"The piecewise-linearity of approximate density functionals revisited: implications for frontier orbital energies"

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In the following, reference to equations from the main text are made by a single number (e.g. Eq. (1)), while equations from this document include the section number, as well (e.g. Eq. (I.1)).

I. DERIVATION OF EQS. (4), (5), (8)

To obtain Eqs. (4) and (5), consider the application of the Coulomb operator

$$\hat{W} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} \qquad (I.1)$$

to a pure state $|\Phi\rangle$ of the KS system, where

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{r_1}) & \varphi_1(\vec{r_2}) & ... & \varphi_1(\vec{r_N}) \\ \varphi_2(\vec{r_1}) & \varphi_2(\vec{r_2}) & ... & \varphi_2(\vec{r_N}) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\vec{r_1}) & \varphi_N(\vec{r_2}) & ... & \varphi_N(\vec{r_N}) \end{vmatrix} \qquad (I.2)$$

is a Slater determinant of the one-electron KS orbitals $\{\varphi_i\}$. The symbol $^{(\alpha)}$ does not accompany here the KS orbitals and other derived quantities, as opposed to the main text, for clarity of presentation.

The quantity $W := \langle\Phi|\hat{W}|\Phi\rangle$ is given by the well-known expression

$$\begin{aligned} W = \ & \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r})\varphi_i(\vec{r})\varphi_j^*(\vec{r'})\varphi_j(\vec{r'})}{|\vec{r} - \vec{r'}|} \\ & - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r'})\varphi_j^*(\vec{r})\varphi_i(\vec{r})\varphi_j(\vec{r'})}{|\vec{r} - \vec{r'}|} \end{aligned}$$
$$(I.3)$$

In the first term above we recognize the pure-state density, defined as $\rho = \sum_{i=1}^{N} |\varphi_i|^2$, and partition the Coulomb energy as

$$W = E_H[\rho] + E_x[\rho], \qquad (I.4)$$

where

$$E_H[\rho] = \frac{1}{2} \iint d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} \qquad (I.5)$$

is the Hartree energy, and

$$E_x[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r'})\varphi_j^*(\vec{r})\varphi_i(\vec{r})\varphi_j(\vec{r'})}{|\vec{r} - \vec{r'}|} \qquad (I.6)$$

is the exchange energy (where φ_i themselves are functionals of the density).

For an ensemble state, W is obtained using the Tr procedure: $W = \text{Tr}\{\hat{\Lambda}_{KS}\hat{W}\}$, where

$$\hat{\Lambda}_{KS} = (1-\alpha)|\Phi_{N_0}\rangle\langle\Phi_{N_0}| + \alpha|\Phi_{N_0+1}\rangle\langle\Phi_{N_0+1}|, \qquad (I.7)$$

and

$$W = (1-\alpha)\langle\Phi_{N_0}|\hat{W}|\Phi_{N_0}\rangle + \alpha\langle\Phi_{N_0+1}|\hat{W}|\Phi_{N_0+1}\rangle. \qquad (I.8)$$

The densities corresponding to the states $|\Phi_{N_0}\rangle$ and $|\Phi_{N_0+1}\rangle$ are ρ_0 and ρ_1, respectively (see definitions in the main text), and therefore

$$W = (1-\alpha)E_H[\rho_0] + \alpha E_H[\rho_1] + (1-\alpha)E_x[\rho_0] + \alpha E_x[\rho_1]. \qquad (I.9)$$

The first two terms are the Hartree energy of the ensemble state, denoted by W_H. The last two terms are the exchange energy of the ensemble state, denoted by W_x. These four terms appear in Eqs. (4) and (5).

To express W_H in terms of $E_H[n]$ and ΔE_{eH}, we insert the definition $n = (1-\alpha)\rho_0 + \alpha\rho_1$ (Eq. (2)) into Eq. (I.5) to obtain

$$\begin{aligned} E_H[n] \ =\ & (1-\alpha)^2 E_H[\rho_0] + \alpha^2 E_H[\rho_1] \\ & + \alpha(1-\alpha) \iint d^3r d^3r' \frac{\rho_0(\vec{r})\rho_1(\vec{r'})}{|\vec{r} - \vec{r'}|} \\ =\ & (1-\alpha)E_H[\rho_0] + \alpha E_H[\rho_1] \\ & + \alpha(1-\alpha)\left(\iint d^3r d^3r' \frac{\rho_0(\vec{r})\rho_1(\vec{r'})}{|\vec{r} - \vec{r'}|} - E_H[\rho_0] - E_H[\rho_1] \right) \end{aligned}$$
$$(I.10)$$

Combining Eqs. (I.5) and (I.10) while using the fact that $\rho_1 - \rho_0 = |\varphi_{N_0+1}|^2$, yields

$$E_H[n] = (1-\alpha)E_H[\rho_0] + \alpha E_H[\rho_1]$$
$$- \frac{1}{2}\alpha(1-\alpha)\iint d^3r d^3r' \frac{|\varphi_{N_0+1}(\vec{r})|^2|\varphi_{N_0+1}(\vec{r'})|^2}{|\vec{r}-\vec{r'}|}.$$
$$(I.11)$$

Thus, we arrive at the relation $W_H = E_H[n] + \Delta E_{eH}[\varphi_{N_0+1};\alpha]$.

To express W_x in terms of $E_x[n]$ and ΔE_{eH}, we rearrange Eq. (5) as

$$W_x = E_x[\rho_0] + \alpha(E_x[\rho_1] - E_x[\rho_0]). \qquad (I.12)$$

Using Eq. (I.6) one then obtains

$$E_x[\rho_1] - E_x[\rho_0] =$$
$$-\frac{1}{2}\sum_{j=1}^{N_0+1}\iint d^3r d^3r' \frac{\varphi_{N_0+1}^*(\vec{r'})\varphi_j^*(\vec{r})\varphi_{N_0+1}(\vec{r})\varphi_j(\vec{r'})}{|\vec{r}-\vec{r'}|}$$
$$(I.13)$$

From Eq. (3) $g_{N_0+1} = \alpha$; considering Eq. (I.12), while substituting Eq. (I.6) for its first term and Eq. (I.13) for the second term, we obtain

$$W_x = -\frac{1}{2}\sum_{i=1}^{\infty}\sum_{j=1}^{N_0} g_i \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r'})\varphi_j^*(\vec{r})\varphi_i(\vec{r})\varphi_j(\vec{r'})}{|\vec{r}-\vec{r'}|}$$
$$- \frac{1}{2}\alpha\iint d^3r d^3r' \frac{|\varphi_{N_0+1}(\vec{r'})|^2|\varphi_{N_0+1}(\vec{r})|^2}{|\vec{r}-\vec{r'}|} \qquad (I.14)$$

Finally, to achieve the form of Eq. (7), we replace the sum $\sum_{j=1}^{N_0}$ by $\sum_{j=1}^{\infty} g_i$. This change introduces an additional term to the double summation, which should be subtracted for maintaining the equality. This manipulation leads to the expression

$$W_x = -\frac{1}{2}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} g_i g_j \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r'})\varphi_j^*(\vec{r})\varphi_i(\vec{r})\varphi_j(\vec{r'})}{|\vec{r}-\vec{r'}|}$$
$$- \frac{1}{2}\alpha(1-\alpha)\iint d^3r d^3r' \frac{|\varphi_{N_0+1}(\vec{r'})|^2|\varphi_{N_0+1}(\vec{r})|^2}{|\vec{r}-\vec{r'}|},$$
$$(I.15)$$

which is equivalent to the form $W_x = E_x[n] - \Delta E_{eH}[\varphi_{N_0+1};\alpha]$.

II. RATIONALE OF EQ. (9)

In the following we explain in more detail the rationale behind the ensemble generalization of an approximate xc-functional to a form which is explicitly linear in α.

The approximate xc-functional can be (and usually is) presented as a sum of an approximate exchange functional and an approximate correlation functional. Because the exact exchange functional is explicitly linear in α, as shown in Eq. (5), it is reasonable to require that the approximate exchange functional exhibit the same property.

The correlation functional for a pure state can be formally expressed, without any approximation, as (see e.g. Eq.(1.68) in Ref. [1])

$$E_c = \langle\Psi|\hat{T}+\hat{W}|\Psi\rangle - \langle\Phi|\hat{T}+\hat{W}|\Phi\rangle, \qquad (II.1)$$

where $\hat{T}$ and $\hat{W}$ are the kinetic and the Coulomb operators, respectively, Ψ is the wavefunction of the interacting system, and Φ is the wavefunction of the KS system.

For ensembles, the wavefunctions Ψ and Φ of the pure state are substituted by the ensemble operators $\hat{\Lambda}$ and $\hat{\Lambda}_{KS}$, respectively (see definitions in the main text). The correlation energy then becomes

$$E_c = (1-\alpha)\langle\Psi_{N_0}|\hat{T}+\hat{W}|\Psi_{N_0}\rangle + \alpha\langle\Psi_{N_0+1}|\hat{T}+\hat{W}|\Psi_{N_0+1}\rangle$$
$$-(1-\alpha)\langle\Phi_{N_0}^{(\alpha)}|\hat{T}+\hat{W}|\Phi_{N_0}^{(\alpha)}\rangle - \alpha\langle\Phi_{N_0+1}^{(\alpha)}|\hat{T}+\hat{W}|\Phi_{N_0+1}^{(\alpha)}\rangle,$$
$$(II.2)$$

being explicitly linear in α. Thus, it is reasonable to require that the approximate correlation functional will also be explicitly linear in α.

Explicit linearization in α of the exchange-correlation functional carries with it an additional advantage. Any successful underlying density functional obeys various exact constraints. In particular, in LSDA a sum rule for the exchange-correlation hole is obeyed [2, 3]. Because the pure-state functional is then generalized into an ensemble one via an appropriate linear combination, exact constraints obeyed by the integer-electron functional will automatically be carried over to the ensemble-generalized functional.

III. DERIVATION OF THE KS POTENTIAL

In our ensemble approach, the KS potential, v_{KS}, cannot be obtained by a straightforward application of a functional derivative, because parts of the energy functional $E[n] = T_{KS} + V_n[n] + E_H[n] + \Delta E_{eH}[\varphi_{N_0+1}^{(\alpha)};\alpha] + E_{exc}[\rho_0^{(\alpha)},\rho_1^{(\alpha)};\alpha]$ depend explicitly on the orbitals and α, rather than on n.

Let us denote $v_{KS} = v_n + v_H + v_{eH} + v_{exc}$, where $v_H = \delta E_H/\delta n$, $v_{eH} = \delta(\Delta E_{eH})/\delta n$ and $v_{exc} = \delta E_{exc}/\delta n$. The two last terms of v_{KS} can be presented as

$$v_T(\vec{r}) = \frac{\delta E_T}{\delta n} = \left(\frac{\partial E_T}{\partial \alpha}\right)_n \frac{\delta\alpha}{\delta n} + \left(\frac{\delta E_T}{\delta n(\vec{r})}\right)_\alpha, \qquad (III.1)$$

where T stands for either the eH term or exc term. For the ensemble of two pure, non-degenerate states discussed throughout, $\alpha[n] = N - \text{floor}(N)$ and $N = \int n d^3r$. We then find $\delta\alpha/\delta n = 1$. The second term of the RHS of Eq. (III.1) is denoted by $v_T^{(1)}$ and can be expressed as

$$v_T^{(1)}(\vec{r}) = \sum_{i=1}^{\infty}\int d^3r' \left(\frac{\delta\varphi_i(\vec{r'})}{\delta n(\vec{r})}\right)_\alpha \left(\frac{\delta E_T}{\delta\varphi_i(\vec{r'})}\right)_\alpha + c.c.,$$
$$(III.2)$$

where α is constant and therefore treated as a parameter. Because $\delta E_T/\delta\varphi_i$ can be obtained from Eqs. (8) and (9), $v_T^{(1)}$ can be found using the OEP procedure [4], as is suitable for an orbital-dependent functional.

The first term of the RHS of Eq. (III.1) is denoted by $v_T^{(0)}$. This term is somewhat unusual, as most functionals do not contain the quantity α explicitly. $v_T^{(0)}$ is α-dependent, but constant in space. As the expressions for ΔE_{eH} and E_{exc} do not depend explicitly on the density n, it is not possible to take the derivative $(\partial E_T/\partial\alpha)_n$ directly. However, the quantity $(\partial E_T/\partial\alpha)_{\{\varphi_i\}}$ is accessible. To relate between the two quantities, we express E_T as a functional of α and n, where the latter is itself a functional of α and $\{\varphi_i\}$: $E_T = E_T[\alpha, n[\{\varphi_i\}, \alpha]]$. Then, we obtain

$$\left(\frac{\partial E_T}{\partial\alpha}\right)_{\{\varphi_i\}} = \left(\frac{\partial E_T}{\partial\alpha}\right)_n + \int d^3r \left(\frac{\delta E}{\delta n(\vec{r})}\right)_\alpha \left(\frac{\partial n(\vec{r})}{\partial\alpha}\right)_{\{\varphi_i\}}.$$
(III.3)

On the right-hand side of this expression we recognize the first term to be $v_T^{(0)}$ and $v_T^{(1)}$ to be the first multiplicand of the second term. From Eq. (2), $(\partial n/\partial\alpha)_{\{\varphi_i\}} = |\varphi_{N_0+1}^{(\alpha)}|^2$. As a result,

$$v_T^{(0)} = \left(\frac{\partial E_T}{\partial\alpha}\right)_{\{\varphi_i\}} - \int |\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 v_T^{(1)}(\vec{r}) d^3r. \quad \text{(III.4)}$$

We remind that in the OEP formalism for the highest occupied orbital

$$\bar{v}_{T,N_0+1}^{(1)} := \int |\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 v_T^{(1)}(\vec{r}) d^3r =$$
$$= \int |\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 u_{T,N_0+1}(\vec{r}) d^3r =: \bar{u}_{T,N_0+1},$$
(III.5)

where

$$u_{T,N_0+1} = \frac{1}{g_{N_0+1}} \frac{1}{\varphi_{N_0+1}^{*(\alpha)}} \frac{\delta E_T}{\delta\varphi_{N_0+1}} \quad \text{(III.6)}$$

(see [4], Sec.II and [5]). An analytical form for $v_T^{(0)}$ can then be obtained from Eqs. (8) and (9). Using this relation, for the eH functional we find:

$$v_{eH}^{(0)} = -\frac{1}{2} \int\int \frac{|\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 |\varphi_{N_0+1}^{(\alpha)}(\vec{r'})|^2}{|\vec{r} - \vec{r'}|} d^3r d^3r', \quad \text{(III.7)}$$

and for the exc-functional:

$$v_{exc}^{(0)} = E_{xc}[\rho_1^{(\alpha)}] - E_{xc}[\rho_0^{(\alpha)}] - \int |\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 v_{xc}[\rho_1^{(\alpha)}] d^3r. \quad \text{(III.8)}$$

During the self-consistent numerical solution of the KS equations with the proposed functionals, the spatial constant $v_T^{(0)}$ can be omitted, as the addition of a constant to the potential does not affect the eigenfunctions, the density, or the total energy E. However, $v_T^{(0)}$ has to be taken into account when addressing KS eigenenergies, in particular when comparing the energy of the frontier orbital to the derivative $\partial E/\partial q$ (see definition in the main text), following the Janak and the IP theorems [6, 7], and when calculating the energy gap as $v_T^{(0)}$ varies with N_0 and thus does not cancel out.

The fact that a constant shift in the KS potential does not lead to a shift in the total energy of the system can be viewed in two different, equivalent ways. In one way, the total energy in DFT is expressed by definition as a sum of the Kohn-Sham kinetic energy, the electron-ion energy, the Hartree energy, and the exchange-correlation energy (see, e.g. Ref. [3], Eq. (7.2.1)). An additive constant in the potential does not affect the KS orbitals, which are obtained from solving the KS equation. Therefore, the density obtained from these orbitals is not affected either. Because all the energy ingredients, i.e. the kinetic, the ion-electron, Hartree, and xc-energy, depend only on the density and/or the KS orbitals, the energy does not change. Alternatively, the total energy in DFT can be obtained using the KS eigenenergies, as in Eq. (7.2.10) in Ref. [3]. In this approach, all eigenenergies are shifted by the same arbitrary constant C, which changes the total energy by $C \cdot N$, where N is the number of electrons. However, this is then compensated by the change in the last term of Eq. (7.2.10), which includes the difference between the xc-energy and the integral over the density-weighted xc-potential. Because the xc-potential shifts by the same constant C, this term yields a change of $-C \cdot N$, i.e., it is equal and opposite to the change in the eigenvalue term, such that the total energy is not affected.

The equations above can be generalized to the spin-polarized case, as well. Because in the spin-polarized version of DFT there exist two potentials, $v_{KS,\sigma}$, where $\sigma = \uparrow$ or $\downarrow$, there also exist two sets of orbitals, $\{\varphi_{i,\sigma}^{(\alpha)}\}$, two densities, n_σ, and also two statistical weights α_σ. As a result, Eq. (III.1) is generalized to be

$$v_{T,\sigma}(\vec{r}) = \left(\frac{\delta E_T}{\delta n_\sigma}\right)_{n_\tau} = \left(\frac{\partial E_T}{\partial\alpha_\sigma}\right)_{n_\tau,\alpha_\tau} + \left(\frac{\delta E_T}{\delta n_\sigma(\vec{r})}\right)_{n_\tau,\alpha_\tau}^{\alpha_\sigma},$$
(III.9)

where τ refers to the other spin channel than σ. Other equations of this section can be generalized accordingly; In particular, Eq.(III.4) reads:

$$v_{T,\sigma}^{(0)} = \left(\frac{\partial E_T}{\partial\alpha_\sigma}\right)_{\substack{\{\varphi_{i,\sigma}\} \\ \{\varphi_{i,\tau}\},\alpha_\tau}} - \int |\varphi_{N_0+1,\sigma}^{(\alpha_\sigma)}(\vec{r})|^2 v_{T,\sigma}^{(1)}(\vec{r}) d^3r.$$
(III.10)

We stress, however, that in all formalism presented in the main text and here only the α of one spin channel is allowed to be fractional.

IV. NUMERICAL DETAILS ON CALCULATION OF THE SYSTEMS H_2 AND C

The calculations presented in this work were performed using the DARSEC [18] code [8]. This program allows to

perform spin-polarized all-electron DFT calculations for single atoms and diatomic molecules using the real-space approach [9–11] with a prolate-spheroidal grid [8, 12–14].

In all calculations the total energy E and the highest occupied orbital energy, ε_{ho}, were obtained within the numerical error of 1 mRy. The bond length of H_2 was found by relaxation to be 1.45 Bohr for LSDA (and therefore, by definition, also for eLSDA), and 1.39 Bohr for the EXX functional. This result is in close correspondence with previous calculations (see Ref. [8] and references therein). The bond length was kept unchanged when varying the number of electrons in the system.

Calculations with the orbital-dependent functionals, eLSDA and EXX, were performed using the OEP procedure exactly with the S-iteration method [15, 16] and the Krieger-Li-Iafrate (KLI) approximation [17], which is less demanding computationally than a full OEP calculation. The differences between the total energy results obtained in the two methods were within the numerical accuracy of 1 mRy for eLSDA and within 4 mRy for EXX. This finding is consistent with a previous observation [16] that KLI deviations from exact OEP results for ground-state energies are generally small. In any case, the remaining deviation of EXX results from the straight line condition is surely not just due to the use of KLI.

This is because for the H_2 system, with (at most) one electron per spin channel, the OEP result is identical to the KLI one as the OEP orbital-shifts vanish, and yet deviation from linearity remains.

Furthermore, we note that incorporating the additional potential term $v^{(0)}$ introduced in this work (Eq. (10) in the main text) in the OEP calculation does not require any other changes to the standard OEP procedure, or approximations thereof. Because $v^{(0)}$ is spatially uniform, it does not affect the KS orbitals and merely shifts the KS eigenvalues.

In the calculations performed for the C atom, it was assumed that the neutral C has a spin $S_z = 1$, the ion C^+ has the spin of $S_z = \frac{1}{2}$, and for the ion C^{++}, $S_z = 0$. Therefore, varying the number of electrons in the system was performed solely in the spin-up channel. In addition, the axial quantum number L_z was restricted to be 0 for $q = -2...-1$, and increased linearly with q for $q = -1...0$, to obtain $L_z = 1$ for the neutral C atom. Calculations with other values of L_z were checked as well: the total energy they produced differed from the reported values by less than 4 mRy. These restrictions for the C system assured that the calculation is performed with an ensemble of two states, which was the one considered in the main text.

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