



HAL
open science

Excited States of the Uniform Electron Gas

Pierre-François Loos

► **To cite this version:**

| Pierre-François Loos. Excited States of the Uniform Electron Gas. 2025. hal-04929937

HAL Id: hal-04929937

<https://hal.science/hal-04929937v1>

Preprint submitted on 5 Feb 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Excited States of the Uniform Electron Gas

Pierre-François Loos*

Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, France

The uniform electron gas (UEG) is a cornerstone of density-functional theory (DFT) and the foundation of the local-density approximation (LDA), one of the most successful approximations in DFT. In this work, we extend the concept of UEG by introducing excited-state UEGs, systems characterized by a gap at the Fermi surface created by the excitation of electrons near the Fermi level. We report closed-form expressions of the reduced kinetic and exchange energies of these excited-state UEGs as functions of the density and the gap. Additionally, we derive the leading term of the correlation energy in the high-density limit. By incorporating an additional variable representing the degree of excitation into the UEG paradigm, the present work introduces a new framework for constructing local and semi-local state-specific functionals for excited states.

The development of state-specific functionals for excited states [1–7] marks a pivotal advancement in density-functional theory (DFT) [8–10]. While the local-density approximation (LDA) [11–15] often serves as the foundational starting point for constructing functionals [16–20], a critical question remains: can we design local and/or semi-local functionals — one that depends solely on local variables such as the electron density — tailored for electronic excited states?

A significant challenge lies in the lack of an established paradigm to construct excited-state uniform electron gases (UEGs). While the ground-state UEG [21–25], also known as the homogeneous electron gas or jellium model, is well-understood and serves as the foundation of most existing local approximations, their excited-state counterparts are far less straightforward. By modifying the UEG paradigm to account for electronic excitations, we aim to create a framework capable of describing excited states in a state-specific manner [1–4, 7, 26–34]. To achieve this, we propose introducing an additional local variable that quantifies the “degree of excitation” of the system. This variable would encode information about the nature and extent of electronic excitations, allowing the functional to adapt to the specifics of the excited states.

To address this, we propose a model for excited-state UEGs constructed by introducing a gap at the Fermi surface through excitations of the electrons near the Fermi level. These excited-state UEGs can be viewed as a generalization of the “jellium with a gap” model, where unoccupied states are rigidly shifted [35–40]. In such systems, while only the correlation functional is affected [35–37, 39, 41–45], both exchange and correlation functionals are influenced by the emergence of a gap in excited-state UEGs. This provides a promising foundation for extending the LDA to incorporate excited states. A related, albeit distinct, approach was explored by Harbola and collaborators, who focused on constructing LDA exchange functionals for excited states [46–48]. However, their strategy clearly lacks generality and is restricted to exchange. Alternative schemes have also been explored [49–52].

Our approach builds on the recent work of Gould and

Pittalis, who proposed incorporating excited-state information via the so-called constant occupation factor ensemble (cofe) UEGs [6]. Here, we move beyond the ensemble framework to focus on a pure-state formalism. We believe this shift offers greater flexibility to capture the unique features of state-specific electronic excitations. By embedding excitation-specific information into the functional, we hope to achieve a more accurate description of excited-state energetics and properties, paving the way for broader applications in quantum chemistry and materials science. Atomic units are used throughout.

The reduced (i.e., per electron) energy of the UEG is expressed as [21, 22, 24, 25]

$$\epsilon(\rho, \zeta) = t_s(\rho, \zeta) + \epsilon_x(\rho, \zeta) + \epsilon_c(\rho, \zeta) \quad (1)$$

where t_s , ϵ_x , and ϵ_c are the kinetic, exchange and correlation energy components, $\rho = \rho_\uparrow + \rho_\downarrow$ is the (uniform) electron density, ρ_σ is the density of the spin- σ electrons, and the spin polarization is $\zeta = (\rho_\uparrow - \rho_\downarrow)/\rho$. The Hartree contribution does not appear in the previous equation as it is exactly canceled by the uniform positively charged background.

Both the kinetic and exchange energies can be written as $t_s(\rho, \zeta) = t_s(\rho)\Upsilon_s(\zeta)$ and $\epsilon_x(\rho, \zeta) = \epsilon_x(\rho)\Upsilon_x(\zeta)$, where $t_s(\rho) \equiv t_s(\rho, \zeta = 0)$ and $\epsilon_x(\rho) \equiv \epsilon_x(\rho, \zeta = 0)$ are spin-unpolarized (or paramagnetic) quantities while the kinetic and exchange spin scaling functions are

$$\Upsilon_s(\zeta) = \frac{t_s(\rho, \zeta)}{t_s(\rho)} = \frac{(1 - \zeta)^{5/3} + (1 + \zeta)^{5/3}}{2} \quad (2a)$$

$$\Upsilon_x(\zeta) = \frac{\epsilon_x(\rho, \zeta)}{\epsilon_x(\rho)} = \frac{(1 - \zeta)^{4/3} + (1 + \zeta)^{4/3}}{2} \quad (2b)$$

The kinetic and exchange energies can also be spin-resolved as follows:

$$t_s(\rho, \zeta) = t_{s\uparrow}(\rho_\uparrow) + t_{s\downarrow}(\rho_\downarrow) \quad (3a)$$

$$\epsilon_x(\rho, \zeta) = \epsilon_{x\uparrow}(\rho_\uparrow) + \epsilon_{x\downarrow}(\rho_\downarrow) \quad (3b)$$

The spin-resolved correlation energy has an additional component and reads

$$\epsilon_c(\rho, \zeta) = \epsilon_{c\uparrow\uparrow}(\rho_\uparrow) + \epsilon_{c\downarrow\downarrow}(\rho_\downarrow) + \epsilon_{c\uparrow\downarrow}(\rho_\uparrow, \rho_\downarrow) \quad (4)$$

In the usual ground-state spin-polarized (or ferromagnetic) UEG, the reduced kinetic energy is

$$t_{s\sigma}(\rho_\sigma) = \frac{1}{\rho_\sigma} \int_0^{k_{F\sigma}} \frac{k^2}{2} \frac{k^2}{2\pi^2} dk = C_F \rho_\sigma^{2/3} \quad (5)$$

where $C_F = -\frac{3}{10}(6\pi^2)^{2/3} \approx 4.5578$ is the Thomas-Fermi coefficient [11, 12] and the uniform spin-density is

$$\rho_\sigma = \int_0^{k_{F\sigma}} \frac{k^2}{2\pi^2} dk = \frac{k_{F\sigma}^3}{6\pi^2} \quad (6)$$

where $k_{F\sigma}$ is the Fermi wave vector associated with the spin- σ channel ($\sigma = \uparrow$ or \downarrow). The exchange energy is given by the well-known Dirac formula [13, 53] which reads

$$\begin{aligned} \epsilon_{x\sigma}(\rho_\sigma) &= \frac{1}{2} \iint \frac{\rho_x(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= C_x \rho_\sigma^{1/3} \end{aligned} \quad (7)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectronic distance and $C_x = -\frac{3}{4}(\frac{6}{\pi})^{1/3} \approx -0.930526$ is the Dirac coefficient. In Eq. (7), $\rho_x(\mathbf{r}_1, \mathbf{r}_2) = -|\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2/\rho(\mathbf{r}_1)$ is the Fermi hole fulfilling the normalization condition $\iint \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = -1$ and $\rho_1(\mathbf{r}_1, \mathbf{r}_2) = j_{k_{F\sigma}}(r_{12})$ is the one-electron reduced density matrix with $j_{k_{F\sigma}}(r_{12}) = 1/(2\pi^2)[\sin(k_{F\sigma}r_{12}) - k_{F\sigma}r_{12}\cos(k_{F\sigma}r_{12})]/(r_{12}^3)$.

Concerning the correlation part, one usually relies on perturbative expansions in the high- and low-density limits [22, 24]. As a function of the Wigner-Seitz radius $r_s = (\frac{3}{4\pi\rho})^{1/3}$, the small- r_s (or high-density) expansion of the correlation energy appears to be [24, 54–64]

$$\epsilon_c(r_s, \zeta) = \lambda_0(\zeta) \ln r_s + \epsilon_0(\zeta) + \lambda_1(\zeta) r_s \ln r_s + \epsilon_1(\zeta) r_s + \dots \quad (8)$$

where, as first proposed by Gell-Mann and Brueckner [55], one must rely on resummation techniques to avoid divergences. This explains the appearance of unusual $\ln r_s$ terms in the high-density perturbative expansion, highlighting the nonanalytic nature of the correlation energy (see below).

The large- r_s (or low-density) expansion reads [24, 65–67]

$$\epsilon_c(r_s, \zeta) = \frac{\eta_0}{r_s} + \frac{\eta_1}{r_s^{3/2}} + \frac{\eta_2}{r_s^2} + \dots \quad (9)$$

which is assumed to be strictly independent of the spin polarization due to the short-range nature of spin interactions. In this strong-coupling (or strictly-correlated) regime, the potential energy dominates over the kinetic energy, causing the electrons to localize at lattice points that minimize their (classical) Coulomb repulsion. These minimum-energy configurations are known as Wigner crystals [68].

Our model for the excited states of the UEG is depicted in Fig. 1. In an excited-state UEG, a gap of magnitude

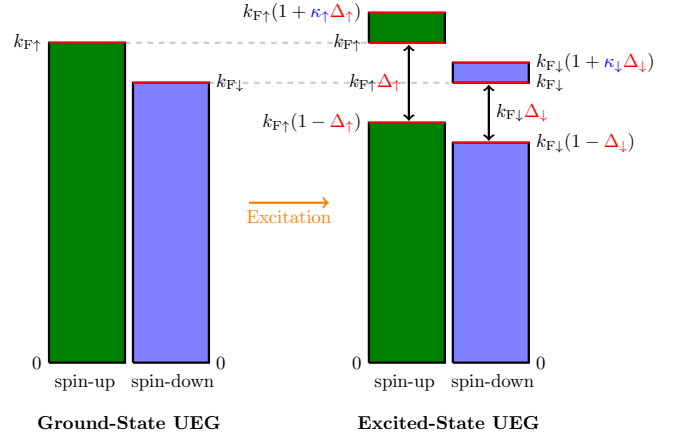


FIG. 1. Schematic representation of ground- and excited-state UEGs. In a ground-state UEG (left), all electronic levels are filled from $k = 0$ to the Fermi level at $k = k_{F\uparrow}$ for the spin-up electrons and $k = k_{F\downarrow}$ for the spin-down electrons. In an excited-state UEG, a gap of magnitude $k_{F\sigma}\Delta_\sigma$ opens at the Fermi level for each spin manifold with $0 \leq \Delta_\sigma \leq 1$. The electrons in the energy levels from $k_{F\sigma}(1 - \Delta_\sigma)$ to $k_{F\sigma}$ are excited to occupy the energy levels from $k_{F\sigma}$ to $k_{F\sigma}(1 + \kappa_\sigma\Delta_\sigma)$. The factor $0 \leq \kappa_\sigma \leq 1$ is determined such that the spin- σ density of the ground- and excited-state UEGs are identical. The red lines indicate regions where the infrared catastrophe may occur due to the vanishing gap between occupied and unoccupied states.

$k_{F\sigma}\Delta_\sigma$ opens at the Fermi level for each spin manifold (with $0 \leq \Delta_\sigma \leq 1$). The electrons in the energy levels from $k_{F\sigma}(1 - \Delta_\sigma)$ to $k_{F\sigma}$ are excited to occupy the energy levels from $k_{F\sigma}$ to $k_{F\sigma}(1 + \kappa_\sigma\Delta_\sigma)$. The parameter $0 \leq \kappa_\sigma \leq 1$ is determined such that the spin- σ density of the ground- and excited-state UEGs are identical (see below). From this model, one can easily recover the ground state by setting $\Delta_\sigma = 0$. Note that the excitation process is independent for each spin channel. A priori, this model is designed to model spin-allowed transitions. Spin-forbidden transitions, such as singlet-triplet excitations, may require a generalization of the present model.

For the spin- σ electrons, the occupation is

$$f_{k\sigma} = \begin{cases} 1 & 0 \leq k \leq k_{F\sigma}(1 - \Delta_\sigma) \\ 0 & k_{F\sigma}(1 - \Delta_\sigma) \leq k \leq k_{F\sigma} \\ 1 & k_{F\sigma} \leq k \leq k_{F\sigma}(1 + \kappa_\sigma\Delta_\sigma) \end{cases} \quad (10)$$

The parameter κ_σ is necessary as the density of states increases with k . (In other words, large values of k accommodate more electrons than smaller values of k .)

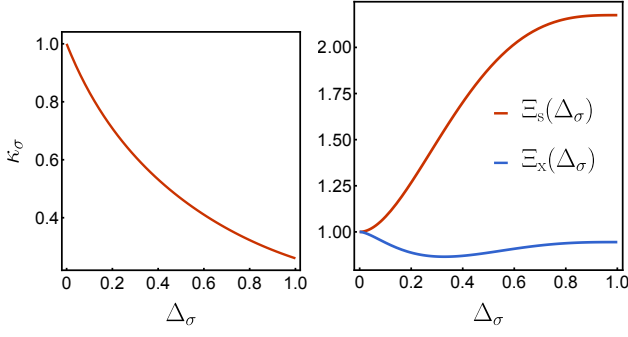


FIG. 2. Left: κ_σ as a function of Δ_σ , as given by Eq. (12). Right: Ξ_s and Ξ_x as functions of Δ_σ , as given by Eqs. (15) and (18), respectively.

Such an excited-state UEG has a uniform spin density

$$\begin{aligned} \rho_\sigma &= \int_0^\infty f_{k_\sigma} \frac{k^2}{2\pi^2} dk \\ &= \int_0^{k_{F\sigma}(1-\Delta_\sigma)} \frac{k^2}{2\pi^2} dk + \int_{k_{F\sigma}}^{k_{F\sigma}(1+\kappa_\sigma\Delta_\sigma)} \frac{k^2}{2\pi^2} dk \\ &= [1 - 3\Delta_\sigma(1 - \kappa_\sigma) + 3\Delta_\sigma^2(1 + \kappa_\sigma^2) - \Delta_\sigma^3(1 - \kappa_\sigma^3)] \frac{k_{F\sigma}^3}{6\pi^2} \end{aligned} \quad (11)$$

If one matches the density of the ground-state UEG and the excited-state UEG, one must set $\rho_\sigma = k_{F\sigma}^3/(6\pi^2)$, which yields

$$\kappa_\sigma = \frac{(1 + 3\Delta_\sigma - 3\Delta_\sigma^2 + \Delta_\sigma^3)^{1/3} - 1}{\Delta_\sigma} \quad (12)$$

and has the following limits

$$\lim_{\Delta_\sigma \rightarrow 0} \kappa_\sigma = 1 \quad (13a)$$

$$\lim_{\Delta_\sigma \rightarrow 1} \kappa_\sigma = 2^{1/3} - 1 \approx 0.259921 \quad (13b)$$

The evolution of κ_σ as a function of Δ_σ is represented in Fig. 2. Note that because the excited-state density is equal to the ground-state density, the Hartree contribution is properly canceled out by the uniform positive background.

Let us now derive the reduced kinetic and exchange energies for these excited-state UEGs. The reduced kinetic energy associated with the spin- σ electrons is

$$\begin{aligned} t_{s\sigma}(\rho_\sigma, \Delta_\sigma) &= \frac{1}{\rho_\sigma} \int_0^\infty f_k \frac{k^2}{2} \frac{k^2}{2\pi^2} dk \\ &= \Xi_s(\Delta_\sigma) \frac{3k_{F\sigma}^2}{10} = \Xi_s(\Delta_\sigma) C_F \rho_\sigma^{2/3} \end{aligned} \quad (14)$$

and the gap-dependent function

$$\begin{aligned} \Xi_s(\Delta_\sigma) &= (1 - \Delta_\sigma)^5 \\ &+ \Delta_\sigma \kappa_\sigma (5 + 10\Delta_\sigma \kappa_\sigma + 10\Delta_\sigma^2 \kappa_\sigma^2 + 5\Delta_\sigma^3 \kappa_\sigma^3 + \Delta_\sigma^4 \kappa_\sigma^4) \end{aligned} \quad (15)$$

is depicted in Fig. 2 and has the following limiting values

$$\lim_{\Delta_\sigma \rightarrow 0} \Xi_s(\Delta_\sigma) = 1 \quad (16a)$$

$$\lim_{\Delta_\sigma \rightarrow 1} \Xi_s(\Delta_\sigma) = 2^{5/3} - 1 \approx 2.1748 \quad (16b)$$

For the exchange, we have

$$\begin{aligned} \epsilon_{x\sigma}(\rho_\sigma, \Delta_\sigma) &= \frac{1}{2} \iint \frac{\rho_x(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \Xi_x(\Delta_\sigma) \frac{3k_{F\sigma}}{4\pi} = \Xi_x(\Delta_\sigma) C_x \rho_\sigma^{1/3} \end{aligned} \quad (17)$$

with the following gap-dependent Dirac coefficient (see Fig. 2)

$$\begin{aligned} \Xi_x(\Delta_\sigma) &= (1 - \Delta_\sigma)^4 + 4\Delta_\sigma \kappa_\sigma (1 + \Delta_\sigma^2 \kappa_\sigma^2) \\ &+ 8\Delta_\sigma^2 \kappa_\sigma^2 \ln 2 - \Delta_\sigma^4 \kappa_\sigma^4 \\ &+ 2\Delta_\sigma^2 \kappa_\sigma^2 \left[\left(1 - \frac{\Delta_\sigma \kappa_\sigma}{2}\right)^2 \ln \left(1 - \frac{\Delta_\sigma \kappa_\sigma}{2}\right) \right. \\ &+ 2 \left(1 - \frac{\Delta_\sigma^2 \kappa_\sigma^2}{4}\right) \ln \left(\frac{\Delta_\sigma \kappa_\sigma}{2}\right) \\ &\left. + \left(1 + \frac{\Delta_\sigma \kappa_\sigma}{2}\right)^2 \ln \left(1 + \frac{\Delta_\sigma \kappa_\sigma}{2}\right) \right] \end{aligned} \quad (18)$$

which admits the following limiting values

$$\lim_{\Delta_\sigma \rightarrow 0} \Xi_x(\Delta_\sigma) = 1 \quad (19a)$$

$$\lim_{\Delta_\sigma \rightarrow 1} \Xi_x(\Delta_\sigma) \approx 0.944717 \quad (19b)$$

In contrast to Ξ_s , Ξ_x exhibits non-monotonic behavior. Initially, it decreases for small gap values, reaching a minimum of 0.865535 at $\Delta_\sigma \approx 0.328476$, before eventually increasing up to $\Delta_\sigma = 1$. The exchange hole of excited-state UEGs remains normalized and can be easily derived using the following expression for the one-electron reduced density matrix (see Fig. 3)

$$\begin{aligned} \rho_1(\mathbf{r}_1, \mathbf{r}_2) &= j_{k_{F\sigma}(1+\kappa_\sigma\Delta_\sigma)}(r_{12}) \\ &- j_{k_{F\sigma}}(r_{12}) + j_{k_{F\sigma}(1-\Delta_\sigma)}(r_{12}) \end{aligned} \quad (20)$$

As readily seen in Eq. (20), the exchange hole of excited-state UEGs is a simple combination of ground-state exchange holes with different values of the Fermi wave vector. Figure 3 evidences that the Fermi hole becomes tighter as Δ_σ increases.

Now, let us study the reduced correlation energy of these excited-state UEGs. Due to the long-range nature of the Coulomb interaction and the neglect of the kinetic energy term, the low-density limit is probably similar to the ground state (at least for the leading order proportional to r_s^{-1}). This remains to be confirmed. We thus focus on the high-density limit and assume a non-polarized gas from hereon for the sake of simplicity.

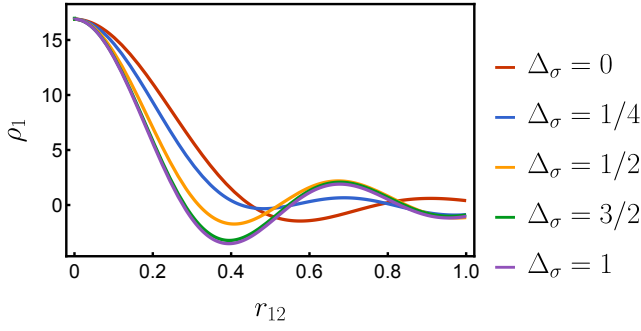


FIG. 3. ρ_1 as a function of r_{12} , as given by Eqs. (20), for $k_{F\sigma} = 10$ and various values of Δ_σ .

Rayleigh-Schrödinger perturbation theory tells us that the second-order contribution can be decomposed as $\epsilon^{(2)} = \epsilon^{(2d)} + \epsilon^{(2x)}$, where, for the ground state, the exchange term, $\epsilon^{(2x)}$, is known to be finite [55, 60] and the direct term, $\epsilon^{(2d)}$, has been first shown to diverge logarithmically as $\lambda_0 \ln r_s$ for small r_s by Macke [54] with $\lambda_0 = (1 - \ln 2)/\pi^2 \approx 0.0310907$.

More explicitly, the direct component reads [69]

$$\epsilon^{(2d)} = -\frac{3}{16\pi^5} \int \frac{d\mathbf{k}}{k^4} \int d\mathbf{q} \int \frac{d\mathbf{p}}{\mathbf{k} \cdot (\mathbf{p} - \mathbf{q} + \mathbf{k})} \quad (21)$$

where, in the case of the ground state, $p < 1$, $q < 1$, $1 < |\mathbf{p} + \mathbf{k}|$, and $1 < |\mathbf{q} - \mathbf{k}|$ in units of k_F . The divergent behavior can be derived by realizing that the main contribution to the integral comes from the small momentum transfer (i.e., $k \approx 0$) or, in other words, from the excitations near the Fermi surface where the energy gap between occupied and vacant states vanishes (infrared catastrophe). This issue is particularly problematic in coupled-cluster theory, where perturbative corrections systematically exhibit infrared divergences [70, 71].

By assuming that $p \approx 1$ and $q \approx 1$ and neglecting the terms proportional to k^2 , one can show that $1 - kx \leq p \leq 1$ and $1 - ky \leq q \leq 1$, where $\mathbf{k} \cdot \mathbf{p} = kpx$ and $\mathbf{k} \cdot \mathbf{q} = -kqy$. This leads to

$$\int d\mathbf{q} \int \frac{d\mathbf{p}}{\mathbf{k} \cdot (\mathbf{p} - \mathbf{q} + \mathbf{k})} \approx (2\pi)^2 \int_0^1 dx \int_0^1 dy \int_{1-kx}^1 dp \int_{1-ky}^1 \frac{dq}{k(x+y)} \quad (22)$$

Finally, the integration over k in the range $\sqrt{r_s} < k < 1$ (where the upper limit is arbitrary and $\sqrt{r_s}$ corresponds to the characteristic wave vector below which the Coulomb interaction is effectively screened [55]) yields

$$\begin{aligned} \epsilon^{(2d)} &\approx -\frac{3}{16\pi^5} \int_{\sqrt{r_s}}^1 \frac{4\pi k^2 dk}{k^4} (2\pi)^2 \frac{2k}{3} (1 - \ln 2) \\ &\sim \frac{1 - \ln 2}{\pi^2} \ln r_s \end{aligned} \quad (23)$$

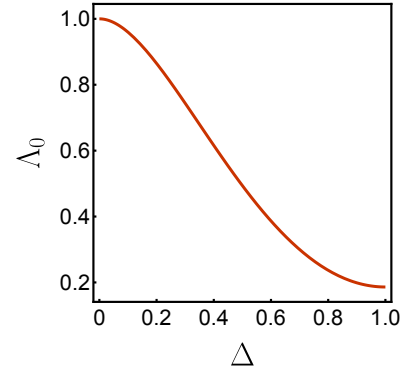


FIG. 4. Λ_0 as a function of Δ , as given by Eq. (24).

For the excited-state UEGs, the infrared divergence originates from various (de)excitation processes in which the energy difference between occupied and vacant states vanishes (see red lines in Fig. 1). By considering the various admissible regions of \mathbf{p} , \mathbf{q} , and \mathbf{k} in Eq. (21), we have identified six divergent terms:

- Excitations from occupied states with $0 < p < 1 - \Delta$ and $0 < q < 1 - \Delta$ to unoccupied states with $1 - \Delta < |\mathbf{p} + \mathbf{k}| < 1$ and $1 - \Delta < |\mathbf{q} - \mathbf{k}| < 1$;
- De-excitations from occupied states with $1 < p < 1 + \kappa\Delta$ and $1 < q < 1 + \kappa\Delta$ to unoccupied states with $1 - \Delta < |\mathbf{p} + \mathbf{k}| < 1$ and $1 - \Delta < |\mathbf{q} - \mathbf{k}| < 1$;
- Excitations from occupied states with $1 < p < 1 + \kappa\Delta$ and $1 < q < 1 + \kappa\Delta$ to unoccupied states with $1 + \kappa\Delta < |\mathbf{p} + \mathbf{k}|$ and $1 + \kappa\Delta < |\mathbf{q} - \mathbf{k}|$;
- Mixed process corresponding to excitations from occupied states with $0 < p < 1 - \Delta$ to unoccupied states with $1 - \Delta < |\mathbf{p} + \mathbf{k}| < 1$, combined with de-excitations from occupied states with $1 < q < 1 + \kappa\Delta$ to unoccupied states with $1 - \Delta < |\mathbf{q} - \mathbf{k}| < 1$;
- Mixed process corresponding to de-excitations from occupied states with $1 < p < 1 + \kappa\Delta$ to unoccupied states with $1 - \Delta < |\mathbf{p} + \mathbf{k}| < 1$, combined with excitations from occupied states with $1 < q < 1 + \kappa\Delta$ to unoccupied states with $1 + \kappa\Delta < |\mathbf{q} - \mathbf{k}|$;
- Excitations from occupied states with $0 < p < 1 - \Delta$ to unoccupied states with $1 - \Delta < |\mathbf{p} + \mathbf{k}| < 1$, combined with excitations from occupied states with $1 < q < 1 + \kappa\Delta$ to unoccupied states with $1 + \kappa\Delta < |\mathbf{q} - \mathbf{k}|$;

Each of these processes leads to a logarithmic divergence of the correlation energy in the high-density limit, with a distinct dependence on Δ . Following a similar procedure as for the ground state (see above), one can show that the corresponding gap-dependent coefficient can be

decomposed as

$$\lambda_0(\Delta) = \Lambda_0(\Delta)\lambda_0 = \frac{1}{\pi^2} \sum_{k=1}^6 \lambda_0^{(k)} \quad (24)$$

with

$$\begin{aligned} \lambda_0^{(1)} &= (1 - \Delta)^3 F(1, 1) & \lambda_0^{(2)} &= F(1, 1) \\ \lambda_0^{(3)} &= (1 + \kappa\Delta)^3 F(1, 1) & \lambda_0^{(4)} &= -2F(1 - \Delta, 1) \\ \lambda_0^{(5)} &= -2F(1, 1 + \kappa\Delta) & \lambda_0^{(6)} &= 2F(1 - \Delta, 1 + \kappa\Delta) \end{aligned}$$

and

$$F(\alpha, \beta) = \alpha^2\beta + \alpha\beta^2 + \alpha^3 \ln \alpha + \beta^3 \ln \beta - (\alpha^3 + \beta^3) \ln(\alpha + \beta) \quad (25)$$

In the limit of a vanishing gap, the ground-state behavior is recovered, i.e., $\lambda_0(\Delta = 0) = \lambda_0 = (1 - \ln 2)/\pi^2$. As Δ approaches 1, the behavior remains logarithmic, though weaker, with $\lambda_0(\Delta = 1) \approx 0.00578826$. The evolution of $\Lambda_0(\Delta) = \lambda_0(\Delta)/\lambda_0$ as a function of Δ is shown in Fig. 4. Higher-order terms in r_s have yet to be explored. This is left for future work.

To conclude, our work introduces a generalization of the UEG paradigm for excited states. We present closed-form expressions for the reduced kinetic and exchange energies of these excited-state UEGs as functions of the density and the gap. Additionally, we derive the leading-order term of the correlation energy in the high-density limit. By modifying the UEG to include a gap at the Fermi surface arising from excitations near the Fermi level, we provide a foundation for constructing state-specific functionals beyond ensemble-based approaches. This pure-state approach represents a significant step toward developing (semi)local approximations capable of accurately describing excited-state properties within DFT.

In terms of perspectives, we are currently developing (semi)local functionals based on excited-state UEGs by embedding an additional variable that quantifies the degree of excitation directly into the functional. This approach opens new avenues for improving density-functional approximations beyond ground-state DFT. Future work will focus on refining this framework and evaluating its performance in practical applications.

The author would like to thank Tim Gould, Andreas Savin, and Hugh Burton for insightful discussions. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

- [1] S. Giarrusso and P.-F. Loos, Exact excited-state functionals of the asymmetric Hubbard dimer, *J. Phys. Chem. Lett.* **14**, 8780 (2023).
- [2] T. Gould, *Stationary conditions for excited states: the surprising impact of density-driven correlations* (2024), [arXiv:2404.12593 \[physics.chem-ph\]](#).
- [3] W. Yang and P. W. Ayers, Foundation for the Δ SCF approach in density functional theory (2024), [arXiv:2403.04604 \[physics.chem-ph\]](#).
- [4] E. Fromager, *Ensemble density functional theory of ground and excited energy levels* (2024), [arXiv:2409.17000 \[physics.chem-ph\]](#).
- [5] T. Gould, S. G. Dale, L. Kronik, and S. Pittalis, *State-specific density functionals for excited states from ensembles* (2024), [arXiv:2406.18105 \[physics.chem-ph\]](#).
- [6] T. Gould and S. Pittalis, Local density approximation for excited states, *Phys. Rev. X* **14**, 041045 (2024).
- [7] P.-F. Loos and S. Giarrusso, *Excited-state-specific Kohn-Sham formalism for the asymmetric Hubbard dimer* (2024), [arXiv:2412.14945 \[physics.chem-ph\]](#).
- [8] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [9] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [10] A. M. Teale, T. Helgaker, A. Savin, C. Adamo, B. Aradi, A. V. Arbuznikov, P. W. Ayers, E. J. Baerends, V. Barone, P. Calaminici, E. Cancès, E. A. Carter, P. K. Chattaraj, H. Chermette, I. Ciofini, T. D. Crawford, F. De Proft, J. F. Dobson, C. Draxl, T. Frauenheim, E. Fromager, P. Fuentealba, L. Gagliardi, G. Galli, J. Gao, P. Geerlings, N. Gidopoulos, P. M. W. Gill, P. Gori-Giorgi, A. Görling, T. Gould, S. Grimme, O. Gritsenko, H. J. A. Jensen, E. R. Johnson, R. O. Jones, M. Kaupp, A. M. Köster, L. Kronik, A. I. Krylov, S. Kvaal, A. Laestadius, M. Levy, M. Lewin, S. Liu, P.-F. Loos, N. T. Maitra, F. Neese, J. P. Perdew, K. Pernal, P. Pernot, P. Piecuch, E. Rebolini, L. Reining, P. Romaniello, A. Ruzsinszky, D. R. Salahub, M. Scheffler, P. Schwerdtfeger, V. N. Staroverov, J. Sun, E. Tellgren, D. J. Tozer, S. B. Trickey, C. A. Ullrich, A. Vela, G. Vignale, T. A. Wesolowski, X. Xu, and W. Yang, DFT exchange: sharing perspectives on the workhorse of quantum chemistry and materials science, *Phys. Chem. Chem. Phys.* **24**, 28700 (2022).
- [11] L. H. Thomas, The calculation of atomic fields, *Math. Proc. Cambridge Philos. Soc.* **23**, 542 (1927).
- [12] E. Fermi, A statistical method for the determination of some atomic properties, *Rendiconti dell'Accademia Nazionale dei Lincei* **6**, 602 (1927).
- [13] P. A. M. Dirac, Note on exchange phenomena in the Thomas atom, *Proc. Cambridge Philos. Soc.* **26**, 376 (1930).
- [14] D. M. Ceperley and B. J. Alder, Ground state of the electron gas by a stochastic method, *Phys. Rev. Lett.* **45**, 566 (1980).
- [15] M. Lewin, E. H. Lieb, and R. Seiringer, The local density approximation in density functional theory, *Pure and Applied Analysis* **2**, 35 (2020).
- [16] J. C. Slater, A simplification of the Hartree-Fock method, *Phys. Rev.* **81**, 385 (1951).
- [17] S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, *Can. J. Phys.* **58**, 1200 (1980).

* loos@irsamc.ups-tlse.fr

- [18] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B* **23**, 5048 (1981).
- [19] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* **45**, 13244 (1992).
- [20] T. Chachiyo, Simple and accurate uniform electron gas correlation energy for the full range of densities, *J. Chem. Phys.* **145**, 021101 (2016).
- [21] R. G. Parr and W. Yang, *Density-functional theory of atoms and molecules* (Oxford, Clarendon Press, 1989).
- [22] G. F. Giuliani and G. Vignale, *Quantum theory of the electron liquid* (Cambridge University Press, Cambridge, 2005).
- [23] P. F. Loos and P. M. W. Gill, Thinking outside the box: The uniform electron gas on a hypersphere, *J. Chem. Phys.* **135**, 214111 (2011).
- [24] P.-F. Loos and P. M. W. Gill, The uniform electron gas, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **6**, 410 (2016).
- [25] M. Lewin, E. H. Lieb, and R. Seiringer, Statistical mechanics of the uniform electron gas, *Journal de l'École polytechnique — Mathématiques* **5**, 79 (2018).
- [26] J. P. Perdew and M. Levy, Extrema of the density functional for the energy: excited states from the ground-state theory, *Phys. Rev. B* **31**, 6264 (1985).
- [27] A. Görling, Density-functional theory for excited states, *Phys. Rev. A* **54**, 3912 (1996).
- [28] A. Görling, Density-functional theory beyond the Hohenberg-Kohn theorem, *Phys. Rev. A* **59**, 3359 (1999).
- [29] M. Levy and A. Nagy, Variational density-functional theory for an individual excited state, *Phys. Rev. Lett.* **83**, 4361 (1999).
- [30] P. W. Ayers and M. Levy, Time-independent (static) density-functional theories for pure excited states: Extensions and unification, *Phys. Rev. A* **80**, 012508 (2009).
- [31] P. W. Ayers, M. Levy, and A. Nagy, Time-independent density-functional theory for excited states of coulomb systems, *Phys. Rev. A* **85**, 042518 (2012).
- [32] P. W. Ayers, M. Levy, and A. Nagy, Kohn-Sham theory for excited states of Coulomb systems, *J. Chem. Phys.* **143**, 191101 (2015).
- [33] P. W. Ayers, M. Levy, and A. Nagy, Time-independent density functional theory for degenerate excited states of coulomb systems, *Theor. Chem. Acc.* **137**, 152 (2018).
- [34] L. Garrigue, Building Kohn–Sham potentials for ground and excited states, *Arch. Ration. Mech. Anal.* **245**, 949 (2022).
- [35] J. Callaway, Correlation energy in a model semiconductor, *Phys. Rev.* **116**, 1368 (1959).
- [36] J. Rey and A. Savin, Virtual space level shifting and correlation energies, *Int. J. Quantum Chem.* **69**, 581 (1998).
- [37] J. B. Krieger, J. Chen, G. J. Iafrate, and A. Savin, Construction of an accurate self-interaction-corrected correlation energy functional based on an electron gas with a gap, in *Electron Correlations and Materials Properties*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Springer, Boston, MA, 1999).
- [38] C. Gutle, A. Savin, J. B. Krieger, and J. Chen, Correlation energy contributions from low-lying states to density functionals based on an electron gas with a gap, *Int. J. Quantum Chem.* **75**, 885 (1999).
- [39] J. B. Krieger, J. Chen, and S. Kurth, Construction and application of an accurate self-interaction-corrected correlation energy functional based on an electron gas with a gap, *AIP Conf. Proc.* **577**, 48 (2001).
- [40] C. Gutle and A. Savin, Orbital spaces and density-functional theory, *Phys. Rev. A* **75**, 032519 (2007).
- [41] P. E. Trevisanutto, A. Terentjevs, L. A. Constantin, V. Olivano, and F. D. Sala, Optical spectra of solids obtained by time-dependent density functional theory with the jellium-with-gap-model exchange-correlation kernel, *Phys. Rev. B* **87**, 205143 (2013).
- [42] E. Fabiano, P. E. Trevisanutto, A. Terentjevs, and L. A. Constantin, Generalized gradient approximation correlation energy functionals based on the uniform electron gas with gap model, *J. Chem. Theory Comput.* **10**, 2016 (2014).
- [43] L. A. Constantin, E. Fabiano, S. Šmiga, and F. Della Sala, Jellium-with-gap model applied to semilocal kinetic functionals, *Phys. Rev. B* **95**, 115153 (2017).
- [44] L. A. Constantin, E. Fabiano, and F. Della Sala, Nonlocal kinetic energy functional from the jellium-with-gap model: Applications to orbital-free density functional theory, *Phys. Rev. B* **97**, 205137 (2018).
- [45] S. Jana, L. A. Constantin, and P. Samal, Density functional applications of jellium with a local gap model correlation energy functional, *J. Chem. Phys.* **159**, 114109 (2023).
- [46] P. Samal and M. K. Harbola, Local-density approximation for the exchange energy functional in excited-state density functional theory, *J. Phys. B At. Mol. Opt. Phys.* **38**, 3765 (2005).
- [47] M. Rahaman, S. Ganguly, P. Samal, M. K. Harbola, T. Saha-Dasgupta, and A. Mookerjee, A local-density approximation for the exchange energy functional for excited states: The band-gap problem, *Phys. B* **404**, 1137 (2009).
- [48] M. Hemanadhan, M. Shamim, and M. K. Harbola, Testing an excited-state energy density functional and the associated potential with the ionization potential theorem, *J. Phys. B At. Mol. Opt. Phys.* **47**, 115005 (2014).
- [49] W. Kohn, Density-functional theory for excited states in a quasi-local-density approximation, *Phys. Rev. A* **34**, 737 (1986).
- [50] A. K. Theophilou and P. G. Papaconstantinou, Local spin-density approximation for spin eigenspaces and its application to the excited states of atoms, *Phys. Rev. A* **61**, 022502 (2000).
- [51] P.-F. Loos and E. Fromager, A weight-dependent local correlation density-functional approximation for ensembles, *J. Chem. Phys.* **152**, 214101 (2020).
- [52] C. Marut, B. Senjean, E. Fromager, and P.-F. Loos, Weight dependence of local exchange–correlation functionals in ensemble density-functional theory: double excitations in two-electron systems, *Faraday Discuss.* **224**, 402 (2020).
- [53] G. Friesecke, Pair correlations and exchange phenomena in the free electron gas, *Commun. Math. Phys.* **184**, 143 (1997).
- [54] W. Macke, *Z. Naturforsch. A* **5a**, 192 (1950).
- [55] M. Gell-Mann and K. A. Brueckner, Correlation energy of an electron gas at high density, *Phys. Rev.* **106**, 364 (1957).
- [56] D. DuBois, Electron interactions: Part I. Field theory of a degenerate electron gas, *Ann. Phys.* **7**, 174 (1959).
- [57] D. DuBois, Electron interactions: Part II. Properties of a dense electron gas, *Ann. Phys.* **8**, 24 (1959).
- [58] W. J. Carr and A. A. Maradudin, Ground-state energy of

- a high-density electron gas, *Phys. Rev.* **133**, A371 (1964).
- [59] S. Misawa, Ferromagnetism of an electron gas, *Phys. Rev.* **140**, A1645 (1965).
- [60] L. Onsager, L. Mittag, and M. J. Stephen, Integrals in the theory of electron correlations, *Ann. Phys.* **18**, 71 (1966).
- [61] Y. Wang and J. P. Perdew, Spin scaling of the electron-gas correlation energy in the high-density limit, *Phys. Rev. B* **43**, 8911 (1991).
- [62] G. G. Hoffman, Correlation energy of a spin-polarized electron gas at high density, *Phys. Rev. B* **45**, 8730 (1992).
- [63] T. Endo, M. Horiuchi, Y. Takada, and H. Yasuhara, High-density expansion of correlation energy and its extrapolation to the metallic density region, *Phys. Rev. B* **59**, 7367 (1999).
- [64] P. F. Loos and P. M. W. Gill, Correlation energy of the spin-polarized uniform electron gas at high density, *Phys. Rev. B* **84**, 033103 (2011).
- [65] K. Fuchs, A quantum mechanical investigation of the cohesive forces of metallic copper, *Proc. R. Soc. London* **151**, 585 (1935).
- [66] W. J. Carr, Jr., Energy, specific heat, and magnetic properties of the low-density electron gas, *Phys. Rev.* **122**, 1437 (1961).
- [67] W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Anharmonic contribution to the energy of a dilute electron gas: Interpolation for the correlation energy, *Phys. Rev.* **124**, 747 (1961).
- [68] E. Wigner, On the interaction of electrons in metals, *Phys. Rev.* **46**, 1002 (1934).
- [69] S. Raimes, *Many-Electron Theory* (Amsterdam, North-Holland, 1972).
- [70] N. Masios, A. Imler, T. Schäfer, and A. Grüneis, Averting the infrared catastrophe in the gold standard of quantum chemistry, *Phys. Rev. Lett.* **131**, 186401 (2023).
- [71] V. A. Neufeld and T. C. Berkelbach, Highly accurate electronic structure of metallic solids from coupled-cluster theory with nonperturbative triple excitations, *Phys. Rev. Lett.* **131**, 186402 (2023).