

the
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international centre for theoretical physics

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Winter College on
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

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**DFT, KS EQUATIONS, XC FUNCTIONALS, SCF VS. MINIMIZATION APPROACH
TO THE NON-LINEAR SCHRÖDINGER EQUATION**

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electrons + ions

$$i \frac{\partial \Psi(\mathbf{r}, \mathbf{R})}{\partial t} = H(\mathbf{r}, \mathbf{p}, \mathbf{R}, \mathbf{P}) \Psi(\mathbf{r}, \mathbf{R})$$

$$\begin{aligned} H(\mathbf{r}, \mathbf{p}, \mathbf{R}, \mathbf{P}) = & T_I(\mathbf{P}) + T_e(\mathbf{p}) + \\ & W_{II}(\mathbf{R}) + W_{ee}(\mathbf{r}) + \\ & W_{eI}(\mathbf{r}, \mathbf{R}) \end{aligned}$$

$$\mathbf{r} = \vec{r}_1, \dots, \vec{r}_N, \quad \mathbf{R} = \vec{R}_1, \dots, \vec{R}_M,$$

3(N + M) variables

Exactly solvable: Hydrogen atom, harmonic oscillator.

Numerically solvable: single-particle problems.

Nevertheless

- GS geometry within 1-2 %
- elastic constants within 5-10 %
- lattice vibrations within a few %
- phase transitions under pressure correctly described
- and much more ...

Thanks to

- Adiabatic Approximation
- Density Functional Theory
- Powerful Computers and Efficient Algorithms

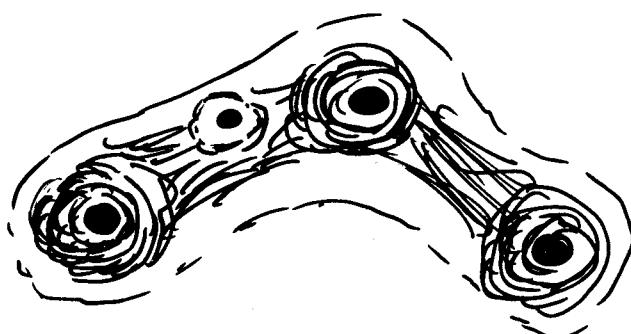
DENSITY FUNCTIONAL THEORY

- Every observable quantity of a stationary quantum mechanical system is determined by the ground-state density alone.
- The ground-state density of the interacting system of interest can be calculated as ground-state density of an auxiliary non-interacting system in an effective potential



$$E_{q\text{-test}}^{(r)} = q \left[\sum_v \frac{Z_v e}{|R_v - r|} + \int \frac{-e n(r')}{|r' - r|} dr' \right]$$

$$q = -e$$



$$E(r) = - \sum_v \frac{Z_v e^2}{|R_v - r|} + e^2 \int \frac{n(r') + \delta n(r')}{|r' - r|} d^3 r'$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + e^2 \int \frac{n(r')}{|r' - r|} d^3 r' + V_{\text{screen}}(r) \right] \varphi_i(r) = \epsilon_i \varphi_i(r)$$

electrons are Fermions

$$\Psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \dots & \varphi_1(r_N) \\ \vdots & & \vdots \\ \varphi_N(r_1) & \dots & \varphi_N(r_N) \end{vmatrix}$$

$$n(r) = \sum_{i=1}^N |\varphi_i(r)|^2$$

Self Consistent Field

the screening term contains contributions due to the statistics (exchange) and statical and dynamical correlations

Many properties are within the scope of DFT...

- Energetics, relative stability of different structures
Phase diagrams
- Structural properties, geometry
- Response to external perturbations
Elastic, Dielectrics, Piezoelectric constants
- Vibrational properties
- Chemical potential, Ionization energies, electron affinities, Fermi energy
- Defect energetics and transport properties

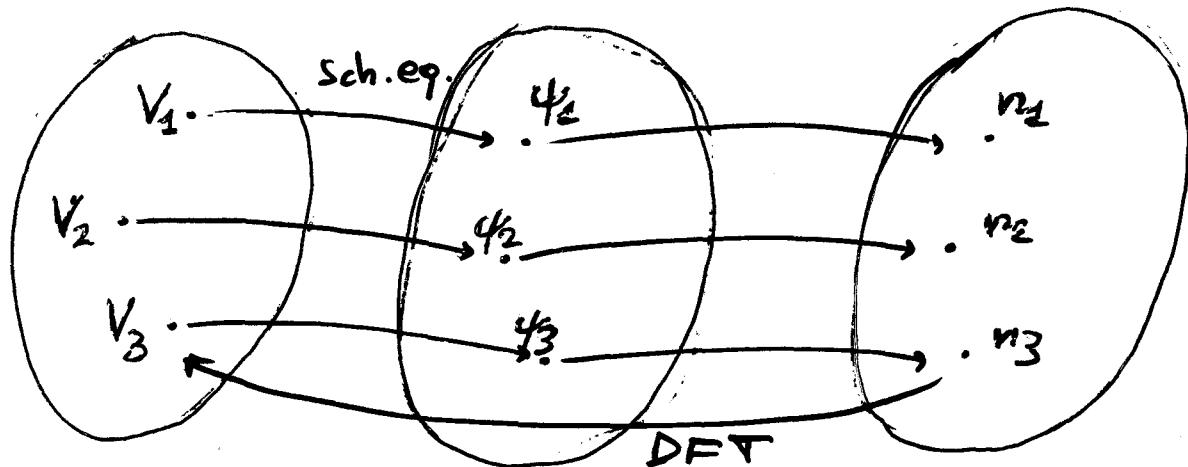
... and many are NOT

- Electronic excitations (unless ΔE_{GS})
- Fermi surfaces and Band structures
- Defect induced electronic structure changes
- electronic transport properties

DENSITY FUNCTIONAL THEORY

the density as the basic variable (for GS properties)

$$[T_e + V_{ee} + V] \psi_{GS} = E_{GS} \psi_{GS} ; \quad n(r) = \langle \psi_{GS} | \hat{n}(r) | \psi_{GS} \rangle$$



Hohenberg & Kohn Theorem Phys. Rev. 136 B864 (1964)

if $V'(r) \neq V(r) + \text{const}$ then $n'(r) \neq n(r)$

$\Rightarrow n(r) \rightarrow V(r) + \text{const} \rightarrow \psi_{GS} \rightarrow E_{GS}, \dots$

$$F[n] = \langle \psi_{GS}^{[n]} | T_e + V_{ee} | \psi_{GS}^{[n]} \rangle$$

$$E[n] = F[n] + \int V(r) n(r) d^3 r$$

$F[n]$ is a well defined functional of $n(r)$

$E[n]$ is minimized by the true GS density
and $E[n_{GS}] = E_{GS}$

$F[n]$ is a very non-trivial functional of the density $n(r)$

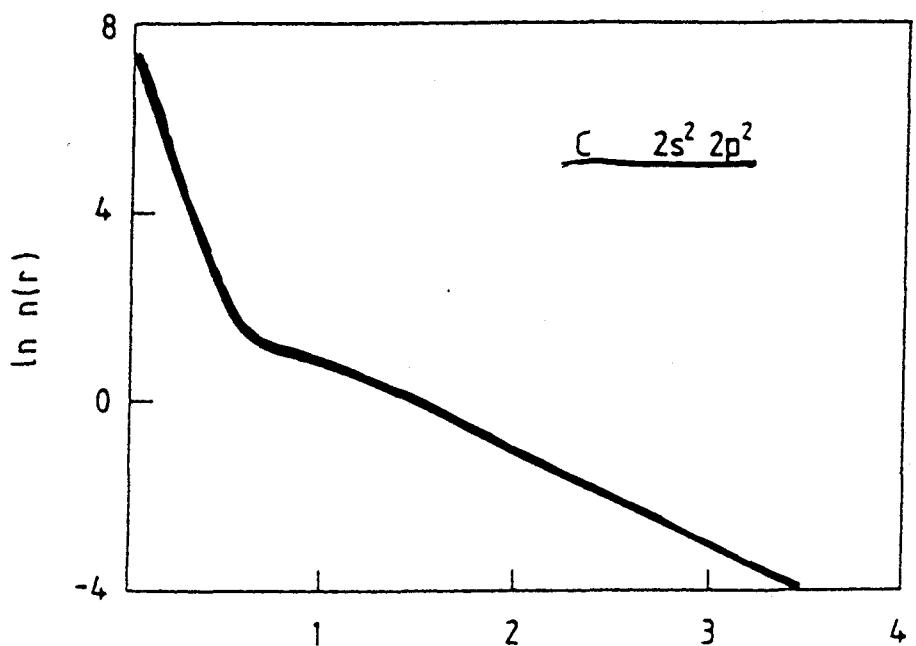


FIG. 1. Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.

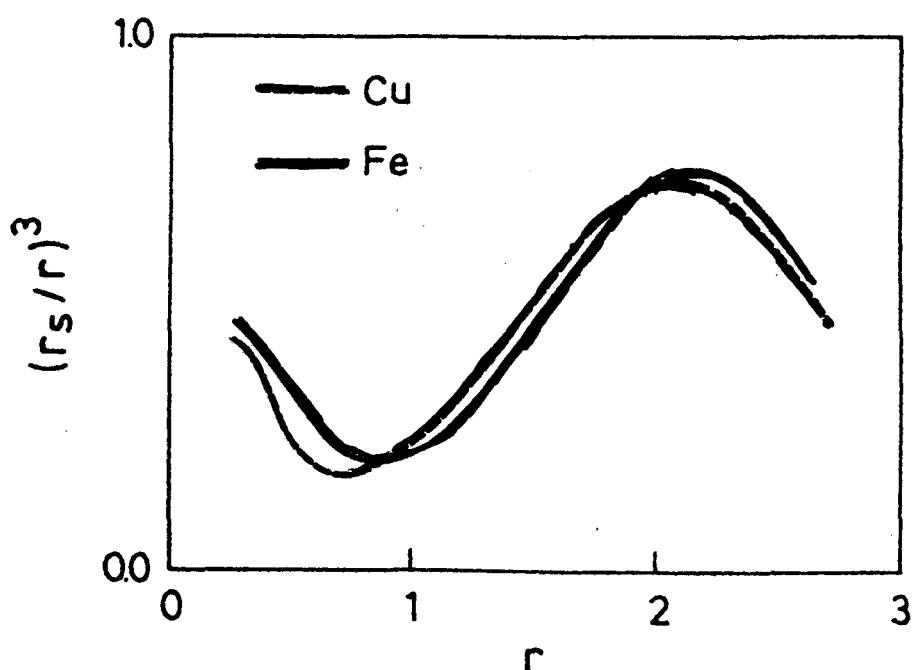


FIG. 6. Density of metallic Fe and Cu as a function of the radius r . The density n is expressed in terms of the parameter r_s , where $n = (4\pi r_s^3/3)^{-1}$.

It is useful to introduce a fictitious system of non-interacting electrons

$$HK: \quad n(r) \rightarrow T_s[n] = \min_{q \rightarrow n} \langle q | \hat{T}_e | q \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$

↑
definition of E_{xc}

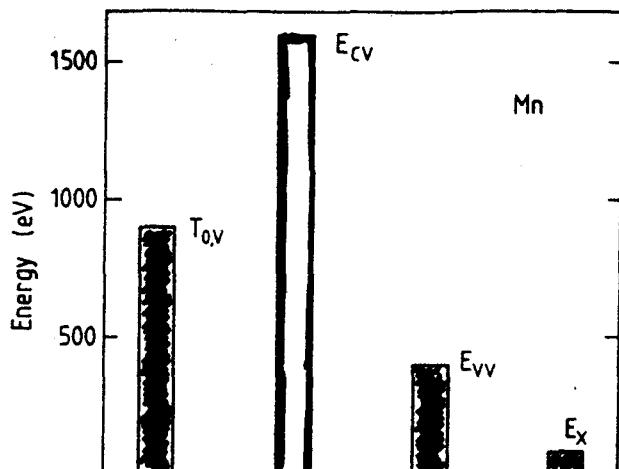


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(r) n(r) d^3r$$

Kohn - Sham equations

the minimum condition for the interacting system is

$$\delta \left[F[n] + \int V_0(r) n(r) d^3r - \mu \left(\int n(r) d^3r - N \right) \right] = 0$$

$$\frac{\delta F[n]}{\delta n(r)} + V_0(r) - \mu = 0$$

$$\frac{\delta T_S[n]}{\delta n(r)} + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)} + V_0(r) - \mu = 0$$

let V_{KS} be the potential of the non-interacting system that gives $n(r)$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

$$\psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \dots & \phi_1(r_N) \\ \vdots & & \vdots \\ \phi_N(r_1) & \dots & \phi_N(r_N) \end{vmatrix}$$

$$n(r) = \sum_i |\phi_i(r)|^2$$

$$\delta \left[T_S[n] + \int V_{KS}(r) n(r) d^3r - \mu \left(\int n(r) d^3r - N \right) \right] = 0$$

$$\frac{\delta T_S}{\delta n(r)} + V_{KS}(r) - \mu = 0$$

$$V_{KS}(r) = V_0(r) + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)}$$

Kohn - Sham eps.

$$E[n] = T_S[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(r) n(r) d^3 r$$

$$\mu' = \frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_S}{\delta n(r)} + V_H^{(r)} + \frac{\delta E_{xc}}{\delta n(r)} + V_{ext}^{(r)} \quad \text{interacting system}$$

$$\mu' = \frac{\delta E_S[n]}{\delta n(r)} = \frac{\delta T_S}{\delta n(r)} + V_{KS}^{(r)} \quad \text{non-interacting system}$$



$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}^{(r)} \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

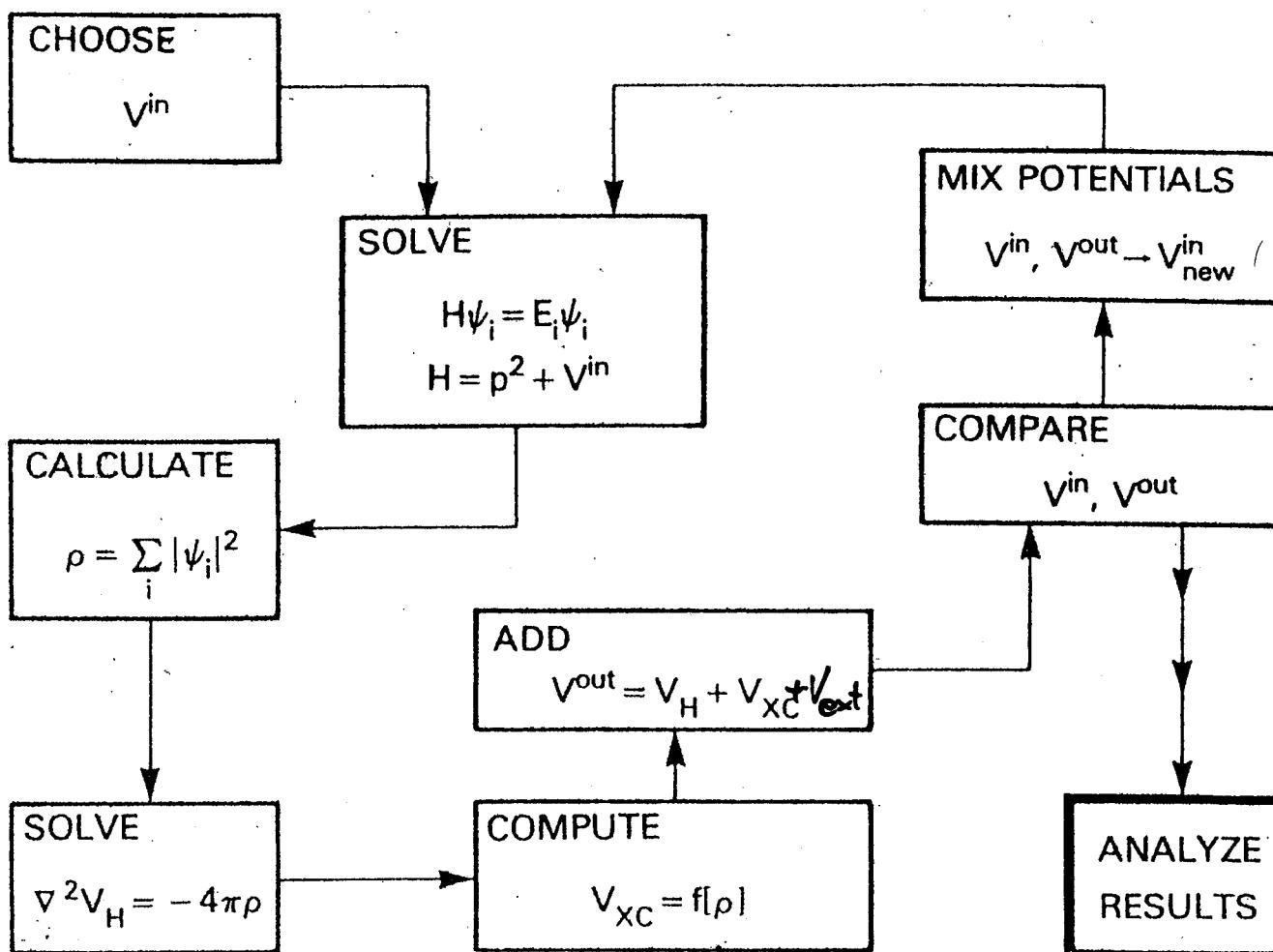
$$n(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}^{(r)} = V_{ext}^{(r)} + V_H^{(r)} + V_{xc}^{(r)}$$

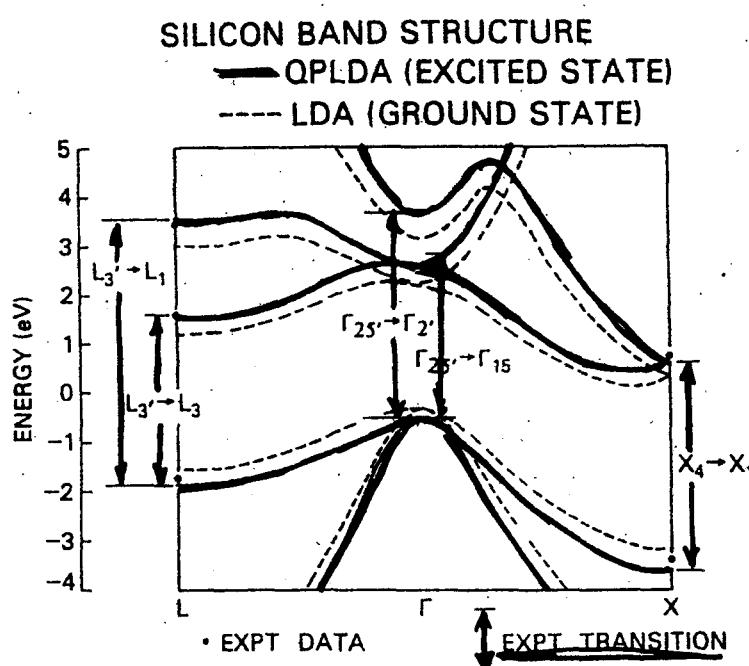
φ_i 's are auxiliary wfs

ε_i 's have no direct physical meaning

SELF-CONSISTENCY IN DENSITY FUNCTIONAL THEORY



WARNING: K-S eigenvalues and wavefunctions are auxiliary quantities without direct physical meaning



- Band gaps are systematically underestimated by DFT
- The shape of the band structure is usually correct
- KS wavefunctions are good approx. of QP amplitudes
- More complex treatments (like GKK) start from KS results
- Together with the charge density, band structure, DOS, wavefunctions give information on the nature of the system studied

in HF theory there are the so called

Koopman's Theorems

$$\text{I) } E_{\text{lost}}^{\text{HF}} \approx -I \quad \text{ionization energy}$$

$$\text{II) } E_{(\text{lost}+1)}^{\text{HF}} \approx -A \quad \text{electron affinity}$$

$$\text{III) } E_{(\text{lost}+1)}^{\text{HF}} - E_{\text{lost}}^{\text{HF}} \approx E_{\text{gap}}$$

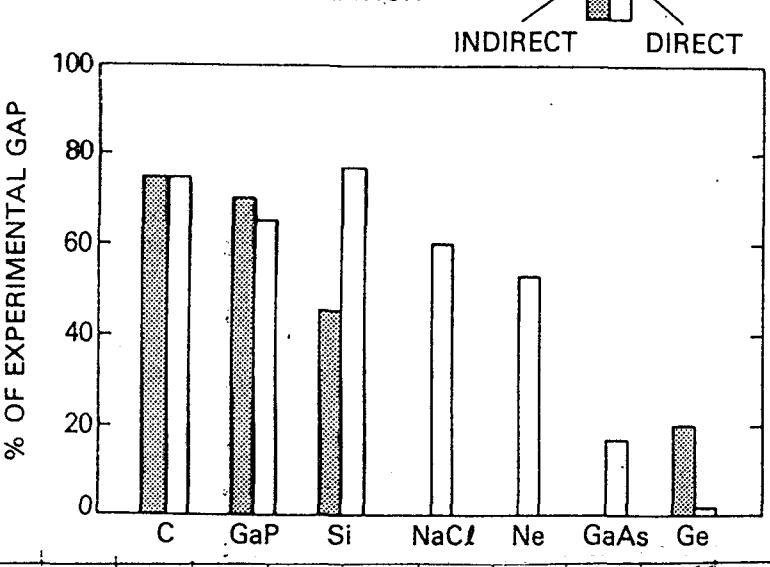
in DFT E 's have no physical meaning (they do not refer to the interacting system but to the fictitious KS's one)

so there's no analogue of Koopman's theorems but for the first one which is exact

$$E_{\text{lost}}^{\text{DFT}} = -I$$

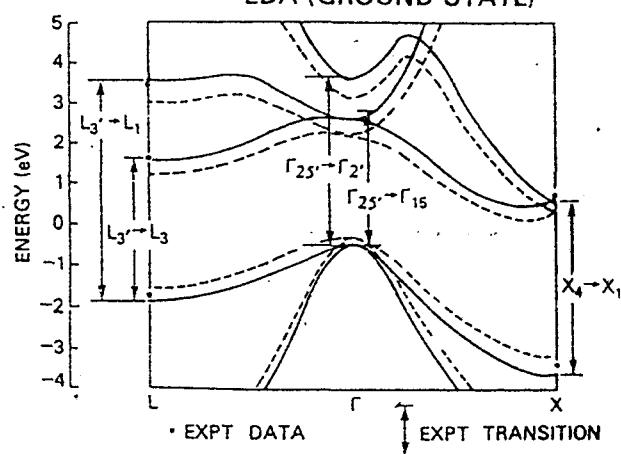
Band Gaps are substantially underestimulated in semiconductors and insulators by DFT (or LDA?)

CALCULATED BAND GAPS
IN LOCAL DENSITY APPROXIMATION



SILICON BAND STRUCTURE

— QPLDA (EXCITED STATE)
--- LDA (GROUND STATE)



Formal expression for $\hat{E}_{xc}^{[n]}$
via coupling constant Integration

$$\hat{H}^{(1)} = \hat{T}_e + \lambda U + V_{ext}^{(1)}$$

$$V_{ee} = \frac{1}{2} \sum \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$F_\lambda[n] = \min_{\psi \rightarrow n} \langle \psi | T + \lambda U | \psi \rangle = \langle \psi_\lambda | T + \lambda U | \psi_\lambda \rangle$$

non-interacting electrons : $\lambda = 0$

$$F_0[n] = T_S[n] \quad V_0 = V_{KS}$$

interacting electrons : $\lambda = 1$

$$F_1[n] = F[n] \quad V_1 = V_{ext}$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \langle \psi_\lambda | U | \psi_\lambda \rangle$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \langle \psi_\lambda | \cup | \psi_\lambda \rangle$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{2} \frac{1}{|r-r'|} n(r) n(r') g(r, r', \lambda)$$

$g(r, r', \lambda)$ = pair correlation function with interaction $\lambda \cup$

$$g(r, r', \lambda) \rightarrow 1 \text{ for } |r-r'| \rightarrow \infty \quad +1 \\ (g(r, r', \lambda) - 1) \rightarrow 0$$

$$F[n] = T_S[n] + \frac{e^2}{2} \int d^3r d^3r' \frac{n(r) n(r')}{|r-r'|} +$$

$$\underbrace{\frac{e^2}{2} \int d^3r d^3r' \frac{n(r) n(r')}{|r-r'|} \int_0^1 d\lambda [g(r, r', \lambda) - 1]}_{E_{xc}}$$

$$n_{xc}(r, r'-r) = n(r') \int_0^1 d\lambda [g(r, r', \lambda) - 1] \quad \text{exchange-correlation hole}$$

$$\int n_{xc}(r, r'-r) d^3r' = -1$$

$$E_{xc} = \frac{e^2}{2} \int d^3r d^3r' n(r) \frac{1}{|r-r'|} n_{xc}(r, r'-r)$$

$$= \frac{e^2}{2} \int d^3r n(r) \int d^3s \frac{1}{|rs|} n_{xc}(r, s)$$

LOCAL DENSITY APPROXIMATION (LDA)

since $g(r, r', \lambda) - 1$ is "short ranged"

$$n_{xc}^{LDA}(r, s) \cong n_{xc}^{\text{hom}}(r, s; n = n(r))$$

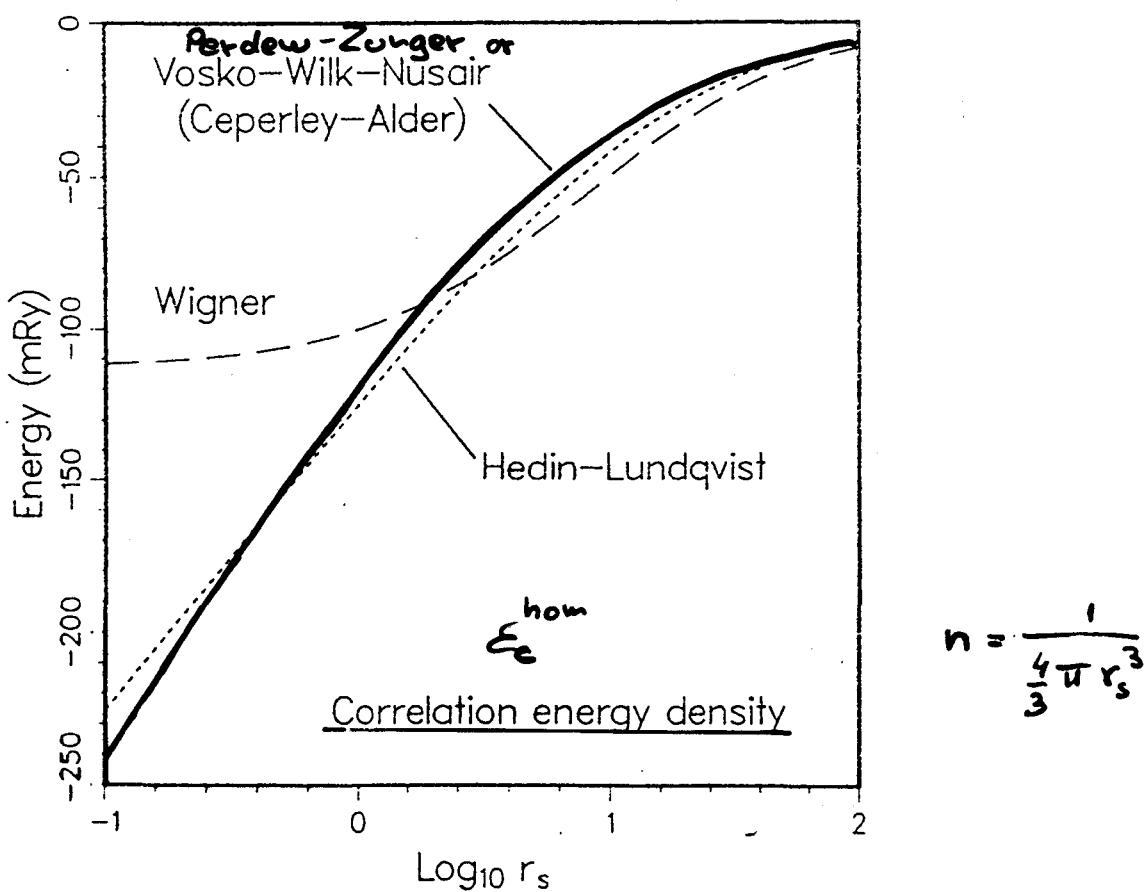
$$E_{xc}^{LDA} = \int d^3r \ n(r) \ E_{xc}^{\text{hom}}(n(r))$$

$$E_{xc}^{\text{hom}}(n) = E_x^{\text{hom}}(n) + E_c^{\text{hom}}(n)$$

$$E_x^{\text{hom}}(n) = -\frac{3}{4\pi} e^2 (3\pi^2 n)^{1/3}$$

$E_c^{\text{hom}}(n)$ from accurate DMC data Ceperley-Alder

Phys. Rev. Lett. 45, 566 (1)



$$V_{xc}^{LDA}(r; [n]) = \frac{d}{dn(r)} E_{xc}^{LDA}[n] = \left. \frac{d(n \cdot E_{xc}^{\text{hom}}(n))}{dn} \right|_{n=n(r)}$$

ZERO PARAMETER THEORY!

Exchange-Correlation Hole in Atoms

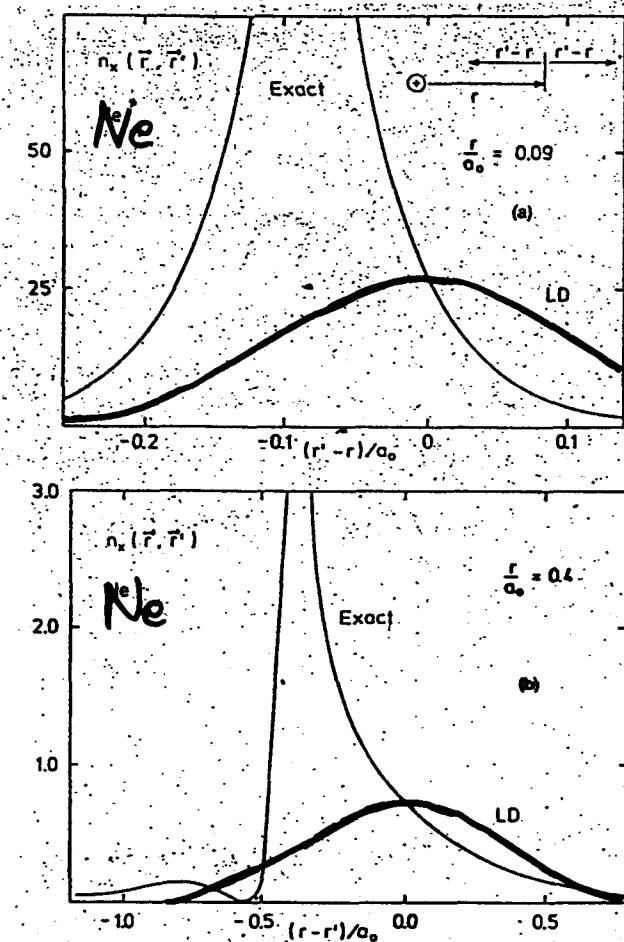


FIG. 5. Exchange hole $n_x(\vec{r}, \vec{r}')$ for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r .

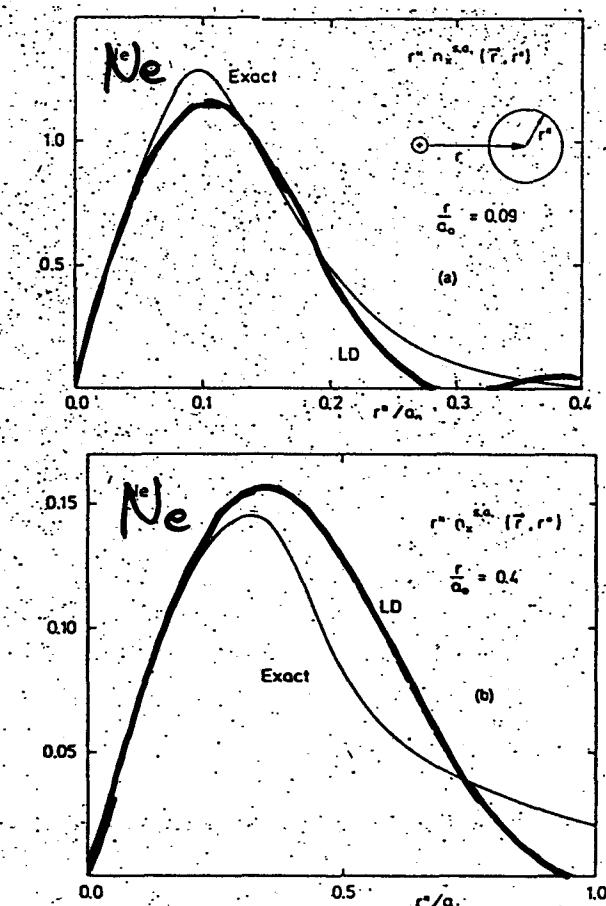


FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times r'' for (a) $r = 0.09$ a. u. and (b) $r = 0.4$ a.u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

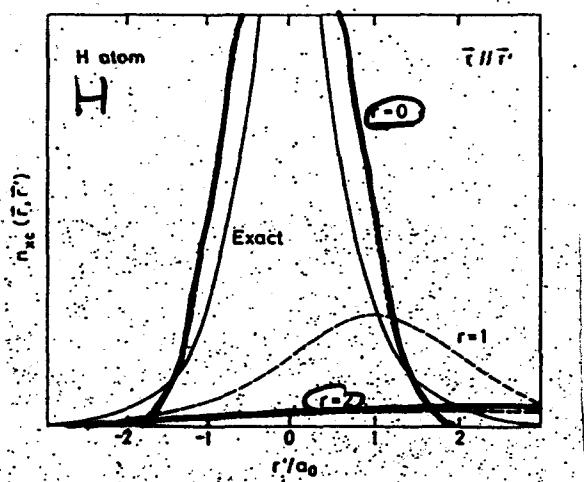


FIG. 4. Exchange-correlation hole $n_{xc}(\vec{r}, \vec{r}')$ (Eq. 15) for a hydrogen atom. The full curve shows the exact hole, while the dashed curves depict the hole in the LD approximation [Eq. (16)] for various positions of the electron (0, 1, and 2 a.u. from the proton), using the dielectric function of Singwi *et al.* (Ref. 37). The x-axis gives the distance from the nucleus.

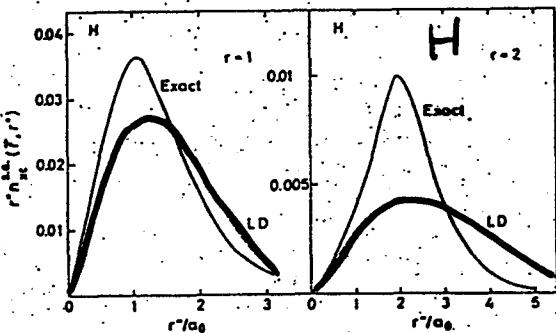


FIG. 6. Spherical average of the hydrogen XC hole [Eq. (16)] times r'' for $r = 1$ and 2 a.u. as a function of r'' . The full curves give the exact results and the dashed curves are calculated in the LD approximation.

The total energy depends directly in terms of the KS orbitals in presence of orthogonality constraints

$$E[\{\varphi_i\}] = \sum_i \langle \varphi_i | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_i \rangle + \frac{e^2}{2} \int \frac{g(r) g(r')}{|r-r'|} d^3r d^3r' + E_{xc}[g] \\ + \int V_{ext}(r) g(r) d^3r + E_{ion} - \sum_{i,j} \lambda_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij})$$

with as usual $g(r) = \sum_i |\varphi_i(r)|^2$

The minimum condition for this functional reads:

$$0 = \frac{\delta E}{\delta \varphi_i^*(r)} = -\frac{\hbar^2}{2m} \nabla^2 \varphi_i(r) + \left\{ V_{ext}(r) + e^2 \int \frac{g(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}}{\delta g(r)} \right\} \varphi_i(r) - \sum_j \lambda_{ij} \varphi_j(r) \\ = \left[\hbar^2 \varphi_i(r) - \sum_j \lambda_{ij} \varphi_j(r) \right]$$

it is equivalent to the KS eqs. up to a unitary transformation in the occupied manifold (that does not change $g(r)$!)

\Rightarrow Global minimization strategies

- steepest descent

$$\varphi_i^{new}(r) = \varphi_i^{old}(r) + \Delta t \cdot \left(-\frac{\partial E}{\partial \varphi_i^*(r)} \right) + \text{orthogonality}$$

- conjugate gradients

- Car-Parrinello dynamics

NB: φ 's at the minimum may not coincide with KS orbitals \rightarrow 2

electrons have spin degrees of freedom and are correlated differently according to it but within DFT V_{xc} is spin independent...

$$\varphi(r, \sigma) = f(r) \cdot \chi(\sigma) \quad \chi = (1), (0)$$

Degenerate GS $\rightarrow n(r)$ is a statistical average
 $n(r) = n_{\uparrow}(r) - n_{\downarrow}(r) = 0$

this is correct but is difficult to implement in simple approximations for E_{xc}

LDA is unsatisfactory in a number of cases

SPIN-DENSITY FUNCTIONAL THEORY

introduce the possibility of coupling to a magnetic field

$$n(r) \rightarrow n_{\alpha\beta}(r) \rightarrow (n_{\uparrow}(r), n_{\downarrow}(r))$$

$$E[n_{\uparrow}, n_{\downarrow}] = T_s[n_{\uparrow}, n_{\downarrow}] + E_H[n] + E_{xc}[n_{\uparrow}, n_{\downarrow}] + \int V_{ext}^{(\alpha)} n(r) d^3r + \int B(r) m(r) d$$

$$T_s = \sum_{\alpha} \sum_i |\nabla \phi_i^{\alpha}(r)|^2 \quad \alpha = \uparrow, \downarrow$$

$$E_{xc}^{LSDA} = \int n(r) E_{xc}^{hom}(n_{\uparrow}(r), n_{\downarrow}(r)) d^3r$$

$$\left. \begin{array}{l} \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ks}^{\alpha}(r) \right] \phi_i^{\alpha}(r) = \varepsilon_i^{\alpha} \phi_i^{\alpha}(r) \\ n_{\alpha}(r) = \sum_i |\phi_i^{\alpha}(r)|^2 \quad n(r) = \sum_{\alpha} n_{\alpha}(r), \quad m(r) = n_{\uparrow}(r) - n_{\downarrow}(r) \\ V_{ks}^{\alpha}(r) = V_{ext}^{(\alpha)} \pm B(r) + V_H(r) + \frac{\delta E_{xc}}{\delta n_{\alpha}} \end{array} \right\}$$

- tendency to favour more homogeneous systems
- Overbinding of molecules and solids
-
- Good chemical trends

in good systems (covalent, metallic, ionic bonds
 bonding from region of high density)

- geometry is good
- bondlengths and angles within a few %
- phonons within a few %,
- dielectric, piezoelectric constant ~10% too large

in bad systems: weakly bonded systems (H-bonded
 Van der Waals)
 much too short bondlengths, large overbinding

Atoms: $-\frac{e^2}{r}$, dissociation limit

- strongly correlated systems

Generalized Gradient Approximations (GGA)

Local Density Approximation

$$E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}^{\text{hom}}(n(r)) d^3r$$

to go beyond LDA make a gradient expansion

$$E_{xc}^{GC}[n] = \int [n(r) \epsilon_{xc}(n(r)) + C(n(r)) \frac{|\nabla n|^2}{h^{4/3}} + \dots] d^3r$$

- improves LDA for slowly varying density $|\nabla n| \ll 1$
- gives worse results for realistic systems
- sum-rules for $\eta_{xc}(r, r')$ are not fulfilled

GGA

$$E_{xc}^{GGA}[n] = \int n(r) \epsilon_{xc}^{(1s)} d^3r + \int \epsilon_{xc}^{(2s)}[n(r), |\nabla n(r)|] d^3r$$

the correction function, ϵ_{xc} , is chosen to satisfy formal conditions for the xc hole and fit to exact xc energies for atoms

NOT A UNIQUE RECIPE

$$E_{xc}[\rho] = \int \epsilon_x(\rho, \nabla\rho, \nabla^2\rho) d^3r$$

$$k_F = (3\pi^2\rho)^{1/3}, \quad k_s = \left(\frac{4}{\pi} k_F\right)^{1/2}, \quad s = \frac{|\nabla\rho|}{2k_F\rho},$$

$$t = \frac{|\nabla\rho|}{2k_F\rho}, \quad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}.$$

All the parameters that appear in the following functionals are in atomic units.

LDA exchange functional:

$$\epsilon_x^{\text{LDA}} = A_x \rho^{4/3}, \quad (\text{A2})$$

where $A_x = -(3/4)(3/\pi)^{1/3}$.

LDA correlation functional (Perdew-Wang¹³):

$$\epsilon_c^{\text{LDA}} = -2ap(1+\alpha_1 r_s) \times \log \left[1 + \frac{1}{2a(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right], \quad (\text{A3})$$

where $a=0.031\ 0907$, $\alpha_1=0.213\ 70$, $\beta_1=7.5957$, $\beta_2=3.5876$, $\beta_3=1.6382$, and $\beta_4=0.492\ 94$.

Langreth-Mehl exchange-correlation functional:¹⁰

$$\epsilon_x = \epsilon_x^{\text{LDA}} - a \frac{|\nabla\rho|^2}{\rho^{4/3}} \left(\frac{7}{9} + 18f^2 \right), \quad (\text{A4})$$

$$\epsilon_c = \epsilon_c^{\text{RPA}}(\rho) + a \frac{|\nabla\rho|^2}{\rho^{4/3}} (2e^{-F} + 18f^2), \quad (\text{A5})$$

where $F=b|\nabla\rho|/\rho^{7/6}$, $b=(9\pi)^{1/6}f$, $a=\pi/(16(3\pi^2)^{4/3})$, and $f=0.15$.

Perdew-Wang '86 exchange functional:¹⁴

$$\epsilon_x = \epsilon_x^{\text{LDA}}(\rho) \left(1 + 0.0864 \frac{s^2}{m} + b s^4 + c s^6 \right)^m, \quad (\text{A6})$$

where $m=1/15$, $b=14$ and $c=0.2$.

Perdew-Wang '86 correlation functional:¹⁵

$$\epsilon_c = \epsilon_c^{\text{LDA}}(\rho) + e^{-\Phi} C_c(\rho) \frac{|\nabla\rho|^2}{\rho^{4/3}}, \quad (\text{A7})$$

where

$$\Phi = 1.745 \int \frac{C_c(\infty)}{C_c(\rho)} \frac{|\nabla\rho|}{\rho^{7/6}},$$

$$C_c(\rho) = C_1 + \frac{C_2 + C_3 r_s + C_4 r_s^2}{1 + C_5 r_s + C_6 r_s^2 + C_7 r_s^3}, \quad (\text{A8})$$

and $\tilde{f}=0.11$, $C_1=0.001\ 667$, $C_2=0.002\ 568$, $C_3=0.023\ 266$, $C_4=7.389 \times 10^{-6}$, $C_5=8.723$, $C_6=0.472$, $C_7=7.389 \times 10^{-2}$.

Perdew-Wang '91 exchange functional:¹¹

$$\epsilon_x = \epsilon_x^{\text{LDA}}(\rho) \left[\frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2}) s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4} \right], \quad (\text{A9})$$

where $a_1=0.196\ 45$, $a_2=7.7956$, $a_3=0.2743$, $a_4=-0.1508$, and $a_5=0.004$.

Perdew-Wang '91 correlation functional:¹¹

$$\epsilon_c = [\epsilon_c^{\text{LDA}}(\rho) + \rho H(\rho, s, t)], \quad (\text{A10})$$

where

$$H = \frac{\beta^2}{2\alpha} \log \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right] + C_{c0} [C_c(\rho) - C_{c1}] t^2 e^{-100s^2},$$

$$A = \frac{2\alpha}{\beta} [e^{-2\alpha\epsilon_c(\rho)/\beta^2} - 1]^{-1},$$

and $\alpha=0.09$, $\beta=0.066\ 726\ 3212$, $C_{c0}=15.7559$, $C_{c1}=0.003\ 521$. The function $C_c(\rho)$ is the same as for the Perdew-Wang '86 correlation functional. $\epsilon_c(\rho)$ is defined so that $\epsilon_c^{\text{LDA}}(\rho)=\rho\epsilon_c(\rho)$.

Becke '88 exchange functional:⁸

$$\epsilon_x = \epsilon_x^{\text{LDA}}(\rho) \left[1 - \frac{\beta}{2^{1/3} A_x} \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \right], \quad (\text{A11})$$

where $x = 2(6\pi^2)^{1/3}s = 2^{1/3}|\nabla\rho|/\rho^{4/3}$, $A_x=(3/4)(3/\pi)^{1/3}$, and $\beta=0.0042$.

Wilson-Levy correlation functional:¹²

$$\epsilon_c = \frac{a\rho + b|\nabla\rho|/\rho^{1/3}}{c + d|\nabla\rho|/(\rho/2)^{4/3} + r_s}, \quad (\text{A12})$$

where $a=-0.748\ 60$, $b=0.060\ 01$, $c=3.600\ 73$, and $d=0.900\ 00$.

Closed shell Lee-Yang-Parr correlation functional:¹⁶

$$\epsilon_c = -a \frac{1}{1+d\rho^{-1/3}} \left[\rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_W + \frac{1}{9} \times \left(t_W + \frac{1}{2} \nabla^2 \rho \right) \right] e^{-c\rho^{-1/3}} \right], \quad (\text{A13})$$

where

$$t_W = \frac{1}{8} \left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2 \rho \right), \quad (\text{A14})$$

and $C_F=3/10(3\pi^2)^{2/3}$, $a=0.049\ 18$, $b=0.132$, $c=0.2533$, and $d=0.349$.

Perdew-Burke-Ernzerhof PRL 72 3855 (1995)

¹P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

²W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1976).

³N. R. Kestner and O. Sinanoglu, Phys. Rev. 128, 2687 (1962).

⁴P. M. Laufer and J. B. Krieger, Phys. Rev. A 33, 1480 (1986).

⁵S. Kais *et al.*, J. Chem. Phys. 99, 417 (1993).

⁶M. Taut, Phys. Rev. A (in press).

⁷C. Umrigar and X. Gonze (unpublished).

⁸A. D. Becke, Phys. Rev. A 33, 3098 (1986).

TABLE IV. Known properties of the exact density functional

Property	E_{xc}^{LDA} Ref. [6]	E_{xc}^{LM} Ref. [34]	E_{xc}^{PW91} Ref. [36]	E_x^{B88} Ref. [37]	E_x^{ECMV} Ref. [38]	E_c^{WL} Ref. [39]	E_c^{LYP} Ref. [40]
1. $\rho_x(r, r') \leq 0$	Y	-	Y	-	-	-	-
2. $\int \rho_x(r, r') dr' = -1$	Y	-	Y	-	-	-	-
3. $\int \rho_c(r, r') dr' = 0$	Y	-	Y	-	-	-	-
4. $E_x[\rho] < 0$	Y	Y	Y	Y	Y	-	-
5. $E_c[\rho] \leq 0$	Y	N	N	-	-	N	N
6. $E_x[\rho], E_{xc}[\rho] \geq -c \int \rho^{4/3} dr$ ^a	Y	N	Y	Y	N	-	-
7. $E_x[\rho_\lambda] = \lambda E_x[\rho]$ ^b	Y	Y	Y	Y	Y	-	-
8. $E_c[\rho_\lambda] < \lambda E_c[\rho], \lambda < 1$ ^c	Y	N	Y	-	-	N	N
9. $\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda] > -\infty$	N	Y	Y	-	-	Y	Y
10. $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_c[\rho_\lambda] > -\infty$	Y	N	Y	-	-	Y	Y
11. $\lim_{\lambda \rightarrow \infty} E_x[\rho_\lambda^x] > -\infty$ ^c	N	N	Y	N	N	-	-
12. $\lim_{\lambda \rightarrow 0} E_x[\rho_\lambda^x] > -\infty$	Y	N	Y	Y	Y	-	-
13. $\lim_{\lambda \rightarrow \infty} \frac{1}{\lambda} E_x[\rho_\lambda^{xy}] > -\infty$ ^d	Y	N	Y	Y	Y	-	-
14. $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_x[\rho_{\lambda\lambda}^{xy}] > -\infty$	N	N	Y	N	N	-	-
15. $\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_\lambda^x] > -\infty$	N	Y	Y	-	-	N	N
16. $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_c[\rho_\lambda^x] = 0$	N	N	Y	-	-	N	N
17. $\lim_{\lambda \rightarrow \infty} E_c[\rho_{\lambda\lambda}^{xy}] = 0$	N	N	Y	-	-	N	N
18. $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda^2} E_c[\rho_{\lambda\lambda}^{xy}] > -\infty$	N	Y	Y	-	-	N	N
19. $\epsilon_x(r) \rightarrow -\frac{1}{2r}, r \rightarrow \infty$	N	N	N	YN ^g	N	-	-
20. $v_x(r) \rightarrow -\frac{1}{r}, r \rightarrow \infty$	N	N	N	N	N	-	-
21. $v_x(r), v_c(r) \rightarrow \text{finite value}, r \rightarrow 0$	Y	N	N	N	N	N	N
22. LDA limit for constant $\rho(r)$	Y	N	Y	Y	Y	N	N

^a $1.44 < c < 1.68$
^b $\rho_\lambda(r) = \lambda^3 \rho(\lambda r); \quad \rho_\lambda^x(r) = \lambda \rho(\lambda x, y, z); \quad \rho_{\lambda\lambda}^{xy}(r) = \lambda^2 \rho(\lambda x, \lambda y, z)$
^c Note that $E_c[\rho_\lambda] < \lambda E_c[\rho], \lambda < 1$ is equivalent to $E_c[\rho_\lambda] > \lambda E_c[\rho], \lambda > 1$.

^f But it diverges to $+\infty$
^g "Y" for exponential $\rho(r)$, but "N" in general, e.g. $\epsilon_x^{\text{B88}}(r) \rightarrow -1/r$ for a gaussian.

GC (or GGA) vs LDA

- improves binding energies (better atomic energies)
(but Be_2 : $E_{\text{exp}} = 0.11 \text{ eV}$ $\text{LDA} = 0.53 \text{ eV}$ $\text{GC} = 0.36 \text{ eV}$)
- bond lengths of IIA and IIB homonuclear dimers are much better
- water clusters and ice: much better geometries and energies
H-bond ok
- Si, Ge, GeAs are better in LDA (not the binding energy)
- 4d-5d metals: it is not clear
- no improvement for the gap problem (nor for dielectric constants)

The improvement is not systematic and probably due
to the wrong reasons.

GGA are fitted on atomic total xc energies: locally they
are not better than LDA

They do not satisfy known asymptotic behaviour

In an atom:

$$V_{xc} \underset{r \rightarrow \infty}{\sim} -\frac{e^2}{r} \quad \text{while} \quad V_{xc}^{\text{LDA, GGA}} \underset{r \rightarrow 0}{\text{vanishes exponentially}}$$

$$V_{xc} \underset{r \rightarrow 0}{\Rightarrow \text{const}} \quad \text{while} \quad V_{xc}^{\text{LDA}} \underset{r \rightarrow 0}{=} \text{const}$$
$$V_{xc}^{\text{GGA}} \underset{r \rightarrow 0}{=} -\infty$$