The Kohn-Sham Method: Basic Principles

Density-Functional Theory of Atoms and Molecules
– Robert G. Parr and Weitao Yang

Chapter 7

Electron density

In an electronic system, the number of electrons per unit volume in a given state is the *electron density* for that state. This quantity will be of great importance in this book; we designate it by $\rho(\mathbf{r})$. Its formula in terms of Ψ is

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \, ds_1 \, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

This is a nonnegative simple function of three variables, x, y, and z, integrating to the total number of electrons,

$$\int \rho(\mathbf{r}) \, d\mathbf{r} = N$$

The Thomas-Fermi model

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r}, \qquad C_F = \tfrac{3}{10}(3\pi^2)^{2/3} = 2.871$$

$$E_{\mathrm{TF}}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{\mathbf{r}}\, d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

The Hohenberg-Kohn theorems

The ground state energy of a many-electron system can be obtained as the minimum of the functional

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + F[\rho]$$

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$

$$\int \rho(\mathbf{r})\, d\mathbf{r} = N$$

Inhomogeneous Electron Gas*

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This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \lll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Kohn-Sham method

Kohn and Sham proposed introducing orbitals into the problem in such a way that the kinetic energy can be computed simply to good accuracy, leaving a small residual correction that is handled separately. To understand what is involved and what Kohn and Sham did, it is convenient to begin with the exact formula for the ground-state kinetic energy,

$$T = \sum_i^N n_i \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle \qquad (7.1.5)$$

where the ψ_i and n_i are, respectively, natural spin orbitals and their occupation numbers.

$$\rho(\mathbf{r}) = \sum_i^N n_i \sum_s |\psi_i(\mathbf{r}, s)|^2$$

Kohn-Sham method

For any *interacting* system of interest, there are an infinite number of terms in (7.1.5) or (7.1.6), which is ponderous at best. Kohn and Sham (1965) showed that one can build a theory using simpler formulas, namely

$$T_s[\rho] = \sum_i^N \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle \qquad (7.1.7)$$

and

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2 \qquad (7.1.8)$$

Kohn-Sham method

In analogy with the Hohenberg–Kohn definition of the universal functional $F_{HK}[\rho]$ (see §3.2 and §3.3), Kohn and Sham invoked a corresponding *noninteracting reference system*, with the Hamiltonian

$$\hat{H}_s = \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_i^N v_s(\mathbf{r}) \qquad (7.1.9)$$

in which there are no electron–electron repulsion terms, and for which *the ground-state electron density is exactly ρ*. For this system there will be an exact determinantal ground-state wave function

$$\Psi_s = \frac{1}{\sqrt{N!}} \det\left[\psi_1 \psi_2 \cdots \psi_N\right] \qquad (7.1.10)$$

Kohn-Sham method

$$\hat{h}_s \psi_i = \left[-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \psi_i = \varepsilon_i \psi_i$$

$$T_s[\rho] = \langle \Psi_s | \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2 \right) |\Psi_s\rangle = \sum_{i=1}^N \langle \psi_i | -\tfrac{1}{2}\nabla^2 |\psi_i\rangle$$

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

Kohn-Sham method

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \qquad (7.1.14)$$

The defined quantity $E_{xc}[\rho]$ is called the *exchange-correlation energy*; it contains the difference between T and T_s, presumably fairly small (see §7.3 below), and the nonclassical part of $V_{ee}[\rho]$.

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

$$= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})$$

Kohn-Sham method

The Kohn–Sham treatment runs as follows. Equation (7.1.15) with the constraint (7.1.4) is precisely the same equation as one obtains from conventional density-functional theory when one applies it to a system of *noninteracting* electrons moving in the external potential $v_s(\mathbf{r}) = v_{\text{eff}}(\mathbf{r})$. Therefore, for a given $v_{\text{eff}}(\mathbf{r})$, one obtains the $\rho(\mathbf{r})$ that satisfies (7.1.15) simply by solving the N one-electron equations

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})]\psi_i = \varepsilon_i\psi_i \qquad (7.1.18)$$

and setting

$$\rho(\mathbf{r}) = \sum_{i}^{N} \sum_{s} |\psi_i(\mathbf{r}, s)|^2 \qquad (7.1.19)$$

Derivation of the Kohn-Sham equations

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}$$

$$= \sum_i^N \sum_s \int \psi_i^*(\mathbf{r})\left(-\tfrac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})\, d\mathbf{r} + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}$$
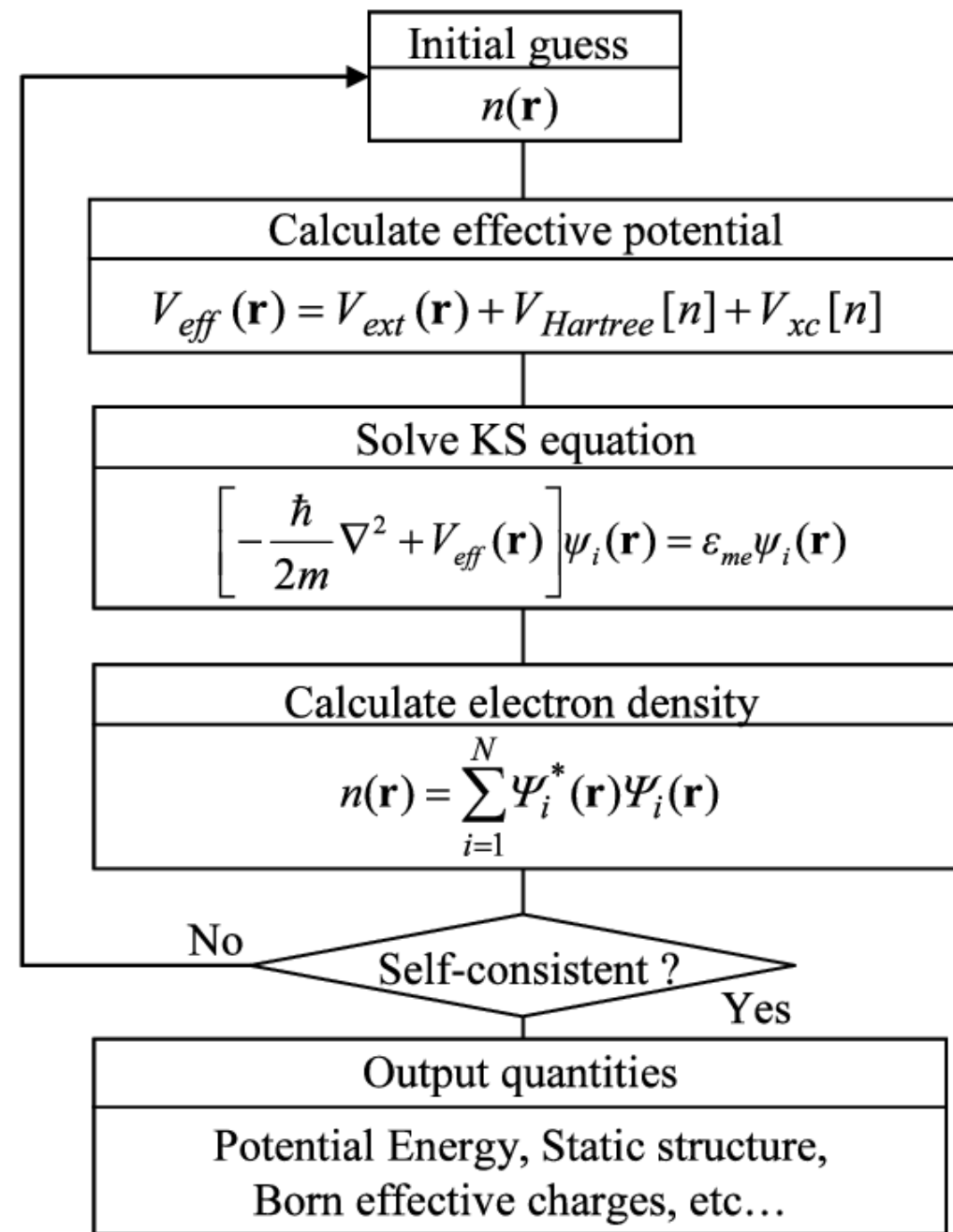
Derivation of the Kohn-Sham equations

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}\right]\psi_i = \varepsilon_i \psi_i$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2$$

Kohn-Sham method

Kohn-Sham method

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}$$

$$\sum_i^N \varepsilon_i = \sum_i^N \langle \psi_i | -\tfrac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) | \psi_i \rangle$$

$$= T_s[\rho] + \int v_{\text{eff}}(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}$$

Self-Consistent Equations Including Exchange and Correlation Effects*

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From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

More on the kinetic-energy functional

Table 7.1 $T[\rho] - T_s[\rho]$ for Some Atoms[a]

Atom	$T[\rho] - T_s[\rho]$ (eV)
H^-	0.8
He	1.0
Li^+	1.1
Be^{2+}	1.1
Li	1.7
Be	2.0

[a] Values from Almbladh and Pedroza (1984).

Local density approximation

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho)\,d\mathbf{r}$$

$$v_{xc}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{LDA}}}{\delta\rho(\mathbf{r})} = \varepsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r})\frac{\delta\varepsilon_{xc}(\rho)}{\delta\rho}$$

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}' + v_{xc}^{\text{LDA}}(\mathbf{r}) \right]\psi_i = \varepsilon_i\psi_i.$$

Local density approximation

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$$\varepsilon_x(\rho) = -C_x\rho(\mathbf{r})^{1/3}, \qquad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

$$\varepsilon_c(r_s) = \frac{A}{2}\left\{\ln\frac{x}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b}\right.$$
$$\left. - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\right\} \quad \text{(E.27)}$$

where $x = r_s^{1/2}$, $X(x) = x^2 + bx + c$, and $Q = (4c - b^2)^{1/2}$. For $\varepsilon_c^0(r_s)$, $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$, and $c = 42.7198$; for $\varepsilon_c^1(r_s)$, $A = \frac{1}{2}(0.0621814)$, $x_0 = -0.743294$, $b = 20.1231$, and $c = 101.578$. These formulas are generally accepted as the most accurate available for the uniform-gas correlation energy per particle.

Xα approximation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{x\alpha}(\mathbf{r}) \right]\psi_i = \varepsilon_i\psi_i$$

$$v_{x\alpha}(\mathbf{r}) = -\frac{3}{2}\alpha\left\{\frac{3}{\pi}\rho(\mathbf{r})\right\}^{1/3}$$

$$\alpha = 2/3$$

Atom (Z)	α
H (1)	0.978
He (2)	0.773
Li (3)	0.781
Be (4)	0.768
B (5)	0.765
C (6)	0.759
N (7)	0.752