Density Functional Theory

Modulo: Funzionale Densità

Chimica Computazionale
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Density functional theory (DFT) has revolutionized the quantun chemistry development of the last 20 years

DFT allows to get information about the energy, the structure and the molecular properties of molecules at lower costs that traditions approaches based on the wavefunction use.

DFT Publications

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Quantum Methods
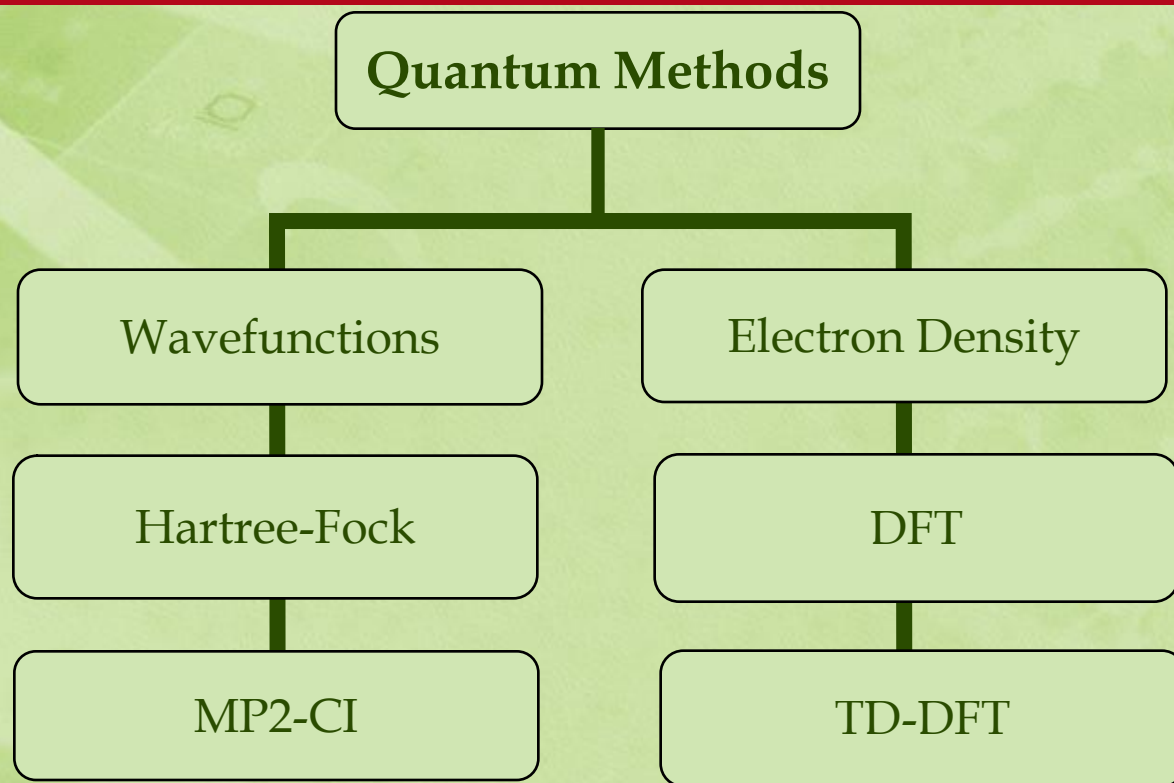
Wavefunctions

Electron Density

Hartree-Fock

DFT

MP2-CI

TD-DFT

The HF equations have to be solved iteratively because V_{HF} depends upon solutions (the orbitals). In practice, one adopts the LCAO scheme, where the orbitals are expressed in terms of N basis functions, thus obtaining matricial equations depending upon N^4 bielectron integrals.
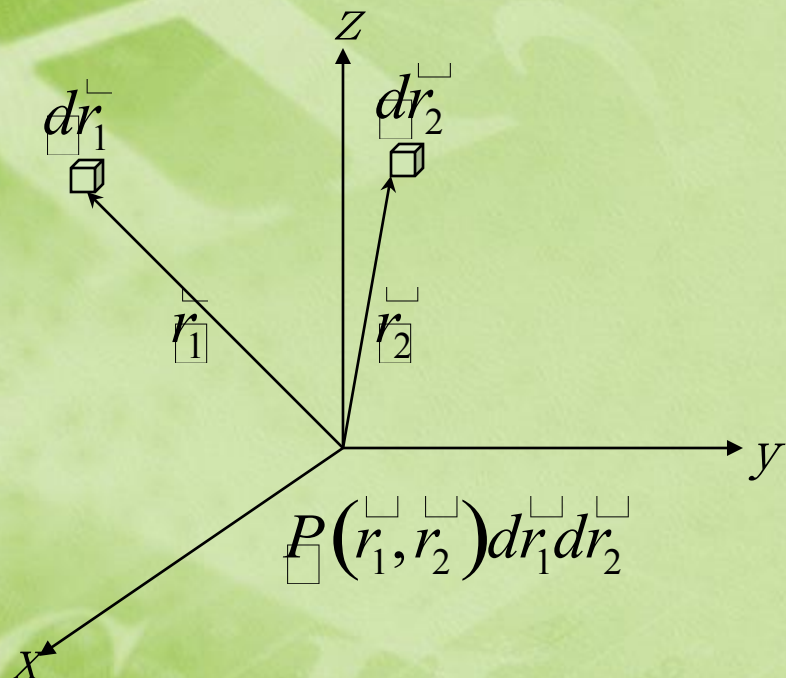
Correlation energy

Exchange correlation: *Electrons with the same spin (m_s) do not move independently as a consequence of the Pauli exclusion principle. $\Psi = 0$ if two electrons with the same spin occupy the same point in space, independently of their charge. HF theory treats exactly the exchange correlation generating a non local exchange correlation potential.*

Coulomb correlation: *Electrons cannot move independently as a consequence of their Coulomb repulsion even though they are characterized by different spin (m_s). HF theory completely neglects the Coulomb correlation thus generating, in principle, significant mistakes. Post HF treatments are often necessary.*

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \left| \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) \right\rangle$$

$$\chi_1(\mathbf{x}_1) = \psi_1(\vec{r}_1)\alpha(\omega_1)$$
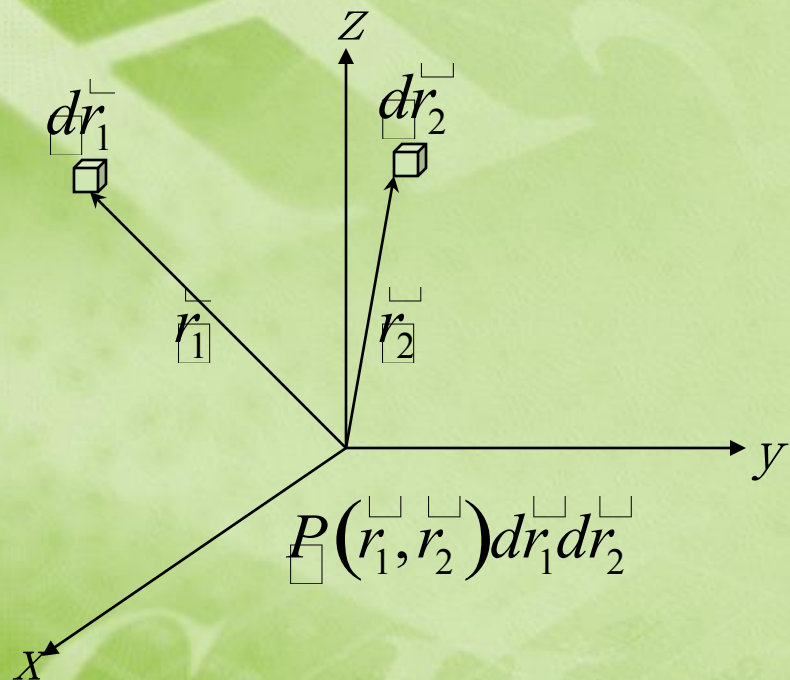
$$\chi_2(\mathbf{x}_2) = \psi_2(\vec{r}_2)\beta(\omega_2)$$

$$d\vec{r}_1 \qquad d\vec{r}_2$$

$$\vec{r}_1 \qquad \vec{r}_2$$

$$P(\vec{r}_1, \vec{r}_2)d\vec{r}_1 d\vec{r}_2$$

$$\Psi\left(\mathbf{x}_1, \mathbf{x}_2\right) = \left|\chi_1\left(\mathbf{x}_1\right)\chi_2\left(\mathbf{x}_2\right)\right\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_1\left(\mathbf{x}_1\right) & \chi_1\left(\mathbf{x}_2\right) \\ \chi_2\left(\mathbf{x}_1\right) & \chi_2\left(\mathbf{x}_2\right) \end{vmatrix}$$

$$\left|\Psi\right|^2 d\mathbf{x}_1 d\mathbf{x}_2 = \frac{1}{2}\left\{ \begin{array}{l} \psi_1\left(\mathbf{r}_1\right)\alpha\left(\omega_1\right)\psi_2\left(\mathbf{r}_2\right)\beta\left(\omega_2\right)- \\ \psi_1\left(\mathbf{r}_2\right)\alpha\left(\omega_2\right)\psi_2\left(\mathbf{r}_1\right)\beta\left(\omega_1\right) \end{array} \right\}^2 d\mathbf{x}_1 d\mathbf{x}_2$$

If the electrons have not the same spin

$$P\left(\vec{r}_1, \vec{r}_2\right)d\vec{r}_1 d\vec{r}_2 = \int d\omega_1 d\omega_2 \left|\Psi\right|^2 =$$

$$\frac{1}{2}\left[\left|\psi_1\left(\vec{r}_1\right)\right|^2 \left|\psi_2\left(\vec{r}_2\right)\right|^2 + \left|\psi_1\left(\vec{r}_2\right)\right|^2 \left|\psi_2\left(\vec{r}_1\right)\right|^2\right]d\vec{r}_1 d\vec{r}_2$$

$$\text{if} \qquad \psi_1 = \psi_2$$

$$P\left(\vec{r}_1, \vec{r}_2\right) = \left|\psi_1\left(\vec{r}_1\right)\right|^2 \left|\psi_1\left(\vec{r}_2\right)\right|^2 \qquad P\left(\vec{r}_1, \vec{r}_1\right) = \left|\psi_1\left(\vec{r}_1\right)\right|^2 \left|\psi_1\left(\vec{r}_1\right)\right|^2 \neq 0$$
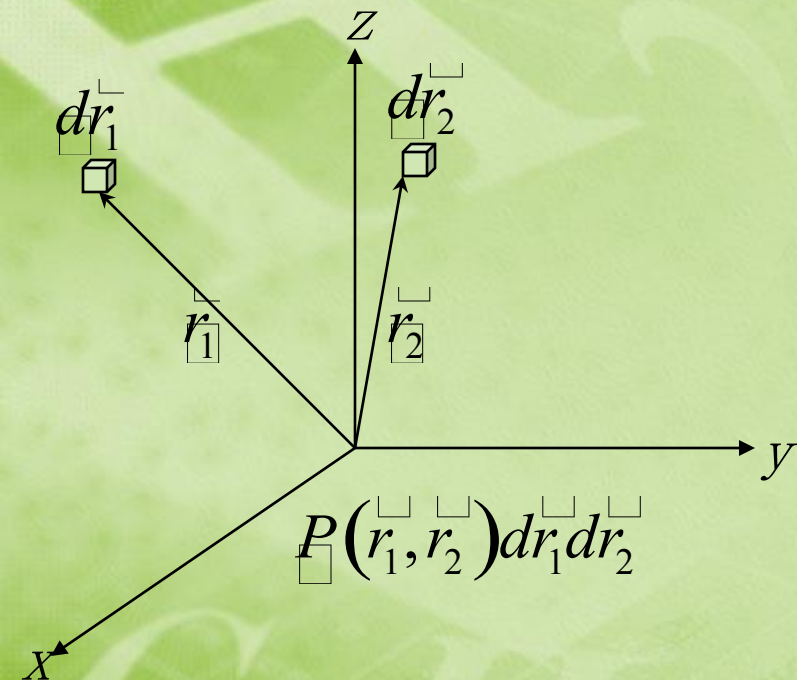
If the electrons have the same spin

$$P\!\left(\vec{r_1},\vec{r_2}\right)dr_1 dr_2$$

$$\chi_1(\mathbf{x_1}) = \psi_1(\mathbf{r}_1)\beta(\omega_1)$$

$$\chi_2(\mathbf{x_2}) = \psi_2(\mathbf{r}_2)\beta(\omega_2)$$

$$P(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{2} \left\{ \begin{array}{l} \left|\psi_1(\mathbf{r}_1)\right|^2 \left|\psi_2(\mathbf{r}_2)\right|^2 + \left|\psi_1(\mathbf{r}_2)\right|^2 \left|\psi_2(\mathbf{r}_2)\right|^2 - \\ \left[\begin{array}{l} \psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2) + \\ \psi_1(\mathbf{r}_1)\psi_2^*(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2) \end{array} \right] \end{array} \right\}$$

$$P(\mathbf{r}_1, \mathbf{r}_1) = 0$$

Information provided by Ψ is redundant

benzene

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$N = 42e^-$

Number of terms in the determinantal form Ψ : N! = 1.4×10^{51}

Number of Cartesian dimensions: 3N = 126

Ψ is a very complex object including more information than we need!

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The use of electron density allows to limit the redundant information

The electron density is a function of three coordinates no matter of the electron number.

Timetable

- *1920s:* **Introduction of the Thomas-Fermi model.**
- *1964:* *Hohenberg-Kohn paper proving existence of exact DF.*
- *1965:* *Kohn-Sham scheme introduced.*
- *1970s and early 80s: LDA. DFT becomes useful.*
- *1985:* *Incorporation of DFT into molecular dynamics (Car-Parrinello) (Now one of PRL's top 10 cited papers).*
- *1988:* *Becke and LYP functionals. DFT useful for some chemistry.*
- *1998:* *Nobel prize awarded to Walter Kohn in chemistry for development of DFT.*

Quotation: "If I have seen further [than certain other men] it is by standing upon the shoulders of giants."*

Isaac Newton (1642–1727), British physicist, mathematician. Letter to Robert Hooke, February 5, 1675.

*With reference to his dependency on Galileo's and Kepler's work in physics and astronomy.

(a) Thomas, L. H. *Proc. Cambridge Philos. Soc.* **1927**, *23*, 542;
(b) Fermi, E. *Z. Phys.* **1928**, *48*, 73;
(c) Dirac, P. A. M. *Cambridge Philos. Soc.* **1930**, *26*, 376;
(d) Wigner, E. P. *Phys. Rev.* **1934**, *46*, 1002.

Thomas, L. H.
1903-1992

Fermi, E.
1901-1954

Dirac, P.M.A.
1902-1984

Wigner, E.
1902-1995

(a)   Hartree, D. R. *Proc. Cambridge Phil. Soc.* **1928**, *24*, 89;
(b)   ibidem **1928**, *24*, 111;
(c)   ibidem **1928**, *24*, 426;
(d)   Fock, V. Z. *Physic* **1930**, *61*, 126;
(e)   Slater, J. C. *Phys. Rev.* **1930**, *35*, 210.

Hartree, D.R.
1897-1958

Fock, D.R.
1898-1974

Slater J. C.
1900 -1976

Definitions

Function: *a prescription which maps one or more numbers to another number:*

$$y = f(x) = x^2$$

Definitions

Operator: a prescription which maps a function onto another function:

$$\hat{F} = \frac{\partial^2}{\partial x^2}$$

$$\hat{F}f(x) = \frac{\partial^2 f(x)}{\partial x^2}$$

Definitions

Functional: A functional takes a function as input and gives a number as output. An example is:

$$F\big[\,f(x)\,\big] = y$$

Here $f(x)$ is a function and y is a number. An example is the functional to integrate x from $-\infty$ to ∞.

$$F[f] = \int_{-\infty}^{\infty} f(x)\,dx$$

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Vito Volterra
1860 - 1940

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In base a un regio decreto emanato il 28 agosto 1931 i docenti delle università italiane avrebbero dovuto giurare di essere fedeli non solo allo statuto albertino e alla monarchia, ma anche al regime fascista.

Francesco ed Edoardo Ruffini e Fabio Luzzatto (giuristi);
Giorgio Levi Della Vida (orientalista);
Gaetano De Sanctis (storico dell'antichità);
Ernesto Buonaiuti (teologo);
Vito Volterra (matematico);
Bartolo Nigrisoli (chirurgo);
Marco Carrara (antropologo);
Lionello Venturi (storico dell'arte);
Giorgio Errera (chimico);
Piero Martinetti (studioso di filosofia).

Nel 1938, con la promulgazione delle Leggi razziali, perdettero il posto i professori considerati di origine ebraica in base alla normativa razziale

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ab-initio methods can be interpreted as a functional of the wavefunction, with the functional form completely known!

$$E[\Psi] = \frac{\int \Psi^*(x_1,\ldots,x_N)\hat{H}\Psi(x_1,\ldots,x_N)dx_1\ldots dx_N}{\int \Psi^*(x_1,\ldots,x_N)\Psi(x_1,\ldots,x_N)dx_1\ldots dx_N}$$

Thomas–Fermi-Dirac Model

Electrons are uniformly distributed over the phase space in cells of $(2\pi h)^3$

Each cell may contain up to two electrons with opposite spins

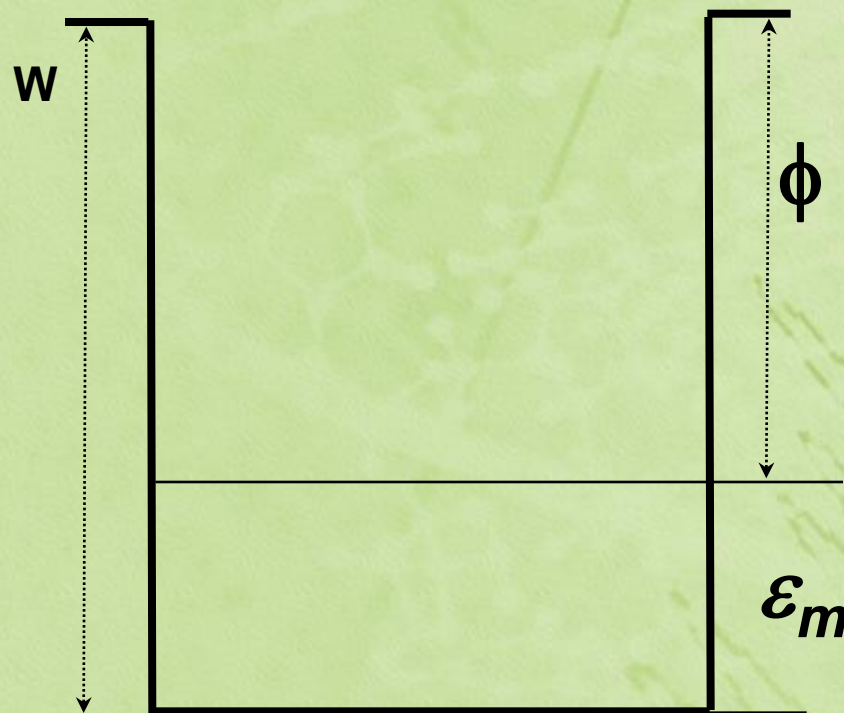Electrons experience a potential field generated by the nuclear charge and by the electron distribution itself.

Let us consider a free electron gas

Let us consider a free electron gas

$$\frac{\mathcal{N}_A}{V} = 6.023 \times 10^{23} \frac{atoms}{mol} \times \frac{8.92 \frac{g}{cm^3}}{63.5 \frac{g}{mol}} = 8.47 \times 10^{22} \frac{electrons}{cm^3}$$

$$\frac{\mathcal{N}_A}{V} = 6.023 \times 10^{23} \frac{atoms}{mol} \times \frac{Z\rho}{at.weight}$$

$$P = \frac{82.06 \left(\frac{cm^3 atm}{mol K}\right) 293K}{7.11 \left(\frac{cm^3}{mol}\right)} = 3381 atm \qquad 7.11 \left(\frac{cm^3}{mol}\right) = \frac{6.023 \times 10^{23} \frac{atoms}{mol}}{8.47 \times 10^{22} \frac{electrons}{cm^3}}$$

$$\frac{V}{\mathcal{N}} = \frac{4\pi}{3} r_s^3 \qquad\qquad r_s = \left(\frac{3V}{4\pi\mathcal{N}} \right)^{\frac{1}{3}}$$

$$r_s = 1.72 \text{ Å (Li)}, \ 2.08 \text{ Å (Na)}, \ 1.12 \text{ Å (Fe)}$$

$$\text{Na}^+ \ radius = 0.95 \text{ Å} \qquad\qquad \left(\frac{r_s}{0.95} \right)^3 > 10$$

$$\varepsilon_m = \frac{mv_m^2}{2} = \frac{3}{2} k_B T$$

$$v_m = 10^7 \ cm/s$$

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$\square \; m$

Let see what happens when QM is applied

Main Assumption:

independent electron approximation

*V(**r**) = constant*

$$\hat{H}\psi = \left[-\frac{\Box^2}{2m}\nabla^2 + V(\overset{\Box}{r}) \right]\psi = E\psi \qquad -\frac{\Box^2}{\Box 2m}\nabla^2\psi = E\psi$$

$$\frac{\Box^2}{\underset{\Box}{2m}}k^2\psi = E\psi \qquad \underset{\Box}{E} = \frac{\Box^2}{2m}k^2 \qquad \underset{\Box}{\psi} = Ae^{ik\cdot r}$$

$$\psi = Ae^{ik\cdot r}$$

$$\hat{p}\psi \equiv -i\hbar\frac{\partial}{\partial r}\psi = -i\hbar\frac{\partial}{\partial r}\left(Ae^{ik\cdot r}\right) = \hbar k\psi$$

De Broglie relation states that

$$p = \frac{h}{\lambda}$$

$$k = \left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

Two kinds of boundary conditions

$$\psi(0) = \psi(L) = 0$$

$$\psi_n = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2$$

$$\psi(x) = \psi(x + L)$$

$$\psi(x) = Ae^{ik_x x} \qquad \psi(x + L) = Ae^{ik_x x} e^{ik_x L} \qquad e^{ik_x L} = 1$$

$$k_x L = 2\pi \bar{m}$$

$$\psi_{\bar{m}}(x) = L^{-\frac{1}{2}} e^{i\frac{2\pi\bar{m}x}{L}}$$

$$E_{\bar{m}} = \frac{\Box^2}{2m} k^2 = \frac{\Box^2}{2m}\left(\frac{2\pi\bar{m}}{L}\right)^2$$

$$\bar{m} = 0, \pm 1, \pm 2, \Box$$

Moving to three dimensions

$$\psi_{\bar{m}}(x,y,z) = L^{-\frac{3}{2}} e^{i\left(\frac{2\pi}{L}\right)\left(\bar{m}_x x + \bar{m}_y y + \bar{m}_z z\right)}$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \left(\bar{m}_x^2 + \bar{m}_y^2 + \bar{m}_z^2\right)$$

$$\bar{m}_x, \bar{m}_y, \bar{m}_z = 0, \pm 1, \pm 2, \dots$$

$$\vec{k} = \frac{2\pi}{L}\vec{m}$$

$$\vec{k} = \frac{2\pi}{L}\vec{m}$$

$$\psi_{\bar{m}}(x,y,z) = L^{-\frac{3}{2}}e^{i\left(\frac{2\pi}{L}\right)\left(\bar{m}_x x + \bar{m}_y y + \bar{m}_z z\right)}$$

$$\psi_{\vec{k}} = V^{-\frac{1}{2}}e^{i\vec{k}\cdot\vec{r}}$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(\bar{m}_x^2 + \bar{m}_y^2 + \bar{m}_z^2\right)$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

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Degeneracies of free electron levels

Typical possibilities				Orbital degeneracy	Total degeneray
$\overline{m}_x$	$\overline{m}_y$	$\overline{m}_z$	$\overline{m}^2$		
0	0	0	0	1	2
±1	0	0	1	6	12
±1	±1	0	2	12	24
±1	±1	±1	3	8	16
±2	0	0	4	6	12

For large m values the degeneracies go up as $\left(\overline{m}^2\right)^{\frac{1}{2}}$

$$\bar{m}_F = \left| \bar{m}_{\max} \right|$$

Energy, temperature and velocity of electrons with m_F

$$\hat{p}\psi \equiv -i\hbar \frac{\partial}{\partial r} \psi = -i\hbar \frac{\partial}{\partial r} \left(A e^{ik \cdot r} \right) = \hbar k \psi$$

$$N = 2\left(\frac{4\pi}{3} \right) \bar{m}_F^3 = 2\left(\frac{4\pi}{3} \right) \frac{V}{(2\pi)^3} k_F^3 \qquad\qquad k = \frac{2\pi}{L} \bar{m}$$

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 \bar{m}_F^2 = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}$$

If we assume that the number of electrons per unit volume is ρ_0, then the Fermi momentum p_F of a uniform free electron gas is:

$$E_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

$$p_F = \hbar\left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$\rho_0 = \frac{N}{V} = \frac{p_F^3}{3\pi^2 \hbar^3}$$

Thomas and Fermi applied such a relation to an inhomogeneous situation as that of atoms, molecules and solids. If the inhomogeneous electron density is denoted by $\rho(\vec{r})$, when the equation defining ρ_0 is applied locally at $\vec{r}$, it yields

$$\rho(\vec{r}) = \frac{p_F^3(\vec{r})}{3\pi^2 \hbar^3}$$

Let us define the density of states $g(\varepsilon)$, i.e. the number of states between ε and $\varepsilon + d\varepsilon$

The number of states with energy up to ε is

$$2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\Box^2}\right)^{\frac{3}{2}} \qquad E_F = \frac{\mathsf{h}^2}{2m}k_F^2$$

$$\int_0^\varepsilon g(\varepsilon)d\varepsilon = 2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\Box^2}\right)^{\frac{3}{2}}$$

$$\int_{0}^{\varepsilon} g(\varepsilon)d\varepsilon = 2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\square^2}\right)^{\frac{3}{2}}$$

$$g(\varepsilon) = \frac{3}{2}\left(\frac{V}{3\pi^2}\right)\left(\frac{2m}{\square^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}} = \sqrt{2}\left(\frac{V}{\pi^2}\right)\left(\frac{m}{\square^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}} = C\varepsilon^{\frac{1}{2}}$$

$$T_0 = \text{total kinetic energy}$$

$$T_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon = C \int_0^{\varepsilon_F} \varepsilon^{\frac{3}{2}} d\varepsilon = \frac{2}{5} C \varepsilon_F^{\frac{5}{2}}$$

$$p_F = \hbar \left(\frac{3\pi^2 N}{V} \right)^{\frac{1}{3}}$$

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}$$

$$\left(\varepsilon_F \right)^{\frac{3}{2}} = \left(\frac{\hbar^2}{2m} \right)^{\frac{3}{2}} \left(\frac{3\pi^2 N}{V} \right)$$

$$T_0 = \frac{2}{5} C \varepsilon_F^{\frac{5}{2}} = \frac{2}{5} \underbrace{\sqrt{2} \left(\frac{V}{\pi^2} \right) \left(\frac{m}{\hbar^2} \right)^{\frac{3}{2}}}_{C} \left(\frac{\hbar^2}{2m} \right)^{\frac{3}{2}} \left(\frac{3\pi^2 N}{V} \right) \varepsilon_F = \frac{3}{5} N \varepsilon_F$$

$$T_0 = \frac{3}{5} N \varepsilon_F \qquad\qquad T_0 = \frac{2}{5} C \varepsilon_F^{\frac{5}{2}}$$

$$T_0[\rho_0] = \frac{2}{5}\sqrt{2}\underbrace{\left(\frac{V}{\pi^2}\right)\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}}}_{C}\underbrace{\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{\frac{2}{3}}\rho_0^{\frac{2}{3}}\right)^{\frac{5}{2}}}_{\varepsilon_F}$$

$$T_0[\rho_0] = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} V \rho_0^{\frac{5}{3}} \qquad\qquad T[\rho(\vec{r})] = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} V \rho(\vec{r})^{\frac{5}{3}}$$

One can next write the classical energy equation for the fastest electrons as

$$\mu = \frac{p_F^2(\vec{r})}{2m} + V(\vec{r})$$

$$\rho(\vec{r}) = \frac{p_F^3(\vec{r})}{3\pi^2 \hbar^3} \qquad\qquad \hbar\left(3\pi^2\right)^{\frac{1}{3}}\left\{\rho(\vec{r})\right\}^{\frac{1}{3}} = p_F(\vec{r})$$

$$\mu = \left(\frac{\hbar^2}{2m}\right)\left(3\pi^2\right)^{\frac{2}{3}}\left\{\rho(\vec{r})\right\}^{\frac{2}{3}} + V(\vec{r})$$

The basic equation of the TF theory. It is a classical expression, and consequently it can be applied only in those cases for which $\mu - V > 0$

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$$T\left[\rho(\vec{r})\right] = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \int^3 \rho(\vec{r})^{\frac{5}{3}}$$

$$T_{TF}\left[\rho(\vec{r})\right] = C_{TF}\int \rho^{\frac{5}{3}}(\vec{r})d\vec{r}$$

$$E_{TF}\left[\rho(\vec{r})\right] = C_{TF}\int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} - Z\int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|r_1 - r_2|}d\vec{r}_1 d\vec{r}_2$$

A results of the free electron gas theory is that the mean kinetic energy per particle is 3/5 of the Fermi energy. The total kinetic energy T_0 of a free electron gas constituted by N particles is then:

$$T_0 = \frac{3}{5}\left(\frac{p_F^2}{2m}\right)N$$

and hence, t_0 (the kinetic energy per unit volume) is

$$t_0 = \frac{T_0}{V} = \frac{3}{5}\left(\frac{p_f^2}{2m}\right)\rho_0 = C_k \rho_0^{5/3}, \qquad C_k = \frac{3\hbar^2}{10m}\left(3\pi^2\right)^{2/3}$$

$$t = C_k \left\{ \rho(r) \right\}^{5/3}$$

$$E = C_k \int \left\{ \rho(r) \right\}^{5/3} dr + \int \rho(r) V_M(r) dr + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} dr dr'$$

The physical meaning of the last equation is that the electronic properties of a system are determined as functionals of the electronic density by applying, locally, relations appropriate to a homogeneous free electron gas. This approximation, known as local density approximation (LDA), is probably one of the most important concept of the modern DFT!

$$N = N\left[\rho(\vec{r})\right] = \int \rho(\vec{r})d\vec{r}$$

$$\delta\left\{E_{TF}\left[\rho\right] - \mu_{TF}\left(\int \rho(\vec{r})d\vec{r} - N\right)\right\} = 0$$

$$\mu_{TF} = \frac{\delta E_{TF}\left[\rho\right]}{\delta\rho(\vec{r})} = \frac{5}{3}C_F\rho^{\frac{2}{3}}(\vec{r}) - \Phi(\vec{r})$$

$$\Phi(\vec{r}) = \frac{Z}{r} - \int \frac{\rho(\vec{r}_2)}{\left|\vec{r} - \vec{r}_2\right|}d\vec{r}_2$$

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$$\hat{v}_X^{HF} \approx v_{X\alpha}\left(\left[\rho(\mathbf{r})\right];\mathbf{r}\right) = -\frac{3}{2}\alpha\left[\frac{3}{\pi}\rho(\mathbf{r})\right]^{\frac{1}{3}}$$

A *non local* operator is characterized by the gener

$$\left\langle r' \left| \hat{A} \right| \Psi \right\rangle = \int dr \hat{A}\left(r',r\right)\Psi\left(r\right) = \Psi'\left(r'\right) \qquad \hat{A}\left(r',r\right) = \left\langle r' \left| \hat{A} \right| r \right\rangle$$

$$\left\langle r' \left| \hat{A} \right| r \right\rangle = \hat{A}\left(r\right)\delta\left(r' - r\right)$$

The Kohn–Sham method

$$T = \sum_{i=1}^{N} q_i \left\langle \psi_i \right| - \tfrac{1}{2} \nabla^2 \left| \psi_i \right\rangle$$

$$\rho(r) = \sum_{i=1}^{N} q_i \sum_s \left| \psi_i(r,s) \right|^2$$

$$T_s = \sum_{i=1}^{N} \left\langle \psi_i \right| - \tfrac{1}{2} \nabla^2 \left| \psi_i \right\rangle$$

$$\rho(r) = \sum_{i=1}^{N} \sum_s \left| \psi_i(r,s) \right|^2$$

In ogni punto si associa alla densita alla densita $\rho(r)$ l'energia XC che avrebbe un gas elettronico uniforme con la stessa densità. Ciò è ripetuto per ogni punto e i valori usati nelle formule

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The seven majar kings of science

Theodor von Kàrmàn

George de Hevesy

Michael Polanyi

Leo Szilard

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Eugene Wigner

John von Neumann

Edward Teller

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P. Hohenberg

W. Kohn

$$E_{HF} = \left\langle \Psi_{HF} \left| \hat{H} \right| \Psi_{HF} \right\rangle = \sum_{i=1}^{N} H_i + \tfrac{1}{2} \sum_{i,j=1}^{N} \left(J_{ij} - K_{ij} \right)$$

$$H_i = \int \psi_i^* \left(\mathbf{x} \right) \left[-\tfrac{1}{2} \nabla^2 + v\left(\mathbf{x} \right) \right] \psi_i \left(\mathbf{x} \right) d\mathbf{x}$$

$$J_{ij} = \iint \psi_i \left(\mathbf{x}_1 \right) \psi_i^* \left(\mathbf{x}_1 \right) \frac{1}{r_{12}} \psi_j^* \left(\mathbf{x}_2 \right) \psi_j \left(\mathbf{x}_2 \right) d\mathbf{x}_1 d\mathbf{x}_2$$

$$K_{ij} = \iint \psi_i^* \left(\mathbf{x}_1 \right) \psi_j \left(\mathbf{x}_1 \right) \frac{1}{r_{12}} \psi_i \left(\mathbf{x}_2 \right) \psi_j^* \left(\mathbf{x}_2 \right) d\mathbf{x}_1 d\mathbf{x}_2$$

Minimization and orthonomalization conditions

$$\hat{H}\psi_i\left(\mathbf{x}\right) = \sum_{j=1}^{N} \varepsilon_{ij}\psi_j\left(\mathbf{x}\right)$$

$$\hat{H} = -\frac{1}{2}\nabla^2 + v + g$$

Background

- 1920s: **Introduction of the Thomas-Fermi model.**
- 1964: **Hohenberg-Kohn paper proving existence of exact DF.**
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA. DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello) (Now one of PRL's top 10 cited papers).
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The first HK theorem legitimates ρ as basic variable.

The external potential is determined, within a trivial additive constant, by the electron density.

$$E_v[\rho] = T[\rho] + V_{em}[\rho] + V_{ee}[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + F_{HK}[\rho]$$

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

$$V_{ee}[\rho] = J[\rho] + \text{non classical terms}$$

The second HK theorem supplies the variational principle for the ground state energy.

$$\int \rho(\vec{r})d\vec{r} = N \qquad\qquad E_0 \leq E_v[\rho]$$

$$\delta\left\{ E_v[\rho] - \mu\left[\int \rho(\vec{r})d\vec{r} - N \right] \right\} = 0$$

The ground state energy and density correspond to the minimum of some functional E_v subject to the constraint that the density contains the correct number of electrons. The Lagrange multiplier of this constraint is the electronic chemical potential μ.

In matematica e in fisica teorica, la derivata funzionale è una generalizzazione della derivata direzionale. La differenza è che la seconda differenzia nella direzione di un vettore, mentre la prima differenzia nella direzione di una funzione. Entrambe possono essere viste come estensioni dell'usuale derivata.

$$E[\rho] = \int f\left(r, \rho, \nabla\rho, \nabla^2\rho, \ldots\right) d^3r$$

$$\frac{\delta F[\rho]}{\delta\rho} = \frac{\delta f}{\delta\rho} - \nabla \cdot \frac{\delta f}{\delta(\nabla\rho)} + \nabla^2 \frac{\delta f}{\delta(\nabla^2\rho)} - \ldots$$

$$J[\rho] = \frac{1}{2} \int \left(\frac{\rho(r)\rho(r')}{|r - r'|} d^3r' \right) d^3r$$

$$\frac{\delta J[\rho]}{\delta \rho} = \frac{\delta j}{\delta \rho} = \int \frac{\rho(r')}{|r - r'|} d^3r'$$

$$j = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} d^3r'$$

$$\frac{\delta^2 J[\rho]}{\delta \rho^2} = \frac{\delta}{\delta \rho} \int \frac{\rho(r')}{|r - r'|} d^3r' = \frac{\delta}{\delta \rho} \frac{\rho(r')}{|r - r'|} = \frac{1}{|r - r'|}$$

$$E_v[\rho] = T[\rho] + V_{em}[\rho] + V_{ee}[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + F_{HK}[\rho]$$

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = v(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})}$$

Despite the importance of the HK theorems, it is noteworthy that the result they give is somehow incomplete. Actually, the first HK theorem refers only to the ground state energy and ground state density. Furthermore, as far as the second HK theorem is concerned, it is *simply* an existence theorem and no information about how to get the ground state energy functional is provided. Nevertheless, the existence of an exact theory justifies the research of new funtionals that, though approximate version of the correct one, are more and more accurate

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The Kohn–Sham method.

The massive usage of DFT is tightly bound to its use in orbitalic theories. This is not very surprising because of the role played by these theories, in particular the HF one, in quantum chemistry. Thus, the major DFT developments have implied either the improvement of existing orbitalic theories, for instance the Xα method [Slater, 1951a–b], or the proposal

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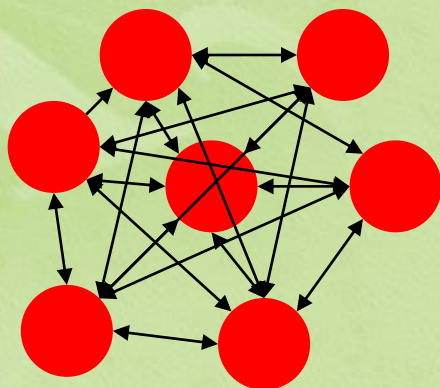TIFF (LZW) decompressor
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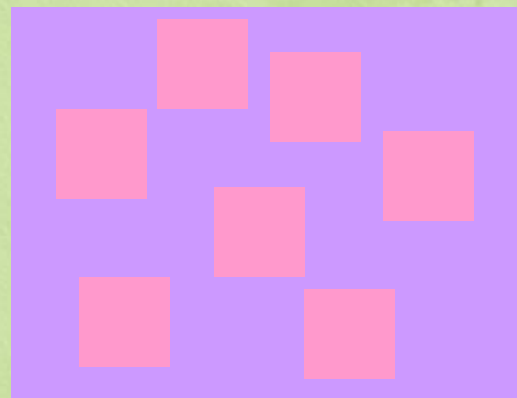QuickTime™ and a
decompressor
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Interacting electrons
+ real potential

Non-interacting fictitious
particles + effective potential

$$\hat{H}_s = \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_i^N v_s\left(\vec{r_i}\right)$$

$$\Psi_s = \tfrac{1}{\sqrt{N!}} \det\left[\psi_1 \psi_2 \cdots \psi_N\right]$$

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

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

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$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \qquad J[\rho] = \tfrac{1}{2} \iint \tfrac{1}{r_{12}} \rho(\vec{r_1}) \rho(\vec{r_2}) d\vec{r_1} d\vec{r_2}$$

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

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = v(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})} \qquad \mu = v_{eff}(\vec{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})}$$

$$v_{eff}(\vec{r}) = v(\vec{r}) + \frac{\delta J[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}(\vec{r})$$

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$

With reference to the single Euler - Lagrange equation, the introduction of *N* orbitals allows us to treat exactly T_s, the dominant part of the true kinetic energy $T[\rho]$. The cost we have to pay is the needed of *N* equations rather than one expressed in terms of the total electron density. The KS equations have the same form of the Hartree equations unless the presence of a more general local potential, $v_{eff}\left(\vec{r}\right)$. The computational effort for their solution is comparable to that required for the Hartree equations and definitely smaller than that pertinent to the HF ones. HF equations are characterized by a one-electron Hamiltonian including a non local potential and for this reason they cannot be considered a special case of the KS equations.
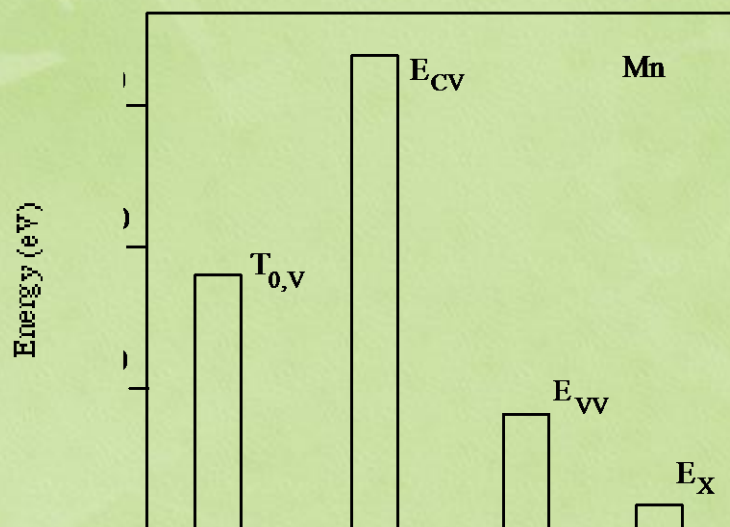
Relative magnitudes of contributions to total valence energy (in eV) of the Mn atom

The exchange-correlation potential

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons.

Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly.

A common approximation is the so-called local density approximation (LDA) which locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density.

The Local Density Approximation (LDA)

The LDA approximation assumes that the density is slowly varying and the inhomogeneous density of a solid or molecule can be calculated using the homogeneous electron gas functional.

While many ground state properties (lattice constants, bulk moduli, etc.) are well described in the LDA, the dielectric constant is overestimated by 10-40% in LDA compared to experiment. This overestimation stems from the neglect of a polarization-dependent exchange correlation field in LDA compared to DFT.

The method can be improved by including the gradient of the density into the functional. The generalized gradient approximation GGA is an example of this type of approach.

The Slater exchange functional

The predecessor to modern DFT is Slater's Xα method. This method was formulated in 1951 as an approximate solution to the Hartree-Fock equations. In this method the HF exchange was approximated by:

$$E_{X\alpha}[\rho] = -\frac{9}{4}\alpha\left(\frac{3}{4\pi}\right)^{1/3}\int_0^\infty \rho^{4/3}(r)dr$$

The exchange energy $E_{X\alpha}$ is a fairly simple function of the electron density ρ.

The adjustable parameter α was empirically determined for each atom in the periodic table. Typically α is between 0.7 and 0.8. For a free electron gas $\alpha = 2/3$.

The VWN Correlation Functional

In ab initio calculations of the Hartree-Fock type electron correlation is also not included. However, it can be included by inclusion of configuration interaction (CI). In DFT calculations the correlation functional plays this role. The Vosko-Wilk-Nusair correlation function is often added to the Slater exchange function to make a combination exchange-correlation functional.

$$E_{xc} = E_x + E_c$$

The nomenclature here is not standardized and the correlation functionals themselves are very complicated functions. The correlation functionals can be seen on the MOLPRO website

http://www.molpro.net/molpro2002.3/doc/manual/node146.html.

Application of the LDA

Application of LDA methods to semi-conductor materials and insulators gives good agreement for the lattice constant and bulk modulus.

The lattice constants are typically accurate to within 1-2% up the second row in the periodic table. Since the crystal volume V is accurately calculated the density is, of course, also obtained.

The bulk modulus is:

$$B = -V\left(\frac{\partial P}{\partial V}\right) = -V\left(\frac{\partial^2 E}{\partial V^2}\right)$$

Bulk moduli are calculated by systematically varying the lattice parameters and plotting the energy as a function of V. The curvature at the minimum of the E(V) plot is proportional to the lattice constant.

Extensions of the LDA approach

Generalized gradient approximation (GGA). Take density gradient into account. Useful for molecules.

Spin density functional theory. Two independent variables: density and magnetization.

$$m(r) = -\mu_0\left(\rho_\uparrow - \rho_\downarrow\right)$$

Exact exchange density functional theory. Calculate exchange exactly and correlation approximately using DFT.

Generalized density functional theory. Modify K-S energy partitioning to obtain a non-local hamiltonian.

Generalized Gradient Approach (GGA)

The GGA approach takes into account variations in the density by including the gradient of the density in the functional. One commonly used GGA functional is that of Becke.

$$V_{xc}^{B} = -\beta\rho^{1/3}\frac{x^2}{\left(1 + 6\beta x \sinh^{-1} x\right)} \quad , \; x = \frac{\nabla\rho}{\rho^{4/3}}$$

This functional has only one adjustable parameter, β. The value of $\beta = 0.0042$ was determined based on the best fit to the energies of six noble gas atoms using the sum of the LDA and GGA exchange terms.

The GGA option in DMol3 is that of Perdew and Wang.

Lee-Yang-Parr Correlation Functional

As was discussed above for the Slater exchange functional (no gradient), the VWN correlation functional provides a significant improvement in the calculation of the energies and properties such as bulk modulus, vibrational frequencies etc. In a similar manner the Becke exchange functional (including a gradient correlation) and the Lee-Yang-Parr functional are used together. The Lee-Yang-Parr or LYP correlation functional is quite complicated. It can be viewed on the MOLPRO website.

Thus, two of the most commonly used functionals are:
S-VWN Slater exchange - VWN correlation (no gradients)
B-LYP Becke exchange - LYP correlation (gradients)