Essentials of Many-Fermion DFT and Their Relationship [or Lack Thereof] to Classical DFT

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Caution

- **A talk of this type must deal in generalities**
- **I've tried to note some of the more important exceptions**
- **Nonetheless, caveat lector**

Context & implications

- **Vast majority of qDFT is T = 0 K**
- **Vast majority of that is for many electrons in an external potential**

$$\hat{\mathcal{H}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right) = -\tfrac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2 + \tfrac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|} + \sum_{i=1}^{N_e} v_{ext}\left(\mathbf{r}_i\right)$$

$$\equiv \hat{\mathcal{T}} + \hat{\mathcal{W}} + \sum_{i=1}^{N_e} v_{ext}\left(\mathbf{r}_i\right)$$

$$:= \hat{\mathcal{H}}_{ee}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right) + V_{ext}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)$$

Hartree atomic units: $m_e = q_e = \hbar = 1$

- **Implication - The interaction potential is non-Coulomb only in comparatively small corners, e.g. atomic nuclei [**Eur. Phys. J. Plus 233, 553 (2018) & refs. therein] **that have not influenced the mainstream. Omitted here.**
- **$\Rightarrow$ most qDFT is conceived of and done in the context of the "electronic structure problem" (AKA "many fermion problem")**

Context & implications

- **The external potential almost always is from a fixed nuclear (ionic) framework**

$$v_{ext}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e};\{\mathbf{R}\}\right)=-\sum_{i,I}^{N_e,N}\frac{Z_I}{\left|\mathbf{r}_i-\mathbf{R}_I\right|}$$

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)=\hat{\mathcal{T}}+\hat{\mathcal{W}}+\sum_{i=1}^{N_{e\{\mathbf{R}\}}}v_{ext}\left(\mathbf{r}_i;\{\mathbf{R}\}\right)$$

- **Exceptions:**

  Harmonic confinement [“Hooke’s atom, Phys. Rev. A 72, 022501 (2005) & refs. therein**]**

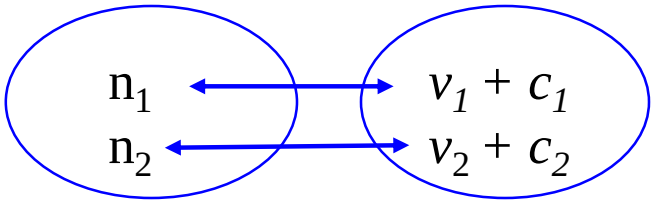
  Hubbard dimer [J. Phys. Cond. Matt. 27, 393001 (2015)]

T= *0 K context & implications*

- **Self-bound systems: atoms, molecules, clusters, ultra-thin films & slabs, 3D periodic solids**
- **Neutral extended systems; neutral and ionized finite systems (e.g. ionization potential I_p & electron affinity E_A); fixed N_e in each case**
- **Can test DFT approximations against nearly exact molecular calculations**
- **But there are approximations that work well on molecules that do badly on solids**

"Universal" functionals (important aside)

Original Hohenberg-Kohn functional



$$F_{HK}[n] = \int \Psi_0^* \hat{\mathcal{H}}_{ee} \Psi_0 d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e} \;;\; \Psi_0 \mapsto n$$

$$E_{v_{ext}}[n_0] = E_0 = \min_{n(\mathbf{r})} \left\{ F_{HK}[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

$$v_{ext} \in \mathcal{V}_N := \left\{ v \,|\, \hat{\mathcal{H}}_v \text{ has } N\text{-electron ground state} \right\}$$

$$n \in \mathcal{A}_N := \left\{ n \,|\, n \text{ from non-degen. } N\text{-electron ground state} \right\}$$

Neither set is known explicitly

Levy-Lieb functional

$$F_{LL}[n] = \inf_{\Psi_{trial} \mapsto n} \int \Psi^*_{trial} \hat{\mathcal{H}}_{ee} \Psi_{trial} d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e}$$

$$E_{v_{ext}}[n_0] = E_0 = \inf_{n(\mathbf{r})} \left\{ F_{LL}[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

$$v_{ext} \in \mathcal{U} := \left\{ v \,|\, \hat{\mathcal{H}}_v \text{ expectation is finite} \right\}$$ This set is known

$$n \in I_N := \left\{ n \,|\, n \text{ comes from N-representable } \Psi \right\}$$ This set is known

It is not guaranteed that there is only one minimizer

"Universal" functionals (important aside)

Lieb functional

$$\mathcal{E}[v] = \inf_{\Psi} \left\{ \langle \Psi | \hat{\mathcal{H}}_{ee} + \mathcal{V} | \Psi \rangle ; \Psi \in \mathcal{W} \right\}; \mathcal{W} \left\{ \psi \middle| \langle \psi | \psi \rangle = 1; \left\langle \psi \middle| \hat{\mathcal{T}} \middle| \psi \right\rangle < \infty \right\}$$

$$F_L[n] = \sup_{v \in \mathcal{X}^*} \left\{ \mathcal{E}[v] - \int d\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) \right\}$$

$$v \in \mathcal{X}^* = L^{3/2} + L^{\infty}$$

H. Eschrig, Phys. Rev. B 82, 205120 (2010):

Lieb allowed the position space to be the real vector space $\mathbb{R}^3$ of infinite volume which caused many problems with the continuous part of the spectrum of Hamiltonians, that is, scattering states toward the infimum of total energy. He then had to restrict $n \in \boldsymbol{L}^3(\mathbb{R}^3) \cap \boldsymbol{L}^1(\mathbb{R}^3)$ since the density must integrate to a finite particle number N over the infinite space $\mathbb{R}^3$. This led him allow for potentials $v \in \boldsymbol{L}^{3/2}(\mathbb{R}^3) + \boldsymbol{L}^{\infty}(\mathbb{R}^3)$. In the three torus every function $n \in \boldsymbol{L}^3(\mathbb{T}^3)$ may be normalized to integrate to a given N, that is, $\boldsymbol{L}^3(\mathbb{T}^3) \subset \boldsymbol{L}^1(\mathbb{T}^3)$.)

Use convexity of F_L to get optimization conditions either by

- **getting functional differentiability by Moreau-Yosida regularization**
- **expression of extremalization via sub-differentials**

Kvaal et al. J. Chem. Phys. 140, 18A518 (2014)

"Universal" functionals (important aside)

$$F_L[n] = \sup_{v \in \mathcal{V}^*} \left\{ \mathcal{E}[v] - \int d\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) \right\}$$

$$\mathcal{E}[v] = \inf_{n \in \mathcal{N}} \left\{ F[n] + \int d\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) \right\}$$

Legendre transform (ex some niceties)

$$\delta F_L / \delta n = -v(\mathbf{r}) \text{ (mod constant)}$$

At least formally; must be alert to odd results

$$F_L[n] \le F_{LL}[n]$$

Lieb fnal is convex hull of Levy-Lieb.

Often it is much easier to think of approximations in terms of LL:

"As a matter of principle, the subsequent development of the DFT formalism should therefore be based explicitly on the Lieb functional. We will nevertheless ignore the issue … and not distinguish between the various flavors …"

[Engel & Dreizler, p. 36]

Kohn-Sham Decomposition

To make the qDFT variational problem tractable, Kohn & Sham introduced a model non-interacting fermion system with the same density (reintroduces v-rep.):

$$E_s[n] \equiv T_s\left[\left\{\varphi[n]\right\}\right] + \int d\mathbf{r}\, n(\mathbf{r}) v_{KS}(\mathbf{r})$$

Non-interacting fermions $\Rightarrow \Phi_{min;n}$ is a Slater determinant.

$$\Phi_{min;n}(1,\ldots,N_e) = \frac{1}{\sqrt{N_e!}} \det\left|\varphi_1 \ldots \varphi_{N_e}\right|$$

$$E_{v_{ext}}[n] = T_S[n] + E_H[n] + \left\{E_x[n] + E_{ee,correl}[n] + T[n] - T_S[n]\right\} + E_{ext}[n] \quad \text{Add \& subtract KS KE}$$

$$\equiv T_S[n] + E_H[n] + E_{xc}[n] + E_{ext}[n]$$

$$T_S[n] \equiv \tfrac{1}{2}\sum_j n_j \int d\mathbf{r} \left|\nabla \varphi_j(\mathbf{r})\right|^2 \quad ; \quad E_H[n] = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}$$

Note self-interaction;
Must cancel with self E_x

$$n(\mathbf{r}) \equiv n(\mathbf{r}) = \sum_{j=1}^{N_F} f_j \left|\varphi_j(\mathbf{r})\right|^2 \quad ; \quad 0 \le f_j \le 1,2 \text{ (depending on spins)}$$

$$\frac{\delta T_s}{\delta n} + v_{eff}(\mathbf{r}) = \mu = \frac{\delta T_s}{\delta n} + \frac{\delta E_H}{\delta n} + \frac{\delta E_{xc}}{\delta n} + \frac{\delta E_{ext}}{\delta n}$$

$$\Rightarrow \left\{-\tfrac{1}{2}\nabla^2 + \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} + v_{xc}(\mathbf{r}_1) + v_{ext}(\mathbf{r}_1)\right\}\varphi_j(\mathbf{r}_1) = \varepsilon_j \phi_j(\mathbf{r}_1)$$

qDFT (T=*0 K*) *uniform scaling example*

$$\langle \Phi | \Phi \rangle = 1 ; \Phi \mapsto n(\mathbf{r})$$

$$\Phi_\lambda(\mathbf{r}_1 \ldots \mathbf{r}_N) := \lambda^{3N/2} \Phi(\lambda x_1, \lambda y_1, \lambda z_1, \ldots, \lambda x_N, \lambda y_N, \lambda z_N)$$

$$\Phi_\lambda \mapsto \lambda^3 n(\lambda \mathbf{r}) := n_\lambda(\mathbf{r}) ; \int d\mathbf{r} n_\lambda(\mathbf{r}) = N$$

If integrated over infinite volume

$$T_s[n_\lambda] = \lambda^2 T_s[n] ; \; E_x[n_\lambda] = \lambda E_x[n] ; \; \lambda \text{ real}, \lambda > 0$$

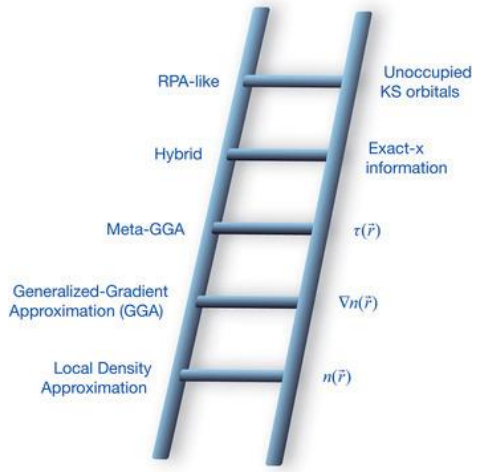
But

$$E_c[n_\lambda] > \lambda E_c[n] \quad \text{for } \lambda > 1$$

$$\lambda E_c[n] > E_c[n_\lambda] \quad \text{for } 0 < \lambda < 1$$

qDFT compared with clDFT even at T=*0 K*

- **Most of the work on density functional approximations (DFAs) is for E_{xc}**
- **Only in a few cases is a DFA for E_c alone constructed**
- **It is commonplace in constraint-based DFAs to cancel errors in E_x against those in E_c**
- **E_x has density scaling equalities; E_c has inequalities because it is a mixture of coulombic and KE contributions.**
- **DFA construction for E_{xc} has proceeded by adding complexity (n, ∇n, ∇^2n, KE density, explicit exact exchange, ….)`**



Perdew-Schmidt Jacob's ladder of DFA complexity

Peter Elliott's alphabet soup

Important qDFT topics perhaps irrelevant (?) to clDFT (even at T=0 K*)*

- **Properties of Kohn-Sham equation eigenvalues & eigenfunctions are very important in qDFT but not in clDFT**
  Koopmans' theorem, Ionization potential theorem, derivative discontinuity, …
- **Self-interaction? Is this encountered in clDFT?**
- **Pseudo-potentials:** $Z_I / |\mathbf{r}_i - \mathbf{R}_I|$
  induces oscillations in KS eigenfns that are costly to represent in plane-wave basis. Is there a clDFT counterpart problem?

qDFT (T=0 K); foretaste of T>0

Lieb functional written in ensemble form

$$F_L[n] = \inf_{\Gamma \mapsto n} Tr\left\{\Gamma \hat{\mathcal{H}}_{ee}\right\}$$

$$n(\mathbf{r}) = \sum_i a_i \left\langle \Psi_i \middle| \hat{n}(\mathbf{r}) \middle| \Psi_i \right\rangle$$

$$\Gamma = \sum_i a_i \left|\Psi_i\right\rangle\left\langle\Psi_i\right|; \quad \sum_i a_i = 1; \quad a_i^* = a_i \ ; \qquad \left\langle \Psi_i \middle| \Psi_j \right\rangle = \delta_{ij}$$

Note N-representability required of every $\left|\Psi_i\right\rangle$

NASC for ensemble N-representability of 1-body reduced density matrices are known and easy to enforce.

Free-energy qDFT vs. ground state formulatoin

Mermin (1965)

I. Universal energy functional F[*n*] → universal free energy functional $\mathcal{F}[n]$

$E_{Vext}[n]$ → grand potential $\Omega_{v_{ext}}[n]$

$$\mathcal{F}[n] := \min_{\Gamma \mapsto n} Tr\left\{\Gamma \hat{\mathcal{H}}_{ee}\right\}$$

II. Hohenberg-Kohn theorems go through as at T=0 K

$$\Omega_{v_{ext}}[n] = \mathcal{F}[n] + \int d\mathbf{r}\,\left\{v_{ext}(\mathbf{r}) - \mu\right\} n(\mathbf{r})$$

$$\Omega_{v_{ext}}\left[n_0\right] = \Omega_0 = \min_{n(\mathbf{r})} \Omega_{v_{ext}}\left[n\right]$$

III. Kohn-Sham procedure is extended to densities with full Fermi-Dirac occupation numbers and potentials that are proper functional derivatives of $\mathcal{F}[n]$

$$\left\{-\tfrac{1}{2}\nabla_{r_1}^2 + v_H\left(\mathbf{r}_1;\{\mathbf{R}\}\right) + v_{xc}\left(\mathbf{r}_1;\{\mathbf{R}\}\right) + v_{ext}\left(\mathbf{r}_1;\{\mathbf{R}\}\right)\right\}\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right) = \varepsilon_j\,\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)$$

$$n\left(\mathbf{r}_1;\{\mathbf{R}\}\right) = \sum_j f(\varepsilon_j;\beta)\left|\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)\right|^2 \quad ; \quad v_{xc}[n] = \frac{\delta \mathcal{F}_{xc}}{\delta n} \quad ; \quad \beta = 1/k_B T$$

T> 0 K qDFT observations & issues

- **Mermin & Eschrig each give the T>0 HK proof in the grand ensemble. Parr &Yang also give a version in the canonical ensemble. So far as I know all computation with T>0 qDFT is de facto with the canonical ensemble, despite the equations having come from the grand ensemble.**
- **Need generalization, extension, or alteration of ground-state constraints**
- **Intrinsic T dependence of $\mathcal{F}_{xc}$ [n(T), T]**
- **For orbital-free version, T > 0 $\Rightarrow$ Three functionals to approximate**

$$\mathcal{T}_s[n,\mathrm{T}],\ \mathcal{S}_s[n,\mathrm{T}],\ \mathcal{F}_{xc}[n,\mathrm{T}]$$

- **Note that counterparts to $\mathcal{T}_s$ & $\mathcal{S}_s$ in clDFT are known – basically the local density approx. with classical ideal gas.**
- **Generalization of variables (implicates gradient expansions for example)**

T>0 *variables example -Generalized Gradient Approx. for Exchange*

Original approach at T = 0

$$E_x^{GGA}[n] = \int d\mathbf{r}\, \varepsilon_x^{HEG}(n)\, F_x\left(n,s\right)$$

"Enhancement factor"

$$s(n,\nabla n) := \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$$

$$E_x[n] = \int d\mathbf{r}\, d\mathbf{r}' \frac{n(\mathbf{r}) n_x\left(\mathbf{r},\mathbf{r}+\mathbf{r}'\right)}{2r'}$$

Exchange hole

$$n_x\left(\mathbf{r},\mathbf{r}+\mathbf{r}'\right) \le 0 \quad ; \quad \int d\mathbf{r}' n_x\left(\mathbf{r},\mathbf{r}+\mathbf{r}'\right) = -1$$

- **2nd order gradient expansion of exchange hole**
- **Spherical average**
- **Zero the contribution wherever expansion goes >0 and set overall cutoff radius to satisfy normalization.**
- **Impose uniform scaling**
- **Numerical $F_x \rightarrow$ fit to analytic form controlled by constraints**
- **More recently – attempt to improve $F_x(n,s)$ by selective application of incompatible constraints.**

T>0 *variables example – Generalized Gradient Approx. for Exchange*

T=0 $E_x^{GGA}[n] = \int d\mathbf{r}\, \varepsilon_x^{HEG}(n)\, F_x\left(n,s\right) \qquad s(n,\nabla n) := \dfrac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$

"Enhancement factor"

T>0 $\mathcal{F}_{\mathrm{x}}^{\mathrm{GGA}}[n,\mathrm{T}] = \int d\mathbf{r}\, n\, f_{\mathrm{x}}^{LDA}(n,\mathrm{T})\, \mathrm{F}_{\mathrm{x}}(s_{2\mathrm{x}}(\mathrm{T}))$

$$s_{2\mathrm{x}}(n,\nabla n,\mathrm{T}) := s^2(n,\nabla n)\, \tilde{B}_{\mathrm{x}}(t) / \tilde{A}_{\mathrm{x}}(t)$$

$$f_{\mathrm{x}}^{\mathrm{LDA}}(n,\mathrm{T}) := \varepsilon_{\mathrm{x}}^{HEG}(n)\, \tilde{A}_{\mathrm{x}}(t) \quad ; \quad t = \mathrm{T}/\mathrm{T}_F$$

Fermi-Dirac integral combos

Constraints:

- **Reproduce finite-T gradient expansion at small *s***
- **Satisfy Lieb-Oxford bound at T=0**
- **Reduce to correct T=0 limit**
- **Reduce to correct high-T limit (HEG)**
- **Correct finite-T uniform scaling**

Karasiev, Dufty, & Trickey: Phys. Rev. Lett. 120, 076401 (2018)

T>0 *variables example – Generalized Gradient Approx. for Correlation*

T=0

$$E_c^{GGA}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \mathrm{f}_c^{GGA}(n, \nabla n)$$

$$\mathrm{f}_c^{PBE}(n, \nabla n) = \mathrm{f}_c^{LDA}(n) + H^{PBE}\left(\mathrm{f}_c^{LDA}, q\right);\ q(n, \nabla n) := |\nabla n| / 2k_s n;\ \ k_s := 2(3n/\pi)^{1/6}$$

T>0

$$\mathcal{F}_c^{GGA}[n, \mathrm{T}] = \int d\mathbf{r}\, n(\mathbf{r})\, f_c^{GGA}(n, \nabla n, \mathrm{T})$$

$$q_c(n, \nabla n, \mathrm{T}) := q(n, \nabla n)\sqrt{\tilde{B}_c(r_s, t)}$$

Fermi-Dirac integral combo

$$\mathrm{f}_c^{KDT16}(n, \nabla n, \mathrm{T}) = \mathrm{f}_c^{LDA}(n, \mathrm{T}) + H^{PBE}\left(\mathrm{f}_c^{LDA}, q_c\right)$$

Constraints:

- **Reproduce finite-T gradient expansion at small *q***
- **Reduce to PBE E_c as T=0 limit**
- **Reduce to correct T=0 & high-T limit (HEG)**
- **Correct finite-T uniform scaling**

Karasiev, Dufty, & Trickey: Phys. Rev. Lett. 120, 076401 (2018)

Correlation – Adiabatic Connection

T=0 $\hat{H}_\lambda := \hat{H}_0 + \lambda \hat{H}_1$ **Pauli coupling constant "trick"**

$$\frac{\partial E_{\lambda,0}}{\partial \lambda} = \langle \Psi_{\lambda,0} | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_{\lambda,0} \rangle$$ **Hellman-Feynman theorem**

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\,\lambda \langle \psi_\lambda | \hat{H}_1 | \psi_\lambda \rangle$$

$$E_\lambda[n] = \min_{\psi_\lambda \mapsto n} \langle \psi_\lambda | \hat{\mathcal{T}} + \lambda \hat{\mathcal{W}} | \psi_\lambda \rangle$$

$$\lambda = 0: \quad E_0[n] = \min_{\Phi \mapsto n} \langle \Phi | \hat{\mathcal{T}} | \Phi \rangle \equiv \langle \Phi_{min,n} | \hat{\mathcal{T}} | \Phi_{min,n} \rangle \equiv T_s[n]$$

$$\lambda = 1: \quad E_1[n] = \min_{\psi_{\lambda=1} \mapsto n} \langle \psi_{\lambda=1} | \hat{\mathcal{T}} + \hat{\mathcal{W}} | \psi_{\lambda=1} \rangle \equiv \langle \psi_{min,n} | \hat{\mathcal{T}} + \hat{\mathcal{W}} | \psi_{min,n} \rangle$$

Adiabatic connection $E_{xc}[n] = \int_0^1 d\lambda \langle \psi_{\lambda,min}[n] | \hat{\mathcal{W}} | \psi_{\lambda,min}[n] \rangle - E_H[n]$

Assumes a Lagrange multiplier potential $v_\lambda(\mathrm{r})$ that keeps the density UNchanged across $0 \le \lambda \le 1$,

Correlation – Adiabatic Connection

T>0

$$\mathcal{F}_\lambda[n,\mathrm{T}] = \min_{\Gamma\mapsto n}\left\{\widehat{\mathcal{T}} + \lambda\widehat{\mathcal{W}} + \beta^{-1}\ln\Gamma\right\}$$

$$\mathrm{U}_{xc}[n,\mathrm{T}] := Tr\left\{\Gamma(n,\mathrm{T})\widehat{\mathcal{W}}\right\} - Tr\left\{\Gamma_s(n,\mathrm{T})\widehat{\mathcal{W}}\right\} \equiv Tr\left\{\Gamma(n,\mathrm{T})\widehat{\mathcal{W}}\right\} - E_H(n(\mathrm{T}))$$

Coulombic correlation

$$\Omega_{xc}[n,T] = \int_0^1 d\lambda U_{xc}[n,T\,|\,\lambda]$$

Adiabatic connection for correlation grand potential

Pitallis et al. Phys. Rev. Lett. 107, 163001 (2011)

qDFT (T>*0 K*) *scaling*

$$n(\mathbf{r}) \to \lambda^3 n(\lambda \mathbf{r}) := n_\lambda(\mathbf{r}); V \to \lambda^{-3} V$$

$$\beta \to \lambda^{-2}\beta;\ \ q_e \to \lambda^{1/2} q_e$$

$$\mu(\mathbf{r}) := \mu - v_{ext}(\mathbf{r}) \to \lambda^2 \mu(\lambda \mathbf{r}) := \mu_\lambda(\mathbf{r})$$

$$\Rightarrow \mathcal{F}[n(\mathbf{r}), \mu(\mathbf{r}); \beta, q_e] = \lambda^{-2} \mathcal{F}[n_\lambda(\mathbf{r}), \mu_\lambda(\mathbf{r}); \lambda^{-2}\beta, \lambda^{1/2} q_e]$$

Pitallis et al. Phys. Rev. Lett. 107, 163001 (2011)
Dufty and Trickey, Phys. Rev. 84, 125118 (2011); Mol. Phys. 114, 988 (2015)

qDFT (T=0 K); another route

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + E_{ext}[n]$$

$$T_s[n] = \int dr\, t_S[n(\mathrm{r})]$$

Keep the KS decomposition but don't use the orbitals explicitly = "orbital-free DFT" [linear scaling with system size]

$$T_s[n] = T_W[n] + T_\theta[n], \quad T_\theta[n] \geq 0$$

M. Levy and H. Ou-Yang, Phys. Rev. A **38**, 625 (1988)

$$T_W[n] := \frac{1}{8}\int d\mathbf{r}\,\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \equiv \int d\mathbf{r}\, t_W[n(\mathbf{r})]$$

Exact for one or two electrons in one orbital (von Weizsäcker)

$$\frac{\delta E[n]}{\delta n} = \mu$$

$$\Rightarrow \quad \frac{\delta T_W[n]}{\delta n} + \frac{\delta T_\theta[n]}{\delta n} + \frac{\delta E_H[n]}{\delta n} + \frac{\delta E_{xc}[n]}{\delta n} + v_{ext} = \mu$$

Single Euler equation

Two functionals to approximate: T_θ , E_{xc}

T>0 ofDFT variables for converting ground-state GGA

$$\mathcal{T}_s[n,\mathrm{T}] = \frac{1}{2}\sum_j f_j \left|\nabla\varphi_j\right|^2 \approx \int d\mathbf{r} n(\mathbf{r})\tau_s\left[n,\nabla n,\mathrm{T}\right]$$

$$\mathcal{S}_s[n,\mathrm{T}] = -k_B\sum_j \left\{ f_j \ln f_j + (1-f_j)\ln(1-f_j)\right\} \approx \int d\mathbf{r} n(\mathbf{r})\sigma_s\left[n,\nabla n,\mathrm{T}\right]$$

$$\mathcal{F}_{\mathrm{s}}^{\,ftGGA}[n] = \int d\mathbf{r}\left[\tau_0^{\mathrm{TF}}(n)\xi(t)F_\tau(s_\tau)\right] - \int d\mathbf{r}\left[\tau_0^{\mathrm{TF}}(n)\zeta(t)F_\sigma(s_\sigma)\right]$$

$$s_\tau(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{\tilde{h}(t)-t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\xi(t)}}$$

$$s_\sigma(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\zeta(t)}}$$

$$t = T/T_F$$

Form of T-dependent reduced density derivative variables motivated by 2nd order gradient expansion.

Fermi-Dirac integral combos

Karasiev, Sjostrom, and Trickey, Phys.Rev.B 86,115101 (2012)

qDFT; two-point non-interacting functionals

T=0

$$T_s[n] = T_W + T_{TF} + T_\theta^{\alpha,\beta}$$

$$T_\theta^{\alpha,\beta} \approx c_0 \int d\mathrm{r} d\mathrm{r}'\, n^\alpha(\mathrm{r})\, n^\beta(\mathrm{r}')\, \mathcal{K}_{\alpha\beta}\left[\mathrm{n(r)}, \mathrm{n(r')}, \mathrm{f(r,r')}\right]$$

$$\alpha = \frac{8}{3} - \beta$$

Witt, del Rio, Dieterich, and Carter; J. Mat. Res. 33, (2018)

T>0

Sjostrom and Daligault,
Phys. Rev. Lett. 113, 155006 (2014)

Not even mentioned

- **Time-dependent qDFT**
- **Multi-species qDFT**
- **Embedding DFT in explicit wave-function formulations (multi-scale treatments)**
- **Current density functional theory**
- **Potential functional approaches (exploit Legendre transform)**
- **Beyond qDFT, e.g. 1-body reduced density matrix schemes**