Density-functional theory or how to connect chemistry with convex analysis

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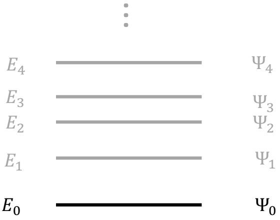
N-electron Schrödinger equation for the *ground* state

$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$



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where $\Psi_0 \equiv \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \hat{V}$ with

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \longrightarrow$$ *universal* kinetic energy operator

$$\hat{W}_{\rm ee} \equiv \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times \longrightarrow$$ *universal* two-electron repulsion operator

$$\hat{V} \equiv \sum_{i=1}^{N} v(\mathbf{r}_i)\times$$ where $$v(\mathbf{r}) = -\sum_{A}^{\rm nuclei}\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \longrightarrow$$ local *nuclear* potential operator

Potential-functional theory

- The basic variable in quantum mechanics is the (many-electron) *wavefunction* Ψ.

- Normalization condition:

$$1 = \langle \Psi | \Psi \rangle = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_1 \ldots \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_N \; \Psi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

- Rayleigh–Ritz *variational principle*:

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

  where

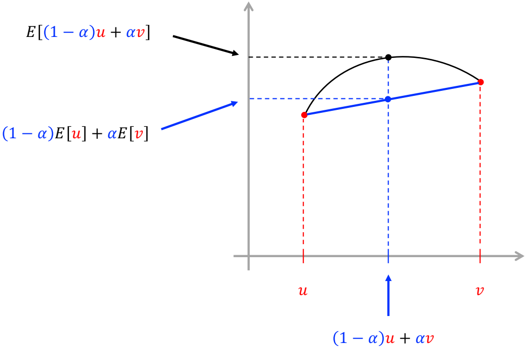
$$\langle \Psi | \hat{H} | \Psi \rangle = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_1 \ldots \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_N \; \Psi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N) \hat{H} \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

- The ground-state energy can be seen as a *functional* of the nuclear potential $v : \mathbf{r} \mapsto v(\mathbf{r})$,

$$v \quad \longrightarrow \quad \hat{H} \equiv \hat{H}[v] \quad \longrightarrow \quad \Psi_0 \equiv \Psi[v] \quad \longrightarrow \quad E_0 \equiv E[v]$$

Potential-functional theory

- The ground-state energy is a *concave* functional of the nuclear potential.



Proof: since $\hat{H}\Big[(1-\alpha)u+\alpha v\Big] = (1-\alpha)\hat{H}\left[u\right]+\alpha\hat{H}\left[v\right]$ we have

$$\begin{aligned}
E\Big[(1-\alpha)u+\alpha v\Big] \quad &= \quad (1-\alpha)\Big\langle\Psi\Big[(1-\alpha)u+\alpha v\Big]\Big|\hat{H}[u]\Big|\Psi\Big[(1-\alpha)u+\alpha v\Big]\Big\rangle \\
&\quad +\alpha\Big\langle\Psi\Big[(1-\alpha)u+\alpha v\Big]\Big|\hat{H}[v]\Big|\Psi\Big[(1-\alpha)u+\alpha v\Big]\Big\rangle \\
&\geq \quad (1-\alpha)E\left[u\right]+\alpha E\left[v\right]
\end{aligned}$$

Potential-functional theory

- We consider two potentials u and v that *differ by more than a constant*.
- In other words $u(\mathbf{r}) - v(\mathbf{r})$ varies with $\mathbf{r}$.
- The corresponding Hamiltonians $\hat{H}[u]$ and $\hat{H}[v]$ have no eigenfunctions in common.

Proof: if Ψ is eigenfunction of both $\hat{H}[u]$ and $\hat{H}[v]$ then

$$\begin{aligned}\left(\hat{H}[u] - \hat{H}[v]\right)\Psi(\mathbf{r},\mathbf{r},\ldots,\mathbf{r}) &= N\left(u(\mathbf{r}) - v(\mathbf{r})\right) \times \Psi(\mathbf{r},\mathbf{r},\ldots,\mathbf{r}) \\ &= \left(E[u] - E[v]\right) \times \Psi(\mathbf{r},\mathbf{r},\ldots,\mathbf{r})\end{aligned}$$

thus leading to $u(\mathbf{r}) - v(\mathbf{r}) = \dfrac{E[u] - E[v]}{N}$, which is absurd.

Density-functional theory (DFT)

- Electron density:

$$n_v(\mathbf{r}) = N \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_2 \ldots \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_N \left|\Psi[v](\mathbf{r}, \mathbf{r}_2 \ldots, \mathbf{r}_N)\right|^2$$

- Note that n_v is a so-called *"v-representable"* density.

- A density n is said to be *"N-representable"* if you can find an N-electron wavefunction Ψ such that

$$n(\mathbf{r}) = N \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_2 \ldots \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_N \left|\Psi(\mathbf{r}, \mathbf{r}_2 \ldots, \mathbf{r}_N)\right|^2$$

- It can be shown that the set of N-representable densities is the set of positive functions $n : \mathbf{r} \mapsto n(\mathbf{r})$ that integrate to the number of electrons N and that give a finite von Weizsäcker kinetic energy*:

$$\frac{1}{2} \int \mathrm{d}\mathbf{r} \, \left|\nabla n^{1/2}(\mathbf{r})\right|^2 < +\infty.$$

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[*] *Principles of DFT*, lecture given by **Trygve Helgaker** at the GDR Correl mini-school on mathematics in electronic structure theory, Paris, January 2017, `http://folk.uio.no/helgaker/talks/Paris_2017.pdf`

Density-functional theory

- The *nuclear potential energy* (unlike the kinetic and repulsion energies) is an *explicit* functional of the density.

Proof: Since electrons are indistinguishable particles,

$$\left|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_N)\right|^2=\left|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_N)\right|^2,$$

thus leading to

$$\begin{aligned}\langle\Psi|\hat{V}|\Psi\rangle &= \sum_{i=1}^{N}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}_1\ldots\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}_N\; v(\mathbf{r}_i)\left|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_N)\right|^2\\ &= N\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}_1\ldots\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}_N\; v(\mathbf{r}_1)\left|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right|^2\\ &= \int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}_1\; v(\mathbf{r}_1)\,n(\mathbf{r}_1)\\ &\overset{\text{notation}}{=} (v|n)\end{aligned}$$

Hohenberg–Kohn theorem

- Let us consider two potentials u and v that *differ by more than a constant*.
- According to the variational principle, the following (strict) inequalities hold:

$$E[u] < \langle \Psi[v] | \hat{H}[u] | \Psi[v] \rangle \quad \text{and} \quad E[v] < \langle \Psi[u] | \hat{H}[v] | \Psi[u] \rangle,$$

or, equivalently,

$$E[u] < E[v] + (u - v | n_v) \quad \text{and} \quad E[v] < E[u] - (u - v | n_u),$$

thus leading to

$$\boxed{(u - v | n_u - n_v) < 0}$$

- **Important consequence** of the above strict inequality:

$$n_u \neq n_v \qquad \longleftarrow \quad \textit{Hohenberg–Kohn theorem}^*$$

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[*] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

Density-functional theory

- The theorem is usually formulated as follows:

  "There is a one-to-one correspondence between the local potential and the ground-state density"

- Let us return to the following inequality:

$$E[v] < E[u] - (u - v|n_u).$$

- If we now include the (missing) particular case where u and v differ by a constant, then

$$E[v] \leq E[u] - (u - v|n_u).$$

- Note that the latter inequality can be seen as holding for *"any"* v and for a *fixed* u.

- **Universal** Hohenberg–Kohn density functional and Lieb maximization:*

$$E[u] - (u|n_u) \quad \equiv \quad F[n_u] \quad = \quad \max_{v}\Big\{E[v] - (v|n_u)\Big\}$$

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

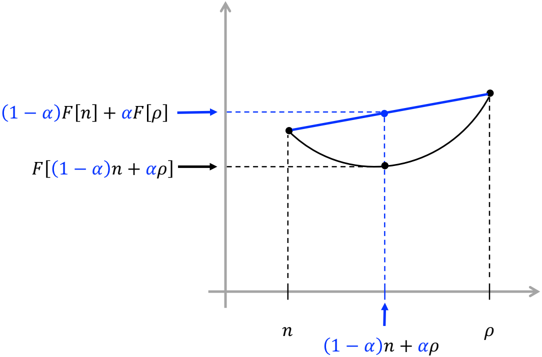
Hohenberg–Kohn variational principle and convexity

- In DFT, if you know $F[n]$, you know "everything":

$$F[n] = \max_{v}\left\{E[v] - (v|n)\right\} \quad \Leftrightarrow \quad \boxed{E[v] = \min_{n}\left\{F[n] + (v|n)\right\}}$$

- Note that the *density* has become our *basic variable*.

- Note also that $F[n]$ is a *convex* functional of the density.



Proof:

$$E[v] - \Big(v\Big|(1-\alpha)n + \alpha\rho\Big)$$

$$= (1-\alpha)\Big(E[v] - (v|n)\Big) + \alpha\Big(E[v] - (v|\rho)\Big)$$

$$\leq (1-\alpha)F[n] + \alpha F[\rho]$$

Kohn–Sham DFT

- Let us now consider DFT for *non-interacting* electrons:

$$\begin{aligned} \hat{W}_{\rm ee} &\longrightarrow 0 \\ F[n] &\longrightarrow T_{\rm s}[n] \leftarrow \textit{non-interacting kinetic energy density functional} \end{aligned}$$

- In a practical (so-called Kohn–Sham) DFT calculation the following (so-called *exchange-correlation*) energy contribution is described as a (approximate) density functional:

$$E_{\rm xc}[n] = F[n] - T_{\rm s}[n] - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

Kohn–Sham DFT

- In Kohn–Sham (KS) DFT, the many-electron problem is formally transformed into a *one-electron-like* problem.

- The "magical" one-electron wavefunctions (so-called KS orbitals) fulfill the following *self-consistent* KS equations:

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r}) + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}\right)\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

where $n(\mathbf{r}) = \sum_{i=1}^{N} \left|\varphi_i(\mathbf{r})\right|^2$.

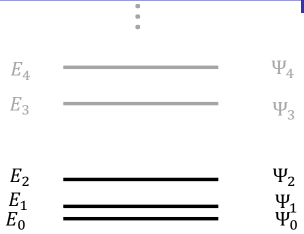
- When convergence is reached, the (in-principle-exact) ground-state energy reads

$$E[v] = -\frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\; \varphi_i^*(\mathbf{r})\nabla^2_{\mathbf{r}}\varphi_i(\mathbf{r}) + (v|n) + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\rm xc}[n].$$

W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

DFT for an ensemble of states

$$\boxed{\hat{H}\Psi_I = E_I\Psi_I}$$



- An ensemble is characterized by the *fixed* weights that are assigned to the excited states:

$$w_1 \geq w_2 \geq \ldots \geq w_M \geq 0.$$

- In this context the *energy of the ensemble*

$$E^{\{w_1,\ldots,w_M\}} = E_0 + \sum_{I=1}^{M} w_I\left(E_I - E_0\right)$$

becomes a *functional of the ensemble density**

$$n^{\{w_1,\ldots,w_M\}}(\mathbf{r}) = n_0(\mathbf{r}) + \sum_{I=1}^{M} w_I\Big(n_I(\mathbf{r}) - n_0(\mathbf{r})\Big).$$

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* E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).

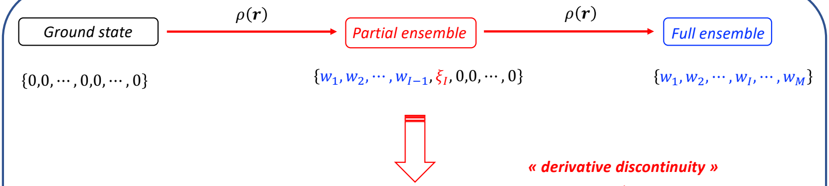
DFT for an ensemble of states

- In ensemble DFT, the exchange-correlation functional becomes *weight-dependent*:

$$\boxed{E_{\rm xc}[n] = E_{\rm xc}^{\{w_1=0,\ldots,w_M=0\}}[n] \qquad \longrightarrow \qquad E_{\rm xc}^{\{w_1,\ldots,w_M\}}[n]}$$

- This weight dependence plays a crucial role in the calculation of *excited energy levels*.[1]

- Generalized adiabatic connection formalism for ensembles (GACE):[2,3]



Ground state $\xrightarrow{\rho(\boldsymbol{r})}$ *Partial ensemble* $\xrightarrow{\rho(\boldsymbol{r})}$ *Full ensemble*

$\{0,0,\cdots,0,0,\cdots,0\}$

$\{w_1,w_2,\cdots,w_{I-1},\xi_I,0,0,\cdots,0\}$

$\{w_1,w_2,\cdots,w_I,\cdots,w_M\}$

$$E_{\rm xc}^{\{w_1,\ldots,w_M\}}[\rho] \quad = \quad E_{\rm xc}[\rho] + \sum_{I=1}^{M} \int_0^{w_I} d\xi_I \; \overbrace{\frac{\partial E_{\rm xc}^{\{w_1,\ldots,w_{I-1},\xi_I,0,\ldots,0\}}[\rho]}{\partial \xi_I}}^{\text{« derivative discontinuity »}}$$

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[1] K. Deur and E. Fromager, J. Chem. Phys. **150**, 094106 (2019).

[2] O. Franck and E. Fromager, *Mol. Phys.* **112**, 1684 (2014).

[3] K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B 95, 035120 (2017).

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