

## Adiabatic connection at negative coupling strengths

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The adiabatic connection of density functional theory (DFT) for electronic systems is generalized here to negative values of the coupling strength  $\alpha$  (with *attractive* electrons). In the extreme limit  $\alpha \rightarrow -\infty$  a simple physical solution is presented and its implications for DFT (as well as its limitations) are discussed. For two-electron systems (a case in which the present solution can be calculated exactly), we find that an interpolation between the limit  $\alpha \rightarrow -\infty$  and the opposite limit of infinitely strong repulsion ( $\alpha \rightarrow +\infty$ ) yields a rather accurate estimate of the second-order correlation energy  $E_c^{\text{GL2}}[\rho]$  for several different densities  $\rho$ , without using virtual orbitals. The same procedure is also applied to the Be isoelectronic series, analyzing the effects of near degeneracy.

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### 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 density  $\rho = \rho(\mathbf{r})$  and ground-state energy  $E_N[v]$  of  $N$  interacting electrons in a given external potential  $v = v(\mathbf{r})$  can be, in principle, obtained by solving single-particle (“Kohn-Sham”) equations for noninteracting electrons. In the practical implementation of Kohn-Sham (KS) DFT, however, we have to rely on approximations for the density functional  $E_{xc}[\rho]$  of the exchange-correlation (xc) energy. Despite the large number of available approximations for this functional and of their successful applications, there are still important cases in which KS DFT can fail, which is why the quest for better xc functionals continues to be a very active research field (for recent reviews see Refs. [3–5]). For example, present-days KS DFT encounters problems in the treatment of near-degeneracy effects (rearrangement of electrons within partially filled levels, important for describing bond dissociation but also equilibrium geometries, particularly for systems with  $d$  and  $f$  unsaturated shells), in the description of van der Waals long-range interactions (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]

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

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

$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle - U[\rho], \quad (2)$$

with the operator of the electronic Coulomb repulsion

$$\hat{V}_{ee} = \frac{e^2}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1 - \delta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3)$$

and the continuum functional of the Hartree energy,

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

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

$$\Psi_\alpha[\rho] = \Psi_\alpha([\rho]; \mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N), \quad (5)$$

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  $\hat{T} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2$ ,

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

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

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

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 noninteracting 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 KS orbitals. Consequently,

$$E_x[\rho] \equiv W_0[\rho] = \langle \Psi_0[\rho] | \hat{V}_{ee} | \Psi_0[\rho] \rangle - U[\rho], \quad (8)$$

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  $\langle |\mathbf{r}_i - \mathbf{r}_j| \rangle$  between two electrons. Consequently, for  $N > 1$ ,

the expectation of  $\hat{V}_{ee}$  in Eq. (2) must be a monotonically decreasing function of  $\alpha$ ,  $\frac{d}{d\alpha} W_\alpha[\rho] < 0$ .

The quantity

$$E_c^{\text{GL2}}[\rho] \equiv \frac{1}{2} \frac{d}{d\alpha} W_\alpha[\rho]|_{\alpha=0}, \quad (9)$$

is the second-order correlation energy in the Görling-Levy perturbation expansion [10,11]. It can be expressed in terms of the KS single-particle orbitals, but, in contrast to  $E_x[\rho]$ , it requires also all the unoccupied orbitals

$$E_c^{\text{GL2}}[\rho] = - \sum_{k=1}^{\infty} \frac{|\langle \Psi_0^k[\rho] | \hat{V}_{ee} - \hat{V}_H[\rho] - \hat{V}_x[\rho] | \Psi_0[\rho] \rangle|^2}{E_0^k - E_0}. \quad (10)$$

Here,  $\Psi_0^k[\rho]$  is the  $k$ th excited state and  $E_0^k$  the corresponding eigenvalue (while  $E_0$  is the ground-state energy) of the noninteracting Hamiltonian  $\hat{H}_0[\rho]$ . The operators  $\hat{V}_H[\rho] = \sum_{i=1}^N v_H([\rho]; \mathbf{r}_i)$  and  $\hat{V}_x[\rho] = \sum_{i=1}^N v_x([\rho]; \mathbf{r}_i)$ , respectively, represent the Hartree potential

$$v_H([\rho]; \mathbf{r}) = \frac{\delta U[\rho]}{\delta \rho(\mathbf{r})} \equiv e^2 \int d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (11)$$

and the exchange potential

$$v_x([\rho]; \mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})}. \quad (12)$$

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  $v_x([\rho]; \mathbf{r})$  for a given density  $\rho$  is a nontrivial problem (see Refs. [12–17]). The resulting weak-interaction expansion of  $W_\alpha[\rho]$  is then

$$W_\alpha[\rho] = E_x[\rho] + 2E_c^{\text{GL2}}[\rho]\alpha + \dots \quad (\alpha \rightarrow 0). \quad (13)$$

The functional  $W_\alpha[\rho]$  and its exact properties have always played a central role for the construction of approximate  $E_{xc}[\rho]$  (see Refs. [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  $\alpha \rightarrow \infty$  limit of  $W_\alpha[\rho]$ . It was shown that, in this limit, the leading terms in  $W_\alpha[\rho]$  are [23–27]

$$W_\alpha[\rho] = W_\infty[\rho] + \frac{W'_\infty[\rho]}{\sqrt{\alpha}} + \frac{W''_\infty[\rho]}{\alpha} + \dots \quad (\alpha \rightarrow \infty). \quad (14)$$

While generally  $W''_\infty[\rho] = 0$  [23,27,28], the functionals  $W_\infty[\rho]$  and  $W'_\infty[\rho]$  were evaluated systematically for spherically symmetric  $N$ -electron densities [26,27]. This  $\alpha \rightarrow \infty$  expansion of  $W_\alpha[\rho]$  is useful in several ways. For example (even if treated in an approximate way [23]), it was used to build an exchange correlation functional (interaction-strength interpolation, or ISI) by interpolating  $W_\alpha[\rho]$  between  $\alpha \rightarrow 0$  [Eq. (13)] and  $\alpha \rightarrow \infty$ , yielding atomization energies of simple molecules with errors within  $\sim 3.4$  kcal/mol [29,30]. Moreover, by properly rescaling a given approximate functional  $E_{xc}[\rho]$ , it is possible to test its performance in the strong-interaction limit, thus adding a new constraint for building approximations [28,31,32]. More recently, the strong-interaction limit was used to directly address strongly

correlated systems [33,34] in a DFT framework completely different with respect to the traditional KS one.

In this work we aim at extending our knowledge on the functional  $W_\alpha[\rho]$  by studying its behavior for  $\alpha < 0$ , thus considering *attractive* electrons. In the very limit  $\alpha \rightarrow -\infty$ , we propose a rather simple and physically appealing solution, which can be evaluated exactly in the case of two-electron systems. The main interest in the exploration of this limit is to find new pieces of information on the unknown functional  $W_\alpha[\rho]$ . Similarly to previous work on the opposite  $\alpha \rightarrow \infty$  limit, we expect that our results will open new possibilities for improving state-of-the-art DFT approximations. Notice that, so far, the  $\alpha < 0$  case was only addressed in the special case of two electrons confined on the surface of a sphere, where accurate numerical calculations for  $\alpha \in (-\infty, \infty)$  were performed [35]. A functional tuned to reproduce these calculations also for  $\alpha < 0$  was recently proposed [36]. The present work fully extends these early results by addressing the  $\alpha \rightarrow -\infty$  limit in a general way.

The article is organized as follows. In Sec. II we present our solution for  $\Psi_\alpha[\rho]$ ,  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$  and  $W_\alpha[\rho]$  in the  $\alpha \rightarrow -\infty$  limit, discussing the implications for DFT, as well as the limitations of our approach. As a first application, we show in Sec. III that for two-electron systems the information on the  $\alpha \rightarrow -\infty$  limit can be used to get a rather accurate estimate of  $E_c^{\text{GL2}}[\rho]$  of Eq. (10) by simply interpolating between the  $\alpha \rightarrow \pm\infty$  limits and thus without using the unoccupied orbitals. The same procedure is also applied to the Be isoelectronic series and the role of near-degeneracy effects in this framework is discussed. Section IV is devoted to conclusions and perspectives.

## II. THE LIMIT $\alpha \rightarrow -\infty$

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  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$ , we consider here the extreme case  $\alpha \rightarrow -\infty$ .

### A. The wave function $\Psi_\alpha[\rho]$ for $\alpha \rightarrow -\infty$

As their attraction becomes very strong ( $\alpha \rightarrow -\infty$ ), 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  $\mathbf{r}_1, \dots, \mathbf{r}_N$  in space that are very close to each other, much closer than any distance over which the density  $\rho(\mathbf{r})$  changes appreciably. For  $N = 2$ , for example, the AEC is a positronium-type object with an average distance of  $\langle |\mathbf{r}_1 - \mathbf{r}_2| \rangle = \frac{2a_B}{|\alpha|}$  between the two electrons (where  $a_B = \hbar^2/m_e e^2$  is the Bohr radius). Notice that here we are only interested in the mathematical limit  $\alpha \rightarrow -\infty$  of the Hamiltonian (7) so that we disregard any relativistic effect.

Exploiting this concept of a compact AEC, we expect that, as  $\alpha \rightarrow -\infty$ , the external potential  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$  approaches a smooth function of  $\mathbf{r}$  which gives the quasipoint-like AEC

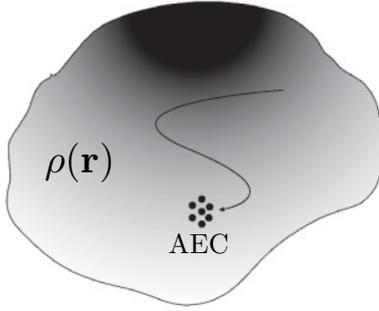


FIG. 1. As the coupling strength  $\alpha \rightarrow -\infty$ , the  $N$  electrons are expected to form a compact (point-like) AEC, whose center-of-mass position has the probability distribution  $\frac{1}{N}\rho(\mathbf{r})$ .

the probability distribution  $\frac{1}{N}\rho(\mathbf{r})$ , as pictorially sketched in Fig. 1.

To formalize this idea, we write

$$\begin{aligned} & \sum_{i=1}^N v_{\text{ext}}^{\alpha}([\rho], \mathbf{r}_i) \Psi_{\alpha}([\rho]; \mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N) \\ & \approx N v_{\text{ext}}^{\alpha}([\rho], \mathbf{R}) \Psi_{\alpha}([\rho]; \mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N) \end{aligned} \quad (\alpha \rightarrow -\infty), \quad (15)$$

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

$$\mathbf{s}_n = \frac{1}{n} \sum_{i=1}^n \mathbf{r}_i - \mathbf{r}_{n+1} \quad (1 \leq n < N), \quad (16)$$

$$\mathbf{s}_N = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \equiv \mathbf{R}. \quad (17)$$

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

$$\mathbf{r}_n = \mathbf{R} - \frac{n-1}{n} \mathbf{s}_{n-1} + \sum_{\ell=n}^{N-1} \frac{\mathbf{s}_{\ell}}{\ell+1}, \quad (18)$$

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

$$\mathbf{r}_1 = \mathbf{R} + \sum_{\ell=1}^{N-1} \frac{\mathbf{s}_{\ell}}{\ell+1}, \quad \mathbf{r}_N = \mathbf{R} - \frac{N-1}{N} \mathbf{s}_{N-1}. \quad (19)$$

In terms of the Jacobi coordinates  $\mathbf{s}_1, \dots, \mathbf{s}_{N-1}$ ,  $\mathbf{s}_N \equiv \mathbf{R}$ , the operator  $\hat{T} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2$  assumes the form

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

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

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

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

$$\hat{V}_{\text{ee}} = \tilde{V}_{\text{ee}}(\mathbf{s}_1, \dots, \mathbf{s}_{N-1}), \quad (22)$$

since  $\mathbf{r}_i - \mathbf{r}_j$  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

$$\Psi_{\alpha}[\rho] \rightarrow \phi_{\alpha}([\rho]; \mathbf{R}) \psi_{\alpha}(\mathbf{s}_1, \dots, \mathbf{s}_{N-1}; \sigma_1, \dots, \sigma_N), \quad (23)$$

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

$$\left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{R}^2} + N v_{\text{ext}}^{\alpha}([\rho], \mathbf{R}) \right\} \phi_{\alpha} = E_{\text{cm}}^{\alpha} \phi_{\alpha}, \quad (24)$$

$$\{ \hat{T}_{\text{rel}} + \alpha \tilde{V}_{\text{ee}}(\mathbf{s}_1, \dots, \mathbf{s}_{N-1}) \} \psi_{\alpha} = E_{\text{rel}}^{\alpha} \psi_{\alpha}. \quad (25)$$

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

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

Here,  $S_N$  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

$$\begin{aligned} & \hat{P}_{\pi} \psi_{\alpha}(\{\mathbf{s}(\mathbf{r}_1, \dots, \mathbf{r}_N)\}; \sigma_1, \dots, \sigma_N) \\ & = \psi_{\alpha}(\{\mathbf{s}(\mathbf{r}_{\pi(1)}, \dots, \mathbf{r}_{\pi(N)})\}; \sigma_{\pi(1)}, \dots, \sigma_{\pi(N)}), \end{aligned} \quad (27)$$

with the short-hand notation  $\{\mathbf{s}\} := \mathbf{s}_1, \dots, \mathbf{s}_{N-1}$  and the explicit functions  $\mathbf{s}_n = \mathbf{s}_n(\mathbf{r}_1, \dots, \mathbf{r}_N)$  of Eq. (16). To recover on the right-hand side a pure function of  $\mathbf{s}_1, \dots, \mathbf{s}_{N-1}$  (and of the  $\sigma_n$ ), the  $\mathbf{r}_{\pi(n)}$  must be re-expressed in terms of the  $\mathbf{s}_n$  by Eqs. (18) and (19), where  $\mathbf{s}_N$  cancels out.

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

## B. The external potential $v_{\text{ext}}^{\alpha}([\rho], \mathbf{r})$ for $\alpha \rightarrow -\infty$

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  $\alpha \rightarrow -\infty$  is given by

$$\begin{aligned} \rho_{\text{cm}}^{\alpha}([\rho], \mathbf{R}) & \rightarrow \sum_{\sigma_1, \dots, \sigma_N} \int d^3 s_1 \dots \int d^3 s_{N-1} |\phi_{\alpha} \psi_{\alpha}|^2 \\ & = \phi_{\alpha}([\rho], \mathbf{R})^2. \end{aligned} \quad (28)$$

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

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

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  $\alpha \rightarrow -\infty$ . The value  $E_{\text{cm}}^{-\infty}$  can be fixed by the condition  $v_{\text{ext}}^{\alpha}([\rho], \mathbf{r}) \rightarrow 0$  for  $|\mathbf{r}| \rightarrow \infty$ . Obviously,  $N v_{\text{ext}}^{-\infty}([\rho], \mathbf{r})$  is simply the external potential for a single particle with mass  $M = Nm_e$  (which is the AEC of the previous Sec. II A) and ground-state density  $\frac{1}{N} \rho(\mathbf{r})$ .

So far, we see that an external potential  $v_{\text{ext}}^{\alpha}([\rho], \mathbf{r})$  can, for  $\alpha \rightarrow -\infty$ , 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 functional $W_\alpha[\rho]$ for $\alpha \rightarrow -\infty$

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

$$\begin{aligned} W_\alpha[\rho] + U[\rho] &\equiv \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle \\ &\rightarrow \sum_{\sigma_1, \dots, \sigma_N} \int d^3 s_1 \cdots \int d^3 s_{N-1} |\psi_\alpha(\dots)|^2 \tilde{V}_{ee}(\mathbf{s}_1, \dots, \mathbf{s}_{N-1}), \end{aligned} \quad (30)$$

where we 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  $W_\alpha[\rho] + U[\rho]$  on the left-hand side of Eq. (30) has the same asymptote when  $\alpha \rightarrow -\infty$ . This point is, of course, very appealing, but has obvious limitations that will be discussed in the next Sec. II D.

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

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

$\hat{H}_\alpha^N$  describes a system of  $N$  attractive electrons in the absence of any localizing external potential  $v_{\text{ext}}(\mathbf{r})$ . 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  $\frac{1}{N}\bar{\rho}$ .

Notice that for the Hamiltonian (31), Eq. (15) is not an approximation, since  $v_{\text{ext}}([\bar{\rho}], \mathbf{r}) \equiv 0$ . Consequently, the product on the right-hand side of Eq. (23), where the factors  $\phi_\alpha$  and  $\psi_\alpha$  satisfy Eqs. (24) [with  $v_{\text{ext}} \equiv 0$ ] 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

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

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

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

in the short-hand notation  $\{\mathbf{r}, \sigma\} \equiv \mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N$ . The resulting scaling law for the ground-state energy  $E_\alpha^N$  of  $\hat{H}_\alpha^N$  reads

$$E_\alpha^N = \alpha^2 E_{\alpha=-1}^N. \quad (34)$$

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

$$\{\hat{T}_{\text{rel}} + \alpha \tilde{V}_{ee}(\mathbf{s}_1, \dots, \mathbf{s}_{N-1})\} \psi_\alpha = E_\alpha^N \psi_\alpha. \quad (35)$$

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

$$\langle \Psi_\alpha^N | \hat{V}_{ee} | \Psi_\alpha^N \rangle = \frac{2}{\alpha} E_\alpha^N = 2\alpha E_{-1}^N. \quad (36)$$

Consequently, according to Eq. (32), the integrand of Eq. (1) asymptotically approaches for  $\alpha \rightarrow -\infty$  a linear function with slope  $2E_{-1}^N < 0$ ,

$$W_\alpha[\rho] \rightarrow 2\alpha E_{-1}^N - U[\rho] \quad (\alpha \rightarrow -\infty). \quad (37)$$

As said, since  $E_{-1}^N$  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  $N = \int d^3 r \rho(\mathbf{r})$ . We discuss in the following 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 noninteracting fragments, to be size consistent the limit of Eq. (37) 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. To be useful to construct approximations for  $W_\alpha[\rho]$ , the  $\alpha \rightarrow -\infty$  asymptote of Eq. (37) 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  $N_\uparrow = 5$  spin-up electrons and  $N_\downarrow = 2$  spin-down electrons, but we may expect that the ground state of the AEC corresponds to  $N_\uparrow = 4$ ,  $N_\downarrow = 3$ , as pairing is usually energetically advantageous for an attractive interaction, so that we will have a spin-flip transition at  $\alpha \leq 0$ . As the number of electrons increases, we may encounter even more difficult cases with possible “exotic” phases. An interesting point is that, however, the  $\alpha \rightarrow -\infty$  potential  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$  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 Sec. III, we construct a simple continuous interpolation between the two limits  $\alpha \rightarrow \pm\infty$  and we use it to estimate  $E_c^{\text{GL2}}[\rho]$  for spherical two and four-electron densities. In the latter case, we will discuss the role of near-degeneracy effects.

### III. $E_c^{\text{GL2}}[\rho]$ FROM THE LIMITS $\alpha \rightarrow \pm\infty$

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 functional  $W_\alpha[\rho]$  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 Sec. IID. In particular, our model will share the correct density-scaling behavior with the unknown exact functional  $W_\alpha[\rho]$ , 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

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

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

$$f(w) \rightarrow \frac{w + U}{2E_{-1}^N} \quad (w \rightarrow \infty), \quad (41)$$

where  $w = f^{-1}(\alpha)$  and  $f(w) = f[f^{-1}(\alpha)] = \alpha$ . Here, we 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

$$f_1(w) = \frac{w + U}{2E_{-1}^N} + \left( \frac{W'_\infty}{w - W_\infty} \right)^2, \quad (42)$$

which, however, ignores condition (40). In particular,  $f_1(w)$  approaches the asymptotic form of Eq. (41) too slowly,  $f_1(w) = (w + U)/2E_{-1}^N + O(w^{-2})$ . Instead, we expect  $f(w) = (w + U)/2E_{-1}^N + O(e^{-w})$ , or equivalently,

$$W_\alpha[\rho] = 2\alpha E_{-1}^N - U[\rho] + O(e^\alpha) \quad (\alpha \rightarrow -\infty). \quad (43)$$

This conjecture is based on Eq. (33), indicating that the size of the AEC shrinks by the factor  $|\alpha|^{-1}$  as  $\alpha \rightarrow -\infty$ , while the external potential  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$  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  $v_{\text{ext}}^\alpha([\rho], \mathbf{r})$  changes appreciably, must be reached at some moderately negative value  $\alpha_0[\rho]$  of the parameter  $\alpha$ ,

$$W_\alpha[\rho] \approx 2\alpha E_{-1}^N - U[\rho] \quad (\alpha < \alpha_0[\rho]). \quad (44)$$

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)

$$f_2(w) = \frac{w + U}{2E_{-1}^N} + \left( \frac{W'_\infty}{w - W_\infty} \right)^2 e^{-(w - W_\infty)/\Gamma}. \quad (45)$$

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), the parameter  $\Gamma = \Gamma[\rho]$  must scale the same way as  $W_\infty[\rho]$ ,  $\Gamma[\rho_\lambda] = \lambda\Gamma[\rho]$ . Therefore, we set

$$\Gamma[\rho] = |W_\infty[\rho]|, \quad (46)$$

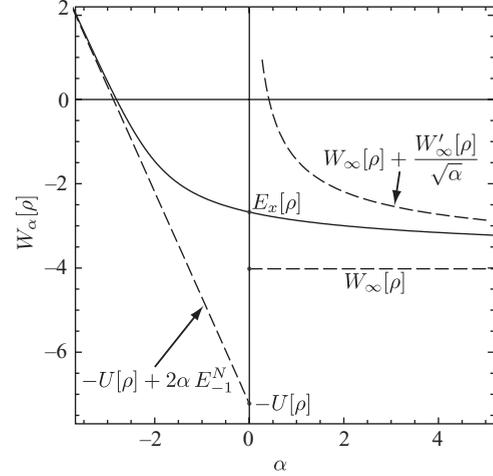


FIG. 2. The functional  $W_\alpha[\rho]$  (in Hartree atomic units) as a function of the dimensionless coupling strength parameter  $\alpha$  (solid curve), as modeled in Sec. III, using the five functionals  $E_x[\rho]$ ,  $U[\rho]$ ,  $W_\infty[\rho]$ ,  $W'_\infty[\rho]$ , and  $E_{-1}^N$  for the Be atom (see Table I).

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

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

see Figs. 2 and 3.

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

$$f(w) = \frac{w + U}{2E_{-1}^N} + \left( \frac{W'_\infty}{w - W_\infty} \right)^2 h_B(w) e^{-(w - W_\infty)/\Gamma}. \quad (48)$$

In terms of the number (with  $\Gamma = |W_\infty|$ )

$$B \equiv \frac{E_x + U}{-2E_{-1}^N} \left( \frac{E_x - W_\infty}{W'_\infty} \right)^2 e^{(E_x - W_\infty)/\Gamma} > 0, \quad (49)$$

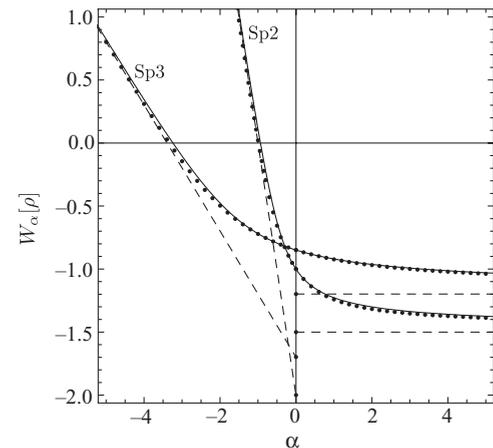


FIG. 3. The functional  $W_\alpha[\rho]$  (in Hartree atomic units) as a function of the dimensionless coupling strength parameter  $\alpha$  for the systems Sp2 and Sp3 defined in the Appendix. The accurate numerical values (dots) are compared with the model of Sec. III (solid curves).

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

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

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  $W_\alpha^{\text{AR}}[\rho] = f^{-1}(\alpha)$  has five parameters:  $E_{-1}^N$ ,  $U[\rho]$ ,  $E_x[\rho]$ ,  $W_\infty[\rho]$ , 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 the Appendix). For these systems, the numerical evaluation of the exact  $W_\alpha[\rho]$  is straightforward since their  $\alpha$ -dependent external potential  $v_{\text{ext}}^{(\alpha)}(\mathbf{r})$  in the Hamiltonian (7) is trivial and thus known from the beginning.

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

$$\tilde{E}_c^{\text{GL2}}[\rho] = E_{-1}^N \left[ 1 + (E_x + U) \left( \frac{B'}{E_x - W_\infty} - \frac{1}{W_\infty} \right) \right]^{-1} \quad (51)$$

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

Unlike the exact functional  $E_c^{\text{GL2}}[\rho]$  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  $E_{-1}^N$ , and explicitly on the density  $\rho$  itself. Nevertheless, the new functional has the correct scaling behavior of the exact  $E_c^{\text{GL2}}[\rho]$  (only valid when the KS system does not become degenerate or quasidegenerate)

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

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

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

TABLE I. The AEC energies  $E_{-1}^N$  and the functionals  $U[\rho]$ ,  $E_x[\rho]$ ,  $W_\infty[\rho]$ , and  $W'_\infty[\rho]$  of the expansions (37), (13), and (14), the dimensionless parameter  $B$ , Eq. (49), and the resulting predictions  $\tilde{E}_c^{\text{GL2}}[\rho]$  of the second-order correlation energy  $E_c^{\text{GL2}}[\rho]$  for various  $D$ -dimensional  $N$ -electron systems. The systems Sp $D$  ( $D = 2, \dots, 5$ ), here with radius  $R = a_B$ , are defined in the Appendix; ‘‘Exp’’ refers to a hypothetical two-electron atom with ground-state density  $\rho(r) = e^{-r/a_B}/4\pi a_B^3$ ; ‘‘Hoo’’ refers to the Hooke atom, consisting of two electrons in the external potential  $v_{\text{ext}}(\mathbf{r}) = \frac{k}{2}r^2$ , with  $k = \frac{1}{4}$ .

System	$N$	$D$	$E_{-1}^N$	$U[\rho]$	$E_x[\rho]$	$W_\infty[\rho]$	$W'_\infty[\rho]$	$B$	$\tilde{E}_c^{\text{GL2}}[\rho]$	$E_c^{\text{GL2}}[\rho]$	Error
Units	–	–			1 Ha = 27.21 eV			–		$10^{-3}$ Ha	$10^{-3}$ Ha
Sp2	2	2	–1.00	2.000	–1.000	–1.500	0.250	2.791	–228.1	–227.4	–0.7(0.3%)
Sp3	2	3	–0.25	1.698	–0.849	–1.198	0.375	1.968	–46.5	–47.6	+1.1(2.3%)
Sp4	2	4	–0.1111	1.6	–0.8	–1.1	0.5	1.702	–18.64	–19.18	+0.5(2.8%)
Sp5	2	5	–0.0625	1.55214	–0.77607	–1.05214	0.625	1.575	–9.87	–10.14	+0.3(2.7%)
Exp	2	3	–0.25	1.250	–0.625	–0.910	0.345	1.167	–43.4	–46.7	+3.3(7.1%)
Hoo	2	3	–0.25	1.030	–0.515	–0.743	0.208	1.682	–47.2	–50.5	+3.3(6.5%)
He	2	3	–0.25	2.049	–1.025	–1.500	0.621	1.649	–48.6	–47.5	–1.1(2.3%)
Ne <sup>8+</sup>	2	3	–0.25	12.055	–6.028	–8.794	8.792	1.631	–48.0	–46.7	–1.3(2.8%)
Be	4	3	–1.255	7.217	–2.673	–4.021	2.59	0.6857	–126.4	–128.4	+2.0(1.6%)
Ne <sup>6+</sup>	4	3	–1.255	21.742	–7.600	–11.563	12	0.8655	–127.5	–320.4	+193(60%)

This law has a simple graphical interpretation: Plotting  $W_\alpha^{\text{AR}}[\rho_\lambda]$  versus  $\alpha$  amounts to zooming the corresponding plot of  $W_\alpha^{\text{AR}}[\rho]$  by the factor  $\lambda$ . This graphical property is satisfied by the function  $f(w)$ , Eq. (48) (and then also for its inverse,  $W_\alpha^{\text{AR}}[\rho]$ ) since we have the general scaling laws  $U[\rho_\lambda] = \lambda U[\rho]$ ,  $E_x[\rho_\lambda] = \lambda E_x[\rho]$ ,  $W_\infty[\rho_\lambda] = \lambda W_\infty[\rho]$ , and  $W'_\infty[\rho_\lambda] = \lambda^{3/2} W'_\infty[\rho]$ .

### A. Application to $N = 2$ systems

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

In Table I we report the prediction of  $\tilde{E}_c^{\text{GL2}}[\rho]$  from Eq. (51) for several two-electron densities and we compare it with accurate values  $E_c^{\text{GL2}}[\rho]$  from the literature. The systems denoted ‘‘Sp $D$ ’’ ( $D = 2, \dots, 5$ ) correspond to electrons confined on the surface of a sphere in  $D$  dimensions and are defined in the Appendix A. For these systems exact values are available [35,38,39]. ‘‘Exp’’ refers to a hypothetical two-electron atom with ground-state density  $\rho(r) = e^{-r/a_B}/4\pi a_B^3$ , whose corresponding accurate  $E_c^{\text{GL2}}[\rho]$  is taken from Ref. [40]. ‘‘Hoo’’ refers to the Hooke atom, consisting of two electrons in the external potential  $v_{\text{ext}}(\mathbf{r}) = \frac{k}{2}r^2$ , with  $k = \frac{1}{4}$ . Its exact density is analytically known [41] and the corresponding  $E_c^{\text{GL2}}[\rho]$  is from Ref. [42]. The accurate densities for He and Ne<sup>8+</sup> and the corresponding values of  $E_c^{\text{GL2}}[\rho]$  are taken from the work of Colonna and Savin [43]. For all the densities considered here, the functionals  $W_\infty[\rho]$  and  $W'_\infty[\rho]$  were evaluated using the procedure described, respectively, in Refs. [26,27].

We see that for all the two-electron systems considered here, the functional  $\tilde{E}_c^{\text{GL2}}[\rho]$  of Eq. (51) is in very good agreement with the corresponding accurate values from the literature, with a maximum error of  $\sim 3$  mHa. Notice in particular how, for the Sp2 system, the unusually high value  $E_c^{\text{GL2}}[\rho] = -227.4$  mHa

is predicted from the unusually high energy  $E_{-1}^2 = -1$  Ha of the AEC in two dimensions (i.e., the slope of the corresponding inclined dashed line at  $\alpha < 0$  in Fig. 3). In contrast, the remaining four functionals  $U$ ,  $E_x$ ,  $W_\infty$ , and  $W'_\infty$  in Table I do not differ dramatically between Sp2 and Sp3. The same happens for the Sp4 and Sp5 systems: Their lower values of  $E_c^{\text{GL2}}[\rho]$  are well predicted by the lower energy of the AEC in four and five dimensions.

### B. Application to the Be series: The effect of near degeneracy

For the Be isoelectronic series, we have closed-shell  $N = 4$  systems so that we may still expect that the  $\alpha \rightarrow -\infty$  limit of Eq. (37) be approached smoothly from  $\alpha = 1$ . However, as the nuclear charge  $Ze$  increases, the  $2s$  and  $2p$  KS-orbital energies become closer and closer, resulting in a large increase of  $E_c^{\text{GL2}}[\rho]$ . Indeed, in this case the scaling property of Eq. (52), satisfied by the present model of Eq. (51), does not hold anymore, so that we can expect a failure of Eq. (51) for large  $Z$ .

As an illustration, we applied the model of Eq. (51) to the Be and the  $\text{Ne}^{6+}$  densities. The cluster energy for  $N = 4$  was estimated from a configuration interaction (CI) calculation [44]. The accurate values of  $U[\rho]$ ,  $E_x[\rho]$ , and  $E_c^{\text{GL2}}[\rho]$  are taken, in both cases, from the work of Colonna and Savin [43]. Using the same densities of Colonna and Savin [43], we calculated here the values of  $W_\infty[\rho]$  and  $W'_\infty[\rho]$ , following the procedures described, respectively, in Refs. [26,27].

We see that 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  $\alpha \rightarrow -\infty$  limit is reached smoothly from  $\alpha = 1$ . However, as the system starts to display strong near degeneracy as in the case of  $\text{Ne}^{6+}$ , we see that the present model fails, making an error of 60% in the estimate of  $E_c^{\text{GL2}}[\rho]$ . When  $Z$  continues to increase beyond the value  $Z = 10$  considered here, the ground-state density becomes no longer pure-state  $v$  representable, but only ensemble  $v$  representable [45–50]. At this point, the definition of both  $E_x[\rho]$  and  $E_c^{\text{GL2}}[\rho]$  should change.

## IV. CONCLUSION AND PERSPECTIVES

We present a comprehensive analysis of the DFT adiabatic connection at negative coupling strengths  $\alpha$ . In the extreme limit  $\alpha \rightarrow -\infty$  we find 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 the application of our results, we show that, for  $N = 2$ , the exact information at  $\alpha \rightarrow -\infty$  can be used, in combination with the opposite  $\alpha \rightarrow +\infty$  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  $\text{Ne}^{6+}$  because of strong near-degeneracy effects.

The analysis carried out here extends our knowledge on the exact properties of the exchange-correlation functional  $E_{xc}[\rho]$  and can be used to test and improve approximations. Another possible application of the present results can 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 needed in the method [51]. For this latter point, the extension to negative coupling  $\alpha$  of the adiabatic connection can prove useful in defining and constructing the appropriate energy functional needed in the method.

## ACKNOWLEDGMENTS

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## APPENDIX: TWO ELECTRONS ON THE SURFACE OF A SPHERE

Sp2 is a system of two electrons that are confined to the two-dimensional surface  $\mathcal{S}_2$  of a sphere with given radius  $R$ . Recently [35,38,39], this system was studied extensively. It is of particular interest for DFT since its two-dimensional ground-state density for all values of the interaction strength  $\alpha \in \mathbb{R}$  is distributed uniformly over the spherical surface. Consequently, the external potential  $v_{\text{ext}}^\alpha([\rho]; \mathbf{r})$  in the Hamiltonian (7) is trivial and known from the beginning. The two-dimensional confinement of these electrons, however, gives rise to an unusually large value [35,38] of

$$E_c^{\text{GL2}}(R) = (4 \ln 2 - 3) \text{ Ha} = -227.4 \text{ mHa}. \quad (\text{A1})$$

This effect can be traced (see Fig. 3) to the strongly negative energy  $E_{-1}^{N=2}$  of an AEC in  $D = 2$  dimensions. For any dimension  $D \geq 2$ , we have [52]

$$E_{-1}^{N=2}(D) = -\frac{1}{(D-1)^2} \text{ Ha}. \quad (\text{A2})$$

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

$$\begin{aligned} E_x(R) &= -\frac{e^2}{R} \equiv -\frac{1}{2}U(R), \\ W_\infty(R) &= -\frac{3}{2}\frac{e^2}{R}, \\ W'_\infty(R) &= \frac{1}{4}\left(\frac{a_B}{R}\right)^{3/2}\frac{e^2}{a_B}, \end{aligned} \quad (\text{A3})$$

with  $R = a_B$  in Table I.

A similar, but more realistic two-electron system is Sp3, which has its electrons confined to the three-dimensional surface  $\mathcal{S}_3$  of a sphere in four-dimensional space

$$\mathcal{S}_3 = \{(x, y, z, u) \in \mathbb{R}^4 \mid x^2 + y^2 + z^2 + u^2 = R^2\}. \quad (\text{A4})$$

Again, the ground-state density is distributed uniformly, but now in a three-dimensional finite (curved) space  $\mathcal{S}_3$ . Consequently, we obtain a value very close to the one for

the He atom (see Table I) [39,53,54]

$$E_c^{\text{GL2}}(R) = \left( \frac{4}{3} - \frac{368}{27\pi^2} \right) \text{Ha} = -47.6 \text{ mHa}; \quad (\text{A5})$$

the exact value was found recently by Loos and Gill [54]. The remaining functionals of Table I are [53]

$$\begin{aligned} E_x(R) &= -\frac{8}{3\pi} \frac{e^2}{R} \equiv -\frac{1}{2}U(R), \\ W_\infty(R) &= \left( \frac{1}{2} - \frac{16}{3\pi} \right) \frac{e^2}{R}, \\ W'_\infty(R) &= \frac{3}{8} \left( \frac{a_B}{R} \right)^{3/2} \frac{e^2}{a_B}, \end{aligned} \quad (\text{A6})$$

with  $R = a_B$  in Table I.

Even more generally, we may consider two electrons on the  $D$ -dimensional surface

$$S_D = \{ (x_1, \dots, x_{D+1}) | x_1^2 + \dots + x_{D+1}^2 = R^2 \}, \quad (\text{A7})$$

for  $D \geq 4$ . For  $D \in \{4, 5\}$ , for example, the corresponding exchange energies are [53]

$$\begin{aligned} E_x(4, R) &= -\frac{4}{5} \frac{e^2}{R} \equiv -\frac{1}{2}U(4, R), \\ E_x(5, R) &= -\frac{256}{105\pi} \frac{e^2}{R} \equiv -\frac{1}{2}U(5, R). \end{aligned} \quad (\text{A8})$$

The remaining coefficients for  $D \geq 4$  are given by [53]

$$\begin{aligned} W_\infty(D, R) &= \frac{e^2}{2R} - U(D, R), \\ W'_\infty(D, R) &= \frac{D}{8} \left( \frac{a_B}{R} \right)^{3/2} \text{Ha}. \end{aligned} \quad (\text{A9})$$

For  $D \in \{4, 5\}$ , we are comparing in Table I our resulting predictions for  $E_c^{\text{GL2}}(D, R)$  with the exact values, recently found by Loos and Gill [54],

$$\begin{aligned} E_c^{\text{GL2}}(4, R) &= \left( \frac{64}{75} \ln 2 - \frac{229}{375} \right) \text{Ha}, \\ E_c^{\text{GL2}}(5, R) &= \left( \frac{24}{35} - \frac{2650112}{385875\pi^2} \right) \text{Ha}. \end{aligned} \quad (\text{A10})$$

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