Surface and nanomaterials science

Presentation Summary on Density Functional Theory

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Density functional theory or DFT is a computational modeling method based in quantum mechanics and used for electronic structure calculation of many-bodies systems as atoms, molecules and especially solids. This method results from the work of P. Hohenberg, W. Kohn and L. J. Sham[1,2] and it is based to the solutions of a Schrödinger equation which depends on the electron density rather than on each individual electron orbital.

By using an effective independent-particle Hamiltonian we arrive to the following Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} + \int \mathrm{d}^3 r'\, n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|} + V_{\mathrm{xc}}[n](\mathbf{r})\right]\psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}).$$

The three first terms of the Hamiltonian are respectively the kinetic energy, the electrostatic electron-nuclei interactions and the electrostatic energy of the electron on a field generated by the total electron density (*n(r)*). As for the last (and the most important) term, it is an exchange-correlation potential containing the many-body effects and it can be formed to depend to the electron density. This is the main result of DFT but unfortunately the XC potential can only be approximated as the exact form is unknown.

For the electron density we have $n(\mathbf{r}) = \sum_{k=1}^{N} |\psi_k(\mathbf{r})|^2,$ which verifies

the self-consistency of the solutions.

The DFT method works like a “loop-machine” in which you put an initial *n* and, by constructing and solving the Schrödinger equation, it gives a new electron density that goes through the machine again.

Although the DFT is not as accurate as the quantum mechanics theory is quite faster and simpler due to the approximations it contains, but also the pseudopotentials we can use in order to construct a simpler Hamiltonian. Thus, in the case of many-bodies and far complicated systems is a powerful tool for electronic structure calculations.

References:

[1]P. Hohenberg and W. Kohn, ‘Inhomogeneous electron gas,’ *Phys. Rev.*, **136** (1964), B864–71.
[2]W. Kohn and L. J. Sham, ‘Self-consistent equations including exchange and correlation effects,’ *Phys. Rev.*, **140** (1965), A1133.
[3] Computational Physics, Second Edition, J. M. Thijssen

[4] Wikipedia/Density Functional Theory