calls for a simpler approach because MC simulations are too expensive to be directly included in simulation of catalytic reactors including mass and heat transfer. Chapter 4 therefore moves from MC simulations to rate equations to estimate surface reaction rates and homogeneous gas-phase reaction rates that also play a role in many catalytic processes. In this so-called mean-field approximation, the details of the molecular process such as diffusion of adsorbates and the dependence of the reaction rate on the crystal phases and defects are not taken directly into account. We now move from the microscopic to the mesoscopic processes. Chapter 5 is then the first part of the book in which the interaction of surface reactions and molecular transport of the reactants and products in the ambience of the catalytic particle is considered. This chapter covers modeling of processes in catalytic porous media and the interaction of diffusion and reactions in those pore structures. The last chapter on fundamentals (Chapter 6) also includes electrochemical charge transfer and couples it with the heterogeneous (thermo-) catalytic reactions and transport in porous media using processes in solid-oxide fuel cells as an illustrating example. Chapter 7 discusses the applicability of molecular-based models, in particular of rate equations, in reactive flow systems and their coupling to the surrounding mass transport processes. The comparison of spatially and temporally resolved species profiles in catalytic laboratory reactors using sophisticated experimental techniques with the profiles computed by coupling chemistry and mass transport models can be used for the evaluation of kinetic schemes developed. The coupling of chemistry and heat and mass transport in catalytic reactors is discussed in Chapter 8, using several multiphase flow systems as examples. Now the book has reached the macroscopic view. The last two Chapters 9 and 10 critically discuss the use, benefits, and limitations of modeling tools in chemical and automobile industry today.

Karlsruhe, August 2011 *Olaf Deutschmann*

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1
Modeling Catalytic Reactions on Surfaces with Density Functional Theory

John A. Keith, Josef Anton, Payam Kaghazchi, and Timo Jacob

1.1
Introduction

Predicting the reactivity of catalytic systems is a nontrivial process that usually requires knowledge about its geometric and electronic structure, properties determined by quantum mechanics (QM). Solving the Schrödinger equation[1)] is a nontrivial task even for small systems, and it becomes especially arduous when the system involves multiple phases as is the case in a surface reaction. Theoretical calculations nevertheless provide useful and important perspectives on chemical reactions that are not accessible through experimental observations alone. Figure 1.1 schematically shows the hierarchy of multiscale modeling, starting from the subatomic regime, over the electronic and atomistic regimes, to the meso- and finally the macroscale. Different theoretical methods have been established to address questions related to each regime (or timescale and length scale); however, realistic processes usually involve effects from all scales. In this chapter, we will focus on the electronic and atomistic regimes, which not only provide the basis for climbing up the hierarchy of multiscale modeling but also provide important mechanistic information on catalytic reactions.

Quantum chemistry is the application of QM to better understand chemical systems. In its purest form, QM calculations solve the Schrödinger equation, which provides the energy of a given configuration of nuclei and their electrons. There are two general approaches to do this. One way is to solve the energy given by the Schrödinger equation approximately using a nonclassical wavefunction. Another popular approach, density functional theory (DFT), uses the electronic density to evaluate the energy of a system via an approximate functional. Both approaches have their merits and provide a nonthermodynamical representation of the energy of a system of electrons.

This chapter gives an introductory overview of the essential concepts behind theoretical calculations of surface reactions, which we then apply to better understand one of the key features in energy conversion and fuel cell technology:

1) For the relativistic case, one has to consider the Dirac equation.

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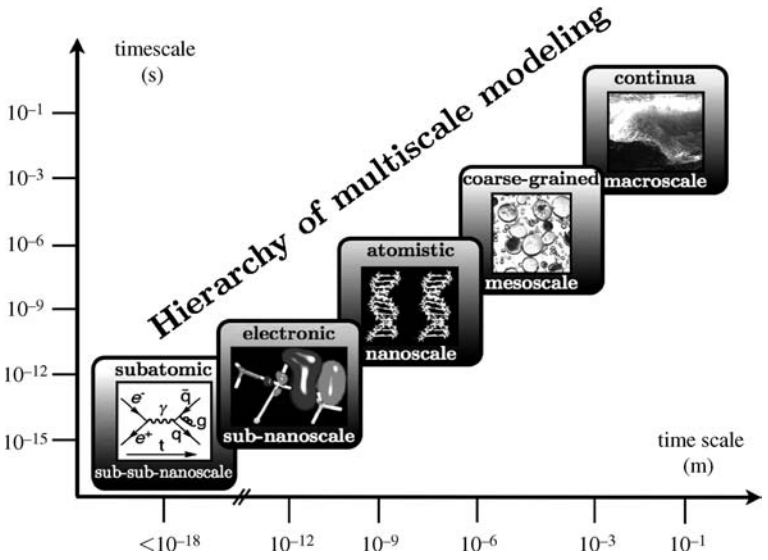

Figure 1.1 Hierarchy of multiscale modeling of different time and length regimes.

the electrocatalytic oxygen reduction reaction (ORR). After describing the multibody problem in quantum mechanics, we will discuss the fundamentals behind wave function- and density-based methods used to solve this problem. We will then focus on density functional theory and its advantages and disadvantages in applications to catalysis. Section 1.2, the first part of this chapter, ends with brief technical details one has to grapple with when modeling surface reactions. This includes thermodynamic approximations and other considerations that extend calculated values from theoretical studies to be more comparable to experiment. Section 1.3, the second part of this chapter, shows an example how quantum mechanical DFT calculations can resolve mechanistic details of a rather complex surface reaction.

1.2
Theoretical Background

1.2.1
The Many-Body Problem

Many material properties of interest to physicists and chemists can be obtained by solving the many-body Schrödinger equation. In stationary, nonrelativistic terms it can be written as

$$\hat{H}\Psi(\mathbf{r}_i\sigma_i, \mathbf{R}_\nu) = E\Psi(\mathbf{r}_i\sigma_i, \mathbf{R}_\nu), \tag{1.1}$$

where $\hat{H}$ is the Hamilton operator, $\Psi(\mathbf{r}_i\sigma_i, \mathbf{R}_\nu)$ is the many-body wave function, E is the total energy of the system, σ_i is the spin coordinate of electron i, and finally $\mathbf{r}_i$

and $\mathbf{R}_\nu$ are the spatial coordinates of electron i and nucleus ν, respectively. The Hamiltonian for a system consisting of a set of nuclei and electrons can be written as[2)]

$$\hat{H} = \sum_{\nu=1}^{N} \hat{T}_\nu + \underbrace{\sum_{i=1}^{M} \hat{t}_i - \sum_{i=1}^{M}\sum_{\nu=1}^{N} \frac{Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{M} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{H}_e} + \frac{1}{2}\sum_{\substack{\nu,\mu=1 \\ \nu\neq\mu}}^{N} \frac{Z_\nu Z_\mu}{|\mathbf{R}_\nu - \mathbf{R}_\mu|}, \tag{1.2}$$

where $\hat{T}_\nu$ and $\hat{t}_i$ are the respective kinetic energy operators for nuclei and electrons, and Z_ν is the charge on a nucleus. The two species (electrons and nuclei) interact with each other and themselves. It is difficult to solve such a coupled system since the motion of any particle is influenced by all other particles. Except for simple systems such as a hydrogen atom, solving Eq. (1.1) with the corresponding Hamiltonian, Eq. (1.2), is nontrivial for most materials that consist of several electrons and nuclei. Therefore, simulations of realistic systems require different applications of approximations.

1.2.2 Born–Oppenheimer Approximation

The Born–Oppenheimer (BO) approximation (introduced by Max Born and J. Robert Oppenheimer in 1927 [1]) treats the electronic and nuclear degrees of freedom as decoupled from each other. Nuclei are much more massive than electrons, so electrons are assumed to instantaneously follow the motion of the nuclei. Consequently, on the timescale of the motion of the electrons, the nuclei appear almost stationary. The total wave function of Eq. (1.1) can then be written as[3)]

$$\Psi(\mathbf{r}_i\sigma_i, \mathbf{R}_\nu) = \psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\})\psi_n(\mathbf{R}_\nu) \tag{1.3}$$

where $\psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\})$ and $\psi_n(\mathbf{R}_\nu)$ are the electronic and nuclei wave functions, and $\{\mathbf{R}_\nu\}$ denotes that nuclear spatial coordinates are parameters and not variables. We then can divide the electronic and nuclear parts into

$$\begin{aligned}\hat{H}_e\psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\}) &= \left(-\sum_{i=1}^{M}\frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{M}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{M}\sum_{\nu=1}^{N}\frac{Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} \right) \psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\}) \\ &= E_e(\mathbf{R}_\nu)\psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\})\end{aligned} \tag{1.4}$$

2) Throughout this chapter, atomic units are assumed.

3) This is an expansion of $\Psi(\mathbf{r}_i\sigma_i, \mathbf{R}_\nu)$ in a series of eigenfunctions of the electronic Hamilton operator $\hat{H}_e$. Since in chemistry electronic excitations usually do not play a substantial role, we restrict our discussion to the eigenfunctions with the lowest energy of the electronic system (ground state) $\psi_e(\mathbf{r}_i\sigma_i, \{\mathbf{R}_\nu\})$.

and

$$\left(-\sum_{\nu=1}^{N}\frac{1}{2m_\nu}\nabla_\nu^2+\frac{1}{2}\sum_{\substack{\nu,\mu=1\\ \nu\neq\mu}}^{N}\frac{Z_\nu Z_\mu}{|\mathbf{R}_\nu-\mathbf{R}_\mu|}+E_\mathrm{e}(\mathbf{R}_\nu)\right)\psi_\mathrm{n}(\mathbf{R}_\nu)=E\psi_\mathrm{n}(\mathbf{R}_\nu). \tag{1.5}$$

In Eq. (1.4), $\hat{H}_\mathrm{e}$ and ψ_e depend only on the positions of the nuclei. In the case of negligible nonadiabatic effects, this approximation introduces a very small error into the energies, and this inaccuracy becomes even smaller for heavier elements [2]. Applying this approximation, we can restrict ourselves to the electronic part[4] (Eq. (1.4)), which can be solved exactly for one-electron systems only. Thus, we need further approximations for systems with many electrons. Many techniques solve the Schrödinger equation approximately from first principles (*ab initio*). Two common types of *ab initio* methods are the wave function-based and the density-based approaches [3]. Both have been applied extensively in material science and catalysis.

1.2.3 Wave Function-Based Methods

The Born–Oppenheimer approximation reduces the many-body problem to the electronic part only (with the positions of the nuclei as parameters), but the electronic wave function is still a function of the spatial coordinates of the electrons and their spin variables. We now describe the Hartree–Fock (HF) approximation, which can be viewed as the basis for all practical *ab initio* developments. This approach does not include any correlation effects, and we will later describe different approaches to account for these.

1.2.3.1 Hartree–Fock Approximation

In 1927, Hartree [4] considered the electron motions as independent (uncorrelated). Each electron could then be treated as moving in an averaged field originating from all other electrons.[5] Three years later, Fock [5] followed Hartree's idea to express the overall electronic wave function as simple product of single-particle wave functions, but he introduced the fermionic character of the electrons by using an antisymmetric sum product of single-particle wave functions. The most simple *ansatz* for such a representation is given by a single Slater determinant [6]:

$$\psi_\mathrm{e}=\frac{1}{\sqrt{M!}}\begin{vmatrix}\varphi_1(\mathbf{r}_1\sigma_1) & \varphi_1(\mathbf{r}_2\sigma_2) & \dots & \varphi_1(\mathbf{r}_M\sigma_M)\\ \varphi_2(\mathbf{r}_1\sigma_1) & \varphi_2(\mathbf{r}_2\sigma_2) & \dots & \varphi_2(\mathbf{r}_M\sigma_M)\\ \vdots & \vdots & & \vdots\\ \varphi_M(\mathbf{r}_1\sigma_1) & \varphi_M(\mathbf{r}_2\sigma_2) & \dots & \varphi_M(\mathbf{r}_M\sigma_M)\end{vmatrix}, \tag{1.6}$$

where $\varphi_i(\mathbf{r}_j\sigma_j)$ describes electron i at the position of electron j. According to Ritz [7], the lowest-energy system state corresponds to the ground state, which is obtainable

4) Although Eq. (1.4) is the main electronic contribution, in practice we usually also consider the second term of Eq. (1.5).

5) This is usually called the model of independent electrons or the effective one-particle model.

by variation under the constraint of an orthonormal[6] set of single-particle wave functions $\varphi_i(\mathbf{r}_j\sigma_j)$:

$$\delta\left\{E_e - \sum_{i,j=1}^{M} \varepsilon_{ij}\langle\varphi_i|\varphi_j\rangle\right\} = 0. \tag{1.7}$$

This finally leads to the well-known Hartree–Fock equations:

$$\hat{F}(\mathbf{r}_i)|\varphi_i\rangle = \sum_{j=1}^{M} \varepsilon_{ij}|\varphi_j\rangle, \quad i = 1, 2, \ldots, M. \tag{1.8}$$

Here, $\hat{F}$ is the Fock operator, which can be written as[7]

$$\hat{F}(\mathbf{r}_i) = \hat{t}_i - \sum_{\nu=1}^{N} \frac{Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} + \sum_{j=1}^{M} \int \varphi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r}_i - \mathbf{r}'|} \varphi_j(\mathbf{r}')\, \mathrm{d}\mathbf{r}' + V_x(\mathbf{r}_i). \tag{1.9}$$

The last term originates from the Pauli principle and describes the nonlocal exchange, for which there is no classical analogue:

$$V_x(\mathbf{r}_i) = -\sum_{j=1}^{M} \int \frac{1}{|\mathbf{r}_i - \mathbf{r}'|} \frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}_i)\varphi_i^*(\mathbf{r}_i)\varphi_i(\mathbf{r}')}{\varphi_i^*(\mathbf{r}_i)\varphi_i(\mathbf{r}_i)} \mathrm{d}\mathbf{r}'. \tag{1.10}$$

Due to the aforementioned nonlocal character of the exchange, practical calculation of this term is extremely demanding. Dirac [8] and Bloch [9] independently showed that the exchange integral for a free electron gas can be expressed as function of the electronic density. In order to generalize this idea, Slater [10, 11] added a scaling factor X_α to the expression for the free electron gas

$$V_x(\mathbf{r}_i) = -3X_\alpha \left(\frac{3}{8\pi}\varrho(\mathbf{r}_i)\right)^{1/3}. \tag{1.11}$$

For the free electron gas, the scaling factor is 2/3. However, a value of $X_\alpha = 0.7$ led to an improved accuracy for atoms [12, 13].

Insertion of the Slater approximation into the exchange term of the HF equations finally leads to the so-called Hartree–Fock–Slater equation (HFS).

1.2.3.2 Post Hartree–Fock Methods

A critical shortcoming of HF theory is its lack of *electronic correlation*, that is, the treatment of systems of electrons interacting with each other. This correlation is often separated into two parts. *Dynamical* correlation relates to responsiveness of electrons interacting with each other, while *nondynamical* electronic correlation relates to how a real system's energy is due to contributions from several accessible electronic states. HF theory treats neither and is not accurate enough to make reliable chemical

6) In the variation, the constraints are usually included as Lagrange multipliers ε_{ij}.

7) Spin variables have not been expressed explicitly.

determinations, but additional corrections have been developed in order to account for these shortcomings such as full CI (configurational interaction), Møller–Plesset perturbation theory (MP*n*), complete active space (CAS), or coupled cluster (CC) methods (see Refs. [14–16] for more details). The majority of these methods are under the umbrella of fully first-principles methods, that is, *ab initio* wave function methods that incorporate no empirical data into their calculation. For problems in catalysis, most of these methods are too expensive in practice; however, the MP2 method is occasionally useful in calculating dispersion forces and van der Waals interactions.

General perturbation theory presumes that the magnitude of a perturbation in a calculation is small compared to the unperturbed value of the calculation itself. This is valid for the electron correlation energy, which is small compared to the HF energy. According to perturbation theory in quantum mechanics, the total Hamiltonian is divided into the unperturbed reference Hamiltonian ($\hat{H}_0$) plus the Hamiltonian corresponding to its correction ($\hat{H}'$) times a scaling factor λ, which determines the strength of the perturbation:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'. \tag{1.12}$$

Based on this separation, perturbation theory yields the different terms of the Taylor expansion of the electronic energy. Consequently, the first two orders of correction to the energy of an electronic state n become

$$\begin{aligned} E_{\mathrm{e},n}^{(1)} &= \left\langle \psi_{\mathrm{e},n}^{(0)} | \hat{H}' | \psi_{\mathrm{e},n}^{(0)} \right\rangle \\ E_{\mathrm{e},n}^{(2)} &= \sum_{j \neq n} \frac{\left| \left\langle \psi_{\mathrm{e},n}^{(0)} | \hat{H}' | \psi_{\mathrm{e},j}^{(0)} \right\rangle \right|^2}{E_{\mathrm{e},n}^{(0)} - E_{\mathrm{e},j}^{(0)}} \end{aligned} \tag{1.13}$$

In Møller–Plesset perturbation theory, $\hat{H}_0$ is taken as the sum of one-electron Fock operators. The sum of $E_{\mathrm{e},n}^{(0)} + E_{\mathrm{e},n}^{(1)}$ is the electronic HF energy,[8] and additional $E_{\mathrm{e},n}^{(i>1)}$ corrects the HF energy for electronic correlation. Calculations including the first additional correction $E_{\mathrm{e},n}^{(2)}$ are called MP2 methods, while MP3, MP4, and so on also treat higher perturbation orders.

Although Møller–Plesset perturbation theory in principle allows for a full inclusion of electronic correlations, evaluating even the first correction terms becomes quite expensive as the number of electrons in the system increases. Even nowadays, MP2 is often considered too expensive for simulating surface reactions.

1.2.4
Density-Based Methods

Instead of employing many-body wave functions, density-based methods use the electron density as the basic variable to evaluate the total energy and other properties. A well-known density-based approach is the density functional theory, which was introduced by Hohenberg and Kohn in 1964 [17] and further developed by Kohn and

8) In HF approximation, $E_{\mathrm{e},n}^{(1)} = 0$.

Sham in 1965 [18]. This method dates back to the works of Thomas and Fermi (TF). Before describing the DFT approach itself, we briefly review the TF model. Although this section focuses on the electronic part of the many-body problem, for simplicity, the index e is not given explicitly.

1.2.4.1 The Thomas–Fermi Model

The electronic part of the many-body wave function containing M electrons, $\psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_M\sigma_M)$, is not easy to calculate since it depends on $4M$ coordinates ($3M$ coordinates if spin is not considered). Thomas and Fermi proposed a simpler approach, the TF model, using the electron density of the system $\varrho(\mathbf{r})$ as the basic variable [19, 20]. A key advantage of this approach is that the electron density of M electrons in a volume element $\mathrm{d}\mathbf{r}$ depends only on three independent coordinates:

$$\varrho(\mathbf{r}) = \sum_{i=1}^{M} \int \psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_M\sigma_M)^{*} \delta(\mathbf{r}_i - \mathbf{r}) \psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_M\sigma_M) d(\mathbf{r}_1\sigma_1) \ldots d(\mathbf{r}_M\sigma_M). \tag{1.14}$$

Here, the ground-state total energy and other properties can be expressed as functionals of the electron density. By assuming that the kinetic energy density is locally equal to that of a homogeneous electron gas, Thomas and Fermi formulated the total energy functional $E^{\mathrm{TF}}[\varrho(\mathbf{r})]$ as

$$E^{\mathrm{TF}}[\varrho(\mathbf{r})] = \frac{3(3\pi^2)^{2/3}}{10} \int \varrho(\mathbf{r})^{5/3} \mathrm{d}\mathbf{r} - \sum_{\nu=1}^{N} \frac{Z_\nu \varrho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_\nu|} \mathrm{d}\mathbf{r} + \frac{1}{2} \int\int \frac{\varrho(\mathbf{r})\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'. \tag{1.15}$$

The first term denotes the kinetic energy of noninteracting electrons, and the second and third terms are the classical electrostatic electron–nucleus attraction and electron–electron repulsion, respectively. Later on, Dirac included the exchange energy, which has no classical analogue, as an additional term to the TF model [8]:

$$E_{\mathrm{x}}^{\mathrm{Dirac}} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \varrho(\mathbf{r})^{4/3} \mathrm{d}\mathbf{r}. \tag{1.16}$$

TF calculated energies are usually too high. The Thomas–Fermi–Dirac (TFD) model accounts for this by adding an appropriate exchange term that gives a negative energy contribution. Despite this correction, calculated total energies are still not accurate for chemical predictions since the kinetic energy is poorly described. Although the TF model was not very successful in quantum chemistry or solid-state physics, it is the starting point for DFT in the sense of using the electron density for solving multielectron systems.

1.2.4.2 The Hohenberg–Kohn Theorems

The theoretical basis of DFT are two fundamental theorems, which were formulated and mathematically proven by Hohenberg and Kohn [17] for nondegenerate ground states. According to the first theorem, the electron density uniquely determines the

external potential (the potential of the ions or nuclei) to within a constant. Therefore, the total electronic energy of a system E can be expressed as a functional of the electron density ϱ,

$$E[\varrho] = T[\varrho] + \int \varrho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \mathrm{d}\mathbf{r} + E_{\text{ee}}[\varrho], \tag{1.17}$$

where $T[\varrho]$ is the kinetic energy functional and $E_{\text{ee}}[\varrho]$ is the electron–electron interaction energy and also a functional. By defining the Hohenberg–Kohn functional

$$F_{\text{HK}}[\varrho] = T[\varrho] + E_{\text{ee}}[\varrho], \tag{1.18}$$

we obtain

$$E[\varrho] = \int \varrho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \mathrm{d}\mathbf{r} + F_{\text{HK}}[\varrho]. \tag{1.19}$$

The exact solution to the Schrödinger equation could be obtained with an explicit expression for the universal functional $F_{\text{HK}}[\varrho]$. Unfortunately, this expression is still unknown, but we will later show different approximations for this term. The remaining electron–electron interaction $E_{\text{ee}}[\varrho]$ can be written as

$$E_{\text{ee}}[\varrho] = J[\varrho] + E^{\text{noncl}}[\varrho], \tag{1.20}$$

where the first term is simply the classical Coulomb repulsion and the second term is the nonclassical part that contains self-interaction correction, exchange, and Coulomb correlation energy.

The second Hohenberg–Kohn theorem provides the energy variational principle for the exact functional. The ground-state density $\varrho_0(\mathbf{r})$ is the density that minimizes $E[\varrho]$

$$E_0 = E[\varrho_0(\mathbf{r})] \leq E[\varrho(\mathbf{r})] \tag{1.21}$$

when

$$\varrho(\mathbf{r}) \geq 0 \quad \text{and} \quad \int \varrho(\mathbf{r}) \mathrm{d}\mathbf{r} - M = 0. \tag{1.22}$$

Energy minimization of the energy functional fulfills the Euler–Lagrange equation under the constraint of a constant number of electrons M (Eq. (1.22)), which can be written as

$$\mu = \frac{\delta E[\varrho(\mathbf{r})]}{\delta \varrho(\mathbf{r})} = V_{\text{ext}}(\mathbf{r}) + \frac{\delta F_{\text{HK}}[\varrho(\mathbf{r})]}{\delta \varrho(\mathbf{r})}, \tag{1.23}$$

where the Lagrange multiplier μ is the chemical potential of the electrons. In principle, this formulation provides all ground-state properties, but the Hohenberg–Kohn theorems do not tell us how to find the universal functional $F_{\text{HK}}[\varrho]$. Later on, Kohn and Sham [18] found rather accurate approximations for $F_{\text{HK}}[\varrho]$, and others still continue this development.

1.2.4.3 The Kohn–Sham Equations

Kohn and Sham decomposed the exact kinetic energy functional $T[\varrho]$ into two parts to approximate the universal functional $F_{HK}[\varrho]$ in terms of Eq. (1.18). The first term is the kinetic energy of a system of noninteracting electrons T_s given by

$$T_s = -\frac{1}{2}\sum_{i=1}^{N} < \phi_i|\nabla^2|\phi_i >, \tag{1.24}$$

where ϕ_i are the so-called Kohn–Sham orbitals. The second term contains all remaining (and neglected) interactions in the noninteracting system ($T-T_s$).

The second contribution is a small correction and it is included along with the nonclassical part of the electron–electron interaction E^{noncl} into a term defined as exchange–correlation (xc) energy:

$$E_{xc}[\varrho] = (T[\varrho]-T_s[\varrho]) + (E_{ee}[\varrho]-J[\varrho]). \tag{1.25}$$

The energy functional Eq. (1.17) is now written as[9)]

$$E[\varrho] = T_s[\varrho] + \int \varrho(\mathbf{r})\, V_{ext}(\mathbf{r})\mathrm{d}r + J[\varrho] + E_{xc}[\varrho]. \tag{1.26}$$

Finding suitable expressions for the $E_{xc}[\varrho]$ term is the main challenge in DFT development since it consists of all contributions that are not yet known exactly. The Euler–Lagrange equation now has the form

$$\varepsilon_i \frac{\delta\varrho(\mathbf{r})}{\delta\phi_i} = \frac{\delta E[\varrho(\mathbf{r})]}{\delta\varrho(\mathbf{r})}\frac{\delta\varrho(\mathbf{r})}{\delta\phi_i} = \frac{\delta T_s[\varrho(\mathbf{r})]}{\delta\phi_i} + V_{eff}(\mathbf{r})\frac{\delta\varrho(\mathbf{r})}{\delta\phi_i} \tag{1.27}$$

with

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + V_{xc}(\mathbf{r}), \tag{1.28}$$

where the exchange–correlation potential $V_{xc}(\mathbf{r})$ is

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\varrho(\mathbf{r})]}{\delta\varrho(\mathbf{r})}. \tag{1.29}$$

The solution of Eq. (1.27) is obtained by solving the following set of one-particle equations

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\phi_i = \varepsilon_i\phi_i, \tag{1.30}$$

9) In principle, the kinetic energy term T_s is a functional of the Kohn–Sham orbitals ϕ_i.

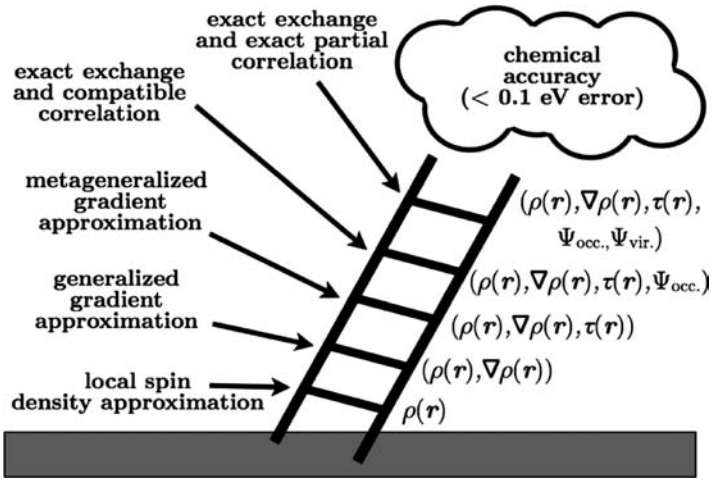

Figure 1.2 Jacob's ladder illustrating the hierarchy of exchange–correlation functionals.

where the electron density of the real system is constructed from the Kohn–Sham orbitals

$$\varrho(r) = \sum_{i=1}^{\text{occ}} |\phi_i(r)|^2. \tag{1.31}$$

Here, the summation runs over all occupied orbitals (occ). Equations (1.28), (1.30) and (1.31) are known as Kohn–Sham equations. The procedure to solve a particular problem is to start with a guessed $\varrho(\mathbf{r})$, determine V_{eff} from Eq. (1.28), and then obtain a new $\varrho(\mathbf{r})$ from Eqs. (1.30) and (1.31). This procedure is then repeated until $\varrho(\mathbf{r})$ is converged, and the total energy is obtained.[10)]

1.2.4.4 Exchange–Correlation Functionals

Density-based formulations reduce the complexity of the many-body problem, but the resulting Kohn–Sham equation (1.30) still requires an xc functional. Different approximations of this term are the key distinction of all DFT implementations.

Perdew [21, 22] has illustratively formulated the hierarchy of different approximations of the xc functional as a "Jacob's ladder," rising from the earth of Hartree to the heaven of chemical accuracy (see Figure 1.2).

Starting from the earth of Hartree, the subsequent rungs of the ladder are defined as follows:

- **Local (spin) density approximation (L(S)DA):** Here the exchange–correlation energy of an inhomogeneous system is obtained by assuming that its density

10) This iterative process is known as the self-consistent field (SCF) approach.

can locally be treated as a uniform electron gas. The xc energy can then be written as

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[\varrho] = \int \varrho(\mathbf{r})\varepsilon_{\mathrm{xc}}(\varrho(\mathbf{r}))\mathrm{d}\mathbf{r}, \tag{1.32}$$

where $\varepsilon_{\mathrm{xc}}(\varrho(\mathbf{r}))$ is the xc energy per particle of the homogeneous electron gas, which can be split into exchange and correlation terms

$$\varepsilon_{\mathrm{xc}}(\varrho(\mathbf{r})) = \varepsilon_{\mathrm{x}}(\varrho(\mathbf{r})) + \varepsilon_{\mathrm{c}}(\varrho(\mathbf{r})). \tag{1.33}$$

The exchange part is given by the Dirac expression (Eq. (1.16))

$$\varepsilon_{\mathrm{x}}(\varrho(\mathbf{r})) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\varrho(\mathbf{r})^{1/3}. \tag{1.34}$$

The correlation component ε_{c} has been determined by Monte Carlo (MC) calculations for a uniform electron gas considering a number of different densities [2]. Although one might expect that the LDA functional is valid only for a slowly varying density that might resemble a uniform electron gas, experience shows that this approximation is surprisingly valuable in a wide range of problems in solid-state physics and material science. LDA is noted to calculate molecular geometries and vibrational frequencies reasonably, but bond energies are strongly overestimated.

- **Generalized gradient approximation (GGA):** Inadequacies in LDA brought about a modified xc functional that, in addition to the density, contains terms for the density gradient:

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[\varrho] = \int \varrho(\mathbf{r})\varepsilon_{\mathrm{xc}}(\varrho(\mathbf{r}), \nabla\varrho(\mathbf{r}))\mathrm{d}\mathbf{r}. \tag{1.35}$$

One form of GGA introduced by Perdew, Burke, and Ernzerhof (PBE) [23] is widely used in surface physics. In this approximation, the correlation energy is expressed as

$$E_{\mathrm{c}}^{\mathrm{GGA}}[\varrho] = \int \varrho\left[\varepsilon_{\mathrm{c}}^{\mathrm{unif}}(\varrho) + K(\varrho, t)\right]\mathrm{d}\mathbf{r}, \tag{1.36}$$

with

$$K(\varrho, t) = \gamma \ln\left[1 + \frac{\beta t^2}{\gamma}\left(\frac{1 + At^2}{1 + At^2 + A^2t^4}\right)\right] \tag{1.37}$$

and

$$\gamma \simeq 0.031091; \quad \beta \simeq 0.066725; \quad A = \frac{\beta}{\gamma}\frac{1}{\mathrm{e}^{-\varepsilon_{\mathrm{c}}^{\mathrm{unif}}/\gamma} - 1}; \quad t = \frac{|\nabla\varrho|}{2\left(\sqrt{4(3\pi^2\varrho)^{1/3}/\pi}\right)\varrho}. \tag{1.38}$$

Here, t is a dimensionless density gradient. The exchange energy in terms of an enhancement factor F_x is written as

$$E_x^{GGA}[\varrho] = \int \varrho \varepsilon_x^{unif}(\varrho) F_x(s) d\mathbf{r}, \tag{1.39}$$

where $\varepsilon_x^{unif}(\varrho)$ and $\varepsilon_c^{unif}(\varrho)$ are, respectively, the exchange and correlation energies per particle of a homogeneous electron gas at point $\mathbf{r}$ (see Eq. (1.34)) and s is another dimensionless density gradient

$$s = \frac{|\nabla \varrho|}{2(3\pi^2\varrho)^{1/3}\varrho}. \tag{1.40}$$

Finally, the function $F_x(s)$ is

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}, \tag{1.41}$$

where $\kappa = 0.804$ and $\mu \simeq 0.21951$.

- **Meta-generalized gradient approximation (MGGA):** The kinetic energy density, $\tau(\mathbf{r})$, is an additional Kohn–Sham contribution that can be calculated. In general, MGGA functionals have the following form:

$$E_{xc}^{MGGA}[\varrho] = \int \varrho(\mathbf{r}) \varepsilon_{xc}(\varrho(\mathbf{r}), \nabla\varrho(\mathbf{r}), \tau(\mathbf{r})) d\mathbf{r}. \tag{1.42}$$

  The main advantage of including kinetic energy densities is that it mostly eliminates self-interaction errors, causing inaccuracies with LDA and GGA functionals at low-density and strong interaction limits. In intermediate regions, however, MGGA functionals usually do not provide substantial improvement to corresponding GGAs.
- **Hybrid DFT with exact exchange:** An entirely different approach to improve deficiencies in GGA functionals is to incorporate the so-called exact exchange energy (EXX) contributions. The exact exchange energy E_x^{exact} is a derivative from the Hartree–Fock approximation (see Section 2.3.1), and is obtained by solving only the exchange part of the exchange–correlation functional exactly. The result is an energy value that when scaled according to

$$E_{xc}^{hybrid} = E_{xc}^{GGA} + a\left(E_x^{exact} - E_x^{GGA}\right) \tag{1.43}$$

  provides a convenient cancellation of errors, making hybrid DFT methods surprisingly accurate. Based on this idea, the highly popular hybrid DFT method B3LYP combines exact HF exchange with the Slater [24] local exchange functional. In addition, it uses the Becke gradient correction [25], the local Vosko–Wilk–Nusair exchange functional [26], and the Lee–Yang–Parr local gradient-corrected functional [27]. Inclusion of the nonlocal exchange, however, limits these methods to be applicable only for finite systems and not in a periodic representation.