

Density Functional Theory: from theory to Applications

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November 12, 2014

Recap of Previous lecture

The Hohenberg-Kohn theorems

The Kohn-Sham equations

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The Hohenberg-Kohn theorems

For a given system described by the Hamiltonian:

$$\hat{H} = \sum_{i=1,}^N \left(-\frac{1}{2} \nabla_i^2\right) + \sum_{i=1,}^N v(r_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \quad (1)$$

N and $v(r)$ determines all properties of the ground state.

The **first Hohenberg-Kohn theorem** states:

The external potential $v(r)$ is determined, within a trivial additive constant, by the electron density $\rho(r)$.

The **second Hohenberg-Kohn theorem** states:

For a trial density $\tilde{\rho}(r)$ such that $\tilde{\rho}(r) > 0$ and $\int \tilde{\rho}(r) dr = N$, there is a variational principle and $E_0 \leq E_v[\tilde{\rho}]$.

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \quad (2)$$

$$= \int \rho(r) v(r) dr + F_{HK}[\rho] \quad (3)$$

and

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \quad (4)$$

$$= T[\rho] + J[\rho] + \text{nonclassical term} \quad (5)$$

The second HK theorem provides the justification for the variational principle in TF, where $E_{TF}[\rho]$ is an approximation to $E[\rho]$.

Orbitals and Kohn-Sham equations

It is quite appealing that we can get the ground-state energy of a many-electron system as minimum of an energy functional

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

we have seen that a drastic approximation to the functional can be obtained by the TF model:

$$V_{ee}[\rho] \rightarrow J[\rho] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

$$T[\rho] \rightarrow \text{uniform electron gas}$$

- ▶ Can we do better?

- ▶ The main problem at this stage is the kinetic energy functional $T[\rho]$ because its explicit expression in term of the density ρ is not known.
- ▶ In 1965 Kohn and Sham invented an ingenious approach to $T[\rho]$. Their idea was to find a system of non-interacting electrons that produces the same density of the interacting system.

Let's consider a *noninteracting reference system* in which there is no electron electron repulsion term and for which the electron density is exactly ρ :

$$\hat{H}_s = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v_s(r_i) \quad (6)$$

For this system we have an exact solution

$$\Psi_s = \frac{1}{\sqrt{N!}} \det [\psi_1 \psi_2 \dots \psi_N] \quad (7)$$

for such a system the kinetic energy is

$$T_s[\rho] = \langle \Psi_s | \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) | \Psi_s \rangle = \quad (8)$$

$$= \sum_i^N \langle \Psi_s | -\frac{1}{2} \nabla_i^2 | \Psi_s \rangle \quad (9)$$

Now the very clever idea by Kohn and Sham was to rewrite

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

as

$$E_v[\rho] = T_s[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (10)$$

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \quad (11)$$

The quantity $E_{xc}[\rho]$ is the *exchange-correlation energy*, which contains the difference between $T[\rho]$ and $T_s[\rho]$ and the non-classical part of $V_{ee}[\rho]$.

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(r)\rho(r)dr = \\ = \sum_i^N \sum_s \int \psi_i^*(x_i) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(x_i) dr + J[\rho] + E_{xc}[\rho] + \int v(r)\rho(r)dr$$

and the electron density

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r, s)|^2 \quad (12)$$

The variational search for the minimum of $E[\rho]$ can be equivalently effected in the space of orbitals ψ_i , constraining the orbitals to be orthonormal:

$$\int \psi_i^*(x) \psi_j(x) dx = \delta_{ij}. \quad (13)$$

If we now define the functional

$$\Omega[\psi_i] = E[\rho] - \sum_i^N \sum_j^N \epsilon_{ij} \int \psi_i^*(x) \psi_j(x) dx \quad (14)$$

where ϵ_{ij} are the Lagrange multiplier for the orthonormality constraints, For $E[\rho]$ to be a minimum it is necessary that:

$$\delta\Omega[\psi_i] = 0, \quad (15)$$

which leads to the equations:

$$\hat{h}_{\text{eff}} \psi_i = \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}} \right] \psi_i = \sum_j^N \epsilon_{ij} \psi_j \quad (16)$$

where

$$v_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{\text{xc}}(r). \quad (17)$$

ϵ_{ij} is Hermitian and can be diagonalized by unitary transformation. Such a transformation leaves invariant the Slater determinant, the density and hence the Hamiltonian.

In this way we can obtain the *Kohn-Sham equations* in their canonical form:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}} \right] \psi_i = \epsilon_i \psi_i \quad (18)$$

$$v_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{\text{xc}}(r) \quad (19)$$

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r, s)|^2 \quad (20)$$

These equations are non-linear and must be solved iteratively.

Then the total energy can be calculated from the energy functional:

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

or in terms of the K-S eigenvalues by:

$$E = \sum_i^N \epsilon_i - \int v_{\text{eff}}(r)\rho(r)dr + J[\rho] + E_{xc}[\rho] + \int v(r)\rho(r)dr$$

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' + E_{xc}[\rho] - \int v_{xc}(r)\rho(r). \quad (21)$$

Here

$$\sum_i^N \epsilon_i = \sum_i^N \langle \psi_i | -\frac{1}{2}\nabla^2 + v_{\text{eff}}(r) | \psi_i \rangle \quad (22)$$

$$= T_s[\rho] + \int v_{\text{eff}}(r)\rho(r)dr \quad (23)$$

- ▶ T_S can be handled *exactly* through the introduction of the N orbitals.
- ▶ The KS eq have the form of Hartree equation where now $v(r)$ has the more general form of $v_{\text{eff}}(r)$. **KS are exact and include all the electron correlation when the exact $E_{xc}[\rho]$ is known.**
- ▶ The computational cost to solve KS is not much more than to solve the Hartree eq and less than for the Hartree-Fock eq.
- ▶ The KS theory, exact in principle, is distinguished from the HF theory by its capacity to incorporate the exchange and correlation potential
- ▶ KS eq are open for improvement with each successive better approximation to $E_{xc}[\rho]$.



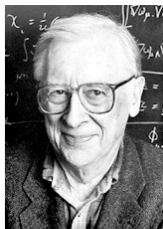
The Nobel Prize in Chemistry 1998

Walter Kohn, John Pople

▶ The Nobel Prize in Chemistry 1998	▼
Nobel Prize Award Ceremony	▼
Walter Kohn	▼
John Pople	▼



Walter Kohn



John A. Pople

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

- ▶ So far $v_{\text{eff}}(r)$ doesn't contain any dependence on the spin. For each eigenvalue ϵ_i there are two independent solutions sharing the same spatial part, they can be chosen as $\phi_i(\mathbf{r})\alpha(s)$ and $\phi_i(\mathbf{r})\beta(s)$.

For an even number of electrons we have:

$$\rho(r) = 2\rho^\alpha(r) = 2\rho^\beta(r) = 2 \sum_i^{N/2} |\phi_i(r)|^2 \quad (24)$$

For an odd number of electrons we have:

$$\rho(r) = \rho^\alpha(r) + \rho^\beta(r) \quad (25)$$

where $\rho^\alpha(r)$ and $\rho^\beta(r)$ differ only by one excess orbital.
(restricted Kohn-Sham method)

Next time we will discuss Spin-DFT which corresponds to an *unrestricted* approach.

- ▶ Which N orbitals should one use to form the density in solving the KS equations? Original proposal by KS is the N lowest eigenstates.
- ▶ Given the auxiliary nature of the KS orbitals - they are just N orbitals the sum of square of which add up to the true total electron density - one should expect no simple physical meaning for the KS orbital energies.
There is none, however one can infer that

$$\epsilon_{max} = -I \quad (26)$$

Eq. 26 requires that $\lim_{|r| \rightarrow \infty} v_{eff}(\mathbf{r}) = 0$.

Local-density

An explicit form of $E_{xc}[\rho]$ is needed!

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}(\rho) dr \quad (27)$$

where $\epsilon_{xc}(\rho)$ is the exchange and correlation energy per particle of a uniform electron gas of density ρ . the corresponding xc potential is

$$v_{xc}^{LDA}(r) = \frac{\delta E_{xc}^{LDA}}{\delta \rho(r)} = \epsilon_{xc}(\rho(r)) + \rho(r) \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho} \quad (28)$$

and the KS orbitals read:

$$\left[-\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}^{LDA}(r) \right] \psi_i = \epsilon_i \psi_i \quad (29)$$

Local-density

$\epsilon_{xc}(\rho)$ can be divided into exchange and correlation contributions:

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho) \quad (30)$$

- ▶ The exchange part is give by the **Dirac (1930) exchange-energy functional**

$$\epsilon_x(\rho) = -C_x \rho(r)^{1/3}, \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \quad (31)$$

- ▶ accurate values of $\epsilon_c(\rho)$ are available thanks to quantum-MC calculations (Ceperly, Alder 1980), and have been interpolated to provide an analytical form for $\epsilon_c(\rho)$.

The Dirac exchange-energy functional

Let's express HF ex in the formalism of first order density matrix:

$$K = \sum_{k,l=1}^{N/2} \iint \phi_k^*(r_1) \phi_l(r_1) \frac{1}{r_{12}} \phi_k(r_2) \phi_l^*(r_2) dr_1 dr_2 \quad (32)$$

$$= \sum_{k,l=1}^{N/2} \iint \phi_k^*(r_1) \phi_k(r_2) \frac{1}{r_{12}} \phi_l^*(r_2) \phi_l(r_1) dr_1 dr_2 \quad (33)$$

$$= \frac{1}{4} \iint \frac{1}{r_{12}} 2 \sum_k^{N/2} \phi_k^*(r_1) \phi_k(r_2) 2 \sum_l^{N/2} \phi_l^*(r_2) \phi_l(r_1) dr_1 dr_2 \quad (34)$$

$$= \frac{1}{4} \iint \frac{1}{r_{12}} \rho_1(r_1, r_2) \rho_1(r_2, r_1) dr_1 dr_2 \quad (35)$$

$$= \frac{1}{4} \iint \frac{1}{r_{12}} |\rho_1(r_1, r_2)|^2 dr_1 dr_2 \quad (36)$$

We need an approximation for the first order density matrix:

$$\rho_1(r_1, r_2) = 2 \sum_k^{N/2} \phi_k^*(r_1) \phi_k(r_2) \quad (37)$$

And we will follow the derivation by Dirac(1930) of calculating the exchange term for a uniform electron gas.

$$\psi(k_x, k_y, k_z) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (38)$$

$$= \frac{1}{l^{3/2}} e^{i(k_x x + k_y y + k_z z)} \quad (39)$$

where

$$k_x = \frac{2\pi}{l} n_x; k_y = \frac{2\pi}{l} n_y; k_z = \frac{2\pi}{l} n_z \quad (40)$$

and

$$E(n_x, n_y, n_z) = \frac{\hbar^2}{8m l^2} [(2n_x)^2 + (2n_y)^2 + (2n_z)^2] \quad (41)$$

$$\rho_1(r_1, r_2) = \frac{2}{V} \sum_n e^{i\mathbf{k} \cdot (r_1 - r_2)} \quad (42)$$

For very many occupied states the sum can be replaced by the integral (dn → dk)

$$\rho_1(r_1, r_2) = \frac{1}{4\pi^3} \int e^{i\mathbf{k} \cdot (r_1 - r_2)} d\mathbf{k} \quad (43)$$

$$= \frac{1}{4\pi^3} \int_0^{k_F} k^2 dk \iint e^{ikr_1^2} \sin \theta d\theta d\phi \quad (44)$$

similarly

$$\rho_1(r, r) = \frac{1}{4\pi^3} \int_0^{k_F} k^2 dk \iint \sin \theta d\theta d\phi \quad (45)$$

$$= \frac{1}{4\pi^3} \frac{k_F^3}{3} 4\pi = \frac{k_F^3}{3\pi^2} \quad (46)$$

from where we get an expression for k_F in terms of the density

$$k_F = (3\pi^2 \rho)^{1/3} \quad (47)$$

Now if we come back to the expression

$$\rho_1(r_1, r_2) = \frac{1}{4\pi^3} \int_0^{k_F} k^2 dk \iiint e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \sin\theta d\theta d\phi$$

we can introduce the new variables:

$$r = \frac{1}{2}(r_1 + r_2) \quad (48)$$

$$s = r_1 - r_2 \quad (49)$$

$$\rho_1(r, s) = \frac{1}{4\pi^3} 2\pi \int_0^{k_F} k^2 dk \int e^{iks \cos\theta} \sin\theta d\theta \quad (50)$$

$$= \frac{1}{2\pi^2} \int_0^{k_F} k^2 \left(-\frac{e^{iks \cos\theta}}{iks} \right) \Big|_0^\pi dk \quad (51)$$

$$= \frac{1}{\pi^2} \int_0^{k_F} k \frac{(e^{iks} - e^{-iks})}{2i} dk \quad (52)$$

$$= \frac{1}{\pi^2 s^3} \int_0^{k_F} ks \sin ksd(ks) \quad (53)$$

defining the new variable $ks = t$ we obtain:

$$\rho_1(r, s) = \frac{1}{\pi^2 s^3} \int_0^{sk_F} t \sin t dt \quad (54)$$

$$= \frac{1}{\pi^2 s^3} \left(-t \cos t \Big|_0^{sk_F} + \int_0^{sk_F} \cos t dt \right) \quad (55)$$

$$= \frac{1}{\pi^2 s^3 k_F^3} k_F^3 [-t \cos t + \sin t] \quad (56)$$

$$= \frac{3\rho(r)}{t^3} [\sin t - t \cos t] \quad (57)$$

Let's now substitute the expression for $\rho_1(r, s)$ into the expression for $K[\rho]$

$$K[\rho] = \frac{1}{4} \iint \frac{1}{r_{12}} |\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

which we now express in the r and s coordinates:

$$K[\rho] = \frac{1}{4} \iint \frac{1}{s} |\rho_1(\mathbf{r}, s)|^2 dr ds \quad (58)$$

$$K[\rho] = \frac{1}{4} \iint \frac{1}{s} |\rho_1(\mathbf{r}, s)|^2 d\mathbf{r} ds \quad (59)$$

$$= \frac{1}{4} \int 9\rho(r)^2 \frac{1}{k_F^2} d\mathbf{r} 4\pi \int_0^\infty \frac{(\sin t - t \cos t)^2}{t^5} dt \quad (60)$$

The integral can be solved with a change of variable $q = \frac{\sin t}{t}$:

$$\int_0^\infty \frac{(\sin t - t \cos t)^2}{t^5} dt = \frac{1}{4} \quad (61)$$

Also recalling that $\rho = \frac{k_F^3}{3\pi^2}$

$$\frac{\rho(r)^2}{k_F^2} = (3\pi^2)^{-2/3} \rho^{4/3} \quad (62)$$

The final expression for $K[\rho]$ is:

$$K[\rho] = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \text{ with } C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} = 0.7386 \quad (63)$$

Quick derivation of the scaling laws

- ▶ Scaling for the density

$$\rho_\lambda(r) = \lambda^3 \rho(\lambda r) \quad (64)$$

- ▶ Scaling for the wavefunction

$$\rho_\lambda(r) = \psi_\lambda^*(r) \psi_\lambda(r) \quad (65)$$

$$\psi_\lambda(r) = \lambda^{3/2} \psi(\lambda r) \quad (66)$$

Quick derivation of the scaling laws

- Scaling for the **kinetic energy** T

$$T_\lambda \sim \int \psi_\lambda^*(r) \nabla_\lambda^2 \psi_\lambda(r) d^3(\lambda r) \quad (67)$$

$$\sim \lambda^{3/2*2} \lambda^2 \lambda^{-3} T(\lambda r) \quad (68)$$

$$\sim \lambda^2 T(\lambda r) \quad (69)$$

$$\text{Also } T[\rho_\lambda] = \int t(\rho_\lambda) dr = \int t(\lambda^3 \rho(\lambda r)) \lambda^{-3} d^3(\lambda r) \quad (70)$$

$$= \int \lambda^{-3} t(\lambda^3 \rho(r)) dr \quad (71)$$

$$\text{equating 69 and 71 we obtain: } \lambda^{-3} t(\lambda^3 \rho(r)) = \lambda^2 t(\rho) \quad (72)$$

$$t(\lambda^3 \rho(r)) = \lambda^5 t(\rho) \quad (73)$$

$$t(\lambda \rho(r)) = \lambda^{5/3} t(\rho) \quad (74)$$

Quick derivation of the scaling laws

- Scaling for the **exchange functional**

$$K[\rho_\lambda] \sim \int \frac{1}{r} \psi^* \psi d^3r = \lambda \lambda^{3/2} \lambda^{-3} K[\rho] \quad (75)$$

$$K[\rho_\lambda] = \lambda K[\rho] \quad (76)$$

$$\text{Also } K[\rho_\lambda] = \int k(\rho_\lambda) dr \quad (77)$$

$$= \int k(\lambda^3 \rho(\lambda r)) \lambda^{-3} d(\lambda r) \quad (78)$$

$$= \int \lambda^{-3} k(\lambda^3 \rho(r)) dr \quad (79)$$

$$\text{Equating 77 and 79 we obtain: } \lambda^{-3} k(\lambda^3 \rho(r)) = \lambda k[\rho] \quad (80)$$

$$k(\lambda^3 \rho(r)) = \lambda^4(\rho) \quad (81)$$

$$k(\lambda \rho) = \lambda^{4/3} k(\rho) \quad (82)$$

Correlation functional

ϵ_c is a difficult problem. Only limiting cases are known in analytic form. In the case of an homogeneous systems,

- ▶ the high density limit is:

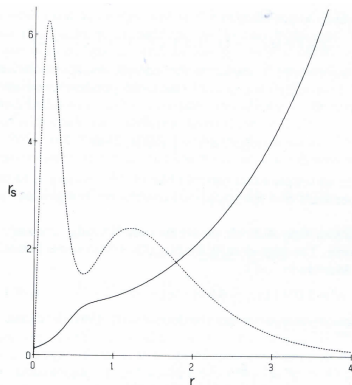
$$\epsilon_c^{hom} = 0.0311 \ln r_s - 0.048 + r_s (A^0 \ln r_s + C^0), \text{ for } r_s \ll 1 \quad (83)$$

- ▶ and the low density limit is:

$$\epsilon_c^{hom} = \frac{1}{2} \left(\frac{g_0}{r_s} + \frac{g_1}{r_s^{3/2}} + \frac{g_2}{r_s^2} + \dots \right) \text{ for } r_s \gg 1 \quad (84)$$

where r_s is the the radius of a sphere whose volume is the effective volume of an electron.

$$\frac{4}{3} \pi r_s^3 = \frac{1}{\rho} \quad (85)$$



¹ Note that

- ▶ large r_s means low density, small r_s means high density

¹The radius r_s for the ground state of the carbon atom as function of the distance from the nucleus. Dotted line: $D(r)=4\pi r^2\rho(r)$.

Early LDA results

The LDA is applicable to systems with slow-varying densities but cannot be formally justified for highly inhomogeneous systems, such as atoms and molecules. The essential justification comes from successful numerical applications.

First LDA calculations on atoms:

THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 144, No. 1

8 APRIL 1966

Application of a Self-Consistent Scheme Including Exchange and Correlation Effects to Atoms*

B. Y. TONG† AND L. J. SHAM

University of California, San Diego, La Jolla, California

(Received 3 November 1965)

Self-consistent schemes including approximations to exchange and correlation proposed by Kohn and Sham are applied to computing atomic energies and densities. These quantities, with and without the correlation correction, are obtained and compared with the results of calculations using the Slater exchange hole or the Hartree-Fock method and with experimental values. The present method, without correlation, gives slightly better results for energies and substantially better results for densities than Slater's method. This was anticipated in the general theory. The correlation corrections of the present scheme are not very good, presumably because the electronic density in atoms has too rapid a spatial variation.

Table 7.3 Total Energies of Atoms, Computed by Various Methods (atomic units)^a

Atom	$X\alpha (\alpha = \frac{2}{3})^b$	$X\alpha (\alpha = 1)^b$	LDA	Hartree-Fock	Experiment
He	-2.72	-2.70	-2.83	-2.86	-2.90
Li	-7.17	-7.15	-7.33	-7.43	-7.48
Ne	-127.49	-127.38	-128.12	-128.55	-128.94
Ar	-524.51	-524.35	-525.85	-526.82	-527.60

^a Atomic $X\alpha$ and LDA calculations by Tong and Sham (1966).

^b Value of α in (7.4.7). In both cases $\alpha = 1$ in (7.4.10).

- ▶ Electron densities are close to HF densities
- ▶ LDA exchange gives $\sim 10\%$ err in the HF exchange
- ▶ inclusion of ϵ_c is not particularly beneficial, indeed the approx used here (Pines, 1963) is not very accurate.

Table 7.4 LDA Calculations for N_2 and $CO^{a,b}$

Molecule	Binding energy (eV)			Bond Length (a_0)			Vibrational Frequency (cm^{-1})		
	LDA	HF	Exptl.	LDA	HF	Exptl.	LDA	HF	Exptl.
N_2	7.8	5.3	9.8	2.16	2.01	2.07	2070	2730	2358
CO	9.6	7.9	11.2	2.22	2.08	2.13	2090	2131	2170

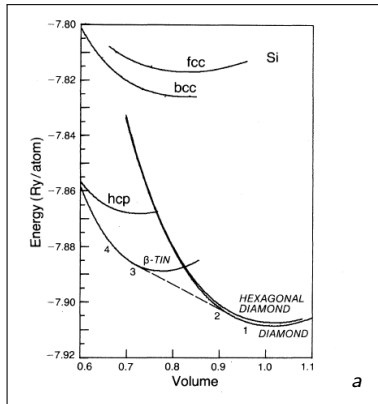
^a Gunnarsson, Harris, and Jones (1977).^b HF designates Hartree-Fock method.

- ▶ Molecular bonding is described relatively well (in contrast with Thomas Fermi theory)
- ▶ LDA accuracy may exceed the Hartree-Fock accuracy

2

²Gunnarson O, Harris J, and Jones, RO (1977) Density Functional Theory and Molecular Bonding. I. First-row diatomic molecules. *J. Chem. Phys.* **67**, 3970.

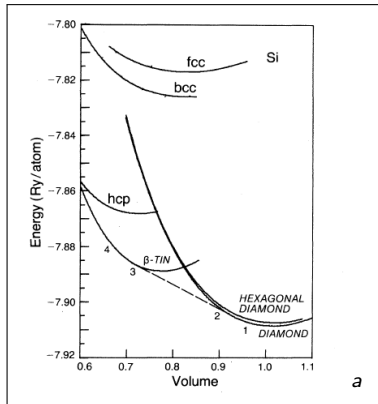
The Si phase diagram from LDA



- The diamond structure is the ground-state phase;

^aYim MT, Cohen ML (1980)
Phys. Rev. Lett. **45**: 1004

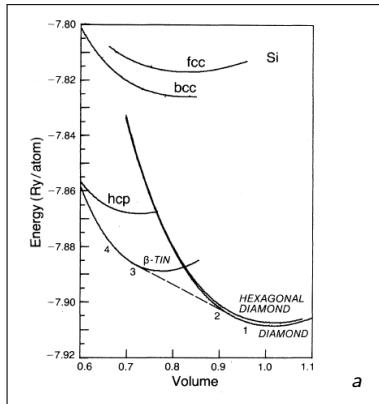
The Si phase diagram from LDA



- ▶ The diamond structure is the ground-state phase;
- ▶ lattice constant predicted within 1-2% of the exp;

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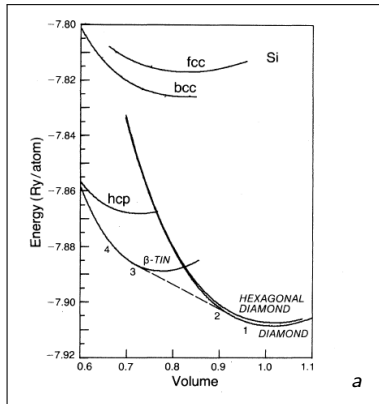
The Si phase diagram from LDA



- ▶ The diamond structure is the ground-state phase;
- ▶ lattice constant predicted within 1-2% of the exp;
- ▶ bulk modulus within 5% of the exp;

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The Si phase diagram from LDA



^aYim MT, Cohen ML (1980)

Phys. Rev. Lett. **45**: 1004

- ▶ The diamond structure is the ground-state phase;
- ▶ lattice constant predicted within 1-2% of the exp;
- ▶ bulk modulus within 5% of the exp;
- ▶ pressure to transform diamond into white-tin structure within 20%.

it is the first application of pseudopotential formalism in DFT. (we discuss this next week)

Gradient expansion

Among limitations of LDA there the fact that inhomogeneities in the density are not taken into account. This can be introduced semi-locally by expanding $E_{xc}[\rho]$ in terms of density and its gradient.

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}[\rho(\mathbf{r})] F_{xc}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r}), \dots] d\mathbf{r} \quad (86)$$

the second order gradient expansion corresponds to:

$$E_{xc}[\rho] = \int A_{xc}[\rho] \rho(\mathbf{r})^{4/3} d\mathbf{r} + \int C_{xc}[\rho] |\nabla[\rho]|^2 / \rho(\mathbf{r})^{4/3} d\mathbf{r} \quad (87)$$

Gradient expansion

GGAs have been obtained following two different approaches:

- ▶ Theoretical derivation of an appropriate expression with coefficients chosen so that number of formal conditions are fulfilled: namely sum rules, long range decay etc...
- ▶ Fit the parameters of the functional in order to reproduce a number of experimental results in a molecular database (structural parameters, formation energies, thermochemical data (possible issue: transferability)).

BLYP functional

An example from the second category is the BLYP functional. The exchange functional has been proposed by Becke in 1988³, fitting the parameters to experimental molecular data.

$$\epsilon_x = \epsilon_x^{LDA} \left(1 - \frac{\beta}{2^{1/3} A_x} \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \right) \quad (88)$$

where $x = 2^{1/3} |\nabla \rho(\mathbf{r})| / \rho(\mathbf{r})$, $A_x = (3/4)(3/\pi)^{1/3}$, and $\beta = 0.0042$. this was complemented by a correlation derived by Lee, Yang and Parr⁴.

$$\epsilon_c = -\frac{a}{1 + d\rho^{-1/3}} \left\{ \rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_w + \frac{1}{9} \left(t_w + \frac{1}{2} \nabla^2 \rho \right) \right] e^{-c\rho^{-1/3}} \right\} \quad (89)$$

where $t_w = \frac{1}{8} \left(\frac{|\nabla \rho|^2}{\rho} - \nabla^2 \rho \right)$, $C_F = 3/10(3\pi^2)^{2/3}$, $a=0.04918$, $b=0.132$, $c=0.2533$ and $d=0.349$.

³ *Phys Rev A* **38**, 3098, number of citations from ISI 18,596

⁴ *Phys Rev B* **37**, 785, number of citations from ISI 30,166