

Chapter 12.

Density functional theory

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Abstract

This chapter gives an introduction to first-principles electronic structure calculations based on the density functional theory (DFT). Electronic structure calculations have a crucial importance in the multi-scale modelling scheme of materials: not only do they enable one to accurately determine physical and chemical properties of materials, they also provide data for the adjustment of parameters (or potentials) in higher-scale methods such as classical molecular dynamics, kinetic Monte Carlo, cluster dynamics, etc. Most of the properties of a solid depend on the behaviour of its electrons, and in order to model or predict them it is necessary to have an accurate method to compute the electronic structure. DFT is based on quantum theory and does not make use of any adjustable or empirical parameter: the only input data are the atomic number of the constituent atoms and some initial structural information. The complicated many-body problem of interacting electrons is replaced by an equivalent single electron problem, in which each electron is moving in an effective potential. DFT has been successfully applied to the determination of structural or dynamical properties (lattice structure, charge density, magnetisation, phonon spectra, etc.) of a wide variety of solids. Its efficiency was acknowledged by the attribution of the Nobel Prize in Chemistry in 1998 to one of its authors, Walter Kohn. A particular attention is given in this chapter to the ability of DFT to model the physical properties of nuclear materials such as actinide compounds. The specificities of the $5f$ electrons of actinides will be presented, i.e., their more or less high degree of localisation around the nuclei and correlations. The limitations of the DFT to treat the strong $5f$ correlations are one of the main issues for the DFT modelling of nuclear fuels. Various methods that exist to better treat strongly correlated materials will finally be presented.

From the Schrödinger Equation to the one-electron Kohn-Sham Equation

The electronic structure of a material is in principle obtained by solving the Schrödinger Equation $H\Psi = E\Psi$ of the system described by the wave-function $\Psi(\mathbf{r}, \mathbf{R})$ of interacting electrons (with positions \mathbf{r}) and nuclei (with positions \mathbf{R}). Such a many-body problem can, however, not be solved exactly and one usually assumes that the movement of the electrons can be decoupled from the movement of the nuclei. It is the *Born-Oppenheimer approximation*, justified by the much greater velocities of the electrons compared to the velocities of the heavier nuclei: electrons respond quasi instantaneously to the movement of the nuclei and one can consider that electrons remain in their ground state during the displacement of the nuclei. As a consequence, the electron wave-function $\Psi(\mathbf{r})$ is determined for fixed positions \mathbf{R} of the nuclei and the dependence in \mathbf{R} can be omitted. This approximation can be considered valid in most cases and in particular as long as the electron-phonon coupling is not fundamental in the properties studied. The Hamiltonian H of the system therefore becomes that of interacting electrons moving in the external field created by the nuclei.

The many-body character of the electron-electron interactions requires further simplification and the next transformation constitutes the fundament of DFT: the Schrödinger Equation is expressed for an equivalent system of independent electrons characterised by single-electron wave functions $\varphi_i(\mathbf{r})$ and whose electron density is the same as the one of the system with interacting electrons. Two theorems by Hohenberg and Kohn [1] show that the single-particle charge density $n(\mathbf{r})$ can be chosen as the fundamental variable for the description of the ground state of a system of interacting electrons. This density $n(\mathbf{r})$ is only a function of the three space coordinates, which simplifies greatly the many-body problem. The two theorems by Hohenberg and Kohn are as follows:

- All physical quantities are a functional of the electron density $n(\mathbf{r})$ of the system, in particular the total energy.
- The physical (or « real ») electron density of a system is the one minimising the total energy functional of the system (variational principle).

The total energy functional is defined as follows:

$$E[n] = -\frac{1}{2} \sum_i \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{ext}(\mathbf{r}, \mathbf{R}) n(\mathbf{r}) d\mathbf{r} + E_{xc}[n(\mathbf{r})] \quad (1)$$

where the first term corresponds to the kinetic energy of non-interacting electrons. The corrections to this term due to the many-body interaction of the electrons are included in the last term, the exchange-correlation term. The second term corresponds to the electron Coulomb interactions. The Coulomb interactions between electrons and nuclei are included in the external potential term $V_{ext}(\mathbf{r}, \mathbf{R})$.

The electron charge density is determined from the single electron wave functions $\varphi_i(\mathbf{r})$ according to the expression:

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 \quad (2)$$

with N the number of occupied states for all atoms of the system.

The minimisation of the energy functional relative to the electron density yields an eigenvalue problem, called the Kohn-Sham Equation [2], which has the form of a single-particle Schrödinger Equation:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (3)$$

The effective potential V_{eff} is given by:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}, \mathbf{R}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (4)$$

with v_{xc} the exchange-correlation potential defined by:

$$v_{xc}(\mathbf{r}) = \frac{\partial E_{xc}}{\partial n(\mathbf{r})} \quad (5)$$

The derivation of the single-particle Kohn-Sham Equation (3) from the many-body Schrödinger Equation is formally exact. Were all interaction terms in Equation 4 known, the solution of the problem would be exact. Unfortunately, the exact analytical expression of the exchange-correlation interaction v_{xc} is not known. Various approximations can be used for this term and they usually determine the accuracy of the calculations. The most usual approximations are the Local Density Approximation (LDA) and the Generalised Gradient Approximation (GGA), which are presented below.

The Bloch theorem and the electron basis set

The resolution of the Kohn-Sham Equation (3) can be simplified by taking advantage of the periodicity of the system. In bulk crystalline systems, the periodicity of the effective potential is straightforward and can be expressed as the condition $V_{eff}(\mathbf{r} + \mathbf{T}) = V_{eff}(\mathbf{r})$, where \mathbf{T} is a translation vector of the crystal lattice. The Bloch theorem then states that all solutions of the Kohn-Sham Equation can be written in the form of a product of a plane wave with a function u that has the periodicity of the crystal: $\varphi_i(\mathbf{k}; \mathbf{r}) = u_{i,\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}$. Due to the periodicity of the crystal, the \mathbf{k} vectors are limited to a primitive cell of the reciprocal lattice, the first Brillouin Zone. In practice, the Brillouin zone has to be sampled by a finite number of \mathbf{k} -points, which is usually achieved by the Monkhorst-Pack scheme [3]. For systems containing point defects or impurities (fission products, helium, oxygen...), the periodicity of the system is retained by the use of the *supercell* method.

In order to solve the Kohn-Sham Equation (3), one needs to choose the analytical form of the electron basis set on which the wave functions will be expanded. The wave

function φ_i is a linear combination of the basis functions χ : $\varphi_{\mathbf{k}}(\mathbf{r}) = \sum_j c_{j,\mathbf{k}} \chi_{j\mathbf{k}}(\mathbf{r})$ where the basis functions χ fulfill the Bloch theorem.

The various methods based on the DFT differentiate by the choice of the basis functions χ , which usually defines the name of the method. The basis functions can be plane waves (in pseudopotentials methods) [4,5] augmented or orthogonalised plane waves (in the PAW [6], the OPW [7] or the APW [8] methods), augmented spherical waves (ASW) [9], Muffin-Tin orbitals (in the LMTO method) [10], linear combination of atomic (LCAO) or Gaussian (LGO) orbitals, etc. The Korringa-Kohn-Rostoker (KKR) [11,12] method makes use of the Green's function of the system instead of the wave function.

For the study of radiation damage in nuclear fuels, which requires large supercells to accommodate point defects or impurities and the relaxation of the atomic positions around the defects, a plane-wave method such as the PAW method is one of the most adapted and accurate. This method is widely used with the code VASP [13] and ABINIT [14].

The Kohn-Sham Equation (3) is solved in a self-consistent manner: an initial charge density (usually calculated by the superposition of atomic densities) is used to derive the various terms of the effective potential (4). The eigenvalue problem is solved for this trial density, and a new electron density is obtained from the eigenvectors according to expression (2). An appropriate mixing of the new and previous densities (or potentials) is used to build the new effective potential in order to solve again the Kohn-Sham Equation. This process is repeated until the results (total energy, charge density, or potential) are converged, i.e., they do not vary anymore (or less than a chosen limit) during the iterative process.

Approximations for the exchange-correlation interaction

The Local Density Approximation (LDA) is one of the first and most standard approximation for the exchange-correlation interaction. It assumes that the exchange-correlation energy of the system is equal to the one of a homogeneous electron gas with the density $n(\mathbf{r})$. The exact expression of the exchange-correlation energy of such a homogeneous electron gas is known:

$$E_{xc}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}[n(\mathbf{r})] d\mathbf{r} \quad (6)$$

where $\varepsilon_{xc}^{\text{hom}}$ is the exchange-correlation energy per electron of a homogeneous electron gas of density n . $\varepsilon_{xc}^{\text{hom}}$ can be expressed in various analytical parameterised forms, among which one finds those by Hedin-Lundqvist [15], Barth-Hedin [16], Vosko-Wilk-Nusair [17], Ceperley-Alder [18], Perdew-Zunger [19], etc. The LDA approximation is, in principle, adequate for system with a low spatial varying electron density, but it revealed good for a wider variety of materials. It, however, significantly fails in the description of many properties of d and f compounds. Binding energies are in particular overestimated [20].

The Generalised Gradient Approximation (GGA) is a more elaborate approximation of the exchange-correlation interaction, which consists in taking into account the non-uniform character of the electron density by replacing $\epsilon_{xc}^{\text{hom}}$ by a semi-local function of the electron density and the magnitude of its gradient:

$$E_{xc}[n] = \int f(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r} \quad (7)$$

where f is an analytical function which can also be parameterised in various ways. The most common ones are the Perdew-Burke-Ernzerhof (PBE) [21] and the Perdew-Wang [22] parametrisations. For most materials, GGA improves the LDA overbinding. However, both GGA and LDA approximations are known to underestimate the band gap of semiconductors by about 30 to 80% and to inaccurately describe the band structure of strongly correlated materials. In the case of UO_2 , which is a Mott insulator, LDA and GGA predict a metallic behaviour. The failure of standard DFT (LDA and GGA) is generally attributed to the use of a local potential to treat exchange or to the inadequate treatment of the many-body electron correlations.

Beyond DFT to treat the strong correlations of the $5f$ electrons in actinide compounds

Most nuclear fuels consist of actinide oxides, which are strongly correlated materials. In UO_2 , the $5f$ electrons of the uranium atoms are strongly localised in space around the nuclei. The standard DFT does not accurately reproduce the thus induced strong correlations of the $5f$ electrons. This flaw is revealed by the metallic behaviour of the actinide oxides obtained by DFT, whereas these materials are insulators. Several methods exist to better treat the correlations of $5f$ electrons: the self-interaction correction (SIC) method, the DFT+U method, hybrid functionals, the DFT+DMFT method:

a. The self-interaction correction (SIC) [23,24]: The unphysical electron self-interaction in DFT is explicitly subtracted from the DFT energy, orbital by orbital, for all the occupied orbitals, namely: $E_{\text{SIC}} = E_{\text{DFT}} - \sum_{\alpha} \delta_{\alpha}^{\text{SIC}}$. Since for the itinerant (delocalised)

electrons the self-interaction vanishes, the above sum runs only over localised orbitals (α). The SIC method thus enables one to select the number of electrons that are considered localised or itinerant. In this approach, the localised and itinerant orbitals are treated on an equal footing, the global energy minimum of the system with different localised/itinerant configurations gives the ground-state valence state of the correlated atoms. The SIC method has been applied to bulk properties of actinide metals [25], oxides [26], carbides and nitrides [27].

b. The DFT+U method [28]: An on-site Hubbard like Coulomb interaction term U is added as a correction to the DFT Hamiltonian to increase the Coulomb repulsion between the localised electrons and better account for their enhanced correlations. The corrective term is only applied for the correlated orbitals (d or f) and the total energy functional takes the following form:

$$E_{\text{DFT}+U}[n(\mathbf{r})] = E_{\text{DFT}}[n(\mathbf{r})] + E_U[n_m^{f,\sigma}] - E_{dc}[n^{f,\sigma}] \quad (8)$$

where E_{DFT} is the DFT (LDA or GGA) energy term as in Equation 1, $n(\mathbf{r})$ the electron density and $n_m^{I\sigma}$ the atomic-orbital occupations with spin σ for the correlated atom I . E_U takes the following form:

$$E_U[n(\mathbf{r})] = \frac{1}{2} \sum_{\langle m, m' \rangle, I, \sigma} [\langle m, m' | V_{ee} | m', m' \rangle n_{mm'}^{I, \sigma} n_{m'm}^{I, -\sigma} + (\langle m, m' | V_{ee} | m', m' \rangle - \langle m, m' | V_{ee} | m'', m'' \rangle) n_{mm'}^{I, \sigma} n_{m'm}^{I, \sigma}] \quad (9)$$

and it can be expressed as a function of the screened on-site Coulomb and exchange parameters U and J :

$$U = \frac{1}{(2l+1)^2} \sum_{m, m'} \langle m, m' | V_{ee} | m, m' \rangle \quad \text{and} \quad J = \frac{1}{2l(2l+1)} \sum_{m \neq m', m''} \langle m, m' | V_{ee} | m', m \rangle \quad (10)$$

E_{dc} is the “double counting term”, i.e., a mean-field evaluation of the Hubbard term removing the same amount of Coulomb repulsion from the DFT part of the Hamiltonian. E_{dc} can be assessed using the Around Mean Field (AMF) scheme [29] or the Fully-Localised Limit (FLL) scheme which is better adapted for strongly correlated materials [30].

There exist two formulations of the DFT+U approach. In Dudarev’s approach [31], only the difference ($U - J$) comes into play in the energy functional whereas in Liechtenstein’s formulation [32] both U and J parameters separately come into play. Thus either the value of the difference ($U - J$) or both U and J parameters have to be chosen. This choice can be based on an adjustment on the material properties or on an analysis of experimental spectroscopic data. Such an approach requiring parameter adjustment can thus be seen as a phenomenological many-body corrections. There, however, exist methods based on a linear response approach [33] or on the Random-Phase Approximation (RPA) [34] to calculate the interaction parameters U and J entering the DFT+U functional from first-principles.

In the case of UO_2 , the values of the parameters U and J widely used in the literature were deduced from photoemission spectra [35] and do not need further adjustment. Their use in DFT+U simulations gives very good bulk properties for UO_2 [36-38]: lattice parameter, elastic constants, cohesive energy, energy gap, non-collinear antiferromagnetic order, Jahn-Teller distortion. Even point defect properties, such as oxygen activation energy of diffusion, are well described [39,40].

c. Hybrid Functionals [41]: Hybrid functionals combine a part of the Hartree-Fock (HF) exact exchange with LDA or GGA exchange-correlation functionals. For instance, the PBE0 hybrid functional [42] yields the following expression for the total energy of the system: $E_{XC} = E_{XC}^{PBE} + \frac{1}{4} [E_x^{HF} - E_x^{PBE}]$, where PBE refers to the Perdew-Burke-Ernzerhof GGA exchange-correlation functional. Another example of hybrid functional is the HSE06 one, in which the exchange energy term is split into short- range and long-range components and the HF long range is neglected but compensated by the PBE long range [43]. A comparison of those functionals with the standard LDA and GGA functionals for UO_2 , PuO_2 and $\beta\text{-Pu}_2\text{O}_3$ is given in [44].

The results yielded by hybrid functionals are comparable or better than DFT+U calculations with the advantage of having no system-dependent parameters U and J . The

$\frac{1}{4}$ ration is considered as adequate for most, if not all, materials. Hybrid functional calculations are computationally much more demanding than DFT+U calculations and are not achievable yet for large systems containing point defects or impurities. Recently, however, P. Novák et al. [45] proposed the Exact Exchange for Correlated Electrons method (EECE) in which the exact exchange functional is only applied to a restricted subspace formed by the correlated electrons. This method is therefore much faster and was applied to the study of actinide oxides [46] and charged defects in UO_2 [47].

It should finally be emphasised that the localisation of the correlated electrons yielded by the above-described methods induces the existence of local energy minima (or metastable states) towards which the calculation can converge, missing thus the ground state of the system. This issue was evidenced in $4f$ [48] and $5f$ systems [46,49,50,51]. For the study of radiation damage in UO_2 using DFT+U, several solutions have been proposed [35,52,53] to avoid such local energy minima.

d. Combination of DFT with Dynamical Mean Field Theory (DFT+DMFT) [54,55]: This method is an extension of the DFT+U method and goes beyond the static mean field approximation. The local correlations are described exactly for each single atom, the effect of the other atoms being gathered in an effective field. The resolution of the problem is based on its mapping onto a single-impurity Anderson model using a Quantum Monte Carlo solver [56] or the Hubbard I approximation [57]. The DFT+DMFT method requires choosing a Hubbard-type U term in the same way as in the DFT+U method (by constrained U -calculations or adjustments to experiments). Besides being able to correctly describe Mott insulators, the DFT+DMFT method is the only method up to now that is able to describe strongly correlated paramagnetic metals. This method is very time-consuming, making the study of radiation damage hardly possible. Only point defects in very small supercells containing few tens of atoms can currently be considered.

Relativistic effects: Spin-orbit coupling

In order to accurately describe the electronic structure of compounds containing heavy elements, relativistic effects must be taken into account. Usually only the Darwin and the mass-velocity relativistic corrections are taken into account, corresponding to the *scalar relativistic approximation*. In the fully relativistic description of the system, the Kohn-Sham Equation should be replaced by its relativistic analogue, the Dirac Equation, in which the spin-orbit coupling is also taken into account. The spin-orbit coupling has a significant influence on the electronic structure of actinide compounds (it accounts in particular for the $5f_{5/2}$ and $5f_{7/2}$ splitting of the actinide $5f$ states) but its effect on the modelling of radiation damage in fuels (formation or migration energies of point defects...) has not been assessed so far due to the increased computational cost.

DFT and Van der Waals interactions

Another limitation of the local and semi-local LDA and GGA approximations of the DFT is that they cannot describe long-range van der Waals interactions (or dispersive interactions). This is a significant flaw for the modelling of nuclear fuels in which rare gas fission products (xenon, krypton) and helium are abundant and tend to aggregate into clusters or bubbles. Such clusters will not be correctly described by these approximations

(energetically and structurally) since the dispersive bonding between rare gas atoms is non-local. The question also arises not only for bonds between rare gas atoms but also for the bonds between a rare gas atom and the host crystal. Improvement of the DFT to describe dispersive bonds is an active field of research. Non-local correlation functionals such as the vdW-DF [58] or the VV09 functionals [59] have been developed recently and have shown success on a wide range of materials. Another way to treat dispersive bonds is by introducing an empirical pair-potential correction to the total energy, as developed in the DFT-D method [60] or the vdW-MLWF method (Maximally Localised Wannier Function) [61] or the DFT-ulg (universal low gradient) approach [62].

Finite temperature effects

DFT is formulated for zero K calculations, i.e., without lattice vibrations. Finite temperature effects can be modelled either by *ab initio* molecular dynamics, in which the forces acting on each atom of the system are calculated from first-principles calculations and the temperature is controlled by a thermostat rescaling the atom velocities, or by the calculation of the phonon spectrum of the material (see Chapter 8). The phonon spectrum can be calculated from the forces that arise due to small displacements of selected atoms from their equilibrium positions in the supercell (frozen phonons in the harmonic approximation) [63] or by the linear response theory (density-functional perturbation theory - DFPT) in which the linear-order variation of the electronic charge density can be calculated using the unperturbed wave-functions [64]. From the phonon spectrum, the vibrational free energy can be obtained, and the link can then be made between first-principles calculations and thermodynamic calculations (using CALPHAD for instance), as already widely done for metallic alloys [65]. Phase diagrams, formation energies of compounds, free energy, heat capacity C_v , thermal expansion, etc. can be predicted and can complete thermodynamic database. For actinide compounds, first-principles thermodynamic calculations, using *ab initio* molecular dynamics or phonon spectra calculations, are only an emerging field due to the difficulties to accurately describe the electronic structure of actinide compounds and to the great computational resources required.

Conclusion and future challenges

DFT-based studies of nuclear fuels have much progressed in the last 15 years, in terms of the complexity of the phenomena which can be treated, and in terms of the approximations which have become available for a more accurate description of the electronic structure of actinide compounds. The importance of DFT calculations in the multiscale modelling scheme of fuel materials is now widely recognised.

It is, however, still a challenge for future studies of radiation damage in nuclear fuels to develop and use first-principles methods beyond the local and semi-local approximations for the exchange-correlation interaction, in particular without a parameterised term to account for the strong correlations. The use of the DFT+DMFT method coupled to the Random Phase Approximation (RPA) [66] is promising to this respect.

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