

1

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 :

$$E = E(r_1, r_2, r_3, \dots, r_n).$$

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,

2 Computational Approaches to Energy Materials

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_{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_{SR} , represents the remainder of the interactions including Pauli repulsion and covalent and dispersive attractive terms. Simple analytical functions are commonly used for E_{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 (α) 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,

4 Computational Approaches to Energy Materials

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

6 Computational Approaches to Energy Materials

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

Code	Method	Basis set	Web site
ABINIT	DFT	Plane waves	http://www.abinit.org
ADF/BAND	DFT	Slater local orbitals	http://www.scm.com
CASTEP	DFT	Plane waves	http://www.castep.org
CONQUEST	DFT/HF	Numerical functions	http://hamlin.phys.ucl.ac.uk
CPMD	DFT/HF	Plane waves	http://www.cpmc.org
CP2K	DFT/HF	Gaussian orbitals/plane waves	http://cp2k.berlios.de
CRYSTAL	DFT/HF	Gaussian local orbitals	http://www.crystal.unito.it
DFTB+	DFTB	Tight binding atomic orbitals	http://www.dftb-plus.info
DMOL ³	DFT	Numerical functions	http://accelrys.com
ELK	DFT/HF	Augmented plane waves	http://elk.sourceforge.net
EXCITING	DFT	Augmented plane waves	http://exciting-code.org
FLEUR	DFT	Augmented plane waves	http://www.flapw.de
FHI-AIMS	DFT/HF	Numerical functions	https://aimsclub.fh-berlin.mpg.de
GAUSSIAN	DFT/HF	Gaussian local orbitals	http://www.gaussian.com
GPAW	DFT	Numerical functions	https://wiki.fysik.dtu.dk/gpaw
ONETEP	DFT	Wannier functions	http://www2.tcm.phy.cam.ac.uk/onetep
PETOT	DFT	Plane waves	https://hpcrd.lbl.gov/~linwang/
SIESTA	DFT	Numerical functions	http://www.icmab.es/siesta
SPHINX	DFT/DFTB	Plane waves	http://www.mpie.de/index.php?id=exlib
QUANTUM-ESPRESSO	DFT/HF	Plane waves	http://www.quantum-espresso.org
VASP	DFT/HF	Plane waves	http://cms.mpi.univie.ac.at/vasp
WIEN2K	DFT/HF	Augmented plane waves	http://www.wien2k.at
Opium		Pseudopotential generator	http://opium.sourceforge.net
BSE		Gaussian basis set/effective core potential database	https://bse.pnl.gov/bse

DFT, density functional theory; HF, Hartree-Fock; DFTB, density functional tight-binding.

For updated descriptions see <http://www.psi-k.org/codes.shtml>

8 Computational Approaches to Energy Materials

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 $e^{i\mathbf{k}\cdot\mathbf{r}}$ 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 ultrasoft 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 Ψ 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:

$$\Psi_0 = \Psi_0(1) \Psi_0(2) \dots \Psi_0(N).$$

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 (Ψ_T) is higher than the true energy obtained using the exact wavefunction (Ψ_0):

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

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.

10 Computational Approaches to Energy Materials

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,

the one-electron HF molecular orbitals themselves are re-optimized when determining the new electronic wavefunction. Sometimes, such methods, which rely on the initial HF solution of particular symmetry, or reference, may become insufficient, and the need for multireference wavefunctions becomes particularly important for systems with low-lying and/or degenerate excited states.

An alternative approach is given by many-body perturbation theory, where the ground-state HF wavefunction is subject to a perturbation with respect to the correlation potential. The most widely used method is second-order Møller–Plesset (MP2) theory, while calculations up to sixth order (MP6) are feasible on small molecules. Of the two approaches, CI is typically the more accurate, but scales poorly with increasing system sizes; for example, HF conventionally scales as $O(N^4)$, MP2 as $O(N^5)$ and CISD as $O(N^6)$, where N is the number of basis functions used to construct the wavefunction. A modern alternative to the Møller–Plesset series is given by the coupled-cluster approaches, which include partial sums over infinite series of different excitations of certain types. While still being very computationally expensive, they provide a highly accurate treatment for both ground and excited states of small molecules. An alternative way of handling the electron correlation problem without the heavy computational burden of post-HF methods is through DFT, which is discussed in Section 1.3.2.

1.3.1.3 Semi-empirical Wavefunction Methods

For large or complex systems, first-principles methods can become too expensive to apply directly. However, further approximations can be made in order to make calculations more affordable. One of the earliest approximate methods is Hückel theory, which describes the π orbitals of aromatic hydrocarbons. Only nearest-neighbor interactions are considered, and all remaining electron integrals are parameterized. This approach is closely related to the tight-binding approximation employed in solid-state theory and, more generally, model Hamiltonian methods. Despite their simplicity, both the original Hückel theory and the extended Hückel method, developed by Hoffmann to treat π and σ bonds, have been highly successful approaches in the field of organic chemistry.

An extended family of more general semi-empirical approaches can be created by reducing the number of two-electron integrals present in the HF approach. These include zero differential overlap, intermediate neglect of differential overlap and so on. Parameterization of integrals can be performed over a large experimental database to reproduce first-principles results. The most advanced of these are the AM1, MNDO and PM3 (PM6) approaches, which are parameterized over a wide range of molecular systems to reproduce structural, thermodynamic and electronic properties. Similar to empirical potentials, the validity of these models for systems or properties that were not in the initial database is not guaranteed, but nonetheless they can produce valuable insight into the processes that are beyond the length and time scales accessible to higher level approaches, such as protein folding and biosolvation.

1.3.2 Density Functional Theory

DFT describes a chemical system in terms of its real-space electron density (n), rather than the $3N$ -dimensional wavefunction associated with solution of the Schrödinger equation. The theory originates from the Thomas–Fermi model (1927), which provided a simple expression for the kinetic energy based on the uniform electron gas model and combined it with a classical description of nuclear–electron and electron–electron interactions. Moreover, the Hartree approximation introduces the mean potential that depends only on the electron density, and likewise the exchange potential models have been advanced for atoms and electron gas by Dirac, Slater, and Gáspár. Building upon these ideas, in 1964 Hohenberg and Kohn [18] reported two important theorems. Firstly, they proved that every observable of a stationary quantum mechanical (QM) system (including energy) could be calculated exactly from the ground-state electron density. Secondly, they showed that the total energy calculated for any trial density could not be lower than the true ground-state energy, and thus could be optimized via the variational principle. There is therefore a direct analogy between HF and DFT methods, except that the latter implicitly includes electron correlation, as it is an exact method by definition.

Within the self-consistent Kohn–Sham approach [19], *independent* (HF-like) one-electron particles are used to construct an *interacting* electron density:

$$n(r) = \sum_{i=1}^N |\Psi_i(r)|^2.$$

In practice, the success of DFT-based approaches relies on the description of exchange–correlation effects, which comes down to the choice of the exchange–correlation functional used to describe the interacting system of electrons.

1.3.2.1 Exchange–Correlation Functionals

While an exchange–correlation functional (E_{XC}) that results in the exact ground-state energy in principle exists, its form is hitherto unknown and only approximate forms are available. However, one reason that DFT is so appealing is that even relatively simple approximations to E_{XC} can give reasonable results for equilibrium atomic and electronic structure. The majority of density functionals are based upon the uniform electron gas model, for which accurate energies are known from quantum Monte Carlo simulations (here, MC techniques described above are used to solve the many-electron Schrödinger equation).

The simplest way to derive an E_{XC} for a real system of variable electron density based on contributions from the uniform electron gas is the local density approximation (LDA), where E_{XC} depends only on the value of the density at a position r in the system of interest. The density calculated at this point is then referenced to the E_{XC} contributions that a uniform electron gas of equivalent density would have. This process is repeated for, and integrated over, each point in space. Such an approach is expected to work well for systems, in which the electron density does not vary rapidly, such as a metal; however, practice shows that the LDA performs

reasonably, at least at a semi-quantitative level across the whole range of chemical compounds and processes. Concerning errors in this approach, calculations based on the LDA generally result in exaggerated binding energies and underestimated bond lengths. The semi-local generalized gradient approximation (GGA) is dependent on both the value of the density at a position r and its variation close to r (the first derivative, or gradient of density). This accounts better for the nonhomogeneity of the true electron density. In contrast to the LDA, the GGA has a tendency to overestimate bond lengths.

Perdew has presented the hierarchy of density functionals metaphorically as Jacob's ladder, which rests upon the "Hartree world" without exchange or correlation and reaches toward the utopia of chemical accuracy [20]. At the bottom, the local potential experienced by each electron at each point is determined by the charge density at the same point. In heaven, the potential at each point is determined by the global electron distribution. To climb the ladder we use auxiliary means in the form of the gradient expansion of the charge density and different constructs using Kohn–Sham orbitals. Above the rungs of the LDA and GGA are the more complex meta-GGA functionals, which depend on second derivatives, or Laplacian, of the charge density along with the Kohn–Sham orbital kinetic energy density:

$$\tau(r) = \frac{1}{2} \sum_{i=1}^N |\nabla \Psi_i(r)|^2.$$

Hybrid exact-exchange functionals, which incorporate an element of nonlocal HF-like electron exchange, can be considered as one of the examples of the next hyper-GGA rung, which makes use of the Kohn–Sham orbital exchange energy. Generally, hyper-GGA functionals can include dependence on the orbital exchange both in exchange and correlation functionals. These methods are now under development and still experimental. While both orbital kinetic and exchange energy densities are local with respect to orbitals, their dependence on the charge density is essentially nonlocal. Finally, unoccupied Kohn–Sham orbitals can be used on the fifth rung, which explicitly includes some correlation effects as they are considered by various post-HF theories, for example in MP2 and the random phase approximations.

The application of hybrid functionals has become increasingly popular in the last decade, for both solid-state and molecular systems: the error cancellation between HF and DFT can generally provide better structural, electronic and thermodynamic properties than either of the pure methods. While the amount of exact-exchange and/or screening of that exchange is not necessarily universal, there has been notable success for a wide range of systems using standard functionals [21, 22]. A number of modern functionals are listed in Table 1.2.

DFT has proved a successful approach applied to a wide range of systems, from insulators to metals, and from the molecular to the solid state. However, the biggest challenge for electron density-based methods can be found in the low- and high-density limits—weak interactions (van der Waals forces) and highly correlated (congested) d and f electron systems.

14 Computational Approaches to Energy Materials

Table 1.2 A selection of commonly used DFT exchange–correlation functionals

Functional	Type	References
AM05	GGA	R. Armiento and A.E. Mattsson, Phys. Rev. B 7, 085108 (2005)
BJ06	Meta GGA	A.D. Becke and E.R. Johnson, J. Chem. Phys. 124, 221101 (2006)
B3LYP	Hybrid GGA/LDA	P.J. Stephens <i>et al.</i> , J. Chem. Phys. 98, 11623 (1994)
B97	Hybrid GGA	A.D. Becke, J. Chem. Phys. 107, 8554 (1997)
B97-3	Hybrid GGA	T.W. Keal and D.J. Tozer, J. Chem. Phys. 123, 121103 (2005)
HSE06	Hybrid GGA	A.V. Krukau <i>et al.</i> , J. Chem. Phys. 125, 224106 (2006)
M05	Hybrid Meta GGA	Y. Zhao <i>et al.</i> , J. Chem. Phys. 123, 161103 (2005)
PBE	GGA	J.P. Perdew <i>et al.</i> , Phys. Rev. Lett. 77, 3865 (1996)
PBE0	Hybrid GGA	C. Adamo and V. Barone, J. Chem. Phys. 110, 6158 (1999)
PBEsol	GGA	J.P. Perdew <i>et al.</i> , Phys. Rev. Lett. 100, 136406 (2008)
PW91	GGA	J.P. Perdew <i>et al.</i> , Phys. Rev. B 46, 6671 (1992)
PW92	LDA	J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)
PZ81	LDA	J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981)
TPSS	Meta GGA	J. Tao <i>et al.</i> , Phys. Rev. Lett. 91, 146401 (2003)
vdW-DF	GGA + dispersion	M. Dion <i>et al.</i> , Phys. Rev. Lett. 92, 246401 (2004)

While nonbonding interactions can be neglected for strongly bound covalent or ionic materials, for molecular solids or physisorbed states, which may be present in gas storage or catalytic systems, their contributions can become critical. A number of exchange–correlation functionals have been developed to account for these terms. One approach is to incorporate an empirical r^{-6} correction as found in the Lennard-Jones potential (termed DFT-D) [23], while an alternative approach derives the dispersion forces from a partitioning of the charge density itself [24]. Such methods have had recent success in the description of phase transitions in metal–organic frameworks [25], as well as the conformational landscape of polypeptides [26].

For highly correlated systems, where electrons occupy localized orbitals, standard LDA or GGA functionals have a tendency to delocalize the electronic states, which affects, for example, the description of magnetism in $3d$ systems. While hybrid functionals are starting to be applied to these systems, a more popular and approximate method formulated for treating d and f shell systems is DFT + U , where U is an orbital-dependent external potential [27]. One of the most prolific applications of DFT + U in recent times has been in the treatment of chemical reductions in the catalytic materials TiO₂ and CeO₂, where standard LDA and GGA functionals have been shown to result in an unphysical description of the excess electron distribution.

1.3.2.2 Semi-empirical Density Functional Approaches

Similar to semi-empirical wavefunction-based methods, it is possible to reduce the cost of DFT through further approximations. The most successful approach in this area, which can facilitate the simulation of thousands of atoms, is density functional tight-binding (DFTB) theory. In solid-state physics, the tight-binding method based on linear combinations of atomic orbitals, where the interaction potentials are

determined empirically or intuitively, has been successful when applied to a range of solids, as reviewed extensively by Harrison [28]. DFTB extends this method to the Kohn–Sham formalism using a minimal localized atomic basis set, and where the level of self-consistency can be controlled, giving rise to different orders of theory. It is a chemically intuitive approach that allows for the calculation of large-system sizes and complex response functions. A detailed discussion of these techniques can be found in the book of Martin [29].

1.3.3 Excited States

Many of the processes relating to energy materials involve excited states, most commonly the absorption or emission of light by materials, which are addressed in Chapters 2 and 8, respectively. In the calculation of excited states, the concepts of excitonic and quasi-particle states are most important, and commonly confused. It is possible to have excitations in which the number of particles is conserved (e.g., optical absorption creating an N^* -excited state), or in which the number of particles changes (e.g., characterized by the $N-1$ ionization potential or $N+1$ electron affinity). For charge-conserving excitations, the dielectric response can be calculated starting from the single-particle density at various levels of theory—a zeroth-order response is based purely on the DFT or HF orbital energies, while higher level theories include electron–hole (excitonic) interactions explicitly (e.g., time-dependent DFT or HF) [30].

Alternatively, one could start with a description of quasi-particle states (e.g., the $N-1/N+1$ excitation spectra) obtained from many-body perturbation theory (e.g., the *GW* method) [31] and include excitonic effects using explicit two-particle calculations (e.g., the Bethe–Salpeter method) [32]. These approaches are currently the state of the art for calculating the optical properties of solids [33], discussed in more detail in the context of solar cell materials in Chapter 2 and solid-state lighting in Chapter 8.

One drawback of one-electron theories is that the band gap (the energy separation between filled and empty states) of semiconducting and insulating materials is typically incorrect by a significant amount: for LDA/GGA-DFT it is too small, while for HF it is too large. For comparison with experimental measurements, a rigid shift (or scissors operator) is generally applied, or a hybrid DFT functional is constructed that results in the correct eigenvalue spectrum. Neither approach is entirely satisfactory, and this is an area where many-body perturbation theory is being rapidly developed for, and applied to [34–36]. The first-principles quantitative prediction of band gaps in nonmetallic materials remains one of the major challenges in contemporary computational materials science.

1.4 Multiscale Approaches

The techniques outlined above are generally applicable directly to small molecules or homogeneous crystalline solids with small- to medium-sized unit cells in

equilibrium. However, often we are interested in large molecules, inhomogeneous solids, complex environments or geometrical arrangements, systems that are far away from equilibrium or have particularly long evolution times. Moreover, when a direct treatment by *ab initio* methods is not viable, and we want to use semi-empirical or interatomic potential-based techniques, suitable parameters will not always be available or easily derivable. Then in many cases, multiscale approaches could be the method of choice. A typical multiscale approach would combine in one model two or three levels of description applied in different regions and/or time intervals.

1.4.1 Hybrid QM/MM Embedding Techniques

Hybrid techniques can be applied to systems with large numbers of atoms, where there is a clearly defined site of interest comprising a small group of atoms, or a cluster with an active site or point defect. The method aims at describing this cluster at the highest affordable level of theory, post-Hartree–Fock or hybrid DFT at present, while the remaining atoms are treated with a parameterized interatomic potential, or molecular mechanical (MM) approach. But other schemes combining different MM or QM methods have also been advanced and widely used. Further, these approaches closely relate to solvation models employed in studies of liquid phase, for example, the behavior of molecular complexes in dielectric solutions.

Hybrid techniques could be broadly divided into two classes [37, 38]: in one, *subtractive* or *multilayered*, more than one level of theory would be applied within the same region of interest [39], whereas in another, *additive* or *multiregion*, each atomic group is treated with one specific approach [40]. As the fundamental extensive measure used in evaluation of system structure and properties is its energy (which could be, for example, potential, internal, including vibrational contributions, or free energy), the terms refer to the way the energy and forces are calculated. Suitable techniques have been developed for both the length and time scales.

Depending on the physicochemical nature of the system of interest, system partitioning may involve (i) only steric constraints on the embedded cluster, which constitutes *mechanical* embedding, (ii) long-range Coulomb interactions included in the Hamiltonian used to describe the electron subsystem of the embedded region, which defines the *electrostatic* embedding, and (iii) short-range Coulomb and exchange–correlation interactions of the electron system of the embedded region with the environment, which could be included into the electronic Hamiltonian as an *embedding potential* [12, 41], a frozen (or relaxed generalized hybrid [42]) orbital or a charge (or spin) density [43].

A distinct problem in hybrid embedding is the termination of the inner QM region. For molecular and ionic systems, the boundary between QM and MM regions can be chosen along the minimum density path, so that all ions or molecules in the QM region remain intact. Then a suitable form of embedding would result in a correct electron localization within the QM region. For extended covalent and metallic systems this is not possible, but additional effort is required. In the

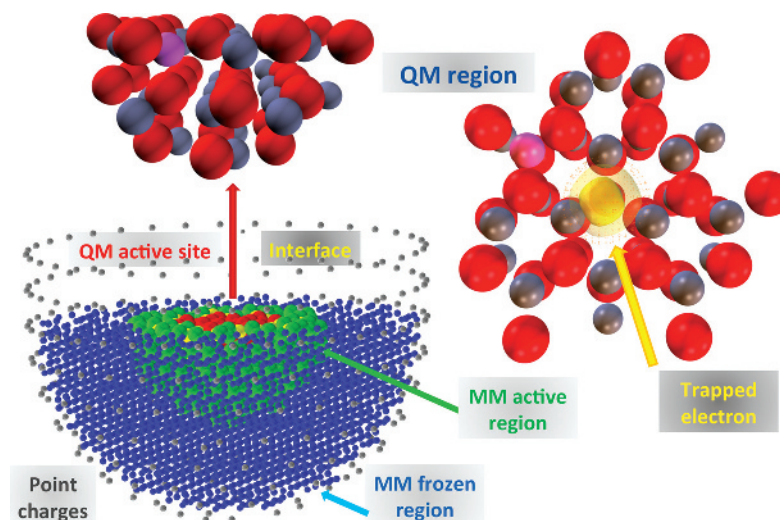


Figure 1.1 A hybrid QM/MM model of a surface-active site. Atoms or ions are shown as spheres while a trapped electron as spin isodensity contours. Auxiliary point charges placed around the large MM cluster emulate the accurate Madelung field in the active region of the model.

case of broken covalent bonds, especially of the sigma character, a QM region necessarily terminates in dangling bonds that need to be saturated. The simplest way to deal with it is by saturation (passivation) of dangling bonds by hydrogen, halide or a molecular group (e.g., methyl) [44]. The metallic systems in turn are characterized by strongly delocalized electrons; to account for their behavior, typically an electron localizing procedure is employed, in which the electrons in the QM cluster are treated as a perturbation of the ideal crystal [4, 45].

As an example of a typical hybrid QM/MM embedded cluster approach, used in the studies of heterogeneous systems, we highlight a ChemShell implementation of the solid-state embedding procedure [46], illustrated in Figure 1.1. Here, simple effective core potentials are centered on the cationic sites around the QM cluster forming an interface region, whose role is to contain the electrons within from spilling over the positive charges in the MM region. Similar models have been widely used in the studies of numerous technologically important materials used in catalysis, energy technologies and electronics [41, 44, 47–53]. The QM treatment used in these types of schemes varies from a straightforward application of a suitable QM method, which is available off the shelf, to sophisticated methods using electron localising procedures to generate a customized embedding potential.

1.4.2 Beyond Atomistic Models

We are often interested in processes that occur at much larger length and longer time scales than atomistic models are appropriate for, where the systems are huge, inhomogeneous and processes are far from equilibrium. At these scales different

18 Computational Approaches to Energy Materials

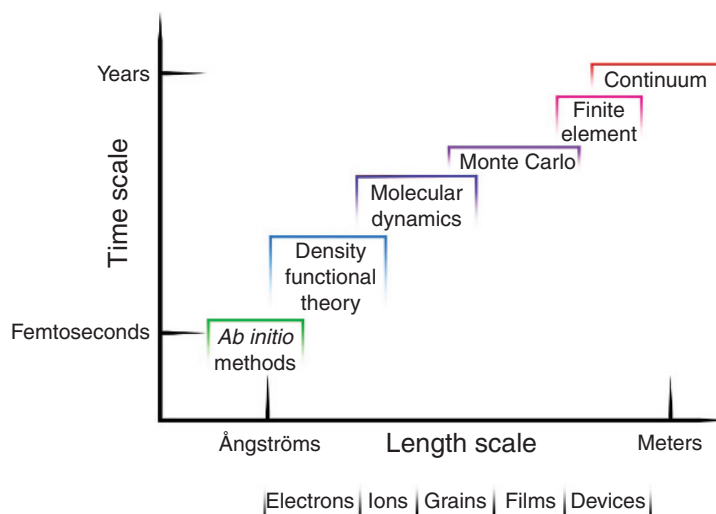


Figure 1.2 Diagrammatic representation of the computational approaches employed at different temporal and spatial scales.

laws govern the motion of matter; sometimes they can be reduced to the underlying quantum mechanics of atoms and electrons, but they can also require new approaches to the understanding of meso- and macrophysics and chemistry of materials. Appropriate methods have been developed, and are widely available, but lie outside the scope of this book. Nevertheless, we give some pointers as to where atomistic simulation techniques fit in this wider picture.

In Figure 1.2, we illustrate the hierarchy of the simulation methods employed to meet the challenges that arise in modeling and design of advanced functional materials, in particular those used in energy technologies.

The typical problems that we wish to tackle at a larger than atomic scale would include modeling macroscopic response to mechanical, thermal, chemical, electromagnetic or high-energy radiation impact on bulk or thin-film materials used for components of devices. One example is the mechanical resistance of a material to deformation and plasticity, which requires an understanding of phase stability, domain or grain structure and evolution, dislocation behavior or microstructure in general. Another, perhaps even more challenging aspect is the growth and self-assembly kinetics of nanoparticulate and nanocomposite materials, and indeed charged particle dynamics in porous systems used as reactors or membranes [38]. In all such situations, we move to the description of rigid or deformable groups of atoms, sometimes comprising quite large entities such as grains, nanoparticles, strands of polymers, or more generally whole macromolecules or residues (*coarse graining*). Thus, the collective motion of an atomic group is modeled explicitly, whereas its internal degrees of freedom and interactions are represented by averaged quantities. As the atomistic detail is lost, vast arrays of data pertinent to

individual electrons or atoms are no longer required, while the necessary time step in dynamical or Monte Carlo stochastic simulations can be increased by orders of magnitude. Both interactions between the new objects and their motion can be described to differing levels of realism according to the simulation approach. For example, simple isotropic Lennard-Jones potentials are often applied in the context of lattice Boltzmann or molecular dynamics, but realistic size and shape, anisotropic potentials are also employed.

The methods to treat inorganic solids, which we are concerned most in this book, strongly overlap with those developed for liquids and soft matter and could be generally related to fluid dynamics. For the description of macroscopic phenomena, including mass and heat transport or kinetics, for which continuum (or continuous media) methods are employed, a number of accurate modern methods have been developed. Solving the corresponding equations of kinetics or hydrodynamics, usually on simulation grids, presents the next step of coarse-graining, now from meso- to macroscale. Finally, we note that “bottom-up” approaches try to make use of electronic techniques or atomistic simulations to parameterize mesoscopic models, the data from, which are used to derive relevant macroscopic parameters. The opposite “top-down” approaches, in which empirical macroscopic data are used to parameterize meso- and microscopic models, are also widespread.

1.5 Boundary Conditions

Electronic structure and atomistic simulations require us to solve relevant “master” equations for particular boundary conditions, which reflect the system dimensionality and complexity. Small clusters of 10–100 atoms would typically be treated as a molecule in the gas phase, that is, in vacuum, whereas simple bulk solids are considered using periodic Born–von Kármán boundary conditions in three dimensions. However, if we wish to reach toward a fully converged basis set for a particular cluster(s), then a plane-wave electronic structure code could be used, and thus artificial periodicity is imposed on this cluster. To reduce the unwanted effects of the periodicity, that is, cluster–cluster interactions, the simulation cell should be chosen to be as large as possible. In turn, systems, extended in one dimension, are often described as periodic in this dimension, even if in reality such a periodicity is not present as is the case for polymers. However, 1D periodic models are valid for the description of nanowires and nanotubes and still serve as effective models for dislocations and polymeric strands. Systems extended in two dimensions are typically material surfaces or interfaces. In practical calculations, 3D boundary conditions are employed, with the third dimension consisting of a finite slab and a large vacuum layer to reduce surface–surface interactions.

Remarkably, however different in nature, the classical vibrational motion of atoms in the harmonic approximation in condensed matter and quantum electronic motion are described by similar homogeneous wave equations, which have

20 Computational Approaches to Energy Materials

qualitatively similar wave solutions, both obeying the Bloch theorem. As a consequence, motion of atoms and electrons can be described as a plane wave propagating in the direction of periodicity modulated by a fully periodic function. When there are two or three periodic directions as in the case of surfaces or bulk crystals, the corresponding waves spread along any vector in which the system is periodic. A wave number of any such wave can always be chosen as a real number between zero and a certain maximum determined by the system period, with all allowed values thus forming a segment (1D), a polygon (2D) or a polyhedron (3D) and referred to as the first Brillouin zone (BZ). The vibrations (phonons) or one-electron orbitals with the period of the unit cell correspond to the first BZ center (Γ point) and form the basis of the entire phonon or electronic structure of the periodic system. For each point in the first BZ, there are only a finite number of solutions of the wave equations: $3N$ vibrations or M orbitals, where N is the number of atoms in the periodic unit cell and M is the number of basis functions. This defines $3N$ vibrational or M electronic energy bands across the first BZ, respectively. Importantly, wave solutions in directions where the system is finite are confined, which results in phonons propagating normal to surfaces being reflected back in the bulk direction and the wavefunctions that describe bound electrons decaying exponentially into free space.

Vibrational or electronic states, based on the plane-wave solutions described above (so-called Bloch states), are fully delocalized in the periodic directions of extended systems, which is often inconvenient if we wish to consider localized processes. For example, to include electronic correlation effects via many-body perturbation theory, CI or coupled cluster techniques would require permutation of delocalized states that lead to severe mathematical problems, generally requiring to sum over divergent series. To avoid this problem, as Bloch states with all allowed wave numbers form a complete basis set, they can be transformed—any linear combination of such states would form another proper solution of the wave equation. Localized solutions could be obtained using a Wannier procedure and then the most relevant localized states could be selected to calculate a desired property of interest, as for example implemented in the code CRYSCOR [54].

The periodic boundary conditions for extended systems are of course suitable for the true periodic systems, which are characterized by sharp X-ray, neutron or electron diffraction patterns. A large class of disordered materials, including glasses, metal and semiconductor alloys on one hand and soft matter on another, do not fit this description. Two types of approaches to modeling such systems have been developed: (i) the atomic or electronic correlation is assumed to decay in real space rapidly, and the system is represented by a large periodic simulation box, usually chosen as a cubic unit cell, with zone-center solutions used to represent the entire extended system; and (ii) effective medium (commonly in the form of mean field or coherent potential) approximations are employed, in which a small representative fragment of the extended system is embedded in a continuous medium characterized by some dispersion, which can in turn be obtained from counterpart crystalline systems, self-consistently or from empirical data. Both approaches work best for

metallic or covalent systems, but experience problems when dealing with ionic systems, characterized by long-range correlation tails.

Ionic or semi-ionic/semi-covalent Coulombic systems in general require a careful treatment in order to avoid artefacts in our simulations. The problem occurs as we try to describe a finite object such as a crystallite as infinite. When charging a molecule or a particle, we allow the long-range Coulomb tail to decay completely in real space, which results in a finite Coulomb energy (excluding of course self-interaction). By charging an infinite object and using a periodic boundary condition, we create an infinite charge, which leads to infinite Coulomb energy density that is unsustainable within a normal physical system. However, often we wish to study local charged centers or nanotubes or surfaces, which are in reality locally compensated. In Section 1.6, we describe how this problem is dealt with when modeling charged point defects.

Even where there is no net charge, the local electrostatic field also has to be considered. For material surfaces, this issue is of particular importance. Depending on the terminating planes, for a binary ionic system, this can lead to dipolar (type III), quadripolar (type II) or nonpolar (type I) surfaces, following the notation developed by Tasker [55]. The presence of an uncompensated surface dipole leads to an infinitely large voltage between opposite surfaces, which necessarily results in a dielectric breakdown. This is the most fundamental reason why models of polar surfaces should always be carefully reconstructed; however, this may not always be evident from experimental analysis.

1.6 Point-Defect Simulations

The role of point defects in determining the properties of condensed matter has been recognized from the onset of solid-state studies in the nineteenth century. These include a combination of lattice site vacancies, interstitials and antisites that may contribute to the optical, electrical, thermal and mechanical response of the material. One of the principal objectives of atomistic simulations is to derive an accurate and coherent approach to the prediction of defect structure, energetics and properties. In Sections 1.6.1 and 1.6.2, we outline two of the most widely employed methods.

1.6.1 Mott–Littleton Approach

The Mott–Littleton approach was originally developed in 1938 as a method to calculate the energy of a charged point defect in alkali salts [10]. The method has since been developed, initially at the Harwell Laboratory, to provide an accurate and flexible description of defects in solids using computer technologies [41].

A charged defect in this approach is treated at the limit of infinite dilution as a local perturbation, the energy of which is minimized to determine the defect equilibrium energy, structure and physical properties. As the total energy of the

22 Computational Approaches to Energy Materials

perfect infinite system is infinite, when using periodic boundary conditions we normally deal with the energy density. This, however, not a useful quantity when dealing with an infinite system containing just one defect, as the change in the mean energy density is negligible. Considering the difference in total energies of the system, with a defect and that of the ideal system, thus proves to be a reasonable course of action. Using the method of interatomic potentials, calculation of such differences is a straightforward procedure as the total energy is summed up over a series of on-site, pairwise, three-body, four-body and so on interaction energies. All contributions from a particular site around the defect center can then be evaluated for the two systems and subtracted from one another to yield a contribution of interest to the defect energy.

On creation of a charged defect, the total energy of an infinite system changes in the first place by the Madelung energy of the introduced charge, qV_{Madelung} . Following the original derivation of Mott and Littleton, the defect energy can be summed up over contributions from the defect site itself (vacant, substitutional or interstitial) and its nearest and, perhaps, next nearest neighbors. To include longer range, polarization effects, a simplified continuous medium approximation of the dielectric material of a given permittivity, ϵ^0 , could be employed, for which one can use the Jost formula, for example $-q^2/2R(1 - 1/\epsilon^0)$, where R is the radius of a sphere containing the defect site with all the neighboring atoms treated explicitly. This approximation is essentially employed in the majority of hybrid QM/MM methods, described in Section 1.4 [46]. Although this approach is robust and provides quite a reasonable estimate of the defect energy, there is still some arbitrariness in how the radius of the dielectric cavity containing defect is chosen or the scalar character of the dielectric constant, which fails for many technologically important materials with a large degree of anisotropy (one celebrated example is TiO_2 rutile for which $\epsilon_{33}^0/\epsilon_{11}^0 \approx 2.3$ at 0 K).

In modern implementations [3], no recourse is made to continuous media approximations; all lattice sums are calculated explicitly until specified criteria of convergence are reached. The system is split into an inner region 1, contained within a sphere of a given radius, and the system remainder referred to as region 2. Within region 1, all ions are treated explicitly and their interactions with each other are calculated exactly (at a given level of theory). In region 2, ions are considered to be perturbed by forces generated by a defect in region 1, but remain in harmonic wells around their perfect crystalline sites and in equilibrium with the defect. The unit cells to which local groups of atoms belong would deform elastically in response to a nearly uniform stress generated by the defect region at a large separation distance. Moreover, parameters of the wells (or curvature) are approximated to be the same as in a perfect crystal. In other words, a response of the crystal with a defect to an external field (electrostatic, short-range or elastic in nature) is equated to the response of the perfect crystal.

In the linear response (or harmonic) approximation for any given defect configuration in region 1, displacements of atoms from their perfect positions in region 2

can be calculated in just one step. Then forces acting on displaced atoms in region 2 can be re-evaluated and new displacements calculated with the procedure applied iteratively until it converges. Following this procedure, the total defect energy is calculated as the sum of (i) the defect energy of atoms in region 1, (ii) the defect energy of atoms in region 1 due to the interaction with atoms in region 2 and (iii) the energy of displacement of atoms in region 2 from their crystalline ideal positions. The latter term is the polarization energy of the system remainder, which provides a much more accurate atomistic expression, thus replacing the simple Jost formula given earlier.

The Mott–Littleton approach has been very successful but still has certain limitations. Firstly, it has slow convergence with respect to region size, where quite reasonable estimates could be obtained on a modern single processor/core machine within seconds, but accurate energetics, converged to 1 meV for example (see Figure 1.3), may require calculations involving explicit sums over many thousands of atoms taking of the order of a hundred processor hours.

Secondly, the method itself may be quite sensitive to the initial (guess) defect configuration and get stuck in an artificial local minimum overstabilized by strong relaxations in region 2a, especially for relatively small region 1 sizes. Thirdly, molecular dynamics and Monte Carlo simulations cannot be routinely performed in this approach although would be possible in principle. The main obstacle is the nonvariational character of the defect energy for nonequilibrated region 1–2

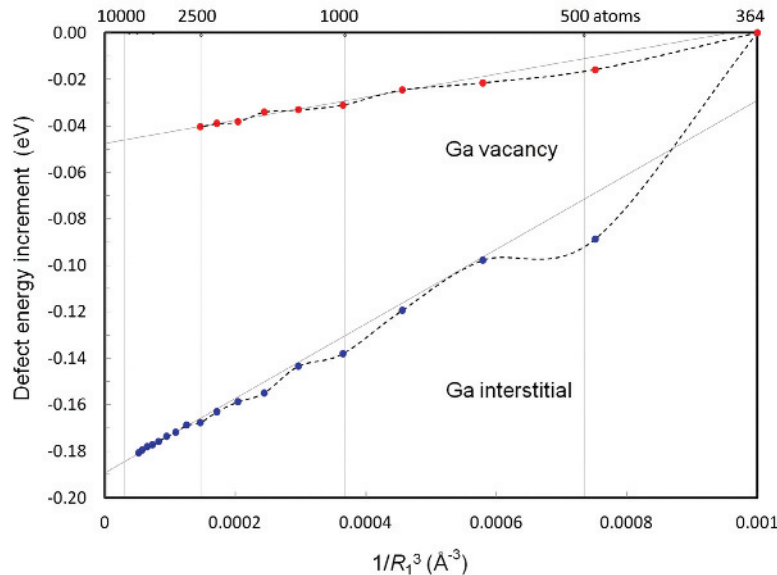


Figure 1.3 Convergence in defect energy of fundamental Ga defects in the hexagonal phase of GaN with region 1 size. The graphs show approximately inverse cubic asymptotes for large values of R_1 .

structures. Finally, a fully *ab initio* counterpart of Mott–Littleton simulations has not been formulated yet, and possibly is mathematically intractable. As a remedy, hybrid QM/MM procedures have been employed, which use simplified *M-L* approaches to calculate defect polarization energy. These problems are mostly avoided in periodic supercell techniques described in Section 1.6.2.

1.6.2 Periodic Supercell Approach

An alternative to the embedded cluster techniques for the calculation of lattice defects is to maintain the 3D boundary conditions of the host material, where the defect is placed at the center of an expanded unit cell, the supercell approach. While in the past, the typical supercell expansion consisted of the order of 64 atoms, developments in high-performance computer architecture mean that calculations involving hundreds or thousands of atoms are now feasible, in particular when combined with linear-scaling electronic structure techniques.

The benefit of the supercell approach is that it requires no methodological advancement and hence works with all existing condensed matter codes. The drawback is that the isolated point defect of interest is treated as a periodic array – for both the total energy and electronic structure, the size of the supercell must be carefully checked for convergence. The issue is most serious for charged defect centers, as the Coulombic interaction is long-ranged, and the error remains significant even for relatively large unit cells, as illustrated in Figure 1.4 for the case of an oxygen vacancy in In_2O_3 . As introduced by Leslie and Gillan [56], the electrostatic correction to the total energy is governed by the supercell length (L), the Madelung

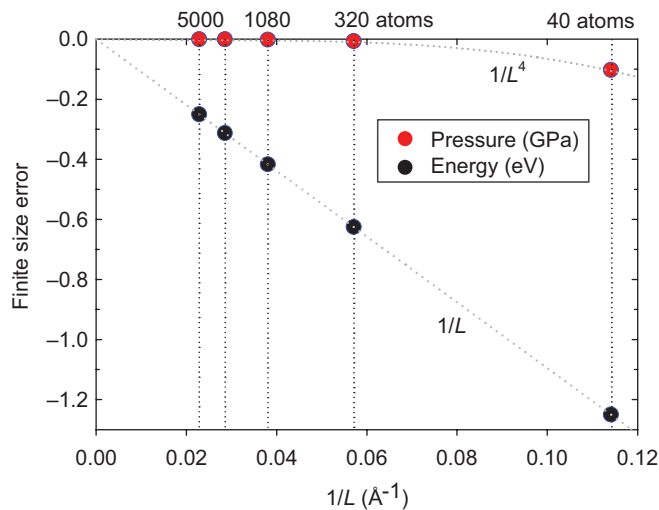


Figure 1.4 Errors in total energy and pressure caused by finite-size effects for a doubly charged oxygen vacancy defect in In_2O_3 , where L represents the length of the supercell expansion.

constant of the material (α_m), the charge of the defect (q) and the dielectric constant (ϵ^0):

$$\Delta E = -\frac{\alpha_m q^2}{2\epsilon^0 L}.$$

The corresponding correction to the pressure is

$$\Delta p = -\frac{\alpha_m q^2}{6\epsilon^0 L^4}.$$

Makov and Payne extended this formalism to include multipole corrections [57]. Such correction methods are now widely used in the community, with a variety of coefficients [58]. Freysolt *et al.* recently presented a straightforward implementation that automates the correction for calculations based on electronic structure techniques [59]; however, it does rely on the input of the dielectric tensor of the material, which may be calculated separately or inferred from experiments.

1.7 Summary

Having introduced the fundamentals of atomistic simulation techniques, their utility for a range of energy-related technologies is illustrated in the following eight chapters. For example, excited-state methods are further developed in Chapters 2 and 8 in relation to solar cells and solid-state lighting, while molecular dynamics approaches are extensively used in Chapters 3 and 4 covering nuclear and energy storage materials. A suggested reading list (Further Reading) is included at the end of the book for any reader interested in the finer details, and especially to those wishing to develop or implement their own techniques in the future.

References

1. Born, M. and Huang, K. (1956) *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford.
2. Bush, T.S., Gale, J.D., Catlow, C.R.A. and Battle, P.D. (1994) Self-consistent interatomic potentials for the simulation of binary and ternary oxides, *J. Mater. Chem.* **4**(6), 831–837.
3. Gale, J.D. and Rohl, A.L. (2003) The general utility lattice program, *Mol. Simul.* **29**(5), 291–341.
4. Daw, M.S. and Baskes, M.I. (1983) Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals, *Phys. Rev. Lett.* **50**, 1285–1288.
5. Dick, B.G. and Overhauser, A.W. (1958) Theory of the dielectric constants of alkali halide crystals, *Phys. Rev.* **112**(1), 90.

26 Computational Approaches to Energy Materials

6. KLMC Potential Database (2011) *Database of Published Interatomic Potential Parameters*, <http://www.ucl.ac.uk/klmc/Potentials/> (accessed 7 November 2012).
7. Lewis, G.V. and Catlow, C.R.A. (1985) Potential models for ionic oxides, *J. Phys. C Solid State Phys.* **18**(6), 1149–1161.
8. Oganov, A.R. (2011) *Modern Methods of Crystal Structure Prediction*, Wiley-VCH Verlag GmbH.
9. Woodley, S.M. and Catlow, R. (2008) Crystal structure prediction from first principles, *Nat. Mater.* **7**(12), 937–946.
10. Mott, N.F. and Littleton, M.J. (1938) Conduction in polar crystals. I. Electrolytic conduction in solid salts, *Trans. Faraday. Soc.* **34**, 485.
11. Walsh, A., Sokol, A.A. and Catlow, C.R.A. (2011) Free energy of defect formation: thermodynamics of anion Frenkel pairs in indium oxide, *Phys. Rev. B* **83**(22), 224105.
12. Bachelet, G.B., Hamann, D.R. and Schlüter, M. (1982) Pseudopotentials that work: from H to Pu, *Phys. Rev. B* **26**(8), 4199–4228.
13. Vanderbilt, D. (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B* **41**(11), 7892.
14. Blöchl, P.E. (1994) Projector augmented-wave method, *Phys. Rev. B* **50**(24), 17953.
15. Hartree, D.R. (1928) The wave mechanics of an atom with a non-coulomb central field. Part I. Theory and methods, *Math. Proc. Camb. Phil. Soc.* **24**(01), 89–110.
16. Fock, V. (1930) Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems, *Z. Phys. A Hadron. Nucl.* **61**(1), 126–148.
17. Slater, J.C. (1963) The electronic structure of atoms—the Hartree-Fock method and correlation, *Rev. Mod. Phys.* **35**(3), 484.
18. Hohenberg, P. and Kohn, W. (1964) Inhomogeneous electron gas, *Phys. Rev.* **136**(3B), B864.
19. Kohn, W. and Sham, L.J. (1965) Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**(4A), A1133.
20. Perdew, J.P., Ruzsinszky, A., Constantin, L. *et al.* (2009) Some fundamental issues in ground-state density functional theory: a guide for the perplexed, *J. Chem. Theory Comput.* **5**, 902.
21. Marsman, M., Paier, J., Stroppa, A. and Kresse, G. (2008) Hybrid functionals applied to extended systems, *J. Phy. Condens. Matter* **20**(6), 064201.
22. Heyd, J. and Scuseria, G.E. (2004) Efficient hybrid density functional calculations in solids: assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional, *J. Chem. Phys.* **121**(3), 1187–1192.
23. Grimme, S. (2004) Accurate description of van der Waals complexes by density functional theory including empirical corrections, *J. Comput. Chem.* **25**(12), 1463–1473.
24. Tkatchenko, A. and Scheffler, M. (2009) Accurate molecular Van Der Waals interactions from ground-state electron density and free-atom reference data, *Phys. Rev. Lett.* **102**(7), 073005.
25. Walker, A.M., Civalleri, B., Slater, B. *et al.* (2010) Flexibility in a metal-organic framework material controlled by weak dispersion forces: the bistability of MIL-53(Al). *Angew. Chem. Int. Ed.* **49**(41), 7501–7503.
26. Tkatchenko, A., Rossi, M., Blum, V. *et al.* (2011) Unraveling the stability of polypeptide helices: critical role of van der Waals interactions, *Phys. Rev. Lett.* **106**(11), 118102.

27. Dudarev, S.L., Savrasov, S.Y., Humphreys, C.J. and Sutton, A.P. (1998) Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA + U study, *Phys. Rev. B* **57**(3), 1505.
28. Harrison, W.A. (1980) *Electronic Structure and the Properties of Solids*, W H Freeman & Co.
29. Martin, R.M. (2004) *Electronic Structure*, Cambridge University Press, Cambridge.
30. Runge, E. and Gross, E.K.U. (1984) Density-functional theory for time-dependent systems, *Phys. Rev. Lett.* **52**(12), 997.
31. Hedin, L. (1965) New method for calculating the one-particle Green's function with application to the electron-gas problem, *Phys. Rev.* **139**, A796.
32. Salpeter, E.E. and Bethe, H.A. (1951) A relativistic equation for bound-state problems, *Phys. Rev.* **84**(6), 1232.
33. Ramos, L.E., Paier, J., Kresse, G. and Bechstedt, F. (2008) Optical spectra of Si nanocrystallites: Bethe-Salpeter approach versus time-dependent density-functional theory. *Phys. Rev. B* **78**(19), 195423.
34. Jiang, H., Gomez-Abal, R.I., Rinke, P. and Scheffler, M. (2009) Localized and itinerant states in lanthanide oxides united by GW@LDA + U, *Phys. Rev. Lett.* **102**, 126403.
35. Rinke, P., Janotti, A., Scheffler, M. and Van de Walle, C.G. (2009) Defect formation energies without the band-gap problem: combining density-functional theory and the GW approach for the silicon self-interstitial, *Phys. Rev. Lett.* **102**, 026402.
36. Vidal, J., Trai, F., Bruneval, F. *et al.* (2010) Effects of electronic and lattice polarization on the band structure of delafossite transparent conductive oxides, *Phys. Rev. Lett.* **104**(13), 136401.
37. Sherwood, P., de Vries, A.H., Guest, M.F. *et al.* (2003) Quasi: a general purpose implementation of the QM/MM approach and its application to problems in catalysis, *J. Mol. Struct. Theochem* **632**(1–3), 1–28.
38. Jorn, R. and Voth, G.A. (2012) Mesoscale simulation of proton transport in proton exchange membranes, *J. Phys. Chem. C* **116**(19), 10476–10489.
39. Svelle, S., Tuma, C., Rozanska, X. *et al.* (2009) Quantum chemical modeling of zeolite-catalyzed methylation reactions: toward chemical accuracy for barriers, *J. Am. Chem. Soc.* **131**(2), 816–825.
40. Harding, J.H., Harker, A.H., Keegstra, P.B. *et al.* (1985) Hartree-Fock cluster computations of defect and perfect ionic crystal properties, *Physica B + C* **131**(1–3), 151–156.
41. Lidiard, A.B. (1989) The Mott-Littleton method: an introductory survey. *J. Chem. Soc. Faraday Trans. 2* **85**(5), 341–349.
42. Gao, J., Amara, P., Alhambra, C. and Field, M.J. (1998) A generalized hybrid orbital (GHO) method for the treatment of boundary atoms in combined QM/MM calculations, *J. Phys. Chem. A* **102**(24), 4714–4721.
43. Wesolowski, T.A. and Warshel, A. (1993) Frozen density functional approach for ab initio calculations of solvated molecules, *J. Phys. Chem.* **97**(30), 8050–8053.
44. Sherwood, P., de Vries, A.H., Collins, S.J. *et al.* (1997) Computer simulation of zeolite structure and reactivity using embedded cluster methods, *Faraday Discuss.* **106**, 79–92.
45. Voloshina, E., Gaston, N. and Paulus, B. (2007) Embedding procedure for ab initio correlation calculations in group II metals, *J. Chem. Phys.* **126**(13), 134115.

28 *Computational Approaches to Energy Materials*

46. Sokol, A.A., Bromley, S.T., French, S.A. *et al.* (2004) Hybrid QM/MM embedding approach for the treatment of localized surface states in ionic materials, *Int. J. Quant. Chem.* **99**(5), 695–712.
47. Nygren, M.A., Pettersson, L.G.M., Barandiarán, Z. and Seijo, L. *et al.* (1994) Bonding between CO and the MgO(001) surface: a modified picture, *J. Chem. Phys.* **100**(3), 2010–2018.
48. Seijo, L. and Barandiarán, Z. (1992) Self-consistent embedded clusters: building block equations for localized orthogonal orbitals, *J. Math. Chem.* **10**(1), 41–56.
49. Shluger, A.L., Sushko, P.V. and Kantorovich, L.N. (1999) Spectroscopy of low-coordinated surface sites: theoretical study of MgO, *Phys. Rev. B* **59**(3), 2417.
50. Grimes, R.W., Catlow, C.R.A. and Stoneham, A.M. (1989) A comparison of defect energies in MgO using Mott-Littleton and quantum mechanical procedures, *J. Phys. Condens. Matter* **1**(40), 7367.
51. Sokol, A.A., French, S.A., Bromley, S.T. *et al.* (2007) Point defects in ZnO, *Faraday Discuss.* **134**, 267–282.
52. Galea, N.M., Scanlon, D.O., Martin, P. and Sherwood, P. (2009) Testing interatomic potentials for QM/MM embedded-cluster calculations on ceria surfaces, *e-J. Surf. Sci. Nanotech.* **7**, 413–420.
53. Stoneham, A.M., Gavartin, J., Shluger, A.L. *et al.* (2007) Trapping, self-trapping and the polaron family, *J. Phys. Condens. Matter* **19**(25), 255208.
54. Pisani, C., Schütz, M., Casassa, S. *et al.* (2012) Cryscor: a program for the post-Hartree-Fock treatment of periodic systems, *Phys. Chem. Chem. Phys.* **14**(21), 7615–7628.
55. Tasker, P.W. (1979) The stability of ionic crystal surfaces, *J. Phys. C Solid State Phys.* **12**(22), 4977.
56. Leslie, M. and Gillan, M.J. (1985) The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method, *J. Phys. C Solid State Phys.* **18**(5), 973.
57. Makov, G. and Payne, M.C. (1995) Periodic boundary conditions in ab initio calculations, *Phys. Rev. B* **51**(7), 4014–4022.
58. Lany, S. and Zunger, A. (2008) Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: case studies for ZnO and GaAs, *Phys. Rev. B* **78**(23), 235104.
59. Freysoldt, C., Neugebauer, J. and Van de Walle, C.G. (2009) Fully ab initio finite-size corrections for charged-defect supercell calculations, *Phys. Rev. Lett.* **102**(1), 016402.