

A mathematical introduction to Density Functional Theory and Kohn-Sham models

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1. **Hohenberg-Kohn theorem**
2. **Constrained search**
3. **Kohn-Sham models**
4. **Homogeneous electron gas**

Some references

- **Hohenberg and Kohn**, *Inhomogeneous electron gas*, **Phys. Rev.** **1964**
- **Kohn and Sham**, *Self-consistent equations including exchange and correlation effects*, **Phys. Rev.** **1965**
- **Lieb**, *Density Functional for Coulomb systems*, **Int. J. Quant. Chem.** **1983**
- **Dreizler and Gross**, *Density Functional Theory*, **Springer-Verlag**, **1990**

1 - Hohenberg-Kohn theorem

Density associated with a normalized wavefunction of $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C})$

$$\rho_{\Psi}(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

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Definition. Let $\mathcal{V} \subset L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ be a class of local potentials and

$$H_N(v) := -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N v(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

We will say that **the Hohenberg-Kohn theorem is satisfied on \mathcal{V}** if two potentials v_1 and v_2 in \mathcal{V} giving rise to the same ground-state density ρ only differ by an additive constant

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i.e.

if for any v_1 and v_2 in \mathcal{V} for which $H_N(v_1)$ and $H_N(v_2)$ admit ground state wavefunctions Ψ_1 and Ψ_2 respectively such that

$$\rho_{\Psi_1} = \rho_{\Psi_2},$$

then $v_2 - v_1$ is constant almost everywhere

Bright Wilson's argument for molecular potentials (reported by Löwdin)

Theorem. The Hohenberg-Kohn theorem is satisfied on

$$\mathcal{V} = \left\{ v(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}, (z_k, \mathbf{R}_k)_{1 \leq k \leq M} \in (\mathbb{N}^* \times \mathbb{R}^3)^M, \mathbf{R}_k \neq \mathbf{R}_l, \text{ if } k \neq l \right\}$$

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Proof. Let $v \in \mathcal{V}$ possessing a normalized ground state wavefunction Ψ . Let $\rho = \rho_\Psi$. The function ρ is smooth (actually analytic¹) away from the nuclei, and at each nucleus of charge z_k , it holds

$$\frac{d[\rho]_{\mathbf{R}_k}}{dr}(0) = -2z_k[\rho]_{\mathbf{R}_k}(0), \quad \text{(Kato's cusp conditions)}$$

where

$$[\rho]_{\mathbf{R}_k}(r) = \frac{1}{4\pi r^2} \int_{S(\mathbf{R}_k, r)} \rho$$

is the average of ρ over the sphere $S(\mathbf{R}_k, r)$ of center \mathbf{R}_k of radius r .

Therefore, there is a unique $v \in \mathcal{V}$ with density ρ .

¹ \longrightarrow see **Thomas Ostergaard Sorensen's talk**

Extension to more general potentials

Denoting by $E_0(v)$ the ground-state energy of $H_N(v)$, we have

$$E_0(v_1) = \langle \Psi_1 | H_N(v_1) | \Psi_1 \rangle = \langle \Psi_1 | H_N(v_2) | \Psi_1 \rangle + \int_{\mathbb{R}^3} \rho(v_1 - v_2) \geq E_0(v_2) + \int_{\mathbb{R}^3} \rho(v_1 - v_2)$$

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By symmetry, we also have

$$E_0(v_2) \geq E_0(v_1) + \int_{\mathbb{R}^3} \rho(v_2 - v_1)$$

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Hence, the above inequalities are in fact equalities, which implies that Ψ_2 is a ground state of $H_N(v_1)$:

$$H_N(v_1)\Psi_2 = E_0(v_1)\Psi_2 \quad \text{and} \quad H_N(v_2)\Psi_2 = E_0(v_2)\Psi_2$$

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This implies,

$$\left(\sum_{i=1}^N (v_2 - v_1)(\mathbf{r}_i) + E_0(v_1) - E_0(v_2) \right) \Psi_2(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0 \quad \text{almost everywhere in } \mathbb{R}^{3N}$$

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that

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from which we easily conclude that

$$(v_2 - v_1)(\mathbf{r}) = \frac{E_0(v_2) - E_0(v_1)}{N} \quad \text{almost everywhere in } \mathbb{R}^3,$$

we need a **unique continuation argument** of the form

$$(H_N(v)\Psi = E\Psi \text{ and } \Psi = 0 \text{ on a set of positive measure}) \Rightarrow (\Psi = 0 \text{ a.e. in } \mathbb{R}^{3N})$$

→ see Louis Garrigue's talk

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Extension of Hohenberg-Kohn theorem to other settings

→ see Andre Laestadius's talk on HK for current densities

2 - Constrained search

Let $\mathcal{H}_k := \bigwedge^k L^2(\mathbb{R}^3, \mathbb{C})$, $\Psi \in \mathcal{H}_N$ such that $\|\Psi\| = 1$, and $1 \leq p \leq N$

- the **p -body (reduced) density matrix (p -RDM)** associated with Ψ is

$$\gamma_{p,\Psi}(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}'_1, \dots, \mathbf{r}'_p) := \binom{N}{p} \int_{\mathbb{R}^{3(N-p)}} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_p, \mathbf{r}_{p+1}, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \dots, \mathbf{r}'_p, \mathbf{r}_{p+1}, \dots, \mathbf{r}_N)^* d\mathbf{r}_{p+1} \cdots d\mathbf{r}_N$$

- the **p -body reduced density operator (p -RDO)** associated with Ψ is the bounded self-adjoint operator on \mathcal{H}_p with kernel $\gamma_{p,\Psi}$. It is also denoted by $\gamma_{p,\Psi}$ and sometimes called density matrix as well;

- the **p -body density** is

$$\begin{aligned} \rho_{p,\Psi}(\mathbf{r}_1, \dots, \mathbf{r}_p) &= \gamma_{p,\Psi}(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}_1, \dots, \mathbf{r}_p) \\ &= \binom{N}{p} \int_{\mathbb{R}^{3(N-p)}} |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_p, \mathbf{r}_{p+1}, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_{p+1} \cdots d\mathbf{r}_N \end{aligned}$$

- for $p = 1$, $\gamma_\Psi := \gamma_{1,\Psi}$, $\rho_\Psi := \rho_{1,\Psi}$

Variational formulation of the ground-state energy

$$E_0 = \inf \{ \langle \Psi | H_N | \Psi \rangle, \Psi \in \mathcal{W}_N \}, \quad \mathcal{W}_N = \left\{ \Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3) \cap H^1(\mathbb{R}^{3N}), \|\Psi\|_{L^2} = 1 \right\}$$

$$H_N = \underbrace{-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i}}_T + \underbrace{\sum_{i=1}^N V(\mathbf{r}_i)}_{V_{\text{ne}}} + \underbrace{\sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{\text{ee}}}, \quad V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

- **kinetic energy:** $\langle \Psi | T | \psi \rangle = \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma_\psi \right)$
- **interaction energy between electrons and nuclei:** $\langle \Psi | V_{\text{ne}} | \psi \rangle = \int_{\mathbb{R}^3} \rho_\Psi V$
- **electron-electron interaction energy:** $\langle \Psi | V_{\text{ee}} | \psi \rangle = \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_{2,\Psi}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

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“Usual” splitting of the electronic Hamiltonian

$$H_N = \underbrace{T + V_{\text{ne}}}_{\text{1-body}} + \underbrace{V_{\text{ee}}}_{\text{2-body}}.$$

Hohenberg-Kohn splitting of the electronic Hamiltonian

$$H_N = \underbrace{T + V_{\text{ee}}}_{\text{generic}} + \underbrace{V_{\text{ne}}}_{\text{specific}}$$

generic specific (to the molecular system considered)

Levy-Lieb functional (Levy '79, Lieb '83, already discussed in previous talks)

$$H_N = H_N^1 + V_{\text{ne}}, \quad H_N^1 = T + V_{\text{ee}} = -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad V_{\text{ne}} = \sum_{i=1}^N V(\mathbf{r}_i)$$

$$E_0 = \inf \left\{ F_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V, \rho \in \mathcal{R}_N \right\}$$

$$F_{\text{LL}}(\rho) := \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle, \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\},$$

$$\mathcal{R}_N := \left\{ \rho, \exists \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\}$$

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Theorem (pure-state N -representability of densities)

$$\mathcal{R}_N = \left\{ \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}$$

$F_{\text{LL}}(\rho)$ is a “universal” functional of the density

Problem: no easy-to-compute expression of $F_{\text{LL}}(\rho)$ is known

Lieb functional (Legendre-Fenchel duality)

For any $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, we can define

$$E_0(v) = \inf \{ \langle \Psi | H_N(v) | \Psi \rangle, \Psi \in \mathcal{W}_N \} = \inf \left\{ \langle \Psi | H_N^1 + \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle, \Psi \in \mathcal{W}_N \right\}$$

and $v \mapsto E_0(v)$ is a real-valued, concave, Lipschitz function on $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$

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Theorem (Lieb '83)

$$E_0(v) = \inf \left\{ F_L(\rho) + \int_{\mathbb{R}^3} \rho v, \rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \right\}$$

where $F_L(\rho)$ is the convex w-l.s.c. function defined on $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$ by

$$F_L(\rho) = \sup \left\{ E(v) - \int_{\mathbb{R}^3} \rho v, v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\}$$

Physical interpretation of $F_L(\rho)$

Mixed states of N -electron systems are described by N -electron density matrices of the form

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle \langle \Psi_n|, \quad \Psi_n \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}), \quad \langle \Psi_m | \Psi_n \rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1$$

the density of Γ being given by

$$\rho_\Gamma(\mathbf{r}) = \sum_{n=1}^{+\infty} p_n \rho_{\Psi_n}(\mathbf{r}).$$

Γ is of finite energy if $\sum_{n=1}^{+\infty} p_n \|\nabla \Psi_n\|_{L^2}^2 < \infty$, its energy being then

$$\mathbf{Tr}(H_N \Gamma) = \sum_{n=1}^{+\infty} p_n \langle \Psi_n | H_N | \Psi_n \rangle = \mathbf{Tr}(H_N^1 \Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V.$$

Let us denote by \mathcal{D}_N the convex set of finite-energy N -electron density matrices

Theorem (ensemble N -representation of densities). It holds

$$\{\rho \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho\} = \mathcal{R}_N = \left\{ \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}$$

Therefore (Valone '80)

$$\begin{aligned} E_0(v) &= \inf \{ \mathbf{Tr} (H_N(v)\Gamma), \Gamma \in \mathcal{D}_N \} \\ &= \inf \left\{ \mathbf{Tr} (H_N^1\Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma v, \Gamma \in \mathcal{D}_N \right\} \\ &= \inf \left\{ \inf \{ \mathbf{Tr} (H_N^1\Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} + \int_{\mathbb{R}^3} \rho v, \rho \in \mathcal{R}_N \right\}. \end{aligned}$$

It holds that $F_L(\rho) = \begin{cases} \inf \{ \mathbf{Tr} (H_N^1\Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} & \text{if } \rho \in \mathcal{R}_N, \\ +\infty & \text{if } \rho \notin \mathcal{R}_N, \end{cases}$
and that F_L is the convex hull of F_{LL} on the convex set \mathcal{R}_N

No explicit expressions of the functionals F_L and F_{LL} are known

Approximations are needed for numerical simulations

Two classes of approximate functionals are available, built from the exact functionals of simple reference systems:

- **orbital-free models**: reference system = homogeneous electron gas

orbital-free functionals are cheap but inaccurate except in a few cases

- **Kohn-Sham models**: reference system = N non-interacting electrons

Kohn-Sham functionals are much more accurate, but more expensive

In orbital-free models, the density functional is explicit in ρ

Examples:

- **Thomas-Fermi (TF) model**

$$\mathcal{E}^{\text{TF}}(\rho) = C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \int_{\mathbb{R}^3} \rho V + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_0 \sim \inf \left\{ \mathcal{E}^{\text{TF}}(\rho), \rho \geq 0, \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}$$

- **Thomas-Fermi-von Weizsäcker (TFW) model**

$$\mathcal{E}^{\text{TFW}}(\rho) = C_{\text{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \int_{\mathbb{R}^3} \rho V + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_0 \sim \inf \left\{ \mathcal{E}^{\text{TFW}}(\rho), \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}$$

3 - Kohn-Sham models

Density functional theory for non-interacting electrons

	Hamiltonian	Levy-Lieb	Lieb
Interacting e⁻	H_N^1	$F_{LL}(\rho)$	$F_L(\rho)$
Non-interacting e⁻	H_N^0	$T_{LL}(\rho)$	$T_J(\rho)$

$$H_N^1 = T + V_{ee} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad H_N^0 = T = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i}$$

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Can $T_{LL}(\rho)$ be "easily" computed? **No**

Can $T_J(\rho)$ be "easily" computed? **Yes! → (extended) Kohn-Sham model**

Kohn-Sham kinetic energy functional (Levy-Lieb approach for H_N^0)

$$\begin{aligned}
 T_{\text{LL}}(\rho) &= \inf \{ \langle \Psi | T | \Psi \rangle, \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \} \\
 &\leq \inf \{ \langle \Psi | T | \Psi \rangle, \Psi \in \mathcal{W}_N \text{ is a Slater determinant s.t. } \rho_\Psi = \rho \} \\
 &= \inf \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \sum_{i=1}^N |\phi_i|^2 = \rho \right\} \\
 &=: T_s(\rho) \quad \text{(Kohn \& Sham '65)}
 \end{aligned}$$

A Slater determinant with finite kinetic energy is a wavefunction Ψ of the form

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \phi_N(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}, \quad \phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$$

Kohn-Sham model ('65)

1. For N *non interacting* electrons, the density functional is (approximatively) given by

$$T_s(\rho) = \inf \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3) \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \sum_{i=1}^N |\phi_i|^2 = \rho \right\}$$

2. For a classical charge distribution of density ρ , the Coulomb interaction reads

$$J(\rho) \stackrel{\text{def}}{=} \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x - y|} dx dy$$

3. Kohn and Sham proposed the following decomposition of F_{LL}

$$F_{LL}(\rho) = T_s(\rho) + J(\rho) + E_{xc}(\rho) \quad \text{where} \quad E_{xc}(\rho) \stackrel{\text{def}}{=} F_{LL}(\rho) - T_s(\rho) - J(\rho)$$

E_{xc} is called the **exchange-correlation functional**

Exchange-correlation functional

Assuming that

- $F_{\text{LL}}(\rho) = \inf_{\Psi | \rho_{\Psi}=\rho} \langle \Psi | H_N^1 | \Psi \rangle$ **has a unique minimizer Ψ_{ρ}^0 (up to a global phase)**
- $T_{\text{s}}(\rho) = \inf_{\Phi \text{ Slater det.} | \rho_{\Phi}=\rho} \langle \Phi | H_N^0 | \Phi \rangle$ **has a unique minimizer Φ_{ρ}^0 (u.t.g.p.)**

one can define

- **the kinetic energy and electron-electron energy functionals**

$$T(\rho) := \langle \Psi_{\rho}^0 | T | \Psi_{\rho}^0 \rangle, \quad V_{\text{ee}}(\rho) := \langle \Psi_{\rho}^0 | V_{\text{ee}} | \Psi_{\rho}^0 \rangle$$

- **the exchange energy functional**

$$E_{\text{x}}(\rho) := -\frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\gamma_{\Phi_{\rho}^0}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

- **the kinetic and e-e contributions to the correlation energy functional**

$$T_{\text{c}}(\rho) := T(\rho) - T_{\text{s}}(\rho) \quad \mathbf{and} \quad U_{\text{c}}(\rho) = V_{\text{ee}}(\rho) - J(\rho) - E_{\text{x}}(\rho)$$

$$E_{\text{xc}}(\rho) = E_{\text{x}}(\rho) + E_{\text{c}}(\rho), \quad E_{\text{c}}(\rho) = T_{\text{c}}(\rho) + U_{\text{c}}(\rho)$$

Orders of magnitude of the various components of the energy (in a.u.)

System	E_{GS}	$T(\rho_{\text{GS}})$	$T_{\text{s}}(\rho_{\text{GS}})$	$T_{\text{c}}(\rho_{\text{GS}})$	$V_{\text{ne}}(\rho_{\text{GS}})$	$V_{\text{ee}}(\rho_{\text{GS}})$	$J(\rho_{\text{GS}})$	$E_{\text{x}}(\rho_{\text{GS}})$	$U_{\text{c}}(\rho_{\text{GS}})$
He	-2.904	2.904	2.867	0.037	-6.753	0.946	2.049	-1.025	-0.079
Be	-14.667	14.667	14.594	0.073	-33.710	4.375	7.218	-2.674	-0.169
Ne	-128.94	128.94	128.61	0.33	-311.12	53.24	66.05	-12.09	-0.39

$$\begin{aligned}
 E_{\text{GS}} &= T(\rho_{\text{GS}}) + V_{\text{ne}}(\rho_{\text{GS}}) + V_{\text{ee}}(\rho_{\text{GS}}) \\
 &= \underbrace{T_{\text{s}}(\rho_{\text{GS}}) + V_{\text{ne}}(\rho_{\text{GS}}) + J(\rho_{\text{GS}}) + E_{\text{x}}(\rho_{\text{GS}})}_{\text{could be "easily" computed from } \rho_{\text{GS}}} + \underbrace{T_{\text{c}}(\rho_{\text{GS}}) + U_{\text{c}}(\rho_{\text{GS}})}_{E_{\text{c}}(\rho_{\text{GS}})}
 \end{aligned}$$

In practice, because of error cancellations, it is better to split the energy as $E(\rho) = T_{\text{s}}(\rho) + V_{\text{ne}}(\rho) + J(\rho) + E_{\text{xc}}(\rho)$ and approximate $E_{\text{xc}}(\rho)$

Local Density Approximation (LDA)

A possible approximation of $E_{xc}(\rho)$ (Kohn and Sham '65) is

$$E_{xc}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} e_{xc}(\rho(x)) dx$$

where $e_{xc}(\bar{\rho})$ is the exchange-correlation energy density in a homogeneous electron gas of density $\bar{\rho}$

Parametrization of $e_{xc} : \mathbb{R}_+ \rightarrow \mathbb{R}$: see **Part 4: Homogeneous electron gas**

Beyond LDA

→ see **Kieron's talk**

Beyond-LDA Kohn-Sham models are poorly understood mathematically

Rewriting the minimization problem in terms of $\Phi = (\phi_1, \dots, \phi_N)$, one obtains

$$E_0 \simeq \inf \left\{ E^{\text{KS,LDA}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\begin{aligned} E^{\text{KS,LDA}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V \\ &+ \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(\mathbf{r})) d\mathbf{r} \end{aligned}$$

with

$$V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

Existence of solutions for neutral and positively charged systems for the $\mathbf{X}\alpha$ model ($e_{\text{xc}}(\rho) = -C \int_{\mathbb{R}^3} \rho^{4/3}$): Le Bris '93

Kohn-Sham equations (Euler-Lagrange + gauge invariance + loc. min.)

$$\begin{cases} -\frac{1}{2}\Delta\phi_i + \mathcal{W}_\Phi\phi_i = \varepsilon_i\phi_i & 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} & 1 \leq i, j \leq N \end{cases}$$

- **In the Hartree-Fock model, the potential \mathcal{W}_Φ is nonlocal**

$$\mathcal{W}_\Phi^{\text{HF}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\cdot|} \right) \phi - \int_{\mathbb{R}^3} \frac{\gamma_\Phi(\cdot, \mathbf{r}')}{|\cdot - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}', \quad \gamma_\Phi(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$$

while it is local in the Kohn-Sham LDA model

$$\mathcal{W}_\Phi^{\text{KS-LDA}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\cdot|} + \frac{de_{\text{xc}}}{d\rho}(\rho_\Phi) \right) \phi$$

- **In the Hartree-Fock model, $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$ are the lowest N eigenvalues of $-\frac{1}{2}\Delta + \mathcal{W}_\Phi$, while it is not known whether this property holds true for the Kohn-Sham LDA model**

Lieb approach (minimizing over N -body density matrices)

Let $\Gamma \in \mathcal{D}_N$

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle\langle\Psi_n|, \quad \Psi_n \in \bigwedge^N L^2(\mathbb{R}^3), \quad \langle\Psi_m|\Psi_n\rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1$$

The first order reduced density operator associated with Γ is

$$\gamma_\Gamma = \sum_{n=1}^{+\infty} p_n \gamma_{\Psi_n} \quad \text{note that} \quad \rho_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r}, \mathbf{r})$$

It holds

$$\gamma_\Gamma^* = \gamma_\Gamma, \quad 0 \leq \gamma_\Gamma \leq 1, \quad \mathbf{Tr}(\gamma_\Gamma) = N, \quad \mathbf{Tr}(H_N^0 \Gamma) = \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma_\Gamma\right)$$

Theorem (ensemble N -representability of 1-RDM)

$$\begin{aligned} \mathcal{C}_N &= \{\gamma \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \gamma_\Gamma = \gamma\} \\ &= \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1, \mathbf{Tr}(\gamma) = N, \mathbf{Tr}(-\Delta\gamma) < \infty\} \end{aligned}$$

Janak functional (Lieb density functional for non-interacting electrons)

$$\begin{aligned}
T_J(\rho) &= \inf \left\{ \mathbf{Tr}(H_N^0 \Gamma), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
&= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma_\Gamma \right), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
&= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right), \gamma \in \mathcal{C}_N \text{ s.t. } \rho_\gamma = \rho \right\} \quad \text{where } \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}) \\
&= \inf \left\{ \sum_{i=1}^{+\infty} \frac{1}{2} n_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \right. \\
&\quad \left. 0 \leq n_i \leq 1, \sum_{i=1}^{+\infty} n_i |\phi_i|^2 = \rho \right\}
\end{aligned}$$

Extended Kohn-Sham LDA model

$$\inf \{ \mathcal{E}(\gamma), \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)), 0 \leq \gamma \leq 1, \mathbf{Tr}(\gamma) = N, \mathbf{Tr}(-\Delta\gamma) < \infty \}$$

$$\mathcal{E}(\gamma) = \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right) + \int_{\mathbb{R}^3} \rho_\gamma V + J(\rho_\gamma) + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_\gamma), \quad \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

The minimization set \mathcal{C}_N is convex and any $\gamma \in \mathcal{C}_N$ can be written as

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle \langle \phi_i|$$

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad 0 \leq n_i \leq 1, \quad \sum_{i=1}^{+\infty} n_i = N, \quad \phi_i \in H^1(\mathbb{R}^3)$$

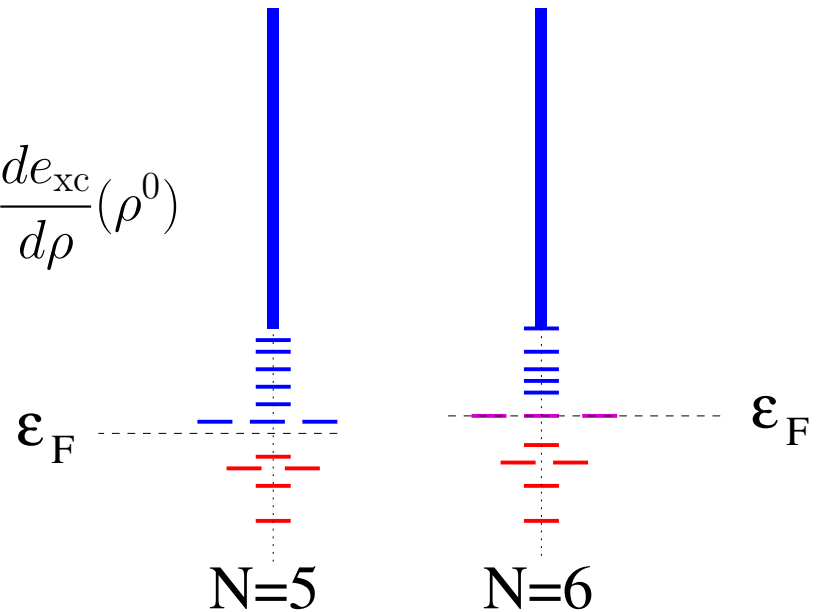
**Existence of solutions for neutral and positively charged systems:
Anantharaman-EC '09 for LDA and GGA $2e^-$, Gontier '15 for LSDA**

Extended Kohn-Sham LDA equations

$$\gamma^0 = \sum_i n_i |\phi_i\rangle \langle \phi_i| \qquad \rho^0(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$$

$$\left\{ \begin{array}{l} H_{\rho^0} \phi_i = \varepsilon_i \phi_i \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \end{array} \right. \quad \mathbf{and} \quad \left\{ \begin{array}{l} n_i = 1 \text{ if } \varepsilon_i < \varepsilon_F, \\ 0 \leq n_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_F, \\ n_i = 0 \text{ if } \varepsilon_i > \varepsilon_F, \end{array} \right. \quad \sum_i n_i = N$$

$$H_{\rho^0} = -\frac{1}{2}\Delta + V + \rho^0 \star |\mathbf{r}|^{-1} + \frac{de_{xc}}{d\rho}(\rho^0)$$



4 - Homogeneous electron gas

Reference: Dreizler and Gross, Springer-Verlag 1990

Supercell model (useful for theoretical calculation and numerical simulations)

supercell $\Omega = [0, L)^3$, spin states $S = \{|\uparrow\rangle, |\downarrow\rangle\}$,
 periodic lattice $\mathcal{R}_L = LZ^3$, dual lattice $\mathcal{R}_L^* = \frac{2\pi}{L}Z^3$

Electronic Hamiltonian (second quantization formalism)

$$H_L = \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \frac{\hbar^2}{2m_e} |\mathbf{k}|^2 a_{\mathbf{k}, \sigma}^\dagger a_{\mathbf{k}, \sigma} + \frac{e^2}{2L^3} \sum_{\mathbf{q} \in \mathcal{R}_L^* \setminus \{0\}} \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \sum_{\mathbf{k}' \in \mathcal{R}_L^*, \sigma' \in S} \frac{4\pi}{|\mathbf{q}|^2} a_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}'-\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}, \sigma} a_{\mathbf{k}', \sigma}$$

→ **rigorous results on the TL by Lieb & Narnhofer '75**

Remark. This is the jellium model, not clear mathematically that this coincides with the HEG (minimizer of the energy per unit volume at constant density)

→ **see Lewin & Lieb '15**

Supercell model (useful for theoretical calculation and numerical simulations)

supercell $\Omega = [0, L)^3$, spin states $S = \{|\uparrow\rangle, |\downarrow\rangle\}$,
 periodic lattice $\mathcal{R}_L = LZ^3$, dual lattice $\mathcal{R}_L^* = \frac{2\pi}{L}Z^3$

Electronic Hamiltonian (second quantization formalism)

$$H_L = \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \frac{\hbar^2}{2m_e} |\mathbf{k}|^2 a_{\mathbf{k}, \sigma}^\dagger a_{\mathbf{k}, \sigma} + \frac{e^2}{2L^3} \sum_{\mathbf{q} \in \mathcal{R}_L^* \setminus \{0\}} \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \sum_{\mathbf{k}' \in \mathcal{R}_L^*, \sigma' \in S} \frac{4\pi}{|\mathbf{q}|^2} a_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}'-\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}, \sigma} a_{\mathbf{k}', \sigma}$$

Dimensional analysis: for the homogeneous electron gas of density $n \in \mathbb{R}_+^*$

$$a_0 = \frac{\hbar^2}{m_e e^2} \text{ (Bohr radius)}, \quad r_0 = \left(\frac{3}{4\pi n} \right)^{1/3} \text{ (Wigner-Seitz radius)}, \quad r_s = \frac{r_0}{a_0}$$

$$H_{La_0 r_s} = \frac{e^2}{a_0 r_s^2} \left(\sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \frac{|\mathbf{k}|^2}{2} a_{\mathbf{k}, \sigma}^\dagger a_{\mathbf{k}, \sigma} + \frac{r_s}{2L^3} \sum_{\mathbf{q} \in \mathcal{R}_L^*} \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in S} \sum_{\mathbf{k}' \in \mathcal{R}_L^*, \sigma' \in S} \frac{4\pi}{|\mathbf{q}|^2} a_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}'-\mathbf{q}, \sigma}^\dagger a_{\mathbf{k}, \sigma} a_{\mathbf{k}', \sigma} \right)$$

r_s small (high-density regime): kinetic energy \gg potential energy

r_s large (low-density regime): potential energy \gg kinetic energy

High-density regime ($r_s \ll 1$)

- leading term in the limit $r_s \rightarrow 0$

$$H_L = \sum_{\mathbf{k} \in \mathcal{R}_L^*, \sigma \in \mathcal{S}} \frac{\hbar^2}{2m_e} |\mathbf{k}|^2 a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma} \xrightarrow{L \rightarrow \infty} -\frac{\hbar^2}{2m_e} \Delta$$

The ground-state density matrix is not spin-polarized

$$\gamma_0 = \mathbb{1}_{(-\infty, \varepsilon_F]} \left(-\frac{\hbar^2}{2m_e} \Delta \right), \quad \varepsilon_F \text{ such that } \underline{\text{Tr}}(\gamma_0) = n$$

The ground-state energy per particle is given by

$$\tilde{e}_0^{\text{HD},0}(r_s) = \frac{\tilde{C}_{\text{TF}}}{r_s^2} = C_{\text{TF}} n^{2/3}, \quad \text{with } C_{\text{TF}} = \frac{3\hbar^2}{10m_e} (3\pi^2)^{2/3}, \quad \tilde{C}_{\text{TF}} = \frac{3}{10} \left(\frac{9\pi}{4} \right)^{2/3} \frac{e^2}{a_0}$$

High-density regime ($r_s \ll 1$) (continued)

- **1st-order perturbation: let $n = n_\uparrow + n_\downarrow$ and $\zeta = \frac{n_\uparrow - n_\downarrow}{n}$**

$$\tilde{e}_0^{\text{HD},0}(r_s, \zeta) + \tilde{e}_0^{\text{HD},1}(r_s, \zeta) = \tilde{C}_{\text{TF}} \frac{(1 + \zeta)^{5/3} + (1 - \zeta)^{5/3}}{2r_s^2} - \tilde{C}_{\text{D}} \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}}{2r_s}$$

→ **rigorous asymptotics when $r_s \rightarrow 0$ (Graf & Solovej '94)**

According to this model, there is a phase transition at $r_s = r_s^{(1)} \simeq 5.45$:

- $r_s < 5.45$: **spin-unpolarized**
- $r_s > 5.45$: **spin-polarized**

According to numerical simulations (see below), the phase transition occurs at much lower density ($r_s^{(\infty)} \gg 5.45$)

For valence electrons in real metals, the local Wigner-Seitz radius is typically

$$1.8 \leq r_s(\mathbf{r}) \leq 5.6$$

→ **see David Gontier's talk on the Hartree-Fock approximation for the HEG**

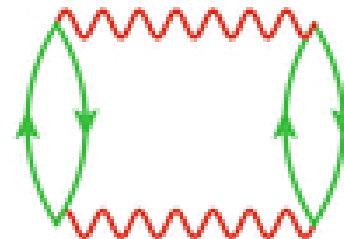
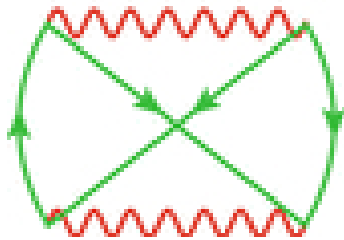
High-density regime ($r_s \ll 1$) (continued)

- 2nd-order perturbation: two diagrams contribute

- 2nd-order exchange diagram:

$$\tilde{\epsilon}_{0,x}^{\text{HD},2}(r_s) = \left(\frac{1}{6} \ln 2 - \frac{3}{4\pi^2} \zeta(3) \right) \frac{e^2}{a_0} \simeq 0.024 \frac{e^2}{a_0} \quad \text{(Onsager et al. '66)}$$

- 2nd-order ring diagram \longrightarrow **divergent**



$$\tilde{\epsilon}_{0,x}^{\text{HD},2}(r_s) = \frac{3e^4}{16\pi^5} \int_{\mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^3} \frac{f_{\mathbf{k}} f_{\mathbf{k}'} (1 - f_{\mathbf{k}+\mathbf{q}}) (1 - f_{\mathbf{k}'+\mathbf{q}})}{|\mathbf{q}|^2 |\mathbf{k} + \mathbf{k}' + \mathbf{q}|^2 \mathbf{q} \cdot (\mathbf{k} + \mathbf{k}' + \mathbf{q})} d\mathbf{k} d\mathbf{k}' d\mathbf{q}, \quad f_{\mathbf{k}} = \mathbb{1}_{|\mathbf{k}| \leq 1}$$

High-density regime ($r_s \ll 1$) (continued)

- 2nd-order perturbation: two diagrams contribute

- 2nd-order exchange diagram:

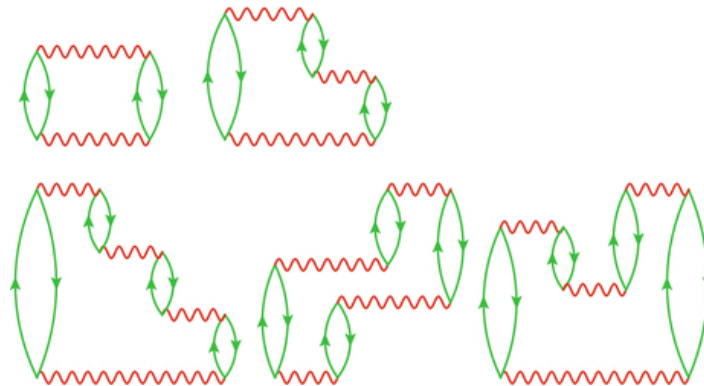
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- 2nd-order ring diagram \longrightarrow **divergent**

- Random Phase Approximation (RPA) = ring approximation

$$\tilde{\epsilon}_{0,c}^{\text{ring}}(r_s) = \left(\frac{(1 - \ln 2)}{\pi^2} \ln r_s - 0.071 + o(1) \right) \frac{e^2}{a_0} \quad \text{(Gell-Mann & Brueckner '57)}$$

(partial resummation of ring diagrams of any orders)



High-density regime ($r_s \ll 1$) (continued)

- **2nd-order perturbation: two diagrams contribute**

- **2nd-order exchange diagram:**

$$\tilde{e}_{0,x}^{\text{HD},2}(r_s) = \left(\frac{1}{6} \ln 2 - \frac{3}{4\pi^2} \zeta(3) \right) \frac{e^2}{a_0} \simeq 0.024 \frac{e^2}{a_0} \quad \text{(Onsager et al. '66)}$$

- **2nd-order ring diagram** \longrightarrow **divergent**

- **Random Phase Approximation (RPA) = ring approximation**

$$\tilde{e}_{0,c}^{\text{ring}}(r_s) = \left(\frac{(1 - \ln 2)}{\pi^2} \ln r_s - 0.071 + o(1) \right) \frac{e^2}{a_0} \quad \text{(Gell-Mann & Brueckner '57)}$$

(partial resummation of ring diagrams of any orders)

- **Correlation energy per particle in the high-density regime**

$$\tilde{e}_{0,c}^{\text{HD}}(r_s) = \left(\frac{(1 - \ln 2)}{\pi^2} \ln r_s - 0.048 + 0.009 r_s \ln r_s - 0.018 r_s + o(r_s) \right) \frac{e^2}{a_0}$$

(last two explicit terms by du Bois '59 and Carr & Maradudin '65)

Low-density regime ($r_s \gg 1$)

- **Wigner crystallization in a BCC lattice**
(conjecture supported by numerical simulations)
- **Energy per particle in the high-density regime**

$$\tilde{e}_0^{\text{HD}}(r_s) = \left(-\frac{1.792}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} + o\left(\frac{1}{r_s^2}\right) \right) \frac{e^2}{2a_0}$$

including

- the BCC lattice energy (first term, Wigner '34)
- the harmonic lattice vibrations (second term, Wigner '38)
- the first anharmonic corrections (third term, Carr-Coldwell et al. '61)

note that there is no consensus on the correctness of this expansion

Intermediate regime

Numerical approximation of the many-body problem

- coupled-clusters (Freeman '77)
- quantum Monte Carlo (VMC: Ceperley '78, GFMC: Ceperley & Alder '80)

Parameterization of the exchange-correlation energy per particle

Two popular parameterizations of $\tilde{e}_c(n, \zeta)$

- Vosko, Wilk & Nusain '80 (VWN)
- Perdew & Zunger '91 (PZ91)

both using

- the high-density expansion
- the QCM results by Ceperley & Alder '80

Perdew & Zunger parameterization (PZ91)**• exchange functional**

$$\tilde{e}_x(r_s, \zeta) = \tilde{e}_x(r_s, 0) + (\tilde{e}_x(n, 1) - \tilde{e}_x(r_s, 0)) f(\zeta)$$

$$\tilde{e}_x(r_s, 0) = -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} \left(\frac{e^2}{a_0}\right), \quad \tilde{e}_x(r_s, 1) = 2^{1/3} \tilde{e}_x(r_s, 0), \quad f(\zeta) = \frac{(1 + \zeta)^{\frac{4}{3}} + (1 - \zeta)^{\frac{4}{3}} - 2}{2(2^{\frac{1}{3}} - 1)}$$

Perdew & Zunger parameterization (PZ91)

- **exchange functional**

$$\tilde{e}_x(r_s, \zeta) = \tilde{e}_x(r_s, 0) + (\tilde{e}_x(n, 1) - \tilde{e}_x(r_s, 0)) f(\zeta)$$

$$\tilde{e}_x(r_s, 0) = -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} \left(\frac{e^2}{a_0}\right), \quad \tilde{e}_x(r_s, 1) = 2^{1/3} \tilde{e}_x(r_s, 0), \quad f(\zeta) = \frac{(1 + \zeta)^{\frac{4}{3}} + (1 - \zeta)^{\frac{4}{3}} - 2}{2(2^{\frac{1}{3}} - 1)}$$

- **correlation functional**

$$\tilde{e}_c^{\text{PZ}}(r_s, \zeta) \simeq \tilde{e}_c^{\text{PZ}}(r_s, 0) + (\tilde{e}_c^{\text{PZ}}(n, 1) - \tilde{e}_c^{\text{PZ}}(r_s, 0)) f(\zeta)$$

with for $\zeta = 0$ or $\zeta = 1$

$$\tilde{e}_c^{\text{PZ91}}(r_s, \zeta) = \begin{cases} \frac{\gamma_\zeta}{1 + \beta_{1,\zeta} r_s^{1/2} + \beta_{2,\zeta} r_s} \left(\frac{e^2}{a_0}\right) & \text{for } r_s \geq 1 \\ (A_\zeta \ln r_s + B_\zeta + C_\zeta r_s \ln r_s + D_\zeta r_s) \left(\frac{e^2}{a_0}\right) & \text{for } 0 \leq r_s \leq 1 \end{cases}$$

Perdew & Zunger parameterization (PZ91) (continued)

- **parameterization of the correlation functional: $\zeta = 0$ or $\zeta = 1$**

$$\tilde{e}_c^{\text{PZ91}}(r_s, \zeta) = \begin{cases} \frac{\gamma_\zeta}{1 + \beta_{1,\zeta} r_s^{1/2} + \beta_{2,\zeta} r_s} \left(\frac{e^2}{a_0} \right) & \text{for } r_s \geq 1 \\ (A_\zeta \ln r_s + B_\zeta + C_\zeta r_s \ln r_s + D_\zeta r_s) \left(\frac{e^2}{a_0} \right) & \text{for } 0 \leq r_s \leq 1 \end{cases}$$

with

$$\begin{aligned} \gamma_0 &= -0.1423 & \beta_{1,0} &= 1.0529 & \beta_{2,0} &= 0.3334 & A_0 &= 0.0311 & B_0 &= -0.0480 & C_0 &= 0.0020 & D_0 &= -0.0116 \\ \gamma_1 &= -0.0843 & \beta_{1,1} &= 1.3981 & \beta_{2,1} &= 0.2611 & A_1 &= 0.0155 & B_1 &= -0.0269 & C_1 &= 0.0007 & D_1 &= -0.0048 \end{aligned}$$

- $\gamma_\zeta, \beta_{1,\zeta}, \beta_{2,\zeta}, \zeta = 0, 1$: **fit of Ceperley-Alder results**
- A_0 and B_0 : **first two terms of the high-density expansion (RPA resummation)**
- A_1 and B_1 : **use the scaling (exact for RPA, valid with a 1% accuracy)**

$$\tilde{e}_c(r_s, 1) = \frac{1}{2} \tilde{e}_c(r_s/2^{4/3}, 0)$$

- C_ζ and $D_\zeta, \zeta = 0, 1$: **chosen so that $\tilde{e}_c^{\text{PZ91}}(n, \zeta)$ is C^1 on \mathbb{R}_+^***