Basics of the Density Functional Theory (DFT) Approach

To calculate the ground-state electronic energy of an atomic system, one normally starts from the time-independent Schrödinger equation. In addition, the Born-Oppenheimer approximation is frequently used because it neglects the motion of the nuclei and allows calculating the total energy of the electrons in the potential created by the nuclei. Therefore, one could calculate the ground-state (lowest-energy configuration) total electronic energy from

$$H \Psi(r_1, r_2, \ldots r_n) = E \Psi(r_1, r_2, \ldots r_n) \quad , \tag{2}$$

where H is the Hamiltonian containing the kinetic energy and all the interactions of the system (electron-electron correlation and exchange and electron-nuclei interactions), $\Psi(r_1, r_2, \ldots r_n)$ is a many-electron wave function of the n-electron system, and E is the total electron energy of the ground state. The input parameters in Equation (2) are the atomic numbers of the atoms and the geometry of the crystal (the lattice constant, the crystal structure, and the atomic positions).

To determine the equilibrium volume theoretically, one could keep the crystal structure fixed and calculate the ground-state electronic energy for different input volumes (or lattice constants). The volume that produced the lowest energy would represent the theoretical equilibrium volume. Similarly, one could compare the total energy of different structures at different volumes and draw conclusions about structural stability and possible structural phase transitions that might occur when the volume is changed (experimentally, one can compress the volume by applying an external pressure). In addition, one could calculate the energy gain when free atoms condense to a solid (the cohesive energy). Unfortunately, there is no practical way to solve Equation (2) for a solid.

Nevertheless, we have been able to carry out this program of calculations because there is an alternative theoretical formulation for determining the electronic structure. In two important theorems (Hohenberg and Kohn 1964, Kohn and Sham 1965, Dreitzler and Gross 1990), it has been shown that the total energy of a solid (or atom) may be expressed uniquely as a functional of the electron density. We can therefore minimize this functional with respect to the density in order to determine the ground-state energy. Therefore, instead of working with a many-electron wave function, $\Psi(r_1, r_2, \ldots r_n)$, one can express the ground-state energy in terms of the electron density at a single point $n(r)$, where that density is due to all the electrons in the solid:

$$n(r) = \sum_{i=1}^{n} \int \Psi^*(r_1, r_2, \ldots r_n) \, \delta(r - r_i) \, \Psi(r_1, r_2, \ldots r_n) \, dr_1 \, dr_2 \cdots dr_n \quad , \tag{3}$$

In addition, Hohenberg and Kohn (1964), Kohn and Sham (1965), and Dreitzler and Gross (1990) demonstrated that, instead of calculating the electron density from the many-electron wave function $\Psi(r_1, r_2, \ldots r_n)$, one may work with the solutions to an effective one-electron problem.

The trick is to use the form of the total-energy functional to identify an effective potential $V_{\mathrm{eff}}(r)$ for one-electron states and then solve for the one-electron states to produce a density equal to the many-electron density. The equation for the one-electron states is

$$\left(\hat{T} + V_{\mathrm{eff}} \right) \psi_i(r) = e_i \psi_i(r) \quad , \tag{4}$$

where $\hat{T}$ is a kinetic energy operator (for example, $-\hbar^2 \nabla^2 / 2m$ in a nonrelativistic approximation)

and the resulting total electron density is given by

$$n(r) = \sum_i \left| \psi_i(r) \right|^2 \quad . \tag{5}$$

To include relativistic effects important in the actinides, one replaces the nonrelativistic, Schrödinger-like one-electron equation—see Equation (4)—by the relativistic Dirac equation. By finding the correct form for the effective potential, the electron density in Equation (5) will be the same as that in Equation (3).

As mentioned in the section "Density Functional Theory" in the main text, the one-electron problem defined by Equation (4) has the same form as the equations solved by band theorists before DFT was invented, and the eigenvalues of those equations as a function of crystal momentum are precisely the energy bands. The contribution of DFT is to provide a rigorous prescription for determining the effective potential and for calculating the total ground-state energy. The DFT prescription for the effective potential in Equation (4) is

$$V_{\text{eff}}(r) = \frac{\delta}{\delta n(r)} \left[E_H(n(r)) + E_{xc}(n(r)) + E_{eN}(n(r)) \right] \quad , \tag{6}$$

where the different terms are derived from the total-energy functional $E(n(r))$:

$$E(n(r)) = T(n(r)) + E_H(n(r)) + E_{xc}(n(r)) + E_{eN}(n(r)) + E_{NN} \quad . \tag{7}$$

In this equation, $T(n(r))$ represents the kinetic energy of the effective one-electron states and is calculated from

$$T(n(r)) = \sum_i \int \psi_i^\dagger(r)\, \hat{T}\, \psi_i(r)\, dr \quad . \tag{8}$$

$E_H(n(r))$ is the classical Hartree interaction (the electrostatic interaction between two charge clouds):

$$E_H(n(r)) = \frac{1}{2} e^2 \int \frac{n(r_1)\, n(r_2)}{\left| r_1 - r_2 \right|}\, dr_1\, dr_2 \quad . \tag{9}$$

$E_{eN}(n(r))$ is the electron-nuclei interaction:

$$E_{eN}(n(r)) = -e^2 \sum_R Z_R \int \frac{n(r)}{\left| r - R \right|}\, dr \quad . \tag{10}$$

$E_{xc}(n(r))$ is the part of the interaction that goes beyond the classical Hartree term as well as the difference between the true kinetic energy and the one-electron kinetic energy. In the LDA, this term has the form

$$E_{xc}(n(r)) = \int n(r)\, \varepsilon_{xc}(n(r))\, dr \quad . \tag{11}$$

Finally, E_{NN} is the Coulomb interaction between the different atomic nuclei of the lattice:

$$E_{NN} = \frac{1}{2} e^2 \sum_R \sum_{R' \neq R} \frac{Z_R\, Z_{R'}}{\left| R - R' \right|} \quad . \tag{12}$$

From these definitions, it becomes obvious that the effective potential in which the electron moves has contributions from the electron's interaction with the nuclei and the other electrons in the solid both by the classical Hartree term and by the quantum mechanical exchange and correlation term.

Because all electron-electron interactions that go beyond the classical Hartree term are found in $E_{XC}(n(r))$, it is crucial to have a good approximation for this term (unfortunately, there is no exact form of this term for a real solid). However, if one assumes the functional to be local, a numerical form may be obtained from many-body calculations (quantum Monte Carlo or perturbation series expansion), and very good values may be obtained for the ground-state energy for different values of the electron density. If the electron density of a real system varies only smoothly in space, one expects that a form of E_{XC} taken from a uniform electron gas should be applicable to the real system as well. This approximation is no other than the LDA. The good agreement, for many solids,[*] on cohesive energy, equilibrium volume, and structural properties between this approximate theoretical approach and experimental values suggests that the LDA form of E_{XC} works even if the electron density varies rapidly in space. As an example of how E_{XC} might look, we quote the full form of the exchange and correlation energy density in Equation (11), as given by Hedin and Lundqvist, with parameters calculated in the random-phase approximation:

$$\mathcal{E}_{xc}(n(r)) = \mathcal{E}_x(r_s) + \mathcal{E}_c(r_s) \quad ,$$

where

$$r_s = \left(\frac{3}{4\pi n(r)}\right)^{\frac{1}{3}}$$

$$\mathcal{E}_x(r_s) = \frac{-0.91633}{r_s}$$

$$\mathcal{E}_c(r_s) = -0.045 \, G\left(\frac{r_s}{21}\right)$$

$$G(x) = (1+x^3)\ln\left(1+\frac{1}{x}\right) - x^2 + \frac{x}{2} - \frac{1}{3} \quad . \tag{13}$$

Thus, one can calculate the total ground-state energy by solving an effective one-electron equation. This tremendous simplification of replacing interacting electrons with effective one-electron states will work only if one can find the correct, effective one-electron potential. ∎

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[*]Among such solids are simple metals, transition metals, actinides, p electron elements, and thousands of compounds formed between these elements.