# 2. Computational design of metal systems

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## 2.1 Pre DFT Models for Metal

## Jellium Model

Consider more than one electron moving in an array of nuclei, the motion can be

described by 
$$\left[\sum_{i=1}^{N} \left( -\frac{\hbar^2 \nabla_i^2}{2m} + v(\vec{r}_i) \right) + \sum_{i < j} U(\vec{r}_i, \vec{r}_j) \right] \Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = E \Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$$

The electron-electron interactions in the equation constitute an unsolvable quantal many-body problem. The most common method for dealing with it is to first consider nuclei to be frozen in space and invoke the mean-field approximation. One can then determines self-consistently an average potential in which the electrons move as independent particles.

The most dramatic but efficient simplification is to ignore the ionic structure totally, replacing the charge distribution of the ions by a constant background charge in a finite volume. The self-consistent mean field of the electrons can be calculated microscopically in this model including the shell effects due to their quantization. It requires, however, the density of the ions (or the Wigner-Seitz radius r<sub>s</sub>) as an external parameter, which characterizes the nature of the metal. The total neglect of the ionic structure is justified: the pseudopotentials have no singularities and their sum is a rather smooth function. This is the combined effect of screening and the Pauli principle, coming from the inner core electrons that fill the lowest orbitals in the Coulomb-like potentials of the individual nuclei. The undoubted virtue of Jellium model is that it can also be applied to large clusters with many hundreds or thousands of atoms, where the more structural models cannot be used for practical reasons.

### **Effective Medium Model**

To relax the assumption of frozen nuclei, it is able to treat the systems dynamically in the adiabatic limit, allowing one to extract thermodynamic properties of complex molecular systems, at least approximately. The price one pays is that not all electrons can be treated fully quantum mechanically. The finite temperature can also be used as a technical means to allow the system to relax into the lowest minimum of its Born-Oppenheimer energy surface and thus to determine the optimal ground-state geometry of the ions. Although this very time consuming, it is crucial in view of the fact that the number of isomeric minima to which the simpler steepest-descent method can lead increases very rapidly with the number of ions.

Another approximation scheme to include electron-ion correlations dynamically is the so-called "efective medium theory" developed some time ago by Norskov and Lang. The effect of an "embedding" electron density  $\rho_e$  on the binding of an atom is first studied with LDA, leading to an energy functional of the atom that depends on

 $\rho_e$  as an external parameter. Then this functional is used for a metal to include in

each Wigner-Seitz cell the effects of the electronic density tails of all neighboring cells. In this model, the Wigner-Seitz radius and the cohesive energy of a given metal can be explicitly calculated..

#### **Embedded Atom Method (EAM)**

A quantum-mechanical many-body potential especially well suited for metals is the so called embedded atom method (EAM), derived by Daw, Baskes, Finnis and Foiles. The agreement between predictions by simulations using EAM-potentials and experiments makes the EAM a practical method for study of defects, surfaces and impurities in metals.

The construction of EAM is based on the use of density functional theory (DFT), according to which the energy of a collection of atoms can be expressed by a functional of its electronic density. Similarly, the energy change associated with embedding an atom into a host background of atoms is a functional of the electronic density of the host before the new atom is embedded. The total electron density of the host atoms is approximated as a linear superposition of the electron densities of individual host atoms. To zeroth order, the embedding energy can be equated to the energy of embedding an atom in a homogenous electron gas, whose density

 $\rho_h(\vec{r_i}) = \rho_{h,i}$  matches the host density at the position of the embedded atom as

$$\rho_{h,i} = \sum_{j \neq i} \rho_j^A(\vec{r}_{ij})$$
, where  $\rho_j^A$  is the electron density of atom *j* as a function of

interatomic separation. Note, that  $\rho_j^A(\vec{r}_{ij})$  is the contribution to the total electron

density due to atom *j*, but  $\rho_h(\vec{r_i})$  is the electron density at the position of atom *i*, created by all the atoms in the solid but with the "impurity atom" *i* absent.

In EAM, The total energy of an elemental system is, therefore, written as

$$E_{tot} = \sum_{i} F_i\left(\rho_{h,i}\right) + \frac{1}{2} \sum_{i} \sum_{j \neq i} \Phi_{ij}(r_{ij}) ,$$

where  $F_i(\rho_{h,i})$  is the embedding functional, *i.e.*, the energy to embed the atom *i* into the background electron density  $\rho_{h,i}$ , and  $\Phi_{ij}(r_{ij})$  is a pairwise central potential between atoms *i* and *j* separated by a distance  $r_{ij}$ , and represents the repulsive core-core electrostatic interaction, is the so-called embedding energy. It is important to note that the embedding functional  $F_i(\rho_{h,i})$  is a universal functional that does not depend on the source of the background electron density. This implies that the same

functional is employed to compute the energy of an atom in an alloy as that employed for the same atom in a pure elemental metal. For a solid at equilibrium, the force to expand, or contract, due to the embedding function is exactly balanced by the force to contract, or expand due to the pairwise interactions. At a defect, this balance is disrupted, leading to the displacements as atoms move to find a new balance.

#### 2.2 Magic Clusters and Shell Model

Many single-particle effects of a metal cluster do not depend crucially on the microscopic self-consistency of the total mean field. One may therefore give up the self-consistency by simply parametrizing the total average potential in an easy-to-use form and then solving just once the Schrodinger equation, in order to obtain single-particle spectra and wave functions. This leads to a considerable gain in numerical simplicity. The cost of such simplicity is a less fundamental description, since contact with the two-body interaction is lost and the parameters of the model have to be determined by fits to experimental observables.

Such a phenomenological shell model is the Woods-Saxon potential, which was successfully introduced into nuclear physics by Maria Goeppert-Mayer (1949) and independently by Haxel, Jensen, and Suess (1949). Nilsson (1955) introduced a shell model for deformed nuclei, which is based on an axially deformed harmonic-oscillator potential including a spin-orbit coupling term and an attractive term proportional to the square l of the single-particle angular momentum operator that simulates a steeper wall. Nilsson model was very successful in explaining the ground-state deformations of many nuclei and their single-particle excitations. Clemenger (1985a, 1985b) adapted the Nilsson model to small axially deformed Na clusters by dropping the spin-orbit term and readjusting the coefficient of the  $l^2$  term. This model has since been frequently used in metal cluster physics and is usually

referred to as the Clemenger-Nilsson model. The model works quite well in reproducing the overall shapes of clusters as calculated by pseudopotential or *ab initio* methods.

The basic idea of the self-consistent jellium model is to replace the distribution of the ionic cores by a constant positive background or jellium density in a finite volume and to treat only the valence electrons explicitly in the mean-field approximation. In density-functional theory the total energy of the cluster is expressed as a functional of the local electron density  $\rho(\vec{r})$ :

$$E[\rho] = T_s[\rho] + E_{xc}[\rho] + \int d^3r \left[ V_I(\vec{r})\rho(\vec{r}) + \frac{e^2}{2}\rho(\vec{r})\int d^3r \left[ \frac{\rho(\vec{r}\,')}{\left|\vec{r} - \vec{r}\,'\right|} \right] + E_I$$

Here  $V_I(\mathbf{r})$  is the ionic background potential, related to the background jellium charge density  $\rho_I(\vec{r})$  by  $V_I(\vec{r}) = e^2 \int \frac{\rho_I(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r'$ . The jellium density is usually

assumed to be uniform, *i.e.*,  $\rho_I(\vec{r}) = \rho_{I0}$  inside the cluster and zero outside.