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Pair Correlations and Exchange Phenomena in the Free Electron Gas

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PAIR CORRELATIONS AND EXCHANGE PHENOMENA
IN THE FREE ELECTRON GAS

By

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Pair correlations and exchange phenomena in the free electron gas

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Abstract

We present a rigorous derivation of the Dirac-Bloch formula for the quantum mechanical exchange energy of the free electron gas. More precisely we establish that for arbitrary determinantal ground states of the underlying finite system of N free electrons in a box, subject to periodic or zero boundary conditions, the error of the Dirac-Bloch formula is of order $N^{-1/3}$.

Mathematics Subject Classification (1991): 81V70, 35P20, 42B, 11L07, 11P21

1. Introduction

The goal of this article is to present a rigorous derivation of the Dirac-Bloch formula [Di30, Bl29]¹ for the exchange energy (quantum minus classical Coulomb repulsion energy) of the free electron gas, and to estimate the accuracy of the formula for the underlying system of N free electrons in a finite box which the gas is meant to be approximating. The formula, which expresses the exchange energy in terms of the single-particle density of the system, plays an important role in numerical ‘ab initio’ electronic structure calculations based on density functional theory.²

The derivations of the formula customary in the density functional theory and quantum chemistry literature (such as the insightful account in [PY89]) concern periodic boundary conditions and pure plane-wave states³ and are not mathematically rigorous: they rest on approximating a lattice sum in momentum space by an integral even though the integrand exhibits oscillations on the length scale of the lattice. As explained below, basic error estimates on this continuum approximation⁴ are insufficient, for instance, to decide on the correct order of magnitude of the exchange energy in terms of the volume of the system.

Hitherto disconnected from the enormous body of DFT literature, a few rigorous results on exchange phenomena can be found in the mathematical physics literature: for periodic plane-wave determinants the Dirac-Bloch formula for the free electron gas is justified to leading order in [Th80, Ch. 4.3], while Graf & Solovej [GS94] have shown it to be asymptotically correct for the *interacting* electron gas in the high density limit (i.e., in the double limit $N \rightarrow \infty$, $\bar{\rho} \rightarrow \infty$ where $\bar{\rho}$ denotes the number of particles per unit

¹A large part of the literature attributes the formula to Dirac but as emphasized recently in [Se95] it was suggested independently and at about the same time by Bloch. In fact, unlike Bloch, Dirac never stated the formula explicitly, but derived a corresponding exchange potential as a correction to the Thomas-Fermi equation.

²Textbook accounts of DFT as initiated in [HK64, KS65] are [PY89, DG90, KL90]; for a rigorous discussion of various aspects see [Li83, Fr96].

³Below arbitrary determinantal ground states of the free electron energy functional, as well as Dirichlet or periodic boundary conditions are admitted; for interesting boundary layer effects observed in the Dirichlet case see Theorems 1.2 and 5.1

⁴like those [LS77 Thm. III.13, RS78 Ch. XIII.15] sufficient to establish the similar-looking but mathematically much simpler Thomas-Fermi kinetic energy formula [Th27, Fe27]

volume). Finally we mention the monumental and by now almost completed series of papers [FS92+] (partially simplified in the beautiful papers [Ba93, GS94]) devoted to establishing an asymptotic expansion, accurate enough to account for exchange, of the ground state energy of heavy atoms as the nuclear charge tends to infinity.⁵

In [Th80] (and [Ba93, GS94] for more intricate systems) control of discreteness effects is achieved on the spatially averaged level of the exchange energy, by exploiting the regularizing effect of its integral kernel $1/|r-r'|$. To extend the result in [Th80] to general ground states and establish error bounds (Theorem 1.1) we do not follow this approach but show instead (Theorem 1.2) that discreteness effects are in fact already small on the *pointwise* level of the pair correlation function, where one faces oscillations genuinely on the length scale of the discretization. In particular our decay estimate on pair correlations (Theorem 1.2) allows a simple and conceptually appealing explanation of the separation of scales between mean field and exchange part of the interelectron repulsion energy (which grow like $N^{5/3}$ and N respectively). Mathematically, these decay properties in the finite systems are caused by cancellation effects in certain exponential sums. To quantify these effects we rely on the help of the stationary phase method [So93, St93], in a variant invented originally [La15, Co23, Ha15] to understand some questions in analytic number theory.

In order to recall the precise definition of exchange energy, we try to follow the notation in standard quantum chemistry texts such as Szabo & Ostlund [SO82], Parr & Young [PY89].⁶ The quantum-mechanical state of an N -electron-system confined to a region $\Lambda \subseteq \mathbb{R}^3$ is described by an N -electron wave function, that is, a square-integrable function ‘of space and spin’ $\psi : (\Lambda \times \{\pm 1/2\})^N \rightarrow \mathbb{C}$ which is normalized,

$$\langle \psi | \psi \rangle_\Lambda = 1 \quad (1.1)$$

where

$$\langle \phi | \psi \rangle_\Lambda = \sum_{s_1, \dots, s_N} \int_{\Lambda^N} \phi(r_1, s_1, \dots, r_N, s_N) \psi(r_1, s_1, \dots, r_N, s_N)^* dr_1 \dots dr_N,$$

and obeys the antisymmetry principle (or Pauli exclusion principle, or Fermi statistics)

$$\psi(\dots, r_i, s_i, \dots, r_j, s_j, \dots) = -\psi(\dots, r_j, s_j, \dots, r_i, s_i, \dots) \quad (i \neq j). \quad (1.2)$$

Important examples of N -electron wave functions are determinantal wave functions (or Slater determinants, or single configurations)

$$\psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(r_1, s_1) & \dots & \psi_1(r_N, s_N) \\ \vdots & & \vdots \\ \psi_N(r_1, s_1) & \dots & \psi_N(r_N, s_N) \end{pmatrix}$$

where $\{\psi_1, \dots, \psi_N\}$ is an orthonormal set ($\langle \psi_i | \psi_j \rangle = \delta_{ij}$) of one-electron wave functions. Now the inconspicuous antisymmetric structure induces the following inequality between the quantum mechanical interelectron energy E_{ee} and the ‘classical’ electrostatic self-repulsion energy J of the electronic charge cloud

$$E_{ee}(\psi) = \frac{1}{2} \langle \psi | \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|r_i - r_j|} \psi \rangle_\Lambda < \frac{1}{2} \int_{\Lambda^2} \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' = J(\rho), \quad (1.3)$$

⁵I thank J. Fröhlich for bringing references [Th80, Ba93, GS94] to my attention.

⁶In particular, atomic units $\hbar = m_e = |e| = 1$ are employed throughout.

valid for any determinantal N -electron wave function with associated one-body density (total electronic charge density)

$$\rho(r) = \langle \psi | (\sum_{i=1}^N \delta_{r_i-r}) \psi \rangle_{\Lambda} = N \sum_{s_1, \dots, s_N} \int_{\Lambda^{N-1}} |\psi(r, s_1, r_2, s_2, \dots, r_N, s_N)|^2 dr_2 \dots dr_N. \quad (1.4)$$

This fascinating many-body effect is measured by the energy difference

$$E_x(\psi) = E_{ee}(\psi) - J(\rho) \quad (1.5)$$

(*exchange energy*).⁷

There is associated with these energy functionals a simple intuition in terms of pair correlations which is crucial for an understanding of the mathematical arguments that follow. Introducing the two-body spin density⁸

$$\rho_2^{spin}(r, s, r', s') = \frac{N(N-1)}{2} \sum_{s_3, \dots, s_N} \int_{\Lambda^{N-2}} |\psi(r, s, r', s', r_3, s_3, \dots, r_N, s_N)|^2 dr_3 \dots dr_N \quad (1.6)$$

and the two-body density

$$\rho_2(r, r') = \sum_{s, s'} \rho_2^{spin}(r, s, r', s') \quad (1.7)$$

we may rewrite

$$E_{ee}(\psi) = \int_{\Lambda^2} \frac{\rho_2(r, r')}{|r - r'|} dr dr'.$$

$J(\rho)$ is then the approximation to E_{ee} obtained by assuming the electrons to be independent,

$$\rho_2(r, r') \approx \frac{1}{2} \rho(r) \rho(r'), \quad (1.8)$$

while $E_x(\psi)$ reflects by how much the independent electron assumption fails: it is a weighted average of the *pair correlation function* $C(r, r') = \rho_2(r, r') - \frac{1}{2} \rho(r) \rho(r')$,⁹

$$E_x(\psi) = \int_{\Lambda^2} \frac{C(r, r')}{|r - r'|} dr dr', \quad (1.9)$$

with the contributions of nearby points $r \approx r'$ being dominant. Note that for nearby points the independent electron assumption (1.8) has no hope of being valid for *any* state ψ , since the antisymmetry principle (or Pauli exclusion principle, or Fermi statistics) enforces $\rho_2^{spin}(r, s, r, s) \equiv 0$.

⁷The Coulomb integral $J(\rho)$, unlike $E_{ee}(\psi)$, contains a positive and unphysical self-interaction contribution, $J_{self}(\psi) = \sum_{i=1}^N J(\rho^{(i)})$ where $\rho^{(i)}(r) = \sum_s |\psi_i(r, s)|^2$ is the charge contributed by the i^{th} electron (note $\rho(r) = \sum_{i=1}^N \rho^{(i)}(r)$ for determinantal wave functions). But (1.3) remains valid with $J(\rho)$ replaced by the self-interaction-corrected Coulomb integral $J_{sic}(\psi) = J(\rho) - J_{self}(\psi)$, with the only caveat that one has equality if all the one-electron orbitals ψ_i have disjoint support. (To see this, use (1.9), (2.4), (2.5) together with the fact that $1/|r - r'|$ is a positive kernel.)

⁸The normalization factor, whose denominator will reappear in (1.8), is determined by the convention that ρ_2 integrate to the number of pairs in the system.

⁹The normalization, here, is not standard, but the above $C(r, r')$ will be more convenient notationally than the standard pair correlation function $h(r, r') = C(r, r') / (\frac{1}{2} \rho(r) \rho(r'))$ or the so-called exchange-correlation hole $\rho_{xc}(r, r') = C(r, r') / (\frac{1}{2} \rho(r))$.

The simplest, and classical, setting for studying these pair correlations and exchange phenomena induced by the Pauli exclusion principle is that of the *free electron gas*. This limiting system is obtained from a large number N of electrons moving freely in a cubical box of volume V by letting $N \rightarrow \infty$, $V \rightarrow \infty$ with the density $\bar{\rho} = N/V$ remaining *finite*. Studying the asymptotics of N -body ground states for such a system reduces, of course, to studying the asymptotics of eigenfunctions of the one-body Laplacian. For convenience of the reader we recall this basic algebraic fact as

Lemma 1.1 *Let Λ be a box $[0, L]^3$ or in fact any bounded domain in \mathbb{R}^3 , and let $\lambda_1 = \lambda_2 \leq \lambda_3 = \lambda_4 \leq \dots$ be an ordered listing of eigenvalues, accounting for multiplicity, of $-\frac{1}{2}\Delta_r$ operating on one-body functions $\psi(r, s)$ ($r \in \Lambda$, $s \in \{\pm\frac{1}{2}\}$, $\psi \in \mathcal{C}$) subject to zero boundary conditions. For a determinantal N -electron wave function ψ the following are equivalent: (i) ψ is a ground state of the free electron gas energy $E_{N,\Lambda}(\psi) = \frac{1}{2}\sum_{i=1}^N \langle \nabla_{r_i} \psi | \nabla_{r_i} \psi \rangle_\Lambda$ subject to zero boundary conditions¹⁰, (ii) ψ is a determinant of N orthonormal eigenfunctions ψ_i of the above one-body problem, corresponding to the lowest N eigenvalues.*

It is instructive to look, for a moment, at the special case of an even number of electrons and doubly occupied spinless one-body orbitals $\psi_{2i-1}(r, s) = \phi_i(r)\delta_{-1/2}(s)$, $\psi_{2i}(r, s) = \phi_i(r)\delta_{1/2}(s)$. By well-known identities from Hartree-Fock theory¹¹, ground state density and pair correlation function are

$$\rho_{N,\Lambda}(r) = 2 \sum_{i=1}^{N/2} |\phi_i(r)|^2, \quad (1.10)$$

$$C_{N,\Lambda}(r, r') = - \left| \sum_{i=1}^{N/2} \phi_i(r)\phi_i(r')^* \right|^2. \quad (1.11)$$

As inferred earlier from more general considerations, one sees again that correlations are large for $r \approx r'$, $C_{N,\Lambda}(r, r) = -\frac{1}{4}\rho(r)\rho(r)$. Now one expects for generic sequences ϕ_i , and in more general situations [Sh74, CV85, HMR87, GL93] than cubical boxes, that the faster and faster oscillations of eigenfunctions lead to ergodic behaviour $|\phi_i|^2 \rightharpoonup 1/\text{vol}(\Lambda)$ as $i \rightarrow \infty$ (where the halfarrow denotes weak convergence for example in $L^1(\Lambda)$) whence the ergodic sum $\rho_{N,\Lambda}(r) \approx N/\text{vol}(\Lambda) = \bar{\rho}$ ($r \in \Lambda$). So if there were no decorrelating effects for $r \neq r'$, or mathematically: cancellation effects in the oscillatory sum $\sum_{i=1}^{N/2} \phi_i(r)\phi_i(r')^*$ not present for $r = r'$, one would infer in the thermodynamic limit

$$E_x(\psi_{N,\Lambda}) \sim \int_{\Lambda \times \Lambda} \frac{1}{|r - r'|} dr dr' \sim (\text{vol}(\Lambda))^{5/3} (= L^5 \text{ for the box.})$$

The true scaling is rather different, illustrating the presence and strength of cancellation effects.

Theorem 1.1 *For $N \in \mathbb{N}$ and $L > 0$ let $Q(L) = [0, L]^3$ and let $\psi_{N,L}$ be any determinantal N -electron wave function which minimizes the free electron gas energy $E_{N,Q(L)}$ (as defined in Lemma 1.1), subject to either zero or periodic boundary conditions. Let*

¹⁰i.e. mathematically: a minimizer of $E_{N,\Lambda}$ not just among determinantal wave functions, but on the full set of antisymmetric wave functions $\{\psi : (\Lambda \times \{\pm 1/2\})^N \rightarrow \mathcal{C}, \psi(\cdot, s_1, \dots, \cdot, s_N) \in H_0^1(\Lambda^N, \mathcal{C}) \text{ for all } (s_1, \dots, s_N) \in \{\pm 1/2\}^N, (1.1) \text{ and } (1.2) \text{ hold}\}$ where H_0^1 denotes the usual Sobolev space of square-integrable functions with square-integrable gradient

¹¹which may be verified by means of straightforward calculations from the definitions

$E_x^{LDA}(\rho) = -c_x \int_Q \rho(r)^{4/3} dr$ denote the Dirac-Bloch-Slater functional, where $c_x = \frac{3}{4}(\frac{3}{\pi})^{1/3}$. In the thermodynamic limit $N \rightarrow \infty$, $L \rightarrow \infty$, $N/L^3 \equiv \bar{\rho} \in (0, \infty)$

$$E_x(\psi_{N,L}) = -c_x \bar{\rho}^{4/3} L^3 + \mathcal{O}(L^2), \quad (1.12)$$

$$E_x^{LDA}(\rho_{N,L}) = -c_x \bar{\rho}^{4/3} L^3 + \mathcal{O}(L^2) \quad (1.13)$$

where $\rho_{N,L}$ is the one-body density of $\psi_{N,L}$. In particular, the quotient $E_x(\psi_{N,L})/E_x^{LDA}(\rho_{N,L})$ converges to 1.

We emphasize that the celebrated approximation $E_{ee}(\psi) \approx J(\rho) + E_x^{LDA}(\rho)$ is justified here in situations not covered by the classical calculation (going back to [Di30], [BI29] and justified in [Th80]) for plane wave orbitals and a homogeneous one-body density $\rho_{N,L} \equiv \bar{\rho}$: Theorem 1.1 shows that both open-shell effects and the long-range density oscillations induced by imposing zero boundary conditions, reminiscent of the Friedel oscillations in realistic systems, contribute only a lower order term to E_x , at most of the order of magnitude of the surface area of the box. – The astonishing accuracy of numerical calculations employing this approximation (or small modifications meant to account for correlation effects) in situations where density homogeneity is violated much more strongly than above¹² remains one of the unsolved mysteries of DFT.

The powers of L in the error estimates can of course be converted, via the thermodynamic relation $N = \bar{\rho}L^3$, into powers of the particle number N , yielding errors of order $N^{2/3}$.

Formula (1.12) admits an interesting mathematical variant which we state, for simplicity, in the case of an even number of electrons and doubly occupied one-body orbitals. Fix $N \in \mathbb{N}$ and pick two indices $i, j \in \{1, \dots, N\}$ at random. Consider the product of the i^{th} and j^{th} eigenfunctions (extended by zero to all of \mathbb{R}^3) of the Laplacian in the 3D unit cube. How large, then, is the expected value of the negative Sobolev norm $\|\phi_i \phi_j^*\|_{H^{-1}(\mathbb{R}^3)}$ squared?¹³

Theorem 1.1' *Let Q denote the three-dimensional unit cube, let $\{\phi_i\}_{i \in \mathbb{N}}$ be any orthonormal basis of $L^2(Q, \mathbb{C})$ of eigenfunctions of the Laplacian subject to zero (or periodic) boundary conditions, and assume the ϕ_i are ordered according to the size of their eigenvalues. Then as $N \rightarrow \infty$*

$$\frac{\mathbb{E} \left(\|\phi_i \phi_j^*\|_{H^{-1}(\mathbb{R}^3)}^2 : i, j \leq N \right)}{\frac{1}{16} \left(\frac{6}{\pi} \right)^{\frac{4}{3}} N^{-\frac{2}{3}}} \rightarrow 1$$

where $\mathbb{E}(a_{ij} : (i, j) \in \mathcal{S} \subset \mathbb{N}^2) = |\mathcal{S}|^{-1} \sum_{(i, j) \in \mathcal{S}} a_{ij}$ denotes the average of a collection of real numbers.

(Let us see how this follows from Theorem 1.1. Note first that the $2N$ -electron Slater determinant with spin orbitals $\phi_i(r)\delta_{s=-1/2}$, $\phi_i(r)\delta_{s=1/2}$ ($i = 1, \dots, N$) is a ground state of $E_{2N,Q}$. Call this determinant $\psi_{2N,1}$ and rewrite formulae (1.9), (1.11) as

$$E_x(\psi_{2N,1}) = - \sum_{i,j=1}^N \int_{Q^2} \frac{\phi_i(r)\phi_j(r)^* \phi_i(r')^* \phi_j(r')}{|r-r'|} dr dr' = -4\pi \sum_{i,j=1}^N \|\phi_i \phi_j^*\|_{H^{-1}(\mathbb{R}^3)}^2. \quad (1.14)$$

¹²For instance, cohesive energies, lattice parameters, and elastic constants for solid metals are typically predicted to within a few percent of experimental values. Current developments in the computational literature may be traced through the recent conference proceedings volumes [EI95, GD95, SP95].

¹³Here $\|f\|_{H^{-1}(\mathbb{R}^3)}^2 = \int_{\mathbb{R}^3} ((-\Delta_{\mathbb{R}^3})^{-1} f)^* f$, where $(-\Delta_{\mathbb{R}^3})^{-1}$ is the inverse Laplacian with zero boundary conditions at infinity: $((-\Delta_{\mathbb{R}^3})^{-1} f)(r) = (4\pi)^{-1} \int_{\mathbb{R}^3} |r-r'|^{-1} f(r') dr'$ or alternatively $(-\Delta_{\mathbb{R}^3})^{-1} = \mathcal{F}^{-1} |\xi|^{-2} \mathcal{F}$ where \mathcal{F} is the Fourier transform (see Sect. 4).

Now use the scaling $E_x(\psi_{M,L}) = L^{-1}E_x(\psi_{M,1})$ and apply (1.12).)

Theorem 1.1' may be regarded as an ergodic theorem, indicating a delocalization and decorrelation of eigenfunctions with growing i and describing the rate of this process. We elaborate on this point in Section 8.

Before proceeding to the proof of Theorem 1.1 let us comment on the exponents 4/3 and 3 appearing in (1.12).

The exponent of $\bar{\rho}$ can be derived *rigorously* from a simple scaling argument if the product structure of the leading order term and the exponent of L are known. Namely, suppose that instead of (1.12) one only knew

$$-E_x(\psi_{N,L}) = f(\bar{\rho})L^3 + o(L^3) \quad (1.15)$$

for some unknown, finite, nonzero function $f(\bar{\rho})$. For any ground state ψ of the $(N, L, \bar{\rho})$ system, the scaled state $\psi_\lambda(r_1, s_1, \dots, r_N, s_N) = \lambda^{3N/2}\psi(\lambda r_1, s_1, \dots, \lambda r_N, s_N)$ ($\lambda > 0$) is a ground state of the $(N, L/\lambda, \bar{\rho}\lambda^3)$ system. Using the scaling of the exchange energy, $E_x(\psi_\lambda) = \lambda E_x(\psi)$, dividing by L^3 and letting $L \rightarrow \infty$ gives $f(\bar{\rho}\lambda^3)\lambda^{-3} = \lambda f(\bar{\rho})$, so $f(\bar{\rho}) = f(1)\bar{\rho}^{4/3} = \text{const} \cdot \bar{\rho}^{4/3}$. Nonrigorous variants of this argument are well known but we emphasize that their validity rests on the physically and mathematically nontrivial assumption (formalized here as (1.15)) that the exchange energy scales at fixed particle density like the volume of the system. (For instance, the total interelectronic energy scales like volume to the 5/3.)

To justify assumption (1.15) and to derive the correct exponent of L is more subtle. That the ' \leq ' part of (1.15) must be true is physically expected from the deeper fact that the total binding energy of the finite systems approximating the *interacting* electron gas, and in fact of any collection of nuclei and electrons, cannot exceed a constant times the number of particles in the system ([LN75]; Dyson-Lenard theorem). At least for plane-wave determinants this part of (1.15) follows rigorously from formula (1.10) and a nontrivial inequality of E. Lieb [Li79] related to the proof in [LT75] of the Dyson-Lenard theorem: for arbitrary N -electron wave functions, $E_x(\psi) \geq -C \int_{\mathbb{R}^3} \rho(r)^{4/3} dr$ for some constant C .¹⁴

For general ground states this argument does not work, due to possible concentration effects in ρ . The desired upper bound on $-E_x$ is contained, via (1.9), in the following much finer result on pair correlations. In case of zero boundary data, a certain role is played by the group $G = \{\sigma \in M^{3 \times 3} : \sigma = \text{diag}(\sigma_1, \sigma_2, \sigma_3) \text{ for some } \sigma_j \in \{\pm 1\}\} \cong (\mathbb{Z}_2)^3$ of reflections at the planes parallel to the faces of the cube.

Theorem 1.2 *Let $\psi_{N,L}$ be a determinantal ground state of the free electron gas energy, let $C_{N,L}$ be its pair correlation function (as defined above (1.9)), and let $N/L^3 \equiv \text{const} = \bar{\rho}$. Then for all $r, r' \in [0, L]^3$, in case of periodic boundary conditions*

$$C_{N,L}(r, r') = -\frac{\bar{\rho}^2}{4} \left(\left(h(p_F |r - r'|_{T(L)}) \right)^2 + A_{N,L} \right), \quad (1.16)$$

$$|C_{N,L}(r, r')| \leq c\bar{\rho}^2 \left(N^{-1} + (1 + p_F |r - r'|_{T(L)})^{-4} \right) \quad (1.17)$$

and in case of Dirichlet boundary conditions

$$C_{N,L}(r, r') = -\frac{\bar{\rho}^2}{4} \left(\left(\sum_{\sigma \in G} (\det \sigma) h(p_F |r - \sigma r'|_{T(2L)}) \right)^2 + B_{N,L} \right), \quad (1.18)$$

$$|C_{N,L}(r, r')| \leq c\bar{\rho}^2 \left(N^{-1} + (1 + p_F |r - r'|)^{-4} \right) \quad (1.19)$$

¹⁴The best constant C is not known, but it must be bigger than c_x .

where $h(s) = 3(\sin s - s \cos s)/s^3$, $p_F = (3\bar{\rho}\pi^2)^{1/3}$, and the error terms satisfy

$$|A_{N,L}| \leq c \left(N^{-1} + N^{-1/2} (1 + p_F |r - r'|_{T(L)})^{-2} \right), \quad (1.20)$$

$$|B_{N,L}| \leq c \left(N^{-1} + N^{-1/2} (1 + p_F |r - r'|)^{-2} \right). \quad (1.21)$$

Here c denotes a universal constant independent of r, r', N, L , and $\bar{\rho}$, and $|r - r'|_{T(L)}$ is the natural distance function on the torus $\mathbb{R}^3/L\mathbb{Z}^3$ inherited from the euclidean norm on \mathbb{R}^3 , $|r - r'|_{T(L)} = \min\{|r - (r' + k)| : k \in L\mathbb{Z}^3\}$.

Estimates (1.17), (1.19)¹⁵ show that despite the nonlocality of the Pauli exclusion principle, statistical independence (1.8) is a valid long range law. The fundamental separation of scales between electrostatic mean field energy ($J = \mathcal{O}(N^{5/3})$) and exchange energy ($E_x = \mathcal{O}(N)$) emerges as an immediate consequence, by multiplying the right hand side of (1.17), (1.19) by $1/|r - r'|$ and integrating over $r, r' \in [0, L]^3$.

The decay exponent -4 in (1.17), (1.19) is optimal, in the sense that $(1 + p_F |r - r'|)^{-4}$ cannot be replaced by any function $g(r - r')$ with $g(s)/(1 + |s|)^{-4} \rightarrow 0$ ($|s| \rightarrow \infty$). See Corollary 4.1.

The finer results of Theorem 1.1 on the exchange energy (explicit identification of the leading order term and error estimates) require the finer results (1.16), (1.18), (1.20), (1.21) of Theorem 1.2 (see Section 6).

The leading order term in (1.16) is well known in the physics literature and appeared first in a paper by Wigner & Seitz [WS33]. We recall its beautiful physical interpretation [e.g. WS33, Sl51, PY89]: Since $h(0) = 1$, $\lim_{N,L \rightarrow \infty} C_{N,L}(r, r')$ equals $-1/2$ times the two-body density $\bar{\rho}^2/2$ of a statistically independent sample. So since the one-body density $\rho_{N,L}(r) = \bar{\rho}(1 + \mathcal{O}(N^{-1/2}))$ (see Theorem 5.1), the two-body density $\lim_{N,L \rightarrow \infty} (\rho_2)_{N,L}(r, r')$ approaches $\bar{\rho}^2/2$ as $|r - r'| \rightarrow \infty$ but only $\bar{\rho}^2/4$ as $|r - r'| \rightarrow 0$.¹⁶ The length scale of this ‘exchange hole’ is given by the Fermi wavelength $1/p_F$; note p_F is the Fermi momentum of a free electron gas at density $\bar{\rho}$, i.e. the limiting momentum as $N \rightarrow \infty$ of the highest occupied eigenstate in the finite system.

In case of zero boundary data, the 7 additional terms $\sigma \neq id$ in the sum in (1.18)¹⁷ represent a boundary layer effect, and may be visualized as correlations between an electron at r and ‘virtual electrons’ at the positions obtained from r' by reflection at the faces of the box. See Figure 1.

Figure 1.1 a.
Pair correlations, periodic boundary conditions

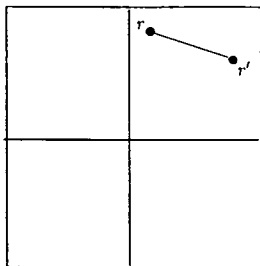
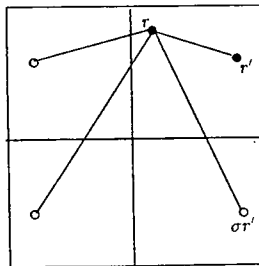


Figure 1.1 b.
Pair correlations, zero boundary conditions



¹⁵ which will be proved without appeal to the explicit formulae for $C_{N,L}$ given above

¹⁶In a fermion system with q spin states the prefactor for $C_{N,L}$ would become $-\frac{1}{q}(\frac{1}{2}\bar{\rho}^2)$ while $(\rho_2)_{N,L}(r, r)$ would approach $\frac{q-1}{q}(\frac{1}{2}\bar{\rho}^2)$, as any given particle is not exchange-correlated to particles of different spin, whose fraction equals $\frac{q-1}{q}$.

¹⁷which we have not previously seen in the literature

Notice that if $\text{dist}(r, \partial[0, L]^3), \text{dist}(r', \partial[0, L]^3) \geq L'$ then $|r - \sigma r'|_{T(2L)} \geq 2L'$ for all $\sigma \neq id$, so

$$C_{N,L}(r, r') = -\frac{1}{4}\bar{\rho}^2 \left((h(p_F|r - r'|))^2 + \mathcal{O}(N^{-1/2}) + \mathcal{O}((p_F L')^{-2}) \right).$$

In particular, away from a boundary layer of thickness $\sim L' = L^{3/4}$ ($\ll L$ for large L) the classical pair correlation function is correct to order $L^{-3/2} \sim N^{-1/2}$.

Starting point for our proof of Theorem 1.2 is the fact that for closed-shell ground states, the pair correlation function is unique and may be expressed as an exponential sum, but as a first novelty, changing to zero boundary data makes the reflection group G appear:

Lemma 1.2 *Let N satisfy the closed-shell condition $\lambda_{N+1} > \lambda_N$, where the λ_i are as in Lemma 1.1. Then for every determinantal ground state of $E_{N,Q(L)}$ subject to zero boundary conditions and all $r, r' \in Q(L)$*

$$C_{N,L}(r, r') = -\left| \frac{1}{8L^3} \sum_{\sigma \in G} \det \sigma \sum_{k \in G\mathcal{L}_N} e^{\frac{i\pi k}{L} \cdot (r - \sigma r')} \right|^2 \quad (1.22)$$

where \mathcal{L}_N is the set of the $N/2$ positive integer lattice points $k \in \mathbb{N}^3$ with smallest euclidean distance to the origin, and G is the reflection group defined above Theorem 1.2. In case of periodic boundary conditions, if N satisfies the above closed-shell condition with the λ_i denoting the analogous periodic one-body eigenvalues, every determinantal ground state satisfies instead

$$C_{N,L}(r, r') = -\left| \frac{1}{L^3} \sum_{k \in \mathcal{L}_N} e^{\frac{2i\pi k}{L} \cdot (r - r')} \right|^2 \quad (1.23)$$

where \mathcal{L}_N is the set of the $N/2$ integer lattice points $k \in \mathbb{Z}^3$ with smallest euclidean distance to the origin.

(For convenience of the reader the elementary calculations are detailed in Section 2 below.)

At this point, the customary derivations of the Dirac-Bloch formula proceed by assuming that the sum over $k \in \mathcal{L}_N$ is well-approximated by the corresponding integral.

But is it? Notice that the function-to-be-summed oscillates in k with amplitude one and with period of order $(r - \sigma r')/L$, i.e. for typical $r, r' \in [0, L]^3$: with period of order one. Thus the function-to-be-summed oscillates on the length scale of the lattice and the obvious error estimate on the continuum approximation only yields the trivial estimate $C(r, r') = \mathcal{O}(1)$. Since the summation over one of the components of k may be carried out explicitly, simple error estimates on the remaining double sum would allow to calculate $C(r, r')$ up to an error of order $L^{-1} \sim N^{-1/3}$, still insufficient to even predict the order of magnitude in L of the exchange energy correctly.

Sufficient – in fact remarkable – error estimates can be obtained through methods of Harmonic Analysis (‘method of stationary phase’).

Lemma 1.3 *In any space dimension n there exists a constant $c_0(n)$ such that for all $R > 0$*

$$\left| \sum_{k \in \mathbb{Z}^n \cap B(R)} e^{ik \cdot z} - \int_{\mathbb{R}^n \cap B(R)} e^{ik \cdot z} dk \right| \leq c_0(1 + R^{n-1-\frac{n-1}{n+1}}), \quad (1.24)$$

for all $|z|_{max} \leq \pi$.¹⁸

¹⁸Here and below $|z|_{max} = \max\{|z_1|, \dots, |z_n|\}$, and $B(R)$ denotes the closed euclidean ball of radius R centered at the origin.

The lemma establishes a uniform bound in one periodic cell of the discrete sum. For a proof see Section 4 below. Estimates of this kind are well known in analytic number theory, but appear not to have been previously considered in the context of exchange and correlation phenomena in many-electron systems. By setting $z = 0$ the lemma reduces to the following classical result on the distribution of lattice points, due to W. Sierpiński [Si06] in dimension $n = 2$ and due to E. Landau [La15] in higher dimensions:

Corollary 1.1 [Si06, La15] *Let $A_n(R)$ be the number of integer points in the ball $B(R) \subset \mathbb{R}^n$, and let τ_n be the volume of the unit ball in \mathbb{R}^n . Then as $R \rightarrow \infty$, $A_n(R) = \tau_n R^n + \mathcal{O}(R^{n-1-\frac{n-1}{n+1}})$.*¹⁹

From Lemma 1.3 together with the fact that the decay at infinity of the continuous term, the Fourier transform of the characteristic function of a ball, is known (Lemma 4.2), it is then not difficult to deduce Theorem 1.2 and our error bounds on the Dirac-Bloch approximation.

The various technical details that remain to be supplied are discussed in Sections 2-6. These are: the elementary calculations leading to the closed-shell result of Lemma 1.2; control of open-shell effects via Corollary 1.1; the demonstration of Lemma 1.3 and Theorem 1.2; control of heterogeneities in the one-body density (Theorem 5.1); and the passage to the limit in the Dirac-Bloch- and the exchange energy functional.

Section 7 is devoted to an issue not discussed in this Introduction: the spurious self-interaction contribution contained in the mean field electrostatic energy $J(\rho)$ (proven to be of lower order than the exchange energy in Theorem 7.1), while Section 8 elaborates on the connection of our work with ergodic theorems for partial differential operators.

2. Pair correlations: closed-shell ground states

Proof of Lemma 1.1. This follows from the fact that the one-body eigenfunctions span the one-body Hilbert space $L^2(\Lambda \times \{\pm \frac{1}{2}\}, \mathcal{C})$, while their Slater determinants span the N -electron Hilbert space $\{\psi \in L^2((\Lambda \times \{\pm \frac{1}{2}\})^N, \mathcal{C}) : (1.2) \text{ holds}\}$.

Proof of Lemma 1.2. The finite-dimensional vector space spanned by the eigenfunctions of $-\frac{1}{2}\Delta$ with eigenvalues $\leq \lambda_N$ has a canonical basis

$$\{\psi_1, \dots, \psi_N\} = \bigcup_{n \in \mathcal{L}_N} \{\phi_n(r)\delta_{s=-\frac{1}{2}}, \phi_n(r)\delta_{s=\frac{1}{2}}\} \quad (2.1)$$

where in the periodic case

$$\phi_n(r) = L^{-3/2} e^{\frac{2\pi i n}{L} \cdot r}, \quad -\frac{1}{2}\Delta\phi_n = \frac{1}{2}\left(\frac{2\pi}{L}\right)^2 |n|^2 \phi_n \quad (2.2)$$

and $\mathcal{L}_N = \mathcal{L}_N^{\text{per}}$ is the set of the $N/2$ integer lattice points $n \in \mathbb{Z}^3$ closest to the origin, and in the Dirichlet case

$$\phi_n(r) = \left(\frac{2}{L}\right)^{3/2} \prod_{j=1}^3 \sin\left(\frac{\pi}{L} n_j r_j\right), \quad -\frac{1}{2}\Delta\phi_n = \frac{1}{2}\left(\frac{\pi}{L}\right)^2 |n|^2 \phi_n \quad (2.3)$$

¹⁹It is almost trivial (and was known to Gauss [Ga63]) that the error is at most of order R^{n-1} . However the precise nature of the error term especially in dimensions 2 and 3 is a fascinating and largely unsolved problem. Note that $A_n(R)R^{-2}$ gives the average number of representations of integers $\leq R^2$ as a sum of n squares. For $n = 3$ Corollary 1.1 seems to entail all that is known about the magnitude of the error. For $n = 2$ the above exponent $2/3$ was improved by many workers beginning with van der Corput [Co23] (to $2/3 - \epsilon$ for some $\epsilon > 0$); the most recent results are $7/11$ [IM88] and $46/73 + \epsilon$ for arbitrarily small $\epsilon > 0$ [Hu91], while it is an old result of Hardy that the optimal exponent cannot be lower than $1/2$ [Ha15].

and $\mathcal{L}_N = \mathcal{L}_N^{\text{Dir}}$ is the set of the $N/2$ positive integer lattice points $n \in \mathbb{N}^3$ closest to the origin.

By the closed shell condition $\lambda_{N+1} > \lambda_N$, the ground state is unique up to multiplication by a phase factor $\alpha \in \{z \in \mathcal{C} : |z| = 1\} = S^1 \cong U(1)$, as is well-known, and easy to see arguing as in the proof of Lemma 1.1. In particular all k -body densities, density matrices, and correlation functions are unique. By Lemma 1.1 the Slater determinant of the canonical basis given by (2.1) and (2.2) resp. (2.3) is a minimizer and thus it suffices to compute its pair correlation function.

To do so we use the following basic formulae from Hartree-Fock theory. For any Slater determinant of one-body orbitals ψ_1, \dots, ψ_N

$$C(r, r') = -\frac{1}{2} \sum_{s, s' = \pm \frac{1}{2}} |\gamma^{\text{spin}}(r, s, r', s')|^2 \quad (2.4)$$

$$\gamma^{\text{spin}}(r, s, r', s') = \sum_{i=1}^N \psi_i(r, s) \psi_i(r', s')^* \quad (2.5)$$

where γ^{spin} is the one-body spin density matrix, while in case (2.1) of doubly occupied spinless one-body orbitals

$$C(r, r') = -\frac{1}{4} |\gamma(r, r')|^2 \quad (2.6)$$

$$\gamma(r, r') = 2 \sum_{i=1}^N \phi_i(r) \phi_i(r')^* \quad (2.7)$$

where $\gamma(r, r') = \sum_{s = \pm 1/2} \gamma^{\text{spin}}(r, s, r', s)$ is the spinless one-body density matrix. The statement in the periodic case follows immediately by substituting (2.2). In the Dirichlet case, substituting (2.3) and using the trigonometric formula $2 \sin \alpha \sin \beta = \cos(\alpha - \beta) - \cos(\alpha + \beta)$ gives

$$\frac{1}{2} \gamma(r, r') = \frac{1}{L^3} \sum_{n \in \mathcal{L}_N} \prod_{j=1}^3 \left(\cos \frac{\pi}{L} n_j (r_j - r'_j) - \cos \frac{\pi}{L} n_j (r_j + r'_j) \right). \quad (2.8)$$

The right hand side can be simplified by invoking the group G twice, through the elementary identity

$$\prod_{j=1}^3 \left(\cos \frac{\pi}{L} n_j (r_j - r'_j) - \cos \frac{\pi}{L} n_j (r_j + r'_j) \right) = \sum_{\sigma \in G} \det \sigma \prod_{j=1}^3 \cos \frac{\pi}{L} n_j (r - \sigma r')_j$$

and the trigonometric formula

$$\prod_{j=1}^3 \cos \alpha_j \beta_j = \frac{1}{8} \sum_{\tau \in G} e^{i\alpha \cdot \tau \beta}.$$

This establishes (1.22).

We conclude this section by noting, for further reference, the following property of the eigenbases introduced above:

Lemma 2.1 *There exists a universal constant c such that for every member ψ_i of the periodic basis (2.1), (2.2) or the Dirichlet basis (2.1), (2.3), $\sup_{r, s} |\psi_i(r, s)|^2 \leq cL^{-3}$.*

3. Pair correlations: open-shell effects

For open-shell determinants, ground state and pair correlation function are no longer unique. The regular structure in the exponential sums (1.22), (1.23) (in which no direction within the integer lattice in k -space is preferred) can become contaminated, and it does not seem obvious that these contaminations are negligible when computing the exchange energy.

To quantify these effects we combine the lattice point estimate from Corollary 1.1 with an observation that the orthonormality of spin orbitals, although only a restriction on averages (L^2 inner products), yields some pointwise smallness of the deviation of the one-body spin density matrix from its closed-shell behaviour.

For either choice of boundary condition (Dirichlet or periodic), let $0 < \lambda_1 = \lambda_2 \leq \lambda_3 = \lambda_4 \leq \dots$ be the corresponding one-body eigenvalues of $-\frac{1}{2}\Delta$ in $[0, L]^3$, and let $\{\psi_1, \psi_2, \dots\}$ be the canonical basis defined in (2.1), (2.3) or (2.1), (2.2). For $N \in \mathbb{N}$ define the number of closed-shell electrons,

$$N_- = \max\{n \leq N : \lambda_n < \lambda_{n+1}\},$$

the number of electrons in the next closed shell state,

$$N_+ = \min\{n \geq N : \lambda_n < \lambda_{n+1}\},$$

and the degeneracy of the open shell,

$$d(N) = N_+ - N_-.$$

These three quantities, while independent of L , of course depend on the boundary conditions, and when necessary this will be indicated by superscripts $(\)^{Dir}$ or $(\)^{per}$.

Lemma 3.1 *Let $N \in \mathbb{N}$, $L > 0$, $N/L^3 = \bar{\rho}$. Then for some universal constant c and every one-body spin density matrix $\gamma_{N,L}$ of a determinantal ground state $\psi_{N,L}$ of $E_{N,Q(L)}$*

$$\sup_{r,s,r',s'} \left| \gamma_{N,L}^{spin}(r,s,r',s') - \gamma_{N-,L}^{spin}(r,s,r',s') \right| \leq c\bar{\rho}N^{-1/2},$$

where $\gamma_{N-,L}^{spin}$ is the spin density matrix of the ground state of $E_{N-,L}$.

The following lemma will be used in the proof of Lemma 3.1.

Lemma 3.2 *There exists a universal constant c such that $d^{Dir}(N) \leq cN^{1/2}$, $d^{per}(N) \leq cN^{1/2}$ for all $N \in \mathbb{N}$.*

Proof. By Corollary 1.1 on lattice points in \mathbb{R}^3 ,

$$\left| S(R) \cap \mathbb{Z}^3 \right| = \inf_{R' > R} A_3(R') - \sup_{R' < R} A_3(R') \leq c(1 + R^{3/2})$$

for all $R > 0$ and some universal constant c . Here $S(R)$ denotes the sphere of radius R in \mathbb{R}^3 centered at the origin. The assertion now follows from the formulae $d^{Dir}(N) = 2|S(R_N^{Dir}) \cap \mathbb{N}^3|$, $d^{per}(N) = 2|S(R_N^{per}) \cap \mathbb{Z}^3|$, with the respective Fermi radii of the discrete systems given by

$$R_N^{Dir} = \max\{|n| : n \in \mathcal{L}_{N_+^{Dir}}\}, \quad (3.1)$$

$$R_N^{per} = \max\{|n| : n \in \mathcal{L}_{N_+^{per}}\}, \quad (3.2)$$

and the elementary estimates $R_N^{Dir} \leq cN^{1/3}$, $R_N^{per} \leq cN^{1/3}$.

Proof of Lemma 3.1. By Lemma 1.1 and (2.5), if $\psi_{N,L}$ is any determinantal ground state, its one-body spin density matrix is

$$\gamma^{spin}(x, x') = \sum_{i=1}^N \psi'_i(x) \psi'^*_i(x') = \sum_{i=1}^{N_-} \psi'_i(x) \psi'^*_i(x') + \sum_{i=N_-+1}^N \psi'_i(x) \psi'^*_i(x')$$

for some collection of orthonormal eigenfunctions satisfying $-\frac{1}{2}\Delta\psi'_i = \lambda_i\psi'_i$. Consider first the first sum on the right hand side. Since N_- corresponds to a closed shell, the vector space over \mathcal{C} spanned by the ψ'_i ($i \in \{1, \dots, N_-\}$) coincides with the space spanned by the canonical eigenfunctions ψ_i ($i \in \{1, \dots, N_-\}$), so $\psi'_i = \sum_{j=1}^{N_-} U_{ij}\psi_j$ for some $U_{ij} \in \mathcal{C}$. By the L^2 -orthonormality of the ψ_i and the ψ'_i , $U = (U_{ij})$ must be unitary,²⁰ i.e. $U(U^*)^T = (U^*)^T U = id$. Consequently $\sum_{i=1}^{N_-} \psi'_i(x) \psi'^*_i(x') = \sum_{i=1}^{N_-} \psi_i(x) \psi^*_i(x') = \gamma_{N_-,L}^{spin}(x, x')$.

Consider now the second sum on the right hand side. The space spanned by the ψ'_i ($i \in \{N_-+1, \dots, N\}$) is a subspace of the eigenspace with eigenvalue $\lambda_{N_-+1} = \dots = \lambda_N = \lambda_{N_+}$. Thus $\psi'_i = \sum_{j=N_-+1}^{N_+} U_{ij}\psi_j$ for some $U_{ij} \in \mathcal{C}$ ($i \in \{N_-+1, \dots, N\}$, $j \in \{N_-+1, \dots, N_+\}$). U can, of course, never be unitary for an open shell ($N_+ > N$), but the L^2 -orthonormality yields $U(U^*)^T = id_{(N-N_-) \times (N-N_-)}$, and consequently $(U^*)^T U$ is a projection operator; in particular $|(U^*)^T U v| \leq |v|$ for all $v \in \mathcal{C}^{N_+-N_-}$. This observation leads to a pointwise estimate:

$$\begin{aligned} \left| \sum_{i=N_-+1}^N \psi'_i(x) \psi'^*_i(x') \right| &= \left| \sum_{j,k=N_-+1}^{N_+} ((U^*)^T U)_{kj} \psi_j(x) \psi^*_k(x') \right| \\ &\leq \left(\sum_{j=N_-+1}^{N_+} |\psi_j(x)|^2 \right)^{\frac{1}{2}} \left(\sum_{k=N_-+1}^{N_+} |\psi_k(x')|^2 \right)^{\frac{1}{2}} \leq d(N) \sup_{j,x} |\psi_j(x)|^2. \end{aligned}$$

One concludes by applying Lemmas 3.2 and 2.1.

4. Pair correlations: discreteness effects

This section touches on the heart of pair correlations and the Dirac-Bloch formula. It shows how the lack of strong a-priori bounds on the oscillating field $e^{i(\pi/L)(r-r') \cdot k}$ can be overcome, by using the special exponential structure, to justify the continuum approximation

$$\sum_{k \in \mathbb{Z}^n \cap B(R)} e^{i(\pi/L)k \cdot (r-r')} \approx \int_{\mathbb{R}^n \cap B(R)} e^{i(\pi/L)k \cdot (r-r')} dk.$$

Proof of Lemma 1.3. Up to uniformity in z , the result is due to E. Landau [La15]. Our proof is an adaptation of the analysis in [So93, Thm 1.2.3] where the lemma is proved for $z = 0$.

We use the Fourier transform $\mathcal{F} : L^2(\mathbb{R}^n; \mathcal{C}) \rightarrow L^2(\mathbb{R}^n; \mathcal{C})$ normalized so that for functions $u \in L^1(\mathbb{R}^n; \mathcal{C}) \cap L^2(\mathbb{R}^n; \mathcal{C})$

$$\hat{u}(k) = (\mathcal{F}u)(k) = \int_{\mathbb{R}^n} e^{-ik \cdot z} u(z) dz.$$

²⁰Beware that in our notation $(\)^*$ denotes complex conjugation, so the adjoint of U is $(U^*)^T$, not U^* .

Its inverse $\mathcal{F}^{-1} : L^2(\mathbb{R}^n; \mathcal{C}) \rightarrow L^2(\mathbb{R}^n; \mathcal{C})$ is then $(\mathcal{F}^{-1}v)(x) = (2\pi)^{-n}\hat{v}(-x)$, and convolutions $(u * v)(z) = \int_{\mathbb{R}^n} u(z-y)v(y) dy$ behave as

$$(\widehat{u*v})(k) = \hat{u}(k)\hat{v}(k), \quad (\widehat{uv})(k) = (2\pi)^{-n}(\hat{u} * \hat{v})(k). \quad (4.1)$$

If u is smooth and decays sufficiently fast to zero at infinity, its Fourier transform is linked to the discrete Fourier series of a certain natural 2π -periodic function associated to u :

Lemma 4.1 (Poisson summation formula) [e.g. So93, Thm 0.1.16]

If, for instance, u or $\hat{u} \in C_0^\infty(\mathbb{R}^n; \mathcal{C})$ then

$$(2\pi)^{-n} \sum_{k \in \mathbb{Z}^n} \hat{u}(k) e^{ik \cdot z} = \sum_{k \in \mathbb{Z}^n} u(z + 2\pi k).$$

Poisson's formula cannot be applied directly to the discontinuous function $\hat{u}(k) = \chi_{B(R)}(k)$ (in fact the sum on the right hand side would diverge, providing a nice example that the formula fails if \hat{u} is not smooth enough). Instead one first smoothens $\chi_{B(R)}$ by local averaging over a small length scale ϵ , later to be adjusted carefully as a suitable negative power of R depending on dimension.

Take $\eta \in C_0^\infty(\mathbb{R}^n; \mathbb{R})$, $\eta(z) = \eta(-z)$, $\int_{\mathbb{R}^n} \eta = 1$, $\eta \geq 0$, $\eta = 0$ outside $B(R')$ for some $R' < 1$, and let $\eta_\epsilon = \epsilon^{-n}\eta(\epsilon^{-1}\cdot)$. Apply Poisson's formula to $(2\pi)^{-n}\hat{u} = \chi_{B(R)} * \eta_\epsilon$, noting $u = \widehat{\chi_{B(R)} * \eta_\epsilon} = \widehat{\chi_{B(R)}} \hat{\eta}_\epsilon$ by (4.1):

$$\sum_{k \in \mathbb{Z}^n} (\chi_{B(R)} * \eta_\epsilon)(k) e^{ik \cdot z} = \sum_{k \in \mathbb{Z}^n} (\widehat{\chi_{B(R)}} \hat{\eta}_\epsilon)(z + 2\pi k).$$

By the scaling of the Fourier transform under dilatation of the domain,

$$\mathcal{F}(u(\lambda \cdot)) = \lambda^{-n}(\mathcal{F}u)(\lambda^{-1}\cdot), \quad (4.2)$$

one has $\hat{\eta}_\epsilon = \hat{\eta}(\epsilon \cdot)$. Splitting off the $k = 0$ term on the right hand side (note $\hat{\eta}(0) = 1$),

$$\sum_{k \in \mathbb{Z}^n} (\chi_{B(R)} * \eta_\epsilon)(k) e^{ik \cdot z} - \widehat{\chi_{B(R)}}(z) \quad (4.3)$$

$$= \sum_{k \in \mathbb{Z}^n \setminus \{0\}} \widehat{\chi_{B(R)}}(z + 2\pi k) \hat{\eta}(\epsilon z + \epsilon(2\pi k)) \quad (4.4)$$

$$+ \widehat{\chi_{B(R)}}(z) (\hat{\eta}(\epsilon z) - \hat{\eta}(0)). \quad (4.5)$$

Lemma 4.2 [e.g. St93 VIII 1.4.1; So93 Cor. 1.2.2]

In any space dimension n the Fourier transform of the characteristic function of the unit ball has the following decay behaviour: $|\widehat{\chi_{B(1)}}(k)| \leq c(n)(1 + |k|)^{-(n+1)/2}$.²¹

(For $n = 3$, from the explicit formula (6.4) below it is not hard to see that $c = 32\pi$ will do.) The term (4.5) is thus in absolute value bounded above by

$$c_1 R^n (1 + |Rz|)^{-(n+1)/2} \epsilon |z| \sup_{\mathbb{R}^n} |\nabla \hat{\eta}| \leq c_2 \epsilon R^{n-1} |Rz| (1 + |Rz|)^{-(n+1)/2},$$

²¹This statement on the volume measure $\chi_{B(1)} d\mathcal{L}^n$ is closely related to the decay of the Fourier transform of surface-carried measures like $\mu = \chi_{S(1)} d\mathcal{H}^{n-1}$, $|\hat{\mu}(k)| \leq c(n)(1 + |k|)^{-(n-1)/2}$ [St93 VIII.3, So93 Thm 1.2.1], for the truth of which radial symmetry could be replaced by appropriate curvature properties, and which underlies the remarkable restriction properties for Fourier transforms of L^p functions onto surfaces [e.g. St93 Thm VIII.3].

where here and below c_1, c_2 etc. denote constants independent of R and z .

Since $\eta \in C_0^\infty(\mathbb{R}^n; \mathbb{R})$, for any $m \in \mathbb{N}$

$$|\hat{\eta}(z)| \leq c(m)(1 + |z|)^{-m}.$$

The term (4.4) is thus in absolute value bounded above by

$$\begin{aligned} & c_3 \sum_{k \in \mathbb{Z}^n \setminus \{0\}} R^n \left(1 + 2\pi R \left|\frac{z}{2\pi} + k\right|\right)^{-(n+1)/2} \left(1 + 2\pi \epsilon \left|\frac{z}{2\pi} + k\right|\right)^{-m} \\ & \leq c_4 \sum_{k \in \mathbb{Z}^n \setminus \{0\}} R^n \left(1 + |Rk|_{max}\right)^{-(n+1)/2} \left(1 + |\epsilon k|_{max}\right)^{-m} \quad \forall |z|_{max} \leq \pi \end{aligned} \quad (4.6)$$

where $|z|_{max} = \max\{|z_1|, \dots, |z_n|\}$ and we have used that z is restricted to one periodic cell, $|z/(2\pi)|_{max} \leq 1/2$, whence

$$\left|\frac{z}{2\pi} + k\right| \geq \left|\frac{z}{2\pi} + k\right|_{max} \geq |k|_{max} - \frac{1}{2} \geq \frac{1}{2}|k|_{max} \geq \frac{1}{2\sqrt{n}}|k|.$$

Now introduce $\Lambda_k = \{k' \in \mathbb{R}^n : k_i - 1 < k'_i \leq k_i \forall k_i \geq 0, k_i \leq k'_i < k_i + 1 \forall k_i < 0\}$, the unit cube with edges parallel to the coordinate axes with k being the farthest corner from the origin. Since every $k' \in \mathbb{R}^n$ is contained in at most 2^n such cubes, (4.6) is bounded by

$$\begin{aligned} & c_4 \sum_{k \in \mathbb{Z}^n \setminus \{0\}} \int_{\Lambda_k} R^n \left(1 + |Rk'|_{max}\right)^{-\frac{n+1}{2}} \left(1 + |\epsilon k'|_{max}\right)^{-m} dk' \\ & \leq 2^n c_4 \int_{\mathbb{R}^n} R^n \left(1 + |Rk'|_{max}\right)^{-\frac{n+1}{2}} \left(1 + |\epsilon k'|_{max}\right)^{-m} dk' = 2^n c_4 \left(\int_{\{|k'| < \epsilon^{-1}\}} + \int_{\{|k'| > \epsilon^{-1}\}} \right) \\ & \leq 2^n c_4 \left(\tau_n R^n \int_0^{1/\epsilon} r^{n-1} (1 + Rr)^{-\frac{n+1}{2}} dr + \frac{(R\epsilon^{-1})^n}{(1 + R\epsilon^{-1})^{(n+1)/2}} \int_{\mathbb{R}^n} (1 + |k'|)^{-m} dk' \right). \end{aligned} \quad (4.7)$$

Choosing $m > n$, the second integral on the right hand side converges. Assuming without loss of generality $n \geq 2$, the first integral in the last expression is bounded by

$$\int_{r=0}^{\epsilon^{-1}} R^{-(n+1)/2} r^{(n-3)/2} dr = \frac{2}{n-1} R^{-(n+1)/2} \epsilon^{-(n-1)/2},$$

hence (4.7) does not exceed $c_5 (R\epsilon^{-1})^{(n-1)/2}$. Summarizing the bounds on (4.4), (4.5),

$$\begin{aligned} & \left| \sum_{k \in \mathbb{Z}^n} (\chi_{B(R)} * \eta_\epsilon)(k) e^{ik \cdot z} - \widehat{\chi_{B(R)}}(z) \right| \\ & \leq c_6 \left((R\epsilon^{-1})^{(n-1)/2} + \epsilon R^{n-1} |Rz| (1 + |Rz|)^{-(n+1)/2} \right) \quad \forall |z| \leq \pi. \end{aligned} \quad (4.8)$$

Next we turn to the error made by smoothing $\chi_{B(R)}$. Recall the notation $A_n(R) = \sum_{k \in \mathbb{Z}^n} \chi_{B(R)}(k)$. Since $\eta_\epsilon = 0$ outside $B(\epsilon)$ and $0 \leq \eta_\epsilon * \chi_{B(R)} \leq 1$,

$$\begin{aligned} & \left| \sum_{k \in \mathbb{Z}^n} (\chi_{B(R)} * \eta_\epsilon)(k) e^{ik \cdot z} - \sum_{k \in \mathbb{Z}^n} \chi_{B(R)}(k) e^{ik \cdot z} \right| \\ & \leq \sum_{k \in \mathbb{Z}^n} |(\chi_{B(R)} * \eta_\epsilon)(k) - \chi_{B(R)}(k)| \leq A_n(R + \epsilon) - A_n(R - \epsilon) \end{aligned} \quad (4.9)$$

and

$$\sum_{k \in \mathbb{Z}^n} (\chi_{B(R-\epsilon)} * \eta_\epsilon)(k) \leq A_n(R) \leq \sum_{k \in \mathbb{Z}^n} (\chi_{B(R+\epsilon)} * \eta_\epsilon)(k). \quad (4.10)$$

By (4.8) with $z = 0$

$$\left| \sum_{k \in \mathbb{Z}^n} (\chi_{B(R')} * \eta_\epsilon)(k) - \widehat{\chi_{B(R')}}(0) \right| \leq c_6 (R' \epsilon^{-1})^{(n-1)/2}$$

and hence

$$\sum_{k \in \mathbb{Z}^n} (\chi_{B(R')} * \eta_\epsilon)(k) = \tau_n (R')^n + \mathcal{O}((R' \epsilon^{-1})^{(n-1)/2}).$$

But now, assuming without loss of generality $\epsilon \leq 1$,

$$\begin{aligned} & \left| \sum_{k \in \mathbb{Z}^n} (\chi_{B(R+\epsilon)} * \eta_\epsilon)(k) - \sum_{k \in \mathbb{Z}^n} (\chi_{B(R-\epsilon)} * \eta_\epsilon)(k) \right| \\ &= \tau_n ((R+\epsilon)^n - (R-\epsilon)^n) + \mathcal{O}((R\epsilon^{-1})^{(n-1)/2}) = \mathcal{O}(\epsilon R^{n-1} + (R\epsilon^{-1})^{(n-1)/2}) \end{aligned}$$

whence by (4.10)

$$A_n(R) = \tau_n R^n + \mathcal{O}(\epsilon R^{n-1} + ((R\epsilon^{-1})^{(n-1)/2})). \quad (4.11)$$

Finally, applying this to $R+\epsilon$ and $R-\epsilon$ and substituting into (4.9) yields

$$\left| \sum_{k \in \mathbb{Z}^n} (\chi_{B(R)} * \eta_\epsilon)(k) e^{ik \cdot z} - \sum_{k \in \mathbb{Z}^n} \chi_{B(R)}(k) e^{ik \cdot z} \right| \leq c_7 (\epsilon R^{n-1} + ((R\epsilon^{-1})^{(n-1)/2})). \quad (4.12)$$

Combining (4.8), (4.12) and the fact that $\epsilon R^{n-1} + ((R\epsilon^{-1})^{(n-1)/2})$ is minimized when $\epsilon = ((n-1)/2)^{2/(n+1)} R^{-(n-1)/(n+1)}$, the assertion of Lemma 1.3 follows.

We proceed next to convert our knowledge gathered in Lemma 1.3 about exponential sums into information about one-body density matrices $\gamma(r, r')$ and pair correlation functions $C(r, r')$. We begin with the case of zero boundary conditions and the closed-shell case $N = N_-$. To understand why away from a boundary layer these quantities closely resemble their periodic counterparts, introduce the set of projections onto the median planes parallel to the faces of the cube $[0, L]^3$, $P = \{\pi_1, \pi_2, \pi_3\}$ where $\pi_i = \sum_{j \in \{1,2,3\} \setminus \{i\}} e_j \otimes e_j$. We may rewrite formula (2.8) as

$$\frac{1}{2} \gamma_{N,L}(r, r') = \sum_{\sigma \in G} (\det \sigma) a_{N,L}(r - \sigma r') \quad \text{for all } r, r' \in [0, L]^3 \quad (4.13)$$

where

$$\begin{aligned} a_{N,L}(y) &= (2L)^{-3} \sum_{k \in G \mathcal{L}_N^{D_{ir}}} e^{i(\pi/L)k \cdot y} = (2L)^{-3} \sum_{k \in (\mathbb{Z} \setminus \{0\})^3 \cap B(R_N^{D_{ir}})} e^{i(\pi/L)k \cdot y} \\ &= (2L)^{-3} \left(\sum_{k \in \mathbb{Z}^3 \cap B(R_N^{D_{ir}})} e^{ik \cdot (\pi/L)y} - \sum_{k' \in \mathbb{Z}^2 \cap B(R_N^{D_{ir}}), \pi_j \in P} e^{i(\pi/L)k' \cdot \pi_j(y)} \right. \\ &\quad \left. + \sum_{k'' \in \mathbb{Z} \cap B(R_N^{D_{ir}}), j \in \{1,2,3\}} e^{i(\pi/L)k'' \cdot y_j} - 1 \right). \end{aligned} \quad (4.14)$$

Now the last three terms on the right hand side of (4.14), when evaluated on $y = r - \sigma r'$ and summed over σ , vanish: indeed $\sum_{\sigma \in G} (\det \sigma) f(\pi_j(r - \sigma r'))$, $\sum_{\sigma \in G} (\det \sigma) g((r - \sigma r')_j)$,

$\Sigma_{\sigma \in G} \det \sigma$ are zero for any functions f, g , since each term appears twice, with opposite sign. So $a_{N,L}$ may and shall be redefined as

$$a_{N,L}(y) = (2L)^{-3} \sum_{k \in \mathbb{Z}^3 \cap B(R_N^{Dir})} e^{ik \cdot (\pi/L)y} \quad (4.15)$$

without affecting the validity of (4.13).

We would like to apply Lemma 1.3 but a little care is needed regarding the range of $y = r - \sigma r'$ for $r, r' \in [0, L]^3$. If $\sigma = id$ then $y \in [-L, L]^3$, or equivalently $z = (\pi/L)y$ satisfies $|z|_{max} \leq \pi$, i.e. lies in the domain where the continuum approximation of the exponential sum is valid. But if $\sigma_{ii} = -1$ then y_i ranges instead over $[0, 2L]$ so we need to introduce the periodically extended continuum approximation

$$a_{N,L}^{cts}(y) = \left(\frac{R_N^{Dir}}{2L}\right)^3 \widehat{\chi_{B^3(1)}} \left(\frac{R_N^{Dir}}{L} \pi (y \bmod 2L)\right) = (2L)^{-3} \widehat{\chi_{B^3(R_N^{Dir})}} \left(\frac{\pi}{L} (y \bmod 2L)\right), \quad (4.16)$$

where $B^n(1)$ stands for the unit ball in \mathbb{R}^n , and for any $y \in \mathbb{R}^3$ we denote by $y \bmod 2L$ the unique element $y' \in [-L, L]^3$ such that $y \in y' + 2L\mathbb{Z}^3$. (With the norm introduced in Theorem 1.2, $|y|_{T(2L)} = |y'|$.)

Now lift the restriction to closed-shell ground states and define for arbitrary N :

$$a_{N,L}^{cts}(y) = a_{N-,L}^{cts}(y). \quad (4.17)$$

Applying Lemma 1.3 to the right hand side of (4.15), denoting $\bar{\rho} = N/L^3$ and using $R_N^{Dir} \leq cN^{1/3}$,

$$\left| a_{N-,L}(r - \sigma r') - a_{N,L}^{cts}(r - \sigma r') \right| \leq c\bar{\rho}N^{-1/2} \quad (4.18)$$

for all $r, r' \in [0, L]^3$ and some universal constant c .

Since the long range behaviour of the Fourier transform $\widehat{\chi_{B^3(1)}}$ is known (Lemma 4.2) and open-shell effects can be controlled (Lemma 3.1) one infers the following version of Theorem 1.2.

Theorem 4.1 (Continuum approximation, zero boundary conditions)

Let $N \in \mathbb{N}$, $L > 0$, $N/L^3 = \bar{\rho}$, $a_{N,L}^{cts}$ as in (4.16), (4.17). Let $\psi_{N,L}$ be any determinantal ground state of the free electron gas energy (subject to zero boundary conditions). Then its one-body density matrix and pair correlation function satisfy

$$\left| \frac{1}{2} \gamma_{N,L}(r, r') - \sum_{\sigma \in G} (\det \sigma) a_{N,L}^{cts}(r - \sigma r') \right| \leq c\bar{\rho}N^{-\frac{1}{2}}, \quad (4.19)$$

$$\left| \gamma_{N,L}(r, r') \right| \leq c\bar{\rho} \left(N^{-\frac{1}{2}} + (1 + \bar{\rho}^{\frac{1}{3}} |r - r'|)^{-2} \right), \quad (4.20)$$

$$\left| C_{N,L}(r, r') + \left| \sum_{\sigma \in G} (\det \sigma) a_{N,L}^{cts}(r - \sigma r') \right|^2 \right| \leq c\bar{\rho}^2 \left(N^{-1} + N^{-\frac{1}{2}} (1 + \bar{\rho}^{\frac{1}{3}} |r - r'|)^{-2} \right), \quad (4.21)$$

$$\left| C_{N,L}(r, r') \right| \leq c\bar{\rho}^2 \left(N^{-1} + (1 + \bar{\rho}^{\frac{1}{3}} |r - r'|)^{-4} \right) \quad (4.22)$$

for all $r, r' \in [0, L]^3$ and some universal constant c .

Proof. The first two inequalities follow immediately from (4.13), (4.15), (4.18), Lemma 3.1, Lemma 4.2, the elementary inequality $c_1 \bar{\rho}^{1/3} \leq R_{N-}/L \leq c_2 \bar{\rho}^{1/3}$, and the fact that $|r - \sigma r' \bmod 2L| \geq |r - r'|$ for all $\sigma \in G$, $r, r' \in [0, L]^3$. The fourth inequality follows by squaring

(4.20). Finally, to prove the third inequality, introduce $\gamma^{cts}(r, r') = 2\sum_{\sigma \in G} (\det \sigma) a_{N,L}^{cts}(r - \sigma r')$, rewrite the pair correlation function as

$$C = -\left|\frac{1}{2}\gamma\right|^2 = -\frac{1}{4}\operatorname{Re}\left((\gamma + \gamma^{cts})(\gamma - \gamma^{cts})^*\right) - \left|\frac{1}{2}\gamma^{cts}\right|^2$$

and note that the absolute value of the first term on the right hand side cannot exceed a constant times the product of the right hand sides of (4.19) and (4.20).

In case of periodic boundary conditions the group G collapses to the identity, but the subtleties regarding the domain of validity of the continuum approximation are slightly different. Begin, again, with the closed shell situation $N = N_-$. The ground state density matrix is then

$$\frac{1}{2}\gamma_{N,L}(r, r') = L^{-3} \sum_{k \in \mathcal{L}_N^{p_{e,r}}} e^{(2i\pi/L)k \cdot (r - r')} = L^{-3} \sum_{k \in \mathbb{Z}^3 \cap B(R_N^{p_{e,r}})} e^{(2i\pi/L)k \cdot (r - r')}.$$

As r, r' vary over one periodic cell $[0, L]^3$, the exponent $z = (2\pi/L)(r - r')$ now ranges over $[-2\pi, 2\pi]^3$; that is: over two periods (in each coordinate) of the exponential sum we wish to approximate. So this time the appropriate periodically extended continuum approximation reads

$$b_{N,L}^{cts}(y) = \left(\frac{R_N^{p_{e,r}}}{L}\right)^3 \widehat{\chi_{B^3(1)}}\left(\frac{2\pi R_N^{p_{e,r}}}{L}(y \bmod L)\right). \quad (4.23)$$

Note $z' = (2\pi/L)((r - r') \bmod L) \in [-L, L]^3$. Lemmas 1.3, 3.1 and 4.2 then yield

Theorem 4.2 (Continuum approximation, periodic boundary conditions)

Let $N \in \mathbb{N}$, $L > 0$, $N/L^3 = \bar{\rho}$, and $b_{N,L}^{cts}$ as defined in (4.23). Let $\psi_{N,L}$ be any determinantal ground state of the free electron gas energy (subject to periodic boundary conditions). Then its one-body density matrix and pair correlation function satisfy

$$\left|\frac{1}{2}\gamma_{N,L}(r, r') - b_{N,L}^{cts}(r - r')\right| \leq c\bar{\rho}N^{-\frac{1}{2}}, \quad (4.24)$$

$$\left|\gamma_{N,L}(r, r')\right| \leq c\bar{\rho}\left(N^{-\frac{1}{2}} + (1 + \bar{\rho}^{\frac{1}{3}}|r - r'|_{T(L)})^{-2}\right), \quad (4.25)$$

$$\left|C_{N,L}(r, r') + |b_{N,L}^{cts}(r - r')|^2\right| \leq c\bar{\rho}^2\left(N^{-1} + N^{-\frac{1}{2}}(1 + \bar{\rho}^{\frac{1}{3}}|r - r'|_{T(L)})^{-2}\right), \quad (4.26)$$

$$\left|C_{N,L}(r, r')\right| \leq c\bar{\rho}^2\left(N^{-1} + (1 + \bar{\rho}^{\frac{1}{3}}|r - r'|_{T(L)})^{-4}\right) \quad (4.27)$$

for all $r, r' \in [0, L]^3$ and some universal constant c .

The long-range decay results (1.17), (1.19) in Theorem 1.2 are thus proved without appeal to the explicit formulae (1.16), (1.18) for the continuum limits. To justify these explicit expressions and complete the proof of Theorem 1.2, it suffices to establish the following

Lemma 4.3 If $N/L^3 \equiv \bar{\rho}$ and h, p_F are as in Theorem 1.2 then

$$\begin{aligned} |a_{N,L}^{cts}(y) - \frac{1}{2}\bar{\rho}h(p_F|y|_{T(2L)})| &\leq c\bar{\rho}N^{-1/2}, \\ |b_{N,L}^{cts}(y) - \frac{1}{2}\bar{\rho}h(p_F|y|_{T(L)})| &\leq c\bar{\rho}N^{-1/2} \end{aligned}$$

for some universal constant c .

Proof. By Lemmas 1.3, 3.2 on lattice points in \mathbb{R}^3

$$\frac{N}{2} = \frac{N_-}{2} + \mathcal{O}(N^{\frac{1}{2}}) = |\mathbb{Z}^3 \cap B(R_{N_-}^{per})| + \mathcal{O}(N^{\frac{1}{2}}) = \frac{4}{3}\pi(R_{N_-}^{per})^3 + \mathcal{O}((R_{N_-}^{per})^{\frac{3}{2}}) + \mathcal{O}(N^{\frac{1}{2}})$$

and thus

$$(R_{N_-}^{per})^3 = \frac{1}{8}\frac{3}{\pi}N + \mathcal{O}(N^{1/2}), \quad \left(\frac{R_{N_-}^{per}}{L}\right)^3 = \frac{1}{8}\frac{3}{\pi}\bar{\rho}(1 + \mathcal{O}(N^{-1/2})). \quad (4.28)$$

Similarly

$$(R_{N_-}^{Dir})^3 = \frac{3}{\pi}N + \mathcal{O}(N^{1/2}), \quad \left(\frac{R_{N_-}^{Dir}}{L}\right)^3 = \frac{3}{\pi}\bar{\rho}(1 + \mathcal{O}(N^{-1/2})). \quad (4.29)$$

By applying the elementary inequality $|a - b| \leq |a^3 - b^3| / \max\{a^2, b^2\}$ ($a, b > 0$)

$$\frac{R_{N_-}^{Dir}}{L} = \left(\frac{3\bar{\rho}}{\pi}\right)^{1/3}(1 + \mathcal{O}(N^{-1/2})), \quad \frac{R_{N_-}^{per}}{L} = \frac{1}{2}\left(\frac{3\bar{\rho}}{\pi}\right)^{1/3}(1 + \mathcal{O}(N^{-1/2})). \quad (4.30)$$

The Fourier transform entering the definitions of $a_{N,L}^{cts}$ and $b_{N,L}^{cts}$ is calculated explicitly in Lemma 6.1 below:

$$a_{N,L}^{cts}(y) = \frac{\pi}{6}\left(\frac{R_{N_-}^{Dir}}{L}\right)^3 h\left(\frac{R_{N_-}^{Dir}}{L}\pi|y|_{T(2L)}\right), \quad b_{N,L}^{cts}(y) = \frac{\pi}{6}\left(\frac{2R_{N_-}^{per}}{L}\right)^3 h\left(\frac{2R_{N_-}^{per}}{L}\pi|y|_{T(L)}\right).$$

In the above expressions discreteness effects are still present, through the discrete Fermi radii $R_{N_-}^{Dir}$, $R_{N_-}^{per}$. By (4.28), replacing the cubic factors in front of h by their limit $\bar{\rho}/2$ produces an error not exceeding $c\bar{\rho}N^{-1/2}$. Finally, a moment's thought shows that if h is any differentiable function on $[0, \infty)$ with $|h'(s)| \leq C(1+s)^{-2}$, as is the case here, one has $\sup_{s \geq 0} |h(\alpha s) - h(\beta s)| \leq C \max\{|\alpha - \beta|, |\alpha^{-1} - \beta^{-1}|\}$, for any $\alpha, \beta > 0$. This observation, together with (4.30) and the choices $\alpha = R_{N_-}^{Dir}\pi L^{-1}p_F^{-1}$, $\beta = 1$, $s = p_F|y|_{T(2L)}$ respectively $\alpha = 2R_{N_-}^{per}\pi L^{-1}p_F^{-1}$, $\beta = 1$, $s = p_F|y|_{T(L)}$ (to ensure $\bar{\rho}$ -independence of α, β), establishes the lemma.

Finally we remark that the decay exponent -4 in Theorem 1.2 is optimal.

Corollary 4.1 *Let $N/L^3 \equiv \text{const} = \bar{\rho}$. Let $\psi_{N,L}$ be any determinantal ground state of the free electron gas energy (subject to zero or periodic boundary conditions), with pair correlation function $C_{N,L}$. Let $f : \mathbb{N} \rightarrow \mathbb{R}$ be a positive function such that*

$$\frac{f(y)}{(1 + \|y\|)^{-4}} \rightarrow 0 \quad (\|y\| \rightarrow \infty), \quad (4.31)$$

where $\|\cdot\| = |\cdot|$ in case of zero boundary data and $\|\cdot\| = |\cdot|_{T(L)}$ in the periodic case. Then

$$\sup_{N \in \mathbb{N}} \sup_{r, r' \in [0, L]^3} \frac{|C_{N,L}(r, r')|}{N^{-1} + f(r - r')} = \infty. \quad (4.32)$$

Proof. For instance, in case of zero boundary conditions, pick $\alpha \in (0, 3/4)$ and let $r_{N,L} = (L/2, L/2, (L+L^\alpha)/2)$, $r'_{N,L} = (L/2, L/2, (L-L^\alpha)/2)$. Then since $|r_{N,L} - \sigma r'_{N,L}| \geq L$ for all $\sigma \in G \setminus \{id\}$ and $|h(s)| \leq c(1+s)^{-2}$, (1.18) implies $C_{N,L}(r_{N,L}, r'_{N,L}) = -(\bar{\rho}^2/2)(h(p_F L^\alpha))^2 + o(L^{-4\alpha})$ as $L \rightarrow \infty$, while by hypothesis $N^{-1} + f(r_{N,L} - r'_{N,L}) = \bar{\rho}^{-1}L^{-3} + f((0, 0, L^\alpha)) = o(L^{-4\alpha})$ ($L \rightarrow \infty$). One concludes since by inspection $\limsup_{s \rightarrow \infty} (h(s))^2 s^{-4} > 0$.

5. One-body density and Dirac-Bloch-Slater functional

The analysis of the previous section allows one to establish, with little effort, the asymptotic behaviour of the Dirac-Bloch-Slater functional on ground state densities. Recall that in the periodic case these finite-system densities may be heterogeneous (due to open-shell effects), while in the case of zero boundary conditions they must be homogeneous (since the wave-functions must decay continuously to zero toward the boundary of the box).

Theorem 5.1 *Let $N/L^3 \equiv \text{const} = \bar{\rho}$, and let $\psi_{N,L}$ be any determinantal ground state of the free electron gas energy, with one-body density $\rho_{N,L}$. In case of periodic boundary conditions*

$$|\rho_{N,L}(r) - \bar{\rho}| \leq c\bar{\rho}N^{-\frac{1}{2}} \text{ for all } r \in [0, L]^3, \quad (5.1)$$

$$\left| \int_{[0,L]^3} \rho_{N,L}(r)^{\frac{4}{3}} dr - \bar{\rho}^{\frac{4}{3}} L^3 \right| \leq c\bar{\rho}^{\frac{1}{3}} N^{\frac{1}{2}} = c\bar{\rho}^{\frac{5}{6}} L^{\frac{3}{2}} \quad (5.2)$$

and in case of zero boundary conditions

$$|\rho_{N,L}(r) - \bar{\rho} \sum_{\sigma \in G} (\det \sigma) h(p_F | (id - \sigma)r |_{T(2L)})| \leq c\bar{\rho}N^{-1/2} \text{ for all } r \in [0, L]^3, \quad (5.3)$$

$$\left| \int_{[0,L]^3} \rho_{N,L}(r)^{\frac{4}{3}} dr - \bar{\rho}^{\frac{4}{3}} L^3 \right| \leq c\bar{\rho}^{\frac{1}{3}} N^{\frac{2}{3}} = c\bar{\rho}L^2, \quad (5.4)$$

for some universal constant c , with G , h , p_F and $|\cdot|_{T(2L)}$ as in Theorem 1.2.

Proof. Recall that $\rho(r) = \gamma(r, r)$. Deal first with the periodic case. By Theorem 4.2

$$|\rho_{N,L}(r) - 2b_{N,L}^{cts}(0)| \leq c\bar{\rho}N^{-1/2}, \quad |\rho_{N,L}(r)| \leq c\bar{\rho}. \quad (5.5)$$

Substituting definitions,

$$2b_{N,L}^{cts}(0) = 2\left(\frac{R_{N,-}^{per}}{L}\right)^3 \widehat{\chi_{B^3(1)}}(0) = \frac{8\pi}{3} \left(\frac{R_{N,-}^{per}}{L}\right)^3.$$

The estimate (5.1) now follows from (4.28). To prove (5.2), apply the elementary inequality $|a^p - b^p| \leq p|a - b| \max\{a^{p-1}, b^{p-1}\}$ ($a \geq 0, b \geq 0, p \geq 1$) to $a = \rho_{N,L}(r)$, $b = \bar{\rho}$, $p = 4/3$, estimate the right hand side through (5.1) and the second inequality in (5.5), and integrate over r .

For zero boundary conditions, Theorem 4.1 and Lemma 4.3 yield (5.3). Without needing Lemma 4.3, by Theorem 4.1 and the decay estimate presented as Lemma 4.2

$$\begin{aligned} \left| \rho_{N,L}(r) - 2 \sum_{\sigma \in G} (\det \sigma) a_{N,L}^{cts}((id - \sigma)r) \right| &\leq c\bar{\rho}N^{-1/2}, \quad |\rho_{N,L}(r)| \leq c\bar{\rho}, \\ a_{N,L}^{cts}(0) &= \frac{1}{2}\bar{\rho}(1 + \mathcal{O}(N^{-1/2})), \quad |a_{N,L}^{cts}((id - \sigma)r)| \leq c\bar{\rho}(1 + \bar{\rho}^{\frac{1}{3}}|(id - \sigma)r|_{T(2L)})^{-2}. \end{aligned}$$

This yields

$$|\rho_{N,L}(r)^{4/3} - \bar{\rho}^{4/3}| \leq c\bar{\rho}^{4/3} \left(N^{-1/2} + \sum_{\sigma \in G \setminus \{id\}} (1 + \bar{\rho}^{\frac{1}{3}}|(id - \sigma)r|_{T(2L)})^{-2} \right).$$

For each $\sigma \in G \setminus \{id\}$ there exists $i \in \{1, 2, 3\}$ such that $\sigma_{ii} = -1$. Consequently

$$\int_0^L (1 + \bar{\rho}^{\frac{1}{3}}|(id - \sigma)r|_{T(2L)})^{-2} dr_i = 2 \int_0^{\frac{L}{2}} (1 + \bar{\rho}^{\frac{1}{3}}|2r_i|)^{-2} dr_i \leq \bar{\rho}^{-\frac{1}{3}} \int_{-\infty}^{\infty} (1 + |s|)^{-2} ds$$

and the last assertion (5.4) follows.

6. The exchange energy functional

Throughout this section $\bar{\rho} > 0$ is fixed, and the thermodynamic relation $N/L^3 \equiv \text{const} = \bar{\rho}$ is assumed. We write $Q(L) = [0, L]^3$ and denote by c any constant which may depend on $\bar{\rho}$ but not on N or L . The value of c may change from line to line.

Proof of Theorem 1.1 (1.12), periodic boundary conditions. By Theorem 4.2 and abbreviating $\int (\cdot) dr dr' = \int (\cdot)$

$$\begin{aligned} & \left| \int_{Q(L)^2} \frac{C_{N,L}(r, r')}{|r - r'|} + \int_{Q(L)^2} \frac{|b_{N,L}^{cts}(r - r')|^2}{|r - r'|} \right| \\ & \leq c \left(L^{-3} \int_{Q(L)^2} \frac{1}{|r - r'|} + L^{-3/2} \sum_{\{d \in LZ^3 : |d|_{\max} \leq L\}} \int_{Q(L)^2} \frac{(1 + |r - r' - d|)^{-2}}{|r - r'|} \right) \\ & \leq c(L^2 + L^{3/2} \log(2+L)). \end{aligned} \quad (6.1)$$

To deal with $b_{N,L}^{cts}$ we need to decode the information hidden in the torus co-ordinate $y \bmod L$. Let $\widetilde{b_{N,L}^{cts}}$ denote the nonperiodic function obtained from the right hand side of (4.23) by replacing $y \bmod L$ with y . Then

$$\begin{aligned} & \left| \int_{Q(L)^2} \frac{|b_{N,L}^{cts}(r - r')|^2}{|r - r'|} - \int_{Q(L)^2} \frac{|\widetilde{b_{N,L}^{cts}}(r - r')|^2}{|r - r'|} \right| \\ & = \left| \int_{Q(L)^2 \cap \{|r - r'|_{\max} \geq \frac{L}{2}\}} \frac{|b_{N,L}^{cts}(r - r')|^2 - |\widetilde{b_{N,L}^{cts}}(r - r')|^2}{|r - r'|} \right| \\ & \leq \frac{c}{L} \sum_{\{d \in LZ^2 : |d| \leq L\}} \int_{Q(L)^2} (1 + |r - r' - d|)^{-4} \leq cL^2. \end{aligned} \quad (6.2)$$

We can now isolate the leading contribution to the exchange energy. Changing variables $y = r - r'$, $y' = r' - \frac{L}{2}(1, 1, 1)^T$,

$$\begin{aligned} & \left| \int_{Q(L)^2} \frac{|\widetilde{b_{N,L}^{cts}}(r - r')|^2}{|r - r'|} - L^3 \int_{\mathbb{R}^3} \frac{|\widetilde{b_{N,L}^{cts}}(y)|^2}{|y|} dy \right| \\ & = \int_{y' \in [-\frac{L}{2}, \frac{L}{2}]^3} \int_{|y'+y|_{\max} > \frac{L}{2}} \frac{|\widetilde{b_{N,L}^{cts}}(y)|^2}{|y|} dy dy' \leq c \int_{y' \in [-\frac{L}{2}, \frac{L}{2}]^3} \int_{|y| > \frac{L}{2} - |y'|_{\max}} \frac{(1 + |y|^2)^{-2}}{|y|} dy dy' \\ & = 2\pi c \int_{y' \in [-\frac{L}{2}, \frac{L}{2}]^3} \frac{1}{1 + (\frac{L}{2} - |y'|_{\max})^2} dy' \quad (\text{with the same constant } c) \\ & \leq cL^2. \end{aligned} \quad (6.3)$$

To find the exchange constant c_x it remains to make explicit the factor of L^3 in the first line of (6.3). This amounts to evaluating the integral

$$I(R, L) = \int_{\mathbb{R}^3} \frac{|L^{-3} \widehat{\chi_{B(R)}}(\frac{\pi y}{L})|^2}{|y|} dy,$$

which encodes all relevant information about the decay and the quantum oscillations of the pair correlation function $C(r, r') \sim |\widehat{\chi_{B(R)}}(\frac{2\pi}{L}(r - r'))|^2$. For the sake of completeness we sketch a derivation of the (elementary) result.

Lemma 6.1 *In three dimensions the Fourier transform of the characteristic function of the unit ball is*

$$\widehat{\chi_{B(1)}}(k) = 4\pi \frac{\sin |k| - |k| \cos |k|}{|k|^3}, \quad (6.4)$$

and

$$I(R, L) = 16\pi \left(\frac{R}{L}\right)^4. \quad (6.5)$$

Proof. Introducing polar coordinates with the z_3 -axis pointing in the direction of k , $(z_1, z_2, z_3) = (r \cos \phi \sin \theta, r \sin \phi \sin \theta, r \cos \theta)$, one has

$$\widehat{\chi_{B(1)}}(k) = \int_{B(1)} e^{ik \cdot z} dz = \int_{r=0}^1 \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} r^2 \sin \theta e^{ir|k| \cos \theta} d\theta d\phi dr$$

and one easily obtains (6.4). Substitution into the definition of $I(R, L)$ and the changes of variables $y' = \frac{\pi R}{L}y$, $s = |y'|$ yield

$$I(R, L) = (4\pi)^2 \left(\frac{R}{L}\right)^6 \int_{\mathbb{R}^3} \frac{1}{|y|} \frac{(\sin t - t \cos t)^2}{t^6} \Big|_{t=\frac{\pi R|y|}{L}} dy = 64\pi \left(\frac{R}{L}\right)^4 \int_0^\infty \frac{(\sin s - s \cos s)^2}{s^5} ds.$$

An elegant evaluation of this last integral can be found in [PY, Sec.6.1]: set $t = (\sin s)/s$, then $dt/ds = -(\sin s - s \cos s)/s^2$, $d^2t/ds^2 = -t - (2/s)dt/ds$, and so

$$\int_0^\infty \frac{(\sin s - s \cos s)^2}{s^5} ds = \int_0^\infty \frac{dt}{ds} \left(\frac{1}{s} \frac{dt}{ds}\right) ds = \int_0^\infty \frac{dt}{ds} \left(-\frac{t}{2} - \frac{1}{2} \frac{d^2t}{ds^2}\right) ds = \frac{1}{4}.$$

This proves the lemma.

By (6.5), (4.28) and the elementary inequality $|a^4 - b^4| \leq (4/3)|a^3 - b^3| \max\{a, b\}$

$$L^3 \int_{\mathbb{R}^3} \frac{|\widehat{b_{N,L}^{cts}}(y)|^2}{|y|} dy = \frac{L^3}{4} I(R_{N_-}^{per}, L) = 4\pi L^3 \left(\frac{R_{N_-}^{per}}{L}\right)^4 = \frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{4}{3}} L^3 + \mathcal{O}(L^{\frac{3}{2}}). \quad (6.6)$$

Assertion (1.12) in Theorem 1.1 now follows by combining (6.1), (6.2), (6.3) and (6.6).

Proof of Theorem 1.1 (1.12), zero boundary conditions. Altering the boundary conditions produces the same leading order exchange energy, but for somewhat subtle reasons.

By multiplying (4.21) by $1/|r-r'|$ and integrating over $Q(L)^2$

$$\left| \int_{Q(L)^2} \frac{C_{N,L}(r, r')}{|r-r'|} + \sum_{\sigma, \tau \in G} \det(\sigma\tau) \int_{Q(L)^2} \frac{a_{N,L}^{cts}(r-\sigma r') a_{N,L}^{cts}(r-\tau r')^*}{|r-r'|} \right| \leq c(L^2 + L^{3/2} \log(2+L)). \quad (6.7)$$

The terms in the sum on the left hand side of (6.7) are at most of the order of magnitude of the surface area of the box, unless $(\sigma, \tau) = (id, id)$:

$$\left| \sum_{\sigma, \tau \in G} \det(\sigma\tau) \int_{Q(L)^2} \frac{a_{N,L}^{cts}(r-\sigma r') a_{N,L}^{cts}(r-\tau r')^*}{|r-r'|} - \int_{Q(L)^2} \frac{|a_{N,L}^{cts}(r-r')|^2}{|r-r'|} \right| \leq c \sum_{\substack{\sigma, \tau \in G \\ (\sigma, \tau) \neq (id, id)}} J_{\sigma, \tau}(L) \quad (6.8)$$

where

$$J_{\sigma,\tau}(L) = \int_{Q(L)^2} \frac{(1+|r-\sigma r'|_{T(2L)})^{-2}(1+|r-\tau r'|_{T(2L)})^{-2}}{|r-r'|} \geq \frac{1}{c} \int_{Q(L)^2} \frac{|a_{N,L}^{cts}(r-\sigma r')a_{N,L}^{cts}(r-\tau r')^*|}{|r-r'|}$$

and we have

Lemma 6.2 *If $(\sigma, \tau) \neq (id, id)$ then $J_{\sigma,\tau}(L) \leq cL^2$.*

(By contrast $J_{id,id}$ is of order L^3 .)

Proof. What is surprising at first sight is that for $\text{tr } \sigma = 1$ the term $J_{\sigma,id}$ is of lower order than the geometric mean of the orders of $J_{\sigma,\sigma}$ and $J_{id,id}$. So we begin with this case. There is exactly one $i \in \{1, 2, 3\}$ with $\sigma_{ii} = -1$. We pick $p \in (1, 2)$ and $j \in \{1, 2, 3\} \setminus \{i\}$ and estimate as follows:

$$J_{\sigma,\tau}(L) \leq \int_{Q(L)^2} \frac{(1+|\pi_i(r-r')|)^{p-2}(1+|(r+r')_i|_{T(2L)})^{-p}}{(1+|\pi_i(r-r')|)|\pi_i(r-r')|^{p/2}(1+|(r-r')_i|)|(r-r')_i|^{1-p/2}} \leq cL^2.$$

Next, consider the case $\text{tr } \sigma \leq -1$, $\tau = id$. Then pick i such that $\sigma_{jj} = -1$ for all $j \neq i$, and calculate

$$J_{\sigma,\tau}(L) \leq c \int_{Q(L)^2} \frac{(1+|\pi_i(r+r')|_{T(2L)})^{-2}}{(1+|r-r'|)^2|r-r'|} \leq cL \log(2+L)^2.$$

Next, assume there exist i, j , $i \neq j$, such that $\sigma_{ii} = -1$, $\tau_{jj} = -1$. Choosing $p, q \in (1, \frac{3}{2})$ and letting $\{k\} = \{1, 2, 3\} \setminus \{i, j\}$, the integrand of $J_{\sigma,\tau}(L)$ is bounded by

$$c \frac{(1+|(r+r')_i|_{T(2L)})^{-p}(1+|(r+r')_j|_{T(2L)})^{-q}(1+|(r-\sigma r')_k|_{T(2L)})^{p-2}(1+|(r-\tau r')_k|_{T(2L)})^{q-2}}{|(r-r')_i|^{1/2}|(r-r')_j|^{1/2}},$$

hence $J_{\sigma,\tau}(L)(L) \leq cL^2$, with the integrals over $(r-r')_i$, $(r-r')_j$, $(r+r')_i$, $(r+r')_j$, and $((r+r')_k, (r-r')_k)$ contributing, respectively, a multiple of $L^{1/2}$, $L^{1/2}$, 1, 1, and L .

The remaining case is $\sigma = \tau$, $\text{tr } \sigma = 1$. We may assume $\sigma = \tau = \text{diag}(-1, 1, 1)$. A moment's thought shows that the seemingly equivalent expression obtained by switching signs in the differences $r - \sigma r'$, $r - r'$,

$$\int_{Q(L)^2} \frac{(1+|((r-r')_1, (r+r')_2, (r+r')_3)|_{T(2L)})^{-4}}{|r+r'|},$$

is of order $L^2 \log L$. But the domain of integration is asymmetric with respect to this switching operation. In fact, changing variables $y = r - r'$, $y'_1 = r_1 + r'_1$, $y'_2 = r_2$, $y'_3 = r_3$, we have $|y_1| \leq \min\{y'_1, 2L - y'_1\}$ and thus (abbreviating $\Lambda(L) = [0, 2L] \times [-L, L]^2$)

$$\begin{aligned} J_{\sigma,\tau}(L) &\leq c \int_{\substack{(y'_2, y'_3) \\ \in [0, L]^2}} \int_{\substack{(y'_1, y_2, y_3) \\ \in \Lambda(L)}} \int_{\substack{|y_1| \leq \\ \min\{y'_1, 2L - y'_1\}}} \frac{(1 + \min_{d \in \{0, 2L\}} |(y'_1 - d, y_2, y_3)|)^{-4}}{|y_1| + |\pi_1 y|} dy_1 d(\pi_1 y) dy' \\ &= 2cL^2 \int_{(y'_1, y_2, y_3) \in \Lambda(L)} \frac{\log(\min\{y'_1, 2L - y'_1\} + |\pi_1 y|) - \log |\pi_1 y|}{(1 + \min_{d \in \{0, 2L\}} |(y'_1 - d, y_2, y_3)|)^4} d(y'_1, y_2, y_3) \\ &= 4cL^2 \int_{[0, L] \times [-L, L]^2} \frac{\log(z_1 + |\pi_1 z|) - \log |\pi_1 z|}{(1 + |z|)^4} dz. \end{aligned}$$

Since the integrand lies in $L^1(\mathbb{R}^3)$, the lemma follows.

It remains to look at the leading order term $\sigma = \tau = id$ in (6.8). Writing $\widetilde{a_{N,L}^{cts}}$ for the function obtained from $a_{N,L}^{cts}$ by replacing $y \bmod 2L$ in (4.16) by y , one has

$$\begin{aligned} & \left| \int_{Q(L)^2} \frac{|a_{N,L}^{cts}(r-r')|^2}{|r-r'|} - L^3 \int_{\mathbb{R}^3} \frac{|\widetilde{a_{N,L}^{cts}}(y)|^2}{|y|} dy \right| = \int_{y' \in [-\frac{L}{2}, \frac{L}{2}]^3} \int_{|y+y'|_{\max} > \frac{L}{2}} \frac{|\widetilde{a_{N,L}^{cts}}(y)|^2}{|y|} dy dy' \\ & \leq c \int_{y' \in [-\frac{L}{2}, \frac{L}{2}]^3} \int_{|y| > \frac{L}{2} - |y'|_{\max}} \frac{(1+|y|^2)^{-2}}{|y|} dy dr' \leq cL^2 \end{aligned} \quad (6.9)$$

where the last inequality follows from (6.3).

The second integral on the left hand side of (6.9) can be evaluated with the help of Lemma 6.1 and (4.29):

$$L^3 \int_{\mathbb{R}^3} \frac{|a_{N,L}^{cts}(y)|^2}{|y|} = \frac{L^3}{64} I(R_{N-}^{Dir}, L) = \frac{L^3}{4} \pi \left(\frac{R_{N-}^{Dir}}{L} \right)^4 = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{4/3} L^3 + \mathcal{O}(L^{3/2}). \quad (6.10)$$

By combining (6.7), (6.8), Lemma 6.2, (6.9), and (6.10) one obtains Theorem 1.1 (1.12).

7. Self-interaction

In the density functional theory literature, the success of the Dirac-Bloch-Slater approximation $E_{ee}(\psi) \approx E_x^{LDA}(\rho) + J(\rho)$ applied to atomic or molecular systems is sometimes attributed to an anticipated ability of E_x^{LDA} to cancel the bulk of the spurious self-interaction energy contained in $J(\rho)$.

It is then interesting to note that such virtues of the local density approximation – if true – must be accidental: I prove below that the self-interaction contribution to E_x (see Footnote 7 in the Introduction) is a lower-order effect which disappears in the thermodynamic limit and contributes nothing to the exchange constant c_x .

Mathematically, my proof relies on Lemma 3.2 (which was a consequence of the lattice point estimate in Corollary 1.1) and the Hardy-Littlewood-Sobolev inequality from the theory of fractional integration.

Theorem 7.1 *Under the assumptions of Theorem 1.1, both for zero and periodic boundary conditions, there exists a universal constant c such that*

$$J_{self}(\psi_{N,L}) \leq c\bar{\rho}^{7/6} L^{5/2} = c\bar{\rho}^{1/3} N^{5/6}. \quad (7.1)$$

In particular, the limit theorem that $E_x(\psi_{N,L})/E_x^{LDA}(\rho_{N,L})$ tends to 1 remains true with E_x replaced by proper exchange $E_x^{sic} = E_x - J_{self}$, with the same exchange constant c_x .

Proof. For a ground state with one-body spin orbitals ψ'_1, \dots, ψ'_N , recall its self-interaction energy, $J_{self}(\psi_{N,L}) = \sum_{i=1}^N J(\rho^{(i)})$ where $\rho^{(i)}(r) = \sum_s |\psi'_i(r, s)|^2$. The ψ'_i must be eigenfunctions of the one-body Laplacian (see Lemma 1.1) and are as usual assumed to be ordered by size of eigenvalue. Hence for any $i \in \{1, \dots, N\}$ we may write $\psi'_i = \sum_{j=i-+}^{i+} \alpha_{ij} \psi_j$ for some $\alpha_{ij} \in \mathcal{C}$, $\sum_{j=i-+}^{i+} |\alpha_{ij}|^2 = 1$, where the ψ_j are the canonical eigenfunctions from Section 2. Thus by Lemmas 2.1, 3.2

$$|\psi'_i(r, s)|^2 \leq \left(\sum_{j=i-+}^{i+} |\alpha_{ij}|^2 \right) \left(\sum_{j=i-+}^{i+} |\psi_j(r, s)|^2 \right) \leq c\bar{\rho} N^{-1/2}. \quad (7.2)$$

This L^∞ -estimate alone does not suffice to infer (7.1). I use Hölder's inequality and the Hardy-Littlewood-Sobolev inequality [e.g. So93 0.2.3, St93 VIII 4.2]

$$\left\| \frac{1}{|\cdot|^{n/\alpha}} * f \right\|_{L^q(\mathbb{R}^n)} \leq c(p, q, n) \|f\|_{L^p(\mathbb{R}^n)} \quad (n \in \mathbb{N}, \alpha > 1, \frac{1}{\alpha} = 1 - (\frac{1}{p} - \frac{1}{q}), 1 < p < q < \infty)$$

with $\alpha = n = 3$, $p = 6/5$, $q = 6$. Extending the $\rho^{(i)}$ by zero to all of \mathbb{R}^3 , for $f = \rho^{(i)}$

$$J(f) = \int_{\mathbb{R}^3} f(r) \left(\frac{1}{|\cdot|} * f \right)(r) dr \leq \|f\|_{L^{\frac{6}{5}}} \left\| \frac{1}{|\cdot|} * f \right\|_{L^6} \leq c \|f\|_{L^{\frac{6}{5}}}^2 \leq c (\|f\|_{L^1})^{\frac{5}{3}} (\|f\|_{L^\infty})^{\frac{1}{3}}.$$

To infer (7.1), use $\|\rho^{(i)}\|_{L^1} = 1$ and the L^∞ -bound (7.2).

8. Concluding remarks

This article by no means exhausts the study of pair correlations and exchange phenomena even in noninteracting systems. A main shortcoming is that I do not know under which changes of domain the pair correlation function away from the boundary, the 'correlation exponent' (3 in Theorem 1.1 and $-2/3$ in Theorem 1.1') and the exchange constant c_x would survive.

Studying more general domains would seem to require a strategy of investigation which bypasses the explicit calculations in Section 2 and could use the differential information on the one-body orbitals $\{\phi_i\}$ more directly. One step in this direction would be to devise, without resorting to explicit calculation of eigenfunctions, a proof of the following consequence of Theorem 1.1':

Corollary 8.1 *Under the assumptions of Theorem 1.1', there exists a set $\mathcal{S} \subseteq \mathbb{N}^2$ of asymptotic density one (that is, $N^{-2}|\mathcal{S} \cap [1, N]^2| \rightarrow 1$ as $N \rightarrow \infty$), such that*

$$\phi_i \phi_j^* \rightarrow 0 \quad \text{in } H^{-1}(\mathbb{R}^3) \quad ((i, j) \in \mathcal{S}, |(i, j)| \rightarrow \infty).$$

Inspection of the diagonal terms $i = j$ shows that the restriction to a subset of asymptotic density one is essential: $\langle (-\Delta_{\mathbb{R}^3})^{-1} |\phi_i|^2, |\phi_i|^2 \rangle_Q \geq (4\pi)^{-1} 3^{-1/2} \langle 1, |\phi_i|^2 \otimes |\phi_i|^2 \rangle_{Q \times Q} = (4\pi)^{-1} 3^{-1/2}$. (If $\{\phi_i\}$ is the standard basis (2.3), $\langle (-\Delta_{\mathbb{R}^3})^{-1} |\phi_i|^2, |\phi_i|^2 \rangle_Q = \langle \hat{C}1, |\phi_i|^2 \otimes |\phi_i|^2 \rangle_{Q \times Q} \rightarrow \langle \hat{C}1, 1 \rangle_{Q \times Q}$ with \hat{C} as below, since $|\phi_i|^2 \otimes |\phi_j|^2 \xrightarrow{*} 1$ in $L^\infty(Q \times Q)$ and $\hat{C}1 \in L^1(Q \times Q)$. But note that if the diagonal terms were the only terms not to converge to zero, the expected value in Theorem 1.1' should behave as $\mathbb{E} \sim N^{-1}$, not $\mathbb{E} \sim N^{-2/3}$.)

While recent advances in weak convergence methods for partial differential equations [Ta90, Ge91] as well as classical ergodic theorems for eigenfunctions of the Laplacian [Sh74, CV85, HMR87, GL93] concern the asymptotic behaviour of quadratic forms $\langle L' \phi_i, \phi_i \rangle_\Lambda$ associated with pseudodifferential operators L' of degree zero, the situation here appears to be slightly different. When working in one-body configuration space,

$$\|\phi_i \phi_j^*\|_{H^{-1}(\mathbb{R}^3)}^2 = \langle (-\Delta_{\mathbb{R}^3})^{-1} (\phi_i \phi_j^*), \phi_i \phi_j^* \rangle_Q$$

so we are dealing with a pseudodifferential operator of degree -2 and a sequence not known to converge weakly to zero in $L^2(Q)$. Alternatively, when working in two-body configuration space, we may write

$$\|\phi_i \phi_j^*\|_{H^{-1}(\mathbb{R}^3)}^2 = \langle \hat{C}(\phi_i \otimes \phi_j), \phi_i \otimes \phi_j \rangle_{Q \times Q}$$

where \hat{C} is a nonlocal operator which switches arguments and multiplies by a weight factor making contributions of nearby points dominant,

$$(\hat{C}\psi)(r, r') = \frac{1}{4\pi|r-r'|} \psi(r', r),$$

but at least the argument of the quadratic form, $\phi_i \otimes \phi_j$, then converges weakly in $L^2(Q \times Q, \mathcal{C})$ to zero as $|(i, j)| \rightarrow \infty$.

Keeping [Sh74, CV85, HMR87, GL93] in mind, what may play a role in Corollary 8.1 is that the underlying classical Hamiltonian system, the geodesic flow in Q (augmented, in case of zero boundary conditions, by reflection at the boundary according to the law of geometrical optics), $(p^{(t)}, q^{(t)}) : \mathbb{R}^3 \times [0, L]^3 \rightarrow \mathbb{R}^3 \times [0, L]^3$, is ergodic at least in the position variable: for almost every $(p_0, q_0) \in \mathbb{R}^3 \times [0, L]^3$ and every $f \in C([0, L]^3)$, $\lim_{T \rightarrow \infty} \int_0^T f(q^{(t)}(p_0, q_0)) dt = \int_{[0, L]^3} f dq$.

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