Density Functional Theory for Electrons in Materials

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OUTLINE

- The many-body electron problem
- Hohenberg-Kohn Theorems
- Kohn-Sham Ansatz
- Functionals for Exchange and Correlation
  - LDA - Local Density Approximation
  - GGA - Generalized Gradient Approximations
- Solution of the Kohn-Sham "Schrodinger-like" Equations
- Results: H, He, H_2
- Results: Solids
- Results: Molecules: GGA
- Failures!

The Fundamental Hamiltonian

$$\begin{aligned}\hat{H} = & - \sum_i \frac{\hbar^2}{2m_e}\boldsymbol{\nabla}_i^2 + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_I \frac{\hbar^2}{2M_I}\boldsymbol{\nabla}_I^2 \quad + \quad \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned} \tag{1}$$

- Born-Openheimer Approximation: There is only one small term, the kinetic energy of the nuclei. If we omit this term, the nuclei are a *fixed external potential acting on the electrons*
- The final term is essential for charge neutrality – but is a classical term that is added to the electronic part
- **The first line is the key problem for** *ab initio* **prediction of the properties of materials**
- The ground state energy as a function of the positions of the nuclei determine:
  - Stable Structures – Phase transitions
  - Mechanical Deformations – Phonons, etc.
- The excited states determine "electronic" properties:
  - Electronic Bands, Optical properties, etc.

Many-Body Electron Problem

The electron Hamiltonian is (we will use atomic units ($\hbar = m_e = 1$) to simplify some equations below)

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int}, \tag{2}$$

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}_{ext}$ is the potential acting on the electrons due to the nuclei,

$$\hat{V}_{ext} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|), \tag{3}$$

$\hat{V}_{int}$ is the many-body electron-electron interaction.

The total energy is the expectation value

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \equiv \langle\hat{H}\rangle = \langle\hat{T}\rangle + \langle\hat{V}_{int}\rangle + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}). \tag{4}$$

The ground state wavefunction Ψ_0 is the state with lowest energy; that obeys the symmetries of the particles and all conservation laws.

"Hellmann-Feynman" Theorem

The force on any nucleus is determined by the wavefunction, despite the fact that the wavefunction changes as the atoms move.

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int d^3r n(\mathbf{r}) \frac{\partial V_{ext}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{II}}{\partial \mathbf{R}_I} \qquad (5)$$

This follows because the energy is at an extremum with respect to any variations in the wavefunction at the exact solution. Only the *explicit* dependence of the nulcear position is needed.

The force is determined by the electron density! (Feynman, 1939)

(The ideas also hold for non-local pseudopotentials, but the force depends upon the wavefunction and not just the density.)

Hohenberg-Kohn Theorems

- Theorem I: For any system of electrons in an external potential $V_{ext}(\mathbf{r})$, that potential is determined uniquely, except for a constant, by the ground state density $n(\mathbf{r})$.

  Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, the full many-body wavefunction and all other properties of the system are also completely determined!

- Theorem II: A *universal functional* for the energy $E[n]$ of the density $n(\mathbf{r})$ can be defined for all electron systems. The exact ground state energy is the global minimum for a given $V_{ext}(\mathbf{r})$, and the density $n(\mathbf{r})$ which minimizes this functional is the exact ground state density.

  Corollary II: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. Excited states of the electrons must be determined by other means.

- Comment: The exact functionals are unknown and must be very complicated!

Proof of Hohenberg-Kohn Theorems

Proof of Theorem I:

Suppose that there were two different external potentials $V_{ext}^{(1)}(\mathbf{r})$ and $V_{ext}^{(2)}(\mathbf{r})$ with the same ground state density $n(\mathbf{r})$. The two external potentials lead to two different hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same density $n(\mathbf{r})$. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \quad (6)$$

which leads to

$$E^{(1)} < E^{(2)} + \int d^3r \{ V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \} n(\mathbf{r}). \quad (7)$$

But changing the labels leads to

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r}) \} n(\mathbf{r}). \quad (8)$$

which is a contradiction!

Theorem II (Not proved here) leads to

$$\begin{aligned} E_{HK}[n] &= T[n] + V_{int}[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) \\ &\equiv F_{HK}[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) \end{aligned} \quad (9)$$

The Levy-Leib Functional

The Hohenberg-Kohn Theorems tell us *nothing* about how to construct a functional. Levy and Lieb gave a derivation that shows what the the functional really is: the minimum energy for all possible many-body wave-functions having the given density.

The idea of Levy and Lieb (LL) is to define a *two-step* minimization procedure:

$$\begin{aligned} E_{LL}[n] &= \min_{\Psi \to n(\mathbf{r})} [\langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{int} | \Psi \rangle] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{II} \\ &\equiv F_{LL}[n] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{II}, \end{aligned} \tag{10}$$

where the Levy-Lieb functional of the density is defined by

$$F_{LL}[n] = \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{int} | \Psi \rangle. \tag{11}$$

In this form $E_{LL}[n]$ is manifestly a functional of the density and the ground state is found by minimizing $E_{LL}[n]$.

The Kohn-Sham Ansatz

The Kohn-Sham approach is to replace the original difficult interacting-particle hamiltonian with a *different* hamiltonian which could be solved more easily.

Kohn-Sham Hamiltonian for *non-interacting "electrons"* **assumed** to have the same density as the true interacting system

$$H_{eff} = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r}). \tag{12}$$

where

$$n_{eff}(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \tag{13}$$

and the kinetic energy T_{eff} is given by

$$T_{eff} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\langle\psi_i|\nabla^2|\psi_i\rangle, \tag{14}$$

The Kohn-Sham energy is the sum

$$\tilde{E} = T_{eff} + \int V_{ext}(\mathbf{r})n_{eff}(\mathbf{r})dr + E_{Hartree}[n_{eff}] + E_{xc}[n_{eff}], \tag{15}$$

The Kohn-Sham Equations

The ground state can be found by minimizing with respect to the independent-electron wavefunctions $\psi_i(\mathbf{r})$

$$\frac{\partial \tilde{E}[n]}{\partial \psi_i(\mathbf{r})} = \frac{\partial T_{eff}}{\partial \psi_i(\mathbf{r})} + \frac{\partial E_{other}}{\partial n_{eff}(\mathbf{r})} \frac{\partial n_{eff}(\mathbf{r})}{\partial \psi_i(\mathbf{r})} = 0 \qquad (16)$$

subject to the orthonormalization constraints

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j} \qquad (17)$$

The Lagrange multiplier method constraints leads to the Kohn-Sham Schroedinger-like equations:

$$(H_{eff} - \epsilon_i)\psi_i(\mathbf{r}) = 0 \qquad (18)$$

where the ϵ_i are the eigenvalues,

$$H_{eff}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r}). \qquad (19)$$

and

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\partial E_{Hart}}{\partial n_{eff}(\mathbf{r})} + \frac{\partial E_{xc}}{\partial n_{eff}(\mathbf{r})} \qquad (20)$$

$$= V_{ext}(\mathbf{r}) + V_{Hart}[n_{eff}] + V_{xc}[n_{eff}]. \qquad (21)$$

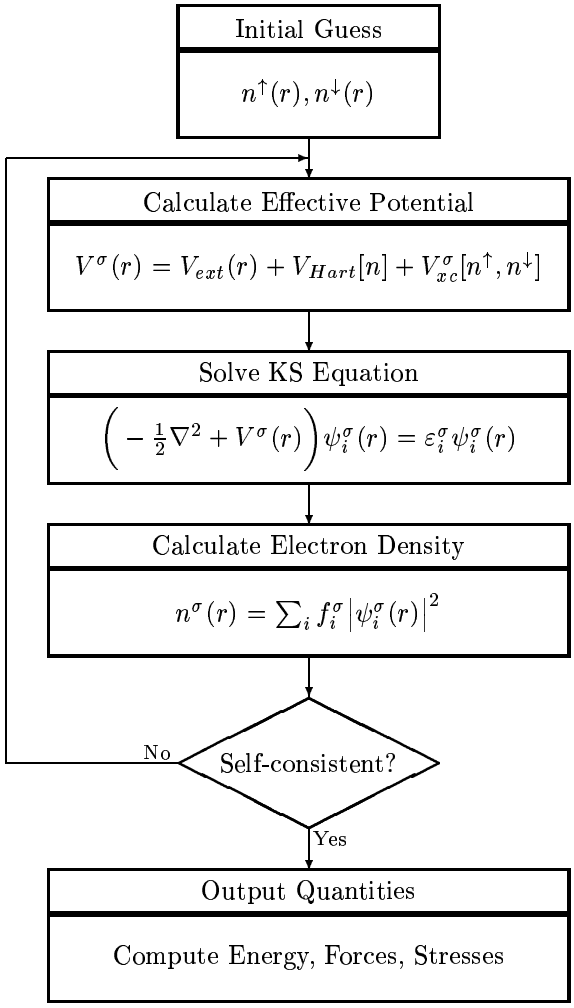
The total energy can be written

$$\tilde{E} = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2}\int V_{Hart}(\mathbf{r}) n_{eff}(\mathbf{r}) dr + (E_{xc}[n] - \int (V_{xc} n_{eff}(\mathbf{r}) dr) \qquad (22)$$

Flow Chart for Kohn-Sham Calculation

Figure 1: Schematic representation of the self-consistent loop for solution of the Kohn-Sham equations. In general one must iterate two such loops simultaneously for the two spins, with the potential for each spin depending upon the density of both spins.

Self-Consistent Kohn-Sham Equations



Exchange-Correlation Functional $E_{xc}[n]$

The Exchange-Correlation energy is defined by

$$\begin{aligned} F_{HK}[n] &= T[n] + V_{int}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle \\ &\equiv T_{eff}[n] + E_{Hartree}[n] + E_{xc}[n] \end{aligned} \quad (23)$$

where

$$E_{Hartree}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}'}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} \quad (24)$$

Key points:

- T_{eff} is really calculated from the wavefunctions!
- $E_{xc}[n]$ contains all the difficult terms is a functional of n by the Hohenberg-Kohn Theorem.
- $E_{xc}[n]$ is reasonably approximated as approximately local – unlike $T_{eff}[n]$ and $E_{Hartree}[n]$

Exchange-Correlation Hole

(See, *e.g.*, *Many-Particle Physics* by Mahan)

Around each electron at point $\mathbf{r}$ other electrons are excluded to form a hole at points $\mathbf{r}'$, $n_{xc}(\mathbf{r}, \mathbf{r}')$.

- The Pauli principle (exchange) causes there to be a hole with *exactly one missing electron* compared to the average density of all electrons including the one under consideration.
- Correlation causes rearrangement but still *exactly one missing electron.*
- The energy is given by the interaction with the hole $\overline{n}_{xc}$ *averaged over all coupling constants* e^2 (not proved here)

$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \int d^3r' \frac{\overline{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (25)$$

LDA - Local Density Approximation

Assume $E_{xc}[n]$ is a sum of contributions from each point in space *depending only upon the density at each point independent of other points*. Then

$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) \tag{26}$$

where $\epsilon_{xc}(n)$ is the x-c energy per electron

- Since $\epsilon_{xc}(n)$ is assumed to be universal, *must be the same as for homogeneous electrons of density* n.
- Exchange (*e.g.,* Aschroft and Mermin, p. 411)

$$\epsilon_x(n) = -\frac{0.458}{r_s} \ \ Hartree, \tag{27}$$

  where r_s is the average distance between electrons given by $\frac{4\pi}{3} r_s^3 = \frac{1}{n}$.

- Correlation found by:
  - RPA approximation - good at high density
  - Interpolation between low and high density - Wigner (1934), Lindberg and Rosen (1970), ...
  - Essentially exact Monte Carlo Calculations done by Ceperley and Alder, 1980

Kohn-Sham Equations in the LDA

In the LDA the potential in Kohn-Sham equations is found as a simple derivative:

$$H_{eff}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r}). \tag{28}$$

and

$$\begin{aligned} V_{eff}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\partial E_{Hart}}{\partial n_{eff}(\mathbf{r})} + \frac{\partial E_{xc}}{\partial n_{eff}(\mathbf{r})} & (29) \\ &= V_{ext}(\mathbf{r}) + V_{Hart}[n_{eff}] + V_{xc}[n_{eff}]. & (30) \end{aligned}$$

where

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}}{\partial n_{eff}(\mathbf{r})} = \frac{\partial n_{eff}(\mathbf{r})\epsilon_{xc}(n_{eff}(\mathbf{r}))}{\partial n_{eff}(\mathbf{r})} \tag{31}$$

The equations are solved self-consistently with the density which results from the eigenfunctions of the independent electron equations

$$n_{eff}(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \tag{32}$$

Kohn-Sham Functional

- The Kohn-Sham solution can be considered a functional of the potential V_{eff}

$$V_{eff}^{in} \rightarrow \psi_i \rightarrow n^{out} \rightarrow E_{KS}[n^{out}]$$

  The energy is given by Eq. 15 (repeated here)

$$\tilde{E} = T_{eff} + \int V_{ext}(\mathbf{r}) n^{out}(\mathbf{r}) dr + E_{Hartree} n^{out}] + E_{xc} n^{out}], \tag{33}$$

- This is a variational expression, *i.e.,* the correct energy is the minimum
- It operationally defines the functional $E_{KS}[n^{out}]$; however, it is not an explicit functional of n^{out}

Explicit Density Functional

- An alternative is to define the energy in terms of the *input* density, *i.e.,* a true density functional. The form proposed by several authors (Weinert, et al (1985), Harris (1985), Foulkes (1989)) is:

$$\begin{aligned}\tilde{E}[n^{in}] &= \sum_{i=1}^{N} \epsilon_i - \frac{1}{2}\int V_{Hart}(\mathbf{r}) n^{in}(\mathbf{r}) dr \\ &- \int ((V_{xc}(n^{in}(\mathbf{r})) - \epsilon_{xc}(n^{in}(\mathbf{r})))n^{in}(\mathbf{r}) dr\end{aligned}$$

  where the eigenvalues are found from the Kohn-Sham hamiltonian with V_{eff} given by the *input* density $n^{in}(\mathbf{r})$

- The solution is the same as the Kohn-Sham solution, but this expression is *not variational*. Usually the energy approaches the correct energy from below. A saddle point.

- The simplest case is where the input density is guessed and never modified

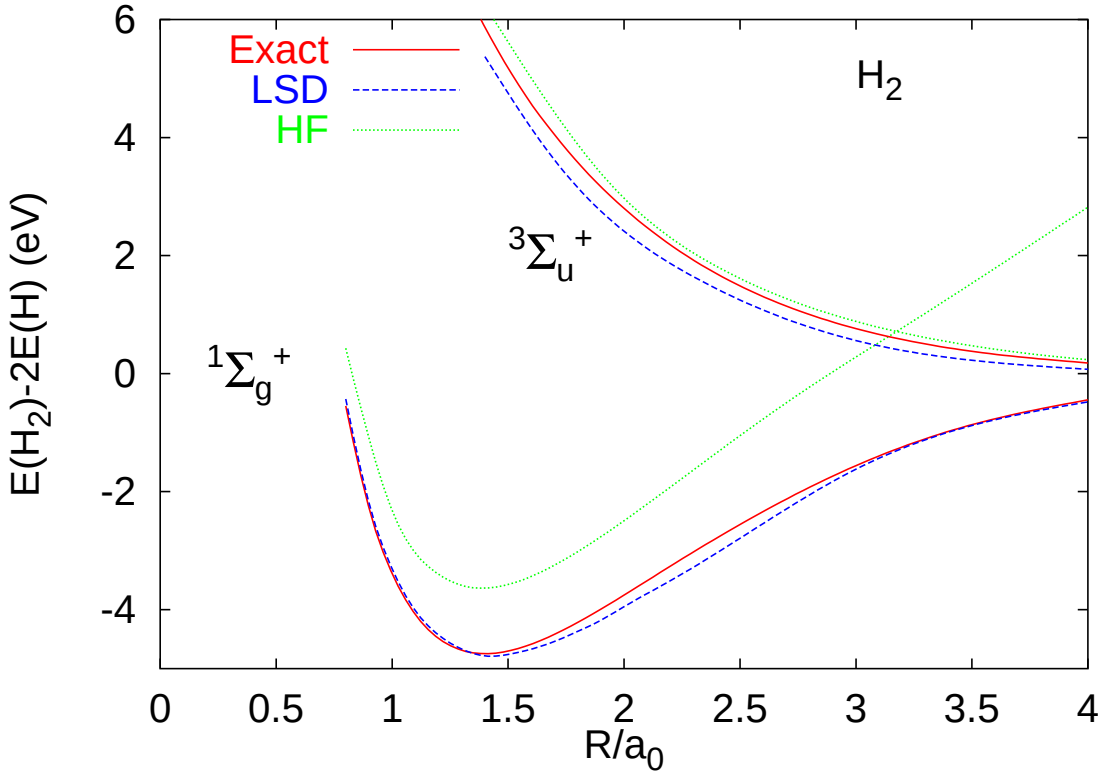
- Example: A sum of atomic densities is very accurate in many cases!

LSD - Local Spin Density Approx.

- It is straightforward to generalize the Hohenberg-Kohn and Kohn-Sham approaches to functions of *two* densities $n_\uparrow$ and $n_\downarrow$.
- The exchange energy is easily generalized since exchange is always a sum of terms for $\uparrow$ and $\downarrow$ spins.
- Correlation involves both spins, so it must be parametrized in terms of both $n_\uparrow$ and $n_\downarrow$.
- Thus we are led to the *LSD* form $E_{xc}[n_\uparrow, n_\downarrow]$. All widely used forms are based upon fitting the energies found by Quantum Monte Carlo calculations for interacting electrons done by Ceperley and Alder.
- Parametrized forms given by Perdew and Zunger, 1981, and Vosko, Wilk, and Nusair, 1980.

GGA - Result for H_2

Figure 2: Energy of H_2 vs. distance (From O. E. Gunnarsson). The limit at large distance are separated atoms. LSD is needed to allow a spin on each atom and get a reasonable answer. (But this is really incorrect because it breaks the symmetry.)



GGA - Generalized Gradient Approx.

Why Kohn got a Nobel prize in Chemistry!

DFT is now widely used in chemistry because the GGA greatly improves the estimates of dissociation energies. The GGA lowers the energy of systems with larger gradients, i.e., to lower the energy to dissociate a molecule into parts.

- Exchange and Correlation are *not* really local.
- Next approximation: consider $\epsilon_{xc}[n]$ a function of the density and the *gradient of the density* at each point
- The function is expressed in terms of the reduced density $s = \frac{|\nabla n|}{2k_F n}$, where $k_F = (3\pi^2 n)^{1/3}$.
- Discussion of forms in paper:
  J. P. Perdew and Kieron Burke, "Comparison Shopping for a gradient-corrected density functional", Int. J. Quant. Chem. 57, 309 (1996).
- Programs for the LDA and various GGA's are available from:
  http://www.phy.tulane.edu/ kieron/dft.html

GGA - Generalized Gradient Approx.

There are many GGA's because the approximations are not universal. The effect of all of them is too:

- Increase the magnitude of the exchange energy, i.e., lower the total energy
- Decrease the magnitude of the correlation energy, i.e., raise the total energy. But this is a smaller effect than the exchange.

The effects can be expressed as a factor F_{xc} multiplying the usual local exchange energy

$$\begin{aligned} & E_{xc}^{GGA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n^{\uparrow}, n^{\downarrow}, \boldsymbol{\nabla} n^{\uparrow}, \boldsymbol{\nabla} n^{\downarrow}) \\ \equiv & \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n^{\uparrow}, n^{\downarrow}, \boldsymbol{\nabla} n^{\uparrow}, \boldsymbol{\nabla} n^{\downarrow}), \end{aligned} \tag{34}$$

where F_{xc} is dimensionless, $\epsilon_x^{hom}(n)$ is the exchange energy of the unpolarized gas, and we can define a reduced dimensionless gradient proportional to the fractional variation in density normalized to the average distance between electrons $r_s \propto 1/k_F$.

$$s = \frac{|\boldsymbol{\nabla} n|}{(2k_F)n} = \frac{|\boldsymbol{\nabla} n|}{2(3\pi^2)^{1/3}(n)^{(4/3)}}. \tag{35}$$

Figure 3: Exchange enhancement factor F_x as a function of the dimensionless density gradient s for various GGAs. (From paper by H. Kim, similar to Figure 1, of Perdew and Burke (1996) but for a larger range of s).

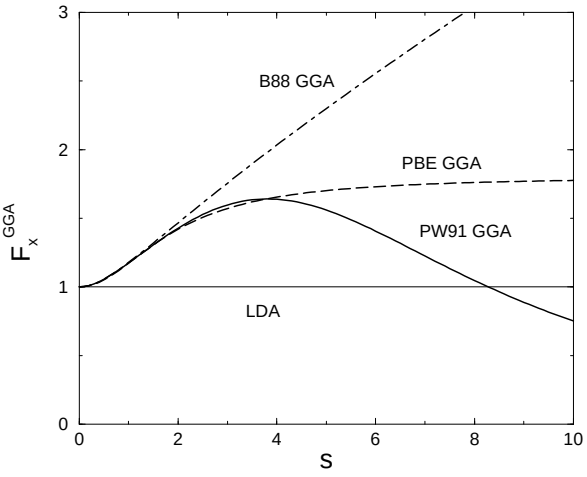
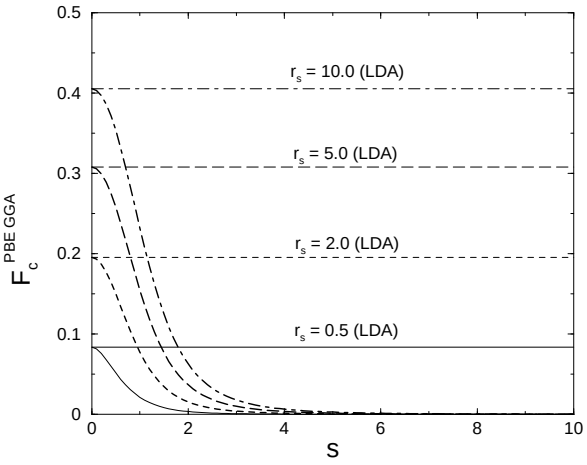


Figure 4: Exchange enhancement factor F_c as a function of the dimensionless density gradient s for various GGAs. (See caption of Fig. 3).



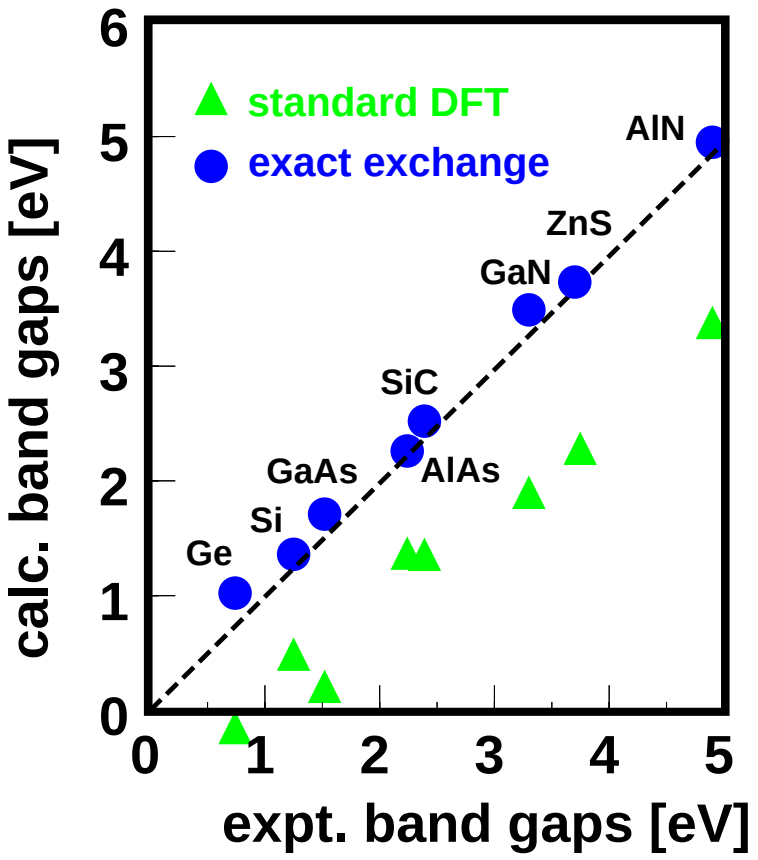
Orbital Functionals E[ψ_i] - OEP

The success of the Kohn-Sham approach over Thomas-Fermi is that *the kinetic energy is not and explicit functional of the density. It is an orbital functional.*

This can also be done with other terms, e.g., the exact Hartree-Fock expression for exchange involves the orbitals. In density functional theory this leads to the "Optimized Effective Potential" (OEP) method, where the potential varied to give the lowest energy for orbitals that are eigenfunctions of that potential.

Recent work (see review by Grabo and papers by Staedele and others) show there is a large improvement in the excited states using the OEP with exchange ("exact exchange" or EXX)..

Figure 5: Gaps of common semiconductors calculated using LDA and EXX. Note that Ge is a metal in the best LDA calculations, but the gaps are in much better agreement with experiment using EXX. From Staedele, et al.)



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