

Density Functional Theory: from theory to Applications

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Recap of Previous lecture

The self interaction error and its correction
Perdew-Zunger SIC

The Hartree-Fock-Kohn-Sham method

The exchange and correlation hole

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The self interaction error

In Thomas Fermi theory the electron electron interaction is:

$$V_{ee}^{TF}[\rho] = J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (1)$$

If we consider the one electron system described by $\phi(\mathbf{r})$, we get

$$J[|\phi(\mathbf{r})|^2] \neq 0 \quad (2)$$

while the exact potential energy functional must give 0 for one electron system:

$$V_{ee}[|\phi(\mathbf{r})|^2] = 0 \quad (3)$$

In 1934 Fermi and Amaldi proposed the simple self-interaction corrected formula:

$$V_{ee}^{FA} = \frac{N-1}{2N} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

No SIE in the Hartree Fock Approximation!

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (5)$$

where

$$H_i = \int \psi_i^*(x) \left[-\frac{1}{2} \nabla^2 + v(x) \right] \psi_i(x) dx \quad (6)$$

$$J_{ij} = \iint \psi_i(x_1) \psi_i^*(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_j(x_2) dx_1 dx_2 \quad (7)$$

$$K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2 \quad (8)$$

$$J_{ii} = K_{ii} \quad (9)$$

this explain the double sum in (5).

- ▶ In DFT the direct (self-interacting) Coulomb energy is large, e.g. for Hydrogen is about 8.5 eV, but about 93% is cancelled by LSD exchange-correlation energy.
- ▶ In LSD a spurious self interaction remains as the price to be paid for a simple, local one-electron potential. The SIE is more severe for localized systems, while it vanishes for orbitals delocalized over extended systems.

Perdew and Zunger¹ Self Interaction Corrections (SIC).

In approximate DFT (including LDA, the exact functional

$$V_{ee} [\rho^\alpha, \rho^\beta] = J [\rho^\alpha, \rho^\beta] + E_{xc} [\rho^\alpha, \rho^\beta] \quad (10)$$

is approximated by the functional:

$$\tilde{V}_{ee} [\rho^\alpha, \rho^\beta] = J [\rho^\alpha, \rho^\beta] + \tilde{E}_{xc} [\rho^\alpha, \rho^\beta] \quad (11)$$


The requirement to exclude the self interaction can be written as

$$V_{ee} [\rho_i^\alpha, 0] = J [\rho_i^\alpha] + E_{xc} [\rho_i^\alpha, 0] = 0 \quad (12)$$

Or in a more detailed form:

$$J [\rho_i^\alpha] + E_x [\rho_i^\alpha, 0] = 0 \quad (13)$$

$$E_c [\rho_i^\alpha, 0] = 0 \quad (14)$$

¹Perdew and Zunger (1981) *Phys Rev B* **23**, 5048. 

Perdew-Zunger self interaction corrected (SIC) version of a given approximate exchange and correlation functional is

$$E_{xc}^{SIC} = \tilde{E}_{xc} [\rho^\alpha, \rho^\beta] - \sum_{i\sigma} \left(J[\rho_i^\alpha] + \tilde{E}_x[\rho_i^\alpha, 0] \right) \quad (15)$$

The SIC one-electron equation become

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^{i\alpha, SIC}(\mathbf{r}) \right] \phi_{i\alpha}^{SIC}(\mathbf{r}) = \epsilon_{i\alpha}^{SIC} \phi_{i\alpha}^{SIC}(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^{j\beta, SIC}(\mathbf{r}) \right] \phi_{j\beta}^{SIC}(\mathbf{r}) = \epsilon_{j\beta}^{SIC} \phi_{j\beta}^{SIC}(\mathbf{r})$$

NOTE: the one electron equation for SIC have different potentials for different orbitals, which causes the orbital to be non-orthogonal.

SIC improves the LSD approximation considerably. For the **exchange energies** we have:

Table 8.3 LSD Calculation of Exchange Energies of Atoms
(in electron volts)^a

Atom	LSD	LSD-SIC	Hartree-Fock
H	-6.9	-8.5	-8.5
He	-23.2	-27.9	-27.9
Ne	-297.6	-337.8	-329.5
Ar	-755.8	-842.4	-821.3
Kr	-2407.5	-2632.0	-2561.9

^a After Perdew and Zunger (1981).

The Hartree-Fock-Kohn-Sham method

The exchange-energy functional

$$E_x [\rho^\alpha, \rho^\beta] = -\frac{1}{2} \iint \frac{1}{r_{12}} \left[|\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)|^2 \right] d\mathbf{r}_1 d\mathbf{r}_2 \quad (18)$$

can be explicitly written in terms of the orbitals for the system of non-interacting electrons with density ρ^α and ρ^β

$$T_s [\rho^\alpha, \rho^\beta] = \text{Min} \left[\sum_{i\sigma} n_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{i\sigma}(\mathbf{r}) \right] \quad (19)$$

$$\begin{aligned} E [\rho^\alpha, \rho^\beta] &= \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{i\sigma}(\mathbf{r}) + J [\rho^\alpha + \rho^\beta] \\ &- \frac{1}{2} \iint \frac{1}{r_{12}} \left[|\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)|^2 \right] d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \int d\mathbf{r} \left[(v(\mathbf{r}) + \beta_e b(\mathbf{r})) \rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r})) \rho^\beta(\mathbf{r}) \right] \quad (20) \end{aligned}$$

Minimization through the orbitals imposing the orthonormalization gives the equations:

$$-\frac{1}{2}\nabla^2\phi_{i\sigma}(\mathbf{r}) + \int v_{\text{eff}}^{\sigma}(\mathbf{r}, \mathbf{r}')\phi_{i\sigma}(\mathbf{r}')d\mathbf{r}' = \epsilon_{i\sigma}\phi_{i\sigma}(\mathbf{r}) \quad (21)$$

where $\epsilon_{i\sigma}$ are the Lagrange multiplier for the constraint

$$\int \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}) = \delta_{ij}.$$

The spin-dependent effective (*non local*) potentials are:

$$v_{\text{eff}}^{\alpha} = \left[v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' + \frac{\delta E_c[\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\alpha}(\mathbf{r})} \right] \delta(\mathbf{r} - \mathbf{r}') - \frac{\rho_1^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2)$$

$$v_{\text{eff}}^{\beta} = \left[v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' + \frac{\delta E_c[\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\beta}(\mathbf{r})} \right] \delta(\mathbf{r} - \mathbf{r}') - \frac{\rho_1^{\beta\beta}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2)$$

The spin density are: $\rho^{\sigma}(\mathbf{r}) = \sum_i |\phi_{i\sigma}(\mathbf{r})|^2$ and $N^{\sigma} = \int d\mathbf{r} \rho^{\sigma}(\mathbf{r})$ and $N = N^{\alpha} + N^{\beta}$.

- ▶ The HFKS equations differs from the KS equations in having a non-local exchange potential;
- ▶ the exchange potential is exact and explicit.
- ▶ The correlation potential is included, if we knew the exact form of $E_c [\rho^\alpha, \rho^\beta]$ we would have the exact solution.

What to use for $E_c [\rho^\alpha, \rho^\beta]$?

One can take the local spin density:

$$E_c^{LSD} [\rho^\alpha, \rho^\beta] = \int \rho \epsilon_c(\rho, \zeta) d\mathbf{r} \quad (24)$$

but it overestimate the the true value by a great deal.

Stoll, Pavlidou, and Preuss² suggested to use LSD only for electron with different spin.

$$E_c^{SPP} [\rho^\alpha, \rho^\beta] = E_c^{LSD} [\rho^\alpha, \rho^\beta] - E_c^{LSD} [\rho^\alpha, 0] - E_c^{LSD} [\rho^\beta, 0] \quad (25)$$

$$= \int \rho \epsilon_c(\rho, \zeta) d\mathbf{r} - \int \rho^\alpha \epsilon_c(\rho^\alpha, 1) d\mathbf{r} - \int \rho^\beta \epsilon_c(\rho^\beta, 1) d\mathbf{r} \quad (26)$$

NOTE: $E_c^{SPP} [|\phi_i(\mathbf{r})|^2, 0] = 0$. This approximation excludes the SI

²Theor. Chem. Acta **49** 143 (1978).

Vosko and Wilk³ proposed a another improvement over LSD.

$$E_c^{VW} [\rho^\alpha, \rho^\beta] = E_c^{LSD} [\rho^\alpha, \rho^\beta] \quad (27)$$

$$- \left(N^\alpha E_c^{LSD} [\rho^\alpha / N^\alpha, 0] + N^\beta E_c^{LSD} [\rho^\beta / N^\beta, 0] \right) \quad (28)$$

$$= \int \rho \epsilon_c(\rho, \zeta) d\mathbf{r} \quad (29)$$

$$- \int \rho^\alpha \epsilon_c(\rho^\alpha / N^\alpha, 1) d\mathbf{r} - \int \rho^\beta \epsilon_c(\rho^\beta / N^\beta, 1) d\mathbf{r} \quad (30)$$

- ▶ For $N = 1$, $E_c^{VW} = 0$
- ▶ For $N \rightarrow \infty$ and slowly-varying densities, $E_c^{VW} = E_c^{LSD}$.

³*J. Phys. B* **16**, 3687 (1983)

The exchange and correlation hole

Let's recall the expression for the E_{xc} :

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

E_{xc} is the sum of two unrelated contributions:

- ▶ $T[\rho] - T_s[\rho]$ is associated to first order reduced density matrix
- ▶ $V_{ee}[\rho] - J[\rho]$ is associated with second order reduced density matrix

The diabatic connection was introduced by Langreth and Perdew⁴ switch on the electron-electron interaction through the parameter λ , so that the density ρ is unchanged along the path.

$$F_\lambda[\rho(\mathbf{r})] = \text{Min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle \quad (31)$$

$$= \langle \Psi_\rho^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\rho^\lambda \rangle \quad (32)$$

where Ψ_ρ^λ is the N-electron wave function that minimize $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$ and yields the density ρ .

⁴Phys. Rev. B **15** 2884 (1977).

The parameter λ characterizes the strength of the electron-electron interaction.

$$F_1[\rho] = F[\rho] = T[\rho] + V_{ee}[\rho] \quad (33)$$

$$F_0[\rho] = T_s[\rho] \quad (34)$$

$$\begin{aligned} E_{xc}[\rho] &= T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \\ &= F_1[\rho] - F_0[\rho] - J[\rho] \end{aligned} \quad (35)$$

$$= \int_0^1 d\lambda \frac{\partial F_\lambda[\rho]}{\partial \lambda} - J[\rho] \quad (36)$$

We want to evaluate E_{xc} from (36).

The condition that $\psi \rightarrow \rho(\mathbf{r})$ can be expressed as:

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \langle \Psi | \sum_i^n \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle \quad (37)$$

It is necessary that Ψ_ρ^λ make stationary the functional:

$$\langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle + \int \left(v_\lambda(\mathbf{r}) - \frac{E_\lambda}{N} \right) \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle d\mathbf{r} \quad (38)$$

$$= \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i) - E_\lambda | \Psi \rangle \quad (39)$$

where $v_\lambda(\mathbf{r}) - \frac{E_\lambda}{N}$ is the Lagrangian multiplier for the constraint (37).

Ψ_ρ^λ has to be an eigenstate of an Hamiltonian \hat{H}_λ

$$\hat{H}_\lambda | \Psi_\rho^\lambda \rangle = \left(\hat{T} + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i) \right) | \Psi_\rho^\lambda \rangle = E_\lambda | \Psi_\rho^\lambda \rangle \quad (40)$$

with eigenvalue E_λ .

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle \Psi_\rho^\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_\rho^\lambda \rangle \quad (41)$$

$$= \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle + \langle \Psi_\rho^\lambda | \frac{\partial}{\partial \lambda} \sum_i^N v_\lambda(\mathbf{r}_i) | \Psi_\rho^\lambda \rangle \quad (42)$$

$$= \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle + \int \rho(\mathbf{r}) \frac{\partial}{\partial \lambda} v_\lambda(\mathbf{r}) d\mathbf{r}. \quad (43)$$

Considering that:

$$E_\lambda = \langle \Psi_\rho^\lambda | \hat{T} + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i) | \Psi_\rho^\lambda \rangle = F_\lambda[\rho] + \sum_i^N v_\lambda(\mathbf{r}_i) \quad (44)$$

We obtain:

$$\frac{\partial F_\lambda[\rho]}{\partial \lambda} = \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle \quad (45)$$

Finally we can now use

$$\frac{\partial F_\lambda[\rho]}{\partial \lambda} = \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle$$

into the exchange and correlation functional:

$$E_{xc}[\rho] = \int_0^1 d\lambda \frac{\partial F_\lambda[\rho]}{\partial \lambda} - J[\rho] \quad (46)$$

$$= \int_0^1 d\lambda \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle - J[\rho] \quad (47)$$

$$= \iint \frac{1}{r_{12}} \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - J[\rho] \quad (48)$$

$$= \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (49)$$

$$= \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (50)$$

where $\int_0^1 d\lambda \rho_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + \bar{h}(\mathbf{r}_1, \mathbf{r}_2)]$.

where the average *exchange and correlation hole*

$$\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) \quad (51)$$

and the average pair correlation functional is given by:

$$\int_0^1 d\lambda \rho_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + \bar{h}(\mathbf{r}_1, \mathbf{r}_2)] \quad (52)$$

The exchange and correlation energy can be viewed as the classical Coulomb interaction between the electron density $\rho(\mathbf{r})$ and a charge $\bar{\rho}_{xc}$, the exchange and correlation hole, averaged over λ

The **sum rule for the exchange and correlation hole** is:

$$\int \bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (53)$$

This can be obtained from

$$\rho(\mathbf{r}_1) = \frac{2}{N-1} \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (54)$$

$$\frac{N-1}{2} \rho(\mathbf{r}_1) = \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (55)$$

$$\text{Inserting } \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] \quad (56)$$

into eq.55 we obtain:

$$\frac{N-1}{2} \rho(\mathbf{r}_1) = \int \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_2 \quad (57)$$

$$\frac{N-1}{2} \rho(\mathbf{r}_1) = \frac{1}{2} \rho(\mathbf{r}_1) \left[N + \int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \right] \quad (58)$$

$$-1 = \int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (59)$$

$$\int \bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$$

From here we see that $\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ represent a hole around \mathbf{r}_1 with unit positive charge.

Such condition can be a test for DFT where an approximation of $\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ is given in term of electron density.

The second consequence of

$$E_{xc}[\rho] = \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

is that E_{xc} only depends on certain spherically averaged behavior of ρ_{xc} , namely

$$E_{xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int_0^\infty 4\pi s ds \rho_{xc}^{SA}(\mathbf{r}, s) \quad (60)$$

where

$$\rho_{xc}^{SA}(\mathbf{r}, s) = \frac{1}{4\pi} \int \bar{\rho}_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (61)$$

The sum rule can be written as:

$$4\pi \int s^2 ds \rho_{xc}^{SA}(\mathbf{r}, s) = -1 \quad (62)$$

We can decompose ρ_{xc} into exchange and correlation contribution.
We can define the exchange hole (for spin-compensated) as:

$$\rho_x(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2} \frac{|\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)}. \quad (63)$$

thus the exchange energy is given by

$$E_x[\rho] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (64)$$

The exchange hole satisfies

$$\int \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1; \quad (65)$$

We define the correlation hole:

$$\bar{\rho}_{xc} = \rho_x(\mathbf{r}_1, \mathbf{r}_2) + \rho_c(\mathbf{r}_1, \mathbf{r}_2). \quad (66)$$

As consequence of the sum rule and of eq.65 we have that

$$\int \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0. \quad (67)$$

- ▶ The exchange energy equals the Coulomb interaction energy of the electrons with a charge distribution contains one unit charge
- ▶ The correlation energy comes from the interaction of the electrons with a neutral charge distribution

For the local density approximation

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r} \quad (68)$$

Recalling:

$$E_{xc} = \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (69)$$

The LDA formula corresponds to:

$$\rho_{xc}^{LDA} = \rho(\mathbf{r}_1) \bar{h}_0(|\mathbf{r}_1 - \mathbf{r}_2|; \rho(\mathbf{r}_1)) \quad (70)$$

Note the difference with the exact formula:

$$\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2)$$

The ρ_{xc}^{LDA} obeys the sum rule:

$$\int \rho_{xc}^{LDA}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (71)$$

Indeed for every \mathbf{r}_1 , ρ_{xc}^{LDA} is the exact exchange-correlation hole of a homogeneous electron gas with density $\rho(\mathbf{r}_1)$.

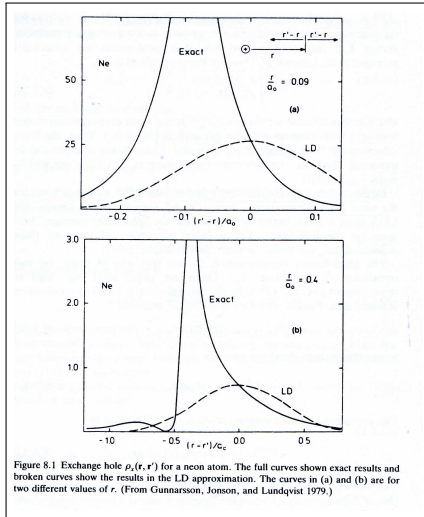


Figure 8.1 Exchange hole $\rho_e(r, r')$ for a neon atom. The full curves show exact results and broken curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r . (From Gunnarsson, Jonson, and Lundqvist 1979.)

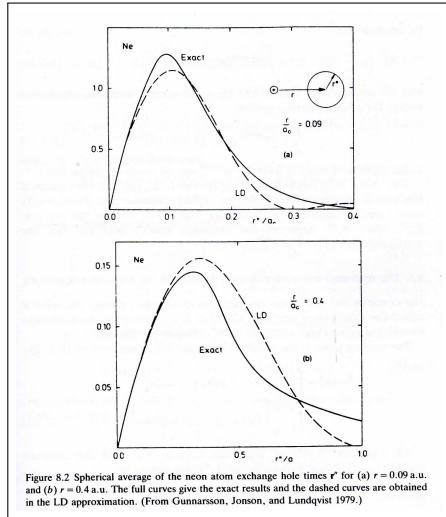
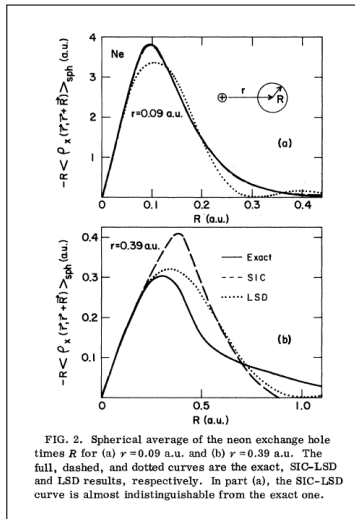
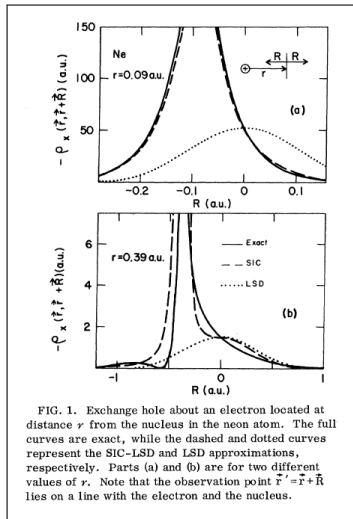


Figure 8.2 Spherical average of the neon atom exchange hole times r^2 for (a) $r = 0.09$ a.u. and (b) $r = 0.4$ a.u. The full curves give the exact results and the dashed curves are obtained in the LD approximation. (From Gunnarsson, Jonson, and Lundqvist 1979.)



Average-density approximation

Average-density (AD) approximation⁵

$$\rho_{xc}^{AD} = \bar{\rho}(\mathbf{r}_1) \bar{h}_0(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) \quad (72)$$

where the average density is given by

$$\bar{\rho}(\mathbf{r}) = \int w(\mathbf{r} - \mathbf{r}'; \bar{\rho}(\mathbf{r})) \rho(\mathbf{r}') d\mathbf{r}' \quad (73)$$

The corresponding exchange and correlation energy is equal to

$$E_{xc}^{AD}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\bar{\rho}(\mathbf{r})) d\mathbf{r} \quad (74)$$

LDA correspond to a weighting factor $w(\mathbf{r} - \mathbf{r}'; \bar{\rho})$ that is a Dirac delta function.

⁵Gunnarsson, Jonson, and Lundqvist, *Phys Lett* **59** A177 (1976)

Weighted density approximation

Other approximations include: weighted density (WD)

$$\rho_{xc}^{WD}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) \bar{h}_0(|\mathbf{r}_1 - \mathbf{r}_2|; \tilde{\rho}(\mathbf{r}_1)) \quad (75)$$

where $\tilde{\rho}(\mathbf{r}_1)$ is determined by the sum rule:

$$\int \rho_{xc}^{WD}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_2) \bar{h}_0(|\mathbf{r}_1 - \mathbf{r}_2|; \tilde{\rho}(\mathbf{r}_1)) d\mathbf{r}_2 = -1 \quad (76)$$

Solving the electronic problem in practice

All electrons vs pseudopotentials

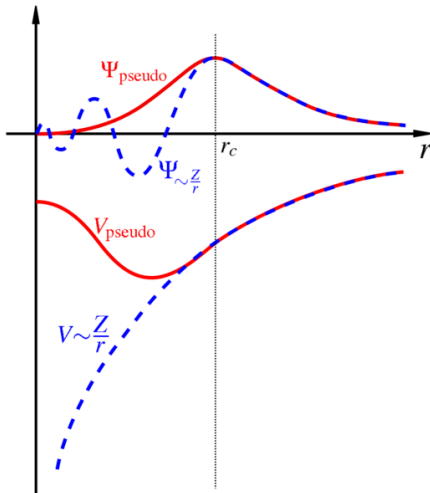
There are two classes of electrons: *valence electrons* (participate to chemical bonds) and *core electrons* (tightly bound to the nuclei). Eventually *semi-core electrons* (close in energy to valence states to feel the presence of the environment)

All-electron methods

- ▶ fixed orbital basis set: core electron minimal number of basis function to reproduce atomic features, valence and semi-core more complete basis set to describe the chemical bond.
- ▶ augmented basis set. Divide the space into spherical regions around the atoms and interstitial regions and requesting that the basis functions are continuous and differentiable across the boundaries.

Pseudopotential methods

- ▶ Core electrons are eliminated. Nuclei effective charge $Z_V = Z - Z_{core}$.
- ▶ Number of electron treated explicitly is reduced
- ▶ The bare Coulomb potential is replaced by a screened Coulomb potential
- ▶ Inner solution, inside the core radius, is replaced with a smooth, node-less pseudo-wave function
- ▶ Pseudopotentials are usually chosen to be dependent on the angular momentum.
E.g. for Pt 6p orbitals are quite external and peaked at around 3.9Å, the 6s peak at around 2.4 Å and the main peak of 5d is located at 1.3 Å.



Classes of Basis-set

- ▶ *Extended basis set*: delocalized, such as plane waves, useful for condensed phase systems. Tends to be inefficient for molecular systems.
- ▶ *Localized basis set*: mainly centered at the atomic positions (but also at position of "ghost" atoms). Mainly used for molecular systems
- ▶ *Mixed basis set*: designed to take best of the two worlds (delocalized + localized). There can be some technical issues (over-completeness).
- ▶ *Augmented basis set*: where an extended or atom centered basis set is augmented with atomic like wf in spherical regions around the nuclei.

Condensed phase: Bloch's th and PBC

Condensed phase: problem of choosing the size of the simulation cell. For periodic system: unit of Wigner-Seitz cell, the minimal choice that contains the whole symmetry of the system. Sometimes it is convenient to choose a larger cell to simplify description of symmetry properties. In an external periodic potential $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{a}_i)$ the wf can be written as:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}) \quad (77)$$

with $u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{a}_i)$.

$$\psi_k(\mathbf{r} + \mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{a}_i} \psi_k(\mathbf{r}) \quad (78)$$

So that the probability density is $|\psi_k(\mathbf{r})|^2$ is exactly the same.

Looking at

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{a}_i) = e^{i\mathbf{k} \cdot \mathbf{a}_i} \psi_{\mathbf{k}}(\mathbf{r})$$

we notice that there is a class of vectors \mathbf{k} such that

$$e^{i\mathbf{k} \cdot \mathbf{a}_i} = 1 \quad (79)$$

The reciprocal lattice vectors are defined by

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (80)$$

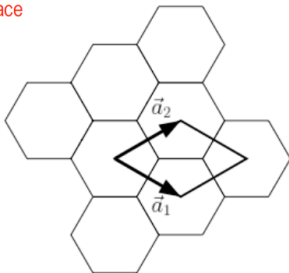
and

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\Omega}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\Omega}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\Omega} \quad (81)$$

The reciprocal lattice vectors define the first Brillouin Zone (BZ).

- Example: honeycomb lattice

real space

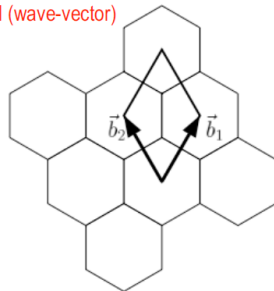


Lattice vectors a_1, a_2, a_3

Unit cell volume Ω

Crystallographic basis consisting of two atoms

Reciprocal (wave-vector)
 space



Reciprocal-lattice vectors b_1, b_2, b_3 , each perpendicular to a pair of lattice vectors

$$\vec{b}_i = \frac{2\pi}{\Omega} (\vec{a}_j \times \vec{a}_k)$$

Bloch's theorem indicates that it is not necessary to determine the electronic wavefunction everywhere in space. It is sufficient to know the solution in the unit cell.

Using the fact that a periodic function can be represented by a Fourier series:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (82)$$

where the sum is over $G = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$, the reciprocal lattice vectors.

\mathbf{k} is restricted to all the vectors in the first Brillouin zone. In practice calculations are done only for a finite number of \mathbf{k} .

The number of \mathbf{k} points depends on the systems we want to study.

Aperiodic systems: molecules, surfaces and defects

- ▶ supercell approach with PBC, making sure that required physical and chemical properties are converged with respect to the size of the supercell.
- ▶ For surfaces and molecules, e.g., introduce a vacuum region large enough that there is no interaction between images.
- ▶ For charged systems difficulties due to the electrostatic interactions (long range). A uniform neutralizing background is introduced.