Computational Approaches to Energy Materials

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A John Wiley & Sons, Ltd., Publication
## Contents

*About the Editors*  
*List of Contributors*  
*Preface*  
*Acknowledgments*

### 1 Computational Techniques

_C. Richard A. Catlow, Alexey A. Sokol, and Aron Walsh_

1.1 Introduction  
1.2 Atomistic Simulations  
  1.2.1 Basic Concepts  
  1.2.2 Parameterization  
  1.2.3 Parameter Sets  
  1.2.4 Implementation  
1.3 Electronic Structure Techniques  
  1.3.1 Wavefunction Methods  
    1.3.1.1 Hartree–Fock Theory  
    1.3.1.2 Post-Hartree–Fock Approaches  
    1.3.1.3 Semi-empirical Wavefunction Methods  
  1.3.2 Density Functional Theory  
    1.3.2.1 Exchange–Correlation Functionals  
    1.3.2.2 Semi-empirical Density Functional Approaches  
1.3.3 Excited States  
1.4 Multiscale Approaches  
  1.4.1 Hybrid QM/MM Embedding Techniques  
  1.4.2 Beyond Atomistic Models  
1.5 Boundary Conditions  
1.6 Point-Defect Simulations  
  1.6.1 Mott–Littleton Approach  
  1.6.2 Periodic Supercell Approach  
1.7 Summary  
References
## Energy Generation: Solar Energy

*Silvana Botti and Julien Vidal*

2.1 Thin-Film Photovoltaics 29
2.2 First-Principles Methods for Electronic Excitations 32
2.2.1 Hedin’s Equations and the \textit{GW} Approximation 34
2.2.2 Hybrid Functionals 38
2.2.3 Bethe–Salpeter Equation 40
2.2.4 Model Kernels for TDDFT 41
2.3 Examples of Applications 42
2.3.1 Cu-Based Thin-Film Absorbers 43
2.3.2 Delafossite Transparent Conductive Oxides 54
2.4 Conclusions 60

References 61

## Energy Generation: Nuclear Energy

*Dorothy Duffy*

3.1 Introduction 71
3.2 Radiation Effects in Nuclear Materials 72
3.2.1 Fission 72
3.2.1.1 Structural Materials 73
3.2.1.2 Fuel 76
3.2.1.3 Cladding 79
3.2.2 Fusion 80
3.2.2.1 Structural Materials 81
3.2.2.2 Plasma-Facing Materials 82
3.2.3 Waste Disposal 83
3.3 Modeling Radiation Effects 85
3.3.1 BCA Modeling 86
3.3.2 Molecular Dynamics 87
3.3.2.1 Cascade Simulations 87
3.3.2.2 Sputtering Simulations 93
3.3.3 Monte Carlo Simulations 94
3.3.3.1 Kinetic Monte Carlo 95
3.3.3.2 Object Kinetic Monte Carlo 96
3.3.3.3 Transition Rates 97
3.3.3.4 Examples 98
3.3.4 Cluster Dynamics 99
3.3.4.1 Examples 99
3.3.4.2 Comparison with OKMC 100
3.3.5 Density Functional Theory 101
3.3.5.1 Interatomic Potentials 101
3.3.5.2 Transition Rates 102
4 Energy Storage: Rechargeable Lithium Batteries

M. Saiful Islam and Craig A.J. Fisher

4.1 Introduction

4.2 Overview of Computational Approaches

4.3 Li–Ion Batteries

4.4 Cell Voltages and Structural Phase Stability

4.5 Li–Ion Diffusion and Defect Properties

4.6 Surfaces and Morphology

4.7 Current Trends and Future Directions

4.8 Concluding Remarks

References

5 Energy Storage: Hydrogen

Viet-Duc Le and Yong-Hyun Kim

5.1 Introduction

5.2 Computational Approach in Hydrogen Storage Research

5.3 Chemisorption Approach

5.4 Physisorption Approach

5.5 Spillover Approach

5.6 Kubas-Type Approach

5.7 Conclusion

References

6 Energy Conversion: Solid Oxide Fuel Cells

E.A. Kotomin, R. Merkle, Y.A. Mastrikov, M.M. Kuklja, and J. Maier

6.1 Introduction

6.2 Computational Details

6.3 Cathode Materials and Reactions

6.3.1 Surfaces: LaMnO$_3$ and (La,Sr)MnO$_3$ Perovskites

6.3.1.1 Surface Termination, Surface Point Defects

6.3.1.2 Oxygen Adsorption and Diffusion

6.3.1.3 Rate-Determining Step of the Surface Reaction

6.3.2 Bulk Properties of Multicomponent Perovskites

6.3.2.1 Oxygen Vacancy Formation in (Ba,Sr)(Co,Fe)O$_{3-\delta}$
6.3.2.2 Oxygen Vacancy Migration in $(\text{Ba, Sr})(\text{Co, Fe})\text{O}_3^{\delta -\delta}$ 167
6.3.2.3 Disorder and Cation Rearrangement in $(\text{Ba, Sr})(\text{Co, Fe})\text{O}_3^{\delta -\delta}$ 170
6.3.3 Defects in $(\text{La, Sr})(\text{Co, Fe})\text{O}_3^{\delta -\delta}$ 173
6.4 Ion Transport in Electrolytes: Recent Studies 175
6.5 Reactions at SOFC Anodes 176
6.6 Conclusions 177
Acknowledgments 178
References 178

7 Energy Conversion: Heterogeneous Catalysis 187
Rutger A. van Santen, Evgeny A. Pidko, and Emiel J.M. Hensen

7.1 Introduction 187
7.1.1 Particle Size Dependence of Catalytic Reactivity 191
7.1.2 Activity and Selectivity as a Function of the Metal Type 192
7.1.3 Reactivity as a Function of State of the Surface 193
7.1.4 Mechanism of Acid Catalysis: Single Site versus Dual Site 193
7.2 Basic Concepts of Heterogeneous Catalysis 195
7.3 Surface Sensitivity in CH Activation 198
7.3.1 Homolytic Activation of CH Bonds 198
7.3.2 Heterolytic Activation of CH Bonds 203
7.3.2.1 Brønsted Acid Catalysis 204
7.3.2.2 Lewis Acid Catalysis 206
7.4 Surface Sensitivity for the C–C Bond Formation 209
7.4.1 Transition Metal Catalyzed FT Reaction 209
7.4.2 C–C Bond Formation Catalyzed by Zeolitic Brønsted Acids 213
7.5 Structure and Surface Composition Sensitivity: Oxygen Insertion versus CH Bond Cleavage 217
7.5.1 Silver-Catalyzed Ethylene Epoxidation 217
7.5.2 Benzene Oxidation by Iron-Modified Zeolite 221
7.6 Conclusion 223
References 224

8 Energy Conversion: Solid-State Lighting 231
E. Kioupakis, P. Rinke, A. Janotti, Q. Yan, and C.G. Van de Walle

8.1 Introduction to Solid-State Lighting 231
8.2 Structure and Electronic Properties of Nitride Materials 234
8.2.1 Density Functional Theory and Ground-State Properties 234
8.2.2 Electronic Excitations: GW and Exact Exchange 236
8.2.3 Electronic Excitations: Hybrid Functionals 240
8.2.4 Band-gap Bowing and Band Alignments 240
8.2.5 Strain and Deformation Potentials 241
8.3 Defects in Nitride Materials 243
8.3.1 Methodology 244
8.3.2 Example: C in GaN 246
8.4 Auger Recombination and Efficiency Droop Problem of Nitride LEDs 248
8.4.1 Efficiency Droop 248
8.4.2 Auger Recombination 249
8.4.3 Computational Methodology 251
8.4.4 Results 252
8.5 Summary 254
Acknowledgments 255
References 255

9 Toward the Nanoscale 261
Phuti E. Ngoepe, Rapela R. Maphanga, and Dean C. Sayle
9.1 Introduction 261
9.2 Review of Simulation Methods 263
9.2.1 Established Computational Methods 263
9.2.2 Evolutionary Methods 263
9.2.2.1 GM Methods 263
9.2.2.2 Amorphization and Recrystallization 264
9.3 Applications 266
9.3.1 Nanoclusters 266
9.3.1.1 ZnO 266
9.3.1.2 ZnS 268
9.3.1.3 MnO₂ 269
9.3.1.4 TiO₂ 271
9.3.2 Nanoarchitectures 272
9.3.2.1 MnO₂ Nanoparticle (Nucleation and Crystallization) 272
9.3.2.2 MnO₂ Bulk 275
9.3.2.3 MnO₂ Nanoporous 279
9.3.2.4 TiO₂ Nanoporous 285
9.3.2.5 ZnS and ZnO Nanoporous 285
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Dr Aron Walsh is a Royal Society University Research Fellow in the Centre for Sustainable Chemical Technologies at the University of Bath. He obtained his BA (Mod) and PhD in computational chemistry from Trinity College Dublin. After receiving the Royal Irish Academy Young Chemist award, he worked for the US Department of Energy at the National Renewable Energy Laboratory and moved to the United Kingdom in 2009 as a Marie Curie Research Fellow at University College London. His research experience to date has followed a coherent path, applying a range of computational techniques to challenging problems in the areas of solid-state chemistry and physics, with a particular emphasis on the description of defect processes in semiconductors. He has authored over 100 peer-reviewed publications.

Dr Alexey A. Sokol, a senior research associate in the Department of Chemistry at University College London (UCL), has worked on the development and applications of computational methods to solid-state physics, chemistry and materials science for over 20 years. His early work concerned disordered materials and interaction of high-energy radiation with semiconductor devices. His PhD project at the Royal Institution of Great Britain and UCL concentrated on the development of a theory of defects in zeolites as centers of chemical activity. On completing this project, Dr Sokol took part in the EU ESPRIT project QUASI, where he has developed a solid-state embedded cluster QM/MM technique implemented in the computational chemistry environment software ChemShell. More recently, these methods have been successfully applied to nanosystems, starting with small clusters and then being extended to larger nanoparticles, wires, tubes and thin films. His current work focuses on excited states of bulk defects and nanostructures.

Professor C. Richard A. Catlow, Dean of Mathematical and Physical Sciences at University College London and Fellow of the Royal Society, has worked for over 30 years in the field of computational and experimental studies of complex inorganic materials. His group has pioneered a wide range of applications of computational techniques in solid-state chemistry to systems and problems including microporous and oxide catalysts, ionic conductors, electronic ceramics and silicate minerals. This applications program has been supported by technique and code
development, including recent work on embedded cluster methodologies for application to the study of catalytic reactions. The computational work has been firmly linked with experimental studies, using both neutron scattering and synchrotron radiation techniques, where the Royal Institution group has also made notable contributions to development as well as application studies. Professor Catlow’s research has led to over 800 publications, and in 2004 he was elected to Fellowship of the Royal Society for “pioneering the development and application of computer modeling in solid state and materials chemistry.”
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Preface

The importance of efficient and sustainable energy technologies has grown enormously over the past decade, driven primarily by concerns over global warming, diminishing fossil-fuel reserves, the need for energy security and increasing consumer demand for portable electronics.

Stricter legislation regarding carbon dioxide emissions from road transport vehicles, combined with increasing fuel prices, will no doubt continue to encourage the introduction of even greater numbers of hybrid electric and fully electric vehicles. Next-generation energy technologies such as these can only come about through the development and optimization of high-performance materials. This, of course, cannot be achieved efficiently without a thorough understanding of the fundamental science of complex solids, an understanding that underpins applied research in this multidisciplinary field.

Computational methods are now an integral and indispensable part of the materials characterization and development process, as experimental techniques are often used at their fundamental limits (i.e., at the atomic and subatomic scales). Today, modeling of structures and properties of materials at this fundamental level is not only useful for confirming experimental results and enabling their correct interpretation but also increasingly being used as a predictive tool that can guide experimental research efforts.

Following an overview of the principles of atomistic modeling, our book focuses on the materials used for clean energy generation and storage, specifically on the development of new materials for thin-film solar cells, radiation-resistant materials for nuclear power and ion-conducting materials for batteries. The challenges involved in using hydrogen as an energy carrier necessitate research into new classes of materials for hydrogen storage. The latter naturally couples to the key issues of alternative energy storage and utilization in fuel cells, batteries and solid-state lighting. We conclude with a general account of the search for stable nanostructures, as nanostructured materials are of key importance in contemporary energy technologies and pose significant challenges for computational structure and property prediction.
Computational materials science represents a vibrant and rapidly expanding subject area. The techniques described in this book have been built from developments spanning across the last century, and we acknowledge all of the scientists who have contributed to their advancement and application, especially those who have not been explicitly referenced in this text.

We thank all authors for their contributions, Déborah Demathieu for her assistance, and the team at Wiley for their help throughout the production process.
Computational Techniques

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1.1 Introduction

In this chapter, we introduce fundamental approaches and ideas, which will be exploited in the rest of the book. These can be divided into two main streams: one dealing with the motion of atoms or ions described at a simplified level of theory and another focusing on electrons. The modeling framework, which covers both streams, is outlined next.

1.2 Atomistic Simulations

1.2.1 Basic Concepts

Methods based on interatomic potentials have a major and continuing role in molecular and materials simulation. The concept of the potential is simple: the energy \( E \) of the system is written as either an analytical or possibly a numerical function of the nuclear coordinates, \( r_i \), of particles \( i = 1 \) to \( n \):

\[
E = E(r_1, r_2, r_3, \ldots, r_n).
\]

The function will normally be written as a sum of terms that depend on the coordinates of two, three or more atoms, although in many potential models,
especially those for ionic and semi-ionic solids, only two body terms are considered; for the latter class of material, the electrostatic term is normally separated, that is,

\[ E = E_{\text{coul}} + E_{\text{SR}}, \]

where the Coulomb energy, \( E_{\text{coul}} \), is obtained by summing over all the interactions between the atomic charges, which are a parameter of the model and must be assigned. The short-range energy, \( E_{\text{SR}} \), represents the remainder of the interactions including Pauli repulsion and covalent and dispersive attractive terms. Simple analytical functions are commonly used for \( E_{\text{SR}} \), including inverse power \((r^{-m})\) and exponential terms \((\exp(-r/r_0))\). Detailed discussions can be found in the seminal book of Born and Huang [1], and more recent literature [2, 3].

In modeling metallic systems, rather different approaches must be adopted; in particular, the effects of the conduction band electrons on atomic interactions must be included—a difficult problem for which there is no simple solution. Nevertheless, a number of effective and useful potential models have been developed for metallic systems, which may be based on the “embedded atom concept.” Details and examples are given in [4].

Accurate models especially for ionic solids must include a representation of polarization. It has long been known that in solid-state modeling simple point dipole models have serious inadequacies, leading to excessive polarization, as they omit any representation of the damping of polarization by the resulting increase in short-range repulsion with neighboring ions. This problem was simply and elegantly solved by the development over 50 years ago of the shell model by Dick and Overhauser [5]. This crude but effective model describes an atom or ion in terms of a “core,” which contains all the mass and represents the nucleus and core electrons, and a “shell” (of charge, \( Y \)), which is massless and represents the polarizable valence shell electrons; the core and the shell are coupled by an harmonic spring (of constant, \( k \)), and the development of a dipole moment is modeled by the displacement of the shell relative to the core. The charge of the shell (\( Y \)) and the value of the spring constant (\( k \)) are parameters of the model; and of course, the sum of core and shell charges must equal the total atomic charge. Moreover, the shell model parameters can be related to the polarizability (\( \alpha \)) by the simple relationship:

\[ \alpha = \frac{Y^2}{k}. \]

Elaborations such as the “breathing shell” model have been developed, but the basic shell model remains the most widely used treatment of polarizability in materials simulation.

A potential model will normally therefore consist of (i) a set of atomic charges, where appropriate, (ii) analytical (or occasionally numerical) functions, containing variable parameters, and (iii) a representation of polarizability for short-range interactions, which will require specification of the parameters \( Y \) and \( k \) when the shell model is used. In Section 1.2.2, we review the methods used to set the variable parameters and then we return to some of the more common potential models.
1.2.2 Parameterization

Once the choice of the form of the potential model has been made, the crucial next step is to parameterize the model, that is, fix the variable parameters, so that the model describes the specific material (or materials) under investigation. Here, there are two broad strategies, which may in some cases be used in concert:

1. **Empirical fitting**: involves variation of the parameters in order to reproduce, as accurately as possible, experimental data of the material. Standard procedures are available for calculating a wide range of properties using potential models (see, e.g., [3]). These are usually coupled to a least-squares minimization procedure to achieve the best fit of calculated to experimental data. Commonly used data include cohesive or lattice energies, crystal structures, elastic and dielectric properties and where available lattice dynamical data. The procedure is simple in concept and highly automated in principle, but in practice it may prove difficult and lengthy and require extensive user intervention and direction to achieve the optimum parameter set. And, of course, it requires that suitable and accurate experimental data be available.

2. **Fitting to energy surfaces**: requires no empirical data, but rather uses energy surfaces calculated by electronic structure methods, with parameters in the potential model being varied to ensure that the surface calculated using the potential model matches as closely as possible that determined by the electronic structure technique. The energy surface is constructed by varying the structural parameters of the material or molecule in a systematic manner, followed by a least squares fitting of the potential parameters. The approach is again in principle straightforward but of course requires an accurate energy surface to which to fit the potential parameters.

Both approaches are widely used and as noted they may be used together, and indeed a potential derived by the latter approach should always be tested in regards to the extent to which it reproduces any available experimental data. More generally, in evaluating a potential model, it is necessary to examine carefully its mode of derivation. When empirical methods are used, the range and accuracy of the data will be crucial; when parameters have been derived from calculated energy surfaces at a higher level of theory, the quality of electronic structure technique will determine the accuracy of the parameterized model.

1.2.3 Parameter Sets

A wide range of parameter sets are available for different classes of material and many can be found in online databases [6]. For oxides, which are extensively used in energy materials, the Born model parameter set derived by Catlow and Lewis [7] may often provide a useful starting point as these parameters have the merit of simplicity and transferability between different materials, which may be an important factor in assessing the suitability of a potential model for applications,
in which several materials are investigated and compared. Other significant considerations when deciding on the suitability of a model are accuracy—that is, the extent to which the model reproduces known crystal properties—and stability—an important consideration as models may perform well around the equilibrium configuration of a crystal but have instabilities for other configurations that may be sampled in dynamical simulations or simulations of defective crystals. More generally the assessment and choice of a potential model is crucially important and needs careful and detailed consideration.

### 1.2.4 Implementation

Having developed or chosen a suitable model for calculating energies and forces as a function of nuclear coordinates, they may be implemented in a wide range of powerful simulation tools (e.g., CP2K, DL-POLY, GULP, GROMACS, KLMC, LAMMPS, METADISE), based on three main concepts:

1. **Minimization**: A conceptually simple approach, in which the aim is to locate the energy minimum configuration of the system modeled, with the energy calculated using an interatomic potential model or by an electronic structure technique. The complexity of energy landscapes may, however, make the identification of the global minimum far from straightforward, and a range of both sophisticated search and minimization algorithms have been developed. Minimization is perhaps at its most effective when refining approximately known structures, although developments in search procedures for energy landscapes have given the techniques an increasingly predictive value [8, 9]. Minimization may be applied to any type of atomic assembly including crystals, molecules and adsorbed species. The approach has been applied with particular effect to defects in solids where the method, originally pioneered by Mott [10], effectively minimizes the energy of a region of crystal surrounding the defect with more approximate quasi-continuum treatments of the more distant regions of the lattice. Energy minimization may also be extended to free energy minimization when entropies can be calculated by, for example, the vibrational partition function in a crystalline solid [11]. The technique has been further developed to study transition states, or more generally, minimum energy pathways as in the popular nudged-elastic band (NEB) approach. Overall, despite its basic simplicity and obvious limitations in omitting any explicit representations of dynamic effects, minimization is a robust and powerful approach and should often be the first approach of a simulation study.

2. **Molecular Dynamics (MD)**: Here, again the basic idea is simple: the time evolution of a system at the molecular level is followed by solving the classical equations of motion—essential Newtonian mechanics for molecules. In practice, the equations of motion are solved using a numerical, iterative procedure, employing repeated applications of a time step, during which both atomic positions and velocities are updated using the known velocities and forces, respectively. The
time step must, of course, be shorter than the characteristic time associated with any important process (e.g., the period of an atomic or molecular vibration) and values of typically 1 fs are chosen. A simulation proceeds by initially setting the positions and velocities of the particles to be included in the simulation; the latter are chosen with target temperature in mind. During the initial “equilibration” stage of the simulation, the system reaches thermal equilibrium, and it is normally necessary to scale the velocities a number of times in order to retain the simulation at the target temperature. Once the system is in equilibrium at the specified temperature, the production stage commences and the data from the simulation (positions and velocities) are stored for subsequent analysis.

MD simulations yield a wealth of information—structural properties via radial distribution functions, information on dynamical properties via a range of correlation factors and diffusion coefficients via the variation of particle mean square displacements with time. Although originally developed to model properties of liquid systems, they have found extensive applications in solids, especially those with high ionic mobility, that is, fast ion conductors, which find important applications in both batteries and fuel cells. The technique does, however, have substantial limitations, most notably the limited amount of “real time” that can be explored with a simulation and the limitations on the size of the simulation cell. The two are, of course, related; but with contemporary simulations with realistic models, implemented on high performance computing (HPC) platforms, simulations are generally confined to the nanosecond time range, with simulation boxes containing several thousand particles. Of course, longer time scales and larger simulation boxes may be achieved given very substantial resources, but in general the phenomena of interest must be accessible within the limitations placed on the technique by the time and size constraints. One major consequence is that standard MD cannot effectively model rare events, which we may define as those involving energies considerably in excess of $k_B T$, as such events will be insufficiently sampled (or not sampled at all) during the course of a simulation. There are a number of recent developments including the increasingly used metadynamics that alleviate this problem, but it does remain intrinsic to the technique. As with minimization techniques, MD can be applied to molecules, clusters and systems with 2D or 3D periodicity. The technique is powerful and flexible, yielding quantitative information can often give valuable insight via graphical displays of configurations and migration mechanisms.

3. Monte Carlo (MC) simulations: A stochastic method alternative to MD for the sampling of large and complex configurational spaces using random numbers. This method is particularly useful to assess higher energy configurations or take the system of interest over a high potential energy barrier, which would be inaccessible in realistic MD time scales. Another advantage of MC is the possibility to explore remote regions of configurational space. In modeling materials structure and thermodynamic properties, the Metropolis algorithm is commonly applied to bias the search toward thermally accessible configurations, which is controlled
by the simulation temperature. The approach can be extended to include variation in the number of particles based on the chemical potential in Grand Canonical MC. In contrast to direct minimization, both MC and MD techniques are suitable to study nonequilibrium, rapidly evolving systems and processes. While MC methods, unlike MD, do not give information on the time evolution of a system, an adaptation of the technique—Kinetic Monte Carlo (KMC)—can allow time dependent processes to be modeled by sampling events, such as atomic migration processes, rather than particle positions.

1.3 Electronic Structure Techniques

The atomistic simulation techniques previously discussed are concerned with describing the energy landscape of individual atoms or ions, where classical mechanics can be usefully employed as the first successful approximation. Electrons are much lighter particles with essential quantum behavior. The goal of quantum chemical approaches, or more broadly, the electronic structure techniques, is to provide the description of electrons. The distribution of electrons in turn determines the structural, optical and magnetic structure of molecules and solids. As electrons are charged particles with spin 1/2 in atomic units, they interact with each other coulombically, and their motion is correlated in different manner depending on mutual orientation of their spins. Quantum mechanics of many-electron systems describes these as effects of electron exchange and correlation, which should be taken into account for a proper quantitative description. Further in materials, the behavior of large numbers of electrons is described using quantum statistical methods suitable for fermions (i.e., Fermi-Dirac statistics), where one typically deals with the Fermi gas or liquid models.

The most advanced quantum chemical methods are based on the (approximate) solution of the Schrödinger equation for the many-electron wavefunction, while density functional theory (DFT) is developed around the electron density, which is a one-electron property. The result for the majority of contemporary electronic structure techniques is the ground-state electron distribution and associated one-electron properties. A distinction is generally made between first-principles (or ab initio) methods that contain no external parameterization beyond fundamental physical constants, and semi-empirical methods, which typically replace more computationally demanding terms with parameters obtained from a fit to a large data set of experimental measurements or calculations at a higher level of theory.

Beyond the one-electron approaches, the full many-body system can be treated, or excited states can be calculated, building up from the ground-state single-particle description. The methods discussed in this section are well developed and have been implemented in a wide range of academic and commercial software packages; a number of such codes are listed in Table 1.1. While any chemical system can, in principle, be calculated using these methods, care must be taken, especially
Table 1.1  A selection of actively developed electronic structure codes suitable for modeling energy materials

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DFT, density functional theory; HF, Hartree–Fock; DFTB, density functional tight-binding.
For updated descriptions see http://www.psi-k.org/codes.shtml
for open-shell or highly correlated \( d \) and \( f \) shell systems to ensure that physically meaningful results are obtained.

For any numerical electronic structure approach, a tractable representation of the one-electron wavefunction (or orbital) is required, which is usually obtained from a linear combination of simple functions referred to as the basis set. These can take many forms, and are one distinguishing factor between computer codes (see Table 1.1). Introduction of a basis set reduces the problem of solving simultaneous differential equations to that of linear algebraic equations with coefficients determined by matrix elements (integrals in real space) between such basis functions. Due to the ease of computing electron integrals, Gaussian functions, \( x^k y^l z^m e^{-\alpha r^2} \), are the most widely used basis for molecular calculations, while for solids, plane waves of the form \( e^{i\mathbf{k}\mathbf{r}} \) act as a more suitable basis (following the Bloch theorem for a periodic potential as discussed below) and offer high accuracy and efficiency.

As the more weakly bound valence electrons make the primary contributions to chemical bonding, a common approximation is to replace the core states by an analytical function that results in the same effective potential for the valence electrons, but at a greatly reduced computational cost. These are known as pseudopotentials or effective core potentials, and exist in many flavors, for example, accurate norm-conserving pseudopotentials [12] or computationally efficient ultra-soft pseudopotentials developed by Vanderbilt [13]. This approach to saving the computational effort has close similarities with a more recent method of projector-augmented wave potentials developed by Blöchl [14], which relies on an explicit but simplified representation of core electronic states in the inner atomic regions. Many codes now come with their own optimized set of potentials, but there are also databases of transferable potentials and pseudopotential generators available for the entire periodic table.

### 1.3.1 Wavefunction Methods

The time-independent, nonrelativistic Schrödinger equation can be expressed concisely as

\[
\hat{H} \Psi = E \Psi,
\]

where \( \Psi \) is the wavefunction, \( E \) is the energy and \( \hat{H} \) is the Hamiltonian, the sum of the kinetic and potential energy operators. The kinetic operator can be divided into the contributions from the nuclei and the electrons, and the potential as the sum of the nuclei–nuclei interactions, the electron–electron interactions and the nuclei–electron interactions:

\[
\hat{H} = \hat{K}_{\text{nuclei}} + \hat{K}_{\text{electrons}} + \hat{V}_{\text{nuclei}} + \hat{V}_{\text{electrons}} + \hat{V}_{\text{nuclei-electrons}}.
\]

Solution of the eigenvalue equation results in the eigenfunctions (state wavefunctions) and the eigenvalues (state energies).
To make solution of the Schrödinger equation practical for many-atom and many-electron systems, we can separate nuclear and electronic degrees of freedom. To this end, we rearrange the Hamiltonian as follows:

\[
\hat{H} = [\hat{K}_{\text{nuclei}} + \hat{V}_{\text{nuclei}}] + \hat{K}_{\text{electrons}} + \hat{V}_{\text{electrons}} + \hat{V}_{\text{nuclei-electrons}}.
\]

Differences in inertia between the nuclei and electrons mean that the nuclei are almost static compared to the electrons and that their kinetic energy and the nuclear–nuclear interactions can be calculated separately. This forms the basis of the Born–Oppenheimer approximation and is valid for most chemical systems of interest, except for the motion of very light atoms (i.e., hydrogen) or where correlations between the ionic and electronic motion are important (e.g., vibrations in solids or the interactions of fast ions with a solid).

1.3.1.1 Hartree–Fock Theory

The Hartree–Fock (HF) method is widely used in quantum chemistry. The predicted equilibrium interatomic distances and bond angles for the majority of molecules are typically within a small percentage of experimental measurements. Many codes now allow for HF calculations of periodic systems, but these are more expensive than simple DFT-based approaches described below, and have inherent difficulties in the description of metallic systems, and hence are less widely used.

In 1928, Hartree introduced a self-consistent field method to evaluate the approximate wavefunctions and energies in many-electron systems [15]. The total electronic wavefunction for \( N \) electrons is constructed as the product of the individual one-electron orbitals:

\[
\Psi_0 = \Psi_0(1) \Psi_0(2) \ldots \Psi_0(N).
\]

Individual electrons are assumed to move as independent particles in the mean field (potential) due to all electrons, hence the probability to find all electrons in a certain configuration can be calculated as a product of probabilities of finding individual electrons. Solving the approximate Schrödinger equation for each one-electron orbital, in a mean field of all electrons, results in a new wavefunction, thus causing a change in the electron distribution and therefore in the potential. The procedure would typically start from a trial set of orbitals (initial guess) to generate a mean-field (Hartree) potential and should be iterated self-consistently until the wavefunctions stop changing (or remain within a certain numerical threshold).

Following the variational principle, the energy calculated with any trial (approximate) wavefunction (\( \Psi_T \)) is higher than the true energy obtained using the exact wavefunction (\( \Psi_0 \)):

\[
[\langle \Psi_T | \hat{H} | \Psi_T \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle] = E_T \geq E_0.
\]

This fact is sometimes used as the basis for an alternative solution to the self-consistent field procedure outlined above, where the energy is minimized with respect to the free coefficients that define the trial wavefunction.
Within the original Hartree approximation, the effect of the electron–exchange interaction is neglected. Fock recognized that the Hartree wavefunction was not antisymmetric with respect to electron interchange [16]. In 1930, he demonstrated that the Hartree approach could be made antisymmetric by appropriately adding and subtracting all possible electron combinations, which was later redefined by Slater as the determinant of the matrix formed by the system of \( N \) electron orbitals [17]. Electron exchange is a nonlocal property as “Pauli repulsion” exists between electrons finite distances apart, and forms the basis of the modern HF theory. In spite of its name, the exchange is a stabilizing interaction as it keeps electrons of the same spin further apart, thus effectively reducing electron–electron Coulomb repulsion. In practical applications, one obtains a large set of orbitals, only a part of which of the lowest energy is occupied by core and valence electrons, while the higher energy virtual orbitals (conduction states in solids) normally remain empty.

The HF approach captures a significant amount of the physics of many-electron systems, but it will never result in an exact wavefunction for an interacting system of electrons. From the definition of the variational principle, the energy of an HF wavefunction will always be greater than the energy of the true wavefunction. Löwdin described this measure of the error as the correlation energy. In the mean-field approach, each electron moves independently of all others in the system, except for having a Coulombic repulsion to the average positions of all electrons. As the motion of electrons is in fact correlated, they tend to “avoid” each other even more than the theory would suggest. This dynamic correlation is the main source of error.

1.3.1.2 Post-Hartree–Fock Approaches

There are a number of methods that go beyond the HF approximation in order to recover the electron correlation that is absent in the original theory. At the heart of such approaches is the use of one-electron excited states (unoccupied orbitals) along with the ground state (occupied orbitals) in constructing more representative many-electron wavefunctions, thus leading to more accurate energies and other fundamental properties. As usual, increased accuracy comes at much greater computational expense, so the applicability of these methods to complex systems remains limited. Importantly, these approaches are typically valid only for localized states, which are not routinely accessible from solid-state calculations. The situation has started changing with the advance of new methods using localized Wannier functions (available in, e.g., CRYSTAL, VASP, and FHI-AIMS).

One such method is known as configuration interaction (CI), and involves the calculation of excited states to create a more accurate electronic wavefunction. Many-electron excited states are obtained by swapping occupied and unoccupied states in Slater determinants. Due to the large number of possible excited states, only a subset are considered to make the problem tractable; for example, the addition of single and double excitations to the ground-state wavefunction produces the CISD method. In the multiconfiguration self-consistent field method, and related approaches such as complete active space self-consistent field (CASSCF) method,