Advanced DFT

Scuola Internazionale Superiore di Studi Avanzati

ma per seguir virtute e conoscenza

- General Variational Formulation
- Adiabatic Connection Formalism
- Exact Exchange
  - *Sharp-Horton, Talman-Shadwick,Sham-Shlueter, KLI*
- Fluctuation-Dissipation for Correlation (vdW aware)
  - *RPA, RPAx, ...*
- ISI Interaction Strength Interpolation
- SCE Strictly Correlated Electrons
  - *Kolmogorov optimal transport dual formulation*
- LIISA Locally Interpolated Interaction Strength Approx
- Homogeneous Electron Gas: HF, RPA, Wigner Crystal
- Lieb-Oxford Bound
- Virial Theorem and Scaling Relations
- Unambiguous Energy Densities

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Hohenberg - Kohn Theorem

Pierre C

Walter

Hohenberg and Kohn Theorem

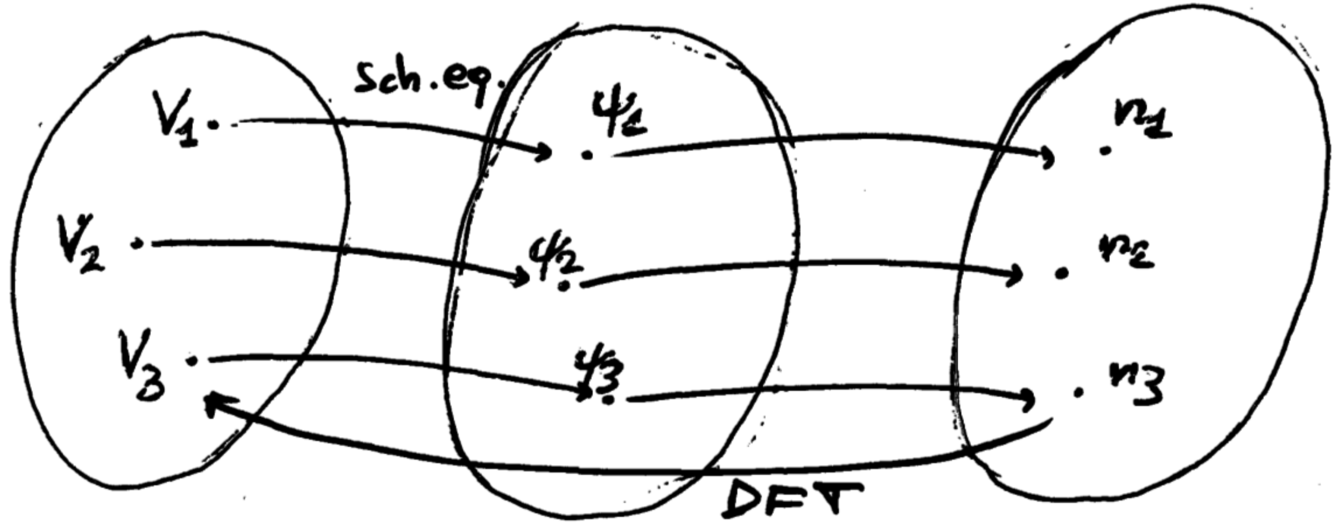
The GS density can be uses as basic variable to describe the status of a quantum many-body system.

All properties of the system are therefore functionals of the GS density.

DENSITY FUNCTIONAL THEORY

the density as the basic variable (for GS properties)

$$[T_e + V_{ee} + V]\psi_{GS} = E_{GS}\psi_{GS} \quad ; \quad n(r) = \langle \psi_{GS} | \hat{n}(r) | \psi_{GS} \rangle$$

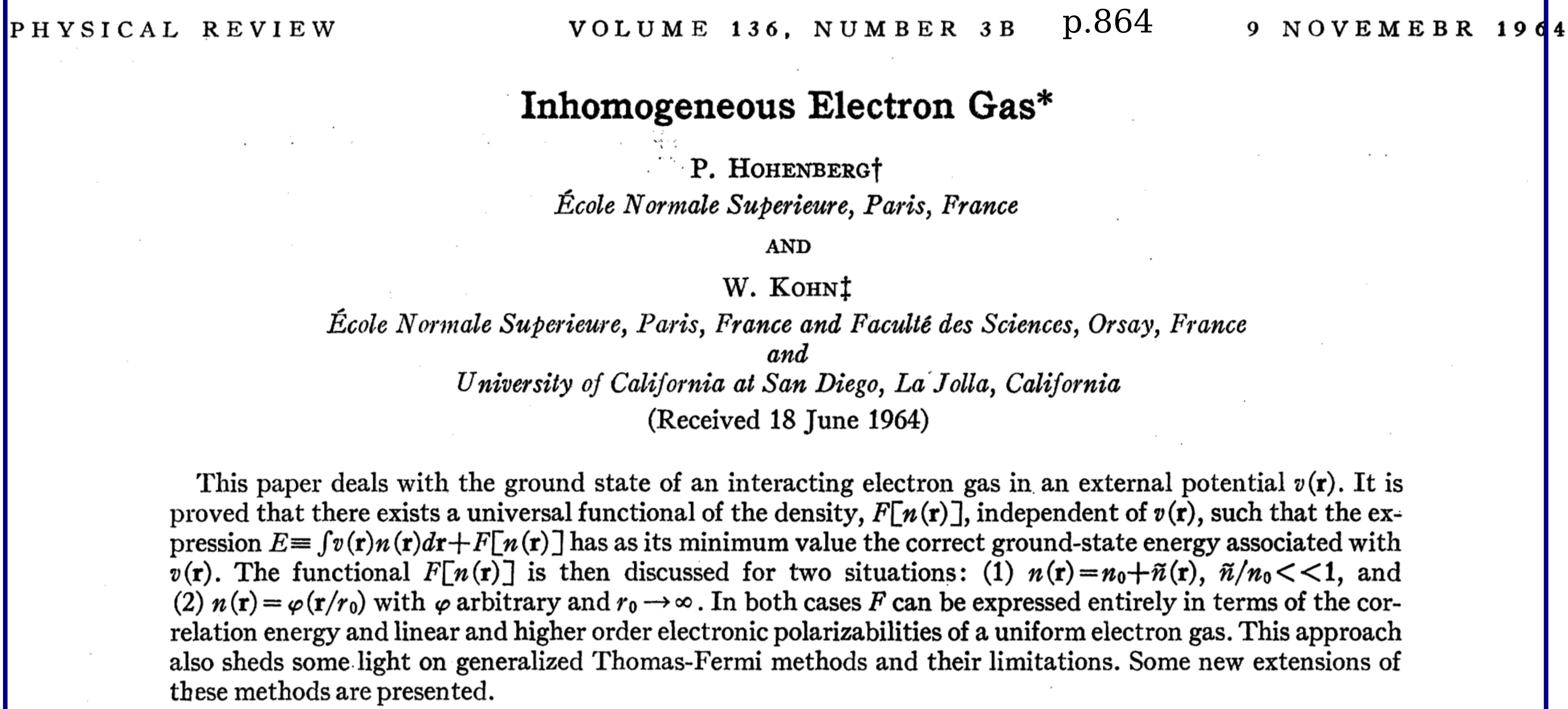


Hohenberg & Kohn Theorem   Phy. Rev. <u>136</u> B864 (1964)

if $V'(r) \neq V(r) + \text{const}$ then $n'(r) \neq n(r)$

$$\Rightarrow n(r) \to V(r) + \text{const} \longrightarrow \psi_{GS} \to E_{GS}, \dots$$

$$F[n] = \langle \psi_{GS}^{[n]} | T_e + V_{ee} | \psi_{GS}^{[n]} \rangle$$



PHYSICAL REVIEW VOLUME 136, NUMBER 3B p.864 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

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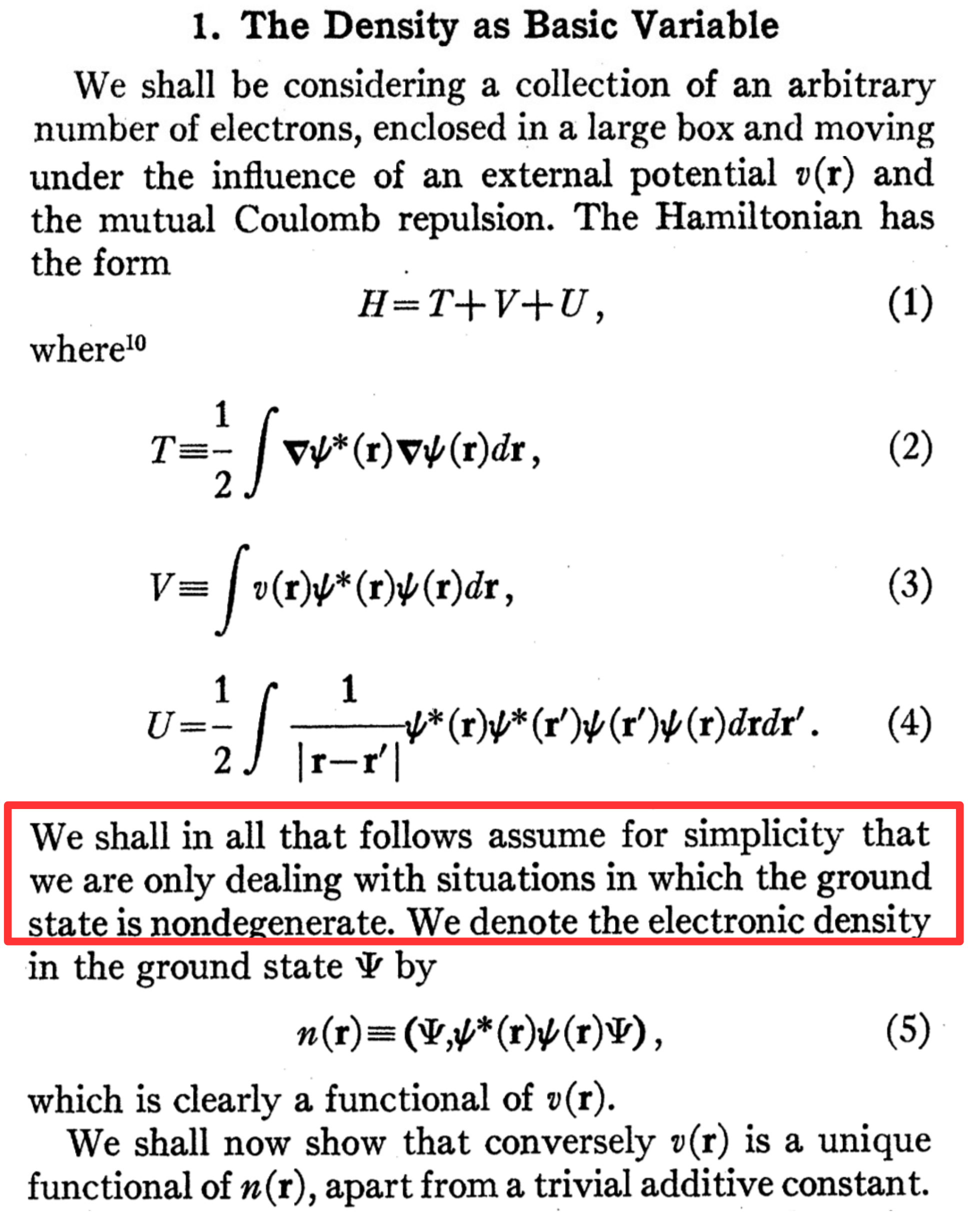
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\rightarrow\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Hohenberg and Kohn Theorem



1. The Density as Basic Variable

We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving under the influence of an external potential $v(\mathbf{r})$ and the mutual Coulomb repulsion. The Hamiltonian has the form

$$H = T + V + U, \qquad (1)$$

where[10]

$$T \equiv \frac{1}{2} \int \nabla\psi^*(\mathbf{r}) \nabla\psi(\mathbf{r}) d\mathbf{r}, \qquad (2)$$

$$V \equiv \int v(\mathbf{r}) \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}, \qquad (3)$$

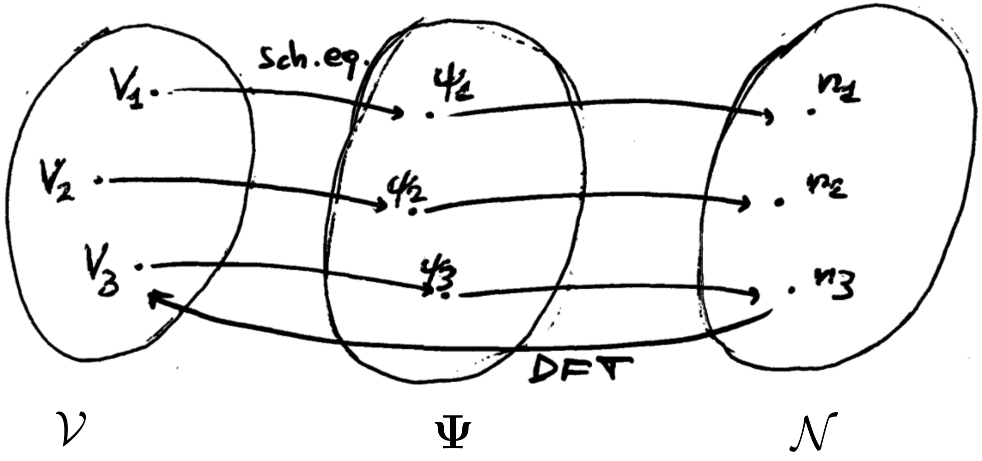
$$U = \frac{1}{2} \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi^*(\mathbf{r}) \psi^*(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) d\mathbf{r} d\mathbf{r}'. \qquad (4)$$

We shall in all that follows assume for simplicity that we are only dealing with situations in which the ground state is nondegenerate. We denote the electronic density in the ground state Ψ by

$$n(\mathbf{r}) \equiv (\Psi, \psi^*(\mathbf{r}) \psi(\mathbf{r}) \Psi), \qquad (5)$$

which is clearly a functional of $v(\mathbf{r})$.

We shall now show that conversely $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant.

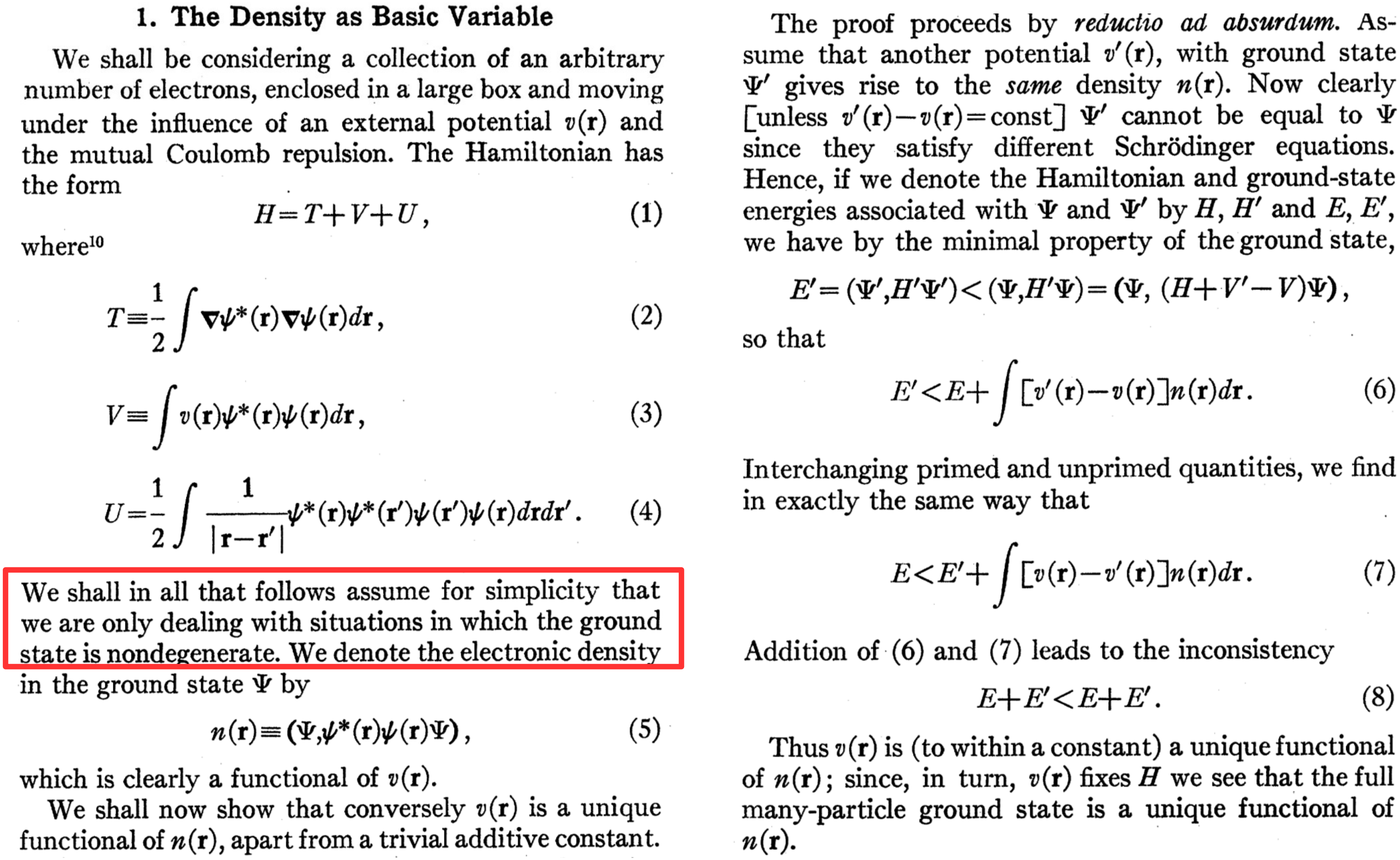


$$\mathcal{V} \longrightarrow \mathbf{\Psi} \longrightarrow \mathcal{N}$$

is invertible for NonDegenerate GS

$$n'(\mathbf{r}) \neq n(\mathbf{r}) \Longrightarrow V'(\mathbf{r}) \neq V(\mathbf{r}) + const$$

Hohenberg and Kohn Theorem



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$$U=\frac{1}{2}\int\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi^*(\mathbf{r})\psi^*(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})d\mathbf{r}d\mathbf{r}'\,. \tag{4}$$

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$$n(\mathbf{r})\equiv(\Psi,\psi^*(\mathbf{r})\psi(\mathbf{r})\Psi)\,, \tag{5}$$

which is clearly a functional of $v(\mathbf{r})$.

We shall now show that conversely $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant.

The proof proceeds by *reductio ad absurdum*. Assume that another potential $v'(\mathbf{r})$, with ground state Ψ' gives rise to the *same* density $n(\mathbf{r})$. Now clearly [unless $v'(\mathbf{r})-v(\mathbf{r})=\text{const}$] Ψ' cannot be equal to Ψ since they satisfy different Schrödinger equations. Hence, if we denote the Hamiltonian and ground-state energies associated with Ψ and Ψ' by H, H' and E, E', we have by the minimal property of the ground state,

$$E'=(\Psi',H'\Psi')<(\Psi,H'\Psi)=(\Psi,\,(H+V'-V)\Psi)\,,$$

so that

$$E'<E+\int[v'(\mathbf{r})-v(\mathbf{r})]n(\mathbf{r})d\mathbf{r}\,. \tag{6}$$

Interchanging primed and unprimed quantities, we find in exactly the same way that

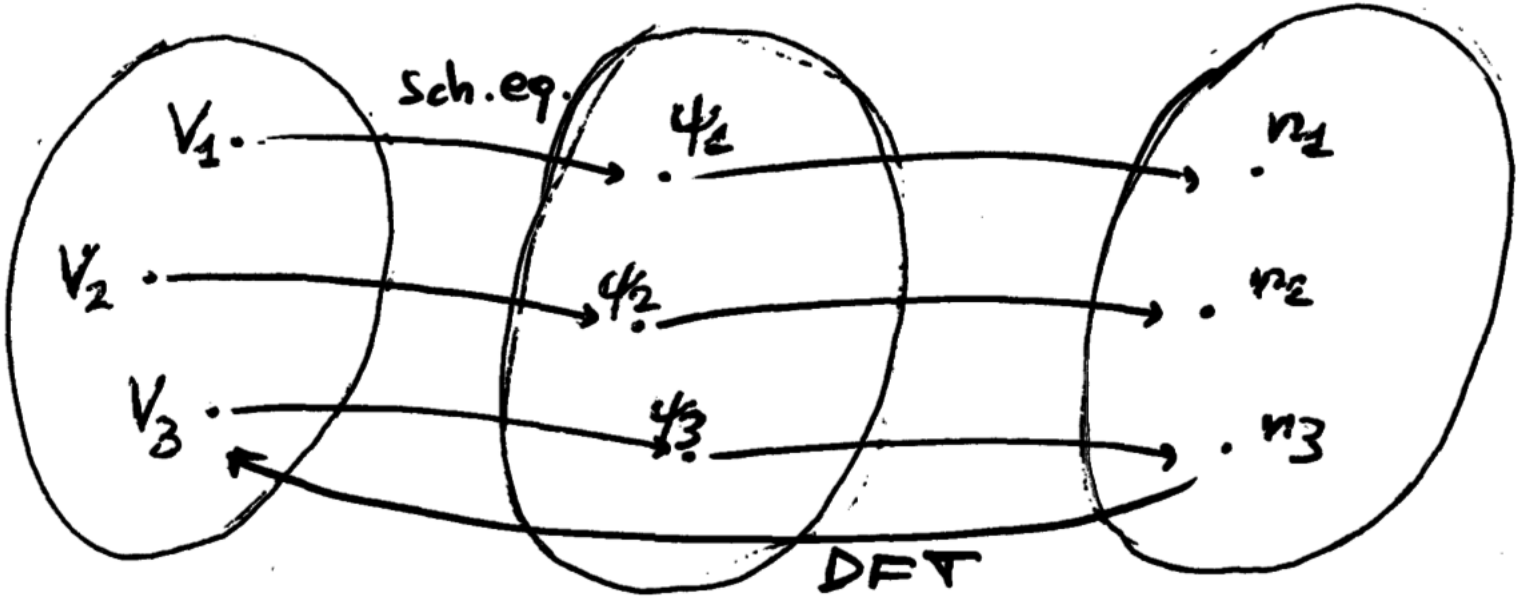
$$E<E'+\int[v(\mathbf{r})-v'(\mathbf{r})]n(\mathbf{r})d\mathbf{r}\,. \tag{7}$$

Addition of (6) and (7) leads to the inconsistency

$$E+E'<E+E'\,. \tag{8}$$

Thus $v(\mathbf{r})$ is (to within a constant) a unique functional of $n(\mathbf{r})$; since, in turn, $v(\mathbf{r})$ fixes H we see that the full many-particle ground state is a unique functional of $n(\mathbf{r})$.

Hohenberg and Kohn Theorem



$\mathcal{V}$ $\quad$ $\boldsymbol{\Psi}$ $\quad$ $\mathcal{N}$

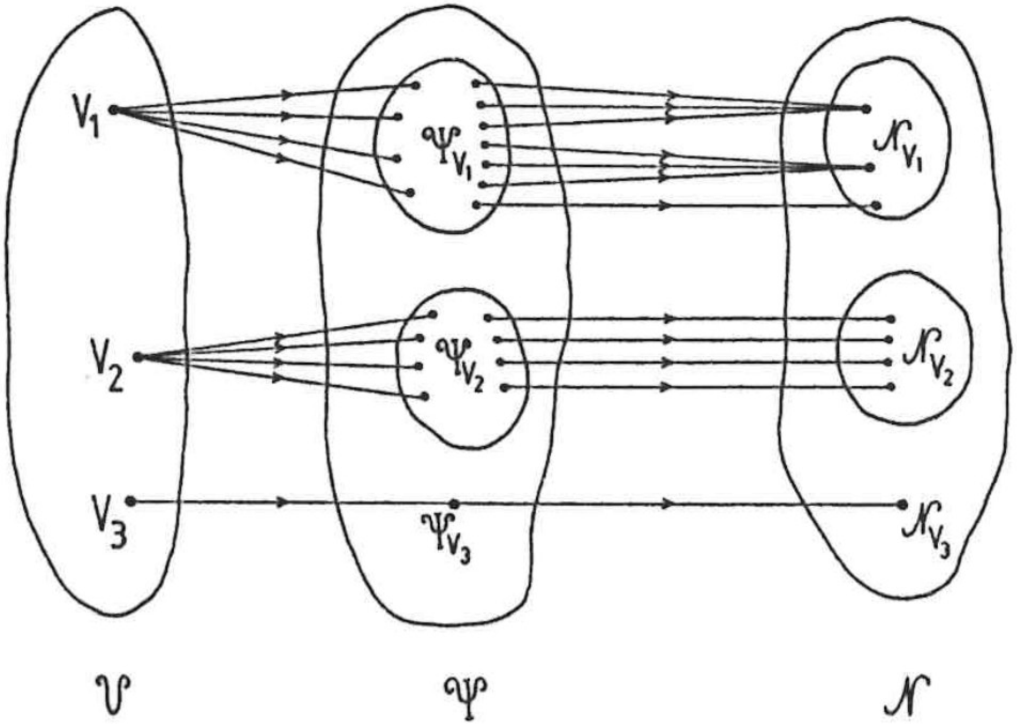
$\mathcal{V} \longrightarrow \boldsymbol{\Psi} \longrightarrow \mathcal{N}$ is invertible for NonDegenerate GS

$F_{HK}[n] = \langle \Psi_{GS}^{[n]} | T + W | \Psi_{GS}^{[n]} \rangle$ with $\Psi_{GS}^{[n]} \longrightarrow n(\mathbf{r})$

$$E_{V_0}[n] = F_{HK}[n] + \int V_0(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

$$E_0(V_0) < E_{V_0}[n] \quad \forall n \in \mathcal{N}, \qquad E_0(V_0) = E_{V_0}[n_0]$$

Degenerate Ground States

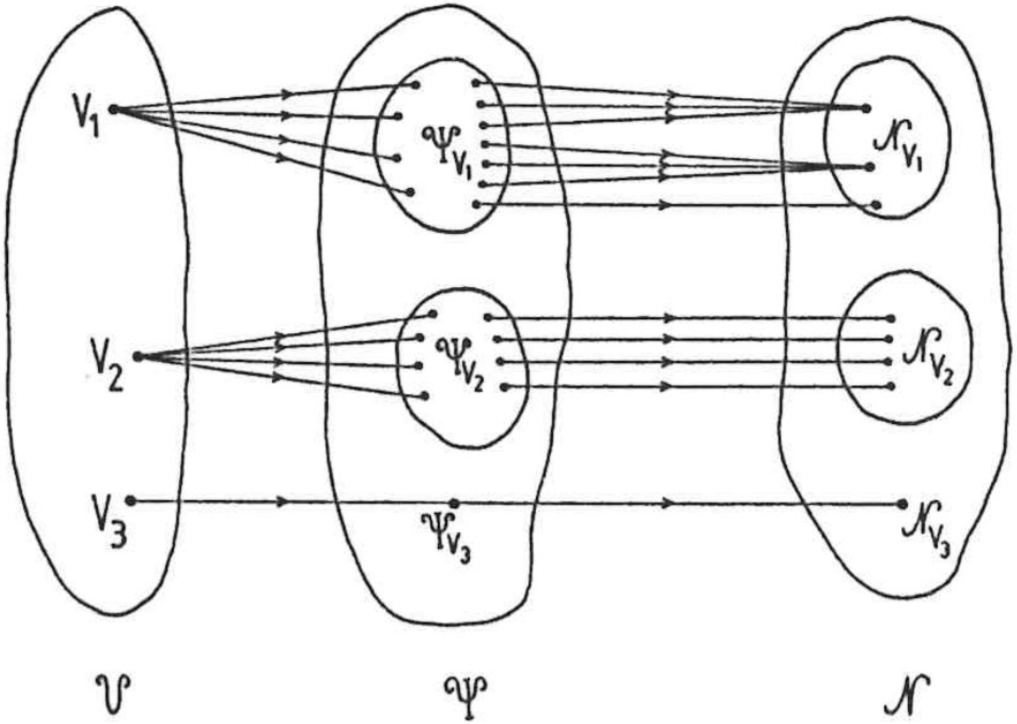


$$\mathbf{\Psi}_V = \left\{ |\Psi\rangle = \sum_{i=1}^{q} c_i |\Psi_i\rangle, \ \ \Psi_i \text{ is GS of V}(\mathbf{r}) \right\}, \qquad \mathbf{\Psi} = \bigcup_{V\in\mathcal{V}} \mathbf{\Psi}_V$$

$$\mathcal{N}_V = \{ n(\mathbf{r}) \mid n(\mathbf{r}) = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle, \ \ |\Psi\rangle \in \mathbf{\Psi}_V \}, \qquad \mathcal{N} = \bigcup_{V\in\mathcal{V}} \mathcal{N}_V$$

$$\mathcal{N}_V \cap \mathcal{N}_{V'} = \varnothing \quad \text{if} \quad V'(\mathbf{r}) \neq V(\mathbf{r}) + const$$

Degenerate Ground States



$n'(\mathbf{r}) \neq n(\mathbf{r}) \Longrightarrow V'(\mathbf{r}) \neq V(r) + const$ also for Degenerate GS

$F_{HK}[n] = \langle \Psi_{GS}^{[n]} | T + W | \Psi_{GS}^{[n]} \rangle$ for any $\Psi_{GS}^{[n]} \longrightarrow n(\mathbf{r})$

$$E_{V_0}[n] = F_{HK}[n] + \int V_0(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

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A few questions about F_{HK}

Are all “reasonably well behaved” densities *pure-state* V-representable ?

NO

If NOT, can one extend the domain to *non pure-state* V-representable densities ?

ensemble V-representable densities

If $V \to \Gamma \to n, \quad V' \to \Gamma' \to n'$ then

$n'(\mathbf{r}) \neq n(\mathbf{r}) \Longrightarrow V'(\mathbf{r}) \neq V(r) + const$ also for Dens. Matrix GS

$F_{EHK}[n] = \mathrm{Tr}\ \Gamma_{GS}^{[n]}(T + W)$ for any $\Gamma_{GS}^{[n]} \longrightarrow n(\mathbf{r})$

$$E_{V_0}[n] = F_{EHK}[n] + \int V_0(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

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ensemble V-representable densities

Still there are innoncent-looking densities that are NOT *pure-state* or *ensemble* V-representable.

$$\frac{\delta}{\delta n(\mathbf{r})} F_{EHK}[n] + V_0(\mathbf{r}) = 0$$

is not well grounded

Levy's constrained search formulation of DFT

M Levy *PNAS* **76**, 6062 (1979); M Levy, *PRA* **26**, 1200 (1982)
EH Lieb *Int.J.Q.Chem* **24**, 243 (1983)

The original HK theorem is obtained for densities that are GS densities of some potential V ...
These densities are named *V-representable*

It can be shown that very reasonable densities *are not* V-representable... Then what ?

The extension

$$n(\mathbf{r}) \longrightarrow F_{LL}[n] = \inf_{\Psi \rightarrow n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

is defined for all *N-representable* densities

$$i.e.\ \ \forall\, n(\mathbf{r}) > 0,\ \int n(\mathbf{r}) d\mathbf{r} = N,\ \int \left(\nabla \sqrt{n(\mathbf{r})} \right)^2 d\mathbf{r} < +\infty$$

N-representable densities

The **inf** exists if the set of $\Psi \to n$ is not empty

In 1 dimension let's set

$$f(x) = n(x)/N \quad \Longrightarrow \quad \phi(x) = 2\pi \int_{-\infty}^{x} f(y)dy$$

$$\psi_k(x) = \sqrt{f(x)}\,\exp[+ik\phi(x)]$$

$$|\psi_k(x)|^2 = n(x)/N \quad \forall k \in \mathcal{Z}, \quad \langle\psi_k|\psi_{k'}\rangle = \delta_{k,k'}$$

$$\Psi = A[\psi_{k_1}(x_1), ..., \psi_{k_N}(x_N)] \longrightarrow n(x)$$

For an extension to 3D see for instance

G Zumbach and K Maschke, *Phys Rev A* **28**, 544 (1983); **29**, 1585 (1984)

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Is a convex set, actually an Hilbert space

N-representable densities

$$(\nabla\sqrt{n})^2 = \frac{(\nabla n)^2}{4n}$$ is a convex function

$$(\nabla\sqrt{(1-\lambda)n+\lambda n'})^2 \leq (1-\lambda)(\nabla\sqrt{n})^2 + \lambda(\nabla\sqrt{n}')^2$$

Let $A = \nabla n,\ \alpha = n,\ B = \nabla n', \beta = n'$

$$\frac{((1-\lambda)A+\lambda B)^2}{(1-\lambda)\alpha+\lambda\beta} \leq (1-\lambda)\frac{A^2}{\alpha} + \lambda\frac{B^2}{\beta}$$

$$((1-\lambda)A+\lambda B)^2 \leq (1-\lambda)^2 A^2 + \lambda^2 B^2 + (1-\lambda)\lambda(A^2\frac{\beta}{\alpha} + B^2\frac{\alpha}{\beta})$$

$$2AB \leq A^2\frac{\beta}{\alpha} + B^2\frac{\alpha}{\beta}$$

$$0 \leq \left(A\sqrt{\frac{\beta}{\alpha}} - B\sqrt{\frac{\alpha}{\beta}}\right)^2$$ ✓

Levy's constrained search formulation of DFT

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Is a convex set, actually an Hilbert space

However $F_{LL}[n]$ is not necessarily a convex functional

Levy's constrained search formulation of DFT

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These densities are named *V-representable*

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The extension

$$n(\mathbf{r}) \longrightarrow F_L[n] = \inf_{\Gamma\to n} \ \mathrm{Tr}\,\Gamma(|T_e + W_{ee})$$

is defined for all *N-representable* densities

$$i.e. \ \forall\, n(\mathbf{r}) > 0, \ \int n(\mathbf{r})d\mathbf{r} = N, \ \int \left(\nabla\sqrt{n(\mathbf{r})}\right)^2 d\mathbf{r} < +\infty$$

Is a convex set, actually an Hilbert space

and $F_L[n]$ $(\le F_{LL}[n])$ is a convex functional !

Hohenberg and Kohn Theorem and Legendre transform

An analogy with a well known case...

Consider the structural stability problem: $E(V) = \min_{\mathbf{R}\to V} E(\mathbf{R})$

Volume V and pressure P are equally legitimate variables to describe the status of the system, each with its own thermodynamic potential, linked by a Legendre transform

$$H(P) = \min_{V} \{E(V) + PV\}, \qquad \frac{\partial H}{\partial P} = V$$

$$E(V) = \max_{P} \{H(P) - PV\}, \qquad \frac{\partial E}{\partial V} = -P$$

Hohenberg and Kohn Theorem and Legendre transform

In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi} \langle \Psi | T_e + W_{ee} + V | \Psi \rangle$$

$$V(\mathbf{r}) \quad \Longrightarrow \quad \Psi \quad \Longrightarrow \quad n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \frac{\delta E_{GS}}{\delta V(\mathbf{r})}$$

$E_{GS}[V]$ is the Legendre transform of $F_{LL}[n]$

$$E_{GS}[V] = \min_{n} \left[\min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right]$$

But $F_{LL}[n]$ is not the Legendre transform of $E_{GS}[V]$

Hohenberg and Kohn Theorem and Legendre transform

In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi} \langle \Psi | T_e + W_{ee} + V | \Psi \rangle$$

$$V(\mathbf{r}) \quad \Longrightarrow \quad \Psi \quad \Longrightarrow \quad n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \frac{\delta E_{GS}}{\delta V(\mathbf{r})}$$

$E_{GS}[V]$ is the Legendre transform of $F_L[n]$

$$E_{GS}[V] = \min_{n} \left[\min_{\Gamma \to n} \mathrm{Tr}\, \Gamma (T_e + W_{ee}) + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right]$$

And $F_L[n]$ is the Legendre transform of $E_{GS}[V]$

Hohenberg and Kohn Theorem and Legendre transform

In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi}\langle\Psi|T_e + W_{ee} + V|\Psi\rangle$$

$$V(\mathbf{r}) \quad \Longrightarrow \quad \Psi \quad \Longrightarrow \quad n(\mathbf{r}) = \langle\Psi|\hat{n}|\Psi\rangle = \frac{\delta E_{GS}}{\delta V(\mathbf{r})}$$

Performing the Legendre transform

$$\begin{aligned} F_L[n] &= \max_{V}\left\{E_{GS}[V] - \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r}\right\} \\ &= \min_{\Gamma\to n}\ \mathrm{Tr}\,\Gamma(T_e + W_{ee}) \end{aligned}$$

$$n(\mathbf{r}) \quad \Longrightarrow \quad \Gamma \quad \Longrightarrow \quad V(\mathbf{r}) = -\frac{\delta F[n]}{\delta n(\mathbf{r})}$$

The GS density n(r) determines the potential V(r)

Fractional Particle Number

$$\int n(\mathbf{r})d\mathbf{r} = N + \omega$$

$$\begin{aligned} F[n] &= \max_{V}\left\{E_{GS}[V] - \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r}\right\} \\ &= \min_{\Gamma\to n}\ \mathrm{Tr}\,\Gamma(T_e + W_{ee}) \end{aligned}$$

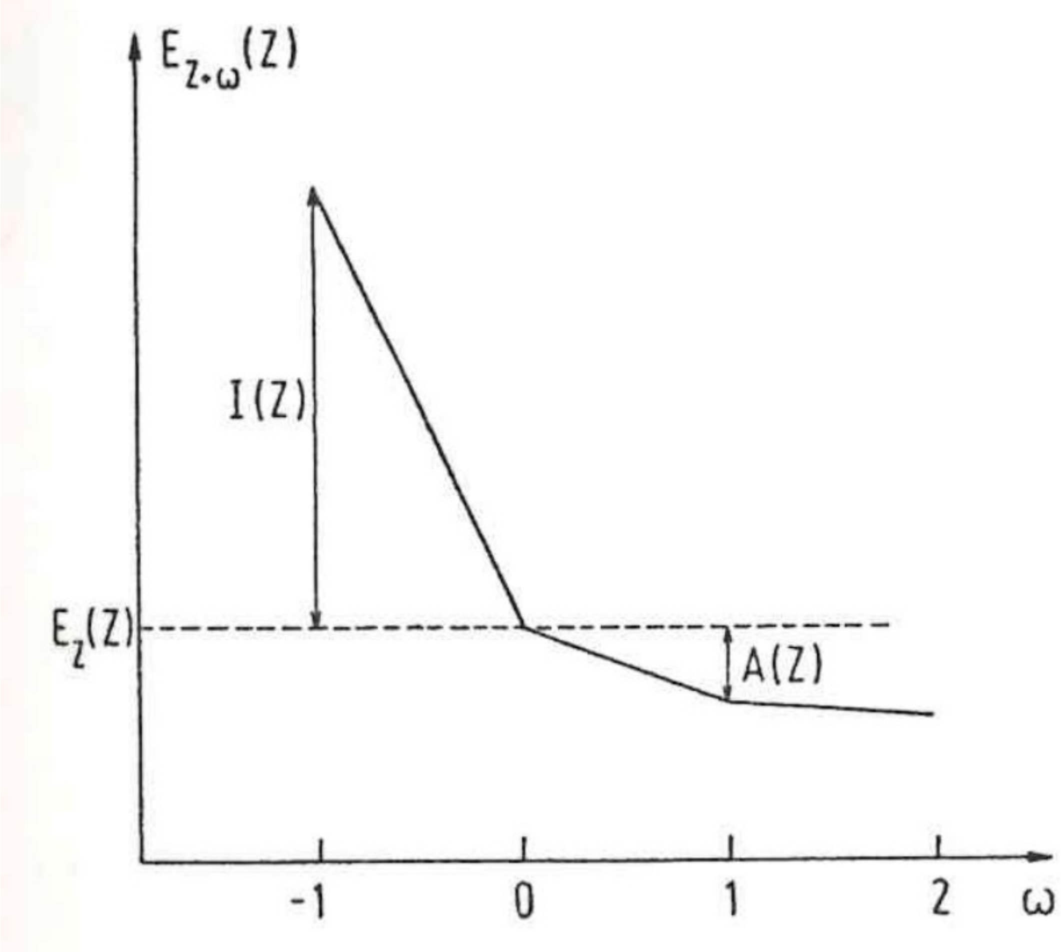
with Γ a mixed particle number Density Matrix

It is well defined if $E_{GS}[V]$ is convex w.r.t. particle number

For Coulomb systems it is believed to be the case

Fractional Particle Number

$$\int n(\mathbf{r})d\mathbf{r} = N + \omega$$



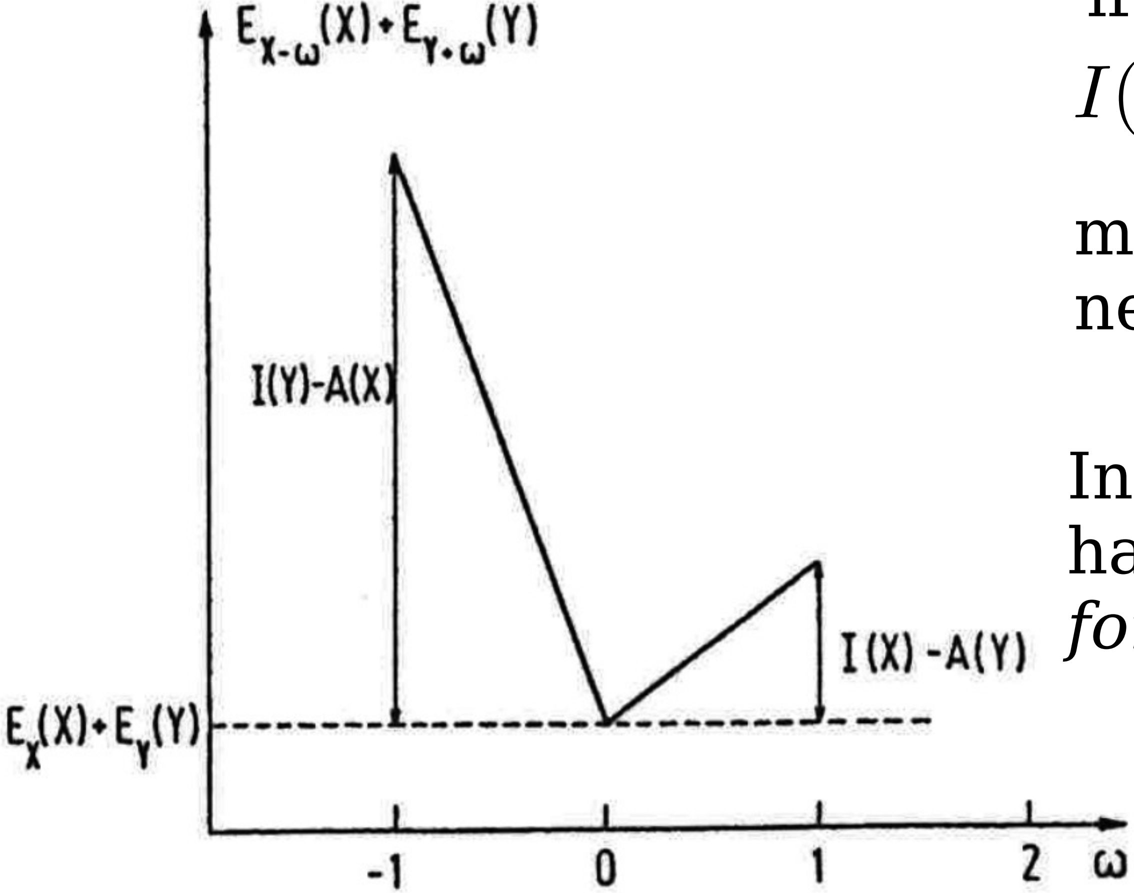
$$\frac{\delta E_v[N]}{\delta N} = \mu(N)$$

$$\frac{\delta E_v[N]}{\delta N}|_{N-} = I(N)$$

$$\frac{\delta E_v[N]}{\delta N}|_{N+} = A(N)$$

Fractional Particle Number

$$\int n(\mathbf{r})d\mathbf{r} = N + \omega$$



if

$$I(X) > A(Y) \quad \forall X, Y$$

molecules dissociate in neutral fragments

In general the fragments have integer charges *for the exact functional*

Finite Temperature DFT

ND Mermin *Phys Rev* **137**, A1441 (1965)

$$\Omega[V] = \min_{\hat\rho} \mathrm{Tr}\, \hat\rho \left(\hat T + \hat W + \hat V - \mu \hat N + \frac{1}{\beta} \ln \hat\rho \right)$$

$$\hat\rho = \exp[-\beta(\hat H - \mu \hat N)]/Z$$

The DFT functional is therefore

$$F[n] = \min_{\hat\rho \to n} \mathrm{Tr}\, \hat\rho \left(\hat T + \hat W + \frac{1}{\beta} \ln \hat\rho \right)$$

and the variational principle becomes

$$\Omega[V] = \min_{n} \left(F[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \mu \int n(\mathbf{r}) d\mathbf{r} \right)$$

It may be convenient to think of the $\beta \to \infty$ limit

HK Theorem: take home messages

- for fixed integer number of particles and fixed interaction it is possible to define a universal functional of the density for all N-representable densities and this functional F[n] is the Legendre transform of the functional E[V].

- the definition can be extended to non integer number of electrons and/or to finite temperature.

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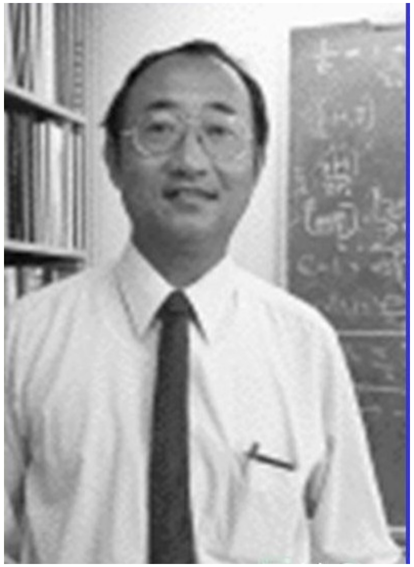
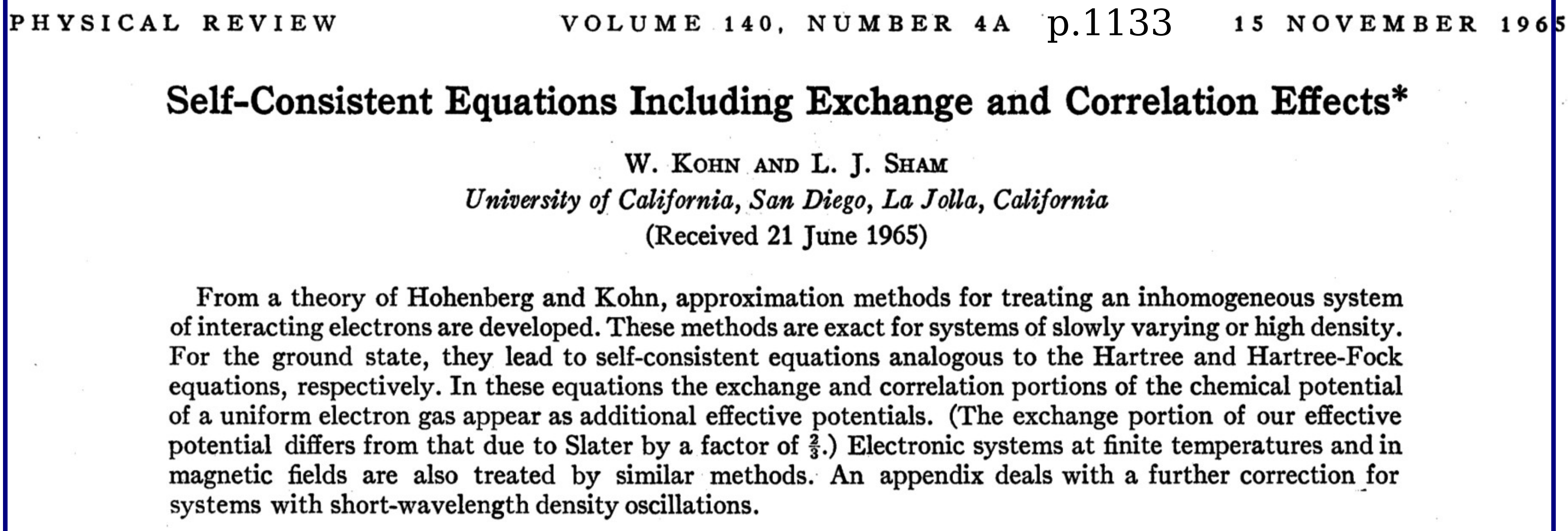
Kohn - Sham equations

Walter



Lu J



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Self-Consistent Equations Including Exchange and Correlation Effects*

W. Kohn and L. J. Sham
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(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

HK: $n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$

It is useful to introduce a ficticious system
of non-interacting electrons

KS: $n(\mathbf{r}) \longrightarrow T_s[n] = \min_{\Psi \to n} \langle \Psi | T_e | \Psi \rangle$

$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$ This defines E_{xc}

The energy becomes

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

Kohn-Sham equations

- interacting system

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$
$$-\mu\left(\int n(\mathbf{r})d\mathbf{r} - N\right)$$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta E_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r})$$

- non-interacting system

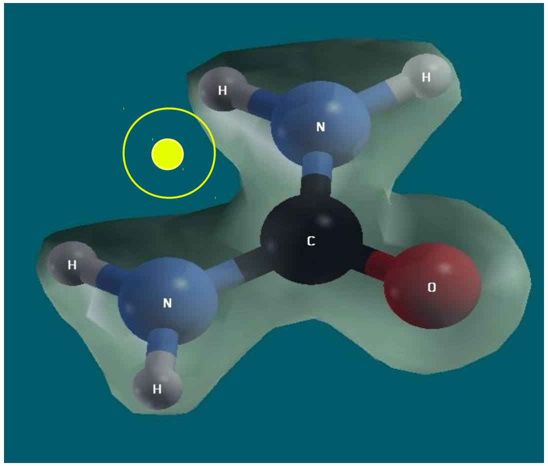
$$E_{KS}[n] = T_s[n] + \int V_{KS}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$
$$-\mu'\left(\int n(\mathbf{r})d\mathbf{r} - N\right)$$

$$\mu' = \frac{\delta E_{KS}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + V_{KS}(\mathbf{r})$$

Self-consistent equations [Kohn-Sham, 1965]

$$V_{KS}(\mathbf{r},\mathbf{R}) = V_{ext}(\mathbf{r},\mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r},\mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$



$$n(\mathbf{r}) = 2\sum_i |\phi_i(\mathbf{r})|^2$$

It is as simple as a Mean-field approach but it is exact !

$E_{xc}[n]$ is not known exactly → approximations

Formal expression for E$_{xc}$[n] via coupling-constant integration

$$\hat{H}^{(\lambda)} = \hat{T}_e + \lambda \hat{W}_{ee} + \hat{V}_{ext}^{(\lambda)}$$

$$F_\lambda[n] = \min_{\Psi \to n} \langle \Psi | \hat{T}_e + \lambda \hat{W}_{ee} | \Psi \rangle$$

$$n(\mathbf{r}) = N \int |\Psi_\lambda(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r_N})|^2 d\mathbf{r}_2 ... d\mathbf{r}_N, \quad \forall\, \lambda$$

non-interacting electrons

$$\lambda = 0 \qquad F_0[n] = T_s[n], \qquad V_{ext}^{(0)} = V_{KS}$$

interacting electrons

$$\lambda = 1 \qquad F_1[n] = F[n], \qquad V_{ext}^{(1)} = V_{ext}$$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

thanks to Hellmann-Feynman theorem ....

$$F[n] = T_s[n] + \int_0^1 d\lambda \langle \Psi_\lambda | \hat{W}_{ee} | \Psi_\lambda \rangle$$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}, \mathbf{r}', \lambda)$$

$g(\mathbf{r}, \mathbf{r}', \lambda)$ pair correlation function for interaction λW_{ee}

$$n(\mathbf{r}) n(\mathbf{r}') g(\mathbf{r}, \mathbf{r}', \lambda) = n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')$$

$$n_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') = N(N-1) \int |\Psi_\lambda(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, ..., \mathbf{r}_N)|^2 d\mathbf{r}_3 ... d\mathbf{r}_N$$

$$\text{if} \quad |\mathbf{r}-\mathbf{r}'| \longrightarrow \infty \qquad \text{then} \qquad g(\mathbf{r},\mathbf{r}',\lambda) \longrightarrow 1$$

$$(g(\mathbf{r},\mathbf{r}',\lambda) - 1) \longrightarrow 0$$

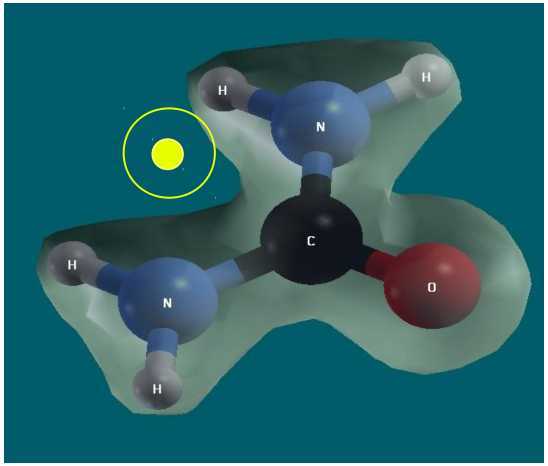
$$F[n] = T_s[n] + \frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$\mathrm{E}_{\mathrm{xc}} \longrightarrow \boxed{+\frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\int_0^1 d\lambda[g(\mathbf{r},\mathbf{r}',\lambda)-1]}$$

Exchange-correlation hole

$$n_{xc}(\mathbf{r};\mathbf{r}'-\mathbf{r}) = n(\mathbf{r}')\int_0^1 d\lambda[g(\mathbf{r},\mathbf{r}',\lambda)-1]$$

$$E_{xc}[n] = \frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n_{xc}(\mathbf{r},\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$



$$F_\lambda[n] = \min_{\Psi\to n}\langle\Psi|\hat{T}_e + \lambda\hat{W}_{ee}|\Psi\rangle = \mathrm{T}_\lambda[n] + \lambda W_\lambda[n]$$

with $\quad T_\lambda[n] = \langle\Psi_\lambda^{[n]}|\hat{T}_e|\Psi_\lambda^{[n]}\rangle, \quad \mathrm{W}_\lambda[n] = \langle\Psi_\lambda^{[n]}|\hat{W}_{ee}|\Psi_\lambda^{[n]}\rangle$

(if need be think of it as the $\beta\to\infty$ limit)

clearly $\qquad T_\lambda[n] > 0, \quad W_\lambda[n] > 0 \quad \forall\lambda$

$F_\lambda[n]$ is variational w.r.t. *isodensity* perturbations

$$\frac{dF_\lambda}{d\lambda} = F'_\lambda = W_\lambda, \quad T'_\lambda + \lambda W'_\lambda = 0, \quad T''_\lambda + \lambda W''_\lambda > 0$$

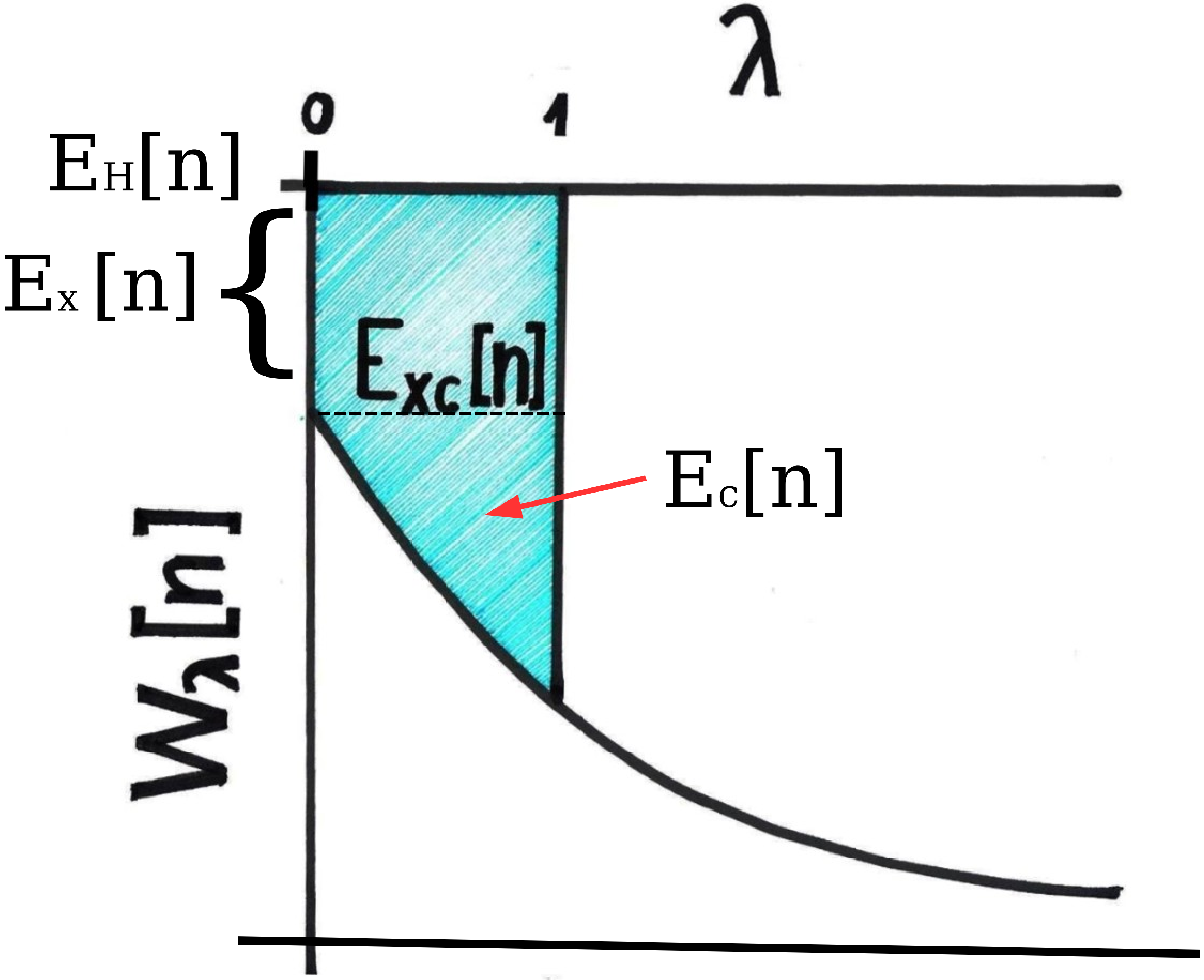
but also $\qquad T''_\lambda + \lambda W''_\lambda + W'_\lambda = 0 \quad \Longrightarrow \quad W'_\lambda < 0$

and $\qquad T'_\lambda = -\lambda W'_\lambda > 0$

$$F[n] = T_s[n] + \int_0^1 d\lambda \langle \Psi_\lambda | \hat{W}_{ee} | \Psi_\lambda \rangle$$

$$F[n] = T_s[n] + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

$$\mathrm{E}_{\mathrm{xc}} \longrightarrow \boxed{+\int_0^1 d\lambda \left[\langle \Psi_\lambda | \hat{W}_{ee} | \Psi_\lambda \rangle - E_H[n] \right]}$$


λ
0
1
$E_H[n]$
$E_x[n]$
$E_{xc}[n]$
$E_c[n]$
$W_\lambda[n]$

THE END