

Ab-initio methods in electronic structure calculations

Methods based on Density Functional Theory

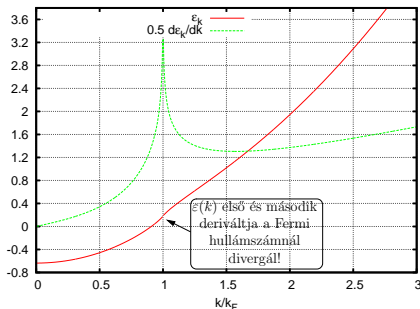
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December 7, 2006

Free electron gas in HF approximation

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{k_F}{\pi} \left(1 + \frac{1 - y^2}{2y} \ln \left| \frac{1 + y}{1 - y} \right| \right), \quad y = \frac{k}{k_F}$$

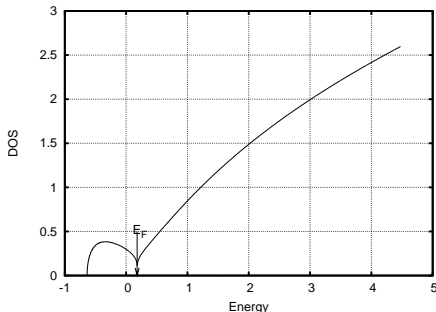


$$\varepsilon_x = \frac{3}{2\pi} k_F = \frac{3}{2\pi} \left(3\pi^2 \rho_0 \right)^{1/3}$$

$$E_x(\rho_0) = \frac{3}{2\pi} \left(3\pi^2 \rho_0 \right)^{1/3} \rho_0$$

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Basic theorems of DFT

Hohenberg - Kohn theorems

- Bijection between V_{ext} and $\rho(r)$ for ground state

- V external potential $\implies \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \implies \rho(\mathbf{r})$

- $\rho(\mathbf{r}) \implies V$

$$E = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' - V' + V | \Psi' \rangle =$$

$$E' + \langle \Psi' | V - V' | \Psi' \rangle = E' + \int \rho(r)(v(r) - v'(r))d^3r$$

$$E' = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H - V + V' | \Psi \rangle = E - \int \rho(r)(v(r) - v'(r))d^3r$$

$$E - E' < E' - E$$

- For a given external potential V the exact density $\rho(r)$ minimizes the ground-state energy E_0 , which is a uniquely determined functional.

Levy-Lieb functional

$$\{\Psi_i\} \text{ where } \int \Psi_i d\mathbf{r}_2^3 d\mathbf{r}_3^3 \dots d\mathbf{r}_N^3 = \rho(\mathbf{r}) \quad E[\rho] = \min\{\langle \Psi | H | \Psi \rangle\}$$

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$$\int \rho(r)d^3r = N, \quad \frac{\delta E[\rho]}{\delta \rho} = \mu$$

Kohn-Sham equation

$$E = T + V + W$$

T : kinetic energy of interacting electrons.

- Kohn-Sham picture

- T : kinetic energy of non interacting electrons

- $\rho(r) = \sum_i \phi_i^*(r)\phi_i(r) \quad |\phi_i\rangle\langle\phi_j| = \delta_{ij}$

$$E[\rho] = \sum_i \int \phi_i \Delta \phi_i d^3r + \int \rho(r)v(r)d^3r + \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho]$$

Kohn-Sham equation

$$-\Delta\phi_i(r) + (v(r) + v_H(r) + v_{xc}(r))\phi_i(r) = \lambda_i\phi_i(r)$$

$$v_H(r) = \int \frac{\rho(r')}{|r-r'|} d^3r',$$

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

Properties of the Kohn-Sham equations

- Expression for total energy:

$$E = \sum_i \lambda_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}^3 - \mu_B \int \mathbf{B}_{xc}(\mathbf{r})\mathbf{m}(\mathbf{r})d\mathbf{r}^3$$

- Interpretation of Kohn-Sham Lagrange multiplier λ_i
 - Local effective potential
 - No Koopman's theorem - can not be interpreted as one-particle energies
 - Exact Fermi level for metals and top and bottom of the valence and conduction band for semiconductors

$$E_N - E_{N-1} = \int \frac{\delta E}{\delta \rho} \delta \rho(\mathbf{r}) d\mathbf{r}^3 = \int \mu \delta \rho(\mathbf{r}) d\mathbf{r}^3 = \mu = \lambda_{HOMO}$$

Local Density Approximation

- $E(\rho_0) = \varepsilon(\rho_0)\rho_0$ is determined for free electron gas
- ρ_0 is substituted by $\rho(\mathbf{r})$

$$E_{xc} = \int \varepsilon(\rho(\mathbf{r}))\rho(\mathbf{r})d^3r$$

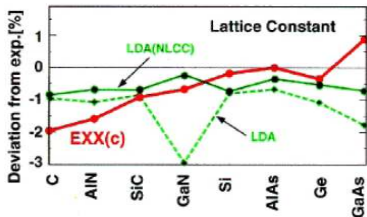
From HF results $E_x \sim \rho^{4/3}$, $v_x(r) \sim \rho^{1/3}$

- Analytic methods
 - U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972)
 - O. Gunnarsson and B. I. Lundqvist, Phys. Rev. **B 13**, 4274 (1976)
 - Vosko, Wilk, and Nusair, Can. J. Phys. **58**, 1200 (1980)
 - Perdew and Zunger Phys. Rev. **B 23**, 5048 (1981)
 - J. P. Perdew and Y. Wang, Phys. Rev. **B 45**, 13244 (1992)
- QMC
 - Ceperley and Alder, Phys. Rev. Lett. **45**, 566 (1980)

Success of LDA

● Geometries

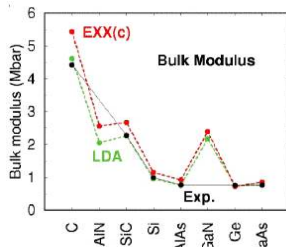
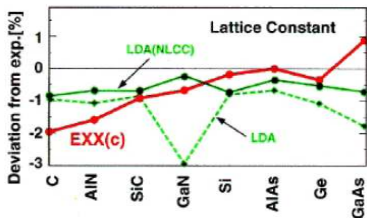
- The accuracy of geometries is better than 0.1 Å
- For certain geometries even comparable to accuracy of CI calculations (10⁻² Å)
- Lattice constants are obtained within 4% or better
- Accuracy for calculated energies better than 0.2 eV/atom, in special cases even better than 0.01 eV/atom.
- Atomization energies in simple molecules: up to 4 kcal/mol (0.2 eV/atom)



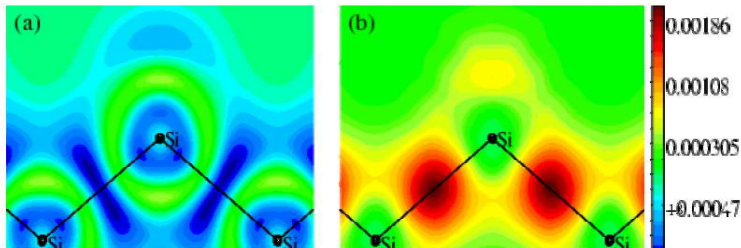
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Success of LDA



The difference between the exchange (left) and correlation (right) energy densities computed using variation quantum Monte Carlo and the local density approximation in bulk Silicon (Phys. Rev. Lett. **78** 3350 1997)

exchange energy underestimated
correlation energy overestimated } **cancellation of errors**

Extensions of LDA

- LSDA $E_{xc}[\rho, m]$, $\rho = \rho_{\uparrow} + \rho_{\downarrow}$, $m = \rho_{\uparrow} - \rho_{\downarrow}$

$$\left(\left(-\frac{\hbar^2}{2m} \Delta + v(r) + v_H(r) + v_{xc}(r) \right) \mathbb{I} + B_{xc} \sigma_z \right) \begin{pmatrix} \phi_{i\uparrow}(r) \\ \phi_{i\downarrow}(r) \end{pmatrix} = \lambda_i \begin{pmatrix} \phi_{i\uparrow}(r) \\ \phi_{i\downarrow}(r) \end{pmatrix}$$

- GGA (Generalized Gradient Correction)

$$E_{xc} = \int F(\rho_{\uparrow}(r), \rho_{\downarrow}(r), \Delta\rho_{\uparrow}(r), \Delta\rho_{\downarrow}(r)) dr^3$$

- Perdew: More ab-initio
- Becke: More semi empirical. Most widely applied
- Hybrid functionals: LDA + GGA + HF

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- **LSDA** $E_{xc}[\rho, m]$, $\rho = \rho_{\uparrow} + \rho_{\downarrow}$, $m = \rho_{\uparrow} - \rho_{\downarrow}$

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SIC

Self Interaction Correction

- Both in the Hartree and in the exchange terms the electrons interact themselves
- For delocalized electrons the error decreases as $1/V$.
- For localized electrons the error could be large.

$$E_{xc}^{SIC}(\rho_{\uparrow}, \rho_{\downarrow}) = E_{xc}(\rho_{\uparrow}, \rho_{\downarrow}) - \sum_i (E_H(\rho_{i\uparrow}) + E_{xc}(\rho_{i\uparrow}, 0)) - \sum_i (E_H(\rho_{i\downarrow}) + E_{xc}(\rho_{i\downarrow}, 0))$$

$$\rho_{i\alpha} = |\phi_{i\alpha}(r)|^2$$

Solution of the Kohn-Sham equation

- Wave-function methods: PW, APW, LMTO, LAPW
- Green's function methods: KKR, LMTO

Plane Wave method

- Basis functions are plane waves:

$$\chi_{\mathbf{k}}(\mathbf{k}, \mathbf{r}) = \frac{1}{V} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}}, \quad \psi(\mathbf{k}) = \sum_{\mathbf{K}} c_{\mathbf{K}}(\mathbf{k}) \chi_{\mathbf{K}}(\mathbf{k}, \mathbf{r})$$

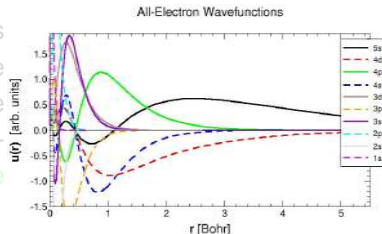
- Eigen value equation for the coefficients:

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 \delta_{\mathbf{K}, \mathbf{K}'} + V_{\mathbf{K}, \mathbf{K}'} \right) c_{\mathbf{K}'}(\mathbf{k}) = \varepsilon(\mathbf{k}) c_{\mathbf{K}}(\mathbf{k})$$

$$V_{\mathbf{K}, \mathbf{K}'} = \frac{1}{V} \int_V V_{\text{eff}}(\mathbf{r}) e^{i(\mathbf{K}' - \mathbf{K})\mathbf{r}} d^3r$$

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Core electrons have nodes close to the nucleus. The smallest distance between the nucleus and the nodes determines the maximum of \mathbf{K} . Huge number of \mathbf{K} points are needed!



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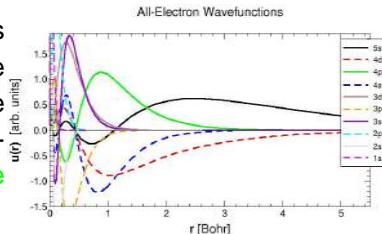
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Pseudo Potentials

- $|\psi_c\rangle$ and $|\psi_v\rangle$ are the core and valence wave-functions.
- Choose a smooth function $|\phi_v\rangle$:

$$|\psi_v\rangle = |\phi_v\rangle - \sum_c |\psi_c\rangle \langle \psi_c | \phi_v \rangle$$

$$(H - (E_c - E_v)|\psi_c\rangle \langle \psi_c|) |\phi_v\rangle = E_v |\phi_v\rangle$$

- Pseudo potential: $w = v - (E_c - E_v)|\psi_c\rangle \langle \psi_c|$
Generally the pseudo potential is looked for in the form of:
 $w(\mathbf{r}, \mathbf{r}') = \sum_L Y_{lm}^*(\hat{\mathbf{r}}) w_l(r) \delta(r - r') Y_{lm}(\hat{\mathbf{r}}')$

Properties of the pseudo wave-functions

- The pseudo and the exact radial wave-functions must be identical if $r > r_l$.
- The norm of the pseudo and exact wave-functions must be the same.
- One-particle energies must be the same.

Example: Troulier-Martins Potential

- Chose a smooth radial wave-functions:

$$R_l(r) = \begin{cases} R_l^{\text{exact}}(r) & \text{if } r > r_l \\ r^l e^{p(r)} & \text{if } r < r_l \end{cases} \quad p(r) = \sum_{n=0}^6 c_n r^{2n}$$

- Find a potential which results in $R_l(r)$ as a solution of the atomic Kohn-Sham equation.

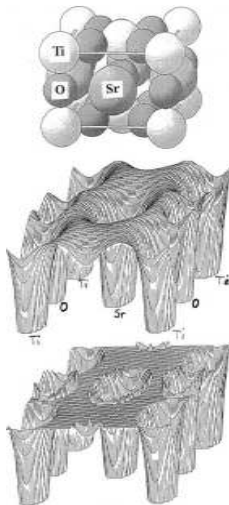
$$w_l(r) = \varepsilon - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_l(r)} \frac{d^2}{dr^2} (rR_l(r))$$

Augmented Plane Wave Method

- Muffin-tin potential
- Basis: linear combination of the radial solution of the KS equation inside MT sphere, plane wave outside

$$\chi(\mathbf{r}, E) = \begin{cases} \sum_L A_{lm} Y_{lm}(\hat{\mathbf{r}}) R_l(r, E) & \text{if } r < r_{MT} \\ e^{i\mathbf{k}\mathbf{r}} & \text{if } r > r_{MT} \end{cases}$$

- The basis is continuous on the MT sphere but the radial derivative is not.



Linearized Augmented Plane Wave Method

- The Wigner-Seitz cell is divided into MT sphere and interstitial space but the potential is not necessary MT potential.
- The radial wave-function is calculated at fixed energy and the basis is linear combination of the radial solution of the KS equation and its derivative with respect of the energy inside MT sphere.

$$\chi(\mathbf{r}, E) = \begin{cases} \sum_L \left(A_{lm} Y_{lm}(\hat{\mathbf{r}}) R_l(r, E) + B_{lm} Y_{lm}(\hat{\mathbf{r}}) \dot{R}_l(r) \right) & (\text{if } r < r_{MT}) \\ e^{i\mathbf{k}\mathbf{r}} & \text{if } r > r_{MT} \end{cases}$$

- The logarithmic derivative of the basis is continuous.