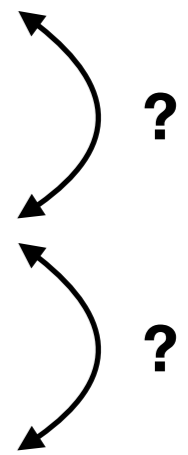


One-body reduced density matrix functional theory

Klaas Giesbertz

Content

- “Reduced stuff” functional theories
- Karush-Kuhn-Tucker conditions
- Approximations
- Making the theory work: finite one-particle basis & temperature



Data compression

Most data in Ψ is not interesting/relevant

explicit

more efficient representation of Ψ

implicit

try to by-pass Ψ and calculate observables directly

Is DFT not enough?

Nuclear potential & electric field

$$v(\mathbf{r}) \quad \Rightarrow \quad \rho(\mathbf{r})$$

The 1RDM

1RDM = One-body reduced density matrix = 1-matrix

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) := N \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\ \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

Equivalent (for fixed N)

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) := \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle \quad \int d\mathbf{x} := \sum_{\sigma} \int d\mathbf{r}$$

One-body operator

$$\hat{O}_1 = \sum_{i=1}^N \hat{o}(\mathbf{x}_i)$$

$$\begin{aligned} \langle \Psi | \hat{O}_1 | \Psi \rangle &= \sum_{i=1}^N \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\ &\quad \hat{o}(\mathbf{x}_i) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &= N \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\ &\quad \hat{o}(\mathbf{x}_1) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &= \int d\mathbf{x} [\hat{o}(\mathbf{x}) \gamma(\mathbf{x}, \mathbf{x}')]_{\mathbf{x}'=\mathbf{x}} \end{aligned}$$

Linear operator

$$\hat{A}(v + w) = \hat{A}v + \hat{A}w$$

Discrete index (vectors)

$$(\hat{A}v)_i = \sum_j A_{ij} v_j$$

Continuous index (functions)

$$(\hat{A}v)(\mathbf{x}) = \int d\mathbf{x}' A(\mathbf{x}, \mathbf{x}') v(\mathbf{x}')$$

non-local

Diagonal operator (multiplication)

$$A_{ij} = a_i \delta_{ij}$$

$$(\hat{A}v)_i = a_i v_i$$

\Rightarrow

$$A(\mathbf{x}, \mathbf{x}') = a(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}')$$

\Rightarrow

$$(\hat{A}v)(\mathbf{x}) = a(\mathbf{x}) v(\mathbf{x})$$

local = multiplicative

Kinetic example

$$\hat{T} = -\frac{1}{2}\nabla^2 \quad \Rightarrow \quad t(\mathbf{x}, \mathbf{x}') = -\frac{1}{2}\nabla_{\mathbf{r}}^2\delta(\mathbf{x} - \mathbf{x}')$$

$$\begin{aligned}(\hat{T}f)(\mathbf{x}) &= \int d\mathbf{x}' t(\mathbf{x}, \mathbf{x}')f(\mathbf{x}') \\ &= -\frac{1}{2}\int d\mathbf{x}' \nabla_{\mathbf{r}}^2\delta(\mathbf{x} - \mathbf{x}')f(\mathbf{x}') \\ &= -\frac{1}{2}\int d\mathbf{x}' \nabla_{\mathbf{r}'}^2\delta(\mathbf{x} - \mathbf{x}')f(\mathbf{x}') \\ &= -\frac{1}{2}\int d\mathbf{x}' \delta(\mathbf{x} - \mathbf{x}')\nabla_{\mathbf{r}'}^2 f(\mathbf{x}') = -\frac{1}{2}\nabla^2 f(\mathbf{r})\end{aligned}$$

Kinetic example

$$\begin{aligned}\hat{T} = -\frac{1}{2}\nabla^2 &\quad \Rightarrow \quad t(\mathbf{x}, \mathbf{x}') = -\frac{1}{2}\nabla_{\mathbf{r}}^2\delta(\mathbf{x} - \mathbf{x}') \\ &= \frac{1}{2}\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'}\delta(\mathbf{x} - \mathbf{x}') \\ &= \frac{1}{2}\sum_k \nabla\chi_k(\mathbf{x}) \cdot \nabla\chi_k^*(\mathbf{x}')\end{aligned}$$

$$\delta(\mathbf{x} - \mathbf{x}') = \sum_k \chi_k(\mathbf{x})\chi_k^*(\mathbf{x}')$$

Sum over complete orthonormal basis

Energy components

Kinetic energy

$$\begin{aligned} T[\gamma] &= \int d\mathbf{x} \left[-\frac{1}{2} \nabla_{\mathbf{x}}^2 \gamma(\mathbf{x}, \mathbf{x}') \right]_{\mathbf{x}'=\mathbf{x}} \\ &= \int d\mathbf{x} \int d\mathbf{x}' t(\mathbf{x}', \mathbf{x}) \gamma(\mathbf{x}, \mathbf{x}') \end{aligned}$$

Scalar potential (nuclei)

$$V[\rho] = \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r})$$

Pair density

$$P(\mathbf{x}_1, \mathbf{x}_2) := N(N-1) \int d\mathbf{x}_3 \cdots \int d\mathbf{x}_N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2$$

Equivalent (for fixed N)

$$P(\mathbf{x}_1, \mathbf{x}_2) := \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle$$

$$W[P] = \frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{P(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$E = T[\gamma] + V[\rho] + W[P]$$

Energy functional

$$E[\Gamma] = T[\gamma] + V[\rho] + W[P]$$

$$\begin{array}{ccc} \rho & \leftarrow & P \\ \uparrow & & \uparrow \\ \gamma & \leftarrow & \Gamma \end{array}$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_2, \mathbf{x}'_1) := \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle$$

$$P(\mathbf{x}_1, \mathbf{x}_2) = \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_2, \mathbf{x}_1)$$

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \frac{1}{N-1} \int d\mathbf{x}_2 \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_2, \mathbf{x}'_1)$$

2RDM functional

$$\inf_{\Gamma} E[\Gamma] = \quad \longrightarrow \quad \min_{\Gamma \in P_N} E[\Gamma] = E_0$$

$$P_N := \{\Gamma : \exists \Psi \rightarrow \Gamma\} \quad = N\text{-representable 2RDMs}$$

$$\text{Tr}\{\Gamma\} = N(N - 1)$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_2, \mathbf{x}'_1) = \Gamma^*(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_2, \mathbf{x}_1)$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_2, \mathbf{x}'_1) = -\Gamma(\mathbf{x}_2, \mathbf{x}_1; \mathbf{x}'_2, \mathbf{x}'_1)$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_2, \mathbf{x}_1) = P(\mathbf{x}_1, \mathbf{x}_2) \geq 0$$

and more!

Comparison

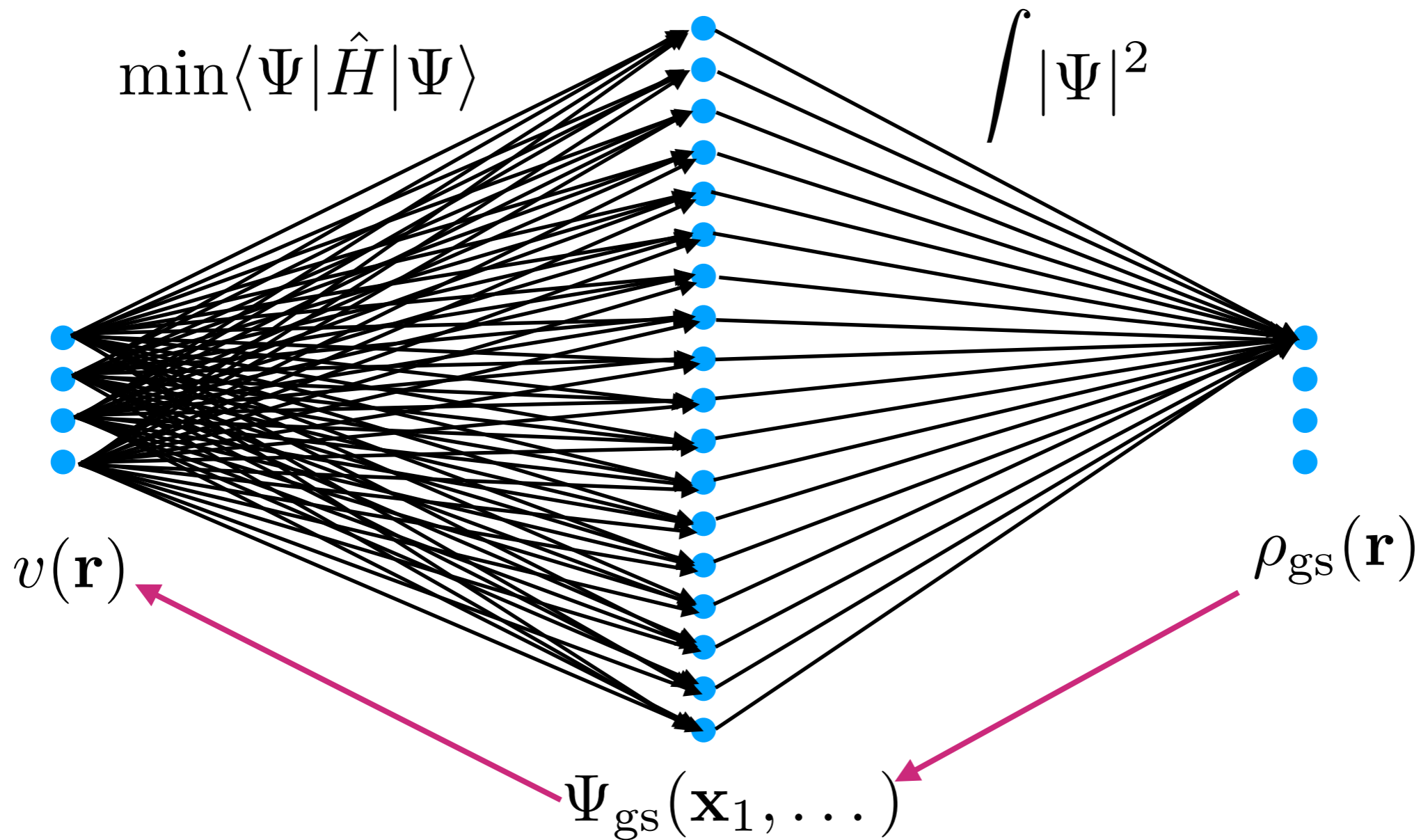
| | complexity | $E[\cdot]$ | P_N | approximated energy |
|----------|------------|------------|----------|---------------------|
| Ψ | m^{dN} | explicit | explicit | $\geq E_0$ |
| Γ | m^{4d} | explicit | tough | $\leq E_0$ |

$$P_N := \{\rho : \exists \Psi \rightarrow \rho\} = \{\rho : \rho \geq 0 \text{ and } \int d\mathbf{r} \rho(\mathbf{r}) = N\}$$

$m = 1\text{D grid size}$

$d = \text{dimension}$

Density Functional Theory



Back mapping: HK

Hohenberg–Kohn I

Suppose v_1 and v_2 yield same Ψ

$$(\hat{T} + \hat{V}_1 + \hat{W})\Psi = E_1\Psi$$

$$(\hat{T} + \hat{V}_2 + \hat{W})\Psi = E_2\Psi$$

$$(\hat{V}_1 - \hat{V}_2)\Psi = (E_1 - E_2)\Psi$$

If Ψ does not vanish on an open set (probably true): divide!

$$\hat{V}_1 - \hat{V}_2 = \sum_{i=1}^N (v_1(\mathbf{r}_i) - v_2(\mathbf{r}_i)) = E_1 - E_2 = \text{const.}$$

Hohenberg–Kohn II

Suppose non-degenerate $\Psi_1 \neq \Psi_2$ both yield ρ

$$\begin{aligned} E_1 &= \langle \Psi_1 | \hat{T} + \hat{V}_1 + \hat{W} | \Psi_1 \rangle \\ &< \langle \Psi_2 | \hat{T} + \hat{V}_1 + \hat{W} | \Psi_2 \rangle \\ &= \langle \Psi_2 | \hat{T} + \hat{V}_2 + \hat{W} | \Psi_2 \rangle + \langle \Psi_2 | \hat{V}_1 - \hat{V}_2 | \Psi_2 \rangle \\ &= E_2 + \int d\mathbf{r} \rho(\mathbf{r}) (v_1(\mathbf{r}) - v_2(\mathbf{r})) \end{aligned}$$

Hohenberg–Kohn II

Suppose non-degenerate $\Psi_1 \neq \Psi_2$ both yield ρ

$$E_1 < E_2 + \int d\mathbf{r} \rho(\mathbf{r}) (v_1(\mathbf{r}) - v_2(\mathbf{r}))$$
$$E_2 < E_1 + \int d\mathbf{r} \rho(\mathbf{r}) (v_2(\mathbf{r}) - v_1(\mathbf{r})) \quad (1 \leftrightarrow 2)$$

$$E_1 + E_2 < E_1 + E_2$$

Impossible! $\rightarrow \Psi_{\text{gs}}[\rho]$ is unique

Density Functionals

Via HK mapping all observables functionals of density

$$O[\rho] = \langle \Psi_{\text{gs}}[\rho] | \hat{O} | \Psi_{\text{gs}}[\rho] \rangle$$

Caveats:

- Degeneracy
- Only works for v-representable densities

V-representable set $V_N := \{ \rho : \exists v \rightarrow \rho = \rho_{\text{gs}} \}$

Energy as (Universal) Density Functional

$$\begin{aligned} E_{\text{gs}} &= \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\ &= \min_{\rho} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle \\ &= \min_{\rho} \left(V[\rho] + \underbrace{\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle}_{= F_L[\rho]} \right) \end{aligned}$$

N -representable densities: Any (positive) density integrating to an integer number of particles

V-repr haunts DFT

To find stationary point:

$$c = \frac{\delta E}{\delta \rho} = \frac{\delta F_L}{\delta \rho} + v(\mathbf{r})$$

$$\frac{\delta F_L}{\delta \rho} = -v(\mathbf{r}) + c$$

$\frac{\delta F_L}{\delta \rho}$ is only defined for v-representable densities...

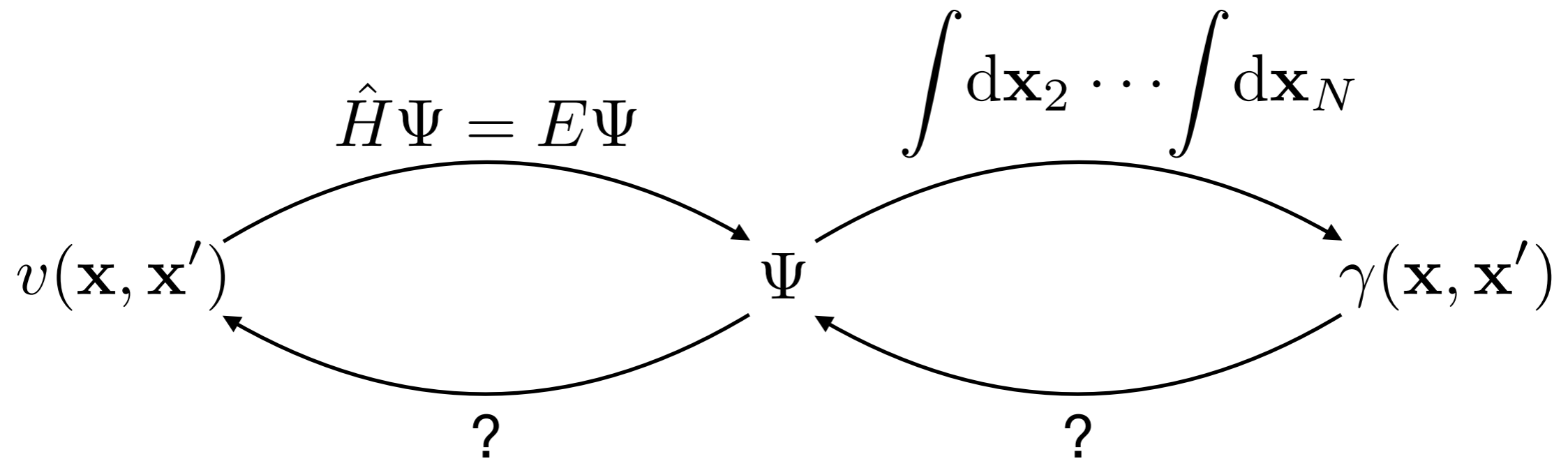
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| Γ | m^{4d} | explicit | tough | $\leq E_0$ |
| ρ | m^d | implicit | easy | $\min_{\Psi \rightarrow \rho} \langle \Psi \hat{T} + \hat{W} \Psi \rangle$ |

$m = 1\text{D grid size}$

$d = \text{dimension}$

1 RDM Functional Theory



Dimensionality of 1RDM requires non-local potential as conjugate variable

$$V[\gamma] = \int d\mathbf{x} \int d\mathbf{x}' v(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x})$$

Diagonalisation 1RDM

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_k n_k \phi_k(\mathbf{x}) \phi_k^*(\mathbf{x}')$$

- $\phi_k(\mathbf{x})$: natural (spin-)orbitals (NOs)
- n_k : (natural) occupation numbers

Bounds on occupations numbers

$$\text{tr}\{\gamma\} = \sum_k n_k = N$$

$$\text{fermions: } 0 \leq n_k \leq 1$$

$$\text{bosons: } 0 \leq n_k < \infty$$

Hohenberg–Kohn I

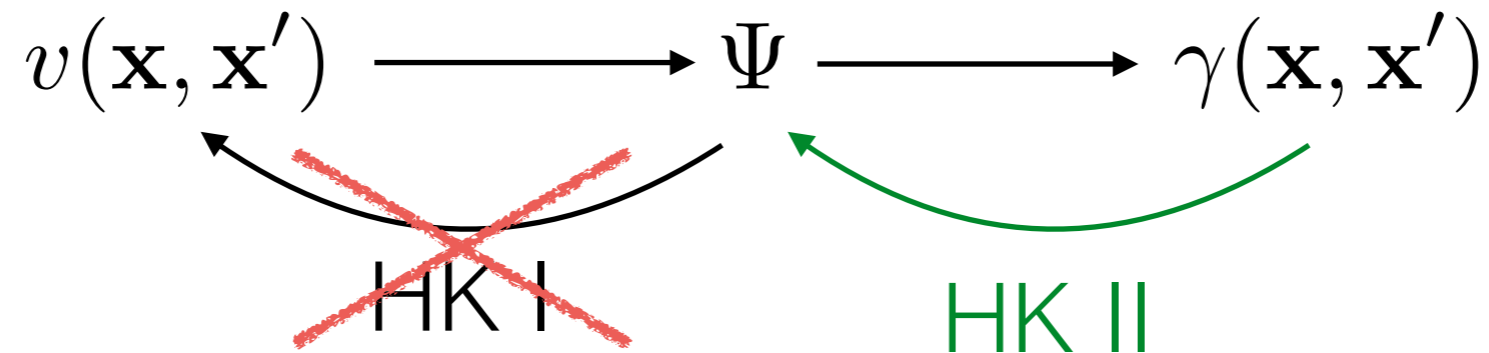
$$(\hat{V}_1 - \hat{V}_2)\Psi = (E_1 - E_2)\Psi$$

No division by Ψ possible! \rightarrow no HK I

$$V[\gamma] = \int d\mathbf{x} \int d\mathbf{x}' \gamma(\mathbf{x}, \mathbf{x}') v(\mathbf{x}', \mathbf{x}) = \sum_k n_k \langle \phi_k | \hat{v} | \phi_k \rangle$$

- Potentials coupling to zero occupation problematic
- Many more [KG, J. Chem Phys. **143**, 054102 (2015)]

Hohenberg–Kohn II



Do not need multiplicativity of potential in HK II

HK II works! $\Psi \leftrightarrow \gamma$

$$O[\gamma] = \langle \Psi[\gamma] | \hat{O} | \Psi[\gamma] \rangle$$

Universal Functionals

$$\begin{aligned} E[\gamma] &= \langle \Psi[\gamma] | \hat{H} | \Psi[\gamma] \rangle \\ &= \sum_k n_k \langle \phi_k | -\frac{1}{2} \nabla^2 + \hat{v} | \phi_k \rangle + \underbrace{\langle \Psi[\gamma] | \hat{W} | \Psi[\gamma] \rangle}_{= W_{\text{HK}}} \end{aligned}$$

Only interaction part implicit!

Same problem: Only defined for 1RDMs generated by ground states. Given a γ , how do we know?

Universal Functionals

$$\begin{aligned} E_{\text{gs}} &= \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\ &= \min_{\gamma} \min_{\Psi \rightarrow \gamma} \langle \Psi | \hat{H} | \Psi \rangle \\ &= \min_{\gamma} \left(T[\gamma] + V[\gamma] + \underbrace{\min_{\Psi \rightarrow \gamma} \langle \Psi | \hat{W} | \Psi \rangle}_{= W_L[\gamma]} \right) \end{aligned}$$

Pure-state N -representable 1RDMs: generalised Pauli constraints

Characterisation of $P_N := \{\Psi \rightarrow \gamma\}$ is difficult in general

Pure state N-repr

Pauli constraints for fermions: $\sum_{i=1}^{N_b} n_i = N \quad 0 \leq n_i \leq 1$

But not sufficient!

Example: $N = 3$ fermions in $N_b = 6$ orbitals

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1$$

$$n_5 + n_6 - n_4 \geq 0$$

(ordered occupations from high to low)

Comparison

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| Ψ | m^{dN} | explicit | explicit | $\geq E_0$ |
| Γ | m^{4d} | explicit | tough | $\leq E_0$ |
| ρ | m^d | implicit | easy | $\min_{\Psi \rightarrow \rho} \langle \Psi \hat{T} + \hat{W} \Psi \rangle$ |
| γ | m^{2d} | implicit | cumbersome | $\min_{\Psi \rightarrow \gamma} \langle \Psi \hat{W} \Psi \rangle$ |

$m = 1D$ grid size

$d =$ dimension

Ensembles

$$O = \sum_K w_K \langle \Psi_K | \hat{O} | \Psi_K \rangle$$

weights: $\sum_K w_K = 1$ $0 \leq w_K (\leq 1)$

density-matrix operator: $\hat{\rho} = \sum_K w_K |\Psi_K\rangle \langle \Psi_K|$

$$\text{Tr}\{\cdot\} = \sum_K \langle \Phi_K | \cdot | \Phi_K \rangle$$

pure-state included as: $w_I = 1$ ($w_{K \neq I} = 0$)

Universal Functionals

Ensemble N -representability: Pauli constraints sufficient!

$$\sum_k n_k = N \qquad 0 \leq n_k (\leq 1)$$

Extend constraint-search over all density matrix-operators

$$W_V[\gamma] = \min_{\hat{\rho} \rightarrow \gamma} \text{Tr}\{\hat{\rho} \hat{W}\}$$

Additional advantage: functional is now convex (also DFT)

A.J. Coleman, Rev. Mod. Phys. **35**, 668 (1963)

S.M. Valone, J. Chem. Phys. **73**, 1344 (1980)

E.H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983)

Comparison

| | complexity | $E[\cdot]$ | P_N | E_N | approximated energy |
|----------|------------|------------|------------|----------|--|
| Ψ | m^{dN} | explicit | explicit | explicit | $\geq E_0$ |
| Γ | m^{4d} | explicit | tough | tough? | $\leq E_0$ |
| ρ | m^d | implicit | easy | easy | $\min_{\Psi \rightarrow \rho} \langle \Psi \hat{T} + \hat{W} \Psi \rangle$ |
| γ | m^{2d} | implicit | cumbersome | easy | $\min_{\hat{\rho} \rightarrow \gamma} \text{Tr}\{\hat{\rho} \hat{W}\}$ |

$m = 1\text{D grid size}$

$d = \text{dimension}$

Advantage for 1RDM-FT in building approximate functionals

- Formal advantage: kinetic energy is known, so less to approximate than in DFT.
- Kinetic energy is known: no Kohn-Sham system needed.
- In practice: natural occupation numbers provide useful information on strong / static correlation.
- This natural occupation numbers can be used to construct approximate functionals, which can properly describe molecular dissociation.