

## Part II: Hohenberg-Kohn Theorems

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## What is DFT for?

As *Density Functional Theory* we understand - following Prof. Kohn's terminology - the formalism dealing with *electronic matter*, i.e., the matter described adequately by means of the non-relativistic Schrödinger equation in Born-Oppenheimer approximation:

$$\hat{H}\Psi = E\Psi$$

$E$  is the electronic energy,

$\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  is the  $N$ -electron wave-function,  
and  $\hat{H}$  is the Hamiltonian operator (in atomic units):

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_{i=1}^N v(\mathbf{r}_i) + \sum_{i=1}^N \sum_{i<j}^N \frac{1}{r_{ij}}$$

$v(\mathbf{r}_i)$  denotes the external potential acting on electron  $i$ .



## What potentials are considered?

$v(\mathbf{r})$  is usually the potential of nuclear charges:

$$v(\mathbf{r}_i) = - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}_i|}$$

$M$  is the number of nuclei,  $Z_{\alpha}$  is the nuclear charge  $\alpha$ ,  $\mathbf{R}_{\alpha}$  is its position.

Following basic quantum mechanics, a given external potential  $v(\mathbf{r})$  and a given number of electron  $N$  determine the ground state wavefunction and the ground state electron density (except for degeneracies).

$$\begin{aligned}\Psi_o(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \Psi_o[v](\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ \rho_o(\mathbf{r}) &= \rho_o[v](\mathbf{r}) \\ E_o &= E_o[v]\end{aligned}$$



## First Hohenberg-Kohn Theorem

According to postulates of QM:

$$N, v(\mathbf{r}) \longrightarrow \Psi_o(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \longrightarrow \rho_o(\mathbf{r}) \text{ and } E_o$$

In 1964, Hohenberg and Kohn proved, that the reverse is also true <sup>1</sup>

## First Hohenberg-Kohn Theorem

*The external potential  $v(\mathbf{r})$  is determined, within a trivial additive constant, by the ground-state electron density  $\rho$ .*

<sup>1</sup> P. Hohenberg, W. Kohn, *Phys. Rev. B*, **136** (1964) 864. Inhomogeneous Electron Gas.



## Exercise

Show that:

For two Hamiltonians  $\hat{H}$  and  $\hat{H}'$  differing in the potential energy term only:

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V}_{ee} + \hat{V} \\ \hat{H}' &= \hat{T} + \hat{V}_{ee} + \hat{V}'\end{aligned}$$

if the ground state functions are the same, the difference between the two potentials is constant ( $v(\mathbf{r}) - v'(\mathbf{r}) = \text{const.}$ )



## Proof of the first HK theorem: reductio ad absurdum

### Assumption:

$v(\mathbf{r})$  and  $v'(\mathbf{r})$  are two potentials such that  $v(\mathbf{r}) - v'(\mathbf{r}) \neq \text{const}$  for which the ground-state densities are the same.

- If  $\hat{H}$ ,  $\hat{H}'$ ,  $\Psi$ , and  $\Psi'$  denote the corresponding Hamiltonians and ground state functions then  $\Psi$  and  $\Psi'$  are different ( $\hat{H}\Psi = E_0\Psi$ ,  $\hat{H}'\Psi' = E_0'\Psi'$ ) unless  $v(\mathbf{r}) - v'(\mathbf{r})$  is a constant (exercise).
- From the variational principle:

$$\begin{aligned} E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E_0' + \int \rho(\mathbf{r}) \{v(\mathbf{r}) - v'(\mathbf{r})\} d\mathbf{r} \end{aligned}$$

$$\begin{aligned} E_0' < \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &= E_0 - \int \rho(\mathbf{r}) \{v(\mathbf{r}) - v'(\mathbf{r})\} d\mathbf{r} \end{aligned}$$

- Adding the two above equations:

$$E_0 + E_0' < E_0' + E_0 \quad \text{Contradiction!}$$



## $v$ -representability

The uniqueness of  $v(\mathbf{r})$  for a given  $\rho$  does not assure that  $v(\mathbf{r})$  exist for *any* electron density.

An electron density, for which the associated  $v(\mathbf{r})$  exists, is called  **$v$ -representable**.





## Universal functional $F_{HK}[\rho]$

The first Hohenberg-Kohn theorem provides the fundamental theoretical basis for all modern variants of density functional theorem. Thomas and Fermi were right in their search for the total energy expression depending explicitly on the electron density. The first Hohenberg-Kohn theorem assures that such an expression **exists generally**. It is denoted by  $E_v[\rho]$  where  $v$  indicates that this functional depends on the system through the external potential  $v(\mathbf{r})$ .

Hohenberg and Kohn introduced a system-independent functional  $F_{HK}[\rho]$ :

$$F_{HK}[\rho] = E_v[\rho] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}$$

The functional  $F_{HK}[\rho]$  exists only for  $v$ -representable electron densities.



## Second Hohenberg-Kohn Theorem

The first Hohenberg-Kohn theorem proves one-to-one mapping between the external potentials and the ground state densities in many-electron systems.

It does not say anything about neither the analytic form of the universal functional  $F_{HK}[\rho]$  nor the practical ways to obtain the ground state electron densities.

The second Hohenberg-Kohn theorem concerns the latter issue.



## Second Hohenberg-Kohn Theorem

For a trial electron density  $\tilde{\rho}(\mathbf{r})$  such that  $\tilde{\rho}(\mathbf{r}) \geq 0$  and  $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$

$$E_0 \leq E_v[\tilde{\rho}]$$



## Second Hohenberg-Kohn Theorem: proof

*(Works only for  $v$ -representable  $\tilde{\rho}$ !)*

Following the first Hohenberg-Kohn theorem, for a trial ground-state electron density  $\tilde{\rho}$  there exists an associated external potential  $\tilde{v}$ . From  $\tilde{v}$ , one can construct a Hamiltonian  $\tilde{H}$  and its ground-state wavefunction  $\tilde{\Psi}$ . Applying the function  $\tilde{\Psi}$  as a trial function in the variational principle leads to:

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho]$$

*End of the proof*



## Generalization of $F_{HK}[\rho]$ : Levy's constrained search

We start with the variational principle

$$E_o = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

with

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}$$

where  $\hat{V}_{ee} = \sum_{i=1}^N \sum_{i < j}^N \frac{1}{r_{ij}}$

and the trial N-electron wavefunctions  $\Psi$  are normalized.



## Levy's constrained search: two step procedure

$$\begin{aligned}
 E_0 &= \min_{\Psi \rightarrow N} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\rho \rightarrow N} [ \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle ] \\
 &= \min_{\rho \rightarrow N} [ \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \min_{\Psi \rightarrow \rho} [ \langle \Psi | \hat{H} | \Psi \rangle - \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} ] ] \\
 &= \min_{\rho \rightarrow N} [ \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho] ]
 \end{aligned}$$

where:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle - \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

If  $\rho$  is  $v$ -representable  $F[\rho]$  and  $F_{HK}[\rho]$  yield the same value. But  $F[\rho]$  is defined for a more general class of densities than is  $F_{HK}[\rho]$ .<sup>2</sup>

<sup>2</sup>M. Levy, *Proc. Natl. Acad. Sci. USA*, **76** (1979) 6062.



## N-representability

The admissible densities, for which the functional  $F[\rho]$  is defined, are called **N-representable**.

**The electron density is N-representable if it can be obtained from some antisymmetric wave-function.**

All electron densities satisfying the following three conditions are N-representable (Gilbert, 1975) <sup>3</sup>.

$$\begin{aligned}\rho(\mathbf{r}) &\geq 0 \\ \int \rho(\mathbf{r}) d\mathbf{r} &= N \\ \int |\nabla \rho(\mathbf{r})^{1/2}|^2 d\mathbf{r} &< \infty\end{aligned}$$

The electron densities constructed in practice are usually N-representable by construction.

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<sup>3</sup>T.L. Gilbert, *Phys. Rev. B*, **12** (1975) 2111-2120. Hohenberg-Kohn theorem for nonlocal external potentials.



## E. Bright Wilson observation

Proof of the first Hohenberg-Kohn theorem for Coulombic systems.<sup>4</sup>

- Assume that we have the **exact** ground-state electron density ( $\rho_0$ ) for an unknown system (from X-ray diffraction experiments for instance).
- The total number of electrons for this system can be obtained trivially by integration:

$$N = \int \rho_0 d\mathbf{r}$$

- The maxima of  $\rho_0$  determine the positions of the nuclei ( $\mathbf{R}_A$ ).
- The cusp condition at each maximum of  $\rho_0$  determines the charge of each nucleus:

$$\left. \frac{\partial}{\partial r_A} \bar{\rho} \right|_{r_A=0} = -2Z_A \bar{\rho}(0)$$

where  $\bar{\rho}$  denotes the spherical average<sup>5</sup>.

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<sup>4</sup>E. Bright Wilson in "Structural Chemistry and Biology". Eds. A. Rich and N. Davidson, W.H. Freeman (San Francisco) (1968) 753-760

<sup>5</sup>Kato, *Comm. Pure. & Appl. Math.*, **10** (1957) 151.





## For curious: A little known theorem

We consider all possible solutions of the equation  $\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \lambda$   
(Perdew and Levy, 1985) <sup>6</sup>

### Theorem

*For each solution  $(\rho_i(\mathbf{r})$  and  $\lambda_i)$ ,  $E_v[\rho_i]$  is the energy and  $\rho_i$  are the energy and density of a stationary state (solution of the SE equation  $\hat{H}\Psi = E\Psi$ ).*

### Attention:

- a) The reverse is not proven.
- b) Does Euler-Lagrange equation has more than one solution?

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<sup>6</sup>J. Perdew and M. Levy, *Phys. Rev. B*, **31** (1985) 6264

