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Minimal composition of Kohn-Sham theory

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— How has an unintelligent physicist appreciated KS theory? —

Contents

I. Introduction

What is Kohn-Sham theory ?

- Hohenberg-Kohn theorem (1964)

  — existence of energy density functional

  Why KS theory, nevertheless ?

  cf. orbital-free DFT

- KS theory (1965)

  — solving many-fermion problem "exactly"

  Under what conditions can a many-body problem be replaced by single-particle equations ?

  ↔ extendability

$\hookrightarrow$ "minimal composition" (= essence) of KS theory

Starting point — variational principle for g.s. energy

$$E_0 = \min_{\Psi \to N} E[\Psi]\,; \qquad E[\Psi] \underline{:= \langle \Psi | H | \Psi \rangle} \; ?$$

$|\Psi\rangle\,(\to N)$: arbitrary (N-)fermion state

— H not necessarily needed $\to$ only $E[\Psi]$

implementation $\cdots$ $\dfrac{\delta E}{\delta Z} = 0$

(Z : appropriate variables)

$\to$ differentiability is crucial !

Density functional

↘ generalize

a set of physical quantities — "principal variables"

S.p. equation ? $\leftarrow$ 1-body density matrix $\varrho_{k\ell}$

(— carrying all information of s.p. quantities)

$$e.g.\ \ n(\boldsymbol{r}) = \sum_{k\ell} \varrho_{k\ell}\, \phi_\ell^*(\boldsymbol{r})\, \phi_k(\boldsymbol{r})$$

Notation:

particle number	N	
general N-particle state	$\lvert\Psi\rangle$	
N-particle Slater det.	$\lvert\Phi\rangle$	
density distribution	$n(\boldsymbol{r})$	[not $\rho(\boldsymbol{r})$]
single-particle basis	ϕ_k	
1-body density matrix	$\varrho_{k\ell}$	[not $\gamma(k,\ell)$]

$$\varrho_{k\ell} = \varrho_{k\ell}[\Psi] := \langle\Psi|a_\ell^\dagger a_k|\Psi\rangle = \varrho_{\ell k}^*$$

1-body potential	$U(\boldsymbol{r})$, Γ	[not $v(\boldsymbol{r})$]

but use the term "v-representability"

interaction	V	[not U]
principal variable	Q^A, $\boldsymbol{Q} = \{Q^A\}$	

II. Hartree-Fock theory in terms of density matrix

ν-body DM — $\langle\Psi|a^\dagger_{\ell_1} a^\dagger_{\ell_2} \cdots a^\dagger_{\ell_\nu} a_{k_\nu} \cdots a_{k_2} a_{k_1}|\Psi\rangle$

$\hookrightarrow$ decomposed with $\varrho_{k\ell}$ & $\mathcal{C}^{(\nu')}$ $(\nu' = 2, 3, \cdots, \nu)$

$\mathcal{C}^{(\nu)} = \mathcal{C}^{(\nu)}[\Psi]$: ν-body correlation function

e.g. $\mathcal{C}^{(2)}_{kk'\ell\ell'} = \langle\Psi|a^\dagger_\ell a^\dagger_{\ell'} a_{k'} a_k|\Psi\rangle - \varrho_{k\ell}\varrho_{k'\ell'} + \varrho_{k\ell'}\varrho_{\ell k'}$

$E[\Psi] = E[\varrho, \mathcal{C}^{(2)}, \mathcal{C}^{(3)}, \cdots, \mathcal{C}^{(N)}]$

($\hookrightarrow$ BBGKY hierarchical equation)

$E[\Psi] \approx E^{\mathrm{HF}}[\varrho]$ $\leftarrow$ neglecting $\mathcal{C}^{(\nu)}$

$\hookrightarrow$ minimize $\quad \tilde{E}^{\mathrm{HF}} := E^{\mathrm{HF}} - \mu\left[\mathrm{tr}(\varrho) - N\right]$

$$\delta\tilde{E}^{\mathrm{HF}} = \mathrm{tr}\left[(h^{\mathrm{HF}} - \mu)\,\delta\varrho\right] - \delta\mu\left[\mathrm{tr}(\varrho) - N\right]$$

$$h^{\mathrm{HF}}_{k\ell} := \frac{\partial E^{\mathrm{HF}}}{\partial \varrho_{\ell k}}$$

HF eq. $\quad \sum_{\ell} h^{\mathrm{HF}}_{k\ell}\,\mathcal{U}^{\mathrm{HF}}_{\ell i} = \epsilon^{\mathrm{HF}}_{i}\,\mathcal{U}^{\mathrm{HF}}_{ki}$ $\qquad i:$ s.p. orbital

$$\rightarrow \quad \epsilon^{\mathrm{HF}}_{i} \;\&\; \varphi^{\mathrm{HF}}_{i} = \sum_{k} \mathcal{U}^{\mathrm{HF}}_{ki}\,\phi_{k}$$

- $\delta \tilde{E}^{\mathrm{HF}} \geq 0$
- $0 \leq \varrho_{ii} \leq 1$ for any representation (Pauli principle)
- $\delta \tilde{E}^{\mathrm{HF}} = \sum_i (\epsilon_i^{\mathrm{HF}} - \mu)\, \delta \varrho_{ii}$ in vicinity of min $\tilde{E}^{\mathrm{HF}}$

$$\rightarrow \begin{cases} \varrho_{ii}^{\mathrm{HF}} = 0 & \text{for } \epsilon_i^{\mathrm{HF}} > \mu \\ \varrho_{ii}^{\mathrm{HF}} = 1 & \text{for } \epsilon_i^{\mathrm{HF}} < \mu \end{cases}$$

viz. $\varrho^2 = \varrho$

$\leftrightarrow \quad |\Phi^{\mathrm{HF}}\rangle$: single Slater determinant

$\mathcal{V}_{\mathrm{full}}$: N-particle full Hilbert space

$\searrow$

$\mathcal{V}_{\mathrm{idem}}$: subspace with idempotency

III. Hohenberg-Kohn theorem

HK (2nd) theorem

- Proof via Legendre transformation (HK 1st theorem)
  $n(\boldsymbol{r}) \leftrightarrow U(\boldsymbol{r})$ ··· conjugate in Leg. transf.
  — v-representability ? (inverse mapping $n \rightarrow U$)
  $\leftrightarrow$ no guarantee of global EDF

- Proof via Levy's constrained search ··· 2-step min.
  $\rightarrow$ link to KS theory
  for principal variables $\boldsymbol{Q} = \{Q^A\}$

$$E^{\mathrm{HK}}[\boldsymbol{Q}] := \min_{\Psi \to \boldsymbol{Q}} E[\Psi] = E[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}] \quad \cdots \text{ global !}$$

$$\rightarrow \quad E_0 = \min_{\boldsymbol{Q} \to N} E^{\mathrm{HK}}[\boldsymbol{Q}]$$

(— N-representability ?)

"Representabilities" for $\boldsymbol{Q} = n(\boldsymbol{r})$

- N-representability :

$^{\exists}\, |\Psi\rangle$: N-fermion w.f.

$$\text{for } {}^{\forall}\, n(\boldsymbol{r}) \left(\geq 0 \,,\ \int d^3r\, n(\boldsymbol{r}) = N \right)$$

$\hookrightarrow$ Harriman's construction

$$|\Phi_{\mathrm{Har}}\rangle \propto \det\left[\varphi_k(x_j)\right] \,;\ \varphi_k(x) = \sqrt{p(x)}\, e^{2\pi i k q(x)}$$

$$p(x) = \frac{n(x)}{N} \,,\ q(x) = \int_{-\infty}^{x} dy\, p(y) \,,\ k \in \mathbf{Z}$$

$$\left(|\Phi_{\mathrm{Har}}\rangle \in \mathcal{V}_{\mathrm{idem}} \right)$$

- v-representability :

$^{\exists}\, U(\boldsymbol{r})$ for $^{\forall}\, n(\boldsymbol{r})\ (\geq 0)$

$\rightarrow$ counterexample (@ degeneracy)

$\rightarrow$ circumvented in Levy's CS ?

v-representability $\underset{(?)}{=}$ differentiability

$$\because\quad U(\boldsymbol{r}) = -\frac{\delta E}{\delta n(\boldsymbol{r})}$$

$\hookrightarrow$ Problem remains @ degeneracy !

(degeneracy = crossing point)

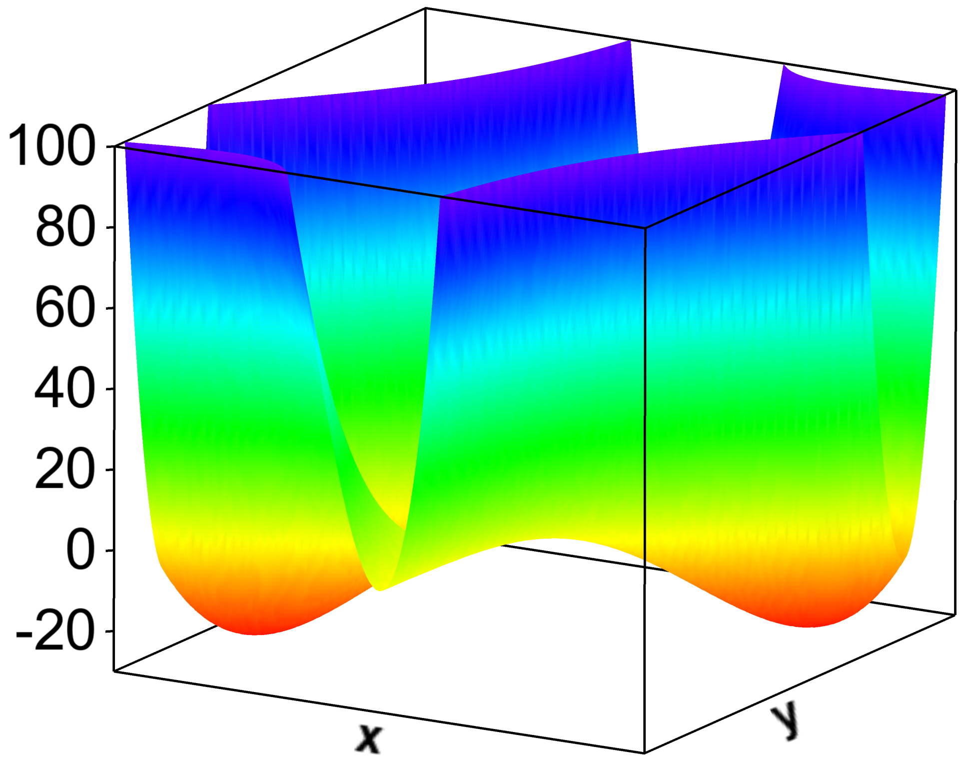
$\cdots\ E^{\mathrm{HK}}[\boldsymbol{Q}]$ exists, but difficult to handle

IV. Elementary examples for irregularities

4.1 *Two-step minimization and differentiability*

$$\phi(x,y) = 3x^4 - 8x^3 y + 6x^2(y^2 - d^2) \quad (d > 0):$$

— analytical everywhere on the xy-plane



$$\min_{(x,y)} \phi(x,y) = -27d^4$$

$$@\ (x,y) = (\pm 3d, \pm 2d)$$

$$\left[\leftarrow \frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial y} = 0 \right]$$

↪ 2-step minimization

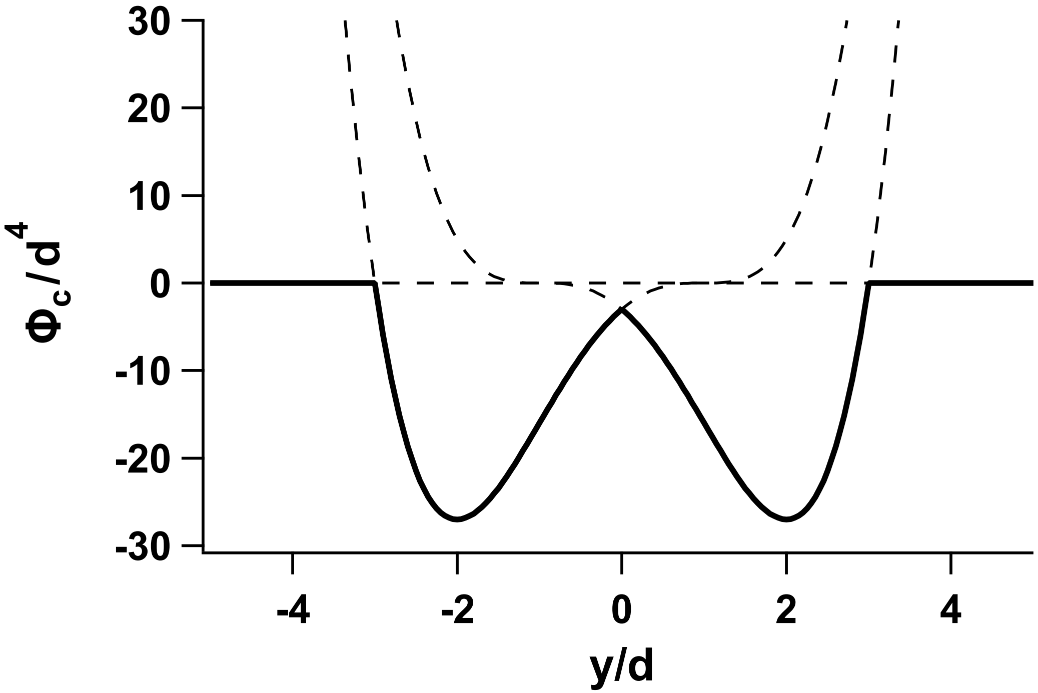
$$\phi_c(y) := \min_x \phi(x, y) \quad \rightarrow \quad \min_y \phi_c(y)$$

$$\phi_c(y) = \min \left[\phi_{c0}(y), \phi_{c+}(y), \phi_{c-}(y)\right]$$

$$= \begin{cases} \phi_{c0}(y) & (\text{for } y \leq -3d \text{ and } y \geq 3d) \\ \phi_{c+}(y) & (\text{for } 0 \leq y < 3d) \\ \phi_{c-}(y) & (\text{for } -3d < y < 0) \end{cases}$$

$$\begin{bmatrix} \phi_{c0}(y) = \phi(0, y) = 0 \\ \phi_{c\pm}(y) = \phi(y \pm d, y) = (y \pm d)^3 (y \mp 3d) \end{bmatrix}$$

$\cdots$ differentiability lost at $y = 0, \pm 3d$!



$$\rightarrow \qquad \min_{y} \phi_c(y) = \min_{(x,y)} \phi(x,y) = -27d^4$$

but $\dfrac{d\phi_c}{dy} = 0$ is not enough !

Cf. Leg. transf. ($\leftrightarrow$ min. constraining y)

$$\psi(x,\lambda) := \phi(x,y) - \lambda y \quad \text{with} \quad \frac{\partial \phi}{\partial y} = \lambda$$

$$\rightarrow \quad \lambda = -4x^2(2x - 3y) \quad i.e. \quad y = \frac{2}{3}\left(x + \frac{\lambda}{8x^2}\right)$$

$$\rightarrow \quad \psi(x,\lambda) = \frac{1}{3}\left[x^4 - 2\lambda x - \frac{\lambda^2}{8x^2} - 18d^2x^2\right]$$

$$\left.\frac{\partial \psi}{\partial x}\right|_{(x_0,\lambda_0)} = 0 \quad \& \quad \lambda_0 = -4x_0^2(2x_0 - 3y)$$

$$\rightarrow \quad x_0 = 0, y \pm d \qquad (\cdots \text{ separated !})$$

$$\rightarrow \quad \phi_c^{(\mathrm{L})}(y) = \psi(x_0,\lambda_0) + \lambda_0 y$$

$$= \text{one of } \left[\phi_{c0}(y), \phi_{c+}(y), \phi_{c-}(y)\right]$$

$\cdots$ regular, but universality lost !

4.2 Fermionic EDF for 1D harmonic oscillator

$$H_\omega = K + U_\omega\,; \quad K = -\frac{1}{2m}\frac{d^2}{dx^2}\,, \;\; U_\omega(x) = \frac{m\omega^2}{2}x^2$$

Ω : degeneracy

$\cdots$ global (HK-)EDF ? $\rightarrow$ EDF w/o ω-dep. ?

$$n^{(0)}_{\omega,N}(x) = \begin{cases} \sqrt{\dfrac{m\omega}{\pi}}\,N\,e^{-m\omega x^2} & (0 < N \le \Omega) \\ \sqrt{\dfrac{m\omega}{\pi}}\left[\Omega + 2(N-\Omega)m\omega x^2\right] \times e^{-m\omega x^2} & (\Omega < N \le 2\Omega) \\ \vdots & \end{cases}$$

→ ω-indep. EDF ?

For $0 < N \leq \Omega$

$$E^{\mathrm{HK}}[n] = \int dx \left[\frac{1}{8m} \frac{\big(n'(x)\big)^2}{n(x)} + U(x)\, n(x) \right]$$

For $\Omega < N \leq 2\Omega$ around a fixed $N = N_0$

$$E^{\mathrm{HK}}[\Delta n] - E^{(0)}_{\omega,N_0} = \int dx \left[\frac{1}{8m} \frac{\big(\Delta n'(x)\big)^2}{\Delta n(x)} + U(x)\, \Delta n(x) \right]$$

$$\Delta n(x) := n(x) - n^{(0)}_{\omega,N_0}(x)$$

(not applicable for $N_0 < \Omega < N$)

⋯ regular & ω-indep. only locally !

EDF for fixed N — similar

deviation of $n(x)$ from $n^{(0)}_{\omega,N}(x)$

$\rightarrow$ ω-dep. and/or irregularity of $E^{\mathrm{HK}}[n]$

$\cdots$ shell structure gives rise to irregularity (as expected) !

V. Kohn-Sham theory in terms of density matrix

Irregularity of $E^{\mathrm{HK}}[\boldsymbol{Q}]$ (loss of differentiability)

$\cdots$ if caused by s.p. mechanism (*e.g.* shell effects)

$\rightarrow$ eased via ϱ

Impose $Q^A = Q^A[\varrho]$ (— for s.p. eqs. to close)

<u>Partitioning of EDF</u>

$$E[\Psi] = E^{\mathrm{KS}}_{\mathrm{irr}}\Big[\varrho; \boldsymbol{Q}[\varrho]\Big] + E_{\mathrm{reg}}[\Psi]$$

$$\rightarrow E^{\mathrm{HK}}[\boldsymbol{Q}] = E^{\mathrm{KS}}_{\mathrm{irr}}\Big[\varrho[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}]; \boldsymbol{Q}\Big] + E^{\mathrm{HK}}_{\mathrm{reg}}[\boldsymbol{Q}]$$

$$E^{\mathrm{HK}}_{\mathrm{reg}}\Big[\boldsymbol{Q}\Big] := E_{\mathrm{reg}}\Big[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}\Big]$$

(*e.g.* $E^{\mathrm{KS}}_{\mathrm{irr}}$: kinetic energy)

Min. $E^{\mathrm{KS}}_{\mathrm{irr}}$ w.r.t. ϱ for a given $\boldsymbol{Q}$?

$$\min_{\varrho\to\boldsymbol{Q}} E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho;\boldsymbol{Q}]\ ?\ \left(\neq E^{\mathrm{KS}}_{\mathrm{irr}}\left[\varrho[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}];\boldsymbol{Q}\right]\ !\right)$$

$$\Rightarrow \quad E^{\mathrm{HK}}[\boldsymbol{Q}] = \min_{\varrho\to\boldsymbol{Q}} E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho;\boldsymbol{Q}] + E^{\mathrm{KS}}_{\mathrm{reg}}[\boldsymbol{Q}]\,;$$

$$E^{\mathrm{KS}}_{\mathrm{reg}}[\boldsymbol{Q}] := E^{\mathrm{HK}}_{\mathrm{reg}}[\boldsymbol{Q}] + \left(E^{\mathrm{KS}}_{\mathrm{irr}}\left[\varrho[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}];\boldsymbol{Q}\right] - \min_{\varrho\to\boldsymbol{Q}} E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho;\boldsymbol{Q}]\right)$$

(— assuming regularity of additional term)

$$\Rightarrow \quad E^{\mathrm{KS}}[\varrho;\boldsymbol{q}] = E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho;\boldsymbol{q}] + E^{\mathrm{KS}}_{\mathrm{reg}}[\boldsymbol{q}] - \sum_A \Lambda^{\mathrm{KS}}_A \left(q^A - Q^A[\varrho]\right)$$

$$\text{Min.} \quad \tilde{E}^{\mathrm{KS}} := E^{\mathrm{KS}} - \mu\Big[\mathrm{tr}(\varrho) - N\Big] \qquad \text{(analogous to HF)}$$

$$\leftrightarrow \quad \frac{\partial \tilde{E}^{\mathrm{KS}}_{\mathrm{irr}}}{\partial \varrho_{k\ell}} = \frac{\partial \tilde{E}^{\mathrm{KS}}_{\mathrm{irr}}}{\partial q^A} = \frac{\partial \tilde{E}^{\mathrm{KS}}_{\mathrm{irr}}}{\partial \mu} = 0$$

$$\rightarrow \quad h^{\mathrm{KS}}_{k\ell} := \frac{\partial E^{\mathrm{KS}}}{\partial \varrho_{k\ell}} = \frac{\partial E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho; \boldsymbol{q}]}{\partial \varrho_{k\ell}} + \Gamma^{\mathrm{KS}}_{k\ell} \,;$$

$$\Gamma^{\mathrm{KS}}_{k\ell} := \sum_A \Lambda^{\mathrm{KS}}_A \frac{\partial Q^A}{\partial \varrho_{k\ell}} \qquad \text{(KS pot.)}$$

$$\Lambda^{\mathrm{KS}}_A = \frac{\partial E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho; \boldsymbol{q}]}{\partial q^A} + \frac{\partial E^{\mathrm{KS}}_{\mathrm{reg}}[\boldsymbol{q}]}{\partial q^A}$$

$$\left(\text{eventually,} \quad h^{\mathrm{KS}}_{k\ell} = \frac{\partial E^{\mathrm{KS}}\Big[\varrho; \boldsymbol{Q}[\varrho]\Big]}{\partial \varrho_{k\ell}}\right)$$

KS eq. $\displaystyle\sum_{\ell} h^{\mathrm{KS}}_{k\ell}\, \mathcal{U}^{\mathrm{KS}}_{\ell i} = \epsilon^{\mathrm{KS}}_{i}\, \mathcal{U}^{\mathrm{KS}}_{k i}$ $\quad i:$ KS orbital

$$\rightarrow \quad \epsilon^{\mathrm{KS}}_{i} \ \& \ \varphi^{\mathrm{KS}}_{i} = \sum_{k} \mathcal{U}^{\mathrm{KS}}_{k i}\, \phi_{k}$$

$$\left\{ \begin{array}{lll} E_0\,,\ Q^A & \cdots & \text{physical} \\ \varrho^{\mathrm{KS}}_{k\ell}\,,\ \epsilon^{\mathrm{KS}}_{i}\,,\ \varphi^{\mathrm{KS}}_{i} & \cdots & \text{not fully physical} \\ & & \quad \left(\because\ |\Phi^{\mathrm{KS}}\rangle \in \mathcal{V}_{\mathrm{idem}} \right) \end{array} \right.$$

cf. Landau's quasiparticle

— possibility of reinterpretation ?

Cf. KS–Bogolyubov - de Gennes theory

$$\{\varrho\} \;\to\; \{\varrho, \kappa, \kappa^*\}\,; \qquad \kappa_{k\ell} := \langle\Psi|a_\ell a_k|\Psi\rangle$$

$\Rightarrow$ fermionic superfluidity (analogous to HFB)

e.g. superconductivity, nuclear pairing

Answer to "Why KS theory ?"

— to remove or ease irregularity in E^{HK}

VI. Discussions

6.1 *Equational equivalence*

KS Hamiltonian : $h^{\mathrm{KS}}_{k\ell} = \dfrac{\partial E^{\mathrm{KS}}\left[\varrho; \boldsymbol{Q}[\varrho]\right]}{\partial \varrho_{k\ell}}$

Even if $\boldsymbol{Q} \neq \boldsymbol{Q}'$,

$$E^{\mathrm{KS}}\left[\varrho; \boldsymbol{Q}[\varrho]\right] = E^{\mathrm{KS}}\left[\varrho; \boldsymbol{Q}'[\varrho]\right] \text{ possible}$$

$\rightarrow$ equivalent KS eq. $\rightarrow$ identical solutions

$\Rightarrow$ Eq. does not tell principal variables

(viz. physical quantities)

$\boldsymbol{Q} \leftrightarrow$ how to construct $E[\boldsymbol{Q}]$

6.2 *Representabilities — HK vs. KS*

Representabilities — distinguished between $\left\{ \begin{array}{l} \text{HK level} \\ \text{KS level} \end{array} \right.$

- v-representability

  HK level $\cdots$ differentiability of $E^{\mathrm{HK}}[\boldsymbol{Q}]$

  $\downarrow$ (looser)

  KS level $\cdots$ differentiability of $E^{\mathrm{KS}}\left[\varrho; \boldsymbol{Q}[\varrho]\right]$

- N-representability

  HK level $\cdots$ existence of $\boldsymbol{Q} \to |\Psi\rangle \in \mathcal{V}_{\mathrm{full}}$

  $\downarrow$ (tighter !)

  KS level $\cdots$ existence of $\boldsymbol{Q} \to |\Phi\rangle \in \mathcal{V}_{\mathrm{idem}}$

6.3 *Choice of Principal variables*

$\boldsymbol{Q}$ — not too few, not too many

$\emptyset$		logically possible, though not useful (∵ only E_0 is physical, 1-step min.)
$\nearrow$	fewer $\rightarrow$	fewer physical quantities N-rep. easier, v-rep. more difficult (∵ proj. on lower-dim. space)
$\boldsymbol{Q}$		
$\searrow$	more $\rightarrow$	more physical quantities v-rep. easier, N-rep. more difficult
$\{\varrho_{k\ell}\}$		impossible within KS (∵ $(\varrho^{\mathrm{KS}})^2 = \varrho^{\mathrm{KS}}$) cf. DMFT

$\Rightarrow$ compromise between $\left\{ \begin{array}{l} \text{physical demand} \\ \text{representabilities} \end{array} \right.$

6.4 *Summary of assumptions for KS theory*

Minimal assumptions to compose KS theory

- Principal variables — $Q^A = Q^A[\varrho]$ (depends only on ϱ)

  $\cdots$ no need to contain $n(\boldsymbol{r})$!

- $E[\Psi] = E^{\mathrm{KS}}_{\mathrm{irr}} + E_{\mathrm{reg}}[\Psi]$;

  $$E^{\mathrm{HK}}_{\mathrm{reg}}[\boldsymbol{Q}] = E_{\mathrm{reg}}\left[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}\right] \quad \cdots \text{ regular w.r.t. } Q^A$$

  $\hookrightarrow$ Irregular part — $E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho; \boldsymbol{Q}]$ (depends only on ϱ)

- Regularity of deviating term of $E^{\mathrm{KS}}_{\mathrm{irr}}$,

  $$\text{viz. } \left(E^{\mathrm{KS}}_{\mathrm{irr}}\left[\varrho[\Psi^{\mathrm{HK}}_{\boldsymbol{Q}}]; \boldsymbol{Q}\right] - \min_{\varrho \to \boldsymbol{Q}} E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho; \boldsymbol{Q}]\right), \text{ w.r.t. } Q^A$$

$\Rightarrow$ Criteria for extendability

(apart from how to construct $E^{\mathrm{KS}}_{\mathrm{irr}}$ & $E^{\mathrm{KS}}_{\mathrm{reg}}$)

VII. Practice of Kohn-Sham theory

7.1 *Many-electron systems*

Conventional KS theory $\quad \boldsymbol{Q} = n(\boldsymbol{r})$

$$H_{\rm irr} = K + U_{ei}\ ,\ \ H_{\rm reg} = V_{ee} \qquad \Big(\to \ \ E^{\rm KS}_{\rm reg} : \ \text{universal} \Big)$$

$$\to \quad E^{\rm KS}_{\rm irr}[\varrho; n(\boldsymbol{r})] = E_K[\varrho] + E_{ei}[n(\boldsymbol{r})]\ ;$$

$$E_K[\varrho] = -\frac{1}{2m} \sum_{k\ell} \langle \ell | \nabla^2 | k \rangle \, \varrho_{k\ell}\ ,$$

$$E_{ei}[n(\boldsymbol{r})] = \int d^3r' \, U_{ei}(\boldsymbol{r'}) \, n(\boldsymbol{r'})$$

$$E^{\mathrm{KS}}_{\mathrm{reg}}[n(\boldsymbol{r})] = E^{\mathrm{HK}}_{\mathrm{reg}}[n(\boldsymbol{r})] + \left(E_K\left[\varrho[\Psi^{\mathrm{HK}}_{n(\boldsymbol{r})}]\right] - \min_{\varrho\to n(\boldsymbol{r})} E_K[\varrho] \right)$$

$$= E_{\mathrm{dir}}[n(\boldsymbol{r})] + E^{\mathrm{KS}}_{\mathrm{xc}}[n(\boldsymbol{r})] \,;$$

$$E_{\mathrm{dir}}[n(\boldsymbol{r})] = \frac{e^2}{2} \int d^3r'\, d^3r''\, \frac{n(\boldsymbol{r}')\, n(\boldsymbol{r}'')}{|\boldsymbol{r}' - \boldsymbol{r}''|} \,,$$

$$E^{\mathrm{KS}}_{\mathrm{xc}}[n(\boldsymbol{r})] = \int d^3r'\, \mathcal{H}_{\mathrm{xc}}[n(\boldsymbol{r}')]$$

$E^{\mathrm{KS}}_{\mathrm{xc}}$ or $\mathcal{H}_{\mathrm{xc}} \leftarrow$ LDA, GGA, meta-GGA, ML, $\cdots$

Spin DFT

$$n(\boldsymbol{r}) = n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r})\,, \qquad \sigma(\boldsymbol{r}) := n_\uparrow(\boldsymbol{r}) - n_\downarrow(\boldsymbol{r})$$

$$E^{\mathrm{KS}}[\varrho; n(\boldsymbol{r}), \sigma(\boldsymbol{r})] = E_K[\varrho] + E_{ei}[n(\boldsymbol{r})] + E_{\mathrm{dir}}[n(\boldsymbol{r})] + E_{\mathrm{xc}}^{\mathrm{KS}}[n(\boldsymbol{r}), \sigma(\boldsymbol{r})]$$

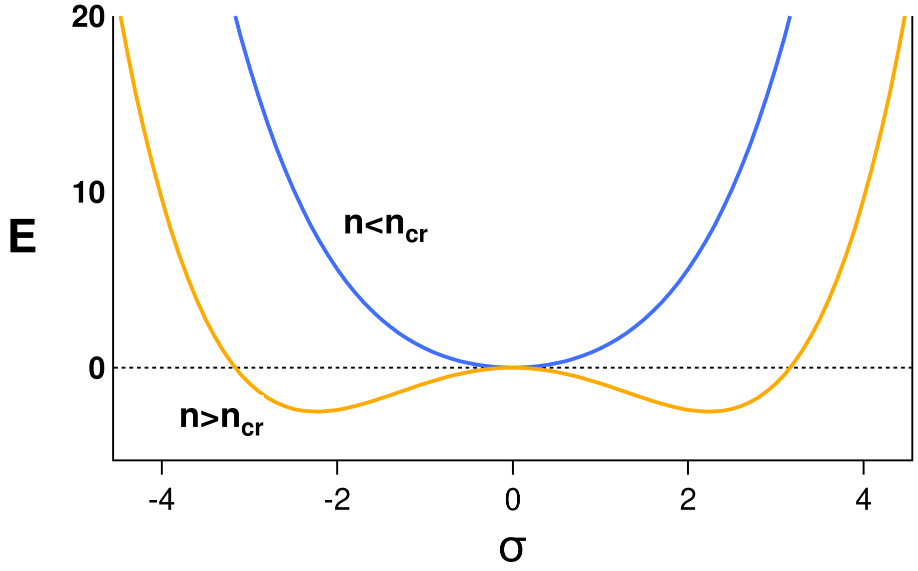
→ Spontaneous magnetization

$$E^{\mathrm{HK}}[n(\boldsymbol{r}), \sigma(\boldsymbol{r})] \approx C_0^{\mathrm{HK}}[n(\boldsymbol{r})] + C_2^{\mathrm{HK}}[n(\boldsymbol{r})] \cdot [\sigma(\boldsymbol{r})]^2 + C_4^{\mathrm{HK}}[n(\boldsymbol{r})] \cdot [\sigma(\boldsymbol{r})]^4 \qquad (|\sigma(\boldsymbol{r})/n(\boldsymbol{r})| \ll 1)$$

$$C_4^{\mathrm{HK}}[n] > 0\,, \qquad \begin{cases} C_2^{\mathrm{HK}}[n] > 0 & \text{for } n < n_{\mathrm{cr}} \\ C_2^{\mathrm{HK}}[n] < 0 & \text{for } n > n_{\mathrm{cr}} \end{cases}$$

$$\rightarrow \min_{\sigma(\boldsymbol{r})} E^{\mathrm{HK}}[n(\boldsymbol{r}), \sigma(\boldsymbol{r})]$$

$$= \begin{cases} C_0^{\mathrm{HK}}[n(\boldsymbol{r})] \quad \text{with } \sigma(\boldsymbol{r}) = 0 & (\text{for } n(\boldsymbol{r}) < n_{\mathrm{cr}}) \\ C_0^{\mathrm{HK}}[n(\boldsymbol{r})] - \dfrac{\left|C_2^{\mathrm{HK}}[n(\boldsymbol{r})]\right|^2}{4\,C_4^{\mathrm{HK}}[n(\boldsymbol{r})]} & \\ \quad \text{with } [\sigma(\boldsymbol{r})]^2 = \dfrac{\left|C_2^{\mathrm{HK}}[n(\boldsymbol{r})]\right|}{2\,C_4^{\mathrm{HK}}[n(\boldsymbol{r})]} & (\text{for } n(\boldsymbol{r}) > n_{\mathrm{cr}}) \end{cases}$$



Reduction to ordinary DFT :

$$\boldsymbol{Q} = \{n(\boldsymbol{r}), \sigma(\boldsymbol{r})\} \to \boldsymbol{Q}' = \{n(\boldsymbol{r})\}$$

$$E^{\mathrm{HK}}[n(\boldsymbol{r})] = \min_{\sigma(\boldsymbol{r})} E^{\mathrm{HK}}[n(\boldsymbol{r}), \sigma(\boldsymbol{r})]$$

$$= C_0^{\mathrm{HK}}[n(\boldsymbol{r})] - \theta\Big(n(\boldsymbol{r}) - n_{\mathrm{cr}}\Big) \frac{\Big|C_2^{\mathrm{HK}}[n(\boldsymbol{r})]\Big|^2}{4\, C_4^{\mathrm{HK}}[n(\boldsymbol{r})]}$$

$\cdots$ irregularity !

$$\hookrightarrow \quad E_{\mathrm{reg}}^{\mathrm{KS}}[n(\boldsymbol{r})] = E_{\mathrm{dir}}[n(\boldsymbol{r})] + C_0^{\mathrm{KS}}[n(\boldsymbol{r})]\,,$$

$$E_{\mathrm{irr}}^{\mathrm{KS}}[\varrho; n(\boldsymbol{r})] = E_K[\varrho] + E_{ei}[n(\boldsymbol{r})] + C_2^{\mathrm{KS}}[n(\boldsymbol{r})] \cdot [\boldsymbol{\sigma}(\boldsymbol{r})]^2 + C_4^{\mathrm{KS}}[n(\boldsymbol{r})] \cdot [\boldsymbol{\sigma}(\boldsymbol{r})]^4$$

$$\Big(C_\nu^{\mathrm{KS}} \;\leftarrow\; E_{\mathrm{xc}}^{\mathrm{KS}}[n, \boldsymbol{\sigma}]\Big)$$

N-representability ? — not yet proven

for $\boldsymbol{Q} = \{n(\boldsymbol{r}), \sigma(\boldsymbol{r})\}$

$\hookrightarrow$ possibility of reinterpretation

$$\boldsymbol{Q} = \{n(\boldsymbol{r}), \sigma(\boldsymbol{r})\} \quad \rightarrow \quad \boldsymbol{Q} = \{n(\boldsymbol{r}), \mathcal{M}\}$$

$$\mathcal{M} := \int d^3r\, \sigma(\boldsymbol{r})$$

$\Big(\rightarrow \quad \mathcal{M}$ physical, $\boldsymbol{\sigma}(\boldsymbol{r})$ not$\Big)$

$\rightarrow$ N-representability easily proven

$\because$) s.p. states $\phi_k(\boldsymbol{r}) = \sqrt{1-c^2}\,\phi_{k\uparrow}(\boldsymbol{r}) + c\,\phi_{k\downarrow}(\boldsymbol{r})$

with $2|c|^2 = 1 - \mathcal{M}/N$

$\rightarrow$ Harriman's construction

7.2 *Many-nucleon systems*

Nucleus $\cdots$ composed of p & n — both #'s conserved

$$\rightarrow \quad \tilde{E}^{\mathrm{KS}} := E^{\mathrm{KS}} - \sum_{\tau=p,n} \mu_\tau \left[\mathrm{tr}_\tau(\varrho) - N_\tau\right]$$

A popular example $\cdots$ Skyrme EDF :

$$E_{\mathrm{Skyrme}} = \int d^3r\, \mathcal{H}_{\mathrm{Skyrme}}[n_\tau(\boldsymbol{r}), \xi_\tau(\boldsymbol{r}), \boldsymbol{\zeta}_\tau(\boldsymbol{r})]\,;$$

$$n_\tau(\boldsymbol{r}) = \sum_{i\in\tau} \varphi_i^*(\boldsymbol{r})\,\varphi_i(\boldsymbol{r})\,, \;\; \xi_\tau(\boldsymbol{r}) = \sum_{i\in\tau} \nabla\varphi_i^*(\boldsymbol{r}) \cdot \nabla\varphi_i(\boldsymbol{r})\,,$$

$$\boldsymbol{\zeta}_\tau(\boldsymbol{r}) = i \sum_{i\in\tau} \varphi_i^*(\boldsymbol{r})\,\boldsymbol{\sigma} \times \nabla\varphi_i(\boldsymbol{r})$$

Parameters in $\mathcal{H}_{\mathrm{Skyrme}}$

$\leftarrow$ fitting to exp. data on some physical quantities

What is $\boldsymbol{Q}$? $\cdots$ obscure !

fitted quantities — possibly physical

$\rightarrow$ belong to $\boldsymbol{Q}$

unfitted quantities — physical meaning questionable

[even $n_\tau(\boldsymbol{r})$]

Basic problems (toward *ab initio* theory)

- How to obtain $E^{\mathrm{KS}}[\varrho; \boldsymbol{Q}]$ — as everyone knows

  $\hookrightarrow$ depends on other problems!

- What $\boldsymbol{Q}$ is appropriate?

  $\cdots$ $n_\tau(\boldsymbol{r})$? what should (can) be added?

  $\leftrightarrow$ how to fix E^{KS} & source of irregularity

- What is $E^{\mathrm{KS}}_{\mathrm{irr}}[\varrho; \boldsymbol{Q}]$? — suppose $\mathcal{C}^{(\nu)}$ unnecessary

  For $\boldsymbol{Q} = \{n_p(\boldsymbol{r}), n_n(\boldsymbol{r})\}$

  shell structure $\leftarrow K$, $V^{(\mathrm{LS})}$ (, $V^{(\mathrm{tensor})}$?)

  $\hookrightarrow E^{\mathrm{KS}}_{\mathrm{irr}}$?

- Center-of-mass [for $n_\tau(\boldsymbol{r}) \in \boldsymbol{Q}$]

True density: $$\tilde{n}_\tau(\boldsymbol{r}) := \Big\langle \Psi \Big| \sum_{i\in\tau} \delta\big(\boldsymbol{r} - (\boldsymbol{r}_i - \boldsymbol{R})\big) \Big| \Psi \Big\rangle$$

$$= \frac{1}{(2\pi)^3} \int d^3q \, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \, \tilde{F}(\boldsymbol{q}) \, ;$$

$$\tilde{F}(\boldsymbol{q}) := \Big\langle \Psi \Big| \sum_{i\in\tau} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_i - \boldsymbol{R})} \Big| \Psi \Big\rangle$$

$\cdots$ many-body op. because of $\boldsymbol{R} := \frac{1}{A} \sum_i \boldsymbol{r}_i$

Note $|\Psi(\mathrm{g.s.})\rangle = |\Psi_{\mathrm{rel.}}(\mathrm{g.s.})\rangle \otimes |\Psi_{\mathrm{c.m.}}\rangle$

$$\Big(|\Psi_{\mathrm{c.m.}}\rangle \propto e^{i\boldsymbol{K}\cdot\boldsymbol{R}} \to \langle\Psi|(\varDelta\boldsymbol{R})^2|\Psi\rangle = \infty \Big)$$

$$\tilde{n}_\tau(\boldsymbol{r}) \underset{?}{\approx} n_\tau(\boldsymbol{r}) = \left\langle \Psi \middle| \sum_{i\in\tau} \delta\Big(\boldsymbol{r} - (\boldsymbol{r}_i - \langle \boldsymbol{R} \rangle)\Big) \middle| \Psi \right\rangle$$

$$= \left\langle \Psi \middle| \sum_{i\in\tau} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \middle| \Psi \right\rangle$$

$\cdots$ not always acceptable

$[R_\alpha, P_\beta] = i\delta_{\alpha\beta} \ \rightarrow \ \langle(\Delta\boldsymbol{R})^2\rangle \neq 0$ (uncertainty)

$\hookrightarrow$ $\boldsymbol{R}$ desired to be controlled ! (with ϱ ?)

Cf. Electrons bound in atom

Born-Oppenheimer approx.

$\rightarrow$ c.m. $\approx$ position of nuclei : classical var.

$\cdots$ well controlled

- Deformation & intrinsic state

  Any even-even nuclei $\cdots$ $J = 0$ @ g.s.

  $\rightarrow n_\tau(\boldsymbol{r}) = n_\tau(r)$!

  — $\min_{\varrho \to \boldsymbol{Q}} E^{\mathrm{KS}} \leftrightarrow$ spherical $n_\tau(\boldsymbol{r})$? $(\leftarrow n_\tau(\boldsymbol{r}) \in \boldsymbol{Q})$

  "Deformed nuclei" $\cdots$ irregularity @ shape transition

  (*e.g.* in $\langle r^2 \rangle$)

  $|\Psi(\mathrm{g.s.})\rangle \approx P_{J=0}|\Phi\rangle \notin \mathcal{V}_{\mathrm{idem}}$ despite $|\Phi\rangle \in \mathcal{V}_{\mathrm{idem}}$

  (intrinsic state)

  $$\left.\begin{array}{l} \text{spherical } n_\tau(\boldsymbol{r}) \\ |\Psi\rangle \in \mathcal{V}_{\mathrm{idem}} \ (\leftarrow \mathrm{KS}) \end{array}\right\} \text{— incompatible!(?)}$$

– Normal interpretation (so far):

$$\min_{\varrho \to \boldsymbol{Q}} E^{\mathrm{KS}} \quad \to \quad |\Phi^{\mathrm{KS}}\rangle \; (\in \mathcal{V}_{\mathrm{idem}}) : \text{ intrinsic state rather than g.s.}$$

$\cdots$ contradictory to KS theory's spirit!

$$\Big(E_0 = \min_{\varrho \to N, \boldsymbol{Q}} E^{\mathrm{KS}} \Big)$$

– Possible reinterpretation: $n_\tau(\boldsymbol{r}) \notin \boldsymbol{Q}$!

$$\Big[n_\tau(r = |\boldsymbol{r}|) \in \boldsymbol{Q} \, ? \Big]$$

VIII. Summary

★ "Minimal composition" of KS theory exposed

- Principal variables generalized : $n(\boldsymbol{r}) \rightarrow \boldsymbol{Q}$

  (KS theory $\not\subset$ DFT ? generalization of 'DFT' ?)

- Reformulation in terms of ϱ

  Levy's constrained search

  $\rightarrow$ differentiability (v-representability) lost in E^{HK}

  $\rightarrow$ partitioning to regular & irregular parts

  $\rightarrow$ E^{KS} (& KS theory)

★ General properties of KS theory

- "Equational equivalence"
- Representabilities

  — distinguished between HK & KS levels

- Principal variables — not too few, not too many

  (no immediate criterion)

★ Practice of KS theory

- Many electron systems
  - ∗ Conventional KS theory
  - ∗ Spin DFT — reinterpretation

    restoring N-representability ?
- Many nucleon systems
  - ∗ Obscurity in principal variables
  - ∗ Problem w.r.t. center-of-mass motion
  - ∗ Problem w.r.t. deformation

    $J = 0$ g.s. & idempotency — incompatible (?)

    $\rightarrow$ abandon describing g.s. or $n_\tau(\boldsymbol{r}) \notin \boldsymbol{Q}$

    ↘ save KS

⇒ Hope to help studies on quantum many-body systems (*e.g.* via KS theory) !