Description of a homogeneous electron gas with simple functionals of the one-particle density matrix

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The momentum distributions of a homogeneous electron gas, arising from a simple one-matrix functional for the electron-electron repulsion energy that generalizes the Hartree-Fock and Goedecker-Umrigar approximations, are analyzed in detail. Their properties are found to depend strongly on the exponent β that enters the functional. Smooth momentum distributions that, together with the corresponding energies per particle, exhibit simple scaling behavior with respect to the electron density ρ, are obtained only for $\frac{4}{5}<\beta<\frac{4}{3}$ and $\rho\leqslant\rho_{\mathrm{crit}}(\beta)$.

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In recent years, there has been a renewed interest in density-matrix functional theory [1–6]. In this formalism, the electron-electron repulsion energy $V_{\mathrm{ee}}[\Gamma]$ is the only contribution to the total electronic energy without a known explicit dependence on the one-particle reduced density matrix (the one-matrix) Γ [7,8]. One of the simplest approximate expressions for $V_{\mathrm{ee}}[\Gamma]$ reads

$$V_{\mathrm{ee}}[\Gamma]=\tfrac{1}{2}\sum_{p\neq q}[n_p n_q\langle\phi_p(\mathbf{x}_1)\phi_q(\mathbf{x}_2)|\hat{r}_{12}^{-1}|\phi_p(\mathbf{x}_1)\phi_q(\mathbf{x}_2)\rangle - (n_p n_q)^{\beta/2}\langle\phi_p(\mathbf{x}_1)\phi_q(\mathbf{x}_2)|\hat{r}_{12}^{-1}|\phi_q(\mathbf{x}_1)\phi_p(\mathbf{x}_2)\rangle], \tag{1}$$

where $\{\phi_p(\mathbf{x})\}$ and $\{n_p\}$ are, respectively, the natural spin orbitals and the occupation numbers that correspond to Γ [in Eq. (1), $\mathbf{x}$ stands for the combined spatial and spin coordinates]. The common Hartree-Fock approximation [9] is recovered for $\beta=2$, whereas setting $\beta=1$ yields the recently proposed Goedecker-Umrigar (GU) functional that, despite the lack of any empirical parameters, produces surprisingly accurate estimates of electron correlation energy in simple Coulombic systems [4].

In the absence of symmetry-breaking phenomena (such as the Wigner crystallization [10]), functional (1) leads to the energy per volume of a homogeneous electron gas equal to $\varepsilon=\varepsilon[n_\uparrow]+\varepsilon[n_\downarrow]$,

$$\varepsilon[n]=(16\pi^3)^{-1}\int n(k)k^2 d\mathbf{k} - (32\pi^5)^{-1}\int\int[n(k)n(k')]^{\beta/2}|\mathbf{k}-\mathbf{k}'|^{-2}d\mathbf{k}d\mathbf{k}', \tag{2}$$

where $n_\uparrow(k)$ and $n_\downarrow(k)$ are the spin-up and spin-down momentum distributions. Extremization of $\varepsilon[n]$ under the constraint of a given density ρ produces the Euler equation

$$\tfrac{1}{2}k^2-(2\pi^2)^{-1}(\beta/2)n(k)^{\beta/2-1}\int n(k')^{\beta/2}|\mathbf{k}-\mathbf{k}'|^{-2}d\mathbf{k}'=\mu, \tag{3}$$

where μ is the chemical potential. Only the solutions of Eq. (3) that satisfy the inequalities $0\leqslant n(k)\leqslant 1$ for all values of k are admissible for fermionic systems [11,12]. Such solutions are readily shown to satisfy the scaling equations [5]

$$n(k)=\rho^{1/(3\beta-2)}\eta[\rho^{(1-\beta)/(3\beta-2)}k], \tag{4}$$

$$e(\rho)=\rho^{(2\beta-2)/(3\beta-2)}, \tag{5}$$

$$\mu(\rho)=(5\beta-4)(3\beta-2)^{-1}e(\rho), \tag{6}$$

$$t(\rho)=(3\beta-4)(3\beta-2)^{-1}e(\rho),\qquad e_{\mathrm{xc}}(\rho)=2(3\beta-2)^{-1}e(\rho), \tag{7}$$

where $A_e(\beta)$ is a proportionality factor that depends only on β, $e(\rho)$ is the energy per particle [equal to $\varepsilon(\rho)/\rho$] as a function of ρ, and $t(\rho)$ and $e_{\mathrm{xc}}(\rho)$ are the corresponding kinetic and exchange-correlation energies. One immediately concludes from these scaling relationships that the admissible solutions of the Euler equation (3) exist only for $\frac{2}{3}<\beta<\frac{4}{3}$, provided $\rho\leqslant\rho_{\mathrm{crit}}(\beta)$ [5]. In all other instances, the physically admissible momentum distributions that minimize $\varepsilon[n]$ do not satisfy Eq. (3). This is indeed the case for $\beta=2$, as asserted by Lieb's theorem [13].

The Euler equation (3) was previously solved for $\beta=1$ [5], yielding

$$n(k)=512\pi\rho(1+4k^2)^{-4},\quad \rho_{\mathrm{crit}}(1)=(512\pi)^{-1},\qquad e(\rho)=\mu(\rho)=-t(\rho)=\tfrac{1}{2}e_{\mathrm{xc}}(\rho)=-\tfrac{1}{8}, \tag{8}$$

in accordance with Eqs. (4)–(7). In this Brief Report, we elucidate properties of the momentum distributions that correspond to other values of β.

A careful analysis of Eq. (3) furnishes the following exact asymptotics for $n(k)$:

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$$\lim_{k\to\infty} n(k)k^{-8/(\beta-2)}=\left[\beta(2\pi)^{-2}\int_0^\infty n(k')^{\beta/2}dk'\right]^{-2/(\beta-2)} \quad \text{for } \beta>\tfrac{6}{7} \tag{9a}$$

and

$$\lim_{k\to\infty} n(k)k^{-1/(\beta-1)} = [(5\beta-4)[2\beta(1-\beta)]^{-1}\sin[\pi(3\beta-2)/(2\beta-2)] \times\{1+\cos[\pi(3\beta-2)/(2\beta-2)]\}^{-1}]^{1/(\beta-1)} \quad \text{for } \beta<\tfrac{6}{7}. \tag{9b}$$

Consequently, as the integrals that enter the expression for $\varepsilon[n]$ diverge for $\beta<\frac{4}{5}$, the interval of β for which admissible solutions of Eq. (3) exist is further reduced to $(\frac{4}{5},\frac{4}{3})$. For $\beta=\frac{4}{5}$, the [3/5] Padé approximant

$$n(k)=(4\pi^2/25)(a+bk+ck^2+k^3)[(4\pi^2/25) \times a+dk+ek^2+fk^3+gk^4+k^5]^{-1}, \tag{10}$$

with $a=0.739\,487$, $b=0.156\,664$, $c=2.388\,30$, $d=0.244\,253$, $e=4.898\,84$, $f=1.644\,95$, and $g=3.833\,14$ [which satisfies the asymptotics (9b)], provides an accurate representation of $n(k)$ at $\rho=\rho_{\rm crit}(\frac{4}{5})\approx 0.0225$. The corresponding chemical potential equals -1.008×10^{-2}, giving rise to the asymptotic behavior of $-8.064\times10^{-4}(\beta-\frac{4}{5})^{-1}$ for $A_e(\beta)$ as $\beta\to\frac{4}{5}^+$ [compare Eq. (6)].

The trial function

$$\tilde{n}(k)=C(1+\zeta k^2)^{-\gamma}, \tag{11}$$

where ζ and γ are variational parameters, and C is a normalization constant, closely approximates the actual $n(k)$ for all $\beta\in[\frac{4}{5},\frac{4}{3}]$. For $\beta=1$, it is identical with the exact solution [Eq. (8)], whereas for $\beta=\frac{4}{5}$ it yields $n(k)$ with the proper asymptotics ($\gamma=\frac{5}{2}$), together with $\rho_{\rm crit}(\frac{4}{5})=4\pi/375\approx0.0335$ and $\lim_{\beta\to4/5^+}A_e(\beta)(\beta-4/5)=-2\pi^3 5^{-7}\approx-7.938\times10^{-4}$. Finally, for $\beta=\frac{4}{3}$, the variational exponent γ attains the value of 3, giving rise to $A_e(\frac{4}{3})=-(\pi/2)^{1/3}$ and $\lim_{\beta\to4/3^-}\rho_{\rm crit}(\beta)(\beta-\frac{4}{3})^{-3}=-(2048\pi)^{-1}$, both of which are exact.

The estimates for $A_e(\beta)$,

$$A_e(\beta)=\min_\gamma((2-3\beta)(4-3\beta)^{-1} \times\{\tfrac{1}{4}[6\pi/(2\gamma-5)]^{3\beta-4}(4-3\beta)^2 \times[\Gamma(\gamma)/\Gamma(\gamma-\tfrac{3}{2})]^{2\beta}[\Gamma(\gamma\beta/2-\tfrac{1}{2})/\Gamma(\gamma\beta/2)]^4 \times(\gamma\beta-2)^{-2}\}^{1/(3\beta-2)}), \tag{12}$$

furnished by the trial function (11), agree very well (Fig. 1) with those obtained numerically for $\beta>\frac{6}{7}$ by a constrained minimization of $\varepsilon[n]$ with respect to the variational parameters A, $\{B_j\}$, and k_0 of the more flexible ansatz

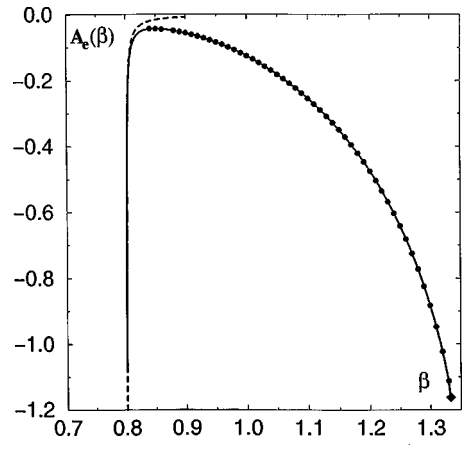

FIG. 1. $A_e(\beta)$ vs β. The solid line corresponds to the upper bound provided by Eq. (12), and the dots mark the results of constrained minimizations carried out with ansatz (13) [the best results for $\rho<\rho_{\rm crit}(\beta)$ are displayed]. The diamond stands for the exact value $A_e(\frac{4}{3})=-(\pi/2)^{1/3}$, and the broken line denotes the asymptotics of $-8.064\times10^{-4}(\beta-\frac{4}{5})^{-1}$.

$$\tilde{n}(k)=\cos^{8/(2-\beta)}\left((\pi/2)(\varphi+A)(\pi/2+A)^{-1} + \sum_{j=1}^{5} B_j[\varphi(\pi/2-\varphi)]^j\right), k=k_0\tan\varphi. \tag{13}$$

A similarly impressive agreement is observed among the computed estimates of $\rho_{\rm crit}(\beta)$ (Fig. 2).

Ansatz (13) also permits an accurate estimation of $e(\rho)$ for $\rho>\rho_{\rm crit}(\beta)$. The results of such a calculation for $\beta=1$ (which corresponds to the GU functional) are presented in Fig. 3. These data are well represented by the empirical fit

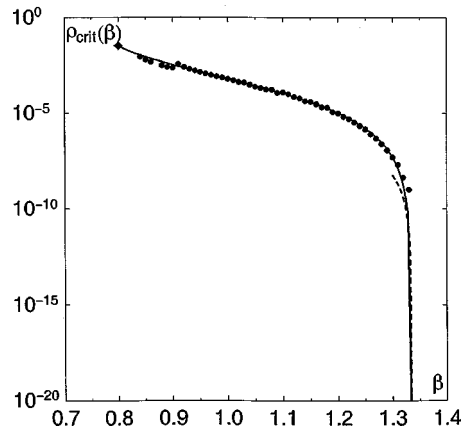

FIG. 2. $\rho_{\rm crit}(\beta)$ vs β. The meaning of the solid line and dots is the same as in Fig. 1. The diamond stands for the exact value $\rho_{\rm crit}(\frac{4}{3})=0.0225$, and the broken line denotes the asymptotics of $-(2048\pi)^{-1}(\beta-\frac{4}{3})^3$.

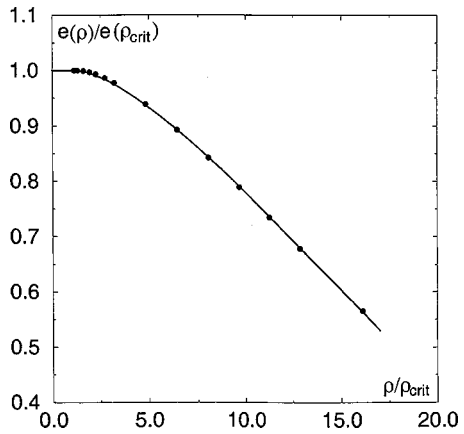

FIG. 3. $e(\rho)/e(\rho_{\mathrm{crit}})$ vs $\rho/\rho_{\mathrm{crit}}$ for $\beta=1$. The results of constrained minimizations carried out with ansatz (13) are marked by dots, and the solid line represents the fit given by Eq. (14).

$$e(\rho)/e(\rho_{\mathrm{crit}})=1-0.007\,331(\rho/\rho_{\mathrm{crit}}-1)^2 \times[1+0.186\,992(\rho/\rho_{\mathrm{crit}}-1)]^{-1} \quad (14)$$

for a wide range of $\rho\geqslant\rho_{\mathrm{crit}}(1)=(512\pi)^{-1}$.

In summary, the description of a homogeneous electron gas arising from functional (1) depends strongly on the exponent β. For $\beta\leqslant\frac{4}{5}$, the energy per volume $\varepsilon[n]$ given by Eq. (2) is unbound from below and thus unphysical. For $\frac{4}{5}<\beta<\frac{4}{3}$, $\varepsilon[n]$ is minimized by smooth momentum distributions provided $\rho\leqslant\rho_{\mathrm{crit}}(\beta)$. These momentum distributions, which become progressively narrower with increasing β (Fig. 4), and the corresponding values of $e(\rho)$, exhibit a simple scaling behavior. The magnitude of $\rho_{\mathrm{crit}}(\beta)$ rapidly decreases with β, becoming vanishingly small for $\beta=\frac{4}{3}$. For $\beta\geqslant\frac{4}{3}$, the physically admissible momentum distributions

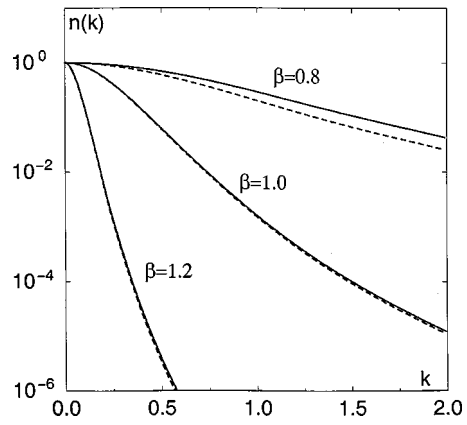

FIG. 4. The momentum distributions for $\rho=\rho_{\mathrm{crit}}(\beta)$. The solid lines stand for the trial function (11). For $\beta=1.0$ and 1.2, the broken lines mark the results of constrained minimizations carried out with ansatz (13), whereas for $\beta=0.8$ it represents the [3/5] Padé approximant [Eq. (10)].

that minimize $\varepsilon[n]$ no longer satisfy the Euler equation (3) for any value of ρ. Such is the case for $\beta=2$, where the Hartree-Fock $n(k)$ is discontinuous at the Fermi level.

We believe that the analysis presented in this Brief Report will facilitate a better understanding of the functionals of natural spinorbitals, and thus aid in the construction of better approximations for $V_{\mathrm{ee}}[\Gamma]$. One should note that many of the properties of $n(k)$ uncovered here [most notably their asymptotics (9)] are readily generalized to functionals in which the expression $(n_p n_q)^{\beta/2}$ that enters Eq. (1) is replaced by $\Omega(n_p,n_q)$ such that $\lim_{n_p\to 0}\Omega(n_p,n_q)n_p^{-\beta/2}=\omega(n_q)$; $0<\omega(n_q)<\infty$.

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