I. INTRODUCTION, DEFINITIONS AND OUTLINE

Combining low computational cost with reasonable accuracy for many molecules and solids, density functional theory (DFT) [1, 2] has become a particularly successful approach for electronic-structure calculations, both in chemistry and in physics. In DFT, the exact electron energy $E$ can be in principle obtained by solving single-particle Schrödinger equations (relevant, for example, for biomolecules and layered materials), and of localization effects due to strong electronic correlations, as those occurring in Mott insulators or in low-density nanodevices.

An exact expression for the xc functional is the coupling-constant integral [6–8],

$$E_{xc}[\rho] = \int_0^1 d\alpha W_\alpha[\rho].$$

The integrand is the $\alpha$-dependent density functional

$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho]|\hat{V}_{ee}|\Psi_\alpha[\rho]\rangle - U[\rho],$$

with the operator of the electronic Coulomb repulsion,

$$\hat{V}_{ee} = \frac{e^2}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1 - \delta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and the continuum functional of the Hartree energy,

$$U[\rho] = \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{\rho(\mathbf{r})\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|}. \quad (4)$$

The crucial quantity in Eq. (2) is the $\alpha$-dependent wave function

$$\Psi_\alpha[\rho] = \Psi_\alpha[\rho]; \mathbf{r}_1, \ldots, \mathbf{r}_N; \sigma_1, \ldots, \sigma_N),$$

where the $\mathbf{r}_n$ and the $\sigma_n$, respectively, are spatial and spin coordinates of the electrons. Out of all antisymmetric $N$-electron wave functions $\Psi$ that are associated with the same given electron density $\rho$, $\Psi_\alpha[\rho]$ denotes the one that yields the minimum expectation of $\hat{T} + \alpha \hat{V}_{ee}$ [9], with the kinetic-energy operator $\hat{T} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2$,

$$\langle \Psi_\alpha[\rho]|\hat{T} + \alpha \hat{V}_{ee}|\Psi_\alpha[\rho]\rangle = \min_{\Psi = \rho - \langle\hat{T} + \alpha \hat{V}_{ee}|\Psi\rangle. \quad (6)$$

If the density $\rho$ is $\alpha$-representable for all $\alpha \geq 0$, there exists an $\alpha$-dependent external potential $v_{ext}^\alpha(\rho, \mathbf{r})$ such that $\Psi_\alpha[\rho]$ is the ground state of the Hamiltonian

$$\hat{H}_\alpha[\rho] = \hat{T} + \alpha \hat{V}_{ee} + \sum_{i=1}^N v_{ext}^\alpha(\rho, \mathbf{r}_i). \quad (7)$$

By construction, this Hamiltonian has for all $\alpha \geq 0$ the same ground-state density $\rho = \rho(\mathbf{r})$ as the real system with $\alpha = 1$.

At the non-interacting limit $\alpha = 0$, the ground state of $\hat{H}_\alpha[\rho]$ is, in most cases, the single Slater determinant $\Psi_0[\rho]$ with the $N$ occupied Kohn-Sham orbitals. Consequently,

$$E_x[\rho] = W_0[\rho] = \langle \Psi_0[\rho]|\hat{V}_{ee}|\Psi_0[\rho]\rangle - U[\rho] \quad (8)$$
is the functional of the DFT exchange energy.

For \( \alpha > 0 \), \( \Psi_\alpha[\rho] \) is no longer a Slater determinant of single-particle orbitals, but a correlated \( N \)-electron wave function. As \( \alpha > 0 \) grows, the electron-electron repulsion in the state \( \Psi_\alpha[\rho] \) increases. So does the average distance \( \langle |r_i - r_j| \rangle \) between two electrons. Consequently, for \( N > 1 \), the expectation of \( \hat{V}_{ee} \) in Eq. (2) must be a monotonically decreasing function of \( \alpha \).

The quantity

\[
E_{c}^{\text{GL2}}[\rho] = \frac{1}{2} \frac{d}{d\alpha} W_\alpha[\rho] \bigg|_{\alpha=0}
\]

is the 2nd-order correlation energy in terms of the density \( \alpha \)-strength, \( \alpha \).

The functional \( E_{c}^{\text{GL2}}[\rho] \) can be expressed in terms of the KS single-particle orbitals, but, in contrast to \( E_\alpha[\rho] \), it requires also all the unoccupied orbitals,

\[
E_{c}^{\text{GL2}}[\rho] = -\sum_{k=1}^{\infty} \frac{|\langle \Psi_0^{k}[\rho]| \hat{V}_{ee} - \hat{V}_{H}[\rho] - \hat{V}_{c}[\rho] |\Psi_0[\rho]\rangle|^2}{E_{c}^{k} - E_{0}}.
\]

Here, \( \Psi_0^{k}[\rho] \) is the \( k \)-th excited state and \( E_{c}^{k} \) the corresponding eigenvalue (while \( E_0 \) is the ground-state energy) of the non-interacting Hamiltonian \( H_0[\rho] \). The operators \( \hat{V}_{H}[\rho] = \sum_{i=1}^{N} \hat{v}_{H}(\rho; \mathbf{r}_i) \) and \( \hat{V}_{c}[\rho] = \sum_{i<j}^{N} \hat{v}_{c}(\rho; \mathbf{r}_i, \mathbf{r}_j) \), respectively, represent the Hartree potential,

\[
\hat{v}_{H}(\rho; \mathbf{r}) = \frac{\delta U(\rho)}{\delta \rho(\mathbf{r})} = e^2 \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\]

and the exchange potential,

\[
\hat{v}_{c}(\rho; \mathbf{r}) = \frac{\delta E_{x}[\rho]}{\delta \rho(\mathbf{r})}.
\]

Since the exchange functional \( E_{x}[\rho] \) is not known explicitly in terms of the density \( \rho \), but only implicitly via the KS orbitals [Eq. (8)], the evaluation of the function \( v_{c}(\rho; \mathbf{r}) \) for a given density \( \rho \) is a non-trivial problem (see, e.g., [12–17]). The resulting weak-interaction expansion of \( W_0[\rho] \) is then

\[
W_\alpha[\rho] = E_{c}[\rho] + 2E_{c}^{\text{GL2}}[\rho]\alpha + \ldots \quad (\alpha \to 0).
\]

The functional \( W_\alpha[\rho] \) and its exact properties have always played a central role for the construction of approximate \( E_{xc}[\rho] \) (see, e.g., [18–22]). Although the integration over \( \alpha \) in Eq. (1) runs between 0 and 1, we can consider values of \( \alpha \) larger than the physical interaction strength, \( \alpha > 1 \). In particular, the strong-interaction (or low-density) limit of DFT is defined as the \( \alpha \to \infty \) limit of \( W_\alpha[\rho] \). It has been shown that in this limit the leading terms in \( W_\alpha[\rho] \) are [23–27],

\[
W_\alpha[\rho] = W_\infty[\rho] + \frac{W_\infty' \rho}{\sqrt{\alpha}} + \frac{W_\infty'' \rho}{\alpha} + \ldots \quad (\alpha \to \infty).
\]

While generally \( W_\infty'' \rho = 0 \) [23, 27, 28], the coefficients \( W_\infty[\rho] \) and \( W_\infty'[\rho] \) have been evaluated systematically for spherically symmetric \( N \)-electron densities [26, 27].

II. THE LIMIT \( \alpha \to -\infty \)

For \( \alpha < 0 \), the Hamiltonian (7) describes attractive electrons with a given ground-state density \( \rho = \rho(\mathbf{r}) \). To understand how attractive fermions can be forced to form a given smooth density distribution \( \rho \) by means of a local external potential \( v_{\text{ext}}(\rho; \mathbf{r}) \), we consider here the extreme case \( \alpha \to -\infty \).
A. The wave function $\Psi_\alpha[\rho]$ for $\alpha \to -\infty$

As their attraction becomes very strong ($\alpha \to -\infty$), we expect that the electrons in the state $\Psi_\alpha[\rho]$ form a compact “attractive-electron cluster” (AEC). With this, we mean that simultaneous measurement of their positions in this state will always yield $N$ points $r_1, \ldots, r_N$ in space that are very close to each other, much closer than any distance over which the density $\rho(\mathbf{r})$ changes appreciably. For $N = 2$, e.g., the AEC is a positronium-type object with an average distance of $\langle |r_1 - r_2| \rangle = \frac{2a_B}{|\alpha|}$ between the two electrons (where $a_B = \hbar^2/m_e c^2$ is the Bohr radius). Notice that here we are only interested in the mathematical limit $\alpha \to -\infty$ of the Hamiltonian (7), so that we disregard any relativistic effect.

Exploiting this concept of a compact AEC, we expect that, as $\alpha \to -\infty$, the external potential $v_{\text{ext}}^\alpha(\rho, \mathbf{r})$ approaches a smooth function of $\mathbf{r}$ which gives the quasi point-like AEC the probability distribution $\frac{1}{N} \rho(\mathbf{r})$, as pictorially sketched in Fig. 1. In order to formalize this idea, we write

$$
\sum_{i=1}^{N} v_{\text{ext}}^\alpha(\rho, r_i) \Psi_\alpha(\rho; r_1, \ldots, r_N; \sigma_1, \ldots, \sigma_N) \\
\approx N v_{\text{ext}}^\alpha(\rho, \mathbf{R}) \Psi_\alpha(\rho; r_1, \ldots, r_N; \sigma_1, \ldots, \sigma_N) \\
(\alpha \ll -1), \quad (15)
$$

where $\mathbf{R} = \frac{1}{N} \sum_{i=1}^{N} r_i$ is the center of mass of the $N$ electrons. The accuracy of this approximation grows indefinitely as $\alpha \to -\infty$, when the radius of the AEC tends to zero. Thus, we introduce relative Jacobi coordinates $s_n (n = 1, \ldots, N - 1)$ and the center-of-mass $s_N \equiv \mathbf{R}$,

$$
\begin{align*}
\rho_1 & = \frac{1}{n} \sum_{i=1}^{n} r_i - r_{n+1} & (1 \leq n < N), \\
\rho_N & = \frac{1}{N} \sum_{i=1}^{N} r_i \equiv \mathbf{R}.
\end{align*} \quad (16)$$

For $1 < n < N$, the inverse transformation reads

$$
\mathbf{r}_n = \mathbf{R} - \frac{n-1}{n} s_{n-1} + \sum_{\ell=n}^{N-1} \frac{s_{\ell}}{\ell + 1}, \quad (17)
$$

while for $n = 1$ and $n = N$ we have

$$
\begin{align*}
r_1 & = \mathbf{R} + \sum_{\ell=1}^{N-1} \frac{s_{\ell}}{\ell + 1}, \quad \mathbf{r}_N = \mathbf{R} - \frac{N-1}{N} s_{N-1}. \quad (18)
\end{align*}
$$

In terms of the Jacobi coordinates $s_1, \ldots, s_{N-1}, s_N \equiv \mathbf{R}$, the operator $\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2$ assumes the form

$$
\hat{T} = -\frac{\hbar^2}{2M} \nabla_\mathbf{R}^2 + \hat{T}_\text{rel}, \quad M = N m_e, \quad (20)
$$

where $\hat{T}_\text{rel}$ acts on the relative coordinates only,

$$
\hat{T}_\text{rel} = -\frac{\hbar^2}{2} \sum_{n=1}^{N-1} \frac{1}{m_n} \nabla_n^2, \quad m_n = \frac{n}{n+1} m_e. \quad (21)
$$

Also, the purely multiplicative operator $\hat{V}_{ee}$ of Eq. (3) depends on the relative coordinates only,

$$
\hat{V}_{ee} = \hat{V}_{ee}(s_1, \ldots, s_{N-1}), \quad (22)
$$

since $r_i - r_j$ is independent of $\mathbf{R}$, see Eqs. (18) and (19).

The resulting structure of the Hamiltonian (7), within the approximation (15), implies a product ansatz for the wave function $\Psi_\alpha[\rho]$ in terms of the new coordinates,

$$
\Psi_\alpha[\rho] \to \phi_\alpha(\rho; \mathbf{R}) \psi_\alpha(s_1, \ldots, s_{N-1}; \sigma_1, \ldots, \sigma_N) \quad (23)
$$

where $\phi_\alpha$ and $\psi_\alpha$ are, respectively, the lowest-eigenvalue solutions of the following Schrödinger Equations,

$$
\begin{align*}
\left\{ -\frac{\hbar^2}{2M} \nabla_\mathbf{R}^2 + N v_{\text{ext}}^\alpha(\rho; \mathbf{R}) \right\} \phi_\alpha & = E_{\text{cm}}^\alpha \phi_\alpha, \quad (24) \\
\left\{ \hat{T}_\text{rel} + \alpha \hat{V}_{ee}(s_1, \ldots, s_{N-1}) \right\} \psi_\alpha & = E_{\text{rel}}^\alpha \psi_\alpha. \quad (25)
\end{align*}
$$

Since $\phi_\alpha(\rho; \mathbf{R})$ is symmetric with respect to permutations of the electronic coordinates $r_n$, the second factor $\psi_\alpha$ of the wave function (23) must be anti-symmetric,

$$
\psi_\alpha(\ldots) = \frac{1}{\sqrt{N!}} \sum_{\pi \in \pi_N} (-1)^\pi \hat{P}_\pi \psi_\alpha(\ldots). \quad (26)
$$

Here, $\pi_N$ is the group of the $N!$ permutations $\pi$ of $N$ elements, and $(-1)^\pi$ is the sign of $\pi$. The operator $\hat{P}_\pi$ is defined by

$$
\hat{P}_\pi \psi_\alpha(\{s(r_1, \ldots, r_N)\}; \sigma_1, \ldots, \sigma_N) = \psi_\alpha(\{s(r_{\pi(1)}, \ldots, r_{\pi(N)})\}; \sigma_{\pi(1)}, \ldots, \sigma_{\pi(N)}), \quad (27)
$$
with the short-hand notation \( \{ s \} := s_1, \ldots, s_{N-1} \) and the explicit functions \( s_n = s_n(r_1, \ldots, r_N) \) of Eq. (16). To recover on the right-hand side a pure function of \( s_1, \ldots, s_{N-1} \) (and of the \( \sigma_n \)), the \( r_\nu(n) \) must be re-expressed in terms of the \( s_n \) by Eqs. (18) and (19), where \( s_n \) cancels out.

The factors \( \phi_\alpha \) and \( \psi_\alpha \) of the wave function (23) are addressed, respectively, in the following two subsections.

**B. The external potential \( v_{\text{ext}}^\alpha(\rho, \mathbf{r}) \) for \( \alpha \to -\infty \)**

In terms of the first factor \( \phi_\alpha \) in Eq. (23), the probability density of the electronic center-of-mass position \( \mathbf{R} \) in the wave function \( \Psi_\alpha[\rho] \) for \( \alpha \to -\infty \) is given by

\[
\rho_{\text{cm}}^\alpha(\rho, \mathbf{R}) \to \sum_{\sigma_1, \ldots, \sigma_N} \int d^3 s_1 \cdots \int d^3 s_{N-1} |\phi_\alpha(\rho)|^2
= |\phi_\alpha(\rho, \mathbf{R})|^2. \tag{28}
\]

For \( \alpha \to -\infty \), when the AEC becomes very compact (point-like), the function \( \rho_{\text{cm}}^\alpha(\rho, \mathbf{R}) \) must approach the electron density \( \rho(\mathbf{r}) \). Then, using \( \phi_\alpha(\mathbf{r}) = \sqrt{\rho_{\text{cm}}^\alpha(\rho, \mathbf{R})} \), Eq. (24) can be resolved for \( v_{\text{ext}}^\alpha(\rho, \mathbf{r}) \),

\[
\lim_{\alpha \to -\infty} v_{\text{ext}}^\alpha(\rho, \mathbf{r}) = \frac{E_{\text{cm}}}{N} + \frac{\hbar^2}{2m_eN^2} \frac{\nabla^2 \rho(\mathbf{r})}{\sqrt{\rho(\mathbf{r})}}. \tag{29}
\]

According to this result, the external potential \( v_{\text{ext}}^\alpha(\rho, \mathbf{r}) \) in the Hamiltonian (7) approaches a smooth and finite function \( v_{\text{ext}}^{-\infty}(\rho, \mathbf{r}) \), as \( \alpha \to -\infty \). The value \( E_{\text{cm}}^{-\infty} \) can be fixed by the condition \( v_{\text{ext}}^{-\infty}(\rho, \mathbf{r}) \to 0 \) for \( |\mathbf{r}| \to \infty \). Obviously, \( Nv_{\text{ext}}^{-\infty}(\rho, \mathbf{r}) \) is simply the external potential for a single particle with mass \( M = Nm_e \) (which is the AEC of the previous Subsec. II A) and ground-state density \( \rho_{\text{cm}}^\alpha(\rho, \mathbf{r}) \).

So far, we see that an external potential \( v_{\text{ext}}^\alpha(\rho, \mathbf{r}) \) can, for \( \alpha \to -\infty \), generate a given smooth density distribution \( \rho(\mathbf{r}) \) for \( N \) attractive electrons. The smooth distribution is achieved by the uncertainty in the center-of-mass position \( \mathbf{R} \) of the AEC. This picture becomes questionable in cases such as the stretched H\(_2\) molecule, where the density is separated spatially into several pieces.

**C. The integrand \( W_\alpha[\rho] \) for \( \alpha \to -\infty \)**

As we have seen in Subsec II A, as \( \alpha \to -\infty \), \( \Psi_\alpha[\rho] \) should be better and better approximated by the product ansatz of Eq. (23). Consequently, the expectation \( \langle \Psi_\alpha[\rho]|\hat{V}_{\text{ee}}|\Psi_\alpha[\rho] \rangle \) can be computed in this limit by using the second factor \( \psi_\alpha \) of Eq. (23), as \( \hat{V}_{\text{ee}} \) only depends on the relative coordinates. Thus, for \( \alpha \to -\infty \) we have

\[
W_\alpha[\rho] + U[\rho] \equiv \langle \Psi_\alpha[\rho]|\hat{V}_{\text{ee}}|\Psi_\alpha[\rho] \rangle \to \sum_{\sigma_1, \ldots, \sigma_N} \int d^3 s_1 \cdots \int d^3 s_{N-1} |\psi_\alpha(\ldots)|^2 \hat{V}_{\text{ee}}(s_1, \ldots, s_{N-1}). \tag{30}
\]

where we have integrated out the center of mass coordinate and used the normalization \( \int d^3 R |\phi_\alpha(\rho, \mathbf{R})|^2 = 1 \).

We now remark that the Schrödinger equation for \( \psi_\alpha \) of Eq. (25) is not affected by the details of the density function \( \rho(\mathbf{r}) \), but only by the electron number \( N = \int d^3 r \rho(\mathbf{r}) \), so that the same is true for its lowest-eigenvalue solution \( \psi_\alpha \) and thus for the right-hand side of Eq. (30). This means that, for all different densities \( \rho \) with the same electron number \( N \), the function \( W_\alpha + U[\rho] \) on the left-hand side of Eq. (30) has the same asymptote when \( \alpha \to -\infty \). This point is of course very appealing, but has obvious limitations that will be discussed in the next Subsec. II D.

To address the solution \( \psi_\alpha \) of Eq. (25), we consider the universal (i.e., density-independent) Hamiltonian

\[
\hat{H}_\alpha^N = \hat{T} + \alpha \hat{V}_{\text{ee}} \quad (\alpha < 0). \tag{31}
\]

\( \hat{H}_\alpha^N \) describes a system of \( N \) attractive electrons in the absence of any localizing external potential \( \hat{V}_{\text{ext}}(\mathbf{r}) \). Such a system has translational symmetry and a uniform ground-state density \( \bar{\rho} \). To make \( \bar{\rho} \) finite, we can introduce a normalization volume \( \Omega = N/\bar{\rho} \) and impose periodic boundary conditions on the wave function. In the ground state of \( \hat{H}_\alpha^N \), the \( N \) electrons are forming a “free” AEC whose center-of-mass position \( \mathbf{R} \) has a uniform probability distribution within \( \Omega \), with density \( \frac{\bar{\rho}}{\Omega} \).

Notice that for the Hamiltonian (31), Eq. (15) is not an approximation, since \( v_{\text{ext}}^{-\infty}(\rho, \mathbf{r}) \equiv 0 \). Consequently, the product on the right-hand side of Eq. (23), where the factors \( \phi_\alpha \) and \( \psi_\alpha \) satisfy Eqs. (24) [with \( v_{\text{ext}}^{-\infty} \equiv 0 \) and (25), respectively, represents the exact ground state \( \Psi_\alpha^N \) of \( \hat{H}_\alpha^N \), for all finite values of \( \alpha \leq 0 \). Therefore, Eq. (30) can be written as

\[
\langle \Psi_\alpha[\rho]|\hat{V}_{\text{ee}}|\Psi_\alpha[\rho] \rangle \rightarrow \langle \Psi_\alpha^N|\hat{V}_{\text{ee}}|\Psi_\alpha^N \rangle \quad (\alpha \to -\infty). \tag{32}
\]

Due to the universal form of the Hamiltonian (31), its ground-state wave functions \( \Psi_\alpha^N \) for different interaction strengths \( \alpha < 0 \) are related by a simple scaling law,

\[
\Psi_\alpha^N(\{r, \sigma\}) = |\alpha|^{3N/2} \Psi_{\alpha=-1}^N(\{(|\alpha|\mathbf{r}, \sigma\}) \tag{33}
\]

in the short-hand notation \( \{r, \sigma\} \equiv r_1, \ldots, r_N; \sigma_1, \ldots, \sigma_N \). The resulting scaling law for the ground-state energy \( E_\alpha^N \) of \( \hat{H}_\alpha^N \) reads

\[
E_\alpha^N = \alpha^2 E_{\alpha=-1}. \tag{34}
\]

Notice that \( E_\alpha^N \) is the eigenvalue in Eq. (25),

\[
\{\hat{T}_{\text{rel}} + \alpha \hat{V}_{\text{ee}}(s_1, \ldots, s_{N-1})\} \psi_\alpha = E_\alpha^N \psi_\alpha. \tag{35}
\]

The virial theorem, \( \langle \Psi_\alpha^N|\hat{T}|\Psi_\alpha^N \rangle = -\frac{1}{2} \langle \Psi_\alpha^N|\hat{\alpha}\hat{V}_{\text{ee}}|\Psi_\alpha^N \rangle \), yields \( E_\alpha^N = \frac{1}{2} \langle \Psi_\alpha^N|\hat{\alpha}\hat{V}_{\text{ee}}|\Psi_\alpha^N \rangle \) or

\[
\langle \Psi_\alpha^N|\hat{V}_{\text{ee}}|\Psi_\alpha^N \rangle = \frac{2}{\alpha} E_\alpha^N = 2 \alpha E_{\alpha=-1}. \tag{36}
\]
Consequently, according to Eq. (32), the integrand of Eq. (1) asymptotically approaches for $\alpha \to -\infty$ a linear function with slope $2E_{N_1}^N < 0$,

$$W_\alpha[\rho] = 2\alpha E_{N_1}^N - U[\rho] \quad (\alpha \to -\infty). \quad (37)$$

As said, since $E_{N_1}^N$ is the ground-state energy of a free AEC at $\alpha = -1$, it cannot depend on details of the density $\rho$, but only on the electron number $N = \int d^3r \rho(r)$. We discuss below the limitations of this result.

D. Limitations of the AEC solution

First of all, as already mentioned, the AEC picture breaks down when the density is composed of several disjointed subsystems (e.g., stretched molecules). In the case of non-interacting fragments, in order to be size consistent, the limit of Eq. (30) should apply separately to each subsystem, which is physically reasonable, but difficult to prove rigorously. The transition from a jointed to a disjointed system (e.g., during molecular stretching) remains also unclear.

An even more important point is the following. In order to be useful to construct approximations for $W_\alpha[\rho]$, the $\alpha \to -\infty$ asymptote of Eq. (30) should be approached in a continuous and smooth way starting from $\alpha = 1$ (i.e., without phase transitions). This is generally not true, so that often the state $\psi_\alpha$ which is smoothly connected with the physical ($\alpha = 1$) system is not the ground state of the hamiltonian of Eq. (25). As a simple example, consider the N atom. At $\alpha = 1$, we have $N_1 = 5$ spin-up electrons and $N_1 = 2$ spin-down electrons, but we may expect that the ground state of the attractive electron cluster corresponds to $N_1 = 4$, $N_1 = 3$, as pairing is usually energetically advantageous for an attractive interaction, so that we will have a spin-flip transition at $\alpha < 0$. This simple case might be solved in a spin-DFT framework (in which we look for the $\alpha < 0$ systems with the same spin densities of the physical system), but we may encounter much more difficult cases as the number of electrons increases, with possible “exotic” phases. An interesting point is that, however, the $\alpha \to -\infty$ potential $
u_\text{ext}^\alpha([\rho], \mathbf{r})$ of Eq. (29) is the same for all the excited states of the cluster, including the one continuously connected with the physical system, if such a state exists. Nonetheless, with all these limitations in mind, we may still expect that the results presented in the previous section be qualitatively correct for many interesting systems.

In simple cases such as closed-shell two- and four-electron systems with a reasonable compact density, we might expect a continuous connection between the limit of Eq. (37) and the $\alpha = 1$ case. In the next Sec. III, we construct a simple continuous interpolation between the two limits $\alpha \to \pm \infty$ and we use it to estimate $E_{\epsilon}^{\text{GL2}}[\rho]$ for spherical two- and four-electron densities. In the latter case, we will discuss the role of near-degeneracy effects.

III. $E_{\epsilon}^{\text{GL2}}[\rho]$ FROM THE LIMITS $\alpha \to \pm \infty$

We now construct an analytic model $W_{\alpha}^{\text{AR}}[\rho]$ (“AR” stands for “attraction-repulsion” here) that shares the properties (13), (14), and (37) with the unknown exact integrand $W_\alpha[\rho]$ of Eq. (1), which we assume here to be a continuous and smooth function of $\alpha$ also for $\alpha \leq 0$, even if we keep in mind the limitations of this assumption discussed in the previous Subsec. II D. In particular, our model will share the correct density-scaling behavior with the unknown exact integrand $W_\alpha[\rho]$, see Eq. (53) below. Since the inverse function is easier to model, we write

$$W_{\alpha}^{\text{AR}}[\rho] = f^{-1}(\alpha). \quad (38)$$

According to Eqs. (13), (14), and (37), respectively, this inverse function $f(w)$ must satisfy the conditions

$$f(w) \to \left(\frac{W_\infty'}{w - W_\infty}\right)^2 \quad (w \to W_\infty), \quad (39)$$

$$f(E_x) = 0 \quad (w = E_x), \quad (40)$$

$$f(w) \to \frac{w + U}{2E_{N_1}^N} \quad (w \to \infty). \quad (41)$$

Here, we have dropped the functional symbol $[\rho]$ for brevity, as we shall do in most of the following equations.

Eqs. (39) and (41) are satisfied by the preliminary choice

$$f_1(w) = \frac{w + U}{2E_{N_1}^N} + \left(\frac{W_\infty'}{w - W_\infty}\right)^2 \quad (42)$$

which, however, ignores condition (40). In particular, $f_1(w)$ approaches the asymptotic form of Eq. (41) too slowly, $f_1(w) = (w + U)/2E_{N_1}^N + O(e^{-w^2})$. Instead, we expect $f(w) = (w + U)/2E_{N_1}^N + O(e^{-w})$ or, equivalently,

$$W_\alpha[\rho] = 2\alpha E_{N_1}^N - U[\rho] + O(e^\alpha) \quad (\alpha \to -\infty). \quad (43)$$

This conjecture is based on Eq. (33), indicating that the size of the AEC shrinks by the factor $|\alpha|^{-1}$ as $\alpha \to -\infty$, while the external potential $\nu_{\text{ext}}^\alpha([\rho], \mathbf{r})$ approaches a smooth finite limit, see Eq. (29). Consequently, the point where the radius of the AEC becomes smaller than any distance $|\mathbf{r}|$ over which $\nu_{\text{ext}}^\alpha([\rho], \mathbf{r})$ changes appreciably, must be reached at some moderately negative value $\alpha_0[\rho]$ of the parameter $\alpha$,

$$W_\alpha[\rho] \approx 2\alpha E_{N_1}^N - U[\rho] \quad (\alpha < \alpha_0[\rho]). \quad (44)$$

This conjecture is also supported by the numerical data sets shown in Fig. 3, where $\alpha_0$ takes values $\approx -3.4$ (‘Sp3’) and $\approx -1.0$ (‘Sp2’). Accordingly, we modify Eq. (42),

$$f_2(w) = \frac{w + U}{2E_{N_1}^N} + \left(\frac{W_\infty'}{w - W_\infty}\right)^2 e^{-(w-W_\infty)/\Gamma}. \quad (45)$$

Note that the exponential factor in Eq. (45) equals 1 at $w = W_\infty[\rho]$, thus preserving the correct limit (39). Due
to the general scaling property of the exact $W_\alpha[\rho]$, see Eq. (53) below, the parameter $\Gamma = \Gamma[\rho]$ must scale the same way as $W_\infty[\rho]$, $\Gamma[p_\alpha] = \lambda \Gamma[\rho]$. Therefore, we set

$$\Gamma[\rho] = |W_\infty[\rho]|,$$

identifying the unknown number $\alpha_0[\rho]$ from Eq. (44) approximately with the zero of $W_\alpha[\rho]$,

$$W_{\alpha_0}[\rho] = 0 \quad \Leftrightarrow \quad f(0) \approx \alpha_0[\rho], \quad (47)$$

see Figs. 2 and 3.

To satisfy condition (40), too, we introduce an extra factor $h_B(w)$ with $h_B(W_\infty) = 1$,

$$f(w) = \frac{w + U}{2E_{N1}} + \left(\frac{W_\infty}{w - W_\infty}\right)^2 h_B(w) e^{-(w-W_\infty)/\Gamma}.$$ 

In terms of the number

$$B = \frac{E_x + U}{2 E_{N1}} \left( \frac{E_x - W_\infty}{W_\infty} \right)^2 e^{(E_x-W_\infty)/\Gamma} > 0, \quad (49)$$

we choose for $w \in [W_\infty, +\infty]$

$$h_B(w) = \begin{cases} 1 + (B - 1) \frac{E_x - W_\infty}{E_x - W_\infty} : & B \geq 1, \\ 1 + \left( \frac{1}{B} - 1 \right) \frac{E_x - W_\infty}{E_x - W_\infty}^{-1} : & B \leq 1. \end{cases} \quad (50)$$

Then, $h_B(W_\infty) = 1$, $h_B(E_x) = B$, and $h_B(w) > 0$ is monotonically increasing ($B > 1$) or decreasing ($B < 1$).

The function $W_\alpha^{AR}[\rho] = f^{-1}(\alpha)$ has five parameters: $E_{N1}^x$, $U[\rho]$, $E_x[\rho]$, $W_\infty[\rho]$, and $W'_\infty[\rho]$, and it is shown in Fig. 2. As an illustration, Fig. 3 shows the true integrand $W_\alpha[\rho]$ (dots), evaluated numerically for the systems ‘Sp2’ and ‘Sp3’ (see Appendix A). The accurate numerical values (dots) are compared with the model of Sec. III (solid curves).

$W_\alpha[\rho]$ (dots), evaluated numerically for the systems ‘Sp2’ and ‘Sp3’ (see Appendix A). For these systems, the evaluation of $W_\alpha[\rho]$ is straightforward, since their $\alpha$-dependent external potential $V_{ext}[\rho]$ in the Hamiltonian (7) is trivial and thus known from the beginning.

Since $2E_c^{GL2}[\rho] \equiv \frac{d}{d\alpha} W_\alpha[\rho] |_{\alpha=0} \approx 1/f'(E_x)$, our model $W_\alpha^{AR}[\rho]$ yields a simple prediction $E_c^{GL2}[\rho] \equiv \frac{1}{f'(E_x)}$ for the second-order correlation energy $E_c^{GL2}[\rho]$,

$$E_c^{GL2}[\rho] = E_{N1}^x \left( 1 + (E_x + U) \left( \frac{B'}{E_x - W_\infty} - \frac{1}{W_\infty} \right) \right)^{-1}$$

$$B' = \begin{cases} 1 + \frac{1}{B} & (B \geq 1), \\ 3 - B & (B \leq 1). \end{cases} \quad (51)$$

Unlike the exact functional $E_c^{GL2}[\rho]$ whose evaluation requires additional knowledge of all the unoccupied KS orbitals, the approximation (51) only depends on the $N$ occupied orbitals (via $E_x[\rho]$), on the universal number $E_{N1}^x$, and explicitly on the density $\rho$ itself. Nevertheless, the new functional has the correct scaling behavior of the exact $E_c^{GL2}[\rho]$ (only valid when the KS system does not become degenerate or quasi-degenerate),

$$\tilde{E}_c^{GL2}[\rho] = E_c^{GL2}[\rho], \quad (52)$$

where $\rho_\lambda[\rho] \equiv \lambda^3 \rho(\lambda \rho)$ (with $\lambda > 0$) is a scaled density. More generally, the model integrand $W_\alpha^{AR}[\rho]$ has the correct scaling property [37] of its exact counterpart $W_\alpha[\rho]$,

$$W_\alpha^{AR}[\rho] = \lambda W_\alpha^{AR}[\rho]. \quad (53)$$

This law has a simple graphical interpretation: Plotting $W_\alpha^{AR}[\rho]$ versus $\alpha$ amounts to zooming the corresponding...
plot of $W_d^{\text{AR}}[\rho]$ by the factor $\lambda$. This graphical property is satisfied by the function $f(u)$, Eq. (48) (and then also for its inverse, $W_{d}^{\text{AR}}[\rho]$), since we have the general scaling laws $U[\rho_\alpha] = \lambda U[\rho]$, $E_\infty[\rho_\alpha] = \lambda E_\infty[\rho]$, $W_\infty[\rho_\alpha] = \lambda W_\infty[\rho]$, and $W_\infty'[\rho_\alpha] = \lambda^{1/2} W_\infty'[\rho]$.

A. Application to $N = 2$ systems

For a closed-shell two-electron system with a reasonable compact density, the cluster energy $E_{N=2}^\infty$ needed in Eq. (37) can be calculated exactly: the AEC defines a positronium-like problem whose ground state energy is $E_2^2 = \frac{1}{4} $ Ha. Moreover, in this special case we expect that the $\alpha \to -\infty$ limit is reached smoothly from $\alpha = 1$.

In Table I we report the prediction of $E_{c}^{\text{GL2}}[\rho]$ from Eq. (51) for several two-electron densities, and we compare it with accurate values from the literature. The systems denoted ‘Sp2’ and ‘Sp3’ correspond to electrons confined on the surface of a sphere (in 2D and 3D, respectively) and are defined in Appendix A. For these systems exact values are available [35, 38, 39]. ‘Exp’ refers to the result for Be is quite accurate, yielding an estimate of $E_{c}^{\text{GL2}}[\rho]$ with an error of only 2 mHa, confirming the hypothesis that, also in this case, the $\alpha \to -\infty$ limit is reached smoothly from $\alpha = 1$. However, as the system starts to display strong near-degeneracy as in the case of Ne$^{6+}$, we see that the present model fails, making an error of 60% in the estimate of $E_{c}^{\text{GL2}}[\rho]$. When $Z_e$ continues to increase beyond the value $Z_e = 10$ considered here, the ground-state density becomes no longer pure-state $\nu$-representable, but only ensemble $\nu$-representable [45–50]. At this point, the definition of both $E_{c}[\rho]$ and $E_{c}^{\text{GL2}}[\rho]$ should change.

IV. CONCLUSIONS AND PERSPECTIVES

We have presented a comprehensive analysis of the DFT adiabatic connection at negative coupling strengths $\alpha$. In the extreme limit $\alpha \to -\infty$ we have found a simple and physically appealing solution, which, albeit suffering from limitations due to the complexity of the many-electron problem with attractive interaction, can be calculated exactly in the case of reasonably compact two-electron systems, and provides insight also when $N > 2$. As a first example of application of our results, we have shown that, for $N = 2$, the exact information at $\alpha \to -\infty$ can be used, in combination with the opposite $\alpha \to +\infty$ limit, to estimate the second-order correlation energy $E_{c}^{\text{GL2}}[\rho]$ without using virtual orbitals. The same procedure works very well also for the Be atom, but breaks down in the case of Ne$^{6+}$, because of strong near-degeneracy effects.

The analysis carried out here extends our knowledge on the exact properties of the exchange-correlation functional $E_{\infty}[\rho]$, and can be used to test and improve approximations. Another possible application of the present results could arise in the framework of a recently proposed approach to the many-electron problem that contains a mixture of Hartree-Fock and Hartree-Fock-Bogoliubov methods [51]. This approach is based on the splitting of the Coulomb electron-electron interaction $1/r$ as $-1/r + 2/r$. The attractive part $-1/r$ triggers the Hartree-Fock-Bogoliubov solution. An energy density functional to describe dynamical correlation is also added to the method [51]. For this latter point, the extension to negative coupling $\alpha$ of the adiabatic connection could prove useful in defining and constructing the appropriate
TABLE I: The AEC energies $E^{N}_{−3}$ and the coefficients $U[ρ]$, $E_{c}[ρ]$, $W_{∞}[ρ]$, and $W'_{∞}[ρ]$ of the expansions (37), (13), and (14), the dimensionless parameter $B$, Eq. (49), and the resulting predictions $E^{GL2}_{c}[ρ]$ of the second-order correlation energy $E^{GL2}_{c}[ρ]$ for various $D$-dimensional $N$-electron systems. The systems ‘Sp2’ and ‘Sp3’, here with radius $R = a_{B}$, are defined in Appendix A; ‘Exp’ refers to a hypothetic two-electron atom with ground state density $ρ(r) = e^{−r/a_{B}}/4πa_{B}^{3}$; ‘Hoo’ refers to the Hooke atom, consisting of two electrons in the external potential $v_{ext}(r) = k/4r^{2}$, with $k = 1/4$.

| System | $N$ | $D$ | $E^{N}_{−3}$ | $U[ρ]$ | $E_{c}[ρ]$ | $W_{∞}[ρ]$ | $W'_{∞}[ρ]$ | $B$ | $E^{GL2}_{c}[ρ]$ | $E^{GL2}_{c}[ρ]$ | error |
|--------|----|----|--------------|--------|------------|------------|----------|-----|----------------|----------------|-------|
| Sp2    | 2  | 2  | $−1.00$     | $2.000$| $−1.000$   | $−1.500$   | $0.250$   | 2.791| $−228.1$      | $−227.4$     | $−0.7$  |
| Sp3    | 2  | 3  | $−0.25$     | $1.500$| $−0.849$   | $−1.198$   | $0.375$   | 1.968| $−46.5$       | $−47.6$      | $+1.1$ |
| Exp    | 2  | 3  | $−0.25$     | $1.500$| $−0.849$   | $−1.198$   | $0.375$   | 1.968| $−46.5$       | $−47.6$      | $+1.1$ |
| Hoo    | 2  | 3  | $−0.25$     | $1.500$| $−0.849$   | $−1.198$   | $0.375$   | 1.968| $−46.5$       | $−47.6$      | $+1.1$ |
| He     | 2  | 3  | $−0.25$     | $1.500$| $−0.849$   | $−1.198$   | $0.375$   | 1.968| $−46.5$       | $−47.6$      | $+1.1$ |
| Ne8+   | 2  | 3  | $−0.25$     | $1.500$| $−0.849$   | $−1.198$   | $0.375$   | 1.968| $−46.5$       | $−47.6$      | $+1.1$ |
| Be     | 4  | 3  | $−1.255$    | $7.217$| $−2.673$   | $−4.021$   | $2.59$    | 0.6857| $−126.4$      | $−128.4$     | $+2.0$ |
| Ne6+   | 4  | 3  | $−1.255$    | $7.217$| $−2.673$   | $−4.021$   | $2.59$    | 0.6857| $−126.4$      | $−128.4$     | $+2.0$ |

energy functional needed in the method.

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APPENDIX A: TWO ELECTRONS ON THE SURFACE OF A SPHERE

‘Sp2’ is a system of two electrons that are confined to the 2D surface $S_{2}$ of a sphere with given radius $R$. Recently [35, 38, 39], this system has been studied extensively. It is of particular interest for DFT, since its 2D ground-state density for all values of the interaction strength $α ∈ R$ is distributed uniformly over the spherical surface. Consequently, the external potential $v_{ext}(ρ; r)$ in the Hamiltonian (7) is trivial and known from the beginning. The 2D confinement of these electrons, however, gives rise to an unusually large value [35, 38] of

$$E^{GL2}_{c}(R) = (4 ln 2 − 3) Ha = −227.4 mHa.$$  (A1)

This effect can be traced (see Fig. 3) to the strongly negative energy of a 2D AEC [35],

$$E^{-3}_{−1} = \begin{cases} \frac{-1}{4} Ha & \text{(2D)}, \\
\frac{-1}{16} Ha & \text{(3D)} \end{cases}$$  (A2)

While the value (A1) is independent of the spherical radius $R$, the remaining functionals of Table I are

$$E_{c}(R) = −\frac{e^{2}}{R} = −\frac{1}{2}U(R),$$
$$W_{∞}(R) = −\frac{3}{2} \frac{e^{2}}{R},$$
$$W'_{∞}(R) = \frac{1}{4} \left(\frac{a_{B}}{R}\right)^{3/2} \frac{e^{2}}{a_{B}}.$$  (A3)

with $R = a_{B}$ in Table I.

A similar, but more realistic two-electron system is ‘Sp3’ which has its electrons confined to the 3D surface $S_{3}$ of a sphere in 4D space,

$$S_{3} = \{ (x, y, z, u) ∈ R^{4} | x^{2} + y^{2} + z^{2} + u^{2} = R^{2} \}. \quad (A4)$$

Again, the ground-state density is distributed uniformly, but now in a 3D finite (curved) space $S_{4}$. Consequently, we obtain a value very close the one for the He atom (see Table I) [39, 52],

$$E^{GL2}_{c}(R) = −47.6 mHa.$$  (A5)

The remaining functionals of Table I are [52],

$$E_{s}(R) = −\frac{8}{3\pi} \frac{e^{2}}{R} = \frac{1}{2}U(R),$$
$$W_{∞}(R) = −\left(\frac{1}{2} − \frac{16}{3\pi}\right) \frac{e^{2}}{R},$$
$$W'_{∞}(R) = \frac{3}{8} \left(\frac{a_{B}}{R}\right)^{3/2} \frac{e^{2}}{a_{B}}.$$  (A6)

with $R = a_{B}$ in Table I.
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