

# Chapter 1

## Born-Oppenheimer Approximation

**Abstract** In condensed matter the motion of the electrons is determined by the electric field generated by the nuclei and their mutual interaction. The conditions for neglecting the vibrations of the nuclei around their fixed positions are discussed. The arrangement of the nuclei rules the symmetry and classification of electronic states. The strength of the electron-nucleus interaction is used to distinguish valence and core electrons.

### 1.1 Solids and Molecules as Many-Body Systems

Systems of condensed matter such as molecules and solids consist of atomic nuclei  $l$  of mass  $M_l$  and charge  $Z_l$  at positions  $\mathbf{R}_l$  and electrons  $i$  with mass  $m$  and charge  $-e$  ( $e > 0$ ) at positions  $\mathbf{x}_i$  and spin variables  $\mathbf{s}_i = \frac{\hbar}{2}\boldsymbol{\sigma}$  with  $\boldsymbol{\sigma}$  as the vector of Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (1.1)$$

The particles can move in the systems, i.e., they possess momentum operators  $\mathbf{P}_l = -i\hbar\nabla_{\mathbf{R}_l}$  (nuclei) or  $\mathbf{p}_i = -i\hbar\nabla_{\mathbf{x}_i}$  (electrons). In the spirit of the ‘first quantization’  $\mathbf{R}_l$  and  $\mathbf{x}_i$  represent canonical position operators. A possible spin of the nuclei is not considered in this book. Each system with all its transport, optical, magnetic, mechanical and thermal properties represents a quantum-mechanical many-body system. For example, in a cube of  $1 \text{ cm}^3$  of a silicon crystal one finds  $5 \times 10^{22}$  nuclei and  $7 \times 10^{23}$  core and valence electrons. For  $N_n$  nuclei the total number of electrons  $N$  in a neutral system is given by  $N = \sum_{l=1}^{N_n} Z_l$ . The Hamiltonian for such a system consists of a sum of five terms: the kinetic energies of the nuclei and electrons, the interactions between nuclei, between electrons and nuclei, and between electrons. The first two types of interactions can be approximately described by Coulomb potentials

$$v(\mathbf{x}) = \frac{e^2}{4\pi\epsilon_0|\mathbf{x}|} \quad (1.2)$$

with the permittivity of vacuum  $\varepsilon_0 = 8.854188 \times 10^{-12}$  As/Vm using consistently SI units in this book. In the non-relativistic limit the Hamiltonian of the system has the form

$$\begin{aligned} \mathcal{H}_{\text{sys}} = & \frac{1}{2} \sum_{l=1}^{N_n} \frac{1}{M_l} \mathbf{P}_l^2 + \frac{1}{2} \sum_{i=1}^N \frac{1}{m} \mathbf{p}_i^2 + \frac{1}{2} \sum_{\substack{l,l'=1 \\ (l \neq l')}}^{N_n} Z_l Z_{l'} v(\mathbf{R}_l - \mathbf{R}_{l'}) \\ & - \sum_{l=1}^{N_n} \sum_{i=1}^N Z_l v(\mathbf{x}_i - \mathbf{R}_l) + \mathcal{H}_{ee}. \end{aligned} \quad (1.3)$$

In this limit it holds  $\mathcal{H}_{ee} = \frac{1}{2} \sum_{\substack{i,i'=1 \\ (i \neq i')}}^N v(\mathbf{x}_i - \mathbf{x}_{i'})$  for the electron-electron interaction.

It is also described by the Coulomb potential (1.2). Relativistic corrections will be discussed in the next chapter.

If  $\mathcal{H}_{ee}$  is known one can solve the Schrödinger equation of the many-body system with the Hamiltonian (1.3) and, in principle, predict all its properties, e.g. its geometric structure including the arrangement of all the nuclei, its thermodynamic behavior, its electrical or thermal transport properties, its excitation spectra, etc. However, such a complete solution of the many-body problem is certainly impossible. Due to the nucleus-nucleus, electron-nucleus, and electron-electron interactions, the Hamiltonian cannot be separated into a sum over Hamiltonians of independent particles. One must therefore solve a coupled system of (differential) equations with a huge number of variables of the order of  $10^{23}$ . This is not feasible numerically and also makes less sense from the viewpoint of physics.

## 1.2 Decoupling of Electron and Nucleus Motion

To make any progress in the theoretical treatment, one is compelled to make certain approximations, mainly motivated by physical considerations. The first obvious fact is that the protons and neutrons in the nuclei are by a factor 1836 more massive than the electrons. For that reason, in general, the nuclei will have a much slower dynamics than the electrons. For instance, the frequencies of atomic vibrations in a typical solid, e.g. a semiconductor, are less than  $10^{13} \text{ s}^{-1}$ . The energy required to excite electrons is given by its fundamental band gap of the order of 1 eV. The frequencies of electronic motion in such a semiconductor are therefore of the order of  $10^{15} \text{ s}^{-1}$ . Consequently, electrons can respond to atomic vibrations almost instantaneously. They follow the atomic motion adiabatically. On the other hand, one may say, nuclei cannot follow the motion of the electrons and only see a time-averaged electronic potential. In the Born-Oppenheimer or adiabatic approximation [1, 2], studying the motion of electrons, the kinetic energy of the nuclei (first term in (1.3)) can be neglected to a first approximation. Experimental observations confirm this idea. Crystallographic

studies show that the ‘atoms’ make up a static, i.e., time-independent, arrangement  $\{\mathbf{R}_l\}$  with small oscillations about their equilibrium positions.

In the older formulation of the adiabatic approximation Born and Oppenheimer [1] expanded the Hamiltonian (1.3) in terms of  $\left(\frac{m}{M_l}\right)^{1/4}$ , the fourth root of the mass ratio between an electron and any of the nuclear masses. The criterion  $\left(\frac{m}{M_l}\right)^{1/4} \ll 1$  has been later reformulated by Born and Huang [2]. In any case it indicates the validity of the adiabatic approximation for not too light elements. Consequently, the treatment of the motion of electrons and nuclei can be decoupled. The neglected interaction can be included in a later step as electron-phonon interaction.

The criterion for semiconductors, insulators, and molecules, small vibrational frequencies compared to the fundamental energy gap, is seemingly violated for metals, while the mass criterion is still fulfilled for sufficiently heavy elements. Nevertheless, more recent investigations [3] showed that in general the adiabatic approximation is also valid for metals. In metals non-adiabaticity is governed by the ratio of a characteristic phonon frequency and the Fermi energy. For a wide range of temperatures the thermal energy  $k_B T$  is usually lower than the Fermi energy  $\varepsilon_F$  of the electron gas in a metal. Therefore, electronic excitations are confined to a narrow region around the Fermi surface, and most of the properties of a metal are little affected by neglecting non-adiabatic contributions due to the motion of the metal electrons.

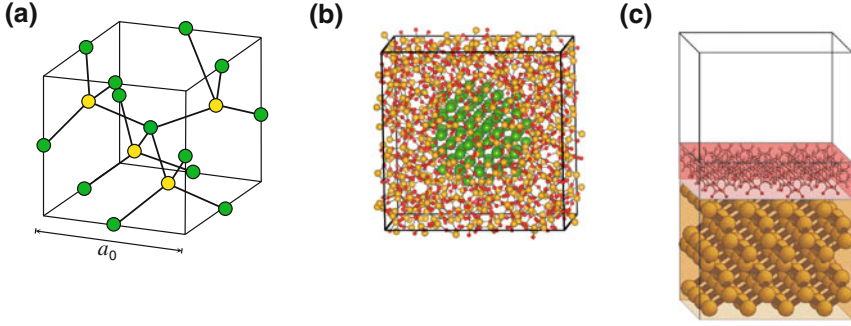
As a result of the Born-Oppenheimer approximation the motion of the electrons will be investigated for fixed positions of the nuclei  $\{\mathbf{R}_l\}$ . Then the third term in (1.3), the energy of repulsion of the nuclei, does not depend on electronic coordinates and, hence, only shifts the total energy of the electrons by the fixed value  $E_{nn} = \frac{1}{2} \sum_{l,l'=1}^{N_n} Z_l Z_{l'} v(\mathbf{R}_l - \mathbf{R}_{l'})$ . Electronic energies and wave functions will be obtained as functions of the nuclei positions. The residual impact of the charged nuclei on the electrons can be described by a potential energy

$$V_n(\mathbf{x}) = - \sum_{l=1}^{N_n} Z_l v(\mathbf{x} - \mathbf{R}_l) \quad (1.4)$$

of an electron at position  $\mathbf{x}$ . The interaction of the spins of nuclei and electrons is not taken into account. Consequently, hyperfine splittings in localized electron systems will not be discussed. We have to point out that in the framework of the description of the pure electronic problem the potential energy (1.4) can be considered as an ‘external’ (from the point of view of the electrons) potential which depends parametrically on the atomic positions.

### 1.3 Atomic Arrangements

The atomic positions in condensed matter can be in general arbitrary, particularly in amorphous systems. However, there are many examples, e.g. molecules and crystals, where the positions of the nuclei underly certain point and/or translational and space symmetries. In addition, for the (numerical) modeling of non-crystalline solids, such



**Fig. 1.1** Illustration of primitive and non-primitive unit cells of three-dimensional periodic atomic arrangements: (a) Cube with edge length  $a_0$  of a zinc-blende crystal with cations (yellow dots) and anions (green dots), (b) Si nanocrystal with 99 atoms (green spheres) in an amorphous  $\text{SiO}_2$  matrix with Si (yellow dots) and oxygen (red dots) atoms arranged in a simple cubic lattice (Reprinted with permission from [5]. Copyright 2012 by the American Physical Society.), and (c) orthorhombic material slab to simulate a Si(001) surface covered by organic molecules together with a separating vacuum region [6]

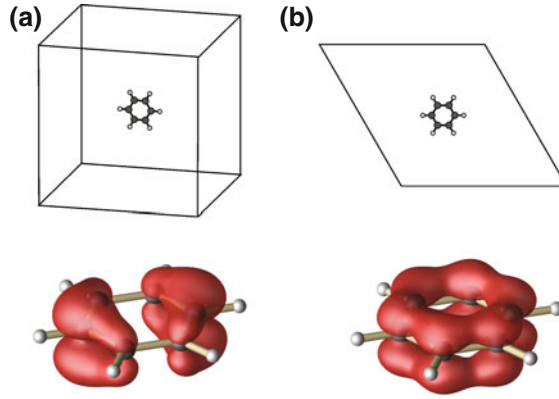
as nanostructures, molecules, clusters, surfaces, and interfaces, frequently periodic arrangements of such objects in supercells are used, i.e., artificial translationally invariant structures. In addition to supercell arrangements repeated slab descriptions are applied [4]. Illustrations of characteristic unit cells and atomic arrangements for a crystal, embedded nanocrystals, and an isolated surface with adsorbate film are displayed in Fig. 1.1. The regularity of the atomic arrangements of such objects in one, two or three dimensions can be mathematically described by a space group of symmetry operations which transforms the arrangement into itself while leaving one space point fixed. Modeling high-symmetric nanoobjects such as a benzene molecule as illustrated in Fig. 1.2, the shape of the supercell and the orientation of the nanoobject in the supercell should be chosen in such away that its point symmetry is not broken. One subgroup of the space group could be a translational symmetry group or simply a translational group of spatial translations  $\{\mathbf{R}\}$ , which can be represented by primitive basis vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  according to

$$\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i \quad (n_i - \text{integer}). \quad (1.5)$$

The set  $\{\mathbf{R}\}$  defines a Bravais lattice [8]. In three dimensions 14 Bravais lattice types exist. The parallelepiped spanned by the basis vectors is a primitive unit cell with the volume

$$\Omega_0 = \mathbf{a}_1 (\mathbf{a}_2 \times \mathbf{a}_3). \quad (1.6)$$

The parallelepiped is not imperative. Other unit cell shapes are possible. The primitive unit cell which represents the point-group symmetry by visual inspection is the so-called Wigner-Seitz cell. The center of this cell lies on a point  $\mathbf{R}$  and its surface is



**Fig. 1.2** Arrangement of a benzene molecule in a (100) plane of an arrangement of cubic supercells (a) or in the (0001) plane of a hexagonal supercell (b). The point groups of the three-dimensional repeated supercell systems  $D_{2h}$  (a) and  $D_{6h}$  (b) strongly influence the computed  $\pi$ -electron density (red clouds) but not the total one. In the case (a) an unphysical symmetry break is clearly visible. Courtesy of M. Preuss, Universität Jena

formed by the perpendicular bisector planes which divide in half the line segments joining the center  $\mathbf{R}$  to adjacent lattice points  $\mathbf{R}'$ .

The arrangements of the nuclei  $\{\mathbf{R}_l\}$  in the natural or artificial translationally invariant structures can be related to Bravais lattice vectors according to

$$\mathbf{R}_l = \mathbf{R} + \mathbf{r}_l. \quad (1.7)$$

The set  $\{\mathbf{r}_l\}$  of vectors  $\mathbf{r}_l$  describes the atomic positions in one unit cell. It is therefore called atomic basis. Together with the Bravais lattice vectors  $\{\mathbf{R}\}$  they describe all atomic positions in the natural or artificial crystal.

The set of all wave vectors  $\mathbf{G}$ , which yield plane waves with the periodicity of a given Bravais lattice, is known as its reciprocal lattice  $\{\mathbf{G}\}$ . These vectors are defined as

$$\mathbf{G} = \sum_{j=1}^3 m_j \mathbf{b}_j \quad (m_j - \text{integer}) \quad (1.8)$$

with basis vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ , and  $\mathbf{b}_3$  which satisfy the relation

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}. \quad (1.9)$$

The construction procedure, which gives in real space the Wigner-Seitz cell, leads in reciprocal space to the Brillouin zone (BZ) with the volume

$$\mathbf{b}_1(\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\Omega_0}. \quad (1.10)$$

Three-dimensional examples are illustrated in Fig. 1.3. It is common to denote the high-symmetry points in the BZ by capital letters. Greek letters are assigned to symmetry points (and lines) in the interior of the BZ but latin letters to symmetry points (and lines) on its surface. The irreducible part of the BZ is also indicated for the (highest) point-group symmetry of the corresponding Bravais lattice.

Each Bravais lattice point  $\mathbf{R}$  is related to a translational operator  $T_{\mathbf{R}} = e^{\mathbf{R}\nabla_{\mathbf{x}}}$  which, when operating on any function  $f(\mathbf{x})$ , shifts the argument according to

$$T_{\mathbf{R}}f(\mathbf{x}) = f(\mathbf{x} + \mathbf{R}). \quad (1.11)$$

The translational operators form an Abelian group with a complete system of eigenfunctions  $\varphi_{\nu\mathbf{k}}(\mathbf{x})$ , which can be classified by means of the eigenvalues  $\mathbf{k}$  of the operator  $-i\nabla_{\mathbf{x}}$ . It holds the Bloch theorem [7]

$$T_{\mathbf{R}}\varphi_{\nu\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\mathbf{R}}\varphi_{\nu\mathbf{k}}(\mathbf{x}) = \varphi_{\nu\mathbf{k}}(\mathbf{x} + \mathbf{R}). \quad (1.12)$$

Since  $e^{i(\mathbf{k}+\mathbf{G})\mathbf{R}} = e^{i\mathbf{k}\mathbf{R}}$  all eigenvalues of  $T_{\mathbf{R}}$  are obtained with  $\mathbf{k} \in \text{BZ}$ . For any given  $\mathbf{k}$ , a countably infinite set of eigenfunctions exists. They can be labeled with an additional index  $\nu$ , following for instance the increasing value of energy. The operator  $T_{\mathbf{R}}$  commutes with the single-particle Hamilton operator  $\hat{H}$  of the electronic system taken in a certain approximation. Since the two operators have a simultaneous system of eigenfunctions, and relation (1.12) represents the Bloch theorem [8], functions  $\{\varphi_{\nu\mathbf{k}}(\mathbf{x})\}$  can be identified with Bloch functions

$$\varphi_{\nu\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\mathbf{x}} u_{\nu\mathbf{k}}(\mathbf{x}) \quad (1.13)$$

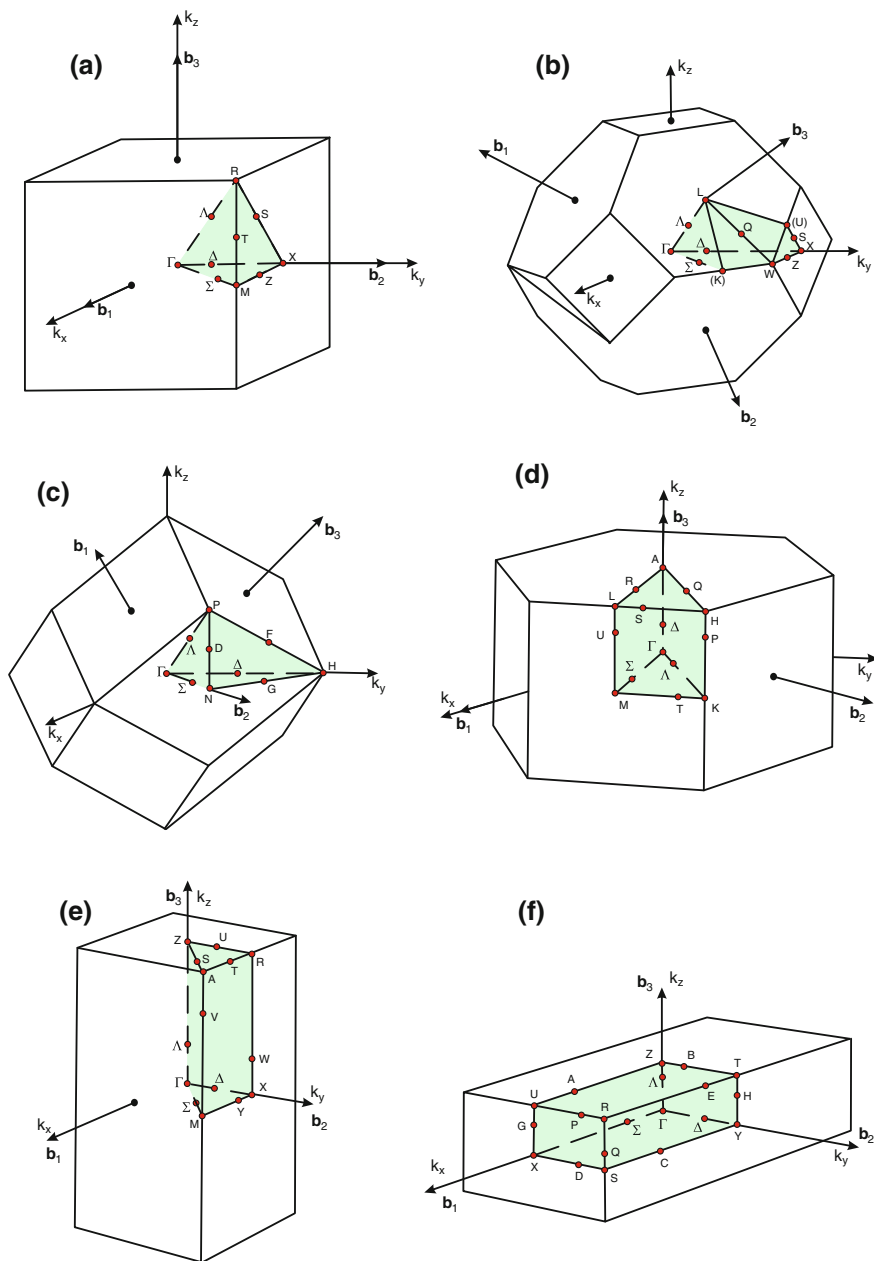
with the periodic Bloch factor  $u_{\nu\mathbf{k}}(\mathbf{x}) = u_{\nu\mathbf{k}}(\mathbf{x} + \mathbf{R})$ , the total volume  $\Omega$  of the condensed-matter system, and the Bloch wave vector  $\mathbf{k} \in \text{BZ}$ . The additional index  $\nu$  may be directly related to the Bloch energy eigenvalues  $\varepsilon_{\nu}(\mathbf{k})$ , i.e., to the Bloch band index.

In many analytical and numerical studies the infinite periodic systems are described by macroscopic (but finite) ones with volume  $\Omega$ . Such a volume can be identified with a parallelepiped with edges  $G_1\mathbf{a}_1$ ,  $G_2\mathbf{a}_2$ , and  $G_3\mathbf{a}_3$ , where  $G_1$ ,  $G_2$ , and  $G_3$  are large (but finite) integer numbers. Then the Born-von Karman periodic boundary conditions [9] on the Bloch eigenfunctions (1.13) require

$$\varphi_{\nu\mathbf{k}}(\mathbf{x}) = \varphi_{\nu\mathbf{k}}(\mathbf{x} + G_i\mathbf{a}_i) \quad (i = 1, 2, 3). \quad (1.14)$$

Together with (1.12) they lead to the conditions  $G_i\mathbf{k}\mathbf{a}_i = 2\pi m_i$  ( $m_i$  – integer) with the solution

$$\mathbf{k} = \sum_{i=1}^3 \frac{m_i}{G_i} \mathbf{b}_i. \quad (1.15)$$



**Fig. 1.3** Brillouin zone and high-symmetry lines/points for the simple cubic (sc) lattice (*cube*) (a), the face-centered cubic (fcc) lattice (*truncated octahedron*) (b), the body-centered cubic (bcc) lattice (*rhombic dodecahedron*) (c), the hexagonal (h) Bravais lattice (d), the simple tetragonal (st) Bravais lattice (e), and the simple orthorhombic (sor) Bravais lattice (f). The green region shows the irreducible part of a BZ

Since the volume of the BZ  $\mathbf{b}_1(\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\Omega_0}$  is given by (1.10), (1.15) asserts that the number of possible wave vectors  $\mathbf{k}$  in such a primitive cell of the reciprocal lattice is equal to the number  $N_c$  of the lattice points in the volume  $\Omega = N_c \Omega_0$ . The numerical advantage of the use of periodic boundary conditions is that it holds

$$\frac{1}{\Omega} \sum_{\mathbf{k}} \rightarrow \frac{1}{(2\pi)^3} \int_{\text{BZ}} d^3\mathbf{k} \quad (1.16)$$

in the limit  $\Omega \rightarrow \infty$ .

## 1.4 Core and Valence Electrons

Obviously, despite fixed nuclei, the eigenvalue problem of the resulting many-particle Hamiltonian (1.3) can generally not be solved without further simplifications. For solids and molecules the electrons can be separated into two groups, valence electrons and core electrons. They can be distinguished according to their contribution to the chemical bonding. For instance, the electronic configuration of a Si atom with  $Z = 14$  is  $1s^2 2s^2 2p^6 3s^2 3p^2$ . The core electrons are those in the energetically lowest, completely filled orbitals  $1s$ ,  $2s$ , and  $2p$ . They are not significantly influenced by the chemical bonding of Si atoms to other ones. They are mostly localized around the nucleus, so they can be ‘lumped’ together with the nucleus to form an ion core with a valence  $Z_{\text{val}} = 4$ . The outer electrons in the incompletely filled shell, such in the  $3s$  and  $3p$  states, are called valence electrons because of their substantial contribution to the chemical bonding.

Several modern electronic-structure codes, e.g. WIEN2k [10], EXCITING [11], CRYSTAL09 [12], and FHI-aims [13, 14], are still all-electron codes and take the motion of the core electrons into account. However, other codes such as VASP [15–17], ABINIT [18, 19], and QUANTUM ESPRESSO [20, 21] are (or can be [13, 14]) restricted to valence electrons. The more localized electrons are frozen into the core. Consequently, instead of bare Coulomb potentials  $Z_l v(\mathbf{x} - \mathbf{R}_l)$  in (1.3), these codes use pseudopotentials (see Sect. 8.3.2), more precisely atomic *ab initio* norm-conserving or ultrasoft pseudopotentials [22], to describe the interaction of valence electrons and ionic cores. The disadvantage of such pseudopotentials, to lead to ‘pseudo-wave functions’ which are too smooth in the core regions, is currently overcome with the projector augmented wave (PAW) formulation [23, 24]. The resulting wave functions of the valence electrons are all-electron wave functions with the correct nodal structure around the cores. There are also examples for efficient total-energy codes such as SIESTA [25, 26] which are based on a description of valence electrons by a few localized orbitals.

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