

INVITED ARTICLE

Finite temperature scaling in density functional theory

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ABSTRACT

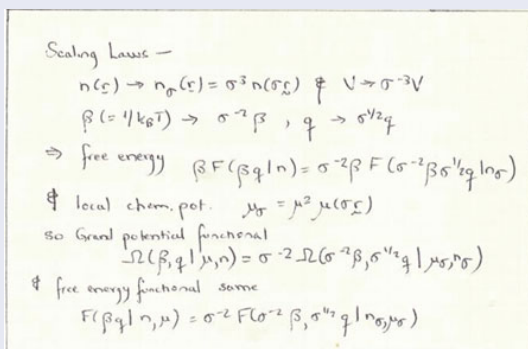
A previous analysis of scaling, bounds, and inequalities for the non-interacting functionals of thermal density functional theory (DFT) is extended to the full interacting functionals. The results are obtained from analysis of the related functionals from the equilibrium statistical mechanics of thermodynamics for an inhomogeneous system. Their extension to the functionals of DFT is described.

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Scaling Laws –
 $n(\mathbf{r}) \rightarrow n_\sigma(\mathbf{r}) = \sigma^3 n(\sigma\mathbf{r})$ & $V \rightarrow \sigma^{-3}V$
 $\beta (= 1/k_B T) \rightarrow \sigma^{-2}\beta$, $q \rightarrow \sigma^{1/2}q$
 \Rightarrow free energy $\beta F(\beta q | n) = \sigma^{-2}\beta F(\sigma^{-2}\beta \sigma^{1/2}q | n_\sigma)$
 & local chem. pot. $\mu_T = \mu^2 \mu(\sigma\mathbf{r})$
 So Grand potential functional
 $\Omega(\beta, q | \mu, n) = \sigma^{-2}\Omega(\sigma^{-2}\beta, \sigma^{1/2}q | \mu_\sigma, n_\sigma)$
 & free energy functional same
 $F(\beta q | n, \mu) = \sigma^{-2}F(\sigma^{-2}\beta, \sigma^{1/2}q | n_\sigma, \mu_\sigma)$

1. Commendation

Andreas Savin has contributed several innovative analyses and insights to the formal and practical development of density functional theory (DFT). They are marked with a characteristic intellectual style which often illuminates points which few, if any, others had considered. One of us (Trickey) has had many conversations of that nature with Andreas – and typically came away from each having learned much. In the context of the present contribution, we note one particular Savin paper: ‘On Degeneracy, Near-degeneracy, and Density Functional Theory’ [1]. It explores ensemble and many-determinant forms of DFT in the context of dissociation limits, symmetries, and invariants. Ensembles, of course, are central to statistical mechanics, hence, the question of their implications for the behaviour of finite-temperature functionals automatically arises. Here, we analyse the scaling behaviour of finite-T ensembles. Though the issues addressed here differ from those in Ref. [1], the underlying approach is closely related, namely the exploration of invariance properties. We hope that Andreas as well as others find

value in it and salute him on his formal (but, we trust, not actual) retirement.

2. Introduction

Thermal DFT is a formally exact structure for the prediction of thermodynamic properties of a quantum or classical system [2–13]. Its application requires specification of certain functionals of the density which are not given a priori and for which no mechanical recipe (e.g. perturbation expansion) is provided by the existence theorems. Development of accurate approximate functionals, therefore, remains the primary challenge for accurate implementation of DFT for a given problem class. An example of current interest is the subject of warm dense matter (WDM). The state conditions of WDM include densities and temperatures for which both traditional zero-temperature solid state or molecular forms and high-temperature plasma forms fail [14,15]. In this context, it is important to have exact properties of the free-energy density functionals for guidance in

construction of approximations. One category of exact results that has proved fruitful at zero temperature is scaling laws, that is, relationships for how the functionals change when the density is transformed under a uniform coordinate scaling which preserves total particle number [16]. Recently, we addressed this problem for the functionals of a non-interacting system at finite temperature [17]. Here, those results are extended to the corresponding functionals for the interacting system and, as a consequence, for the exchange–correlation components.

Similar results have been obtained by Pittalis *et al.* [18]. The primary simplifying feature of the approach used here and in Ref. [17] is recognition of the origin of the density functionals in the statistical mechanics of a non-uniform system at equilibrium [19]. The scaling properties then follow directly from their explicit representations as equilibrium ensemble averages via invariance of corresponding dimensionless forms. One consequence is that coupling constant scaling (i.e. electronic charge scaling) appears intrinsically in the dimensional analysis, rather than as a separate consequence of adiabatic connection as in Ref. [18].

In the next section, the thermodynamic context is noted and the density functionals for free energy, internal energy, and entropy are defined. In Section 4, the treatment is specialised to the important case of systems of electrons and ions. A coordinate scaling transformation for the electron number density is extended to include a scaling of the temperature and the Coulomb coupling constant that leaves the dimensionless functionals invariant. The consequences of this invariance are the scaling laws of interest. These results are discussed further in Section 5.

3. Equilibrium statistical mechanics and density functional theory

3.1. Thermodynamics

Here, we recall the relevant functionals of local thermodynamics on the basis of their statistical mechanical definitions in the grand canonical ensemble. Their relationship to the functionals and variational context of DFT then is noted. Recently, Eschrig [20] discussed this relationship for the general quantum case and a pedagogical version for the classical case is in Ref. [21]. The relationship provides the basis for establishing scaling laws from dimensional analysis and their relationship to thermodynamic transformations.

The grand canonical ensemble describes a system at equilibrium, exchanging energy and particles with its surroundings. The thermodynamic parameters are the temperature $T = 1/k_B\beta$, volume V , and local chemical

potential $\mu(\mathbf{r}) = \mu - v_{\text{ext}}(\mathbf{r})$. The presence of an external potential $v_{\text{ext}}(\mathbf{r})$ implies that, in general, the system is inhomogeneous (lacks translational invariance). The thermodynamic properties are defined in terms of the grand potential

$$\beta\Omega(\beta | \mu) \equiv -\ln \sum_{N=0}^{\infty} \text{Tr}^{(N)} e^{-\beta(\hat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \hat{n}(\mathbf{r}))}, \quad (1)$$

where \hat{H} is the Hamiltonian operator (see below; note the usual assumption that \hat{H} is bounded below), $\hat{n}(\mathbf{r})$ is the particle number density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i), \quad (2)$$

and $\hat{\mathbf{r}}_i$ is the position operator for the i th particle. The traces are taken over N -particle Hilbert space with an appropriate restriction on the symmetry of states (Bosons or Fermions). The grand potential and pressure $p(\beta|\mu)$ are proportional: $p(\beta|\mu)V = -\Omega(\beta|\mu)$.

The primitive functional of interest in the present context is the grand potential $\beta\Omega(\beta | \cdot)$ defined over the class of functions $\mu(\mathbf{r})$ for which the right-hand side of (1) exists. An important property that follows from this definition is its concavity,

$$\beta\Omega(\beta | \alpha\mu_1 + (1-\alpha)\mu_2) > \alpha\beta\Omega(\beta | \mu_1) + (1-\alpha)\beta\Omega(\beta | \mu_2) \quad (3)$$

for $0 < \alpha < 1$ and arbitrary $\mu_1(\mathbf{r})$ and $\mu_2(\mathbf{r})$ in the defining class. A closely related functional is the local number density defined by

$$n(\mathbf{r}, \beta | \mu) \equiv -\frac{\delta\Omega(\beta | \mu)}{\delta\mu(\mathbf{r})}. \quad (4)$$

Whenever this last definition is invertible, it identifies the chemical potential as a functional of the density

$$\mu(\mathbf{r}) \equiv \mu(\mathbf{r}, \beta | n). \quad (5)$$

Thus, at thermodynamical equilibrium there are dependent pairs μ, n , such that one determines the other. It then is possible to define a change of variables from $\beta, V, \mu(\mathbf{r})$ to $\beta, V, n(\mathbf{r})$. This is effected by the Legendre transformation

$$\begin{aligned} F(\beta | n) &\equiv \left[\Omega(\beta | \mu) - \int d\mathbf{r} \mu(\mathbf{r}) \frac{\delta\Omega(\beta | \mu)}{\delta\mu(\mathbf{r})} \right]_{\mu(\mathbf{r}, \beta | n)} \\ &= \left[\Omega(\beta | \mu) + \int d\mathbf{r} \mu(\mathbf{r}) n(\mathbf{r}) \right]_{\mu(\mathbf{r}, \beta | n)} \end{aligned} \quad (6)$$

whose differential with respect to $\mu(\mathbf{r})$ at constant $n(\mathbf{r})$ manifestly vanishes. Hence, $F(\beta | \cdot)$ is a universal functional of the density, in the sense that it is independent of $\mu(\mathbf{r})$ (hence, of v_{ext}). Also $F(\beta | n)$, the thermodynamic free energy, is a convex functional of $n(\mathbf{r})$.

$$\beta F(\beta | \alpha n_1 + (1 - \alpha)n_2) < \alpha \beta F(\beta | n_1) + (1 - \alpha) \beta F(\beta | n_2) \quad (7)$$

for $0 < \alpha < 1$ and arbitrary $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$.

The equivalent relationship between the pair μ, n of (6) now is expressed as

$$\mu(\mathbf{r}) = \frac{\delta F(\beta | n)}{\delta n(\mathbf{r})}. \quad (8)$$

Other thermodynamic functionals of interest are defined in terms of the foregoing two. For example, the energy and entropy functionals are

$$U(\beta | n) = \frac{\partial \beta \Omega(\beta | \mu)}{\partial \beta} \Big|_{\beta \mu}, \quad TS(\beta | n) = U(\beta | n) - F(\beta | n). \quad (9)$$

3.2. Connection with density functional theory

The connection to DFT is established by defining a bi-linear functional $\Omega(\beta | \mu, n)$ which is closely related to $\Omega(\beta | \mu)$. The new functional is defined for the density $n(\mathbf{r})$ and for an *independently specified* $\mu(\mathbf{r})$,

$$\Omega(\beta | \mu, n) \equiv F(\beta | n) - \int d\mathbf{r} \mu(\mathbf{r}) n(\mathbf{r}). \quad (10)$$

The density functional $F(\beta | \cdot)$ in this definition is the same as the thermodynamic functional given by (6). However, $\Omega(\beta | \mu, n)$ differs from $\Omega(\beta | \mu)$ because

$$\int d\mathbf{r} \mu(\mathbf{r}) n(\mathbf{r}) \neq - \int d\mathbf{r} \mu(\mathbf{r}) \frac{\delta \Omega(\beta | \mu)}{\delta \mu(\mathbf{r})} \quad (11)$$

for *separately and arbitrarily* specified $\mu(\mathbf{r})$ and $n(\mathbf{r})$. The same statement is true if $\Omega(\beta | \mu, n)$ appears on the right-hand side of (11). The two functionals, $\Omega(\beta | \mu, n)$ and $\Omega(\beta | \mu)$, do become equal when $\mu(\mathbf{r}), n(\mathbf{r})$ are the matched pair related by Equation (8). Furthermore, the special density which provides that pair for given $\mu(\mathbf{r})$ is that density \bar{n} which minimises $\Omega(\beta | n, \mu)$

$$\min_n \Omega(\beta | n, \mu) \equiv \Omega(\beta | \mu, \bar{n}) = \Omega(\beta | \mu). \quad (12)$$

The Euler equation associated with (12) which defines the special density is

$$\mu(\mathbf{r}) = \frac{\delta F(\beta | n)}{\delta n(\mathbf{r})} \Big|_{n=\bar{n}}. \quad (13)$$

This recovers the thermodynamic relationship (8) as expected. Equation (10) defines the fundamental functional of DFT, while (12) and (13) are the variational applications of it [2]. Those follow from the convexity properties of the thermodynamic functionals. In particular, it can be shown that $\Omega(\beta | \mu, n)$ is a convex functional of n for which the minimum is the desired special density [22].

The customary formulation and application of DFT is to determine the density for given $\mu(\mathbf{r})$. From the foregoing thermodynamic discussion it is evident, however, that $n(\mathbf{r})$ and $\mu(\mathbf{r})$ have dual roles at equilibrium with corresponding thermodynamic potentials $F(\beta | n)$ and $\Omega(\beta | \mu)$, respectively. It might be expected, for example, as a parallel to the original Hohenberg–Kohn [23] bijectivity proof at $T = 0$ K [3,4], that a complementary version of the thermal DFT could be formulated in terms of variation of $\mu(\mathbf{r})$ at given density $n(\mathbf{r})$. This is indeed the case [20,21,24]. Define the bi-linear functional for given $n(\mathbf{r})$ but arbitrary $\mu(\mathbf{r})$

$$F(\beta | n, \mu) \equiv \Omega(\beta | \mu) + \int d\mathbf{r} \mu(\mathbf{r}) n(\mathbf{r}). \quad (14)$$

The functional $\Omega(\beta | \cdot)$ is the same as the grand potential functional given by (1). However, $F(\beta | n, \mu)$ differs from $F(\beta | n)$ because of the inequality (11) for general $\mu(\mathbf{r})$. It can be shown that $F(\beta | n, \mu)$ is a concave functional of μ , and

$$\sup_{\mu} F(\beta | n, \mu) = F(\beta | n, \bar{\mu}) = F(\beta | n), \quad (15)$$

where the extremum is attained for $\mu(\mathbf{r}) = \bar{\mu}(\mathbf{r})$ determined from

$$n(\mathbf{r}) = - \frac{\delta \Omega(\beta | \mu)}{\delta \mu(\mathbf{r})} \Big|_{\mu=\bar{\mu}}. \quad (16)$$

This is the required thermodynamic relationship given in (4), while the last equality of (15) shows that the thermodynamic free energy is recovered for this particular value of the chemical potential. Equations (14)–(16) comprise a representation of DFT that is fully equivalent to the customary form displayed in Equations (10), (12), and (13). For the $T = 0$ K analogue, see Lieb [24].

In summary, this section has defined the relevant functionals for the thermodynamics of an inhomogeneous system within the framework of the grand ensemble of

equilibrium statistical mechanics. The simple relationship of the central ingredients of DFT to those equilibrium functionals then was indicated. The advantage of this perspective is that the functionals have an unambiguous representation within statistical mechanics, for both formal and practical analysis.

4. Scaling properties of functionals

Most commonly, the systems of interest for DFT applications are comprised of electrons and ions, denoted in the following by subscript ‘e’ and ‘i’. For simplicity without loss of generality, we restrict discussion to a single ion species. The grand potential reads

$$\beta\Omega(\beta, \mu_e, \mu_i) \equiv -\ln \sum_{N_e=0, N_i=0}^{\infty} T r^{(N_e)} T r^{(N_i)} e^{-\beta(\hat{H}_e + \hat{H}_i + \hat{H}_{ei} - \mu_e N_e - \mu_i N_i)}. \quad (17)$$

The two chemical potentials are related by charge neutrality

$$q_e N_e(\beta, \mu_e, \mu_i) + q_i N_i(\beta, \mu_e, \mu_i) = 0, \quad (18)$$

or

$$q_e \frac{\partial \Omega(\beta, \mu_e, \mu_i)}{\partial \mu_e} + q_i \frac{\partial \Omega(\beta, \mu_e, \mu_i)}{\partial \mu_i} = 0. \quad (19)$$

In the following discussion, it is assumed that μ_e is given and μ_i is determined from this charge neutrality condition.

Because of the comparatively large mass of the ions, typically the ionic thermal de Broglie wavelength λ_i and average inter-ionic separation r_0 are much different: $\lambda_i \ll r_0$. The ions, therefore, can be treated in a semi-classical limit. The motive for doing so is to have a purely electronic DFT with the ions providing an external potential. The average over the electron subsystem can be performed formally to give

$$\beta\Omega(\beta, \mu_e, \mu_i) \rightarrow -\ln \sum_{N_i=0}^{\infty} \frac{1}{\lambda_i^{3N_i} N_i!} \int d\mathbf{X}_i e^{-\beta(U_{ii} + \Omega_e(\beta, q_e | \mu_e) - \mu_i N_i)}. \quad (20)$$

Here, U_{ii} is the ion-ion Coulomb repulsion energy and the set of ionic coordinates $\{\mathbf{X}_{i,1} \dots \mathbf{X}_{i,N_i}\}$ is denoted \mathbf{X}_i . The electronic grand potential Ω_e that appears in (20) is defined by

$$\beta\Omega_e(\beta, q_e | \mu) = -\ln \sum_{N_e=0}^{\infty} T r^{(N_e)} e^{-\beta(\hat{H}_e - \int d\mathbf{r} \mu(\mathbf{r}) \hat{n}_e(\mathbf{r}))}, \quad (21)$$

where the dependence on the electronic charge q_e now has been made explicit for purposes of the scaling analysis of the next subsection. The electronic local chemical potential

$$\mu(\mathbf{r}) = \mu_e - v_{\text{ext}}(\mathbf{r}), \quad v_{\text{ext}}(\mathbf{r}) = \sum_{i=1}^{N_i} \frac{q_e q_i}{|\mathbf{r} - \mathbf{X}_{i\eta}|}. \quad (22)$$

The dependence of $\beta\Omega_e$ and μ on the ion coordinates \mathbf{X}_i has been left implicit in this notation.

In this approximation, the calculation of the thermodynamic properties for the electron-ion system is separated into two parts. First, the quantum mechanical treatment of the electrons is addressed through the calculation of $\beta\Omega_e(\beta | \mu_e)$, the task of DFT. Next, the classical ion average is performed (typically in the Born-Oppenheimer approximation). That can be done via molecular dynamics simulation under the assumption of ergodicity. The effective ion forces for such a simulation are

$$\begin{aligned} \mathbf{F}_i &= -\nabla_{\mathbf{X}_i} (U_{ii} + \Omega_e(\beta, q_e | \mu)) \\ &= -\nabla_{\mathbf{X}_i} U_{ii} - \int d\mathbf{r} n_e(\mathbf{r}, \beta | \mu) \nabla_{\mathbf{X}_i} v_{\text{ext}}(\mathbf{r}), \end{aligned} \quad (23)$$

where the definition of the density, (4), has been used in the second equality. It can be shown that this same result is obtained from the microscopic ion force averaged over the electron subsystem. (As an aside, we remark that such a simulation calculates one member of the grand ensemble. For large systems, the fluctuations about the average number of electrons are small, hence, so are the fluctuations around the average number of ions. Thus, a single simulation can be sufficient and operationally equivalent to working in the canonical ensemble. More generally, fluctuation corrections can be calculated. These issues of precise relationship between theory and simulational practice are worth keeping in mind but are not of consequence here. See Ref. [25] for an analysis.)

The remainder of this work addresses only the electron subsystem, namely, the calculation of $\Omega_e(\beta, q_e | \mu)$ from DFT. Therefore, from now on, we drop the subscript ‘e’ on the grand potential and charge and write $\Omega(\beta, q | \mu)$ and do the same with the associated free energy functional $F(\beta, q | n)$.

4.1. Scaling properties of $\Omega(\beta, q | \mu)$ and $F(\beta, q | n)$

Begin, as before, with the thermodynamic functionals and introduce the dimensionless variables/operators

$$\begin{aligned} v(\mathbf{r}^*) &= \beta \mu(\mathbf{r}), & \hat{n}^*(\mathbf{r}^*) &= \lambda^3 \hat{n}(\mathbf{r}), \\ \hat{y}_\alpha &\equiv \sqrt{\frac{\beta}{2m}} \hat{\mathbf{p}}_\alpha, & \hat{\mathbf{r}}_\alpha^* &= \frac{\hat{\mathbf{r}}_\alpha}{\lambda}, & \xi &= \beta q^2 / \lambda \end{aligned} \quad (24)$$

with $\hat{\mathbf{p}}_\alpha$, $\hat{\mathbf{r}}_\alpha$ the momentum and position operators, respectively, for electron α and λ the electron thermal de Broglie wavelength

$$\lambda(\beta) = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{1/2}. \quad (25)$$

Conversion to these dimensionless variables gives the dimensionless grand potential

$$\begin{aligned} \Omega^*(\xi | v) &= \beta \Omega(\beta, q | \mu) \\ &= -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-(\hat{H}^* - \int d\mathbf{r}^* v(\mathbf{r}^*) \hat{n}^*(\mathbf{r}^*))}. \end{aligned} \quad (26)$$

The dimensionless Hamiltonian is

$$\hat{H}^* = \beta \hat{H} = \sum_{\alpha=1}^N \hat{y}_\alpha^2 + \frac{1}{2} \xi \sum_{\alpha \neq \eta=1}^N \frac{1}{|\hat{\mathbf{r}}_\alpha^* - \hat{\mathbf{r}}_\eta^*|}. \quad (27)$$

The dimensionless electron number density follows from

$$n^*(\mathbf{r}^*, \xi | v) = - \frac{\delta \Omega^*(\xi | v)}{\delta v(\mathbf{r}^*)} \Big|_{\xi}. \quad (28)$$

Assuming invertibility as usual, this relationship establishes $v(\mathbf{r}^*)$ as a functional of $n^*(\mathbf{r}^*)$

$$v(\mathbf{r}^*) = v(\mathbf{r}^*, \xi | n^*). \quad (29)$$

The dimensionless free energy functional of the density is defined by the Legendre transformation

$$\begin{aligned} F^*(\xi | n^*) &= \beta F(\beta, q | n) = \Omega^*(\xi | v) \\ &+ \int d\mathbf{r}^* v(\mathbf{r}^*, \xi | n^*) n^*(\mathbf{r}^*). \end{aligned} \quad (30)$$

The corresponding dimensionless internal energy and entropy functionals are

$$U^*(\xi | n^*) = \beta U(\beta, q | n) = \beta \frac{\partial \beta \Omega(\beta | n, \mu)}{\partial \beta} \Big|_v, \quad (31)$$

$$S^*(\xi | n^*) = k_B^{-1} S(\beta, q | n) = U^*(\xi | n^*) - F^*(\xi | n^*). \quad (32)$$

Now, consider the usual uniform coordinate scaling transformation of the density and volume,

$$n(\mathbf{r}) \rightarrow n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r}), \quad V \rightarrow \gamma^{-3} V, \quad (33)$$

with γ a real, positive constant. Include scalings of both β and q in the transformation as well,

$$\beta \rightarrow \gamma^{-2} \beta, \quad q \rightarrow \gamma^{1/2} q. \quad (34)$$

The result is to leave ξ invariant

$$\xi = \beta q^2 / \lambda \rightarrow \gamma^{-2} \beta (\gamma^{1/2} q)^2 / \lambda (\gamma^{-2} \beta) = \xi, \quad (35)$$

and preserve the total number of particles

$$\int_V n(\mathbf{r}) d\mathbf{r} = N = \int_{\gamma^{-3}V} n_\gamma(\mathbf{r}) d\mathbf{r}. \quad (36)$$

Also $n^*(\mathbf{r}^*)$ is invariant

$$\begin{aligned} n^*(\mathbf{r}^*) &\equiv \lambda^3(\beta) n(\lambda(\beta) \mathbf{r}^*) \rightarrow \lambda^3(\gamma^{-2} \beta) \gamma^3 n(\gamma \mathbf{r}) \\ &= \lambda(\gamma^{-2} \beta)^3 \gamma^3 n(\gamma \lambda(\gamma^{-2} \beta) \mathbf{r}^{**}) \\ &= \lambda^3(\beta) n(\lambda(\beta) \mathbf{r}^{**}) = n^*(\mathbf{r}^{**}), \end{aligned} \quad (37)$$

where $\mathbf{r}^* \rightarrow \mathbf{r}^{**} = \mathbf{r} / \lambda(\gamma^{-2} \beta)$ is the dimensionless coordinate in the transformed system.

These invariances for ξ and n^* then imply the invariance of the dimensionless free energy $F^*(\xi | n^*)$ which is a function or functional of only these properties. Consequently, the scaling law for the free energy functional is obtained

$$\beta F(\beta, q | n) = \gamma^{-2} \beta F(\gamma^{-2} \beta, \gamma^{1/2} q | n_\gamma). \quad (38)$$

It also follows that $v(\mathbf{r}^*, \xi | n^*) \rightarrow v(\mathbf{r}^{**}, \xi | n^*)$ and so $\Omega^*(\xi | v)$ is also invariant under this transformation, leading to the scaling law for the grand potential

$$\beta \Omega(\beta, q | \mu) = \gamma^{-2} \beta \Omega(\gamma^{-2} \beta, \gamma^{1/2} q | \mu_\gamma), \quad (39)$$

where μ_γ follows from (29)

$$\mu_\gamma = \gamma^2 \mu(\gamma \mathbf{r}). \quad (40)$$

This last result may seem a bit surprising, since one naïvely might expect the same scaling as for the density (33). But that does not follow because of the assumed

invertibility of n and $\mu(\mathbf{r})$. Instead (40) comes from

$$\begin{aligned} v(\mathbf{r}^*) &= \beta\mu(\mathbf{r}), \quad v(\mathbf{r}^*, \xi | n^*) \rightarrow v(\mathbf{r}^{**}, \xi | n^*) \\ &= v\left(\frac{\lambda}{\lambda_\gamma}\mathbf{r}^*, \xi | n^*\right) = v(\gamma\mathbf{r}^*, \xi | n^*), \end{aligned} \quad (41)$$

whence

$$v(\gamma\mathbf{r}^*, \xi | n^*) = \beta\mu(\gamma\mathbf{r}) = \beta_\gamma\mu_\gamma(\mathbf{r}). \quad (42)$$

Here, the abbreviated notation is $\lambda_\gamma := \lambda(\gamma^{-2}\beta) = \gamma^{-1}\lambda(\beta)$ and $\beta_\gamma = \gamma^{-2}\beta$. The result is (40).

Finally, the dimensionless internal energy and entropy of (31) and (32) are also invariant under this transformation, giving their scaling laws

$$\beta U(\beta, q | n) = \beta\gamma^{-2}U(\gamma^{-2}\beta, \gamma^{1/2}q | n_\gamma), \quad (43)$$

$$S(\beta, q | n) = S(\gamma^{-2}\beta, \gamma^{1/2}q | n_\gamma). \quad (44)$$

For $q = 0$, the results of Ref. [17] for the non-interacting case are recovered. An independent proof of these scaling laws is given in the Appendix by direct coordinate scaling of the Hamiltonian in (1).

4.2. Scaling properties of $\Omega(\beta|\mu, n)$ and $F(\beta|\mu, n)$

Now consider the dimensionless functionals of DFT. From (10), the dimensionless grand potential functional is

$$\begin{aligned} \Omega^*(\xi | v, n^*) &= \beta\Omega(\beta, q | \mu, n) \\ &= F^*(\xi | n^*) - \int d\mathbf{r}^* v(\mathbf{r}^*) n^*(\mathbf{r}^*), \end{aligned} \quad (45)$$

as a functional of $n^*(\mathbf{r}^*)$ for given $v(\mathbf{r}^*)$. Concurrently, consider the dimensionless free energy density functional from (14),

$$\begin{aligned} F^*(\xi | n^*, v) &= \beta F(\beta, q | n, \mu) \\ &= \Omega^*(\xi | v) + \int d\mathbf{r}^* v(\mathbf{r}^*) n^*(\mathbf{r}^*), \end{aligned} \quad (46)$$

as a functional of $v(\mathbf{r}^*)$ for given $n^*(\mathbf{r}^*)$. The dimensionless density $n^*(\mathbf{r}^*)$ and independent dimensionless local chemical potential $v(\mathbf{r}^*)$ were defined at (24) as

$$n^*(\mathbf{r}^*) = \lambda^3 n(\mathbf{r}), \quad v(\mathbf{r}^*) = \beta\mu(\mathbf{r}). \quad (47)$$

The first terms on the right-hand sides of (45) and (46) have the invariance defined in (38) and (39), respectively.

The remaining term transforms as

$$\begin{aligned} \int d\mathbf{r}^* v(\mathbf{r}^*) n^*(\mathbf{r}^*) &= \int d\mathbf{r} \beta\mu(\mathbf{r}) n(\mathbf{r}) \\ &\rightarrow \int d\mathbf{r} \beta_\gamma\mu_\gamma(\mathbf{r}) n_\gamma(\mathbf{r}) = \int d\mathbf{r} (\gamma^{-2}\beta) \gamma^2\mu(\gamma\mathbf{r}) \gamma^3 n(\gamma\mathbf{r}) \\ &= \int d\mathbf{r} \beta\mu(\mathbf{r}) n(\mathbf{r}). \end{aligned} \quad (48)$$

Consequently, the DFT functionals $\Omega^*(\xi | v, n^*)$ and $F^*(\xi | n^*, v)$ have the same invariance as the thermodynamic functionals $\Omega^*(\xi | v)$ and $F^*(\xi | n^*)$,

$$\Omega(\beta, q | \mu, n) = \gamma^{-2}\Omega(\gamma^{-2}\beta, \gamma^{1/2}q | \mu_\gamma, n_\gamma) \quad (49)$$

$$F(\beta, q | n, \mu) = \gamma^{-2}F(\gamma^{-2}\beta, \gamma^{1/2}q | n_\gamma, \mu_\gamma). \quad (50)$$

4.3. Exchange–correlation scaling

The free energy functional $\beta F(\beta, q | n)$ typically is decomposed into separate contributions for practical analysis

$$F(\beta, q | n) = F^{(0)}(\beta | n) + E_H(q | n) + F^{xc}(\beta, q | n). \quad (51)$$

The first term on the right-hand side $F^{(0)}$ is the free energy functional for the non-interacting system,

$$F^{(0)}(\beta | n) = F(\beta, q = 0 | n), \quad (52)$$

while the second is the Hartree energy

$$E_H = q^2 \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}'). \quad (53)$$

The last term F^{xc} is the exchange–correlation free energy, defined as the residual free energy incorporating all exchange and correlation effects due to interactions. It is easily seen that $\beta F^{(0)}(\beta | n)$ and $\beta E_H(q | n)$ are invariant under the transformation defined by (33) and (34). Consequently, βF^{xc} is invariant as well

$$\beta F^{xc}(\beta, q | n) = \gamma^{-2}\beta F^{xc}(\gamma^{-2}\beta, \gamma^{1/2}q | n_\gamma). \quad (54)$$

5. Discussion

At first reading, familiarity with ground-state DFT scaling laws may make Equations (49) and (50) a bit surprising because they both scale the same way. Thus,

$$\beta Q(\beta, q | \mu, n) = \gamma^{-2}\beta Q(\gamma^{-2}\beta, \gamma^{1/2}q | n_\gamma, \mu_\gamma), \quad (55)$$

for Q any of Ω , F , U , or TS . Though not the more commonly discussed ground-state DFT pattern (which

involves inequalities), such scaling has been discussed for the ground state by Levy; see Section 2.11 of Ref. [26]. The relevant point there and here is the inclusion of charge scaling, (34). Pittalis *et al.* [18] arrived at the result (55) by a route analogous to Levy's ground-state procedure, namely, by considering the coupling constant scaling in the adiabatic connection procedure. This is the same charge scaling as in (34) above but introduced separately from the uniform coordinate scaling, (33). The present analysis provides the alternative perspective of invariance properties of the thermodynamical functionals, (38), (39), (43), and (44) leading to the scaling of the DFT functionals. There is a similar parallel with the recent discussion by Pribram-Jones and Burke of connecting charge and temperature scaling [27].

Without the charge scaling but with temperature scaling as well as coordinate scaling, the homogeneous scaling of the internal energy as γ^{-2} (43) does not hold, since the Coulombic contributions with unscaled charge go as γ^{-1} , whereas the non-interacting parts T_s (KE) and TS_s (entropy) scale as γ^{-2} (obviously irrespective of charge scaling) [17]. Since the exchange contribution $U_x(\beta, q|\mu, n)$ to the internal energy functional is defined in DFT (both finite-T and ground-state) as a Coulomb energy (from the 1-body reduced density matrix), its scaling is the same as the Hartree contribution $U_H(\beta, q - \mu, n)$: both go as γ^{-2} with charge scaling, γ^{-1} without. As with the ground-state theory, the difference between the scaling procedures shows up in the correlation internal energy $U_c(\beta, q|\mu, n)$ because it has both a Coulombic contribution,

$$U_{\text{Coul}}^c(\beta, q|\mu, n) = W_{ee}(\beta, q|\mu, n) - U_H(\beta, q|\mu, n) - U_x(\beta, q|\mu, n) \quad (56)$$

(with W_{ee} the entire Coulomb internal energy functional) and two contributions that scale as does a kinetic energy, namely,

$$\mathcal{T}^c(\beta, q|\mu, n) = \mathcal{T}(\beta, q|\mu, n) - \mathcal{T}_s(\beta, q|\mu, n), \quad (57)$$

$$T\mathcal{S}^c(\beta, q|\mu, n) = T\mathcal{S}(\beta, q|\mu, n) - T\mathcal{S}_s(\beta, q|\mu, n). \quad (58)$$

Here, \mathcal{T}, \mathcal{S} are the kinetic energy and entropy functionals and subscript s labels their non-interacting (Kohn–Sham) counterparts. Thus,

$$U^c(\beta, q|\mu, n) = U_{\text{Coul}}^c(\beta, q|\mu, n) + \mathcal{T}^c(\beta, q|\mu, n) + T\mathcal{S}^c(\beta, q|\mu, n). \quad (59)$$

Without charge scaling, this combination leads [18] to inequalities, such as

$$\Omega^c(\beta, q|\mu, n) \geq \gamma \Omega^c(\gamma^{-2}\beta, q|\mu, n), \quad \gamma \geq 1 \quad (60)$$

for the correlation contribution to the grand potential. In contrast, with charge scaling, the equality (55) holds. Both forms are potentially useful for constraining the design of approximate functionals.

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Appendix. Scaling of $\Omega(\beta, q | \mu)$ and $F(\beta, q | n)$

The scaling properties for the functionals of thermodynamics follow directly from the statistical mechanical definition (1). In our earlier work on the non-interacting functionals [17], a unitary operator was constructed that implements scaling of the particle coordinate and momentum operators

$$\widehat{U}_\gamma A(\widehat{\mathbf{q}}_\alpha, \widehat{\mathbf{p}}_\alpha) \widehat{U}_\gamma^{-1} = A(\gamma \widehat{\mathbf{q}}_\alpha, \gamma^{-1} \widehat{\mathbf{p}}_\alpha), \quad 0 < \gamma < \infty, \quad (\text{A1})$$

where γ again is a positive, real-valued scalar. The detailed form of \widehat{U}_γ is not required here; the interested reader is referred to Appendix B of Ref. [17]. Then, from the cyclic invariance of the trace Equation (1) of the main

text can be written as

$$\begin{aligned} \beta \Omega(\beta, q | \mu) &= -\ln \sum_{N=0}^{\infty} T r^{(N)} \widehat{U}_\gamma e^{-\beta(\widehat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \widehat{n}(\mathbf{r}))} \widehat{U}_\gamma^{-1} \\ &= -\ln \sum_{N=0}^{\infty} T r^{(N)} e^{-\widehat{U}_\gamma \beta(\widehat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \widehat{n}(\mathbf{r})) \widehat{U}_\gamma^{-1}}, \end{aligned} \quad (\text{A2})$$

and by application of (A1)

$$\begin{aligned} &\widehat{U}_\gamma \beta \left(\widehat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \widehat{n}(\mathbf{r}) \right) \widehat{U}_\gamma^{-1} \\ &= \beta \gamma^{-2} \left(\sum_{\alpha=1}^N \left(\frac{\widehat{p}_\alpha^2}{2m} - \gamma^2 \mu(\gamma \widehat{\mathbf{q}}_\alpha) \right) + \frac{1}{2} \gamma q^2 \sum_{\alpha \neq \eta=1}^N \frac{1}{|\widehat{\mathbf{q}}_\alpha - \widehat{\mathbf{q}}_\eta|} \right) \\ &= \beta_\gamma \left(\sum_{\alpha=1}^N \frac{\widehat{p}_\alpha^2}{2m} + \frac{1}{2} q_\gamma^2 \sum_{\alpha \neq \eta=1}^N \frac{1}{|\widehat{\mathbf{q}}_\alpha - \widehat{\mathbf{q}}_\eta|} - \int d\mathbf{r} \mu_\gamma(\mathbf{r}) \widehat{n}(\mathbf{r}) \right) \end{aligned} \quad (\text{A3})$$

with

$$\beta_\gamma = \beta \gamma^{-2}, \quad q_\gamma = \gamma^{1/2} q, \quad \mu_\gamma(\mathbf{r}) = \gamma^2 \mu(\gamma \mathbf{r}). \quad (\text{A4})$$

Consequently, the desired scaling property is obtained

$$\beta \Omega(\beta, q | \mu) = \beta_\gamma \Omega(\beta_\gamma, q_\gamma | \mu_\gamma). \quad (\text{A5})$$

To interpret the transformed local chemical potential μ_γ , note that it gives rise to the density

$$n_\gamma(\mathbf{r}, \beta_\gamma, q_\gamma | \mu_\gamma) = \gamma^3 \frac{\delta \Omega(\beta_\gamma, q_\gamma | \mu_\gamma)}{\delta \mu_\gamma(\mathbf{r})}. \quad (\text{A6})$$

This density is related to that in the original variables by

$$\begin{aligned} &e^{\beta_\gamma \Omega(\beta_\gamma, q_\gamma | \mu_\gamma)} \sum_{N=0}^{\infty} T r^{(N)} \widehat{n}(\mathbf{r}) e^{-\widehat{U}_\gamma \beta(\widehat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \widehat{n}(\mathbf{r})) \widehat{U}_\gamma^{-1}} \\ &= e^{\beta \Omega(\beta, q | \mu)} \sum_{N=0}^{\infty} T r^{(N)} \widehat{U}_\gamma^{-1} \widehat{n}(\mathbf{r}) \widehat{U}_\gamma e^{-\beta(\widehat{H} - \int d\mathbf{r} \mu(\mathbf{r}) \widehat{n}(\mathbf{r}))}, \end{aligned} \quad (\text{A7})$$

or

$$n(\mathbf{r}, \beta_\gamma, q_\gamma | \mu_\gamma) = \gamma^3 n(\gamma \mathbf{r}, \beta, q | \mu), \quad (\text{A8})$$

i.e. it is the transformed density $n_\gamma(\mathbf{r})$.

Now consider the Legendre transform for the new free energy $F(\beta_\gamma, Q_\gamma | n_\gamma)$

$$\begin{aligned} \beta_\gamma F(\beta_\gamma, q_\gamma | n_\gamma) &= \beta_\gamma \Omega(\beta_\gamma, q_\gamma | \mu_\gamma) \\ &+ \beta_\gamma \int d\mathbf{r} \mu_\gamma(\mathbf{r}) n_\gamma(\mathbf{r}) \end{aligned}$$

$$\begin{aligned} &= \beta \Omega(\beta, q | \mu) + \beta \int d\mathbf{r} \mu(\gamma \mathbf{r}) \gamma^3 n(\gamma \mathbf{r}) \\ &= \beta F(\beta, q | n). \end{aligned} \tag{A9}$$

This is the expected invariance corresponding to that for $\beta \Omega(\beta, q | \mu)$ in (A5).