On the exactness of simple natural spin-orbital functionals for a high-density homogeneous electron gas

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Detailed analysis of the Euler equation pertaining to the natural spin-orbital functional of the form $V_{ee}=\frac{1}{2}\Sigma_{p\neq q}[n_p n_q J_{pq}-\Omega(n_p,n_q)K_{pq}]$, where V_{ee} is the electron-electron repulsion energy, $\{n_p\}$ are the occupancy numbers, and $\{J_{pq}\}$ and $\{K_{pq}\}$ are the respective Coulomb and exchange integrals, reveals that the large- and small-k asymptotics of the momentum distribution $n(k)$ of a high-density homogeneous electron gas rigorously determine the behavior of the function $\Omega(x,y)$ for each of its arguments approaching either 0 or 1. However, since the resulting $\Omega(x,y)$ does not give rise to $n(k)$ with a proper discontinuity at the Fermi level, such functionals cannot be exact for this system.

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I. INTRODUCTION

There has been recent interest[1–5] in a particular type of one-electron reduced density matrix (1-matrix) functionals for the electron-electron repulsion energy. These natural spin-orbital functionals are of the general form

$$V_{ee}[\Gamma]=\frac{1}{2}\sum_{p\neq q}[n_p n_q\langle\phi_p(x_1)\phi_q(x_2)|\hat{r}_{12}^{-1}|\phi_p(x_1)\phi_q(x_2)\rangle -\Omega(n_p,n_q)\langle\phi_p(x_1)\phi_q(x_2)|\hat{r}_{12}^{-1}|\phi_q(x_1)\phi_p(x_2)\rangle]. \tag{1}$$

where $\{\phi_p(x)\}$ and $\{n_p\}$ are, respectively, the natural spin orbitals and the occupation numbers that correspond to the 1-matrix Γ, and $\Omega(x,y)$ is a symmetrical function, $\Omega(y,x)=\Omega(x,y)$ [in Eq. (1) x stands for the combined spatial and spin coordinates; here and in the following, atomic units are employed]. The common Hartree-Fock approximation[6] is recovered for $\Omega(x,y)=xy$, whereas setting $\Omega(x,y)=(xy)^{1/2}$ yields the recently proposed Goedecker-Umrigar functional that, despite the lack of any empirical parameters, produces surprisingly accurate estimates of electron correlation energy in simple Coulombic systems.[1]

In the absence of symmetry-breaking phenomena (such as the Wigner crystallization),[7] the functional (1) leads to the energy per volume $e(\rho)$ of a spin-unpolarized homogeneous electron gas equal to $\min_{n\rightarrow\rho}\varepsilon[n]$,

$$\varepsilon[n]=(8\pi^3)^{-1}\int n(k)k^2 d\mathbf{k} -(16\pi^5)^{-1}\int\int\Omega(n(k),n(k'))|\mathbf{k}-\mathbf{k}'|^{-2}d\mathbf{k}\,d\mathbf{k}', \tag{2}$$

where ρ is the particle density and $n\equiv n(k)$ is the momentum distribution.[2,3] Extremization of $\varepsilon[n]$ under a density constraint produces the Euler equation

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

where $\mu\equiv\mu(\rho)=\partial e(\rho)/\partial\rho$ is the chemical potential. Only those solutions of Eq. (3) that satisfy the inequalities $0\leqslant n(k)\leqslant 1$ for all values of k are admissible for fermionic systems.[8,9]

For homogeneous functions $\Omega(x,y)$ such as $\Omega(x,y)=(xy)^{\beta}$, the solutions of Eq. (3) are unphysical for large values of ρ.[2,3] This failure has prompted our investigation into the connections between the analytical properties of the momentum distributions of a homogeneous electron gas at the high-density limit and those of the function $\Omega(x,y)$. The resulting set of constraints upon $\Omega(x,y)$, which turn out to be mutually incompatible, is presented in this paper.

II. THEORY

A. Properties of a high-density homogeneous electron gas

For a spin-unpolarized homogeneous electron gas with density ρ,[10]

$$k_F=(3\pi^2\rho)^{1/3},\quad (4\pi/3)r_s^3\rho=1,\quad \alpha k_F r_s=1, \tag{4}$$

where k_F is the Fermi momentum, r_s measures the mean interelectron distance and thus the correlation strength, and

$$\alpha=(4/9\pi)^{1/3}\approx 0.521\,06. \tag{5}$$

The weakly correlated (high-density) limit corresponds to $r_s\rightarrow 0$. At this limit, the correlation energy per volume $e_c(\rho)$ is given by the expansion[11,12]

$$e_c(\rho)/\rho=(1-\ln 2)\pi^{-2}\ln r_s+e_0+\cdots,\quad e_0=-0.047. \tag{6}$$

By virtue of the virial theorem,[13] the correlation contributions to the potential and kinetic energies per volume and to the chemical potential are

$$v_c(\rho)/\rho = 2(1-\ln 2)\pi^{-2}\ln r_s + [2e_0 + (1-\ln 2)\pi^{-2}] + \cdots, \tag{7}$$

$$t_c(\rho)/\rho = -(1-\ln 2)\pi^{-2}\ln r_s - [e_0 + (1-\ln 2)\pi^{-2}] + \cdots, \tag{8}$$

and

$$\mu_c(\rho) = (1-\ln 2)\pi^{-2}\ln r_s + [e_0 - \tfrac{1}{3}(1-\ln 2)\pi^{-2}] + \cdots, \tag{9}$$

respectively. Within the random-phase approximation (RPA) formalism, which is valid at the high-density limit,[14] the dependence of the momentum distribution $n(k)$ on r_s and the reduced momentum $\kappa = k/k_F$ is described by the equations[15,16]

$$\begin{aligned} n(k) = 1 &- (\alpha r_s/\pi^2)\kappa^{-1}\int_{1-\kappa}^{1+\kappa} q\,dq \int_0^{\pi/2} \{[q^2 + (\alpha r_s/\pi^2) Q(q,(\kappa+q/2)\tan\varphi)]^{-1} \\ &- [q^2 + (\alpha r_s/\pi^2) Q(q,(1-\kappa^2)\tan\varphi/2q)]^{-1}\} d\varphi - (\alpha r_s/\pi^2)\kappa^{-1}\int_{1+\kappa}^{\infty} q\,dq \\ &\times \int_0^{\pi/2} \{[q^2 + (\alpha r_s/\pi^2) Q(q,(\kappa+q/2)\tan\varphi)]^{-1} - [q^2 + (\alpha r_s/\pi^2) Q(q,(q/2-\kappa)\tan\varphi)]^{-1}\} d\varphi \quad \text{for} \quad \kappa<1, \end{aligned} \tag{10}$$

$$\begin{aligned} n(k) = (\alpha r_s/\pi^2)\kappa^{-1}\int_{\kappa-1}^{\kappa+1} q\,dq \int_0^{\pi/2} &\{[q^2 + (\alpha r_s/\pi^2) Q(q,(\kappa-q/2)\tan\varphi)]^{-1} \\ &- [q^2 + (\alpha r_s/\pi^2) Q(q,(\kappa^2-1)\tan\varphi/2q)]^{-1}\} d\varphi \quad \text{for} \quad \kappa>1, \end{aligned} \tag{11}$$

where

$$Q(x,y) = 2\pi\left\{1 + (2x)^{-1}[1+y^2-(x^2/4)]\ln\frac{(2+x)^2+(2y)^2}{(2-x)^2+(2y)^2} - y\arctan[(2+x)/(2y)] - y\arctan[(2-x)/(2y)]\right\}. \tag{12}$$

Equations (10) and (11) possess small-r_s asymptotics

$$n(k) = \begin{cases} 1-(\alpha r_s/\pi^2)^2 F_<(\kappa), & \kappa<1 \\ (\alpha r_s/\pi^2)^2 \quad F_>(\kappa), & \kappa>1 \end{cases} \tag{13}$$

that are valid for $|1-\kappa| \gg (4\alpha r_s/\pi)^{1/2}$. The functions $F_<(x)$ and $F_>(x)$, which are given by

$$\begin{aligned} F_<(x) = x^{-1}\int_{1-x}^{1+x} q^{-3}dq \int_0^{\pi/2} [Q(q,(1-x^2)\tan\varphi/2q) - Q(q,(x+q/2)\tan\varphi)] d\varphi \\ + x^{-1}\int_{1+x}^{\infty} q^{-3}dq \int_0^{\pi/2} [Q(q,(q/2-x)\tan\varphi) - Q(q,(x+q/2)\tan\varphi)] d\varphi \end{aligned} \tag{14}$$

and

$$F_>(x) = x^{-1}\int_{x-1}^{x+1} q^{-3}dq \int_0^{\pi/2} [Q(q,(x^2-1)\tan\varphi/2q) - Q(q,(x-q/2)\tan\varphi)] d\varphi, \tag{15}$$

have the properties

$$F_<(0) = 4\int_1^{\infty} q^{-4}dq \int_0^{\pi/2} Q(q,(q/2)\tan\varphi)\cos 2\varphi\, d\varphi \approx 4.112\,34, \tag{16}$$

$$\lim_{x\to\infty} F_>(x)x^8 = 8\pi^2/9 \approx 8.772\,98, \tag{17}$$

and

$$\begin{aligned} \lim_{x\to 1^-} F_<(x)x^2(1-x)^2 &= \lim_{x\to 1^+} F_>(x)x^2(x-1)^2 \\ &= 4\pi\int_1^{\infty} q^{-3}dq \int_0^{\pi/2} [R(q^{-1}\tan\varphi) - R(\tan\varphi)] d\varphi \\ &= (\pi^2/3)(1-\ln 2) \approx 1.009\,51, \end{aligned} \tag{18}$$

where

$$R(u)=(4\pi)^{-1}Q(0,u)=1-u\arctan u^{-1}. \tag{19}$$

In the region where the inequality $|1-\kappa|\gg(4\alpha r_s/\pi)^{1/2}$ is not satisfied, the behavior of $n(k)$ is described by the asymptotics[16]

$$n(k)=\begin{cases}1-(\alpha r_s/2\pi^2)G((4\alpha r_s/\pi)^{-1/2}(1-\kappa)), & \kappa<1\\ (\alpha r_s/2\pi^2)G((4\alpha r_s/\pi)^{-1/2}(\kappa-1)), & \kappa>1\end{cases} \tag{20}$$

that are valid for $|1-\kappa|\ll 1$. The function $G(x)$, which is given by

$$G(x)=-\int_0^\infty R'(u)[R(u)-x^2/u^2]^{-1}\times[\arctan u^{-1}-xu^{-1}R(u)^{-1/2}\times\arctan[R(u)^{1/2}x^{-1}]]du, \tag{21}$$

has the properties

$$G(0)=-\int_0^\infty R'(u)[R(u)]^{-1}\arctan u^{-1}du\approx 3.353\,34 \tag{22}$$

and

$$\lim_{x\to\infty}G(x)x^2=-\int_0^\infty R'(u)R(u)u\,du=(\pi/6)(1-\ln 2)\approx 0.160\,67, \tag{23}$$

The asymptotics (13) and (20) are readily reconciled by the following stitching:

$$n(k)=\begin{cases}1-(\alpha r_s/\pi^2)^2F_<(\kappa) & 0\leqslant\kappa\leqslant 1-\xi\\ 1-(\alpha r_s/2\pi^2)\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa)) & 1-\xi<\kappa<1\\ (\alpha r_s/2\pi^2)\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(\kappa-1)) & 1<\kappa<1+\xi\\ (\alpha r_s/\pi^2)^2F_>(k) & 1+\xi\leqslant\kappa<\infty\end{cases} \tag{24}$$

where ξ is an arbitrary cutoff such that $(4\alpha r_s/\pi)^{1/2}\ll\xi\ll 1$.

It is easy to show that this stitched momentum distribution is properly normalized and yields a correct logarithmic term in Eq. (8). On the other hand, since $n(k)$ given by Eqs. (10) and (11) arises from the RPA formalism that does not include exchange effects, its large-k asymptotics [compare Eq. (17)]

$$\lim_{k\to\infty}n(k)k^8=8\pi^2\rho^2 \tag{25}$$

is incompatible with the well-known relationship[17,18]

$$\lim_{k\to\infty}n(k)k^8=\tfrac{8}{9}(\alpha r_s/\pi)^2g(0)k_F^8=8\pi^2\rho^2g(0), \tag{26}$$

where $g(0)$ is the pair correlation function with the small-r_s asymptotics[19]

$$g(0)=\tfrac{1}{2}-5\pi^{-1}(\pi^2+6\ln 2-3)\alpha r_s-(3-\pi^2/4)\times(3\alpha r_s/2\pi)^2\ln r_s+O(r_s^2). \tag{27}$$

Combining Eqs. (26) and (27) yields

$$\lim_{k\to\infty}n(k)k^8=4\pi^2\rho^2[1-10\pi^{-1}(\pi^2+6\ln 2-3)\alpha r_s-(6-\pi^2/2)(3\alpha r_s/2\pi)^2\ln r_s+\cdots], \tag{28}$$

which at the limit of $r_s\to 0$ produces only half of the RPA value given by the right-hand side rhs of Eq. (25), as expected from the influence of the exchange effects[15] that also affect the constant e_0 in Eqs. (6)–(9).[12]

B. Constraints upon $\Omega(x,y)$ imposed by the large-k asymptotics of the momentum distribution

Stringent constraints are imposed upon $\Omega(x,y)$ by the large-k asymptotics of $n(k)$. At the large-k limit, Eq. (3) affords[3]

$$\lim_{k\to\infty}n(k)k^{4/(1-\beta)}=\left[\beta\pi^{-2}\int\omega(n(k'))d\mathbf{k}'\right]^{1/(1-\beta)}, \tag{29}$$

where

$$\omega(y)=\lim_{x\to 0}\Omega(x,y)x^{-\beta},\quad 0<|\omega(y)|<\infty. \tag{30}$$

Comparison of Eq. (29) with Eq. (28) immediately yields

$$\beta=\tfrac{1}{2} \tag{31}$$

and

$$\int \omega(n(k))d\mathbf{k}=4\pi^3\rho[1-5\pi^{-1}(\pi^2+6\ln 2-3)\alpha r_s - (3-\pi^{-2}/4)(3\alpha r_s/2\pi)^2\ln r_s+\cdots] \tag{32}$$

as a constraint for $\omega(x)$. In turn, setting $r_s=0$ in Eq. (32) produces

$$\int_0^{k_F}\omega(1)k^2dk+\int_{k_F}^{\infty}\omega(0)k^2dk=\pi^2\rho, \tag{33}$$

from which one readily infers that

$$\omega(1)=1,\quad \omega(0)=0. \tag{34}$$

Since $\Omega(x,y)$ is a symmetrical function, Eq. (30) implies that

$$C_1=\lim_{x\to 0}\omega(x)x^{-\beta},\quad 0<|C_1|<\infty \tag{35}$$

from which the latter of the conditions (34) also follows. On the other hand, the former of these conditions is consistent with the asymptotic behavior

$$\lim_{x\to 1}[1-\omega(x)](1-x)^{-\gamma}=C_2,\quad 0<|C_2|<\infty. \tag{36}$$

Thus, at the limit of small r_s [compare Eq. (24)],

$$\begin{aligned}\int \omega(n(k))d\mathbf{k}&=(4\pi/3)k_F^3-4\pi C_2\int_0^{k_F}[1-n(k)]^{\gamma}k^2dk+4\pi C_1\int_{k_F}^{\infty}[n(k)]^{1/2}k^2dk\\&=4\pi^3\rho\Bigg\{1-3C_2(\alpha r_s/\pi^2)^{2\gamma}\int_0^{1-\xi}[F_<(\kappa)]^{\gamma}\kappa^2d\kappa\\&\quad-3C_2(\alpha r_s/2\pi^2)^{\gamma}\int_{1-\xi}^{1}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{\gamma}\kappa^2d\kappa\\&\quad+3C_1(\alpha r_s/2\pi^2)^{1/2}\int_1^{1+\xi}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(\kappa-1))]^{1/2}\kappa^2d\kappa+3C_1(\alpha r_s/\pi^2)\int_{1+\xi}^{\infty}[F_>(\kappa)]^{1/2}\kappa^2d\kappa\Bigg\}.\end{aligned} \tag{37}$$

Owing to the asymptotics (18) and (23), the following estimates are valid for small r_s:

$$\begin{aligned}&\int_1^{1+\xi}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(\kappa-1))]^{1/2}\kappa^2d\kappa\\&=(4\alpha r_s/\pi)^{1/2}\int_0^{(4\alpha r_s/\pi)^{-1/2}\xi}[G(\kappa)]^{1/2}[(4\alpha r_s/\pi)^{1/2}\kappa+1]d\kappa\\&=(4\alpha r_s/\pi)^{1/2}[g_0+g_1(4\alpha r_s/\pi)^{1/2}]+(4\alpha r_s/\pi)^{1/2}[(\pi/6)(1-\ln 2)]^{1/2}\int^{(4\alpha r_s/\pi)^{-1/2}\xi}\kappa^{-1}[(4\alpha r_s/\pi)^{1/2}\kappa+1]d\kappa\\&=(4\alpha r_s/\pi)^{1/2}[g_0+g_1(4\alpha r_s/\pi)^{1/2}]+(4\alpha r_s/\pi)^{1/2}[(\pi/6)(1-\ln 2)]^{1/2}\{\xi+\ln[(4\alpha r_s/\pi)^{-1/2}\xi]\}\end{aligned} \tag{38}$$

and

$$\begin{aligned}\int_{1+\xi}^{\infty}[F_>(\kappa)]^{1/2}\kappa^2d\kappa&=f_2^>+[(\pi^2/3)(1-\ln 2)]^{1/2}\int_{1+\xi}(\kappa-1)^{-1}\kappa\,d\kappa=f_2^>+[(\pi^2/3)(1-\ln 2)]^{1/2}\int_{\xi}\kappa^{-1}(\kappa+1)d\kappa\\&=f_2^>-[(\pi^2/3)(1-\ln 2)]^{1/2}(\xi+\ln\xi),\end{aligned} \tag{39}$$

where g_0, g_1, and $f_2^>$ are integration constants. Consequently,

$$\begin{aligned}&3C_1(\alpha r_s/2\pi^2)^{1/2}\int_1^{1+\xi}[\kappa^{-2}G((4\pi r_s/\pi)^{-1/2}(\kappa-1))]^{1/2}\kappa^2d\kappa+3C_1(\alpha r_s/\pi^2)\int_{1+\xi}^{\infty}[F_>(\kappa)]^{1/2}\kappa^2d\kappa\\&=3C_1\{(2/\pi^3)^{1/2}\alpha r_s[g_0+g_1(4\alpha r_s/\pi)^{1/2}]+(3\pi^2)^{-1/2}(1-\ln 2)^{1/2}\alpha r_s\ln[(4\alpha r_s/\pi)^{-1/2}]+f_2^>(\alpha r_s/\pi^2)\}.\end{aligned} \tag{40}$$

Inspection of Eq. (32) reveals that the term proportional to $\alpha r_s \ln r_s$ in the rhs of Eq. (40) has to be canceled out by an analogous term in the remaining two contributions to the rhs of Eq. (37), hence $\gamma=\frac{1}{2}$. Upon insertion of the small-r_s estimates

$$\int_0^{1-\xi}[F_<(\kappa)]^{1/2}\kappa^2 d\kappa = f_2^< - [(\pi^2/3)(1-\ln 2)]^{1/2}(-\xi+\ln\xi) \tag{41}$$

and

$$\int_{1-\xi}^{1}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{1/2}\kappa^2 d\kappa = (4\alpha r_s/\pi)^{1/2}[g_0 - g_1(4\alpha r_s/\pi)^{1/2}] + (4\alpha r_s/\pi)^{1/2}[(\pi/6)(1-\ln 2)]^{1/2}\{-\xi+\ln[(4\alpha r_s/\pi)^{-1/2}\xi]\}, \tag{42}$$

these contributions become

$$3C_2(\alpha r_s/\pi^2)^{2\gamma}\int_0^{1-\xi}[F_<(\kappa)]^{\gamma}\kappa^2 d\kappa + 3C_2(\alpha r_s/2\pi^2)^{\gamma}\int_{1-\xi}^{1}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{\gamma}\kappa^2 d\kappa$$
$$= 3C_2\{f_2^<(\alpha r_s/\pi^2) + (2/\pi^3)^{1/2}\alpha r_s[g_0 - g_1(4\alpha r_s/\pi)^{1/2}] + (3\pi^2)^{-1/2}(1-\ln 2)^{1/2}\alpha r_s \ln[(4\alpha r_s/\pi)^{-1/2}]\}. \tag{43}$$

Combining Eqs. (37), (40), and (43) yields

$$\int \omega(n(k))d\mathbf{k} = 4\pi^3\rho\{1 + (3/\pi^2)^{1/2}(C_1 - C_2)(1-\ln 2)^{1/2}\alpha r_s \ln[(4\alpha r_s/\pi)^{-1/2}] + (18/\pi^3)^{1/2}(C_1 - C_2)g_0\alpha r_s + (72/\pi^4)^{1/2}(C_1 + C_2)g_1(\alpha r_s)^{3/2} + (3/\pi^2)(C_1 f_2^> - C_2 f_2^<)\alpha r_s\}, \tag{44}$$

from which one immediately concludes that $C_1 = C_2 = C$, where

$$C = -(5\pi/3)(\pi^2 + 6\ln 2 - 3)(f_2^> - f_2^<)^{-1} \approx -16.594\,7. \tag{45}$$

Since exchange effects reduce $n(k)$ for $k \gg k_F$ (see the preceding section), the actual value of the constant C is slightly more positive (by at most a few percent) than that given by the above equation.

In summary, the large-k asymptotics of the momentum distribution furnishes the following constraints upon the function $\Omega(x,y)$:

$$\Omega(x,y) \to C(xy)^{1/2} \quad \text{for } x\to 0, \quad y \to 0 \tag{46}$$

and

$$\Omega(x,y) \to [1 - C(1-x)^{1/2}]y^{1/2} \quad \text{for } x\to 1, \quad y\to 0, \tag{47}$$

where, quite unexpectedly, the constant C turns out to be negative.

C. Constraints upon $\Omega(x,y)$ imposed by the small-k asymptotics of the momentum distribution

The asymptotic behavior of $\Omega(x,y)$ for both of its arguments approaching unity is readily derived from the constraint

$$-(2\pi^2)^{-1}\int \Omega_x(n(0),n(k'))k'^{-2}d\mathbf{k}' = \mu, \tag{48}$$

which follows from the Euler equation (3) upon setting $k = 0$. The chemical potential of a high-density homogeneous electron gas is given by the equation

$$\mu(\rho) = \tfrac{1}{2}(\alpha r_s)^{-2} - \pi^{-1}(\alpha r_s)^{-1} + (1-\ln 2)\pi^{-2}\ln r_s + [e_0 - \tfrac{1}{3}(1-\ln 2)\pi^{-2}] + \cdots. \tag{49}$$

where the first two terms arise from the kinetic and exchange energy components, respectively. It should be emphasized that Eq. (48) is satisfied only for functionals that yield admissible momentum distributions as solutions of Eq. (3). Thus, as the lhs of the constraint (48), the Hartree-Fock functional yields

$$-2\pi^{-1}\int_0^{\infty}\Omega_x(n(0),n(k))dk = -2\pi^{-1}(\alpha r_s)^{-1}, \tag{50}$$

rather than the first two terms of Eq. (49).

With the help of the asymptotics (46) and (47), the $k > k_F$ contribution to the integral that enters Eq. (48) is easily evaluated as

$$
\begin{aligned}
&-2\pi^{-1}\int_{k_F}^{\infty}\Omega_x(n(0),n(k))dk\\
&\quad=-C\pi[F_<(0)]^{-1/2}(\alpha r_s)^{-2}\left\{(\alpha r_s/2\pi^2)^{1/2}\int_1^{1+\xi}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(\kappa-1))]^{1/2}d\kappa+(\alpha r_s/\pi^2)\int_{1+\xi}^{\infty}[F_>(\kappa)]^{1/2}d\kappa\right\}\\
&\quad=-C[F_<(0)]^{-1/2}(\alpha r_s)^{-1}\{\pi^{-1}f_0^>+(2/\pi)^{1/2}[g_0-g_1(4\alpha r_s/\pi)^{1/2}]+3^{-1/2}(1-\ln 2)^{1/2}\ln[(4\alpha r_s/\pi)^{-1/2}]\}.
\end{aligned}
\tag{51}
$$

Thus, the term proportional to $(\alpha r_s)^{-2}$ in the rhs of Eq. (49), has to stem from the $k<k_F$ contribution, implying that, as $x\to 1$ and $y\to 1$, either

$$\Omega(x,y)\to[1-D(1-x)^{1/2}][1-D(1-y)^{1/2}] \tag{52}$$

or

$$\Omega(x,y)\to 1-\tilde{D}(1-x)^{1/4}(1-y)^{1/4}, \tag{53}$$

where D and $\tilde{D}$ are constants. For the former asymptotics,

$$
\begin{aligned}
-2\pi^{-1}\int_0^{k_F}\Omega_x(n(0),n(k))dk=&-\pi D[F_<(0)]^{-1/2}(\alpha r_s)^{-2}\Bigg(\int_0^{1-\xi}\{1-D(\alpha r_s/\pi^2)[F_<(\kappa)]^{1/2}\}d\kappa\\
&+\int_{1-\xi}^{1}\{1-D(\alpha r_s/2\pi^2)^{1/2}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{1/2}\}d\kappa\Bigg)\\
=&-\pi D[F_<(0)]^{-1/2}(\alpha r_s)^{-2}\{1-D(\alpha r_s/\pi^2)f_0^<-D\alpha r_s(2/\pi^3)^{1/2}[g_0+g_1(4\alpha r_s/\pi)^{1/2}]\\
&-D\alpha r_s(3\pi^2)^{-1/2}(1-\ln 2)^{1/2}\ln[(4\alpha r_s/\pi)^{-1/2}]\},
\end{aligned}
\tag{54}
$$

which fixes the value of D,

$$D=-(2\pi)^{-1}[F_<(0)]^{1/2}\approx-0.322\,75. \tag{55}$$

On the other hand, upon insertion of the small-r_s estimates

$$\int_0^{1-\xi}[F_<(\kappa)]^{1/4}d\kappa=\tilde{f}_0^<-(\pi^2/3)^{1/4}(1-\ln 2)^{1/4}[2\xi^{1/2}+\tfrac{1}{3}\xi^{3/2}] \tag{56}$$

and

$$
\begin{aligned}
&\int_{1-\xi}^{1}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{1/4}d\kappa\\
&\quad=(4\alpha r_s/\pi)^{1/2}[\tilde{g}_0+(\alpha r_s/\pi)^{1/2}\tilde{g}_1]+(4\alpha r_s/\pi)^{1/4}[(\pi/6)(1-\ln 2)]^{1/4}[2\xi^{1/2}+\tfrac{1}{3}\xi^{3/2}],
\end{aligned}
\tag{57}
$$

the latter asymptotics leads to

$$
\begin{aligned}
-2\pi^{-1}\int_0^{k_F}\Omega_x(n(0),n(k))dk=&-(\pi^2/2)\tilde{D}(\alpha r_s)^{-5/2}[F_<(0)]^{-3/4}\Bigg\{(\alpha r_s/\pi^2)^{1/2}\int_0^{1-\xi}[F_<(\kappa)]^{1/4}d\kappa\\
&+(\alpha r_s/2\pi^2)^{1/4}\int_{1-\xi}^{1}[\kappa^{-2}G((4\alpha r_s/\pi)^{-1/2}(1-\kappa))]^{1/4}d\kappa\Bigg\}\\
=&-(\pi/2)\tilde{D}(\alpha r_s)^{-2}[F_<(0)]^{-3/4}\{\tilde{f}_0^<+2(\alpha r_s/2)^{1/4}[\tilde{g}_0+(\alpha r_s/\pi)^{1/2})\tilde{g}_1]\}.
\end{aligned}
\tag{58}
$$

The rhs of Eq. (58) contains an unphysical term proportional to $(\alpha r_s)^{-7/4}$ that cannot be canceled out by the $k>k_F$ contributions [Eq. (51)]. For this reason, the asymptotics (53) has to be ruled out in favor of expressions consistent with Eq. (52).

One of such expressions, which reads

$$\Omega(x,y)\rightarrow[1-(D/\lambda)(1-x)^{1/2}]^{\lambda}[1-(D/\lambda)(1-y)^{1/2}]^{\lambda}, \tag{59}$$

produces

$$\mu=-\pi D[F_<(0)]^{-1/2}(\alpha r_s)^{-2}+\pi^{-1}[F_<(0)]^{-1/2}\{(1-\lambda^{-1})D^2[F_<(0)]^{1/2}+(D^2f_0^<-Cf_0^>)+(2\pi)^{1/2}(D^2-C)g_0\}(\alpha r_s)^{-1}$$
$$+(D^2-C)3^{-1/2}(1-\ln 2)^{1/2}[F_<(0)]^{-1/2}(\alpha r_s)^{-1}\ln[(4\alpha r_s/\pi)^{-1/2}]+(D^2+C)(8/\pi^2)^{1/2}g_1[F_<(0)]^{-1/2}(\alpha r_s)^{-1/2}+\cdots, \tag{60}$$

which, upon setting

$$\lambda=(1+D^{-2}[F_<(0)]^{-1/2}\{(D^2f_0^<-Cf_0^>)+(2\pi)^{1/2}(D^2-C)g_0+[F_<(0)]^{1/2}\})^{-1}, \tag{61}$$

yields the first two terms in the rhs of Eq. (49). On the other hand, the unphysical term that scales like $(\alpha r_s)^{-1}\ln r_s$ would be canceled out only if

$$D^2=C. \tag{62}$$

Although for obvious reasons this condition cannot be satisfied, it is clear that, in principle, asymptotic expressions going beyond that given by Eq. (59) would be capable of not only eliminating this spurious term but also furnishing proper constant and logarithmic contributions in the expansion (49).

D. A constraint upon $\Omega(x,y)$ imposed by the discontinuity of the momentum distribution at $k=k_F$

Having established the asymptotics of $\Omega(x,y)$ for x and y approaching either 0 or 1, one may now proceed to demonstrate that such a function cannot give rise to the momentum distribution $n(k)$ with a discontinuity at $k=k_F$. The location of this discontinuity is unaffected by exchange effects beyond RPA (Ref. 20) that contribute to its magnitude only through orders higher than linear in r_s.[21] Since the Euler equation (3) has to be satisfied as k approaches k_F from both below and above, one has

$$\int \Omega_x(n(k_F^-),n(k'))|\mathbf{k}-\mathbf{k}'|^{-2}d\mathbf{k}'$$
$$=\int \Omega_x(n(k_F^+),n(k'))|\mathbf{k}-\mathbf{k}'|^{-2}d\mathbf{k}', \tag{63}$$

where $|\mathbf{k}|=k_F$. Integrating out the angular coordinates and inserting the aforederived asymptotics (46), (47), and (52) produces

$$\int_0^{k_F}\{(D-1)+(C-D^2)[1-n(k)]^{1/2}\}k\ln\left|\frac{k+f_F}{k-k_F}\right|dk=0, \tag{64}$$

which immediately implies $D=1$ together with the condition (62), thus contradicting Eq. (55).

III. DISCUSSION AND CONCLUSIONS

The large- and small-k asymptotics of the momentum distribution $n(k)$ rigorously determine the behavior of the function $\Omega(x,y)$ for each of its arguments approaching either 0 or 1. Unfortunately, the resulting $\Omega(x,y)$ does not give rise to $n(k)$ with a proper discontinuity as a solution of the Euler equation (3). Consequently, functionals of the form given by Eq. (1) cannot be exact for a high-density homogeneous electron gas.

In principle, this problem can be rectified in two different ways. One possibility is to consider more involved functionals in which the function Ω does not depend on the occupancies of the two spin orbitals in question but also on those of the others, i.e., $\Omega\equiv\Omega(n_p,n_q,\{n_r\})$. Such a function would ''know'' the value of k_F, circumventing the scaling arguments presented in the above derivations. Another possibility would be to abandon the concept of the natural spin-orbital functionals altogether in favor of alternative approaches to $V_{ee}[\Gamma]$.[22]

In light of the above discussion, the remarkable performance of the functional (1) with $\Omega(x,y)=(xy)^{1/2}$ for simple Coulombic systems[1] remains unexplained. The present findings appear to imply that either the satisfaction of the constraints imposed by the properties of a homogeneous electron gas is of little relevance to the accuracy of predictions for atoms or that poor performance of such functionals should be expected for systems with narrow gaps or degeneracies at the Fermi level. The research aiming at the elucidation of these issues is in progress.

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