

Density functionals

Thomas-Fermi-Dirac approximation

Assumption:

Kinetic energy of electrons is an explicit functional of density of non-interacting electrons of a homogeneous electron gas equal to the local density at a given point.

Dirac -> local approximation for an exchange functional

Energy functional reads:

$$E_{TFD}[\rho] = \overset{\text{Kin.Ener.}}{C_1 \int d\mathbf{r} \rho(\mathbf{r})^{5/3}} + \int d\mathbf{r} V_{ext} \rho(\mathbf{r}) + \overset{\text{Exchange}}{C_2 \int d\mathbf{r} \rho(\mathbf{r})^{4/3}} + \overset{\text{Classical Coulomb}}{\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}$$

Minimize functional using Lagrange multipliers

$$\Omega[\rho] = E[\rho] - \mu \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right)$$

with the constraint of conservation of particle number

$$\int d\mathbf{r} \rho(\mathbf{r}) = N$$

$$C_1 = \frac{3}{10} (3\pi^2)^{2/3}$$
$$C_2 = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}$$

For small variations of density

$$\int d\mathbf{r} \left[\frac{5}{3} C_1 \rho(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu \right] \delta \rho(\mathbf{r}) = 0$$

The effective potential

$$V(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_X(\mathbf{r})$$

Leads to

$$\frac{1}{2} (3\pi^2)^{2/3} \rho(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu = 0$$

Not successful: the assumption for K.E. was too crude

Failure of the atoms binding into molecules

Lack of shell structure in atoms (periodic variation with Z is not reproduced)

Slater's $X\alpha$ method

Exchange energy can be expressed as

$$E_X = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) h_X(\mathbf{r}_1; \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Slater's approximation

Exchange hole is spherically symmetric and centered around the reference electron. Also, within the sphere, the exchange hole density is constant.

$$\int h_X(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$$

Let r_s be the radius of the sphere

$$\frac{4}{3}\pi r_s^3 \times \rho(\mathbf{r}_1) = 1$$

$$r_s = \left(\frac{3}{4\pi}\right)^{1/3} \rho(\mathbf{r}_1)^{-1/3}$$

Wigner Seitz radius (average distance between 2 electrons)

Regions of high density \rightarrow small value of r_s & vice-versa

In electrostatics, the potential of a uniformly charged sphere of radius r_s is $1/r_s$, hence to $\rho(\mathbf{r}_1)^{1/3}$

The exchange energy can be written as

$$E_X[\rho] = C_X \int d\mathbf{r}_1 \rho(\mathbf{r}_1)^{4/3}$$

The non-local exchange term has been replaced by a **local** term depending on the **local** electron density.

Hartree-Fock-Slater exchange

$$E_{X\alpha}[\rho] = -\frac{9}{8} \left(\frac{3}{\pi}\right)^{1/3} \alpha \int d\mathbf{r}_1 \rho(\mathbf{r}_1)^{4/3}$$

$$\frac{2}{3} < \alpha < 1$$

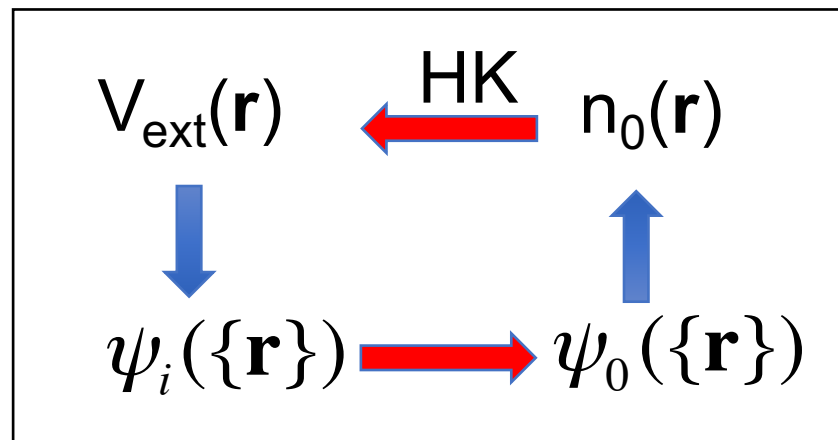
Semi-empirical adjustable parameter

Density Functional Theory

Hohenberg-Kohn theorems

Theorem I: The ground state density $n_0(\mathbf{r})$ determines uniquely the external potential $V_{\text{ext}}(\mathbf{r})$ except for a constant, for any system of interacting particles subjected to $V_{\text{ext}}(\mathbf{r})$.

Theorem II: For any $V_{\text{ext}}(\mathbf{r})$, a universal energy functional $E[n]$ can be defined in terms of density $n(\mathbf{r})$. For a particular $V_{\text{ext}}(\mathbf{r})$, the ground state energy is the global minimum of $E[n]$ obtained by the exact ground state density $n_0(\mathbf{r})$.



Proof of Theorem I

Suppose $V_{\text{ext}}^{(1)}$ and $V_{\text{ext}}^{(2)}$ lead to the same ground state density $n_0(\mathbf{r})$
 $V_{\text{ext}}^{(1)} \rightarrow H^{(1)}, V_{\text{ext}}^{(2)} \rightarrow H^{(2)}$

$$\begin{aligned} E^{(1)} &= \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle < \langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle \\ &< \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle = \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle + \langle \psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \psi^{(2)} \rangle \\ &< \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle = E^{(2)} + \int d^3r [V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r})] n_0(\mathbf{r}) \end{aligned}$$

$$E^{(1)} < E^{(2)} + \int d^3r [V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r})] n_0(\mathbf{r}) \quad (\text{i})$$

$$E^{(2)} < E^{(1)} + \int d^3r [V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r})] n_0(\mathbf{r}) \quad (\text{ii})$$

(i)+(ii),

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)} \quad \text{absurd !!!!}$$

Density uniquely determines the external potential

The energy functional

Hohenberg-Kohn energy functional

$$E_{HK}[n] = T[n] + E_{\text{int}}[n] + \int dr V_{\text{ext}}(r)n(r) + E_{II}$$

Kohn Sham ansatz:

Replace the interacting many body system by a **non-interacting auxiliary system** with the **same ground state density**

$$E_{KS} = T_S[n] + \int dr V_{\text{ext}}(r)n(r) + E_H[n] + E_{II} + E_{XC}[n]$$

$$T_S = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\nabla \psi_i^{\sigma}|^2 \quad \text{Non-interacting}$$

$$E_H = \frac{1}{2} \int dr dr' \frac{n(r)n(r')}{|r - r'|}$$

$$E_{XC}[n] = \langle T \rangle - T_S[n] + \langle V_{\text{int}} \rangle - E_H[n]$$

Single particle Kohn-Sham theory

Kohn-Sham variational equation

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma*}(r)} = \frac{\delta T_S}{\delta \psi_i^{\sigma*}(r)} + \left[\frac{\delta V_{ext}}{\delta n(r,\sigma)} + \frac{\delta E_H}{\delta n(r,\sigma)} + \frac{\delta E_{XC}}{\delta n(r,\sigma)} \right] \frac{\delta n(r,\sigma)}{\delta \psi_i^{\sigma*}(r)}$$

$$\frac{\delta T_S}{\delta \psi_i^{\sigma*}(r)} = -\frac{1}{2} \nabla^2 \psi_i^\sigma(r)$$

$$\frac{\delta n(r,\sigma)}{\delta \psi_i^{\sigma*}(r)} = \psi_i^\sigma(r)$$

Single particle Kohn-Sham equation

$$(H_{KS}^\sigma(r) - \varepsilon_i^\sigma) \psi_i^\sigma(r) = 0$$

$$H_{KS}^\sigma(r) = -\frac{1}{2} \nabla^2 + V_{KS}^\sigma(r)$$

$$V_{KS}^\sigma(r) = V_{ext}(r) + V_H(r) + V_{XC}^\sigma(r)$$

Inhomogeneous Electron Gas,
P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

Self Consistent Equations Including Exchange and Correlation Effects,
W.Kohn and L.J.Sham, Phys. Rev. 140, A1133 (1965)

Many body effects dumped in to XC term: **How to get a proper form of it ?**

Meaning of Kohn-Sham eigenvalue

Slater-Janak theorem:

the eigenvalue is the derivative of the total energy with respect to the occupation of the state

$$\epsilon_i = \frac{dE_{total}}{dn_i} = \int d\mathbf{r} \frac{dE_{total}}{dn(\mathbf{r})} \frac{dn(\mathbf{r})}{dn_i}$$

But, total energy contains the exchange-correlation part for an interacting system

$$\begin{aligned} E_{XC}[n] &= \int d\mathbf{r} n(\mathbf{r}) \epsilon_{XC}([n], \mathbf{r}) \\ V_{XC}(\mathbf{r}) &= \frac{dE_{XC}}{dn(\mathbf{r})} \\ &= \epsilon_{XC}([n], \mathbf{r}) + n(\mathbf{r}) \frac{\delta \epsilon_{XC}([n], \mathbf{r})}{\delta n(\mathbf{r}, \sigma)} \end{aligned}$$

The derivative causes discontinuity between states: band gap discontinuity

The eigenvalues of the ground state Kohn-Sham potential should not produce the correct gap

Exchange-correlation energy

$$E_{XC}[n] = \langle T \rangle - T_S[n] + \langle V_{\text{int}} \rangle - E_H[n]$$

Adiabatic connection: coupling between non-interacting & interacting systems (through coupling constant λ)

$$E_{XC}[n] = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \int_0^1 d\lambda \frac{n_{XC,\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Harris, PRA (1984)

For isotropic Coulomb interaction,

$$E_{XC}[n] = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int_0^\infty dR R^2 \frac{1}{R} \int d\Omega \int_0^1 d\lambda n_{XC,\lambda}(\mathbf{r}, \mathbf{R})$$

Exchange-correlation hole

$$\lim_{|\mathbf{r}-\mathbf{r}'|\rightarrow\infty} n_{XC}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = 0 \quad n_{XC} \text{ is local}$$

$$n_{XC}(\mathbf{r}\sigma, \mathbf{r}\sigma) = -n_{\sigma}(\mathbf{r}) \quad \text{Pauli exclusion principle}$$

$$n_{XC}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_X(\mathbf{r}\sigma, \mathbf{r}'\sigma') + n_C(\mathbf{r}\sigma, \mathbf{r}'\sigma')$$

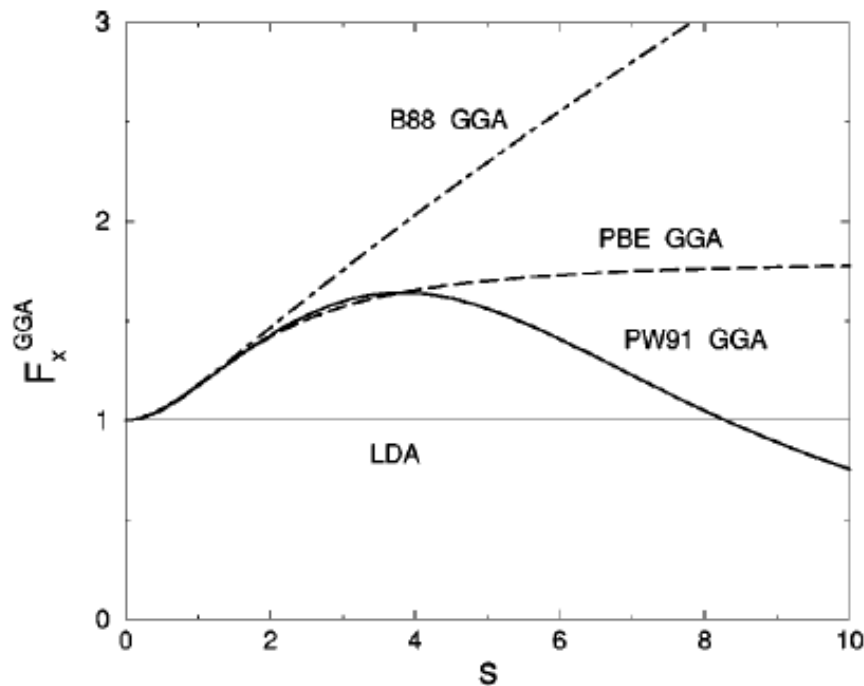
$$n_X(\mathbf{r}\sigma, \mathbf{r}'\sigma') \leq 0$$

$$\int d\mathbf{r}' n_X(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\delta_{\sigma, \sigma'}$$

$$\int d\mathbf{r}' n_C(\mathbf{r}\sigma, \mathbf{r}'\sigma') = 0$$

Approximations for exchange correlation term

$$\begin{aligned}
 E_{XC}^{LSDA}[n^\uparrow, n^\downarrow] &= \int dr n(r) \varepsilon_{XC}^{\text{hom}}(n^\uparrow(r), n^\downarrow(r)) \\
 &= \int dr n(r) [\varepsilon_X^{\text{hom}}(n^\uparrow(r), n^\downarrow(r)) + \varepsilon_C^{\text{hom}}(n^\uparrow(r), n^\downarrow(r))] \\
 E_{XC}^{GGA}[n^\uparrow, n^\downarrow] &= \int dr n(r) \varepsilon_{XC}(n^\uparrow(r), n^\downarrow(r), |\nabla n^\uparrow(r)|, |\nabla n^\downarrow(r)|) \\
 &= \int dr n(r) \varepsilon_X^{\text{hom}}(n(r)) F_{XC}(n^\uparrow(r), n^\downarrow(r), |\nabla n^\uparrow(r)|, |\nabla n^\downarrow(r)|)
 \end{aligned}$$



Reduced density gradient

$$s = \frac{|\nabla n|}{2k_F n}$$

(i) $0 < s < 3$: similar for PBE & PW91

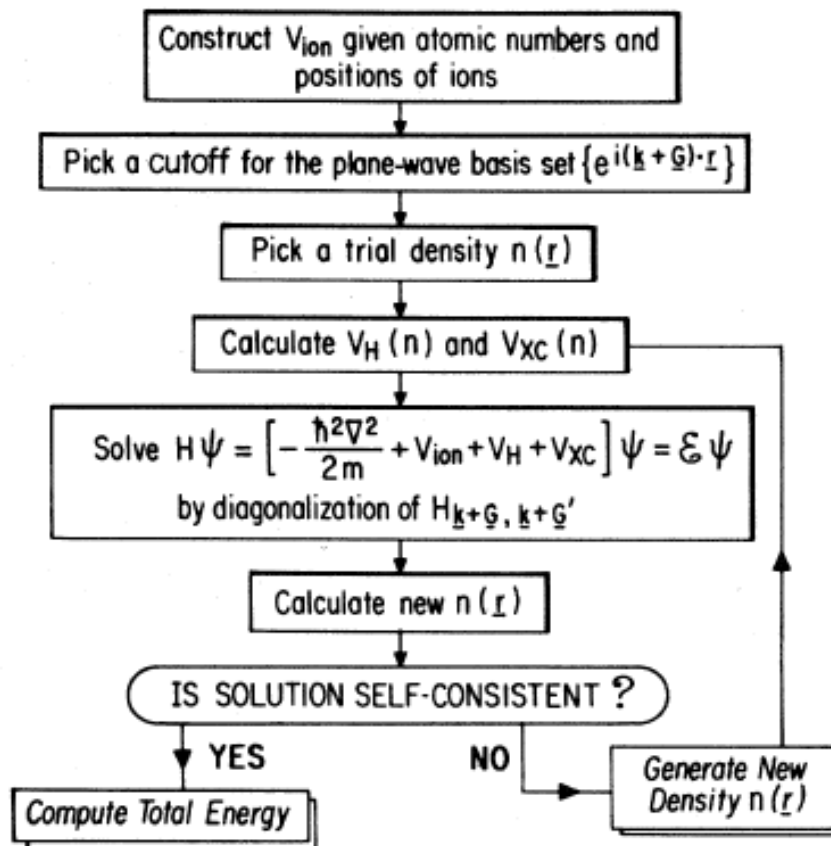
(ii) $s > 3$: different asymptotics

Spin-unpolarized $F_X(n, |\nabla n|)$

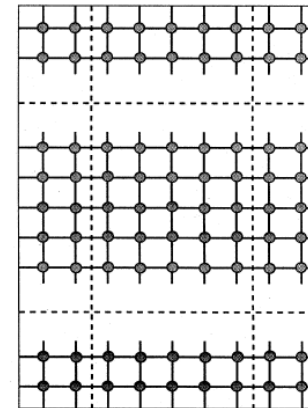
PW: Perdew and Wang

PBE: Perdew, Burke and Ernzerhof

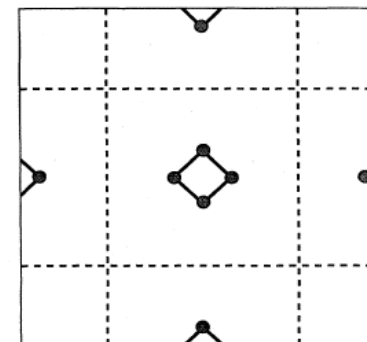
Self-consistency procedure (ex. plane wave basis set)



Construction of unit cell



Surface



Molecule

Payne et al., Rev. Mod. Phys. (1992)

Some essential things to remember

- **Achieving self-consistency: mixing schemes**

Linear mixing

$$n_{i+1}^{in} = \alpha n_i^{out} + (1 - \alpha) n_i^{in} = n_i^{in} + \alpha (n_i^{out} - n_i^{in})$$

More complex Broyden's mixing based on Jacobians

- **Smearing**

Band structure energy

$$\sum_{nk} \omega_k \epsilon_{nk} f\left(\frac{\epsilon_{nk} - \mu}{\sigma}\right)$$

Fermi-Dirac: $f = \frac{1}{1 + \exp\left(\frac{\epsilon_{nk} - \mu}{k_B T}\right)}$

Gaussian: $f = \frac{1}{2\sqrt{\pi}} \exp\left\{-\left(\frac{\epsilon_{nk} - \mu}{\sigma}\right)^2\right\}$

- **Hellmann-Feynman force**

$$F_I = -\frac{\partial E}{\partial R_I} = -\left\langle \Psi \left| \frac{\partial \hat{H}}{\partial R_I} \right| \Psi \right\rangle - \left[\left\langle \frac{\partial \Psi}{\partial R_I} \left| \hat{H} \right| \Psi \right\rangle - \left\langle \Psi \left| \hat{H} \right| \frac{\partial \Psi}{\partial R_I} \right\rangle \right] - \frac{\partial E_{II}}{\partial R_I}$$

$$F_I = -\int d\mathbf{r} n(\mathbf{r}) \frac{\partial V_{ext}(\mathbf{r})}{\partial R_I} - \frac{\partial E_{II}}{\partial R_I}$$

$n(\mathbf{r})$ is unperturbed density in presence of other fixed nuclei

Basis sets: diverse electronic structure methods

- Gaussian (GAUSSIAN)
- Plane wave (VASP, CASTEP, QUANTUM ESPRESSO, ABINIT,.....)
- Localized orbitals (SIESTA, FPLO,.....)
- Linearized muffin tin orbital (Stuttgart LMTO, Uppsala Rspt,.....)
- Linearized augmented plane wave (ELK, EXCITING, WIEN2K, FLEUR,....)
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