A CORRELATION ESTIMATE WITH APPLICATIONS TO QUANTUM SYSTEMS WITH COULOMB INTERACTIONS

Gian Michele Graf[1]
Institut für theoretische Physik
ETH Hönggerberg
CH–8093 Zürich, Switzerland

Jan Philip Solovej[2]
Department of Mathematics
Princeton University
Princeton, N.J. 08544

Dedicated to Elliott H. Lieb on his 60th birthday

Abstract: We consider some two-body operators acting on a Fock space with either fermionic or no statistics. We prove that they are bounded below by one-body operators which mimic exchange effects. This allows us to compare two-body correlations of fermionic and bosonic systems with those in Hartree-Fock, respectively Hartree theory. Applications of the fermionic estimate yield lower bounds for the ground state energy of jellium at high densities and of molecules with large nuclear charges.

I. INTRODUCTION

One of the striking differences between classical and quantum mechanics is the existence of non-trivial correlations in the ground state of a quantum mechanical system. From a rigorous point of view very little is known about these correlations. By neglecting these correlations one arrives at an approximating theory for the ground state energy. In the case of a fermionic system this theory is the Hartree-Fock approximation while in the case of a bosonic system the theory is the Hartree approximation. We shall define these approximations below.

The first step in understanding the ground state correlations is to investigate the validity of these approximating theories. Although such an investigation will not give any

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information about the actual physical implications due to the correlations it will, however, give an estimate on their effects.

In a recent very beautiful paper [1] Bach gives an estimate on the ground state correlations of Coulomb systems which proves the exactness of the Hartree-Fock approximation in the high density limit. The importance of this result motivated us to simplify and generalize the method of Bach. It is this simplification and generalization that we present here.

An important ingredient in the method is to prove that there is condensation. By this we mean in the case of fermions that the ground state is a fairly well-defined Fermi sea. It turns out that this is not too difficult to prove in the high density limit of Coulomb systems. In the case of bosons, condensation means Bose-Einstein condensation, i.e., that in the ground state almost all particles are in one state.

In the case of bosons it can actually be very difficult to prove condensation. An example of this is the bosonic jellium model which we define below. Here condensation has to the best of our knowledge never been rigorously established. However, in this case a very impressive method (avoiding the issue of condensation) for obtaining a correlation estimate of the right order was given by Conlon [4,5] and by Conlon, Lieb and Yau [6]. Assuming condensation in the bosonic jellium model is also the essential feature of the Bogoliubov approximation (where correlations are not neglected) which was used by Foldy [10] to compute the ground state energy to leading order in the high density limit. It is a very interesting open problem to give a rigorous derivation of this result.

In the present paper we shall be concerned with Coulomb systems. By this we mean that we consider N-body Hamiltonians of the form

$$H(N,V)=\sum_{i=1}^{N}(-\Delta_i-V(x_i))+\sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|}\quad , \tag{1.1}$$

acting on the many-body space $\mathcal{H}(N)=\bigotimes^{N}\mathcal{H}$, where the one-body space is $\mathcal{H}=L^2(\mathbf{R}^3;\mathbf{C}^m)$ and $x_i\in\mathbf{R}^3$, $i=1,\ldots,N$. The space $\mathbf{C}^m$ refers to the spin variable. It corresponds to particles having m spin states.

The operator $H(N,V)$ acts also on the fermionic (antisymmetric) subspace $\mathcal{H}_{\mathrm{F}}(N)=\bigwedge^{N}\mathcal{H}$ and on the bosonic (symmetric) subspace. In general for any operator A on $\mathcal{H}$ we define operators A_i, $i = 1, 2, \ldots, N$ on $\mathcal{H}(N)$ by simply letting A act on the i^{th} particle (i.e., on the i^{th} factor in the tensor product). The one-body operator $\sum_i^N A_i$ and the two-body operator $\sum_{1\le i<j\le N} A_i A_j$ then act on $\mathcal{H}(N)$ as well as on the fermionic and bosonic subspaces.

We shall only be interested in the ground state energy, i.e., the lowest eigenvalue (or in general the bottom of the spectrum) of $H(N, V)$. The bottom of the spectrum of $H(N, V)$ restricted to the bosonic subspace is identical to the bottom of the spectrum of the operator acting on the full space $\mathcal{H}(N)$. The unrestricted operator is therefore often refered to as the bosonic case. We shall here mainly be interested in the fermionic case.

The fermionic ground state energy is

$$E(N, V) = \inf_{\langle\ \cdot\ \rangle_{\mathrm{F}}} \langle H(N, V)\rangle_{\mathrm{F}} \quad , \tag{1.2}$$

where the infimum is over all fermionic states $\langle\ \cdot\ \rangle_{\mathrm{F}}$. By a fermionic state we mean a positive linear functional on the bounded operators on $\mathcal{H}_{\mathrm{F}}(N)$ satisfying the normalization condition that its value on the identity I is $\langle I\rangle_{\mathrm{F}} = 1$. Although, $H(N, V)$ is not bounded we only consider potentials V for which $H(N, V)$ is bounded from below. The expectation $\langle H(N, V)\rangle_{\mathrm{F}}$ of $H(N, V)$ in a fermionic state is then a meaningful quantity (possibly having the value infinity). As explained above the bosonic ground state energy can be defined as in (1.2) but with the infimum being over states on the full space $\mathcal{H}(N)$. The bosonic energy is thus clearly smaller than the fermionic energy.

Corresponding to states $\langle\cdot\rangle_{\mathrm{F}}$ on $\mathcal{H}_{\mathrm{F}}(N)$ and $\langle\cdot\rangle$ on $\mathcal{H}(N)$ we define operators γ_{F} and γ on the one-body space $\mathcal{H}$. These operators are called *one-particle density matrices* for the states and are defined by the following relations which should hold for all bounded operators A on $\mathcal{H}$.

$$\left\langle \sum_i A_i \right\rangle = \mathrm{Tr}[\gamma A] \quad \text{and} \quad \left\langle \sum_i A_i \right\rangle_{\mathrm{F}} = \mathrm{Tr}[\gamma_{\mathrm{F}} A] \quad .$$

It is easy to see that $\mathrm{Tr}\gamma = N$ and $\mathrm{Tr}\gamma_{\mathrm{F}} = N$. Moreover, γ_{F} satisfies that as an operator $0 \le \gamma_{\mathrm{F}} \le I$.

We shall restrict our attention to two different systems (when dividing into bosonic and fermionic models we in fact get four systems). The first is a molecule in the Born-Oppenheimer approximation. Such a molecule with N electrons and with K nuclei having prescribed positive charges $\underline{Z} = (Z_1, \ldots, Z_K)$ and positions $\underline{\mathcal{R}} = (\mathcal{R}_1, \ldots, \mathcal{R}_K)$ is described by a Hamiltonian $H(N, \underline{Z}, \underline{\mathcal{R}}) := H(N, V)$ as in (1.1) where

$$V(x) = \sum_{k=1}^{K} \frac{Z_k}{|x - \mathcal{R}_k|} \quad . \tag{1.3}$$

We denote the ground state energy of the molecule by $E(N, \underline{Z}, \underline{\mathcal{R}}) = E(N, V)$. We are using the term Born-Oppenheimer here to indicate that we are neglecting the nuclear motion completely. We shall not, as is often done in the Born-Oppenheimer approximation, study the nuclear motion in the potential $\underline{\mathcal{R}} \mapsto E(N, \underline{Z}, \underline{\mathcal{R}})$. We are interested in the limit as the total nuclear charge $Z = \sum_{k=1}^{K} Z_k$ tends to infinity. We shall not discuss the bosonic molecule here, but refer the reader to [3] where the atomic case ($K = 1$) is treated. (In [3] a somewhat weaker version of inequality (2.8) given below is used. Our proof of (2.8) would slightly simplify the presentation in [3].)

The second system is the neutral jellium model on a cube Λ in $\mathbf{R}^3$ with volume $|\Lambda|$. This model is again described by a Hamiltonian $H(N, \Lambda) := H(N, V)$ as in (1.1) but this time with the potential V coming from a uniform charge background

$$V(x) = \begin{cases} \frac{N}{|\Lambda|} \int_\Lambda dy |x - y|^{-1} & \text{if } x \in \Lambda \\ -\infty & \text{if } x \notin \Lambda \end{cases} \quad . \tag{1.4}$$

(The value $-\infty$ amounts to choosing the Dirichlet condition on the boundary of the cube Λ.) The energy of jellium is denoted by $E(N, \Lambda) = E(N, V)$. The existence of the thermodynamic limit of the ground state energy with the self-energy of the background included, i.e.,

$$E_{\mathrm{J}}(\overline{\rho}) = \lim_{\substack{N, |\Lambda| \to \infty \\ N/|\Lambda| = \overline{\rho}}} |\Lambda|^{-1} \left(E(N, \Lambda) + \tfrac{1}{2} \overline{\rho}^2 \iint_{\Lambda \times \Lambda} dx dy |x - y|^{-1} \right) \quad , \tag{1.5}$$

was proved in [15] . We are interested in the high density limit ($\overline{\rho} \to \infty$) of $E_{\mathrm{J}}(\overline{\rho})$. Again we shall not discuss the bosonic case, but this time the reason, as explained above, is that the method presented here does not work. We have to refer to [4–6].

We now introduce three approximations to the ground state energy of the Hamiltonian (1.1). All statements below should be understood to hold for the potentials in (1.3) and (1.4), but not necessarily for potentials in general.

Hartree-Fock Theory: In Hartree-Fock theory one restricts attention to states $\langle\cdot\rangle_{\mathrm{F}}$ that have *no correlations*. By this we mean that the expectation of any operator H is $\langle H\rangle_{\mathrm{F}} = \langle\Psi|H\Psi\rangle$ where $\Psi \in \mathcal{H}_{\mathrm{F}}(N)$ is of the Slater determinant type, i.e., of the form $\Psi = (N!)^{-1/2}\psi_1 \wedge \ldots \wedge \psi_N$, where $\psi_1, \ldots, \psi_N \in \mathcal{H}$ are orthonormal one-particle wave functions. For such a state the one-particle density matrix is the projection operator P in $\mathcal{H}$ projecting onto the space spanned by $\psi_1, \ldots, \psi_N$ (i.e., the Fermi sea). It is easy to see that the one-particle density matrix P determines the uncorrelated state uniquely. A straightforward computation shows that the expectation $\langle\Psi|H(N,V)\Psi\rangle$ is equal to

$$\mathcal{E}_{\mathrm{HF}}(P) = \mathrm{Tr}_{\mathcal{H}}[(-\Delta - V)P] + D(\rho_P, \rho_P) - \tfrac{1}{2}\sum_{\sigma,\sigma'}\iint dxdy\frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|} \quad , \tag{1.6}$$

where $P(x,\sigma;y,\sigma')$ is the integral kernel for P with σ and σ' denoting the spin variables. The density is $\rho_P(x) = \sum_\sigma P(x,\sigma;x,\sigma)$ and we have introduced the positive definite quadratic form

$$D(\rho_1,\rho_2) = \tfrac{1}{2}\iint dxdy\rho_1(x)|x-y|^{-1}\rho_2(y) \quad . \tag{1.7}$$

We call the functional $\mathcal{E}_{\mathrm{HF}}$ the Hartree-Fock functional. If we allow the value infinity this functional is defined on all trace class operators P on $\mathcal{H}$. The term in (1.6) involving the quadratic form D is called the *direct Coulomb energy* while the last term in (1.6) is the *exchange energy*.

The Hartree-Fock energy is

$$\begin{aligned} E_{\mathrm{HF}}(N,V) &= \inf\Big\{\mathcal{E}_{\mathrm{HF}}(P) \mid P \text{ is an } N \text{ dimensional projection}\Big\} \\ &= \inf\Big\{\mathcal{E}_{\mathrm{HF}}(P) \mid 0 \le P \le I,\ \mathrm{Tr}P = N\Big\} \quad . \end{aligned} \tag{1.8}$$

That the variational problem can be formulated by the second line was realized by Lieb in [14] (for a simple proof of this fact see also [1]) . From the minimax principle it follows that $E(N,V) \le E_{\mathrm{HF}}(N,V)$.

Remarks: (a) We shall measure the degree of non-condensation of a general state $\langle\cdot\rangle_{\mathrm{F}}$, with one-particle density matrix γ_{F}, into the Fermi sea, given by the projection P, by the positive quantity (see also [2])

$$N^{-1}\delta(\gamma_{\mathrm{F}}, P) := N^{-1}\mathrm{Tr}[\gamma_{\mathrm{F}}(I-P)] \quad ,$$

i.e., the relative number of particles outside the Fermi sea. Thus if $N^{-1}\delta(\gamma_{\rm F},P) \ll 1$ we say that the state is well condensated. As in (1.8) we shall not limit P to be a projection but in general allow P to satisfy $0 \le P \le I$ in the definition of $\delta(\gamma_{\rm F},P)$.

(b) In case of bosons an uncorrelated state is given by a product wave function $\Psi = \bigotimes^N \psi$ where ψ is a normalized function in $\mathcal{H}$. The one-particle density matrix is $\gamma = NP$ where P is the projection onto ψ. Hartree theory is the restriction to these states. Condensation is defined as in (a).

Thomas-Fermi Theory: The second approximating theory which is much simpler than Hartree-Fock theory is the statistical description given by the Thomas-Fermi functional

$$\mathcal{E}_{\rm TF}(\rho) = \int dx \Big(\tfrac{3}{5} c_{\rm TF} \rho(x)^{5/3} - V(x)\rho(x) \Big) + D(\rho,\rho) \quad , \tag{1.9}$$

where $c_{\rm TF} = (6\pi^2/m)^{2/3}$. More precisely the statistical description is given by the minimization problem

$$E_{\rm TF}(N,V) = \inf \Big\{ \mathcal{E}_{\rm TF}(\rho) \mid \rho \ge 0, \int dx\ \rho \le N \Big\} \quad . \tag{1.10}$$

It is known [13,16] that there is a unique minimizer $\rho_{\rm TF}$. Together with the potential V, this charge distribution gives raise to the Thomas-Fermi potential

$$\phi_{\rm TF} = V - \rho_{\rm TF} * \frac{1}{|x|} \quad . \tag{1.11}$$

Dirac-Schwinger Theory: What we here call the Dirac-Schwinger theory is an intermediate model between Hartree-Fock theory and Thomas-Fermi theory defined in terms of the Hamiltonian

$$H_{\rm DS}(N,V) = \sum_{i=1}^N h_i - D(\rho_{\rm TF},\rho_{\rm TF}) - c_{\rm D} \int dx \rho_{\rm TF}(x)^{4/3} \quad , \tag{1.12}$$

$$h = -\Delta - \phi_{\rm TF}(x) \quad , \tag{1.13}$$

acting on $\mathcal{H}_{\rm F}(N)$. Here $c_{\rm D} = (2\pi)^{-3} m c_{\rm TF}^2$ is the Dirac [7] constant. In this model noninteracting electrons move in the Thomas-Fermi mean-field potential. The term $D(\rho_{\rm TF},\rho_{\rm TF})$ is subtracted because the first term overcounts the Coulomb repulsion between the electrons.

The exchange energy is taken into account simply by subtracting a constant. Correspondingly we have

$$E_{\mathrm{DS}}(N,V) = \inf_{\langle\,\cdot\,\rangle_{\mathrm{F}}} \langle H_{\mathrm{DS}}(N,V)\rangle_{\mathrm{F}} \quad . \tag{1.14}$$

The limits we are interested in (i.e., $Z \to \infty$ for the molecular problem and $|\Lambda| \to \infty$ for jellium) can be considered as quasiclassical limits for the Hamiltonian H_{DS}. Thomas-Fermi theory is the leading order quasiclassical approximation to H_{DS} with the exchange term neglected.

In the molecular case the quasiclassical approximation of H_{DS} was studied in [12,13, 16,20]. It is known that the energies

$$E(N,\underline{Z},\underline{\mathcal{R}}),\ E_{\mathrm{HF}}(N,\underline{Z},\underline{\mathcal{R}}),\ E_{\mathrm{DS}}(N,\underline{Z},\underline{\mathcal{R}}) \text{ and } E_{\mathrm{TF}}(N,\underline{Z},\underline{\mathcal{R}})$$

agree to the leading order which is $O(Z^{7/3})$ (for N of order Z) as $Z \to \infty$.

In the atomic case ($K = 1$) it was realized by Schwinger [18] that the second correction† to the leading order quasiclassical approximation is of the same order as the exchange energy originally computed by Dirac in [7]. The order of the exchange energy is $O(Z^{5/3})$. It would therefore not be adequate in this case to replace H_{DS} by what is called the Thomas-Fermi-Dirac functional which is the Thomas-Fermi functional with the exchange integral (the last term in (1.12)) included. The non-rigorous analysis of Schwinger was proved to be mathematically correct in the atomic case in the monumental work of Fefferman and Seco announced in [9]. We shall not here go into this very involved analysis.

Our main result in the molecular case is the following theorem first proved in [1] and [2].

THEOREM 1. *For some $\varepsilon > 0$ we have*

$$E_{\mathrm{HF}}(N,\underline{Z},\underline{\mathcal{R}}) \geq E(N,\underline{Z},\underline{\mathcal{R}}) \geq E_{\mathrm{HF}}(N,\underline{Z},\underline{\mathcal{R}}) - \mathrm{O}(Z^{5/3-\varepsilon}) \tag{1.15}$$

$$E(N,\underline{Z},\underline{\mathcal{R}}) \geq E_{\mathrm{DS}}(N,\underline{Z},\underline{\mathcal{R}}) - \mathrm{O}(Z^{5/3-\varepsilon}) \quad , \tag{1.16}$$

as $Z \to \infty$ uniformly in $\underline{Z}$, $\underline{\mathcal{R}}$ and $N \leq Z$.

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† The first correction is the Scott correction due to the Coulomb singularities at the positions of the nuclei

In (1.16) we can only prove the lower bound. An upper bound presumably requires an analysis similar to the one described in [9]. In [2] it was shown how, assuming the results announced in [9], one can prove an upper bound.

In the case of fermionic jellium the semiclassical analysis becomes exact in the thermodynamic limit and the main result in this case has a more explicit form.

THEOREM 2. *For* $\overline{\rho} \geq \mathrm{const}\, m^2$ *we have*

$$E_{\mathrm{J}}(\overline{\rho}) = \tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}\overline{\rho}^{5/3} - \mathrm{c}_{\mathrm{D}}\overline{\rho}^{4/3} - \mathcal{C}(\overline{\rho})\overline{\rho}^{4/3} \quad , \tag{1.17}$$

where $0 \leq \mathcal{C}(\overline{\rho}) \leq C_\varepsilon m^{2/15}\overline{\rho}^{\;-1/15+\varepsilon}$ *for all* $\varepsilon > 0$ *small enough.*

Remark: A perturbative computation of Gell-Mann and Brueckner [11] leads to the asymptotic behavior $\mathcal{C}(\overline{\rho}) \sim \overline{\rho}^{\;-1/3}\log\overline{\rho}$.

The paper is organized as follows. In Sect. II we give a purely algebraic inequality which allows one to estimate correlations. It estimates a two-body operator below in terms of one-body operators. The estimate involves a one-body operator P on $\mathcal{H}$. The error term in the algebraic inequality is (almost) proportional to the operator $I-P$. In the applications P will (almost) be the projection which minimizes the Hartree-Fock functional and thus $I-P$ is the orthogonal projection and the error term can be controlled by the degree of condensation. In Sect. III we show how the algebraic inequality can be applied to the Coulomb potential. In Sect. IV we study the jellium problem and in Sect. V the more complicated molecular problem.

II. THE ALGEBRAIC INEQUALITY

We present here a purely algebraic inequality for operators acting on tensor products of a Hilbert space. Let $\mathcal{H}$ be a complex Hilbert space. For an integer $N > 0$ we shall consider the N-fold tensor product $\mathcal{H}(N) = \bigotimes^N \mathcal{H}$ and its antisymmetric subspace $\mathcal{H}_{\mathrm{F}}(N) = \bigwedge^N \mathcal{H}$. In terms of particle language $\mathcal{H}(N)$ is a full N particle space and $\mathcal{H}_{\mathrm{F}}(N)$ is its fermionic subspace.

THEOREM 3. *Let X and P be bounded operators on $\mathcal{H}$ satisfying $0 \le X$ and $0 \le P \le I$ (where I is the identity operator on $\mathcal{H}$). For all $\alpha \ge 0$ we have the following operator inequality on the N-particle space $\mathcal{H}(N)$*

$$\sum_{1\le i<j\le N} X_iX_j \ge \sum_i \Big(\alpha X_i - \tfrac{1}{2}X_iP_iX_i\Big) - \tfrac{1}{2}\alpha^2 - \sum_i B_i \quad , \tag{2.1}$$

where the error term is given by the following operator on $\mathcal{H}$ depending on an arbitrary parameter $\lambda \ge 0$

$$\begin{aligned} B =& \Big[\alpha + \tfrac{1}{2}\left(1 + 2\lambda + (4+\lambda+\lambda^{-1})(N-1)\right)\|PXP\|\Big](I-P)X(I-P) \\ &+ \tfrac{1}{2}\lambda^{-1}(X^2 + PX^2P) \quad . \end{aligned} \tag{2.2}$$

However, if we restrict to the fermionic subspace $\mathcal{H}_{\mathrm{F}}$ inequality (2.1) holds with the operator B replaced by

$$\begin{aligned} B_{\mathrm{F}} =& \Big[\alpha + \tfrac{1}{2}(5+3\lambda+\lambda^{-1})\mathrm{Tr}[PX]\Big](I-P)X(I-P) \\ &+ \tfrac{1}{2}\lambda^{-1}(X^2 + PX^2P) \quad . \end{aligned} \tag{2.3}$$

(Notice that in contrast to B the operator B_{F} has no N dependence.)

Remark: We want to emphasize that inequality (2.1) estimates a two-body operator in terms of one-body operators.

Proof: For simplicity we shall denote $Q = I - P$. Then $0 \le Q \le I$. There are two main ingredients in the proof of (2.1). The first is an operator identity which we write as $\sum_{1\le i<j\le N} X_iX_j = A_1 + A_2 + A_3$, where

$$A_1 = \sum_{1\le i<j\le N} \Big(Q_iQ_j + Q_iP_j + P_iQ_j\Big)X_iX_j\Big(Q_iQ_j + Q_iP_j + P_iQ_j\Big) \quad , \tag{2.4}$$

and

$$\begin{aligned} A_2 =& \tfrac{1}{2}\sum_{i\ne j}\Big(P_iP_jX_iX_jP_iP_j + 2P_iP_jX_iX_jP_iQ_j + 2Q_iP_jX_iX_jP_iP_j\Big) \\ =& \tfrac{1}{2}\Big|\alpha - \sum_i P_iX_i(I+Q_i)\Big|^2 - \tfrac{1}{2}\alpha^2 \\ &+ \sum_i\Big\{\alpha X_i - \tfrac{1}{2}(I+Q_i)X_iP_i^2X_i(I+Q_i) - \alpha Q_iX_iQ_i\Big\} \\ &- 2\sum_{i\ne j} Q_iX_iP_iP_jX_jQ_j \quad , \end{aligned} \tag{2.5}$$

where we have used the convention $|T|^2 = T^*T$ and

$$A_3 = \sum_{i<j}\Big(P_iP_jX_iX_jQ_iQ_j + Q_iQ_jX_iX_jP_iP_j\Big) = \tfrac{1}{2}\Big|\lambda^{-1/2}\sum_i Q_iX_iP_i + \lambda^{1/2}\sum_i P_iX_iQ_i\Big|^2$$
$$- \tfrac{1}{2}\sum_i\Big\{\lambda Q_iX_iP_i^2X_iQ_i + \lambda^{-1}P_iX_iQ_i^2X_iP_i + P_iX_iQ_iP_iX_iQ_i + Q_iX_iP_iQ_iX_iP_i\Big\}$$
$$- \tfrac{1}{2}(\lambda+\lambda^{-1})\sum_{i\neq j} Q_iX_iP_iP_jX_jQ_j \quad . \tag{2.6}$$

Since $X \geq 0$, the expression $A_1 \geq 0$. Furthermore, the first terms in the above expressions for both A_2 and A_3 are also positive and can thus be neglected for the lower bound.

The second main ingredient in the proof is the estimate of the only remaining two-body term, namely the last term in the expressions for A_2 and A_3. In estimating this term the positivity of the operator X is again essential, as it was in concluding that $A_1 \geq 0$. It is also here that the difference between the full N-body space $\mathcal{H}(N)$ and the antisymmetric fermionic subspace $\mathcal{H}_{\mathrm{F}}(N)$ plays an important role. We proceed as follows

$$\sum_{i\neq j}Q_iX_iP_iP_jX_jQ_j = \sum_{i\neq j}P_iX_iP_iQ_jX_jQ_j - \tfrac{1}{2}\sum_{i\neq j}(Q_jP_i - Q_iP_j)X_iX_j(Q_jP_i - Q_iP_j)$$
$$\leq \sum_{i\neq j}(Q_jX_jQ_j)^{1/2}(P_iX_iP_i)(Q_jX_jQ_j)^{1/2} \leq \begin{cases} (N-1)\|PXP\|\sum_i Q_iX_iQ_i & \text{on } \mathcal{H}(N) \\ \mathrm{Tr}[PX]\sum_i Q_iX_iQ_i & \text{on } \mathcal{H}_{\mathrm{F}}(N) \end{cases} .$$

The last inequality follows since the operator $\sum_{i=1}^{N-1} P_iX_iP_i$ on $\mathcal{H}(N-1)$ is bounded in norm by $(N-1)\|PXP\|$ and as an operator on $\mathcal{H}_{\mathrm{F}}(N-1)$ it is bounded in norm by $\mathrm{Tr}[PX]$.

The proof of the theorem is now essentially complete, since we have found a lower bound in terms of one-body operators. It only remains to write this lower bound in as simple a form as possible. Since we are now only dealing with one-body operators this last step involves only estimates on operators on the one-body space $\mathcal{H}$.

In estimating A_2 we single out the estimate

$$(I+Q)XP^2X(I+Q) = XPX - XPQX + QXP^2X + XP^2XQ + QXP^2XQ$$
$$\leq XPX - XPQX + (1+\lambda)QXP^2XQ + \lambda^{-1}XP^2X \quad .$$

Combining this with the simple operator estimate $XPQX \geq PXPQXQ + QXPQXP$ we arrive at

$$A_2 + A_3 \geq \sum_i \Big(\alpha X_i - \tfrac{1}{2} X_i P_i X_i\Big) - \tfrac{1}{2}\alpha^2 - \sum_i B_i' \\ - (2 + \tfrac{1}{2}(\lambda + \lambda^{-1})) \begin{cases} (N-1)\|PXP\| \sum_i Q_i X_i Q_i & \text{on } \mathcal{H}(N) \\ \mathrm{Tr}[PX] \sum_i Q_i X_i Q_i & \text{on } \mathcal{H}_{\mathrm{F}}(N) \end{cases} , \quad (2.7)$$

where

$$B' = \alpha QXQ + \tfrac{1}{2}(1+2\lambda) QXP^2XQ + \tfrac{1}{2}\lambda^{-1}(PXQ^2XP + XP^2X) \quad .$$

Finally, using $\|X^{1/2}P^2X^{1/2}\| = \|PXP\|$ we get that $QXP^2XQ \leq \|PXP\| QXQ \leq \mathrm{Tr}[PX]QXQ$. Using this together with the trivial estimates $P^2 \leq P \leq I$ and $Q^2 \leq Q \leq I$ we see that (2.7) leads to the estimate (2.1) with (2.2) and (2.3) respectively. ■

As a simple consequence of this theorem we shall now give the estimates of Bach [1] (see also [3]). Consider states $\langle \cdot \rangle$ and $\langle \cdot \rangle_{\mathrm{F}}$ on the algebra of bounded operators on $\mathcal{H}(N)$ and $\mathcal{H}_{\mathrm{F}}(N)$ respectively. Let γ and γ_{F} be the corresponding one-particle density matrices.

COROLLARY 4 (Bach's inequalities). *If X is a projection, i.e., $X^2 = X = X^*$ we have*

$$\Big\langle \sum_{1 \leq i < j \leq N} X_i X_j \Big\rangle \geq \tfrac{1}{2}\Big((\mathrm{Tr}[X\gamma])^2 - N^{-1}\mathrm{Tr}[\gamma X \gamma X]\Big) \\ - \tfrac{1}{2}\mathrm{Tr}[X\gamma] \min\Big\{1, \sqrt{\tfrac{57}{2}}\left[\mathrm{Tr}[X(\gamma - N^{-1}\gamma^2)]\right]^{1/2}\Big\} \quad (2.8)$$

and

$$\Big\langle \sum_{1 \leq i < j \leq N} X_i X_j \Big\rangle_{\mathrm{F}} \geq \tfrac{1}{2}\Big((\mathrm{Tr}[X\gamma_{\mathrm{F}}])^2 - \mathrm{Tr}[\gamma_{\mathrm{F}} X \gamma_{\mathrm{F}} X]\Big) \\ - \tfrac{1}{2}\mathrm{Tr}[X\gamma_{\mathrm{F}}] \min\Big\{1, \sqrt{\tfrac{77}{2}}\left[\mathrm{Tr}[X(\gamma_{\mathrm{F}} - \gamma_{\mathrm{F}}^2)]\right]^{1/2}\Big\} \quad (2.9)$$

Proof: In both (2.8) and (2.9) the case of the min being equal to 1 is proved from (2.1) by simply choosing $\alpha = \mathrm{Tr}[X\gamma]$ or $\alpha = \mathrm{Tr}[X\gamma_{\mathrm{F}}]$ and $P = I$ and $\lambda = \infty$. In this case the operators B and B_{F} are both zero.

We next turn to the case when the min in (2.8) and (2.9) is smaller than 1. We consider first (2.8). We shall use (2.1) and (2.2) with $\lambda^{-1} = \frac{1}{4}\sqrt{\frac{57}{2}}\left[\mathrm{Tr}[X(\gamma - N^{-1}\gamma^2)]\right]^{1/2}$ and $\alpha = \mathrm{Tr}[X\gamma]$ and $P = N^{-1}\gamma$. Since the min in (2.8) is assumed to be smaller than 1 we have $\lambda \geq 4$. To arrive at (2.8) we need the additional simple observation that $N\|PXP\| \leq N\mathrm{Tr}[PX] = \mathrm{Tr}[\gamma X]$. We can then estimate the error term in (2.2) in the following way using that $\lambda \geq 4$.

$$
\begin{aligned}
\mathrm{Tr}[B\gamma] \leq& \tfrac{1}{2}(6 + 2\lambda + \lambda^{-1})\mathrm{Tr}[X\gamma]\mathrm{Tr}[X(\gamma - N^{-1}\gamma^2)] + \lambda^{-1}\mathrm{Tr}[X\gamma] \\
\leq& \tfrac{1}{2}\sqrt{\tfrac{57}{2}}\mathrm{Tr}[X\gamma]\left[\mathrm{Tr}[X(\gamma - N^{-1}\gamma^2)]\right]^{1/2} \quad .
\end{aligned}
$$

To get (2.9) we choose $\lambda^{-1} = \frac{1}{4}\sqrt{\frac{77}{2}}\left[\mathrm{Tr}[X(\gamma_{\mathrm{F}} - \gamma_{\mathrm{F}}^2)]\right]^{1/2}$ and $\alpha = \mathrm{Tr}[X\gamma_{\mathrm{F}}]$ and $P = \gamma_{\mathrm{F}}$. As before we have $\lambda \geq 4$. Inserting this into (2.3) easily gives (2.9).■

In the next section we will use the following inequality, which we state for fermions only:

COROLLARY 5. *Let X and P be bounded operators on $\mathcal{H}$ satisfying $X = X^2 = X^*$ and $0 \leq P \leq I$, and let $\alpha \geq 0$. Then*

$$
\begin{aligned}
\left\langle \sum_{1\leq i<j\leq N} X_i X_j \right\rangle_{\mathrm{F}} \geq& \alpha\mathrm{Tr}[X\gamma_{\mathrm{F}}] - \tfrac{1}{2}\alpha^2 - \tfrac{1}{2}\mathrm{Tr}[PXPX] \\
&- \mathrm{const}(\alpha + \mathrm{Tr}[XP] + \mathrm{Tr}[X\gamma_{\mathrm{F}}]) \min\left\{1, [\mathrm{Tr}[X(I-P)\gamma_{\mathrm{F}}(I-P)]]^{1/2}\right\} \quad .
\end{aligned}
\tag{2.10}
$$

Proof: The case where the min is 1 is done as before. In the other case we first note that for fermions we have

$$
\begin{aligned}
\sum_i X_i P_i X_i \leq& (1+\lambda^{-1})\sum_i P_i X_i P_i X_i P_i + (1+\lambda)\sum_i Q_i X_i P_i X_i Q_i \\
\leq& \mathrm{Tr}[PXPX] + \lambda^{-1}\sum_i P_i X_i P_i + (1+\lambda)\mathrm{Tr}[XP]\sum_i Q_i X_i Q_i
\end{aligned}
$$

since $\sum_i P_i X_i P_i X_i P_i \leq \mathrm{Tr}[PXPXP] = \mathrm{Tr}[P^{1/2}XP^2XP^{1/2}] \leq \mathrm{Tr}[P^{1/2}XPXP^{1/2}] = \mathrm{Tr}[PXPX]$ and $\|X^{1/2}PX^{1/2}\| = \|P^{1/2}XP^{1/2}\| \leq \mathrm{Tr}[XP]$. This shows that in (2.1) $\sum_i X_i P_i X_i$ can be replaced by $\mathrm{Tr}[PXPX]$ at the expense of changing the numerical constants in (2.3). We then let $\lambda^{-1} = \mathrm{Tr}[XQ\gamma_{\mathrm{F}}Q]^{1/2}$ and use $\lambda \geq 1$:

$$
\begin{aligned}
\mathrm{Tr}[B_{\mathrm{F}}\gamma] \leq& \mathrm{const}\lambda(\alpha + \mathrm{Tr}[XP])\mathrm{Tr}[QXQ\gamma_{\mathrm{F}}] + \mathrm{const}\lambda^{-1}(\mathrm{Tr}[X\gamma_{\mathrm{F}}] + \mathrm{Tr}[PXP\gamma_{\mathrm{F}}]) \\
\leq& \mathrm{const}(\alpha + \mathrm{Tr}[XP] + \mathrm{Tr}[X\gamma_{\mathrm{F}}])\mathrm{Tr}[XQ\gamma_{\mathrm{F}}Q]^{1/2}
\end{aligned}
$$

since $\mathrm{Tr}[PXP\gamma_{\mathrm{F}}] = \mathrm{Tr}[(PXP)^{1/2}\gamma_{\mathrm{F}}(PXP)^{1/2}] \leq \mathrm{Tr}[XP]$. ■

Remark: One may ask whether the exponent 1/2 appearing in (2.8) and (2.9) is optimal. The following example shows that, indeed, it is. The example is for the fermionic case (2.9), but it is easy to give a similar example in the case of (2.8). The idea behind the example is to construct fermionic states depending on a parameter ε such that $\mathrm{Tr}[X(\gamma_{\mathrm{F}} - \gamma_{\mathrm{F}}^2)] \to 0$ as $\varepsilon \to 0$ and such that the leading contribution to the error in Theorem 3 comes from A_3 estimated in (2.6).

Example: Let $\psi_1, \ldots, \psi_{N+2}$ be an orthonormal family of functions. Define normalized N-body functions by $\Psi_1 = (N!)^{-1/2}\psi_1 \wedge \ldots \wedge \psi_N$ and $\Psi_2 = (N!)^{-1/2}\psi_3 \wedge \ldots \wedge \psi_{N+2}$ and let $\Psi = (1-\varepsilon)^{1/2}\Psi_1 - \varepsilon^{1/2}\Psi_2$. Then Ψ is also normalized and if P and P' are the one-particle density matrices (projections) for Ψ_1 and Ψ_2 respectively, one easily sees that the one-particle density matrix corresponding to Ψ is $\gamma_{\mathrm{F}} = (1-\varepsilon)P + \varepsilon P'$. Hence $\gamma_{\mathrm{F}} - \gamma_{\mathrm{F}}^2 = \varepsilon(1-\varepsilon)P''$ where P'' is the projection onto $\mathrm{span}\{\psi_1, \psi_2, \psi_{N+1}, \psi_{N+2}\}$. Now let X be the projection onto $\mathrm{span}\{\psi_1 + \psi_{N+1}, \psi_2 + \psi_{N+2}\}$. Then $\mathrm{Tr}[\gamma_{\mathrm{F}}X] = 1$ and $\mathrm{Tr}[X(\gamma_{\mathrm{F}} - \gamma_{\mathrm{F}}^2)] = 2\varepsilon(1-\varepsilon)$. We can also compute $\langle\Psi_1|\sum_{i<j} X_iX_j\Psi_1\rangle = \frac{1}{2}\Big(\mathrm{Tr}[XP]^2 - \mathrm{Tr}[PXPX]\Big)$ and likewise for Ψ_2. Moreover, we find that the cross-term is $\langle\Psi_1|\sum_{i<j} X_iX_j\Psi_2\rangle = \frac{1}{4}$. Notice, that if we write $\sum_{i<j} X_iX_j = A_1 + A_2 + A_3$ as in the proof of Theorem 3 corresponding to the decompostion of the one-body space by P and $Q = I - P$ then the cross-term gets a contribution from A_3 only. Hence as $\varepsilon \to 0$

$$\langle\Psi|\sum_{1\leq i<j\leq N} X_iX_j\Psi\rangle - \tfrac{1}{2}\Big((\mathrm{Tr}[X\gamma_{\mathrm{F}}])^2 - \mathrm{Tr}[\gamma_{\mathrm{F}}X\gamma_{\mathrm{F}}X]\Big) = -\tfrac{1}{2}\varepsilon^{1/2} + O(\varepsilon).$$

III. APPLICATIONS TO QUANTUM SYSTEMS

The results of the preceding section have applications to Coulomb systems thanks to the Fefferman-de la Llave representation [8] of the Coulomb potential:

$$\frac{1}{|x-y|} = \frac{1}{\pi}\int dz \int_0^\infty \frac{dr}{r^5}\chi_{B(r,z)}(x)\chi_{B(r,z)}(y) \quad , \tag{3.1}$$

where $\chi_{B(r,z)}$ is the characteristic function of the ball $B(r,z) = \{x \in \mathbf{R}^3 \mid |x-z| \leq r\}$.

For any density matrix $0 \leq P \leq I$ with $\mathrm{Tr}P < +\infty$ acting on $\mathcal{H} = \mathrm{L}^2(\mathbf{R}^3, \mathbf{C}^m)$ let $\rho_P \in \mathrm{L}^1(\mathbf{R}^3)$ be its density. It satisfies $\mathrm{Tr}[Pf] = \int dx\rho_P(x)f(x)$ for all $f \in \mathrm{L}^\infty(\mathbf{R}^3)$. As before, we consider an N-particle fermionic state $\langle\ \cdot\ \rangle_{\mathrm{F}}$ with corresponding one-particle density matrix γ. The following is a generalization of Lemma 5 in [1]:

LEMMA 6. *Fix $0 < \varepsilon \le 1/6$. For any density matrix P and any density $\rho_0(x) \ge 0$ we have*

$$\left\langle \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} \right\rangle_{\mathrm{F}} \ge 2D(\rho_0,\rho_\gamma) - D(\rho_0,\rho_0) - \tfrac{1}{2}\sum_{\sigma,\sigma'}\iint dxdy \frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|} - \mathrm{const}\|\rho\|_{5/3}^{5/6}\|\rho\|_1^{1/6+\varepsilon}\delta(\gamma,P)^{1/3-\varepsilon} \tag{3.2}$$

where $\rho = \rho_0 + \rho_P + \rho_\gamma$.

Remark: The best choice for ρ_0 is $\rho_0 = \rho_\gamma$, since $2D(\rho_0,\rho_\gamma) - D(\rho_0,\rho_0) = -D(\rho_\gamma,\rho_\gamma) - D(\rho_0-\rho_\gamma,\rho_0-\rho_\gamma)$.

Proof: Let $X_{r,z}$ denote the operator on $\mathcal{H}$ acting by multiplication with $\chi_{B(r,z)}$; let $\alpha_{r,z} = \int_{B(r,z)} dx\rho_0(x)$. Then (2.10) yields

$$\left\langle \sum_{1\le i<j\le N} (X_{r,z})_i (X_{r,z})_j \right\rangle_{\mathrm{F}} \ge \alpha_{r,z}\mathrm{Tr}[X_{r,z}\gamma] - \tfrac{1}{2}\alpha_{r,z}^2 - \tfrac{1}{2}\mathrm{Tr}[PX_{r,z}PX_{r,z}] - \mathrm{const}\ E(r,z)$$

where $E(r,z) = (\int_{B(r,z)} dx\rho(x)) \min\{1, (\int_{B(r,z)} dx\rho_{Q\gamma Q}(x))^{1/2}\}$. The claim follows from this and from (3.1), except for the error term which we now estimate. Let f^* be the Hardy-Littlewood maximal function of $f \in \mathrm{L}^1(\mathbf{R}^3)$. Then

$$E(r,z) \le (4\pi/3)r^3\rho^*(z)\min\{1, (4\pi/3)^{1/2}r^{3/2}\rho^*_{Q\gamma Q}(z)^{1/2}\}$$

and

$$\begin{aligned}\int_0^\infty \frac{dr}{r^5}E(r,z) &\le \mathrm{const}\rho^*(z)\Big(\rho^*_{Q\gamma Q}(z)^{1/2}\int_0^R drr^{-1/2} + \int_R^\infty drr^{-2}\Big)\\ &\le \mathrm{const}\rho^*(z)\rho^*_{Q\gamma Q}(z)^{1/3}\end{aligned}$$

for $R = \rho^*_{Q\gamma Q}(z)^{-1/3}$. Thus, for fixed $0 < \varepsilon \le 1/5$,

$$\begin{aligned}\int dz\int_0^\infty \frac{dr}{r^5}E(r,z) &\le \mathrm{const}\|\rho^*(\rho^*_{Q\gamma Q})^{1/3}\|_1 \le \mathrm{const}\|\rho^*\|_{3/(2+\varepsilon)}\|\rho^*_{Q\gamma Q}\|_{1/(1-\varepsilon)}^{1/3}\\ &\le \mathrm{const}\|\rho\|_{3/(2+\varepsilon)}\|\rho_{Q\gamma Q}\|_{1/(1-\varepsilon)}^{1/3}\\ &\le \mathrm{const}\|\rho\|_{5/3}^{(5-5\varepsilon)/6}\|\rho\|_1^{(1+5\varepsilon)/6}\|\rho_{Q\gamma Q}\|_{5/3}^{5\varepsilon/6}\|\rho_{Q\gamma Q}\|_1^{(2-5\varepsilon)/6}\end{aligned} \tag{3.3}$$

by using the Hölder inequality, the Hardy-Littlewood maximal inequality [19] and $\|f\|_p \leq \|f\|_{5/3}^{\frac{5}{2}-\frac{5}{2p}} \|f\|_1^{\frac{5}{2p}-\frac{3}{2}}$ for $1 \leq p \leq 5/3$. From $Q\gamma Q \leq (I-P)\gamma(I-P)+(I+P)\gamma(I+P) = 2(\gamma+P\gamma P) \leq 2(\gamma+P)$ we obtain $\rho_{Q\gamma Q} \leq 2\rho$. On the other hand, $\|\rho_{Q\gamma Q}\|_1 = \mathrm{Tr}[Q\gamma Q] \leq \delta(\gamma, P)$. The error estimate in (3.2) follows by applying these last two inequalities to the last two factors in (3.3). ■

IV. THE JELLIUM MODEL

We shall here prove Theorem 2. The proof is divided into a proof of an upper bound and a lower bound on the energy $E_{\mathrm{J}}(\overline{\rho})$. We first turn to the upper bound, i.e., to the proof that $\mathcal{C}(\overline{\rho}) \geq 0$.

Proof of upper bound in (1.17): Since the thermodynamic limit is independent of the shape of the domain Λ as proved in [15] we may for convenience assume that Λ is a ball centered at the origin. For the lower bound we shall return to Λ being a cube.

We shall use that $E(N,\Lambda) \leq E_{\mathrm{HF}}(N,\Lambda)$ and appeal to the Lieb variational principle (the second line in (1.8)). We define an operator P on $\mathcal{H}$ by the integral kernel

$$P(x,\sigma;y,\sigma') = \delta_{\sigma,\sigma'}(2\pi)^{-3}\int_{|p|\leq F} dp g(x)e^{ip(x-y)}g(y) \quad , \tag{4.1}$$

where g is a function we shall choose below to be spherically symmetric, supported in the ball Λ and satisfying $0 \leq g \leq 1$. The parameter F is to be chosen such that $\mathrm{Tr}P = N$. By Parseval's identity $0 \leq P \leq I$ and the density corresponding to P is

$$\rho_P(x) = (m/6\pi^2)F^3 g(x)^2.$$

Thus $F = \left(6\pi^2 N/(m\int g^2)\right)^{1/3} = \mathrm{c}_{\mathrm{TF}}^{1/2}(N/\int g^2)^{1/3}$. It is easy to compute the integral kernel of P explicitly indeed

$$P(x,\sigma;y,\sigma') = \delta_{\sigma,\sigma'}F^3 g(x)G_0(|x-y|F)g(y) \quad , \tag{4.2}$$

where $G_0(t) = (2\pi^2)^{-1}t^{-3}(\sin t - t\cos t)$.

We shall let $\overline{\rho}$ denote both the value $N/|\Lambda|$ and the background density which is equal to the constant $N/|\Lambda|$ in Λ and is zero outside Λ. From (1.6) we now see that the right side of (1.5) can be estimated as follows

$$|\Lambda|^{-1}\Big(E(N,\Lambda)+D(\overline{\rho},\overline{\rho})\Big) \le |\Lambda|^{-1}\Big(\mathrm{Tr}[-\Delta P]+D(\rho_P-\overline{\rho},\rho_P-\overline{\rho}) - \tfrac{1}{2}\sum_{\sigma,\sigma'}\iint dxdy\frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|}\Big). \tag{4.3}$$

A simple computation gives $\mathrm{Tr}[-\Delta P]=\frac{3}{5}\mathrm{c}_{\mathrm{TF}}\int\rho_P(x)^{5/3}+(m/6\pi^2)F^3\|\nabla g\|_2^2$.

Let $R=(3|\Lambda|/4\pi)^{1/3}$ be the radius of Λ we can choose $g=g_R$ such that (a) $g_R(x)=1$ if $|x|\le R(1-R^{-\alpha})$ and (b) $\|\nabla g_R\|_2^2\le \mathrm{const}\,R^{1+\alpha}$ for any α satisfying $1<\alpha<2$. It is then clear that in the thermodynamic limit $|\Lambda|\to\infty$ with $N/|\Lambda|=\overline{\rho}$ fixed we have

$$|\Lambda|^{-1}\mathrm{Tr}[-\Delta P]\to\tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}\overline{\rho}^{5/3} \quad . \tag{4.4}$$

From the choice of g_R it follows that $|\Lambda|(1-R^{-\alpha})^3\le\int g_R^2\le|\Lambda|$. We then have $\rho_P(x)=(N/\int g_R^2)-\widetilde{\rho}(x)$ where $\widetilde{\rho}$ is a positive density supported in $R(1-R^{-\alpha})\le|x|\le R$ and with $\int\widetilde{\rho}\le N[(1-R^{-\alpha})^{-3}-1]$. Since $\iint_{\Lambda\times\Lambda}dxdy|x-y|^{-1}=\mathrm{const}\,R^5$ and $N/|\Lambda|-N/(\int g_R^2)\le 0$ we obtain

$$\begin{aligned} D(\rho_P-\overline{\rho},\rho_P-\overline{\rho}) =&\tfrac{1}{2}\Big(\frac{N}{|\Lambda|}-\frac{N}{\int g_R^2}\Big)^2\iint_{\Lambda\times\Lambda}dxdy|x-y|^{-1}\\ &+\Big(\frac{N}{|\Lambda|}-\frac{N}{\int g_R^2}\Big)\int dx\widetilde{\rho}(x)\int_\Lambda dy|x-y|^{-1}+D(\widetilde{\rho},\widetilde{\rho})\\ &\le\mathrm{const}\left(\frac{N}{|\Lambda|}\right)^2[(1-R^{-\alpha})^{-3}-1]^2R^5\left(1+(1-R^{-\alpha})^{-1}\right) \quad , \end{aligned}$$

where in the last inequality we have used $D(\widetilde{\rho},\widetilde{\rho})\le(\int\widetilde{\rho})^2R^{-1}(1-R^{-\alpha})^{-1}$. Since $\alpha>1$ we find in the thermodynamic limit that

$$\lim_{|\Lambda|\to\infty}|\Lambda|^{-1}D(\rho_P-\overline{\rho},\rho_P-\overline{\rho})\le\mathrm{const}\,\overline{\rho}^2\lim_{R\to\infty}R^{2-2\alpha}=0 \quad . \tag{4.5}$$

Finally, using (4.2) and the change of variables $s=\frac{x+y}{2}$, $r=F(x-y)$ (whose Jacobian is $(FR^{-1})^3$) we compute

$$\begin{aligned} &\tfrac{1}{2}|\Lambda|^{-1}\sum_{\sigma,\sigma'}\iint dxdy\frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|}\\ &\qquad=\frac{m}{2}(|\Lambda|^{-1}R^3)F^4\iint drdsg_R(Rs+F^{-1}\frac{r}{2})^2\frac{G_0(|r|)^2}{|r|}g_R(Rs-F^{-1}\frac{r}{2})^2 \quad . \end{aligned}$$

In the termodynamic limit $F \to c_{\rm TF}^{1/2}\overline{\rho}^{1/3}$ and $g_R(Rs \pm F^{-1}\frac{r}{2})^2 \to \chi_{B(1,0)}(s)$ pointwise. By dominated convergence the above expression tends to

$$\frac{m}{2}c_{\rm TF}^2\overline{\rho}^{4/3}\int dr \frac{G_0(|r|)^2}{|r|} = 2\pi m c_{\rm TF}^2\overline{\rho}^{4/3}\int_0^\infty dt\; t\; G_0(t)^2 = c_{\rm D}\overline{\rho}^{4/3} \quad , \tag{4.6}$$

where we used the value $(2\pi)^{-4}$ of the last integral. Combining (4.6) with (4.3–5) proves the upper bound.

Proof of lower bound in (1.17): We now assume that Λ is a cube of length $L = |\Lambda|^{1/3}$ and we consider states $\langle\cdot\rangle_{\rm F}$ such that in the thermodynamic limit

$$|\Lambda|^{-1}\left(\Big\langle H(N,\Lambda)\Big\rangle_{\rm F} + D(\overline{\rho},\overline{\rho})\right) \to E_{\rm J}(\overline{\rho}) \quad . \tag{4.7}$$

We shall use Lemma 6 with $\rho_0 = \overline{\rho}$ and P being the projection with integral kernel

$$P(x,\sigma;y,\sigma') = \begin{cases} |\Lambda|^{-1}\delta_{\sigma,\sigma'} \displaystyle\sum_{\substack{p\in 2\pi L^{-1}\mathbf{Z}^3,\\ |p|\le p_{\rm TF}}} e^{ip(x-y)} & , \text{if } x,y\in\Lambda \\ 0 & , \text{otherwise} \end{cases} \tag{4.8}$$

where $p_{\rm TF} = c_{\rm TF}^{1/2}\overline{\rho}^{1/3}$. Notice that P is a spectral projection of the Laplacian with *periodic* boundary conditions on Λ and that $\rho_P(x)$ converges to $\overline{\rho}$ in the thermodynamic limit. Since $\langle V\rangle_{\rm F} = 2D(\overline{\rho},\rho_\gamma)$ we get from Lemma 6 that

$$\begin{aligned}\Big\langle H(N,\Lambda)\Big\rangle_{\rm F} + D(\overline{\rho},\overline{\rho}) \ge &\Big\langle \sum_i -\Delta_i\Big\rangle_{\rm F} - \tfrac{1}{2}\sum_{\sigma,\sigma'}\iint dxdy \frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|} \\ &- {\rm const}\,\|\rho\|_1^{1/6+\varepsilon'}\|\rho\|_{5/3}^{5/6}\delta(\gamma,P)^{1/3-\varepsilon'} \quad .\end{aligned} \tag{4.9}$$

Recall that $\rho = \rho_\gamma + \rho_P + \overline{\rho}$.

We first point out that the same computation which led to (4.6) gives

$$\lim_{|\Lambda|\to\infty} \tfrac{1}{2}|\Lambda|^{-1}\sum_{\sigma,\sigma'}\iint dxdy\frac{|P(x,\sigma;y,\sigma')|^2}{|x-y|} = c_{\rm D}\overline{\rho}^{4/3} \quad . \tag{4.10}$$

Secondly, we use (4.7) (and the upper bound on $E_{\rm J}$ proved above), (4.9) and (4.10) together with the Lieb-Thirring estimate [17] $\Big\langle \sum_i -\Delta_i\Big\rangle_{\rm F} \ge {\rm const}\, m^{-2/3}\int \rho_\gamma^{5/3}$ and the trivial estimate $\delta(\gamma,P) \le {\rm Tr}\gamma = N$ to obtain that for $\overline{\rho} \ge {\rm const}\, m^2$

$$\limsup_{|\Lambda|\to\infty} |\Lambda|^{-1}\int \rho_\gamma^{5/3} \le {\rm const}\,\overline{\rho}^{5/3} \quad . \tag{4.11}$$

Since the form domain of the Dirichlet Laplacian is included in the form domain of the Laplacian with periodic boundary conditions we may write

$$\Big\langle \sum_i -\Delta \Big\rangle_{\mathrm{F}} = \mathrm{Tr}[(-\Delta)\gamma] = \sum_{p\in 2\pi L^{-1}\mathbf{Z}^3} |p|^2 M(p) \quad , \tag{4.12}$$

where $M(p) = |\Lambda|^{-1}\sum_\sigma \iint dxdy e^{ip(y-x)}\gamma(x,\sigma;y,\sigma)$. In order to control $\delta(\gamma,P) = \langle\sum_{i=1}^N (I - P_i)\rangle_{\mathrm{F}}$ we view $\langle\,\cdot\,\rangle_{\mathrm{F}}$ as an approximate ground state of $\sum_{i=1}^N \Delta_i$ which we probe by means of the perturbation $\sum_{i=1}^N (I-P)_i$, a method known as the Feynman-Hellmann technique. More precisely we want to estimate

$$\Big\langle \sum_i -\Delta \Big\rangle_{\mathrm{F}} - \alpha\delta(\gamma,P) = \sum_{p\in 2\pi L^{-1}\mathbf{Z}^3} (p^2 - p_{\mathrm{TF}}^2 + \alpha\theta(p_{\mathrm{TF}}^2 - p^2))M(p) + (p_{\mathrm{TF}}^2 - \alpha)N \quad ,$$

where we have used that $\sum_p M(p) = \mathrm{Tr}\gamma = N$ and $\delta(\gamma,P) = \mathrm{Tr}[\gamma(I-P)] = \sum_{|p|>p_{\mathrm{TF}}} M(p)$. Here θ is the step function $\theta(t) = 1$ if $t\geq 0$ and $\theta(t) = 0$ if $t<0$. Note that $0\leq M(p)\leq m$. The sum is thus bounded below by

$$\inf\Big\{ \sum_{p\in 2\pi L^{-1}\mathbf{Z}^3} (p^2 - p_{\mathrm{TF}}^2 + \alpha\theta(p_{\mathrm{TF}}^2 - p^2))M(p) \mid 0\leq M(p)\leq m \Big\} \quad ,$$

whose minimizer is $M(p) = m\theta(p_{\mathrm{TF}}^2 - p^2 - \alpha\theta(p_{\mathrm{TF}}^2 - p^2)) = m\theta(p_{\mathrm{TF}}^2 - \alpha_+ - p^2)$ with $t_+ = \max(t,0)$. For $\alpha\geq 0$ we then have

$$\begin{aligned}
&\Big\langle \sum_i -\Delta \Big\rangle_{\mathrm{F}} - \tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}|\Lambda|\overline{\rho}^{5/3} - \alpha\delta(\gamma,P) \\
&\qquad \geq m \sum_{p^2\leq p_{\mathrm{TF}}^2 - \alpha} (p^2 - p_{\mathrm{TF}}^2 + \alpha) - \mathrm{c}_{\mathrm{TF}}^{-3/2}|\Lambda|(\tfrac{3}{5}p_{\mathrm{TF}}^5 - (p_{\mathrm{TF}}^2 - \alpha)p_{\mathrm{TF}}^3) \\
&\qquad = -\mathrm{c}_{\mathrm{TF}}^{-3/2}|\Lambda|\Big(\tfrac{2}{5}(p_{\mathrm{TF}}^2 - \alpha)_+^{5/2} - \tfrac{2}{5}p_{\mathrm{TF}}^5 + p_{\mathrm{TF}}^3\alpha\Big) + \mathrm{o}(|\Lambda|) \\
&\qquad = -\mathrm{c}_{\mathrm{TF}}^{-3/2}|\Lambda|\tfrac{1}{2}\cdot\tfrac{3}{2}(p_{\mathrm{TF}}^2 - \alpha')_+^{1/2}\alpha^2 + \mathrm{o}(|\Lambda|) \\
&\qquad \geq -\mathrm{const}\, m^{2/3}|\Lambda|\overline{\rho}^{1/3}\alpha^2 + \mathrm{o}(|\Lambda|)
\end{aligned}$$

for some $0\leq\alpha'\leq\alpha$ (by Taylor's formula). Optimization over $\alpha\geq 0$ then yields

$$|\Lambda|^{-1}\Big\langle \sum_i -\Delta \Big\rangle_{\mathrm{F}} \geq \tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}\overline{\rho}^{5/3} + \mathrm{const}\, m^{-2/3}\overline{\rho}^{-1/3}(|\Lambda|^{-1}\delta(\gamma,P))^2 + \mathrm{o}(1) \tag{4.13}$$

Inserting (4.10), (4.11) and (4.13) into (4.9) gives for large $\overline{\rho}$ the following estimate:

$$\begin{aligned}|\Lambda|^{-1}\Big(\Big\langle H(N,\Lambda)\Big\rangle + D(\overline{\rho},\overline{\rho})\Big) \geq &\tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}\overline{\rho}^{5/3} - \mathrm{c}_{\mathrm{D}}\overline{\rho}^{4/3} + \mathrm{const}\, m^{-2/3}\overline{\rho}^{-1/3}(|\Lambda|^{-1}\delta(\gamma,P))^2 \\ &- \mathrm{const}\,\overline{\rho}^{1+\varepsilon'}(|\Lambda|^{-1}\delta(\gamma,P))^{1/3-\varepsilon'} + \mathrm{o}(1) \\ \geq &\tfrac{3}{5}\mathrm{c}_{\mathrm{TF}}\overline{\rho}^{5/3} - \mathrm{c}_{\mathrm{D}}\overline{\rho}^{4/3} - \mathrm{const}\, m^{2/15}\overline{\rho}^{4/3-1/15+\varepsilon} + \mathrm{o}(1) \quad .\end{aligned}$$

The last inequality which proves the lower bound was found by minimizing over the quantity $|\Lambda|^{-1}\delta(\gamma, P)$. ■

V. BORN-OPPENHEIMER MOLECULES

The proof of (1.15,16) is a local version of that given in the previous section. We begin by reviewing the classical picture of the quantum ground state as it emerges e.g. from [13]. The minimizer ρ_{TF} of (1.10) satisfies $\int dx\, \rho_{\mathrm{TF}}(x) = \min(N, Z) = N$ and the Thomas-Fermi equation

$$\mathrm{c}_{\mathrm{TF}}\rho_{\mathrm{TF}}^{2/3} = (\phi_{\mathrm{TF}} + \mu)_+ \tag{5.1}$$

for some $\mu \leq 0$ called the chemical potential. Let $M(p,q)$ be the ensemble over phase space ($\mathbf{R}^6$, $(2\pi)^{-3}dpdq$) obtained by placing N electrons in such a way as to minimize the expectation of the Hamiltonian function $h(p,q) = p^2 - \phi_{\mathrm{TF}}(q)$ under the constraint of putting at most m particles per unit cell. That is, $M(p,q) = m\theta(\mu - h(p,q))$. Indeed, $(2\pi)^{-3}\int dp\ M(p,q) = \rho_{\mathrm{TF}}(q)$ and

$$E_{\mathrm{C}} = (2\pi)^{-3}m\iint_{h(p,q)\leq\mu} dpdq\ h(p,q) = E_{\mathrm{TF}} + D(\rho_{\mathrm{TF}},\rho_{\mathrm{TF}}) \quad ,$$

as it is seen by carrying out the p-integration and by using (5.1).

This picture is translated into quantum mechanics by means of coherent states $f_{pq}(x) = g(x-q)e^{ipx}$ with g even and $\|g\|_2 = 1$. The corresponding projections are $\Pi_{pq} = f_{pq}\langle f_{pq} \mid \ \cdot\ \rangle$. A semiclassical approximation for the one-particle density matrix γ of the quantum ground state should then be given by the weak integral

$$P_{\mathrm{SC}} = (2\pi)^{-3}\iint_{h(p,q)\leq\mu} dpdq\ \Pi_{pq} \quad .$$

We note that $0 \leq P_{\mathrm{SC}} \leq I$ and that $\mathrm{Tr}P_{\mathrm{SC}} = N$. Its integral kernel is $P(x,y)\delta_{\sigma,\sigma'}$ with

$$P(x,y) = (2\pi)^{-3}\iint_{h(p,q)\leq\mu} dpdq\, g(x-q)\bar{g}(y-q)e^{ip(x-y)} = \int dq\, G(q,x-y)g(x-q)\bar{g}(y-q) \quad ,$$

where $G(q,r) = p_{\rm TF}(q)^3 G_0(p_{\rm TF}(q)|r|)$, $p_{\rm TF} = c_{\rm TF}^{1/2}\rho_{\rm TF}^{1/3}$ and G_0 is as in (4.2). By setting $f(s,r) = g(s+\frac{r}{2})\bar{g}(s-\frac{r}{2})$ we can rewrite this as $P(x,y) = G *_1 f(\frac{x+y}{2}, x-y)$, where $*_1$ stands for convolution in the first variable only. In particular, $P_{\rm SC}$ has density $\rho_{\rm SC} = \rho_{\rm TF} * |g|^2$. We now turn to the exchange energy: Since the Jacobian of the change of variables $s=(x+y)/2$, $r = x-y$ is 1, it is estimated as

$$\frac{m}{2}\iint dxdy \frac{|P(x,y)|^2}{|x-y|} = \frac{m}{2}\iint \frac{dr}{r} ds |G *_1 f(s,r)|^2 \le \frac{m}{2}\iint \frac{dr}{r} ds |G(s,r)|^2 = c_{\rm D}\int dx \rho_{\rm TF}^{4/3} \tag{5.2}$$

by using Young's inequality. The last equality follows as in (4.6).

The constants appearing below are uniform in the variables of the theorem, namely in $\underline{Z}$, $\underline{\mathcal{R}}$ and $N \le Z$. They may however depend on m, K and ε.

Also of interest will be the operator

$$\begin{aligned} h_{\rm SC} &= (2\pi)^{-3}\iint dpdq\ h(p,q)\Pi_{pq} \\ &= -\Delta - \phi_{\rm TF} * |g|^2 + \|\nabla g\|_2^2 = h + (\phi_{\rm TF} - \phi_{\rm TF} * |g|^2) + \|\nabla g\|_2^2 \end{aligned} \tag{5.3}$$

with h as in (1.13). We will need that $\|\phi_{\rm TF} - \phi_{\rm TF} * |g|^2\|_{5/2} \le {\rm const}\, Z \||x|^{1/2}|g|^2\|_1^{2/5}$. Indeed,

$$\begin{aligned} \big||x|^{-1} - |x|^{-1} * |g|^2\big| &\le \int dy \big||x|^{-1} - |x-y|^{-1}\big| |g(y)|^2 \\ &\le \left(\int dy \big||x|^{-1} - |x-y|^{-1}\big|^{5/2} |g(y)|^2\right)^{2/5} \left(\int dy |g(y)|^2\right)^{3/5} \end{aligned}$$

so that

$$\||x|^{-1} - |x|^{-1} * |g|^2\|_{5/2}^{5/2} \le \int dy \left(\int dx \big||x|^{-1} - |x-y|^{-1}\big|^{5/2}\right) |g(y)|^2 \quad .$$

Clearly, $|x|^{-1} - |x-y|^{-1} \in {\rm L}^{5/2}(\mathbf{R}^3)$ for fixed y. By scaling, $\int dx \big||x|^{-1} - |x-y|^{-1}\big|^{5/2} = {\rm const}|y|^{1/2}$. Hence $\|\phi_{\rm TF} - \phi_{\rm TF} * |g|^2\|_{5/2} \le {\rm const}(\sum_{k=1}^K Z_k + \|\rho_{\rm TF}\|_1)\||x|^{1/2}|g(x)|^2\|_1^{2/5}$.

As a final preliminary we give a bound for the ${\rm L}^{5/3}$ norms of the densities met so far: $\|\rho\|_{5/3}^{5/3} \le {\rm const}\, Z^{7/3}$ either for $\rho = \rho_{\rm TF}$ (and hence for $\rho = \rho_{\rm SC}$) or, using the notation of Sect. III, for $\rho = \rho_\gamma$ provided $\langle H(N, \underline{Z}, \underline{\mathcal{R}})\rangle_{\rm F} \le 0$. To see this we write $|x|^{-1} = V_1 + V_2$ with $V_1 = \min(|x|^{-1}, \lambda)$, $V_2 = (|x|^{-1} - \lambda)_+$ for any $\lambda > 0$. Then $\|V_1\|_\infty = \lambda$, $\|V_2\|_{5/2} =$

const $\lambda^{-1/5}$. Hence $\int dx\rho|x|^{-1} \leq \lambda\|\rho\|_1 + \mathrm{const}\,\lambda^{-1/5}\|\rho\|_{5/3}$, which is $\leq \mathrm{const}\|\rho\|_1^{1/6}\|\rho\|_{5/3}^{5/6}$ after optimizing λ. For $\rho = \rho_{\mathrm{TF}}$ this implies

$$0 \geq E_{\mathrm{TF}} \geq \mathrm{const}\|\rho\|_{5/3}^{5/3} - \mathrm{const}\, Z N^{1/6}\|\rho\|_{5/3}^{5/6} \geq \mathrm{const}\|\rho\|_{5/3}^{5/6}(\|\rho\|_{5/3}^{5/6} - \mathrm{const}\, Z^{7/6}) \quad ,$$

where we dropped the repulsion between electrons. The Lieb-Thirring inequality [17] yields a lower bound for $\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}}$ of the same form but with $\rho = \rho_\gamma$.

Proof of (1.16): We take $\rho_0 = \rho_{\mathrm{TF}}$, $P = P_{\mathrm{SC}}$ in (3.2) and use the bounds for the $\mathrm{L}^{5/3}$ norms of the occurring densities, as well as (5.2). The result is

$$\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \geq \langle H_{\mathrm{DS}}(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} - \mathrm{const}\, Z^{7/6} Z^{1/6+\varepsilon}\delta(\gamma, P_{\mathrm{SC}})^{1/3-\varepsilon}$$

provided $\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \leq 0$. Since $E(N,\underline{Z},\underline{\mathcal{R}}) \leq E(1,\underline{Z},\underline{\mathcal{R}}) < 0$ for $Z > 0$, we see that all is needed is an estimate of the form $\delta(\gamma, P_{\mathrm{SC}}) = \mathrm{O}(Z^{1-\varepsilon})$ for states with $\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}}$ arbitrarily close to $E(N,\underline{Z},\underline{\mathcal{R}})$. Just by using the trivial estimates $\delta(\gamma, P_{\mathrm{SC}}) \leq \mathrm{Tr}\,\gamma = N \leq Z$ and $\|\rho_{\mathrm{TF}}\|_{4/3}^{4/3} \leq \|\rho_{\mathrm{TF}}\|_1^{1/2}\|\rho_{\mathrm{TF}}\|_{5/3}^{5/6} \leq \mathrm{const}\, Z^{5/3}$ we have

$$\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \geq \mathrm{Tr}[h\gamma] - D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \mathrm{const}\, Z^{5/3} \quad ,$$

a fact which can also be derived [13] without using the lemma. Now (5.3) implies

$$\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \geq \mathrm{Tr}[h_{\mathrm{SC}}\gamma] - D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - \mathrm{const}(Z^{12/5}\||x|^{1/2}|g|^2\|_1^{2/5} + Z\|\nabla g\|_2^2 + Z^{5/3}) \tag{5.4}$$

since $\mathrm{Tr}[(\phi_{\mathrm{TF}} - \phi_{\mathrm{TF}} * |g|^2)\gamma] \leq \|\phi_{\mathrm{TF}} - \phi_{\mathrm{TF}} * |g|^2\|_{5/2}\|\rho_\gamma\|_{5/3}$. We set $g(x) = \lambda^{-3/2}g_0(x/\lambda)$ for some smooth, even g_0 with $\|g_0\|_2 = 1$, so that $\|g\|_2 = 1$ as required. Then the above error is $\mathrm{O}(Z^{12/5}\lambda^{1/5} + Z\lambda^{-2} + Z^{5/3})$, i.e. $\mathrm{O}(Z^{7/3-2/33})$ once we take the optimal value $\lambda = Z^{-7/11}$.

We will now estimate $\delta(\gamma, P_{\mathrm{SC}}) = \langle\sum_{i=1}^N (I - P_{\mathrm{SC}})_i\rangle_{\mathrm{F}}$ by using the Feynman-Hellmann technique, as in the previous section. Specifically,

$$\begin{aligned}\mathrm{Tr}[h_{\mathrm{SC}}\gamma] - E_{\mathrm{C}} - \alpha\delta(\gamma, P_{\mathrm{SC}}) &= \mathrm{Tr}[(h_{\mathrm{SC}} - \alpha(I - P_{\mathrm{SC}}))\gamma] - E_{\mathrm{C}} \\ &= (2\pi)^{-3}\left(\iint dpdq(h - \mu + \alpha\theta(\mu - h))\mathrm{Tr}[\Pi_{pq}\gamma] - m\iint_{h\leq\mu} dpdq(h - \mu + \alpha)\right) \quad ,\end{aligned}$$

since Tr $\gamma = N = (2\pi)^{-3} m \iint_{h\leq\mu} dpdq$. Note that $0 \leq \mathrm{Tr}[\Pi_{pq}\gamma] \leq \mathrm{Tr}\ \Pi_{pq} \leq m$. The first integral is therefore bounded below by

$$\inf\Big\{\iint dpdq[h(p,q)-\mu+\alpha\theta(\mu-h(p,q))]M(p,q)\mid 0\leq M(p,q)\leq m\Big\} \quad .$$

The obvious minimizer is $M(p,q) = m\theta(\mu-h(p,q)-\alpha\theta(\mu-h(p,q))) = m\theta(\mu-\alpha_+-h(p,q))$. For $\alpha \geq 0$ we thus have

$$\begin{aligned}
\mathrm{Tr}[h_{\mathrm{SC}}\gamma] - E_{\mathrm{C}} - \alpha\delta(\gamma,P_{\mathrm{SC}}) &\geq (2\pi)^{-3} m \left(\iint_{h\leq\mu-\alpha} - \iint_{h\leq\mu}\right) dpdq(h-\mu+\alpha) \\
&= -(2\pi)^{-3} m \iint_{-\alpha\leq h-\mu\leq 0} dpdq(h-\mu+\alpha) \\
&= -(2\pi)^{-3} m \int_0^\alpha d\alpha' \iint_{-\alpha'\leq h-\mu\leq 0} dpdq \\
&= -(2\pi)^{-3} m \int_0^\alpha d\alpha' \frac{4\pi}{3} \int dq[(\phi_{\mathrm{TF}}+\mu)_+^{3/2} - (\phi_{\mathrm{TF}}+\mu-\alpha')_+^{3/2}] \\
&= -(2\pi)^{-2} m \int_0^\alpha d\alpha' \int_0^{\alpha'} d\alpha'' \int dq(\phi_{\mathrm{TF}}+\mu-\alpha'')_+^{1/2}
\end{aligned}$$

since $h-\mu+\alpha = \int_0^\alpha d\alpha'\theta(h-\mu+\alpha')$ if $-\alpha\leq h-\mu\leq 0$. The innermost integral is bounded by a constant times $\alpha''^{-1/4}$, as will be shown in the lemma below. This yields

$$\mathrm{Tr}[h_{\mathrm{SC}}\gamma] - E_{\mathrm{C}} \geq \alpha\delta(\gamma,P_{\mathrm{SC}}) - \mathrm{const}\,\alpha^{7/4} \quad ,$$

which is $\geq$ const $\delta(\gamma,P_{\mathrm{SC}})^{7/3}$ after optimizing $\alpha\geq 0$. Inserting this into (5.4) we obtain

$$\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \geq E_{\mathrm{TF}} + \mathrm{const}\ \delta(\gamma,P_{\mathrm{SC}})^{7/3} - \mathrm{const}\ Z^{7/3-2/33} \quad .$$

This is an extension of the lower bound contained in the result of [13,16,20] which we mentioned in the introduction, namely $E = E_{\mathrm{TF}} + \mathrm{O}(Z^{7/3-2/33})$. By the upper bound therein there are states with $\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \leq E_{\mathrm{TF}} + \mathrm{const}\ Z^{7/3-2/33}$. For such states we conclude that

$$\delta(\gamma,P_{\mathrm{SC}}) \leq \mathrm{const}\, Z^{1-2/77} \quad , \tag{5.5}$$

which is what we needed.■

Proof of (1.15): By taking $\rho_0 = \rho_\gamma$, $P=\gamma$ in (3.2) we obtain

$$\langle H(N,\underline{Z},\underline{\mathcal{R}})\rangle_{\mathrm{F}} \geq \mathcal{E}_{\mathrm{HF}}(\gamma) - \mathrm{const}\ Z^{4/3+\varepsilon}\delta(\gamma,\gamma)^{1/3-\varepsilon} \quad .$$

We note that $\delta(\gamma, P_{\rm SC}) = N - {\rm Tr}[\gamma P_{\rm SC}] = \delta(P_{\rm SC}, \gamma)$ and that

$$\begin{aligned}\delta(\gamma,\gamma) &= {\rm Tr}[P_{\rm SC}^{1/2}\gamma(I-\gamma)P_{\rm SC}^{1/2}] + {\rm Tr}[(I-P_{\rm SC})^{1/2}\gamma(I-\gamma)(I-P_{\rm SC})^{1/2}] \\ &\le {\rm Tr}[P_{\rm SC}^{1/2}(I-\gamma)P_{\rm SC}^{1/2}] + {\rm Tr}[(I-P_{\rm SC})^{1/2}\gamma(I-P_{\rm SC})^{1/2}] = \delta(P_{\rm SC},\gamma) + \delta(\gamma, P_{\rm SC}) \ .\end{aligned}$$

We then conclude as before using (5.5). ■

Left to be proved is the following estimate which is similar to one in [1].

LEMMA 7. *For $\alpha > 0$,*

$$\int dx (\phi_{\rm TF}(x) + \mu - \alpha)_+^{1/2} \le {\rm const}\,\alpha^{-1/4} \quad .$$

Proof: [13] Let $\phi_k(x) = {\rm c}_{\rm TF}^3(3/\pi)^2|x-\mathcal{R}_k|^{-4}$, $k = 1,\ldots,K$ and $\phi(x) = \sum_{k=1}^K \phi_k(x)$. For $x \ne \mathcal{R}_k$, $k=1,\ldots,K$ we then have $(4\pi)^{-1}\Delta\phi_k(x) = {\rm c}_{\rm TF}^{-3/2}\phi_k(x)^{3/2}$ and $(4\pi)^{-1}\Delta\phi(x) \le {\rm c}_{\rm TF}^{-3/2}\phi(x)^{3/2}$, due to $\sum_{k=1}^K \phi_k^{3/2} \le (\sum_{k=1}^K \phi_k)^{3/2}$. We claim that

$$\phi_{\rm TF} + \mu \le \phi \quad . \tag{5.6}$$

To show this, let $\psi = \phi_{\rm TF} + \mu - \phi$ and $B = \{x \in \mathbf{R}^3 \mid \psi(x) > 0\}$. Then (1.11) implies $\mathcal{R}_k \notin \bar{B}$ and, on the open set B, $-(4\pi)^{-1}\Delta\psi = (4\pi)^{-1}\Delta\phi - \rho_{\rm TF} \le {\rm c}_{\rm TF}^{-3/2}[\phi^{3/2} - (\phi_{\rm TF}+\mu)_+^{3/2}] \le 0$ because $\phi_{\rm TF} + \mu > \phi \ge 0$. That is, ψ is subharmonic on B. Since $\psi\big|_{\partial B} = 0$ and $\lim_{|x|\to\infty}\psi = \mu \le 0$, we have $\psi \le 0$ on B. Hence $B = \emptyset$ and (5.6) holds true. We can now estimate

$$\begin{aligned}\int dx(\phi_{\rm TF} + \mu - \alpha)_+^{1/2} &\le \int dx(\phi-\alpha)_+^{1/2} = \int dx \Big[\sum_{k=1}^K(\phi_k - \alpha K^{-1})\Big]_+^{1/2} \\ &\le \int dx\Big[\sum_{k=1}^K(\phi_k - \alpha K^{-1})_+\Big]^{1/2} \le \int dx \sum_{k=1}^K (\phi_k - \alpha K^{-1})_+^{1/2} \\ &= K\int dx({\rm c}_{\rm TF}^3(3/\pi)^2|x|^{-4} - \alpha K^{-1})_+^{1/2} = {\rm const}\,K^{5/4}\alpha^{-1/4}\end{aligned}$$

by scaling the last integral. ■

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REFERENCES

[1] Bach, V.: Error bound for the Hartree-Fock Energy of Atoms and Molecules. *Commun. Math. Phys.* **147**, 527–548 (1992)

[2] Bach, V.: Accuracy of Mean Field Approximations for Atoms and Molecules. To appear in *Commun. Math. Phys.*

[3] Bach, V., Lewis, R., Lieb, E.H., Siedentop, H.: On the number of Bound states of a (boltzonic and) bosonic N-particle Coulomb system. To appear in *Mathematische Zeitschrift*

[4] Conlon, J.G.: The ground state energy of a Bose gas with Coulomb interaction I. *Commun. Math. Phys.* **100**, 355–397 (1985)

[5] Conlon, J.G.: The ground state energy of a Bose gas with Coulomb interaction II. *Commun. Math. Phys.* **108**, 363–374 (1987)

[6] Conlon, J.G., Lieb, E.H., Yau, H.-T.: The $N^{7/5}$ law for for charged bosons. *Commun. Math. Phys.* **116**, 417–448 (1988)

[7] Dirac, P.A.M.: Note on exchange phenomena in the Thomas-Fermi atom. *Proc. Cambridge Phil. Soc.* **26**, 376–385 (1931)

[8] Fefferman, C.L., de la Llave, R.: Relativistic stability of matter-I. *Revista Matematica Iberoamericana* **2**, 119–161 (1986)

[9] Fefferman, C.L., Seco, L.: The ground-state energy of a large atom. *Bull. A.M.S.* **23**, 525–530 (1990)

[10] Foldy, L.L.: Charged Boson Gas. *Phys. Rev. Lett.* **124**, 649–651 (1961).

[11] Gell-Mann, M., Brueckner, K.A.: Correlation energy of an electron gas at high density. *Phys. Rev.* **106**, 364–368 (1957)

[12] Ivrii, V.J., Sigal, I.M.: Asymptotics of the ground state energies of large Coulomb systems. Preprint.

[13] Lieb, E.H.: Thomas-Fermi theory and related theories of atoms and molecules. *Rev. Mod. Phys.* **53**, 603–641 (1981)

[14] Lieb, E.H.: Variational principle for many-fermion systems. *Phys. Rev. Lett.* **46**, 457–459 (1981); Errata ibid. **47**, 69 (1981)

[15] Lieb, E.H., Narnhofer, H.: The thermodynamic limit for jellium. *J. Stat. Phys.* **12**, 291–310 (1975); Errata ibid. **14**, 465 (1976)

[16] Lieb, E.H., Simon, B.: The Thomas-Fermi theory of atoms, molecules, and solids. *Adv. Math.* **23**, 22–116 (1977)

[17] Lieb, E.H., Thirring, W.: Bound for the kinetic energy of fermions which proves the stability of matter. *Phys. Rev. Lett.* **35**, 687–689 (1975); Errata ibid. **35**, 1116 (1975)

[18] Schwinger, J.: Thomas-Fermi model: The second correction. *Phys. Rev. A* **24**, 2353–2361 (1981)

[19] Stein, E.M., Weiss, G.: Introduction to Fourier analysis on Euclidean spaces. Princeton University Press, 2nd edition (1971)

[20] Thirring, W.: A lower bound with the best possible constant for Coulomb Hamiltonians. *Commun. Math. Phys.* **79**, 1–7 (1981)