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Can we make exchange energy virial?

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Exchange-correlation virial relation (Levy & Perdew 1985)

$$E_{\mathrm{xc}}(\rho) + T_{\mathrm{c}}(\rho) = -\int_{\mathbb{R}^3} \rho(\mathbf{r})\, \mathbf{r} \cdot \nabla v_{\mathrm{xc}}(\mathbf{r}) \mathrm{d}\mathbf{r}$$

- $\rho(\mathbf{r})$ particle density, $\mathbf{r} \in \mathbb{R}^3$
- $E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$ exchange-correlation energy
- T_{c} kinetic correlation energy
- v_{xc} exchange-correlation potential (non trivial part of v_{KS})

Do we have

$$\boxed{E_{\mathrm{x}}(\rho) = -\int_{\mathbb{R}^3} \rho(\mathbf{r})\, \mathbf{r} \cdot \nabla v_{\mathrm{x}}(\mathbf{r}) \mathrm{d}\mathbf{r} \text{ ?}}$$

Lieb (constrained-search) functional

$$F(\rho) = \inf_{\Gamma \mapsto \rho} \mathrm{Tr}((\hat{T} + \hat{W})\Gamma), \qquad \Gamma = \sum_j p_j |\psi_j\rangle\langle\psi_j|$$

$F(\rho)$ **not** differentiable (Lammert 2007)

Given ρ and $\varepsilon > 0$, we can construct $\{\rho_n\} \subset L^1 \cap L^3$

$$\|\rho - \rho_n\| < \varepsilon$$

and $F(\rho_n) > n$.

In *exact* theory we **cannot** use

$$v_{\mathrm{xc}} = \frac{\delta}{\delta \rho} E_{\mathrm{xc}} \; !$$

λ coupling constant:

$$\boxed{\hat{H}^{\lambda}[v] = \hat{T} + \lambda\hat{W} + \hat{V}}$$

ρ fixed:

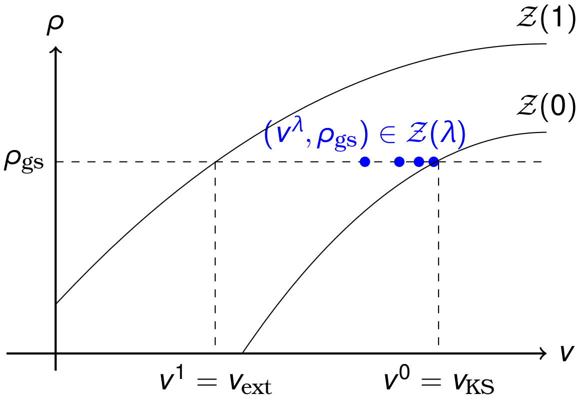
$$\boxed{\hat{H}^{\lambda}[v^{\lambda}] \quad \text{has ground-state density } \rho}$$

Question:

$$E_{\mathrm{xc}}(\lambda) + T_{\mathrm{c}}(\lambda) = -\lambda \int_{\mathbb{R}^3} \rho(\mathbf{r})\, \mathbf{r} \cdot \nabla v_{\mathrm{xc}}^{\lambda}(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{1}$$

What can we say about Eq. (1) in the limit $\lambda \to 0+$?

$$\boxed{\mathcal{Z}(\lambda) = \left\{(v,\rho) : \rho \text{ is a ground-state density of } \hat{H}^{\lambda}[v]\right\}}$$



$$v^0 = v^{\lambda} + \lambda v_{\mathrm{H}} + \lambda v_{\mathrm{xc}}^{\lambda} \tag{2}$$

Properties of $F(\lambda)$

$$\boxed{F(\lambda) = \inf_{\Gamma \mapsto \rho} \mathrm{Tr}((\hat{T} + \lambda \hat{W})\Gamma)}$$

- $F(\lambda) = \mathrm{Tr}((\hat{T} + \lambda \hat{W})\Gamma(\lambda))$
- $F(\lambda)$ infimum over linear function of $\lambda \implies F(\lambda)$ is **concave**
- Left- and right-derivative exist: $\partial_- F(\lambda)$, $\partial_+ F(\lambda)$

$$\overline{\partial} F = \text{super-differential} = [\partial_+ F, \partial_- F] \neq \emptyset$$

$$\partial_+ F(\lambda) = \lim_{\mu \to 0+} \frac{F(\lambda + \mu) - F(\lambda)}{\mu}$$

Decomposition of $F(\lambda)$

$$\boxed{F(\lambda) = \mathrm{Tr}(\hat{T} + \lambda \hat{W})\Gamma(\lambda)} \qquad \boxed{T(0) = F(0) = \mathrm{Tr}\,\hat{T}\Gamma(0)}$$

$$\begin{aligned} F(\lambda) &= T(0) + \lambda \left(\frac{F(\lambda) - T(0)}{\lambda} \right) \\ &= T(0) + \underbrace{\lambda \left(\frac{F(\lambda) - T(0)}{\lambda} - J \right)}_{\lambda E_{\mathrm{xc}}(\lambda)} + \lambda J, \qquad \lambda > 0 \end{aligned}$$

$$\boxed{E_{\mathrm{xc}}(\lambda) = \begin{cases} \frac{F(\lambda) - T(0)}{\lambda} - J & \lambda > 0 \\ ? & \lambda = 0 \end{cases}} \tag{3}$$

Study the limit:

$$\boxed{\lim_{\lambda \to 0+} \frac{F(\lambda) - T(0)}{\lambda} - J}$$

Proposition

$$\partial_+ F(0) - J = \lim_{\gamma \to \infty} \frac{1}{\gamma} E_{\mathrm{xc}}(\rho_\gamma)$$

Idea of proof.

$\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma \mathbf{r})$, use scaling relation for terms involving $\hat{T}$ and $\hat{W}$
$\gamma \to \infty \implies \lambda = 1/\gamma \to 0+$

Definition

$$\boxed{E_{\mathrm{x}} = \partial_+ F(0) - J}$$

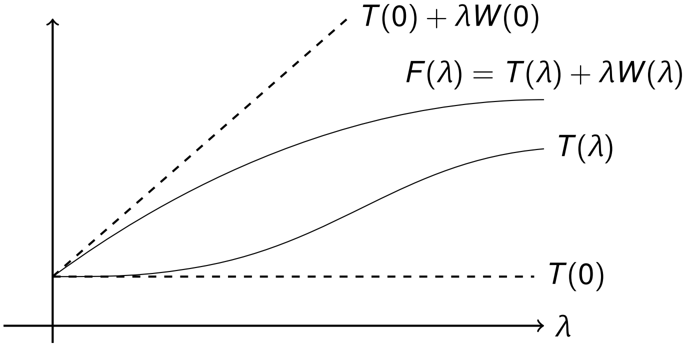
- No need to reference wave function or density matrix
- Also note that we have the proper scaling:

$(\rho_\gamma)_\mu = \rho_{\gamma\mu} \implies$

$$\begin{aligned} E_{\mathrm{x}}(\rho_\mu) &= \lim_{\gamma \to 0+} \frac{1}{\gamma} E_{\mathrm{xc}}((\rho_\mu)_\gamma) \\ &= \mu \lim_{\nu \to 0+} \frac{1}{\nu} E_{\mathrm{xc}}(\rho_\nu) = \mu E_{\mathrm{x}}(\rho) \end{aligned}$$

Write $F(\lambda) = \mathrm{Tr}(\hat{T} + \lambda\hat{W})\Gamma(\lambda) = T(\lambda) + \lambda W(\lambda)$

$$\text{with} \quad \begin{cases} T(\lambda) & = \mathrm{Tr}\ \hat{T}\Gamma(\lambda) \\ W(\lambda) & = \mathrm{Tr}\ \hat{W}\Gamma(\lambda) \end{cases}$$



Adiabatic connection

$$F(\lambda) = F(0) + \int_0^\lambda f(t)\,\mathrm{d}t, \qquad f \in \overline{\partial} F$$

$W(\lambda) \in \overline{\partial} F(\lambda)$

$$\begin{aligned} F(\lambda') &= T(\lambda') + \lambda' W(\lambda') \\ &\leq T(\lambda) + \lambda' W(\lambda) = F(\lambda) + (\lambda' - \lambda) W(\lambda), \end{aligned}$$

since $T(\lambda)$ and $W(\lambda)$ is constructed from $\Gamma(\lambda)$, which in general is not a minimizer for $F(\lambda')$.

Ehrenfest theorem for mixed states

$\mathrm{i}\,\mathrm{Tr}[\hat{H},\hat{O}]\Gamma = 0$ and $\hat{O} = \sum_{j=1}^{N} \mathbf{r}_j \cdot \nabla_j \implies$

$$2T(\lambda) + \lambda W(\lambda) = \int \rho(\mathbf{r})\,\mathbf{r}\cdot\nabla v^{\lambda}(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{4}$$

Rearranging Eq. (4)

$$T(\lambda) = \mathrm{Tr}\,\hat{T}\Gamma(\lambda) = \int \rho(\mathbf{r})\,\mathbf{r}\cdot\nabla v^{\lambda}(\mathbf{r})\mathrm{d}\mathbf{r} - F(\lambda), \tag{5}$$

Rhs. of Eq. (5) uniquely determined by ρ

Virial expressions

$$F(\lambda) + T(\lambda) = \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v^{\lambda}(\mathbf{r})\mathrm{d}\mathbf{r}$$
$$F(0) + T(0) = \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v^{0}(\mathbf{r})\mathrm{d}\mathbf{r}$$

Subtract and divide by $\lambda \neq 0$

$$\frac{1}{\lambda}(F(\lambda) - F(0)) + \frac{1}{\lambda}(T(\lambda) - T(0)) \quad = - \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla \overbrace{v^{\lambda}_{\mathrm{Hxc}}(\mathbf{r})}^{v^0 - v^\lambda} \mathrm{d}\mathbf{r}. \tag{6}$$

$$\boxed{\partial^+ F(0) + \partial^+ T(0) = - \lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v^{\lambda}_{\mathrm{Hxc}}(\mathbf{r})\mathrm{d}\mathbf{r}} \tag{7}$$

Proposition

$$\partial^+ T(0) = \lim_{\lambda \searrow 0} \frac{1}{\lambda}(T(\lambda) - T(0)) = \lim_{\lambda \searrow 0} \frac{T_\mathrm{c}(\lambda)}{\lambda} = 0 \tag{8}$$

Idea of proof.

$F(\lambda) = T(\lambda) + \lambda W(\lambda) \implies$

$$\frac{F(\lambda) - F(0)}{\lambda} - \frac{T(\lambda) - T(0)}{\lambda} = W(\lambda) \in [\partial_+ F(\lambda), \partial_- F(\lambda)] \tag{9}$$

$F(\lambda)$ concave, a countable number of points $\{\lambda_i\}_i$, $0 < \lambda_{i+1} < \lambda_i$, where it is non-differentiable $\implies \lim_{i\to\infty} W(\lambda_i) = \lim_{i\to\infty} \partial^+ F(\lambda_i)$

$$\underbrace{\partial^+ F(0)}_{E_{\mathrm{x}}+J} + \underbrace{\partial^+ T(0)}_{0} = -\lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{Hxc}}^{\lambda}(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{10}$$

Exchange-only virial relation

$$E_{\mathrm{x}} = -\lim_{\lambda \searrow 0} \int \rho(\mathbf{r})\,\mathbf{r} \cdot \nabla v_{\mathrm{xc}}^{\lambda}(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{11}$$

Result from the force-based treatment: additional transversal term next to the gradient of the force-based local exchange potential v_{fx},

$$E_{\mathrm{x}} = \int \rho(\mathbf{r})\,\mathbf{r} \cdot (-\nabla v_{\mathrm{fx}}(\mathbf{r}) + \nabla \times \alpha_{\mathrm{fx}}(\mathbf{r}))\mathrm{d}\mathbf{r}. \tag{12}$$

Thank you for your attention!