Constrained density-functional theory extended to finite temperatures, non-integer particle numbers, and non-local constraints

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We present a generalization of the constrained density-functional theory approach to metallic and finite-temperature electronic systems, both in the canonical and grand-canonical ensembles. We find that the free-energy attains a unique maximum with respect to Lagrange multipliers whenever the applied constraints are satisfied, in each case. Analytical expressions are provided for the free-energy curvatures with respect to the Lagrange multipliers, as required for their automated non-linear optimization. Our extension is general to arbitrary constraints on the spin-polarized density, or on the density-matrix in the case of orbital-dependent constrained density-functional theory constrained non-locally. Our conclusion that the ground-state free-energy is concave with respect to Lagrange multipliers for finite-temperature systems is corroborated by numerical tests on a disparate pair of systems, namely a metallic hydrogen chain and a ferromagnetic metal oxide.

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Interfacial charge and spin excitation or transfer is crucial for the functioning of biological enzymes and effectively ubiquitous among established and developmental technologies for energy generation, conversion, and storage as well as electronics, opto-electronics, and spintronics. Atomistic insight into and understanding of these physical processes is expected to greatly accelerate the development of improved solutions, which motivates growing efforts in the characterization and understanding of charge (spin) transfer at functional interfaces. The experimental challenges and costs in atom- and time-resolved characterization of charge (spin) transfer at functional interfaces prompts increasing interest in the development of accurate simulation methods of favorable computational costs applicable to realistically extended models.

In this context, constrained Density Functional Theory (cDFT) has emerged as a very convenient approach of acceptable accuracy and favorable computational costs. These advantages can in principle be maximized leveraging on existing linear-scaling implementations of DFT. Although density-constraints have been long used by the DFT community, numerically efficient application of cDFT was first made possible by the mathematical proof of Wu et al. The proof establishes the general concavity of a constrained functional with respect to a constraining potential, expressed as a Langrange multiplier. This results allows direct, thence automatable, optimization of the constraining potential needed to obtain the lowest-energy cDFT-solution consistent with the enforced constraint. Besides insight into the fundamentals of charge and spin transfer, cDFT has been shown to hold great potential for the use of differently constrained solutions as basis of more elaborate configuration interaction (CI-cDFT) approaches to electron correlation, and in practical/effective/pragmatic approximations to electron hole screening effects intrinsically neglected by standard DFT.

The significance of metal substrates and metal-semiconductor (-insulator) interfaces for >0 K technological applications, has driven strong interest in the development of numerically robust and efficient extension of the DFT formalism to finite (>0 K) temperatures (FT-DFT), capable of capturing the dependence of the DFT solution on the system temperature. Recent developments have led to further numerical optimization of FT-DFT via use of minimal, in situ optimized, atomic basis sets and ensuing reduction of the size of the FT-DFT Hamiltonian. These advances have made possible to simulate metallic systems up to over two thousands atoms on academically accessible hardware.

Towards viable simulation of biased electrochemical interfaces, interest has also been growing in extending DFT methods to open-boundary grand-canonical formalisms, capable of modelling electrodes and their interfaces at constant potential (variable number of electrons).

Prompted by these advances and derivation of the original cDFT proof for close-boundary 0K DFT only, here we explore possible extension of the cDFT-theorem to FT-DFT in both the canonical and grand-canonical ensembles. In both cases, we find that the constrained FS-DFT free-energy attains a maximum with respect to Lagrange multipliers whenever the applied constraints are satisfied. These results lay the basis for canonical and grand-canonical constrained FT-DFT simulation of (metallic) systems, which should be useful for fundamental research in charge and spin transfer and excitation at functional interfaces.

We begin by summarizing the main result of Ref[?], valid for zero-temperature systems of integer occupancy, to the effect that if a constraint on a fermionic density

can be satisfied, it will be so only at a unique maximum of the total-energy of the constrained system with respect to the Lagrange multiplier of the constraint. Without loss of generality, however, we will extend this result to allow for the possibility of non-local potentials, such as those introduced by the widely-used pseudopotential approximation in DFT, subject to a non-local constraint, albeit limited to two spatial indices. While a number of existing implementations of cDFT already make use of non-local constraints, such as those constructed from projections onto subspaces spanned by atomic orbitals, this extension to true constrained *density*-functional theory has not yet been shown, to our knowledge. As such, the single-particle density-matrix describing a non-interacting reference (i.e., Kohn-Sham) system, from which the energy is computed, is promoted as the central variable. Here, we may restrict ourselves to the diagonal density-matrices of the form $\hat{\rho}^\sigma = \sum_i |\psi_i^\sigma\rangle f_i^\sigma \langle\psi_i^\sigma|$, where σ is the spin index, and the index i runs over sufficiently many orbitals to converge any properties of interest.

treat the case of constrained density functional theory to allow for finite-temperature fermionic systems subject to non-local potentials,

The occupancy of the single-particle orbital $|\psi_i^\sigma\rangle$ is described by the Fermi-Dirac distribution $f_i^\sigma = (1 + \exp(\beta(\epsilon_i^\sigma - \mu)))^{-1}$, where ϵ_i^σ is the corresponding eigenvalue of the non-interacting Hamiltonian, μ is the chemical potential, and $\beta = (k_B T)^{-1}$. The density is then given by the local part of the density-matrix, that is $\rho^\sigma(\mathbf{r}) = \langle\mathbf{r}|\hat{\rho}^\sigma|\mathbf{r}\rangle = \sum_i f_i^\sigma |\psi_i^\sigma(\mathbf{r})|^2$. In the canonical ensemble, the chemical potential is defined such that the electron number is kept fixed, i.e., such that $\sum_{i\sigma} f_i^\sigma = N$, whereas otherwise, in the grand canonical ensemble, the electron number may vary and the chemical potential is treated as a free parameter.

The electronic free-energy functional, allowing for finite temperatures or metallic densities of states, and including a number of spin-density constraints with pre-factors $U^{I\sigma}$, may be written as $A[\hat{\rho}, \{U^{I\sigma}\}; \beta] = W[\hat{\rho}, \{U^{I\sigma}\}; \beta] - S[\hat{\rho}]/\beta$, where the electronic enthalpy is written in dimensionless form as $S[\hat{\rho}] = -\sum_\sigma \text{Tr}[\hat{\rho}^\sigma \ln\hat{\rho}^\sigma + (\hat{1} - \hat{\rho}^\sigma)\ln(\hat{1} - \hat{\rho}^\sigma)]$, and the quantity to be made stationary in the grand canonical ensemble is instead $\Omega = A - \mu N$. The total energy, $W[\hat{\rho}, \{U^{I\sigma}\}] = E[\hat{\rho}] + \sum_{I\sigma} U^{I\sigma} C^{I\sigma}[\hat{\rho}^\sigma]$, comprises the unconstrained total-energy $E[\hat{\rho}] = \sum_\sigma \text{Tr}[(\hat{v}_{\text{ext}}^\sigma - \hat{\nabla}^2/2)\hat{\rho}^\sigma] + E_{\text{Hxc}}[\rho^\uparrow, \rho^\downarrow]$ (where $\hat{v}_{\text{ext}}^\sigma$ is a possibly non-local external potential, Hxc denotes Hartree plus exchange-correlation, and we neglect the temperature-dependence of the latter) together with a number of spin-density constraints in which the $U^{I\sigma}$ appear as pre-factors. Here, we consider constraints of the form $C^{I\sigma}[\hat{\rho}^\sigma] = \text{Tr}[\hat{\rho}^\sigma \hat{P}^{I\sigma}] - N^{I\sigma}$, where $\hat{P}^{I\sigma}$ is an projection operator (i.e., idempotent, Hermitian) onto some subspace, and $N^{I\sigma}$ is a real-valued constant target. The

special case of pure spin-density functional constraints, for which constrained DFT was originally derived, may be recovered by setting $\hat{P}^{I\sigma} = |\mathbf{r}\rangle w_c^{I\sigma}(\mathbf{r})\langle\mathbf{r}|$, for some weighting function $w_c^{I\sigma}(\mathbf{r})$. Another appropriate choice are operators of the form $\hat{P}^{I\sigma} = \sum_m^{M^I} |\varphi_m^{I\sigma}\rangle\langle\varphi_m^{I\sigma}|$, where the $M^{I\sigma}$ projecting orbitals $|\varphi_m^{I\sigma}\rangle$ for each subspace I are considered to be fixed and orthonormal, in which case the constraint term may be re-written in powers of the occupancy matrix $n_{mm'}^{I\sigma} = \langle\varphi_m^{I\sigma}|\hat{\rho}^\sigma|\varphi_{m'}^{I\sigma}\rangle$. We refer the reader to Ref. **?** for the invariance-preserving generalization to nonorthogonal projecting orbitals.

The ground state density-matrix $\hat{\rho}_0$, for a given temperature and set of parameters $U^{I\sigma}$ is defined as that which minimizes the free-energy, subject to Fermi-Dirac statistics, i.e., $A_0[\{U^{I\sigma}\}; \beta] = \min_{\hat{\rho}} A[\hat{\rho}, \{U^{I\sigma}\}; \beta]$.

$$\hat{V}^{I\sigma}[\hat{\rho}] = \frac{\delta A^{I\sigma}}{\delta\hat{\rho}^\sigma} = \hat{H}^\sigma + \sum_I U^{I\sigma}\frac{\delta C^{I\sigma}}{\delta\hat{\rho}^\sigma} \qquad (1)$$
$$+ \text{Tr}[\ln\hat{\rho}^\sigma - \ln(\hat{1} - \hat{\rho}^\sigma)]/\beta$$

$\text{Tr}[\ln\hat{\rho}^\sigma - \ln(\hat{1} - \hat{\rho}^\sigma)]/\beta = \sum_i(\mu - \epsilon_i^\sigma)$

The DFT+U method acts, via the addition of an idempotency constraint of the form

$$C^I[\hat{\rho}] = \sum_\sigma \frac{1}{2}\sum_m^{M^I}\left[n_{mm}^{I\sigma} - \sum_{m'}^{M^I} n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}\right] \qquad (2)$$
$$= \sum_\sigma \frac{1}{2}Tr[\hat{\rho}^\sigma\hat{P}^I - \hat{\rho}^\sigma\hat{P}^I\hat{\rho}^\sigma\hat{P}^I],$$

for each subspace, to partially enforce the idempotency of the each subspace density matrix up to a pre-factor U^I, so that the grand energy functional reads

$$W[\hat{\rho}, \{U^I\}] = E[\hat{\rho}] + \sum_I U^I C^I[\hat{\rho}]. \qquad (3)$$

This functional adds a corrective potential to each subspace given by $\hat{v}_U^{I\sigma} = U^I\hat{w}_U^{I\sigma}$, where

$$\hat{w}_U^{I\sigma}[\hat{\rho}] = \frac{\partial C^I[\hat{\rho}]}{\partial\hat{\rho}^\sigma} = \left(\frac{1}{2} - \hat{P}^I\hat{\rho}^\sigma\right)\hat{P}^I, \qquad (4)$$

so that the most direct effect of subspace idempotency penalization is to suppress (enhance) diagonal subspace occupancies less (greater) than one-half.

Extremization of the grand functional W with respect to idempotent density-matrices,

$$\delta_{\hat{\rho}=\hat{\rho}^2}[W[\hat{\rho}, \{U^I\}]] = 0, \qquad (5)$$

yields the density-matrix expression of the Kohn-Sham equations, modified by the corrective potential, so that

$$E_{IP}^\sigma\hat{\rho}^\sigma = \begin{pmatrix} \frac{-\hat{\nabla}^2}{2} + v_{ext}(\mathbf{r}) \\ + \int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \hat{v}_{xc}^\sigma[\rho^\uparrow, \rho^\downarrow] \\ + \sum_I \hat{v}_U^{I\sigma}[\hat{\rho}] \end{pmatrix}\hat{\rho}^\sigma, \qquad (6)$$

where $E_{IP}^\sigma = \sum_i f_i^\sigma \epsilon_i^\sigma$ is the occupancy-weighted sum of Kohn-Sham eigenvalues. We seek the solution of Eq. 6 for the set of pre-factors $\{U^I\}$ at which the constraint defined by Eq. 2 vanishes. There is a unique solution $\hat{\rho}_0^\sigma$ of the former for any set of Hubbard U parameters, however, so that we may write

$$\hat{\rho}_0^\sigma = \hat{\rho}_0^\sigma \left[\{U^I\}\right] \quad \Rightarrow \quad W_0 = W_0 \left[\{U^I\}\right], \quad (7)$$

where W_0 is defined as the lowest-energy extremum of W for a given set of U parameters.

Following the prescription of Refs. **?** **?** , we now show that W_0 is strictly concave. Beginning with its first derivative,

$$\frac{dW_0}{dU^I} = Tr_\sigma Tr \left[\overbrace{\frac{\delta W_0}{\delta \hat{\rho}^\sigma}}^{0} \frac{d\hat{\rho}^\sigma}{dU^I} \right] + \frac{\partial W_0}{\partial U^I} \quad (8)$$

we find that extrema with respect to the U^I occur when the corresponding constraint vanishes, more explicitly

$$\frac{dW_0}{dU^I} = 0 \quad \leftrightarrow \quad C^I\left[\hat{\rho}_0\right] = 0 \quad (9)$$

$$\leftrightarrow \quad \sum_m^{M^I} n_{0mm}^{I\sigma} = \sum_{mm'}^{M^I} n_{0mm'}^{I\sigma} n_{0m'm}^{I\sigma}.$$

The nature of such extrema is determined by the second derivative of the constraint, so that

$$\frac{d^2 W_0}{dU^{I2}} = \frac{dC^I\left[\hat{\rho}_0\right]}{dU^I} \quad (10)$$

$$= Tr_\sigma \frac{1}{2} \sum_{mm'}^{M^I} \left[\left(\delta_{mm'} - 2n_{0mm'}^{I\sigma}\right) \frac{dn_{0m'm}^{I\sigma}}{dU^I} \right]$$

$$= Tr_\sigma \frac{1}{2} Tr \left[\left(\hat{P}^I - 2\hat{P}^I \hat{\rho}_0^\sigma \hat{P}^I\right) \frac{d\hat{\rho}_0^\sigma}{dU^I} \right]$$

$$= Tr_\sigma Tr \left[\hat{w}_U^{I\sigma} \frac{d\hat{\rho}_0^\sigma}{dU^I} \right],$$

and the density-matrix depends on the U parameters only via perturbation of the Hamiltonian, were we find simply that

$$\frac{d\hat{\rho}^\sigma}{dU^I} = Tr \left[\frac{\delta \hat{\rho}^\sigma}{\delta \hat{H}^\sigma} \frac{\partial \hat{H}^\sigma}{\partial U^I} \right] \quad (11)$$

$$= Tr \left[\frac{\delta \hat{\rho}^\sigma}{\delta \left[\hat{v}_U^{I\sigma}\right]} \hat{w}_U^{I\sigma} \right].$$

The variation of the density-matrix may be performed using conventional perturbation theory, since the idempotency of the density-matrix for any choice of parameters allows us to order states such that

$$f_i^\sigma = \begin{cases} 1 & \text{if } 1 \leq i \leq N^\sigma; \\ 0 & \text{otherwise}, \end{cases} \quad (12)$$

and the generalization to wave-vector dependent occupancies is straightforward. The variation thus proceeds via the orbitals only, such that

$$\frac{\delta \hat{\rho}^\sigma}{\delta \left[\hat{v}_U^{I\sigma}\right]} = \sum_i^{N^\sigma} \left(\begin{array}{c} |\psi_i^\sigma\rangle \frac{\delta \langle \psi_i^\sigma|}{\delta \left[U^I \hat{w}_U^{I\sigma}\right]} \\ + \frac{\delta |\psi_i^\sigma\rangle}{\delta \left[U^I \hat{w}_U^{I\sigma}\right]} \langle \psi_i^\sigma| \end{array} \right), \quad (13)$$

where we may then make use of the familiar expression

$$\frac{\delta |\psi_i^\sigma\rangle}{\delta \left[U^I \hat{w}_U^{I\sigma}\right]} = \sum_{a > N^\sigma} |\psi_a^\sigma\rangle \left(\frac{|\psi_i^\sigma\rangle \langle \psi_a^\sigma|}{\epsilon_i^\sigma - \epsilon_a^\sigma} \right). \quad (14)$$

We finally combine the resulting expression for the derivative of the density matrix with respect to the Hubbard U parameters, momentarily suppressing σ,

$$\frac{d\hat{\rho}}{dU^I} = \sum_{\substack{i \leq N \\ a > N}} \left(\begin{array}{c} |\psi_i\rangle \left(\frac{\langle \psi_i | \hat{w}_U^{I\sigma} | \psi_a\rangle}{\epsilon_i - \epsilon_a} \right) \langle \psi_a| \\ + |\psi_a\rangle \left(\frac{\langle \psi_a | \hat{w}_U^{I\sigma} | \psi_i\rangle}{\epsilon_i - \epsilon_a} \right) \langle \psi_i| \end{array} \right) \quad (15)$$

with Eq. 10, to find that the functional W_0 is strictly concave, since

$$\frac{d^2 W_0}{dU^{I2}} = 2 Tr_\sigma \sum_{\substack{i \leq N^\sigma \\ a > N^\sigma}} \left(\frac{\left|\langle \psi_i^\sigma | \hat{w}_U^{I\sigma} | \psi_a^\sigma\rangle\right|^2}{\epsilon_i^\sigma - \epsilon_a^\sigma} \right)$$

$$\leq 0, \quad (16)$$

and that, moreover, there exists a unique extremum with respect to each U parameter.

Thus, the task of minimizing the total energy subject to the constraint that the idempotency penalty functional of Eq. 2 vanishes, for each subspace, is re-cast as an iterative maximization of the grand functional $W_0\left[\{U^I\}\right]$ with respect to the set of Hubbard U parameters. On every such iteration, in practice, the total energy must be re-minimized self-consistently, so that the algorithm takes the form of two nested loops – albeit with no resort to numerical finite differences or perturbation theory. The corrective term in the total-energy vanishes at the self-consistent solution, however the corrective potential generally does not.

$$\frac{d^2 W_0}{dU^{I2}} = \left(\frac{\partial}{\partial U^I} + Tr \left[\frac{\delta \hat{\rho}_0^\sigma}{\delta U^I} \frac{\delta}{\delta \hat{\rho}_0^\sigma} \right] \right)^2 W_0 \quad (17)$$

$$= \frac{\partial^2 W_0}{\partial U^{I2}} + Tr \left[\frac{\delta \hat{\rho}_0^\sigma}{\delta U^I} \frac{\partial \delta W_0}{\partial U^I \delta \hat{\rho}_0^\sigma} + \frac{\partial \delta \hat{\rho}_0^\sigma}{\partial U^I \delta U^I} \frac{\delta W_0}{\delta \hat{\rho}_0^\sigma} \right]$$

$$+ Tr \left[\frac{\delta \hat{\rho}_0^\sigma}{\delta U^I} \left(\frac{\delta \partial W_0}{\delta \hat{\rho}_0^\sigma \partial U^I} + \frac{\delta^2 \hat{\rho}_0^{'\sigma}}{\delta \hat{\rho}_0^\sigma \delta U^I} \frac{\delta W_0}{\delta \hat{\rho}_0^{'\sigma}} \right) \right]$$

$$+ Tr \left[\frac{\delta \hat{\rho}_0^\sigma}{\delta U^I} \frac{\delta^2 W_0}{\delta \hat{\rho}_0^\sigma \delta \hat{\rho}_0^{'\sigma}} \frac{\delta \hat{\rho}_0^{'\sigma}}{\delta U^I} \right]$$

$$= \frac{\partial^2 W_0}{\partial U^{I2}} + Tr \left[\frac{\delta \hat{\rho}_0^\sigma}{\delta U^I} \left(\frac{\partial \delta W_0}{\partial U^I \delta \hat{\rho}_0^\sigma} + \frac{\delta \partial W_0}{\delta \hat{\rho}_0^\sigma \partial U^I} \right) \right],$$

since, by definition of W_0 we have $\delta W_0/\delta\hat{\rho}_0^\sigma = 0$ and we may neglect the final term of order $(\delta\hat{\rho}_0^\sigma)^2$.

$$0 = \frac{d}{d\epsilon_i^\sigma} \sum_{j,\sigma'} f_j^{\sigma'} = \sum_{j,\sigma'} \frac{d}{d\epsilon_i^\sigma} \left(1 + \exp\left(\beta\left(\epsilon_j^{\sigma'} - \mu\right)\right)\right)^{-1}$$

$$= \sum_{j,\sigma'} f_j^{\sigma'2} \exp\left(\beta\left(\epsilon_j^{\sigma'} - \mu\right)\right) \beta \left(\frac{d\mu}{d\epsilon_i^\sigma} - \delta_j^i \delta_\sigma^{\sigma'}\right)$$

$$= \sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right) \beta \left(\frac{d\mu}{d\epsilon_i^\sigma} - \delta_j^i \delta_\sigma^{\sigma'}\right)$$

$$\Rightarrow \quad \frac{d\mu}{d\epsilon_i^\sigma} = \left(f_i^\sigma - f_i^{\sigma 2}\right) \left(\sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right)\right)^{-1}$$

$$\frac{\partial f_i^\sigma}{\partial \epsilon_i^\sigma} = -\frac{\partial f_i^\sigma}{\partial \mu} = -\beta\left(f_i^\sigma - f_i^{\sigma 2}\right) \tag{18}$$

$$\frac{df_i^\sigma}{d\epsilon_i^\sigma} = \frac{\partial f_i^\sigma}{\partial \epsilon_i^\sigma} + \frac{\partial f_i^\sigma}{\partial \mu} \frac{d\mu}{d\epsilon_i^\sigma} = \frac{\partial f_i^\sigma}{\partial \epsilon_i^\sigma} \left(1 - \frac{d\mu}{d\epsilon_i^\sigma}\right) \tag{19}$$

$$= -\beta\left(f_i^\sigma - f_i^{\sigma 2}\right) \tag{20}$$

$$\times \left(1 - \left(f_i^\sigma - f_i^{\sigma 2}\right) \left(\sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right)\right)^{-1}\right) \tag{21}$$

$$f_i^\sigma - f_i^{\sigma 2} > 0$$
$$\sum_{j,\sigma'} f_j^{\sigma'} \geq f_i^\sigma$$
$$\sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right) \geq f_i^\sigma - f_i^{\sigma 2}$$
$$1 \geq \left(f_i^\sigma - f_i^{\sigma 2}\right) \left(\sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right)\right)^{-1}$$
$$0 \leq 1 - \left(f_i^\sigma - f_i^{\sigma 2}\right) \left(\sum_{j,\sigma'} \left(f_j^{\sigma'} - f_j^{\sigma'2}\right)\right)^{-1}$$
$$\frac{df_i^\sigma}{d\epsilon_i^\sigma} \leq 0$$

$$= \frac{df_i^\sigma}{d\left(U\hat{P}\right)} = \sum_{k,\sigma''} \frac{df_i^\sigma}{d\epsilon_k^{\sigma''}} \frac{d\epsilon_k^{\sigma''}}{d\left(U\hat{P}\right)} \tag{22}$$