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Müller Density-Matrix-Functional Theory: Existence of Solutions and their Properties

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MÜLLER DENSITY-MATRIX-FUNCTIONAL THEORY: EXISTENCE OF SOLUTIONS AND THEIR PROPERTIES

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Abstract. This report is mainly concerned about one of density-matrix-functionals, namely Müller functional and the existence of its minimizer. This functional is similar to the Hartree-Fock functional, but with a modified exchange term in which the square of the density matrix $\gamma(\mathbf{x}, \mathbf{x}')$ is replaced by its square root operator $\gamma^{1/2}(\mathbf{x}, \mathbf{x}')$. We show that minimizers exist for Müller functional and furthermore, all minimizers have unique trace if $N \leq Z$. Moreover, combing with the convexity of this functional with respect to γ we show that this functional is convex with respect to the density $\rho(\mathbf{r})$ and the energy minimizing $\gamma's$ have unique densities $\rho(\mathbf{r})$ as well.

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1. Introduction

1.1. **Density functional theory.** In Quantum mechanics, the time-independent state of a particle is described by a complex-valued function of position, namely wave function $\psi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^{\mathbf{3}}$. The space of all possible states of the particle at a given time is called the state space. For us, the state space of a particle will usually be the normalized square-integrable functions:

$$\{\psi : \mathbb{R}^3 \to \mathbb{C}; \psi \in L^2(\mathbb{R}^3), \int_{\mathbb{R}^3} |\psi(\mathbf{x})|^2 \mathrm{d}\mathbf{x} = 1\}.$$

It is a Hilbert space with an inner product given by

$$\langle \psi, \varphi \rangle = \int \overline{\psi} \varphi \mathrm{d}\mathbf{x}, \quad \psi, \varphi \in \mathrm{L}^2(\mathbb{R}^3)$$

The classical electron structure methods, for example, Hartree-Fock method, are based on these electronic wave function. Observables are quantities that can be experimentally measured in a given physical framework. Mathematically speaking, an observable is a self-adjoint operator on the state space $L^2(\mathbb{R}^3)$. In this paper, for example, the Hamiltonian operator: $H = -\frac{\hbar^2}{2m}\nabla^2 + V$. For a N-electron system, therefore, an observable will depend on 3N variables, since every electron has 3 spacial variables, and this may really lead us into thouble, even in such a centrary that the computational power is fast developed. For example, the electron wave function of the nitrogen atom, having 7 electrons, depends on 21 spatial variables. If we create a rough table of the electronic wave function of this system at 10 different positions in each variable, this amounts to 10^{21} double precision entries. Storing it on DVDs the stack of discs would easily reach the moon (See [14]). Density Functional Theory aims to replace the wave function by electronic densities, for instance, express the energy of a quantum mechanical state in terms of its one-particle density $\rho(\mathbf{r})$, where

$$\rho(\mathbf{r}) = N \sum_{\sigma_1,\cdots,\sigma_N} \int \psi^2(\mathbf{x}, \mathbf{x}_2, \cdots, \mathbf{x}_N) \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_\mathrm{N} \tag{1.1}$$

and then minimize the resulting functional with respect to $\rho(\mathbf{r})$, thereby we can calculate the ground state energy of the system. Its idea can go back to L. H. Thomas and E. Fermi in 1926 that a large atom, with many electrons, can be approximately modeled by a simple nonlinear problem for a 'charge density' $\rho(\mathbf{x})$. The exploration of its mathematical foundation can be traced to Hohenberg-Kohn theorem([15]). However, Hohenberg and Kohn proved the remarkable theorem [15, Theorem 1] which states that the non-degenerate ground-state wave function of a many-particle system is a unique functional of the particle density and that leads to the existence of a universal energy functional of the external potential and particle density, but the proof was for the case of a local external potential. Also, the external potential energy can easily be expressed in terms of the one-particle density, whereas it is unknown how to express the kinetic energy and the interaction energy in terms of $\rho(\mathbf{x})$. Nevertheless, all expectations of one-particle operators can be expressed in term of the one-particle density matrix. So going from density-functional theory to density-matrix-functional theory appears to be reasonable, and in fact, it does work and the new model was established by Gilbert [9].(See also [19])

The most difficult part of the density-functional to estimate is the exchange-correlation energy (exchange energy for short), and it is this energy which concern us here. And recently, it has been the tendency to replace the energy as a functional of $\rho(\mathbf{x})$ by a functional of the one-body density matrix $\gamma(\mathbf{x},\mathbf{x}')$. In this case it is hoped to have more flexibility and achieve more accurate answers.

1.2. **Physical explanation.** Fermions have spin and we write a particle's coordinates as $\mathbf{x} = (\mathbf{r}, \sigma)$ for a pair consisting of a vector $\mathbf{r}$ in space and an integer σ taking values from 1 to q. Here q is the number of spin states for the particles which in the physical case of electrons is equal to 2. Moreover, we write for any function f depending on space and spin variables

$$\int f(\mathbf{x})\mathrm{d}\mathbf{x} = \sum_{\sigma=1}^{q} \int_{\mathbb{R}^3} f(\mathbf{r},\sigma)\mathrm{d}\mathbf{r}, \tag{1.2}$$

which means that $\int \mathrm{d}\mathbf{x}$ indicates integration over the whole space and summation over all spin indices. This allows us to take the density matrix γ as an operator on the Hilbert space of spinors ψ for which $\int |\psi(\mathbf{x})|^2\mathrm{d}\mathbf{x} = 1$ with integral kernel $\gamma(\mathbf{x},\mathbf{x}')$. Consider a system with K nuclei and N electrons, the Schrödinger Hamiltonian we will consider is

$$H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m}\nabla_i^2 - e^2 V_c(\mathbf{r}_i) \right) + e^2 R \tag{1.3}$$

where

$$V_c(\mathbf{r}) = \sum_{j=1}^{K} \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} \tag{1.4}$$

is the Coulomb potential and

$$R = \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1.5}$$

is the electron-electron repulsion. The j^{th} nucleus has charge $+Z_j e > 0$ and is located at some fixed point $\mathbf{R}_j \in \mathbb{R}^3$. Let $Z = \sum_{j=1}^{K} Z_j$ be the total nuclear charge. Since through this paper we will consider the model with all the nuclei fixed, we do not take into account the nucleus-nucleus repulsion $e^2 U$, where

$$U = \sum_{1 \le i < j \le N} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}. \tag{1.6}$$

What will be discussed is the one of three density-matrix-functionals, namely Müller model, the other two, better known models, are Hartree-Fock model and Thomas-Fermi model. The aim of this report which is mainly following the work of R. L. Frank, E. H. Lieb, R. Seiringer and H. Siedentop [7] in 2007 is to present a thorough understanding on the Müller energy functional theory which was elaborately discussed by R. L. Frank et al. As we will see, the energy functional in Müller theory is quite similar to the Hartree-Fock functional, but with a modified exchange energy. Thus next we introduce briefly the best known Hartree-Fock functional.

1.3. **Hartree-Fock Model.** The Hartree-Fock functional is

$$\mathcal{E}^{HF}(\gamma) = \frac{\hbar^2}{2m}\,\mathrm{tr}\,(-\nabla^2\gamma) - e^2\int_{\mathbb{R}^3} V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + e^2 D(\rho_\gamma,\rho_\gamma) - e^2 X(\gamma). \tag{1.7}$$

where

$$\rho_\gamma(\mathbf{r}) = \sum_{\sigma=1}^{q}\gamma(\mathbf{x},\mathbf{x}) = \sum_{\sigma=1}^{q}\gamma(\mathbf{r},\sigma;\mathbf{r},\sigma) \tag{1.8}$$

is the particle density,

$$D(\rho,\mu) = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\mu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{1.9}$$

is the repulsion among electrons and

$$X(\gamma) = \frac{1}{2}\iint \frac{|\gamma(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \tag{1.10}$$

is the exchange energy.

It is well known that the functional $\mathcal{E}^{HF}$ is the expectation value of H in a determinantal wavefunction Ψ made of orthonormal functions ϕ_i, where

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N) = (N!)^{-1/2}\det\phi_i(\mathbf{x}_j)|_{i,j=1}^{N}, \tag{1.11}$$

in this case

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_{i=1}^{N}\phi_i(\mathbf{x})\phi_i(\mathbf{x}'). \tag{1.12}$$

We refer people interested in the derivation of these forms above to [26] and [5] for details. We want to mention here that any one-body density matrix γ for fermions always has two properties:

a) γ as an operator is self-adjoint, i.e.,

$$\gamma(\mathbf{x}, \mathbf{x}') = \gamma(\mathbf{x}', \mathbf{x})^*; \tag{1.13}$$

b) It is necessary and sufficient to ensure that it comes from a normalized N-body state satisfying the Pauli exclusion principle:

$$0 \leq \gamma \leq 1 \text{ as an operator and } \quad \mathrm{tr}\ \gamma = \mathrm{N} \tag{1.14}$$

where tr denotes the trace$= \int \gamma(\mathbf{x}, \mathbf{x})\mathrm{d}\mathbf{x}$ =sum of the eigenvalues of γ.

Recalling the definition of the integral given in (1.2), a consequence of (1.14) is that the spin-summed density matrix

$$(\mathrm{tr}_{\sigma}\,\gamma)(\mathbf{r}, \mathbf{r}') = \sum_{\sigma} \gamma(\mathbf{r}, \sigma; \mathbf{r}', \sigma), \tag{1.15}$$

which satisfies

$$0 \leq \mathrm{tr}_{\sigma}\,\gamma \leq q \text{ as an operator and } \quad \mathrm{tr}\,(\mathrm{tr}_{\sigma}\,\gamma) = \mathrm{N} \tag{1.16}$$

when γ acts on functions of space alone.

We define the HF energy (for all $N \geq 0$) by

$$E^{HF}(N) = \inf_{\gamma}\{\mathcal{E}^{HF}(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma = N\} \tag{1.17}$$

We choose infimum in (1.17) instead of minimum since perhaps there is no actual minimizer for Hartree-Fock functional, for instance, the minimizer does not exist in the case of $N >> Z = \Sigma_{i=1}^{K} Z_i$, but it does really exist when $N < Z + 1$. E. H. Lieb showed in [23] that $E^{HF}(N)$ is the infimum over all γ's of the determinantal form (1.12). Therefore, $E^{HF}(N) \geq E_0(N)$, where $E_0(N)$ is the true ground state energy of the Hamiltonian (1.3).

Whereas the HF density-matrix-functional theory provides an upper bound to E_0, but it still has some disadvantage and inconsistency theoretically ([7]):

a) The energy minimizer γ^{HF}, if it exists, may not be unique.

Remark 1.1. This assertion shall not be completely correct any longer to this very day. Since Dr. Fabian Clemens Hantsch had shown in his doctoral thesis ([11]) in 2012 that the minimizer of H-F functional is unique, if the number of electrons satisfies a certain closed shell condition and the nuclear charge is large enough.

b) The quantity that replaces the two particle density $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ does not satisfy the correct integral condition.

In the HF theory the electron Coulomb repulsion is modeled by $D(\rho_\gamma, \rho_\gamma) - X(\gamma)$. This energy really should be $\iint \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$, where $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ is the two-particle density,

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{2} \sum_{\sigma_1,\cdots,\sigma_N} \int \psi^2(\mathbf{x},\mathbf{x}',\mathbf{x}_3,\cdots,\mathbf{x}_N)\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_\mathrm{N} \tag{1.18}$$

which represents the probability to find one particle with arbitrary spin at position $\mathbf{r}$ and simultaneously a second particle with arbitrary spin at position $\mathbf{r}'$. By direct calculation, one can conclude the integral condition between one-particle density (1.1) and two-particle density (1.18), that is

$$\begin{aligned}\int \rho^{(2)}(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' &= \frac{N(N-1)}{2} \sum_{\sigma_1,\cdots,\sigma_N} \int \psi^2(\mathbf{x},\mathbf{x}',\mathbf{x}_3,\cdots,\mathbf{x}_N)\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_\mathrm{N}\mathrm{d}\mathbf{r}' \\ &= \frac{(N-1)}{2}N \sum_{\sigma_1,\cdots,\sigma_N} \int \psi^2(\mathbf{x},\mathbf{x}',\mathbf{x}_3,\cdots,\mathbf{x}_N)\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_\mathrm{N} \\ &= \frac{(N-1)}{2}\rho(\mathbf{r}). \end{aligned} \tag{1.19}$$

In HF case, we replace $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ by

$$G^{(2)}(\mathbf{r},\mathbf{r}') = \frac{1}{2}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}') - \frac{1}{2}\sum_{\sigma,\sigma=1}^{q} |\gamma(\mathbf{x},\mathbf{x}')|^2. \tag{1.20}$$

If this $G^{(2)}(\mathbf{r},\mathbf{r}')$ is the two-body density of any state, $G^{(2)}(\mathbf{r},\mathbf{r}')$ is supposed to satisfy (1.19), namely, $\int G^{(2)}(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' = \frac{\mathrm{N}-1}{2}\rho(\mathbf{r})$. In fact, this equality fails unless the state is a HF state since $\iint G^{(2)}(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \geq \frac{\mathrm{N}(\mathrm{N}-1)}{2}$ and the equality only holds for the HF state.

1.4. **Müller density-matrix-functional theory.** As we have mentioned before, we obtain Müller density-matrix-functional via replacing the operator γ in $X(\gamma)$ by $\gamma^{1/2}$. This square root operator is well defined since γ is self-adjoint (1.13) and positive (1.14),see [18]. And the Müller functional and the Müller energy become

$$\mathcal{E}^M(\gamma) = \frac{\hbar^2}{2m}\,\mathrm{tr}\,(-\nabla^2\gamma) - e^2\int_{\mathbb{R}^3} V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + e^2 D(\rho_\gamma,\rho_\gamma) - e^2 X(\gamma^{1/2}), \tag{1.21}$$

and

$$E^M(N) = \inf_\gamma\{\mathcal{E}^M(\gamma) : 0 \le \gamma \le 1, \mathrm{tr}\ \gamma = N\} \tag{1.22}$$

For the density matrix operator, we have

$$\gamma(\mathbf{x},\mathbf{x}') = \int \gamma^{1/2}(\mathbf{x},\mathbf{x}'')\gamma^{1/2}(\mathbf{x}'',\mathbf{x}')\mathrm{d}\mathbf{x}'', \tag{1.23}$$

and in terms of spectral representations, with eigenvalues λ_i and orthonormal eigenfunctions ϕ_i,

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_{i=1}^{\infty} \lambda_i \phi_i(\mathbf{x})\phi_i(\mathbf{x}')^* \tag{1.24}$$

$$\gamma^{1/2}(\mathbf{x},\mathbf{x}') = \sum_{i=1}^{\infty} \lambda_i^{1/2} \phi_i(\mathbf{x})\phi_i(\mathbf{x}')^*. \tag{1.25}$$

Note that in the spectral representations, we sum from $i = 1$ to ∞, we shall prove that γ has infinitely many positive eigenvalues. This feature holds for the whole Schrödinger theory (See [8] and [20]). But the problem that how many orbitals are contained in a minimizing γ is still open. As a comparison, we have known that there are only N orbitals that are contained in a minimizing γ in HF theory.

From now on we will use atomic units, i.e., $\hbar = m = e = 1$. Then the Müller functional becomes

$$\mathcal{E}^M(\gamma) = \mathrm{tr}\,(-\nabla^2\gamma) - \int_{\mathbb{R}^3} V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + D(\rho_\gamma, \rho_\gamma) - X(\gamma^{1/2}) \quad (1.26)$$

and we define the relaxed problem as

$$E^M_{\leq}(N) = \inf_\gamma\{\mathcal{E}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\} \quad (1.27)$$

Müller's functional (1.26) has several advantages ([7]):

a) The quantity that effectively replaces $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ in the functional is now

$$\frac{1}{2}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}') - \frac{1}{2}\sum_{\sigma,\sigma=1}^{q} |\gamma^{1/2}(\mathbf{x}, \mathbf{x}')|^2, \quad (1.28)$$

and this satisfies the correct integral condition (1.19), namely,

$$\frac{1}{2}\int \left[\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}') - \sum_{\sigma,\sigma=1}^{q} |\gamma^{1/2}(\mathbf{x}, \mathbf{x}')|^2\right]\mathrm{d}\mathbf{r}' = \frac{\mathrm{N}-1}{2}\rho_\gamma(\mathbf{r}). \quad (1.29)$$

$\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}') - \sum_{\sigma,\sigma=1}^{q} |\gamma^{1/2}(\mathbf{x}, \mathbf{x}')|^2$, however, is not necessarily positive as a function of $\mathbf{r}, \mathbf{r}'$, whereas the HF choice $\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}') - \sum_{\sigma,\sigma=1}^{q} |\gamma(\mathbf{x}, \mathbf{x}')|^2 > 0$ which is true for any positive semi-definite operator (See [16]).

b) A special choice of γ is a HF type of γ, namely one in which all the eigenvalues are 0 or 1. In this case it follows from (1.24) and (1.25) that $\gamma^{1/2} = \gamma$ and the value of the Müller energy equals the HF energy. Thus, the Müller functional is a generalization of the HF functional , and its energy satisfies $E^M(N) \leq E^{HF}(N)$.

1.5. **Convexity.** Dr. R. L. Frank et al. mentioned in [7] as a surprising fact that $\mathcal{E}^M$ is a convex functional of γ, which means that for any $0 < \mu < 1$ and density matrices γ_1, γ_2,

$$\mathcal{E}^M(\mu\gamma_1 + (1-\mu)\gamma_2) \leq \mu\mathcal{E}^M(\gamma_1) + (1-\mu)\mathcal{E}^M(\gamma_2). \tag{1.30}$$

To prove this convexity, the key step is to prove the concavity of the functional $X(\gamma^{1/2})$ ([7]). Following this idea, we shall prove this fact in Subsection 9.3. This convexity will lead to several important properties. One is the convexity of the energies $E^M(N)$ with respect to N (see Proposition 7.2), as it is in Thomas-Fermi theory. As for Thomas-Fermi case, we refer readers to check papers [21] and [23]. Further, we shall prove that the electron density $\rho_\gamma(\mathbf{r})$ of the minimizer, if it exists, is the same for all minimizers with the same N by proving the strictly convexity of $\mathcal{E}^M$ with respect to ρ, see Subsection 9.4.

1.6. **The Müller variation equations.** If the Müller functional has a minimizing γ with $\operatorname{tr}\gamma = N$ then this γ should satisfy an Euler equation, but whether a γ that satisfies the Euler equation is necessarily a minimizer?

In deed, a minimizer does exist when $N \leq Z$ as we shall show in Theorem 3.4, but it is not trivial to write down an equation satisfied by a minimizing γ. Now we are trying to find an equation defining a minimizer of (1.26).

Suppose that γ satisfies $\operatorname{tr}\gamma = N$ and meanwhile minimizes $\mathcal{E}^M(\gamma)$, i.e., $\mathcal{E}^M(\gamma) = E^M(N)$. Then by the definition of the minimizer we have

$$\mathcal{E}^M((1-s)\gamma + s\gamma') \geq \mathcal{E}^M(\gamma) \tag{1.31}$$

for any admissible γ' with tr $\gamma' = N$ and all $0 \leq s \leq 1$. Conversely, if tr $\gamma = N$ and if (1.31) is true for all possible γ' and for some $0 < s \leq 1$ (not necessarily for all $s \in [0,1]$ and s could depend on γ') then γ is a minimizer. In other words, to identify the condition that a minimizer γ satisfies, it suffices to require that for all such γ',

$$\frac{\mathrm{d}}{\mathrm{ds}}\mathcal{E}^M((1-s)\gamma + s\gamma')\bigg|_{s=0} = \lim_{s\to 0}\frac{\mathcal{E}^M((1-s)\gamma + s\gamma') - \mathcal{E}^M(\gamma)}{s} \geq 0. \tag{1.32}$$

Note that the convexity of $\mathcal{E}^M$ with respect to γ (1.30) gives

$$\mathcal{E}^M((1-s)\gamma + s\gamma') \leq (1-s)\mathcal{E}^M(\gamma) + s\mathcal{E}^M(\gamma'). \tag{1.33}$$

Hence from (1.31), (1.32) and (1.33) we conclude that $\mathcal{E}^M(\gamma) \leq \mathcal{E}^M(\gamma')$.

1.7. **Energy associated to the system of no nuclei.** If there are no nuclei at all (Z=0), and we try to minimize $\mathcal{E}^M(\gamma)$ with tr $\gamma = N$, we shall show that there will be no energy minimizing γ (See Proposition 4.1). We can surely find a minimizing sequence $\gamma_j, j = 0, 1, \cdots$ such that $\mathcal{E}^M(\gamma_j) \to E^M(N)$ as $n \to \infty$, such a sequence will tend to "spread out" and get smaller and smaller as it spreads ([7]). But we can prove exactly that $E^M(N)$ is given by $E^M(N) = -N/8$ when all

$Z_j = 0$ (See Proposition 7.1). This situation is reminiscent of Thomas-Fermi-Dirac theory where, in the absence of nuclei, the energy equals $-(constant)N$ (See [23]). This negative energy comes from balancing the kinetic energy against the negative exchange. In such a case it is convenient to add $+(constant)\,\mathrm{tr}\,\gamma$ to $\mathcal{E}^M(\gamma)$ in order that $E^M(N) \equiv 0$ for a system with no nuclei.

Another explanation for this case, given by R. L. Frank et al., is that the energy, -N/8, is the self-energy of a N-particle system in this theory. It has no physical or chemical meaning but we have to pay attention to it. It is the quantity

$$\widehat{E}^M(N) = E^M(N) + \frac{N}{8} \tag{1.34}$$

that might properly be regarded as the energy of N electrons in the presence of the nuclei, in fact, $-\widehat{E}^M(N)$ is the physical binding energy. On the other hand, if we are interested in the binding energy with fixed N, for example, the binding energy fo two atoms to form a molecule, then it is safe to use the $\widehat{E}^M(N)$ instead of $E^M(N)$.

The idea is to ensure that the ground state energy of free electrons is zero. This can be compared with the formulation in [10] in which the "self-energy" corrections obtained by omitting certain diagonal terms in the energy, and the energy is written in terms of the orbitals of γ. This consideration allows us to consider the functional

$$\widehat{\mathcal{E}}^M(\gamma) = \mathcal{E}^M(\gamma) + \frac{1}{8}\,\mathrm{tr}\,\gamma \tag{1.35}$$

and its corresponding infimum $\widehat{E}^M(N)$

$$\widehat{E}^M(\gamma) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma = N\}. \tag{1.36}$$

Similarly, we define a relaxed problem for the new functional as

$$\widehat{E}^M_{\leq}(\gamma) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}. \tag{1.37}$$

Note that $\widehat{\mathcal{E}}^M(\gamma)$ is a convex functional of γ due to the convexity of $\mathcal{E}^M(\gamma)$ (See Subsection 9.3) and the linearity of the new term $\frac{1}{8}\,\mathrm{tr}\ \gamma$. Similarly, $\widehat{E}^M(N)$ is a convex function of N. The main problem that has been addressed and solved in [7] is whether ot not there is a minimizer γ for (1.36). The way to solve this problem, as E. H. Lieb and B. Simon did for Thomas-Fermi model in [21], is to consider the relaxed problem (1.37). The equivalence of these two energy $\widehat{E}^M(\gamma)$ and $\widehat{E}^M_{\leq}(\gamma)$ for all N will be shown in the Proposition 7.1.

2. Preliminaries

Lemma 2.1. *Let $l \in \mathbb{R}$ and*

$$\chi_{B(\mathbf{z},l)}(\mathbf{r}) = \begin{cases} 1, & |\mathbf{r}-\mathbf{z}| < l, \\ 0, & |\mathbf{r}-\mathbf{z}| \geq l. \end{cases}$$

Then $|\mathbf{r}-\mathbf{r}'|^{-1}$ can be written as

$$|\mathbf{r}-\mathbf{r}'|^{-1} = \frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5}.$$

(This expression was proposed in [6], here I specify the elementary proof.)

Proof. Let's consider first for a fixed l the integral

$$\int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z}.$$

Initiating a spherical polar co-ordinates systems (l, θ, φ), let $t = \frac{|\mathbf{r}-\mathbf{r}'|}{2}$. In fact, the integral above is the volume of the intersection of two $l-$radius balls that centered at $\mathbf{r}$ and $\mathbf{r}'$. Thus

$$\begin{aligned} V &:= \int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z} \\ &= 2\int_t^l \pi(l^2 - x^2)\mathrm{d}x \\ &= \frac{4}{3}\pi l^3 + \frac{2}{3}\pi t^3 - 2\pi r^2 t. \end{aligned}$$

Noting that $l = t/\cos\varphi (t = l\cos\varphi)$, $\mathrm{d}l = t\mathrm{d}(\sec\varphi) = t\sec\varphi\tan\varphi\mathrm{d}\varphi$. Therefore,

$$\begin{aligned}
&\frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5} \\
= \ &\frac{1}{\pi}\int_0^\infty \frac{\frac{4}{3}\pi l^3 + \frac{2}{3}\pi l^3(\cos\varphi)^3 - 2\pi l^2 l\cos\varphi}{l^5}\mathrm{d}l \\
= \ &\int_0^{\pi/2} \frac{\left(\frac{4}{3}(\cos\varphi)^2 + \frac{2}{3}(\cos\varphi)^5 - 2(\cos\varphi)^3\right)\sec\varphi\tan\varphi}{t}\mathrm{d}\varphi \\
= \ &\frac{1}{t}\int_0^{\pi/2}\left(\frac{4}{3}\cos\varphi\tan\varphi + \frac{2}{3}(\cos\varphi)^4\tan\varphi - 2(\cos\varphi)^2\tan\varphi\right)\mathrm{d}\varphi \\
= \ &\frac{1}{2t},
\end{aligned}$$

which gives $\frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5} = |\mathbf{r}-\mathbf{r}'|^{-1}$. □

Next we deal with the monotonicity of the square root operator. We will consider for a general case, namely

$$A^\mu \le B^\mu,\ 0 \le \mu \le \mathbf{1} \tag{2.1}$$

provided that A and B are semi-positive definite operators and B is bounded. This inequality (2.1) is one of several useful inequalities for linear operators in Hilbert space that were deduced by E. Heinz in 1951 ([13]). The proof we give here is due to T. Kato ([17]).

Lemma 2.2. *Let A and B be self-adjoint operators and let $A \ge 0$, $B \ge 0$, B is bounded. If $A \le B$, then $A^\mu \le B^\mu$ for $0 \le \mu \le \mathbf{1}$.*

Proof. Firstly, we assume that B has a positive lower bound ι. Suppose now that the Lemma is already proved for $\mu = \alpha$ and $\mu = \beta$, $0 \le \alpha < \beta$, namely,

$$A^{\alpha} \leq B^{\alpha}, \ A^{\beta} \leq B^{\beta}. \tag{2.2}$$

Let λ be any real number belonging to the spectrum of the bounded self-adjoint operator $H = B^{\alpha+\beta} - A^{\alpha+\beta}$. Then for every $\epsilon > 0$, there exists a $x_0 \in \mathcal{H}$, $\mathcal{H}$ is a Hilbert space, such that $\|x_0\| = 1$ and $\|(H - \lambda I)x_0\| < \epsilon$. Now set

$$y_0 = (H - \lambda I)x_0 = B^{\alpha+\beta}x_0 - A^{\alpha+\beta}x_0 - \lambda x_0$$

Then we have $\|y_0\| < \epsilon$ and

$$\langle y_0, B^{\beta-\alpha}x_0\rangle = \|B^{\beta}x_0\|^2 - \langle A^{\beta}x_0, A^{\alpha}B^{\beta-\alpha}x_0\rangle - \lambda\langle x_0, B^{\beta-\alpha}x_0\rangle. \tag{2.3}$$

By applying Schwarz inequality several times to the equality (2.3) and with the assumption (2.2) we have

$$\|B^{\beta}x_0\|^2 - \lambda\langle x_0, B^{\beta-\alpha}x_0\rangle \leq \epsilon\|B^{\beta-\alpha}x_0\| + \|B^{\beta}x_0\|^2, \tag{2.4}$$

hence we have

$$\begin{aligned} \lambda &> \frac{-\epsilon\|B^{\beta-\alpha}x_0\|}{\langle x_0, B^{\beta-\alpha}x_0\rangle} \\ &\geq \frac{-\epsilon\|B^{\beta-\alpha}x_0\|}{\iota^{\beta-\alpha}\|x_0\|} \\ &\geq \frac{-\epsilon\|B\|^{\beta-\alpha}}{\iota^{\beta-\alpha}}. \end{aligned} \tag{2.5}$$

Since (2.5) holds for every $\epsilon > 0$, we must have $\lambda \geq 0$—-that is , the spectrum of H contains no negative numbers. This implies $H \geq 0$. In deed, this can indicates that $A^{\frac{\alpha+\beta}{2}} \leq B^{\frac{\alpha+\beta}{2}}$ as well. On the one hand,

$$\langle x_0, (B^{\alpha+\beta} - A^{\alpha+\beta})x_0\rangle = \langle x_0, Hx_0\rangle \geq 0. \tag{2.6}$$

On the other hand,

$$\begin{aligned} \langle x_0, (B^{\alpha+\beta} - A^{\alpha+\beta})x_0\rangle &= \langle x_0, B^{\alpha+\beta}x_0\rangle - \langle x_0, A^{\alpha+\beta}x_0\rangle \\ &= \langle B^{\frac{\alpha+\beta}{2}}x_0, B^{\frac{\alpha+\beta}{2}}x_0\rangle - \langle A^{\frac{\alpha+\beta}{2}}x_0, A^{\frac{\alpha+\beta}{2}}x_0\rangle \\ &= \|B^{\frac{\alpha+\beta}{2}}x_0\|^2 - \|A^{\frac{\alpha+\beta}{2}}x_0\|^2. \end{aligned} \tag{2.7}$$

Combining (2.6) and (2.7), one has

$$\|B^{\frac{\alpha+\beta}{2}}x_0\| \geq \|A^{\frac{\alpha+\beta}{2}}x_0\|,$$

i.e., $B^{\frac{\alpha+\beta}{2}} \geq A^{\frac{\alpha+\beta}{2}}$.

So far we have shown that the set Ω of real numbers μ for which the lemma holds contains $\frac{\alpha+\beta}{2}$ whenever it contains α, β such that $0 \leq \alpha < \beta$. Trivially Ω consists of 0 and 1, it follows that it contains all μ of the form $\mu = \frac{m}{2^n}$ for $n = 0, 1, 2, \cdots, m \leq 2^n$. Thus we have $\|A^\mu x_0\| \leq \|B^\mu x_0\|$ for a set of μ dense in the interval $0 \leq \mu \leq 1$. As $\|A^\mu x_0\|$ and $\|B^\mu x_0\|$ are continuous functions of μ, it follows that it holds for all μ of $0, 1, i.e.,$A$^\mu \leq B^\mu$ for $0 \leq \mu \leq 1$.

Next we prove the Lemm with the only assumption that B is bounded. For any $\epsilon > 0$, let $B_\epsilon = (B^2 + \epsilon^2 I)^{1/2}$. B_ϵ is bounded and has positive lower bound. Indeed,

$$\|B_\epsilon x_0\|^2 = \langle B_\epsilon x_0, B_\epsilon x_0\rangle = \|Bx_0\|^2 + \epsilon^2\|x_0\|^2$$

gives $\|B_\epsilon\| \geq \epsilon$. Also, from the equality above one has $A \leq B \leq B_\epsilon$. This is the case we have proved above. So we have $A^\mu \leq B_\epsilon^\mu$ for $0 \leq \mu \leq 1$, i.e., $\|A^\mu x_0\| \leq \|B_\epsilon^\mu x_0\|$. Let $\epsilon \to 0$, since $\|B_\epsilon^\mu x_0\|$ is continuous in ϵ, $\|A^\mu x_0\| \leq \|B^\mu x_0\|$. □

Remark 2.3. A special case of the Lemma above is that the square root function $f(t) = t^{1/2}$ is operator monotone for all positive definite operators. In fact, one can also reach this end by considering eigenvalues λ of the Hermitian $T - H$ (see [2]). Without loss of generality, let u be a unit vector that is an eigenvector with the eigenvalue λ of $T - H$. We just need show $\lambda > 0$. Note that $(T - H)u = \lambda u$ gives that $(T - \lambda I)u = Hu$, and then we have

$$\langle Tu, (T - \lambda I)u\rangle = \langle Tu, Hu\rangle. \tag{2.8}$$

For the LHS of (2.8),

$$\langle Tu, (T - \lambda I)u\rangle = \langle Tu, Tu\rangle - \lambda\langle Tu, u\rangle = \|Tu\|^2 - \lambda\langle Tu, u\rangle. \tag{2.9}$$

For the RHS of (2.8), by Schwarz Inequality,

$$\begin{aligned}
\langle Tu, Hu\rangle &\leq \|Tu\|\|Hu\| \\
&= \langle u, T^2u\rangle^{1/2}\langle u, H^2u\rangle^{1/2} \\
&< \langle u, T^2u\rangle^{1/2}\langle u, T^2u\rangle^{1/2} \\
&= \langle u, T^2u\rangle \\
&= \|Tu\|^2.
\end{aligned}$$

Hence, $\|Tu\|^2 - \lambda\langle Tu, u\rangle < \|Tu\|^2$, which gives that $\lambda\langle Tu, u\rangle > 0$. Since T is positive definite, we conclude that $\lambda > 0$.

3. Assumption and main theorems

Definition 3.1. Let $\mathcal{H}$ be a separable Hilbert space. The trace class $\mathfrak{S}^1$ is the set of $A \in \mathcal{L}(\mathcal{H})$ so that $\mathrm{tr}\,(|A|) < \infty$. We define a $\mathfrak{S}^1$-norm on $\mathfrak{S}^1$ by $\|A\|_1 = \mathrm{tr}\,(|A|)$.

Definition 3.2. Let $\mathcal{H}$ be a separable Hilbert space. For $1 \le p < \infty$, we denote the space of Schatten-Von Neumann operator of class p as

$$\mathfrak{S}^p = \{A \in \mathcal{L}(\mathcal{H}); |A|^p \in \mathfrak{S}^1\}$$

with norm $\|A\|_p = (\mathrm{tr}\,(|A|^p))^{1/p}$.

Especially when $p = 2$, we call $\mathfrak{S}^2$ Hilbert-Schmidt space, $A \in \mathfrak{S}^2$ is a Hilbert-Schmidt operator and

$$\|A\|_2 = (\mathrm{tr}\ |A|^2)^{1/2} = (\mathrm{tr}\ |A^*A|)^{1/2} < \infty.$$

Sometimes we also denote the norm $\|\cdot\|_2$ by $\|\cdot\|_{HS}$.

We always assume that $(-\nabla^2+1)^{1/2}\gamma^{1/2} \in \mathfrak{S}^2$, then $(-\nabla^2+1)\gamma \in \mathfrak{S}^1$, i.e.,

$$\begin{aligned}\mathrm{tr}\,((-\nabla^2+1)\gamma) &= \mathrm{tr}\,(\gamma^{1/2}(-\nabla^2+1)^{1/2}(-\nabla^2+1)^{1/2}\gamma^{1/2}) \\ &= \iint (|\nabla\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 + |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' < \infty\end{aligned}$$

As I have mentioned in the introduction, the main task that has been addressed is whether ot not there is a minimizer γ for (1.36). Our strategy is to consider the relaxed problem (1.37), inspired by what E.

H. Lieb and B. Simon did for Thomas-Fermi model in [21]. I reformulate two main theorems as below, which readers can definitely find in the work of R. L. Frank, E. H. Lieb, R. Seiringer and H. Siedentop [7] and their elegant proofs. The rest of this report will go through his proofs again, but with far more details.

Theorem 3.3. *For any $Z > 0$ and $N > 0$, one has $\widehat{E}^M_{\leq}(N) < 0$ and $\widehat{E}^M_{\leq}(N)$ attained its infimum. Here*

$$\widehat{E}^M_{\leq}(N) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}$$

Theorem 3.4. *Assume that $N \leq Z$. Then a minimizer of $\widehat{E}^M_{\leq}(N)$ has trace N.*

4. CASE Z=0

In this section we shall show the energy of free electrons $E^M(N)$ is not zero but is proportional to N. Precisely speaking, $E^M(N) = -N/8$ when there are no nuclei. This negative energy could be $-\infty$ if it were not controlled by the positive kinetic energy, which leads to a finite result. We recall that the Müller functional is

$$\mathcal{E}^M(\gamma) = \frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma) - \int V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + D(\rho_\gamma,\rho_\gamma) - X(\gamma^{\frac{1}{2}}). \quad (4.1)$$

Since $Z = \Sigma_j Z_j = 0$, it's obvious that

$$\int V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} = 0$$

when

$$V_c(\mathbf{r}) = \Sigma_{j=1}^K \frac{Z_j}{|\mathbf{r} - R_j|}.$$

We just need to consider the functional

$$\mathcal{E}^M(\gamma) = \frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma) + D(\rho_\gamma,\rho_\gamma) - X(\gamma^{\frac{1}{2}}).$$

Proposition 4.1. *If $Z = 0$,then for any $N > 0$,*

$$E^M(N) = E^M_{\leq}(N) = -N/8$$

and there is no minimizing γ.

Proof. Firstly, we use the lower semi-boundedness of the hydrogenic Hamiltonian

$$-\frac{1}{2}\nabla^2 - \frac{1}{2|\mathbf{r}-\mathbf{r}'|} \geq -\frac{1}{8}, \quad \forall \mathbf{r}' \in \mathbb{R}^3 \tag{4.2}$$

(See [24, 11.10]) to find the lower bound. Indeed, by the direct calculation, and together with the fact (9.1), we have

$$\begin{aligned}
\mathcal{E}^M(\gamma) &= \frac{1}{2}\operatorname{tr}(-\nabla^2\gamma) + D(\rho_\gamma,\rho_\gamma) - X(\gamma^{\frac{1}{2}}) \\
&\geq \frac{1}{2}\operatorname{tr}(-\nabla^2\gamma) - X(\gamma^{\frac{1}{2}}) \\
&= \frac{1}{2}\operatorname{tr}((-\nabla^2+1)\gamma) - \frac{1}{2}\operatorname{tr}\gamma - X(\gamma^{\frac{1}{2}}) \\
&= \frac{1}{2}\iint \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\big(|\nabla\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 + |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\big) - \frac{1}{2}\operatorname{tr}\gamma - X(\gamma^{\frac{1}{2}}) \\
&= \frac{1}{2}\iint \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\big(|\nabla\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\big) - \frac{1}{2}\iint \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \frac{1}{2}\iint \big(-\nabla^2\gamma(\mathbf{x},\mathbf{x}')\big)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' - \frac{1}{2}\iint \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \iint \Big(-\frac{1}{2}\nabla^2 - \frac{1}{2|\mathbf{r}-\mathbf{r}'|}\Big)|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\geq (-\frac{1}{8})\operatorname{tr}\gamma. \qquad (4.3)
\end{aligned}$$

This exactly gives the lower bound on $E^M(N)$ and $E^M_{\leq}(N)$.

To show the non-existence of a minimizer we denote by $g(\mathbf{r}-\mathbf{r}')$ the ground state of $-\nabla^2 - |\mathbf{r}-\mathbf{r}'|^{-1}$, such that

$$\big(-\nabla^2 - |\mathbf{r}-\mathbf{r}'|^{-1}\big)g(\mathbf{r}-\mathbf{r}') = E_0 g(\mathbf{r}-\mathbf{r}') \tag{4.4}$$

where

$$g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{r}'|} \tag{4.5}$$

and $E_0 = -\frac{1}{4}$.

It follows from the eigenvalue equation for g that the inequality $\leq$ in (4.2) is strict except for multiples of the function $g(\mathbf{r}-\mathbf{r}')$. Hence the above lower bound on $\mathcal{E}^M(\gamma)$ is strict unless $\gamma^{1/2}(\mathbf{x},\mathbf{x}') = c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')$. For any $\phi(\mathbf{r})$ and $\psi(\mathbf{r}) \in L^2(\mathbb{R}^3)$,

$$\begin{aligned}
\langle \phi(\mathbf{r}), c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}')\rangle &= \int \overline{\phi(\mathbf{r})}\Big(\int c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}')\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r} \\
&= \iint \overline{\phi(\mathbf{r})}c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}')\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r} \\
&= \int \overline{\int \phi(\mathbf{r})\overline{c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')}\mathrm{d}\mathbf{r}}\psi(\mathbf{r}')\mathrm{d}\mathbf{r}' \\
&= \langle \overline{c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')}\phi(\mathbf{r}), \psi(\mathbf{r}')\rangle \\
&= \langle \overline{c_{\sigma\sigma'}(\mathbf{r}')}g(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}), \psi(\mathbf{r}')\rangle
\end{aligned}$$

Because of the adjointness of $\gamma^{1/2}$, we requires

$$\overline{c_{\sigma\sigma'}(\mathbf{r}')}g(\mathbf{r}-\mathbf{r}') = c_{\sigma\sigma'}(\mathbf{r})g(\mathbf{r}-\mathbf{r}'),$$

Thus $c_{\sigma\sigma'}$ is a real constant.

Moreover, since $\gamma \in \mathfrak{G}^1$, i.e.,

$$\begin{aligned}
\infty > \operatorname{tr}\gamma &= \iint |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \Sigma_{\sigma,\sigma'} \iint |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \Sigma_{\sigma,\sigma'} \iint c^2_{\sigma\sigma'}g(\mathbf{r}-\mathbf{r}')^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \Sigma_{\sigma,\sigma'}c^2_{\sigma\sigma'} \iint \pi^{-1}e^{-2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'
\end{aligned}$$

Since the integral is divergent, the constant $c_{\sigma\sigma'}$ has to be 0. This, however, illustrates that there exists no minimizer.

Next we turn to the upper bound of the energy functional. We define a trial density matrix $\tilde{\gamma}$ by defining its square root:

$$\widetilde{\gamma}^{1/2}(\mathbf{x},\mathbf{x}') = \chi(\mathbf{r})^* g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}')q^{-1/2}\delta_{\sigma,\sigma'}. \tag{4.6}$$

Here $\chi(\mathbf{r})$ is a smooth function on $\mathbb{R}^3$ and $g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{r}'|}$ as defined in (4.5). Applying Lemma 9.2 to the $g(\mathbf{r}-\mathbf{r}')$ we can calculate the Fourier transform of g,

$$\begin{aligned}
\widehat{g}(\mathbf{p}) : &= \frac{1}{(2\pi)^{3/2}}\int_{\mathbb{R}^3} e^{-i\mathbf{p}\cdot\mathbf{x}} g(\mathbf{x})\mathrm{d}\mathbf{x} \\
&= \frac{1}{(2\pi)^{3/2}}\frac{1}{k}\int_0^\infty 4\pi x g(x)\sin(kx)\mathrm{d}x \\
&= \frac{2^{1/2}}{\pi k}\int_0^\infty xe^{-x}\sin(kx)\mathrm{d}x \\
&= \frac{2^{1/2}}{\pi k}\cdot\frac{2k}{(1+k^2)^2} \\
&= \frac{2^{3/2}}{\pi}\frac{1}{(1+k^2)^2},
\end{aligned}$$

which shows that the definition of $\widetilde{\gamma}^{1/2}$ given above does make sense, since the operator is non-negative. Noting that in view of the eigenvalue function of g, i.e.,

$$\big(-\nabla_{\mathbf{r}}^2 - |\mathbf{r}-\mathbf{r}'|^{-1}\big)g(\mathbf{r}-\mathbf{r}') = -\frac{1}{4}g(\mathbf{r}-\mathbf{r}')$$

so

$$-\nabla_{\mathbf{r}}^2 g(\mathbf{r}-\mathbf{r}') = |\mathbf{r}-\mathbf{r}'|^{-1} g(\mathbf{r}-\mathbf{r}') - \frac{1}{4} g(\mathbf{r}-\mathbf{r}').$$

Combining with the fact (see Lemma 9.4) that

$$\begin{aligned}
&\operatorname{tr}(-\nabla_{\mathbf{r}}^2 \gamma) \\
&= \iint \Big(|\chi(\mathbf{r})|^2 |\chi(\mathbf{r}')|^2 (-\nabla_{\mathbf{r}}^2 g(\mathbf{r}-\mathbf{r}')) g(\mathbf{r}-\mathbf{r}') - |\nabla \chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2 |\chi(\mathbf{r}')|^2 \Big) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',
\end{aligned}$$

we have

$$\operatorname{tr}(-\nabla_{\mathbf{r}}^2 \widetilde{\gamma}) = 2X(\widetilde{\gamma}^{1/2}) - \frac{1}{4} \operatorname{tr} \widetilde{\gamma} + \iint |\nabla \chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2 |\chi(\mathbf{r}')|^2 \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.$$

The upper bound will be easily found from this if we can find functions χ_L such that for $\widetilde{\gamma}_L \le 1$, as an operator, satisfying

$$\operatorname{tr} \widetilde{\gamma}_L \to N, \tag{4.7}$$

$$\iint |\nabla \chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2 |\chi_L(\mathbf{r}')|^2 \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \to 0 \tag{4.8}$$

and

$$D(\rho_{\widetilde{\gamma}_L}, \rho_{\widetilde{\gamma}_L}) \to 0 \tag{4.9}$$

as $L \to \infty$. Indeed, assuming momentarily that (4.7)-(4.9) hold, then we find that

$$\begin{aligned}
\operatorname{tr}(-\frac{1}{2}\nabla_{\mathbf{r}}^2 \widetilde{\gamma}_L) &= X(\widetilde{\gamma}_L^{1/2}) - \frac{1}{8} \operatorname{tr} \widetilde{\gamma}_L + \frac{1}{2} \iint |\nabla \chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2 |\chi_L(\mathbf{r}')|^2 \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&\to X(\widetilde{\gamma}_L^{1/2}) - \frac{1}{8} N, \ L \to \infty.
\end{aligned}$$

whence

$$\begin{aligned}\mathcal{E}^M(\widetilde{\gamma}_L) &= \frac{1}{2}\operatorname{tr}(-\nabla^2\widetilde{\gamma}_L) + D(\rho_{\widetilde{\gamma}_L},\rho_{\widetilde{\gamma}_L}) - X(\widetilde{\gamma}_L^{\frac{1}{2}}) \\ &\to X(\widetilde{\gamma}_L^{1/2}) - \frac{1}{8}N - X(\widetilde{\gamma}_L^{1/2}) = -\frac{1}{8}N,\ \textit{as}\ L\to\infty.\end{aligned}$$

Hence it suffices to prove the claims (4.7)-(4.9).

We shall take $\chi_L(\mathbf{r}) = L^{-3/4}\chi(\mathbf{r}/L)$ for a fixed smooth function $\chi \geq 0$ satisfying

$$\|\chi\|_4^4 = \int_{\mathbb{R}^3} |\chi(\mathbf{r})|^4 \mathrm{d}\mathbf{r} = N.$$

Indeed, $\|\chi_L\|_4^4 = \int_{\mathbb{R}^3} |L^{-3/4}\chi(\mathbf{r}/L)|^4\mathrm{d}\mathbf{r} = N$. Here we define an operator denoted by γ with its kernel $\gamma(\mathbf{r},\mathbf{r}')$. We note that for any L^2 function ψ,

$$\langle\psi(\mathbf{r}),\widetilde{\gamma}_L^{1/2}\psi(\mathbf{r}')\rangle \leq (2\pi)^{3/2}\|\widehat{g}\|_\infty\|\chi_L\|_\infty^2\|\psi\|_2^2.$$

Indeed,

$$\begin{aligned}
\langle\psi(\mathbf{r}),\widetilde{\gamma}_L^{1/2}\psi(\mathbf{r}')\rangle &= \int\psi(\mathbf{r})\Big(\int\widetilde{\gamma}_L^{1/2}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r}\\
&= \int\psi(\mathbf{r})\int\chi_L^*(\mathbf{r})g(\mathbf{r}-\mathbf{r}')\chi_L(\mathbf{r}')\psi(\mathbf{r}')\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}\\
&= \int\psi(\mathbf{r})\chi_L^*(\mathbf{r})\Big(\int g(\mathbf{r}-\mathbf{r}')\chi_L(\mathbf{r}')\psi(\mathbf{r}')\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r}\\
&= \int\widehat{\psi\chi_L^*}(\mathbf{p})\widehat{g*(\chi_L\psi)}(\mathbf{p})\mathrm{d}\mathbf{p}\quad (\textit{Plancherel Theorem})\\
&= (2\pi)^{3/2}\int\widehat{\psi\chi_L^*}(\mathbf{p})\widehat{g(\mathbf{p})}\widehat{(\chi_L\psi)}(\mathbf{p})\mathrm{d}\mathbf{p}\\
&= (2\pi)^{3/2}\int\widehat{g}(\mathbf{p})|\widehat{(\chi_L\psi)}(\mathbf{p})|^2\mathrm{d}\mathbf{p}\\
&\leq (2\pi)^{3/2}\|\widehat{g}\|_\infty\int|\widehat{(\chi_L\psi)}(\mathbf{p})|^2\mathrm{d}\mathbf{p}\\
&= (2\pi)^{3/2}\|\widehat{g}\|_\infty\int|\chi_L(\mathbf{r})\psi(\mathbf{r})|^2\mathrm{d}\mathbf{r}\quad (\textit{Plancherel Theorem})\\
&\leq (2\pi)^{3/2}\|\widehat{g}\|_\infty\|\chi_L\|_\infty^2\int|\psi(\mathbf{r})|^2\mathrm{d}\mathbf{r}\\
&= (2\pi)^{3/2}\|\widehat{g}\|_\infty\|\chi_L\|_\infty^2\|\psi\|_2^2,
\end{aligned}$$

which is less than or equal to $\|\psi\|_2^2$ for L large, since $\|\widehat{g}\|_\infty<\infty$ and $\|\chi_L\|_\infty\to 0$. This proves $\widetilde{\gamma}_L\leq 1$ provided L is large enough. To check $\iint|\nabla\chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\to 0$, we note that

$$\mathrm{tr}\ \widetilde{\gamma}_L=(2\pi)^{3/2}\int\widehat{g}^2(\mathbf{p})|\widehat{(\chi_L^2)}(\mathbf{p})|^2\mathrm{d}\mathbf{p},$$

Then since

$$\begin{aligned}
|\widehat{(\chi_L^2)}(\mathbf{p})|^2 &= |\int\chi_L^2(\mathbf{r})e^{-i\mathbf{r}\mathbf{p}}\mathrm{d}\mathbf{r}|^2\\
&= L^3|\widehat{\chi^2}(L\mathbf{p})|^2
\end{aligned}$$

and by the Lemma 9.5 we know that as $L \to \infty$

$$L^3|\widehat{\chi^2}(L\mathbf{p})|^2 \to N\delta(\mathbf{p}).$$

Besides, in the spirit of Lemma 9.2 , one can calculate

$$\widehat{g^2}(\mathbf{p}) = \frac{2^{5/2}}{\pi^{3/2}}\frac{1}{(4+|\mathbf{p}|^2)^2}$$

and $\|g\|_2 = 1$. Therefore,

$$\mathrm{tr}\ \widetilde{\gamma}_L \to (2\pi)^{3/2}\widehat{g^2}(0)N = N,$$

which proves (4.7). Next, (4.8) is a consequence of

$$\iint |\nabla\chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi_L(\mathbf{r}')|^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \le L^{-2}\|\chi\|_\infty^2\|\nabla\chi\|_2^2,$$

which follows from the estimate

$$\begin{aligned}
\iint |\nabla\chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi_L(\mathbf{r}')|^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' &= \int |\nabla\chi_L(\mathbf{r})|^2\Big(\int g(\mathbf{r}-\mathbf{r}')^2|\chi_L(\mathbf{r}')|^2\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r} \\
&\le \|\chi_L\|_\infty^2\int |\nabla\chi_L(\mathbf{r})|^2\Big(\int g(\mathbf{r}-\mathbf{r}')^2\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r} \\
&= \|\chi_L\|_\infty^2\|g\|_2^2\int |\nabla\chi_L(\mathbf{r})|^2\mathrm{d}\mathbf{r} \\
&= \|\chi_L\|_\infty^2\|\nabla\chi_L\|^2 \qquad (\|g\|_2^2 = 1) \\
&= L^{-2}\|\chi\|_\infty^2\|\nabla\chi\|_2^2.
\end{aligned}$$

where we used that $\|\chi_L\|_\infty^2 = L^{-3/2}\|\chi\|_\infty^2$ and $\|\nabla\chi_L\|_2^2 = L^{-1/2}\|\nabla\chi\|_2^2$.

To verify (4.9), we consider

$$\begin{aligned}
\rho_{\widetilde{\gamma}_L}(\mathbf{r}) &= \int |\chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2 |\chi_L(\mathbf{r}')|^2 \mathrm{d}\mathbf{r}' \\
&= |\chi_L(\mathbf{r})|^2 \int g(\mathbf{r}-\mathbf{r}')^2 |\chi_L(\mathbf{r}')|^2 \mathrm{d}\mathbf{r}' \\
&= L^{-3/2}|\chi(\mathbf{r}/L)|^2 \int g(\mathbf{r}-\mathbf{r}')^2 L^{-3/2}|\chi(\mathbf{r}'/L)|^2 \mathrm{d}\mathbf{r}' \qquad (\mathit{let}\ \mathbf{z} = r/L, \mathbf{z}' = \mathbf{r}'/L) \\
&= L^{-3}|\chi(\mathbf{z})|^2 \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 L^3 \mathrm{d}\mathbf{z}' \\
&= |\chi(\mathbf{z})|^2 \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 \mathrm{d}\mathbf{z}',
\end{aligned}$$

and therefore,

$$\begin{aligned}
D(\rho_{\widetilde{\gamma}_L}, \rho_{\widetilde{\gamma}_L}) &= \frac{1}{2}\iint \frac{\rho_{\widetilde{\gamma}_L}(\mathbf{r})\rho_{\widetilde{\gamma}_L}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \frac{1}{2}\iint \frac{|\chi(\mathbf{z})|^2 \int g(L(\mathbf{z}-\mathbf{z}'))^2|\chi(\mathbf{z}')|^2\mathrm{d}\mathbf{z}' |\chi(\mathbf{z}')|^2 \int g(L(\mathbf{z}-\mathbf{z}'))^2|\chi(\mathbf{z})|^2\mathrm{d}\mathbf{z}}{L|\mathbf{z}-\mathbf{z}'|} \\
&\quad L^6 \mathrm{d}\mathbf{z}\mathrm{d}\mathbf{z}' \\
&= \frac{1}{2L}\iint \frac{|\chi(\mathbf{z})|^2\varphi_L(\mathbf{z})\varphi_L(\mathbf{z}')|\chi(\mathbf{z}')|^2}{|\mathbf{z}-\mathbf{z}'|}\mathrm{d}\mathbf{z}\mathrm{d}\mathbf{z}',
\end{aligned}$$

where

$$\varphi_L(\mathbf{z}) = L^3 \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 \mathrm{d}\mathbf{z}'.$$

Again using the fact that $\|g\|_2 = 1$, one can see Lemma 9.5 that

$$\varphi_L(\mathbf{z}) \to \chi^2(\mathbf{z}) \tag{4.10}$$

as $L \to \infty$ with

$$L^3 g(L(\mathbf{z}-\mathbf{z}'))^2 \to \delta(\mathbf{z}-\mathbf{z}'). \tag{4.11}$$

In fact, let's denote the distribution of $f(\mathbf{x})$ on $\mathbb{R}^3$ by T_f such that

$$\langle T_f, \varphi(\mathbf{x})\rangle = \int_{\mathbb{R}^3} f(\mathbf{x})\varphi(\mathbf{x})\mathrm{d}\mathbf{x},$$

for any test function $\varphi(\mathbf{x})$. By the continuity of φ, we know that for an arbitrary small ε, there exists a $\delta > 0$, such that

$$|\varphi(\mathbf{z}') - \varphi(\mathbf{z})| < \varepsilon \textit{ whenever } |\mathbf{z}' - \mathbf{z}| < \delta.$$

And for the same ε there also exists an M such that

$$\int_{|\mathbf{x}|\geq M} g(\mathbf{x})^2\mathrm{d}\mathbf{x} < \varepsilon.$$

Then when $L > M/\delta$,

$$\begin{aligned}
&\left|\langle T_{L^3 g(L(\mathbf{z}-\mathbf{z}'))^2}, \varphi(\mathbf{z}')\rangle - \langle \delta(\mathbf{z}-\mathbf{z}'), \varphi(\mathbf{z}')\rangle\right| \\
= &\left|\int L^3 g(L(\mathbf{z}-\mathbf{z}'))^2\varphi(\mathbf{z}')\mathrm{d}\mathbf{z}' - \varphi(\mathbf{z})\right| \\
= &\left|\int g(L(\mathbf{z}-\mathbf{z}'))^2(\varphi(\mathbf{z}') - \varphi(\mathbf{z}))\mathrm{d}(L\mathbf{z}')\right| \\
\leq &\left|\int_{|\mathbf{z}-\mathbf{z}'|<\delta} g(L(\mathbf{z}-\mathbf{z}'))^2(\varphi(\mathbf{z}') - \varphi(\mathbf{z}))\mathrm{d}(L\mathbf{z}')\right| \\
&+\left|\int_{|\mathbf{z}-\mathbf{z}'|\geq\delta} g(L(\mathbf{z}-\mathbf{z}'))^2(\varphi(\mathbf{z}') - \varphi(\mathbf{z}))\mathrm{d}(L\mathbf{z}')\right| \\
< &\ 1\cdot\varepsilon + \varepsilon\cdot\max\{\varphi\}.
\end{aligned}$$

It follows from Lebesgue dominant convergence theorem that

$$D(\rho_{\tilde{\gamma}_L}, \rho_{\tilde{\gamma}_L}) = L^{-1}D(\chi^4, \chi^4) + o(L^{-1}). \tag{4.12}$$

Indeed, since $\|\chi\|_4^4 = N$, χ is square integrable, i.e., $\int |\chi(\mathbf{z})|^2 \mathrm{d}\mathbf{z} < \infty$, otherwise $|\chi(\mathbf{z})|^2$ must be unbounded on a subset of $\mathbb{R}^2$ with positive measure, which ruins the convergence of $|\chi(\mathbf{z})|^4$. So that for any L

$$
\begin{aligned}
\varphi_L(\mathbf{z}) &= L^3 \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 \mathrm{d}\mathbf{z}' \\
&= \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 \mathrm{d}(L\mathbf{z}') \\
&= \int g(L(\mathbf{z}-\mathbf{z}'))^2 |\chi(\mathbf{z}')|^2 \mathrm{d}(L\mathbf{z} - L\mathbf{z}') \\
&= \int g(\mathbf{u})^2 |\chi(\mathbf{z}-\mathbf{u}/L)|^2 \mathrm{d}\mathbf{u} \quad (\mathbf{u} = L\mathbf{z} - L\mathbf{z}') \\
&:= G(\mathbf{z}).
\end{aligned}
$$

Clearly, $\int G(\mathbf{z})\mathrm{d}\mathbf{z}$ exists. □

5. Proof of Theorem 3.3

Firstly, let's prove the first part of Theorem 3.3, that is for any $Z > 0$ *and* $N > 0$, $\widehat{E}^M_{\leq} < 0$.

Lemma 5.1. *For any* $Z > 0$ *and* $N > 0$ *one has* $\widehat{E}^M_{\leq}(N) < 0$.

Proof. Without loss of generality, we may assume that there is only one nucleus of charge Z located at the origin $\mathbf{r} = 0$. We use the same family $\widetilde{\gamma}_L$ of trial density matrices as (4.6) in the proof of the upper bound in Proposition 4.1.

We investigate the functional $\widehat{\mathcal{E}}^M$ first. We have known that

$$\widehat{\mathcal{E}}^M(\gamma) = \mathcal{E}^M(\gamma) + \frac{1}{8}\,\mathrm{tr}\;\gamma.$$

As $L \to \infty$, one has $\widehat{\mathcal{E}}^M(\widetilde{\gamma}_L) = -Z\,\mathrm{tr}\,\frac{\widetilde{\gamma}_L}{|\mathbf{r}|} + L^{-1}D(\chi^4, \chi^4) + o(L^{-1})$. Indeed, by using the asymptotic behavior in (4.12),

$$\begin{aligned}
\widehat{\mathcal{E}}^M(\widetilde{\gamma}_L) &= \mathcal{E}^M(\widetilde{\gamma}_L) + \frac{1}{8}\,\mathrm{tr}\;\widetilde{\gamma}_L \\
&= \mathrm{tr}\,(-\frac{1}{2}\nabla^2\widetilde{\gamma}_L) + D(\rho_{\widetilde{\gamma}_L}, \rho_{\widetilde{\gamma}_L}) - X(\widetilde{\gamma}_L^{1/2}) - \int V_c(\mathbf{r})\rho_{\widetilde{\gamma}_L}\mathrm{d}\mathbf{r} \\
&\quad + \frac{1}{8}\,\mathrm{tr}\;\widetilde{\gamma}_L. \\
&\to X(\widetilde{\gamma}_L^{1/2}) - \frac{1}{8}\,\mathrm{tr}\;\widetilde{\gamma}_L + \frac{1}{8}\,\mathrm{tr}\;\widetilde{\gamma}_L - X(\widetilde{\gamma}_L^{1/2}) - Z\int \frac{\widetilde{\gamma}_L}{|\mathbf{r}|}\mathrm{d}\mathbf{r} \\
&\quad + L^{-1}D(\chi^4, \chi^4) + o(L^{-1}) \qquad (\textit{use (4.12) here}) \\
&= -Z\int \frac{\widetilde{\gamma}_L}{|\mathbf{r}|}\mathrm{d}r + L^{-1}D(\chi^4, \chi^4) + o(L^{-1}) \\
&= -Z\,\mathrm{tr}\,\frac{\widetilde{\gamma}_L}{|\mathbf{r}|} + L^{-1}D(\chi^4, \chi^4) + o(L^{-1}).
\end{aligned}$$

Now we see that tr $\frac{\widetilde{\gamma}_L}{|\mathbf{r}|} \to L^{-1}\int \frac{\chi^4(\mathbf{r})}{|\mathbf{r}|}\mathrm{d}\mathbf{r} + o(L^{-1})$ by using the argument we claimed in (4.10) that $\varphi_L(\mathbf{r}) = L^3\int g^2(L(\mathbf{r}-\mathbf{r}'))\chi^2(\mathbf{r}')\mathrm{d}\mathbf{r}' \;\to\; \chi^2(\mathbf{r})$, which comes from

$$\begin{aligned}
\mathrm{tr}\ \frac{\widetilde{\gamma}_L}{|\mathbf{r}|} &= \iint \frac{\chi_L^2(\mathbf{r})g^2(\mathbf{r}-\mathbf{r}')\chi_L^2(\mathbf{r}')}{|\mathbf{r}|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \iint \frac{L^{-\frac{3}{2}}\chi_L^2(\frac{\mathbf{r}}{L})g^2(\mathbf{r}-\mathbf{r}')L^{-\frac{3}{2}}\chi_L^2(\frac{\mathbf{r}'}{L})}{|\mathbf{r}|}L^6\mathrm{d}\frac{\mathbf{r}}{L}\mathrm{d}\frac{\mathbf{r}'}{L} \\
&= \iint \frac{L^3\chi_L^2(\mathbf{r})g^2(L(\mathbf{r}-\mathbf{r}'))\chi_L^2(\mathbf{r}')}{|L\mathbf{r}|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= L^{-1}\int \frac{\chi^2(\mathbf{r})}{|\mathbf{r}|}\int L^3 g^2(L(\mathbf{r}-\mathbf{r}'))\chi^2(\mathbf{r}')\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r} \\
&\to L^{-1}\int \frac{\chi^4(\mathbf{r})}{|\mathbf{r}|}\mathrm{d}\mathbf{r} + o(L^{-1}) \quad \textit{as } L\to\infty.
\end{aligned}$$

Hence,

$$\widehat{\mathcal{E}}^M(\widetilde{\gamma}_L) = L^{-1}\Big(- Z\int \frac{\chi^4(\mathbf{r})}{|\mathbf{r}|}\mathrm{d}\mathbf{r} + D(\chi^4,\chi^4)\Big) + o(L^{-1}) \qquad \textit{as } L\to\infty.$$

For $Z > 0$, by choosing an appropriate χ such that $N = \|\chi\|_4^4$ being small enough, one can impose the first term in brackets being negative. And this completes the proof of Lemma 5.1. □

Next, we want to prove the existence of the infimum, namely

$$\widehat{E}^M_{\leq}(N) = \inf_\gamma\{\widehat{\mathcal{E}}^M(\gamma) : 0\leq\gamma\leq 1, \mathrm{tr}\ \gamma \leq N\}.$$

But note that a minimizing sequence $\{\gamma_j\}$, satisfying

$$\widehat{\mathcal{E}}^M(\gamma_0) \geq \widehat{\mathcal{E}}^M(\gamma_1) \geq \widehat{\mathcal{E}}^M(\gamma_2) \geq \dots \geq \widehat{\mathcal{E}}^M(\gamma),$$

does not necessarily convergent. So let's give a quick glance to the frame of variational method. If there exists a minimizing sequence $\{\gamma_j\}_0^\infty$ for the functional $\widehat{\mathcal{E}}^M(\gamma)$, i.e.,

$$\widehat{\mathcal{E}}^M(\gamma_j) \to \widehat{E}^M_{\leq}(N) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}, \tag{5.1}$$

and if the functional turns out to be weakly lower semicontinuous, namely,

$$\liminf_{j\to\infty} \widehat{\mathcal{E}}^M(\gamma_j) \geq \widehat{\mathcal{E}}^M(\gamma) \tag{5.2}$$

provided $\gamma_j \rightharpoonup \gamma$. Then γ is the minimizer, i.e., $\widehat{\mathcal{E}}^M(\gamma) = \widehat{E}^M_{\leq}(N)$, since

$$\widehat{E}^M_{\leq}(N) = \liminf_{j\to\infty} \widehat{\mathcal{E}}^M(\gamma_j) \geq \widehat{\mathcal{E}}^M(\gamma) \geq \widehat{E}^M_{\leq}(N). \tag{5.3}$$

The first problem therefore is whether there is a convergent minimizing sequence $\{\gamma_j\}$ such that $\gamma_j \to \gamma$ in $\mathfrak{G}^1$. This question will be answered in Proposition 5.4.

Then the problem remains to show is the weakly lower semicontinuity of the energy functional that will be answered in Proposition 5.5.

First, however, we begin with two Lemmas.

Lemma 5.2. *For every* $\varepsilon > 0$

$$\iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon} \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \leq 4\varepsilon\, \mathrm{tr}\,(-\nabla^2\gamma) \tag{5.4}$$

and

$$X(\gamma^{1/2}) \leq \frac{\varepsilon}{4}\, \mathrm{tr}\,(-\nabla^2\gamma) + \frac{1}{4\varepsilon}\, \mathrm{tr}\ \gamma. \tag{5.5}$$

Proof. The first formula is a consequence of Hardy's inequality $\frac{1}{4|\mathbf{r}|^2} \leq -\nabla^2$(see Lemma 9.6). Indeed,

$$\begin{aligned}
\iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon} \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' &= \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon} |\mathbf{r}-\mathbf{r}'| \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|^2} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\leq \varepsilon \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon} \left(\frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|}{|\mathbf{r}-\mathbf{r}'|} \right)^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\leq 4\varepsilon \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon} \left(\nabla \gamma^{1/2}(\mathbf{x},\mathbf{x}') \right)^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\leq 4\varepsilon \iint \left(\nabla \gamma^{1/2}(\mathbf{x},\mathbf{x}') \right)^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= 4\varepsilon \, \mathrm{tr}\,(-\nabla^2\gamma).
\end{aligned}$$

For the second inequality (5.5), we shall use the expression for the ground state energy of the hydrogen atom, namely

$$-\nabla^2 - \frac{z}{|\mathbf{r}|} \geq -\frac{z^2}{4}.$$

Put $z = 2/\varepsilon$, one can shift this expression to

$$\frac{2}{|\mathbf{r}|\varepsilon} \leq -\nabla^2 + \frac{1}{\varepsilon^2}$$

$$\Leftrightarrow \frac{\varepsilon}{4}\frac{2}{|\mathbf{r}|\varepsilon} \leq \frac{\varepsilon}{4}(-\nabla^2) + \frac{\varepsilon}{4}\frac{1}{\varepsilon^2}$$

$$\Leftrightarrow \frac{1}{2|\mathbf{r}|} \leq \frac{\varepsilon}{4}(-\nabla^2) + \frac{1}{4\varepsilon}.$$

Thus

$$\int \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x} \leq \frac{\varepsilon}{4} \int |\nabla_{\mathbf{x}} \gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 \mathrm{d}\mathbf{x} + \frac{1}{4\varepsilon} \int |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 \mathrm{d}\mathbf{x}$$

and, by integrating on $\mathbf{x}'$, we get

$$\begin{aligned} X(\gamma^{1/2}) &= \frac{1}{2}\iint \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\ &\leq \frac{\varepsilon}{4}\iint |\nabla_{\mathbf{x}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \frac{1}{4\varepsilon}\iint |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\ &= \frac{\varepsilon}{4}\,\mathrm{tr}\,(-\nabla^2\gamma) + \frac{1}{4\varepsilon}\,\mathrm{tr}\;\gamma, \end{aligned}$$

which is exactly what we want. □

Lemma 5.3. *Let* $\chi(\mathbf{r})$ *satisfy* $|\chi(\mathbf{r})| \leq 1$. *Then*

$$X(\chi^*\gamma^{1/2}\chi) \leq X((\chi^*\gamma\chi)^{1/2}). \tag{5.6}$$

Proof. We introduce the characteristic function of a ball of radius l centered at $\mathbf{z}$ as defined in the Lemma 2.1

$$\chi_{B_{\mathbf{z},l}}(\mathbf{r}) = \begin{cases} 1 & |\mathbf{r}-\mathbf{z}| < l \\ 0 & |\mathbf{r}-\mathbf{z}| \geq l. \end{cases}$$

From Lemma 2.1 we know that the Coulmb kernel can be expressed as

$$|\mathbf{r}-\mathbf{r}'|^{-1} = \frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{B_{\mathbf{z},l}}(\mathbf{r})\chi_{B_{\mathbf{z},l}}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5}$$

Then for any density matrix δ

$$\begin{aligned} X(\delta) &= \frac{1}{2}\iint |\delta|^2|\mathbf{r}-\mathbf{r}'|^{-1}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\ &= \frac{1}{2\pi}\iint |\delta|^2\int_0^\infty\int_{\mathbb{R}^3} \chi_{B_{\mathbf{z},l}}(\mathbf{r})\chi_{B_{\mathbf{z},l}}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\ &= \frac{1}{2\pi}\int_0^\infty\int_{\mathbb{R}^3}\left(\iint |\delta|^2\chi_{B_{\mathbf{z},l}}(\mathbf{r})\chi_{B_{\mathbf{z},l}}(\mathbf{r}')\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\right)\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5} \\ &= \frac{1}{2\pi}\int_0^\infty\int_{\mathbb{R}^3}\mathrm{tr}\,(\delta\chi_{B_{\mathbf{z},l}}\delta\chi_{B_{\mathbf{z},l}})\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5} \end{aligned} \tag{5.7}$$

It follows from $|\chi| \leq 1$ and the monotonicity of the operator square root (Lemma 2.2) that

$$\chi^*\gamma^{1/2}\chi = ((\chi^*\gamma^{1/2}\chi)(\chi^*\gamma^{1/2}\chi))^{1/2} \leq (\chi^*\gamma^{1/2}\gamma^{1/2}\chi))^{1/2} = (\chi^*\gamma\chi)^{1/2}.$$

Hence

$$\mathrm{tr}\,(\chi^*\gamma^{1/2}\chi\chi_{B_{\mathbf{z},l}}\chi^*\gamma^{1/2}\chi\chi_{B_{\mathbf{z},l}}) \leq \mathrm{tr}\,((\chi^*\gamma\chi)^{1/2}\chi_{B_{\mathbf{z},l}}(\chi^*\gamma\chi)^{1/2}\chi_{B_{\mathbf{z},l}}).$$

and, in conjunction with (5.7) we conclude that

$$X(\chi^*\gamma^{1/2}\chi) \leq X((\chi^*\gamma\chi)^{1/2}).$$

□

Now we are ready to deal with the next Proposition.

Proposition 5.4. *Let $Z > 0$ and $N > 0$. There exists a minimizing sequence $\{\gamma_j\}$ for*

$$\widehat{E}^M_{\leq}(N) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}$$

which converges in $\mathfrak{S}^1$, i.e., there is a γ such that $\mathrm{tr}\ |\gamma_j - \gamma| \to 0$.

Proof. Choose an arbitrary minimizing sequence $(\gamma_j)_{j\geq 1}$, which is convergent in the sense of trace, for

$$\widehat{E}^M_{\leq}(N) = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}.$$

If it is necessary, we can extract a convergent subsequence instead. Thus assume that tr $\gamma_j \to \widetilde{N} \in [0, N]$. Recall that we have proved in Lemma 5.2 that (5.5) holds, and we know the hydrogen bound,

$$\mathrm{tr}\,(Z_k|\mathbf{r}-\mathbf{R}_k|^{-1}\gamma) \leq (Z_k\varepsilon/4Z)\,\mathrm{tr}\,(-\nabla^2\gamma) + (Z_kZ/\varepsilon)\,\mathrm{tr}\ \gamma. \qquad (5.8)$$

It follows that

$$\frac{1}{2}(1-\varepsilon)\,\mathrm{tr}\,(-\nabla^2\gamma_j) \leq \widehat{\mathcal{E}}^M(\gamma_j) + \frac{1}{\varepsilon}(Z^2+\frac{1}{4})\,\mathrm{tr}\ \gamma_j,$$

as demonstrated below

$$\begin{aligned}
\widehat{\mathcal{E}}^M(\gamma_j) &= \mathcal{E}^M(\gamma_j) + \frac{1}{8}\,\mathrm{tr}\ \gamma_j \\
&= \mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma_j) + D(\rho_{\gamma_j},\rho_{\gamma_j}) - X(\gamma_j^{1/2}) - \int V_c(\mathbf{r})\rho_{\gamma_j}\mathrm{d}\mathbf{r} \\
&\quad +\frac{1}{8}\,\mathrm{tr}\ \gamma_j \\
&\geq \mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma_j) - X(\gamma_j^{1/2}) - \int V_c(\mathbf{r})\rho_{\gamma_j}\mathrm{d}\mathbf{r} \\
&\geq \mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma_j) - \frac{\varepsilon}{4}\,\mathrm{tr}\,(-\nabla^2\gamma_j) - \frac{1}{4\varepsilon}\,\mathrm{tr}\ \gamma_j - (Z_k\varepsilon/4Z)\,\mathrm{tr}\,(-\nabla^2)\gamma_j \\
&\quad -(Z_kZ/\varepsilon)\,\mathrm{tr}\ \gamma_j \\
&\quad (\mathit{let}\ Z_k = Z) \\
&= \frac{1}{2}(1-\varepsilon)\,\mathrm{tr}\,(-\nabla^2\gamma_j) - \frac{1}{\varepsilon}(Z^2+\frac{1}{4})\,\mathrm{tr}\ \gamma_j.
\end{aligned}$$

Hence the sequence $(-\nabla^2+1)^{1/2}\gamma_j(-\nabla^2+1)^{1/2}$ is bounded in $\mathfrak{G}^1$, this is because

$$\begin{aligned}\mathrm{tr}\left((-\nabla^2+1)^{1/2}\gamma_j(-\nabla^2+1)^{1/2}\right) &= \mathrm{tr}\left((-\nabla^2+1)^{1/2}(-\nabla^2+1)^{1/2}\gamma_j\right)\\ &= \mathrm{tr}\left((-\nabla^2+1)\gamma_j\right) < \infty.\end{aligned}$$

Note that if $(-\nabla^2+1)^{1/2}\gamma_j(-\nabla^2+1)^{1/2}$ is bounded in $\mathfrak{G}^1$, then $(-\nabla^2+1)^{1/2}\gamma_j^{1/2}$ is bounded in $\mathfrak{G}^2$. Since $\mathfrak{G}^2$ is reflexive, in view of the Banach-Alaoglu theorem [24, Theorem 2.18], there exists a γ such that, after passing to a subsequence (if necessary), $\mathrm{tr}\,(K\gamma_j) \to \mathrm{tr}\,(K\gamma)$ for any operator K such that $(-\nabla^2+1)^{-1/2}K(-\nabla^2+1)^{-1/2}$ is compact (this argument is given in [7], it is true because one can build an isometric isomorphism between $\mathfrak{G}^1$ and the dual space of compact operators, namely, $\mathfrak{G}^1(\mathcal{H}) \cong Com'(\mathcal{H})$, see [31, Theorem VI.26]. For the pedagogical purpose, we refer readers to [33] and [3]). This compactness condition is satisfied if K is simply multiplication by some function $f \in L^p(\mathbb{R}^3)$ for some $p = 3/2$ (See Section 9.5). In this case we have that

$$\int f(\mathbf{r})\rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} = \mathrm{tr}\ f\gamma_j \to \mathrm{tr}\ f\gamma = \int f(\mathbf{r})\rho_{\gamma}(\mathbf{r})\mathrm{d}\mathbf{r}.$$

In particular one can take such an f to be the Coulomb potential since this potential can be written as the sum of two functions, one of which is in $L^p(\mathbb{R}^3)$ and the other in $L^q(\mathbb{R}^3)$ with $p = 3/2$ and $q = \infty$.

Observe that $0 \leq \gamma \leq 1$. By the lower semi-continuity of the $\mathfrak{G}^1$ norm,

$$M := \mathrm{tr}\ \gamma \leq \liminf_{j\to\infty} \mathrm{tr}\ \gamma_j = \widetilde{N} \leq N.$$

Then $\gamma \not\equiv 0$ and, consequently $M > 0$ as we shall demonstrate now.

From Lemma 5.1, $\widehat{E}^M_{\leq}(N) < 0$, we can know that $\widehat{\mathcal{E}}^M(\gamma_j) \leq -\varepsilon$ for some $\varepsilon > 0$ and all sufficiently large j. By Proposition 4.1,

$$-\varepsilon \geq \widehat{\mathcal{E}}^M(\gamma_j) = \mathcal{E}^M_{Z=0}(\gamma_j) + \frac{1}{8}\,\mathrm{tr}\,(\gamma_j) - \mathrm{tr}\,(V_c\gamma_j) \geq -\,\mathrm{tr}\,(V_c\gamma_j),$$

It follows that $\mathrm{tr}\,(V_c\gamma_j) \geq \varepsilon$, so that $\mathrm{tr}\,(V_c\gamma) \geq \varepsilon$. The assertion $\gamma \not\equiv 0$ follows.

We have noted $\gamma_j \rightharpoonup \gamma$ in the sense of weak operator convergence. If $M = \widetilde{N}$, then $\mathrm{tr}\ \gamma_j \to \mathrm{tr}\ \gamma$, and thus $\gamma_j \to \gamma$ in $\mathfrak{G}^1$ (See [29, Theorem 2.16]), we are done with the case $M = \widetilde{N}$ for proposition 5.4 .

It remains to examine the case $M < \widetilde{N}$.

First we describe the strategy. We are supposed to construct a minimizing sequence γ_j^0 out of γ_j which converges to γ in $\mathfrak{G}^1$.

On this purpose we choose a quadratic partition of unity, $(\chi^0)^2+(\chi^1)^2 \equiv 1$, where χ^0 is a smooth, symmetric decreasing function with $\chi^0(\mathbf{0}) = 1, \chi^0(\mathbf{r}) < 1$ if $|\mathbf{r}| > 0$ and $\chi^0(\mathbf{r}) = 0$ if $|\mathbf{r}| \geq 2$. Clearly, for a fixed j, $\mathrm{tr}\ \big((\chi^0(\mathbf{r}/R))^2\gamma_j\big)$ is a continuous function of R which increases from 0 to $\mathrm{tr}\ \gamma_j$ as $R \to \infty$. When j large enough, we can restrict ourselves to such $j's$ that $\mathrm{tr}\ \gamma_j > M$ and choose an appropriate R_j such that $\mathrm{tr}\ \big((\chi^0(\mathbf{r}/R_j))^2\gamma_j\big) = M$.

We write $\chi_j^\nu(\mathbf{r}) = \chi^\nu(\mathbf{r}/R_j)$ and $\gamma_j^\nu = \chi_j^\nu \gamma_j \chi_j^\nu$ for $\nu = 0, 1$. We prove the following fact first.

Claim $R_j \to \infty$ as $j \to \infty$.

Verification We argue by contradiction.

Assume that there is a subsequence that converges to some $R < \infty$. Then for this subsequence,

$$\chi_j^0(\mathbf{r})^2 = \chi^0(\mathbf{r}/R_j)^2 \to \chi^0(\mathbf{r}/R)^2$$

in any L^p. In view of formula $\int f(\mathbf{r})\rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} = \mathrm{tr}\ f\gamma_j \to \mathrm{tr}\ f\gamma = \int f(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}$, $\rho_{\gamma_j} \rightharpoonup \rho_\gamma$ weakly in L^p for $1 < p < 3$ and, therefore,

$$\int \chi_j^0(\mathbf{r})^2 \rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} \to \int \chi^0(\mathbf{r}/R)^2 \rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}.$$

Note that, by the definition, the left-hand side is independent of j and it equals $\int \chi_j^0(\mathbf{r})^2\rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} = \mathrm{tr}\ \big((\chi^0(\mathbf{r}/R_j))^2\gamma_j\big) = M = \mathrm{tr}\ \gamma = \int \rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}$. But the right-hand side is strictly less than$\int \rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}$ because $(\chi^0)^2 < 1$ *a.e.* and $\gamma \not\equiv 0$. We reach a contradiction. Therefore $\lim_{j\to\infty} R_j = \infty$.

Now we observe that

$$\gamma_j^0 = \chi_j^0\gamma_j\chi_j^0 = \chi^0(\mathbf{r}/R_j)\gamma_j\chi^0(\mathbf{r}/R_j),$$

and as a consequence, $\mathrm{tr}\ \gamma_j^0 = \mathrm{tr}\ \Big(\chi^0(\mathbf{r}/R_j)\gamma_j\chi^0(\mathbf{r}/R_j)\Big) \to \mathrm{tr}\ \gamma_j$ in $\mathfrak{G}^1$, which means $\gamma_j^0 \rightharpoonup \gamma_j$ in $\mathfrak{G}^1$. Moreover, since $\gamma_j \rightharpoonup \gamma$, we deduce that $\gamma_j^0 \rightharpoonup \gamma$ in the sense of weak operator convergence. On the other hand, by the construction of γ_j^0 and R_j, $\mathrm{tr}\ \gamma_j^0 = \mathrm{tr}\ \gamma = M$, so that $\gamma_j^0 \to \gamma$ in $\mathfrak{G}^1$.

The last thing for completing the proof of Proposition 5.4 rests on the minimizing property of γ_j^0.

For this purpose, we need to show that

$$\liminf_{j\to\infty} \widehat{\mathcal{E}}^M(\gamma_j) \geq \liminf_{j\to\infty} \widehat{\mathcal{E}}^M(\gamma_j^0). \tag{5.9}$$

For the kinetic energy we use the IMS formula (Lemma 9.3),

$$\mathrm{tr}\,(-\nabla^2\gamma_j) = \mathrm{tr}\,(-\nabla^2\gamma_j^0) + \mathrm{tr}\,(-\nabla^2\gamma_j^1) - \mathrm{tr}\,[(|\nabla\chi_j^0|^2 + |\nabla\chi_j^1|^2)\gamma_j].$$

Since $R_j \to \infty$, we have $\||\nabla\chi_j^0|^2 + |\nabla\chi_j^1|^2\|_\infty \to 0$ and therefore

$$\mathrm{tr}\,(-\nabla^2\gamma_j) = \mathrm{tr}\,(-\nabla^2\gamma_j^0) + \mathrm{tr}\,(-\nabla^2\gamma_j^1) + o(1). \tag{5.10}$$

For the attraction term, we again use the fact that $R_j \to \infty$, so

$$\mathrm{tr}\,\frac{\gamma_j^1}{|\mathbf{r}-\mathbf{R_k}|} = \int \frac{\chi^1(\frac{\mathbf{r}}{R_j})\gamma_j\chi^1(\frac{\mathbf{r}}{R_j})}{|\mathbf{r}-\mathbf{R_k}|}\mathrm{d}\mathbf{r} \to 0$$

since $\chi^1(0) = 0$. So

$$\mathrm{tr}\,\frac{\gamma_j}{|\mathbf{r}-\mathbf{R_k}|} = \mathrm{tr}\,\frac{\gamma_j^0}{|\mathbf{r}-\mathbf{R_k}|} + o(1). \tag{5.11}$$

For the repulsion term we use that $\rho_{\gamma_j^0} \leq \rho_{\gamma_j}$ pointwise and note that

$$\gamma_j = \gamma_j^0 + \gamma_j^1,$$

$$\mathrm{tr}\,(\gamma_j) = \mathrm{tr}\,(\gamma_j^0) + \mathrm{tr}\,(\gamma_j^1),$$

and we get

$$D(\rho_{\gamma_j^0}, \rho_{\gamma_j^0}) \leq D(\rho_{\gamma_j}, \rho_{\gamma_j}). \tag{5.12}$$

At last, we turn to the exchange term , to which we apply the quadratic partition of unity first:

$$\begin{aligned}
X(\gamma_j^{1/2}) &= \frac{1}{2}\iint \frac{|\gamma_j^{1/2}|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \frac{1}{2}\iint \frac{|(\chi_j^0)^2\gamma_j^{1/2}+(\chi_j^1)^2\gamma_j^{1/2}|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \frac{1}{2}\iint \frac{|(\chi_j^0)^2\gamma_j^{1/2}|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \frac{1}{2}\iint \frac{|(\chi_j^1)^2\gamma_j^{1/2}|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\quad + \frac{1}{2}\iint \frac{2|(\chi_j^0)\gamma_j^{1/2}(\chi_j^1)|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= X(\chi_j^0\gamma_j^{1/2}\chi_j^0) + X(\chi_j^1\gamma_j^{1/2}\chi_j^1) + 2X(\chi_j^0\gamma_j^{1/2}\chi_j^1).
\end{aligned}$$

We claim that

$$X(\gamma_j^{1/2}) \le X((\gamma_j^0)^{1/2}) + X((\gamma_j^1)^{1/2}) + o(1) \tag{5.13}$$

holds. Indeed, it follows from Lemma 5.3 that

$$X(\chi_j^\nu\gamma_j^{1/2}\chi_j^\nu) \le X((\chi_j^\nu\gamma_j\chi_j^\nu))^{1/2}. \tag{5.14}$$

For the off-diagonal term we decompose, for any $\varepsilon > 0$,

$$\begin{aligned}
X(\chi_j^0\gamma_j^{1/2}\chi_j^1) &= \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2} \frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&\quad + \iint_{|\mathbf{r}-\mathbf{r}'|\ge\varepsilon/2} \frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'.
\end{aligned}$$

The term with the singularity is controlled by Lemma 5.2:

$$
\begin{aligned}
&\iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2} \frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
\leq\ & \varepsilon\cdot\operatorname{tr}\left((-\nabla^2)\chi_j^0\gamma_j^{1/2}(\chi_j^1)^2\gamma_j^{1/2}\chi_j^0\right) \\
\leq\ & \varepsilon\cdot\operatorname{tr}\left((-\nabla^2)\chi_j^0\gamma_j\chi_j^0\right).
\end{aligned}
$$

Clearly this can be made arbitrarily small by choosing ε small enough. For any $A>0$, $0<R_j-A<\varepsilon/2$ as long as j large enough. We decompose the term without singularity into two pieces,

$$
\begin{aligned}
&\iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2} \frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
\leq\ & \iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2,|\mathbf{r}|\geq A} \frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&+\iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2,|\mathbf{r}|<A} \frac{|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
\leq\ & \varepsilon^{-1}\iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2,|\mathbf{r}|\geq A} \chi_j^0(\mathbf{r})^2|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&+(2(R_j-A))^{-1}\iint |\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
=\ & \varepsilon^{-1}\operatorname{tr}\left(\chi\{|\mathbf{r}|\geq A\}\gamma_j^0\right)+(2(R_j-A))^{-1}\operatorname{tr}\gamma_j. \qquad (5.15)
\end{aligned}
$$

In the next to last line we used that $|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2>R_j-A$ and $\chi_j^1(\mathbf{r}')\neq 0$. Since $\gamma_j^0\to\gamma$ in $\mathfrak{S}^1$, one has $\operatorname{tr}\left(\chi\{|\mathbf{r}|\geq A\}\gamma_j^0\right)\to\operatorname{tr}\left(\chi\{|\mathbf{r}|\geq A\}\gamma\right)$, this can be made arbitrarily small by choosing A large enough. Since $R_j\to\infty$, the second summand converges to 0. Hence we have shown that (5.13) holds. Finally, By (5.10)-(5.13)we obtain a lower bound of

$\widehat{\mathcal{E}}^M(\gamma_j)$,

$$\begin{aligned}\widehat{\mathcal{E}}^M(\gamma_j) &= \mathcal{E}^M(\gamma_j) + \frac{1}{8}\,\mathrm{tr}\;\gamma_j \\ &= \frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma_j) + D(\rho_{\gamma_j},\rho_{\gamma_j}) - X(\gamma_j^{1/2}) - \int \frac{Z_k\gamma_j}{|\mathbf{r}-\mathbf{R_k}|}\mathrm{d}\mathbf{r} \\ &\quad + \frac{1}{8}\,\mathrm{tr}\;\gamma_j \\ &\geq \frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma_j^0) + \frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma_j^1) + o(1) + D(\rho_{\gamma_j^0},\rho_{\gamma_j^0}) - X((\gamma_j^0)^{1/2}) \\ &\quad - X((\gamma_j^1)^{1/2}) + o(1) - \mathrm{tr}\;\frac{Z_k\gamma_j^0}{|\mathbf{r}-\mathbf{R_k}|} + o(1) + \frac{1}{8}\,\mathrm{tr}\;\gamma_j^0 + \frac{1}{8}\,\mathrm{tr}\;\gamma_j^1 \\ &= \widehat{\mathcal{E}}^M(\gamma_j^0) + \left(\frac{1}{2}\,\mathrm{tr}\,(-\nabla^2\gamma_j^1) - X(\gamma_j^1) + \frac{1}{8}\,\mathrm{tr}\;\gamma_j^1\right) + o(1).\end{aligned}$$

Recall that in the proof of Proposition 4.1 we have shown that the term in brackets is non-negative. Hence

$$\liminf_{j\to\infty}\widehat{\mathcal{E}}^M(\gamma_j) \geq \liminf_{j\to\infty}\widehat{\mathcal{E}}^M(\gamma_j^0).$$

This concludes the proof of Proposition 5.4. □

Proposition 5.5. *Suppose $\gamma_j \to \gamma$ in $\mathfrak{G}^1$. Then*

$$\liminf_{j\to\infty}\widehat{\mathcal{E}}^M(\gamma_j) \geq \widehat{\mathcal{E}}^M(\gamma). \tag{5.16}$$

Proof. The bound

$$\frac{1}{2}(1-\varepsilon)\,\mathrm{tr}\,(-\nabla^2\gamma_j) \leq \widehat{\mathcal{E}}^M(\gamma_j) + \frac{1}{\varepsilon}(Z^2+\frac{1}{4})\,\mathrm{tr}\;\gamma_j$$

shows that

$$E = \liminf_{j\to\infty}\widehat{\mathcal{E}}^M(\gamma_j) > -\infty. \tag{5.17}$$

Moreover, we may assume that $E < \infty$, for otherwise there is nothing to prove. After passing to a subsequence (if necessary), we may assume that $\widehat{\mathcal{E}}^M(\gamma_j) \to E$. As in the proof of Proposition 5.4, there exists a γ such that, after passing to a subsequence (if necessary), $\operatorname{tr}(K\gamma_j) \to \operatorname{tr}(K\gamma)$ for any operator K such that $(-\nabla^2+1)^{-1/2}K(-\nabla^2+1)^{-1/2}$ is compact.

Since $\gamma_j \rightharpoonup \gamma$ in $\mathfrak{G}^1$, by the weakly lower semi-continuity, we have

$$\liminf_{j\to\infty} \operatorname{tr}\big((-\frac{1}{2}\nabla^2 + \frac{1}{8})\gamma_j\big) \geq \operatorname{tr}\big((-\frac{1}{2}\nabla^2 + \frac{1}{8})\gamma\big). \tag{5.18}$$

Next we turn to the repulsion term. Since $D(\rho_{\gamma_j}, \rho_{\gamma_j})$ is bounded, passing to a subsequence (if necessary), we may assume that $\rho_{\gamma_j} \rightharpoonup \rho$ with respect to the D-scalar product, namely $D(\rho_{\gamma_j}, \rho_{\gamma_j}) \to D(\rho, \rho)$. On the other hand, from the proof of Proposition 5.4, we have known that $\int f(\mathbf{r})\rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} = \operatorname{tr} f\gamma_j \to \operatorname{tr} f\gamma = \int f(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}$, then $D(\rho_{\gamma_j}, \rho_{\gamma_j}) \to D(\rho_\gamma, \rho_\gamma)$. It follows that $\rho = \rho_\gamma$. Again the weak convergence lead to the weakly lower semi-continuity with respect to the D-norm:

$$\liminf_{j\to\infty} D(\rho_{\gamma_j}, \rho_{\gamma_j}) \geq D(\rho_\gamma, \rho_\gamma). \tag{5.19}$$

For the attraction term, since the Coulomb potential V_c can be written as $v(\mathbf{r}) + w(\mathbf{r})$, where $v(\mathbf{r}) \in L^{3/2}, w(\mathbf{r}) \in L^\infty$. Therefore, using the equality $\int f(\mathbf{r})\rho_{\gamma_j}(\mathbf{r})\mathrm{d}\mathbf{r} = \mathrm{tr}\ f\gamma_j \to \mathrm{tr}\ f\gamma = \int f(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r}$ again

$$\begin{aligned}
\mathrm{tr}\ V_c\gamma_j &= \int V_c\gamma_j \mathrm{d}\mathbf{r} \\
&= \int V_c\gamma_j \mathrm{d}\mathbf{r} \\
&= \int v\gamma_j \mathrm{d}\mathbf{r} + \int w\gamma_j \mathrm{d}\mathbf{r} \\
&\to \int v\gamma \mathrm{d}\mathbf{r} + \int w\gamma \mathrm{d}\mathbf{r} \\
&= \int V_c\gamma \mathrm{d}\mathbf{r} = \mathrm{tr}\ V_c\gamma.
\end{aligned}$$

At last, we prove the continuity of the exchange term. We decompose, for any $\varepsilon > 0$,

$$\begin{aligned}
& |X(\gamma_j^{1/2}) - X(\gamma^{1/2})| \\
= & \left| \iint \frac{|\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right| \\
= & \left| \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2} \frac{|\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2} \frac{|\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right| \\
\leq & \left| \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2} \frac{|\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right| + \left| \iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2} \frac{|\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right| \\
\leq & \iint_{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2} \frac{|\gamma_j^{1/2}|^2 + |\gamma^{1/2}|^2}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \iint_{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2} \frac{\left||\gamma_j^{1/2}|^2 - |\gamma^{1/2}|^2\right|}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}',
\end{aligned}$$

The first term can be bounded by $\varepsilon\, \mathrm{tr}\, \big((-\nabla^2)(\gamma_j + \gamma)\big)$ according to Lemma 5.2 and $\mathrm{tr}\, \big((-\nabla^2)(\gamma_j+\gamma)\big)$ is bounded since $\frac{1}{2}(1-\varepsilon)\, \mathrm{tr}\, (-\nabla^2\gamma_j) \leq \widehat{\mathcal{E}}^M(\gamma_j) + \frac{1}{\varepsilon}(Z^2 + \frac{1}{4})\ \mathrm{tr}\ \gamma_j$. To treat the term without the singularity we use the fact that the mapping $K \mapsto |K|^{1/2}$ is continuous from $\mathfrak{G}^1$ to $\mathfrak{G}^2$ (See Lemma 9.18 in Appendix) . Hence $\gamma_j^{1/2} \to \gamma^{1/2}$ in $\mathfrak{G}^2$, and we can estimate as follows

$$
\begin{aligned}
& \left(\iint_{|\mathbf{r}-\mathbf{r}'|\geq \varepsilon/2} \frac{\big||\gamma_j^{1/2}|^2 - |\gamma_j^{1/2}|^2\big|}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right)^2 \\
= & \left(\iint_{|\mathbf{r}-\mathbf{r}'|\geq \varepsilon/2} \big||\gamma_j^{1/2}| - |\gamma_j^{1/2}|\big| \frac{\big||\gamma_j^{1/2}| + |\gamma_j^{1/2}|\big|}{2|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right)^2 \\
\leq & \left(\iint_{|\mathbf{r}-\mathbf{r}'|\geq \varepsilon/2} \big|\gamma_j^{1/2} - \gamma_j^{1/2}\big|^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right) \left(\iint_{|\mathbf{r}-\mathbf{r}'|\geq \varepsilon/2} \frac{\big||\gamma_j^{1/2}| + |\gamma_j^{1/2}|\big|^2}{4|\mathbf{r}-\mathbf{r}'|^2} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \right) \\
\leq & \ \|\gamma_j^{1/2} - \gamma_j^{1/2}\|_2^2 \varepsilon^{-2} \iint \big||\gamma_j^{1/2}| + |\gamma_j^{1/2}|\big|^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
\leq & \ 2\|\gamma_j^{1/2} - \gamma_j^{1/2}\|_2^2 \varepsilon^{-2} \iint \left(|\gamma_j^{1/2}|^2 + |\gamma_j^{1/2}|^2 \right) \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
= & \ \|\gamma_j^{1/2} - \gamma_j^{1/2}\|_2^2 \varepsilon^{-2} \operatorname{tr}(\gamma_j + \gamma).
\end{aligned}
$$

The first factor tend to 0 by convergence of $\gamma_j^{1/2}$ due to the fact mentioned above and the second one remains bounded. Hence we have proved that

$$\lim_{j\to\infty} X(\gamma_j^{1/2}) = X(\gamma^{1/2}). \tag{5.20}$$

Proposition 5.5 follows immediately. □

Proof of Theorem 3.3. By now, we have proved the existence of minimizer of $\widehat{\mathcal{E}}^M$. That is to say we complete the proof of Theorem 3.3 □

6. Proof of Theorem 3.4

Assume that $N \le Z$. Under this assumption we show that a minimizer γ of $\widehat{\mathcal{E}}^M(\gamma)$ satisfies the constraint $\mathrm{tr}\ \gamma = N$.

Proof. We argue by contradiction. Assume $\mathrm{tr}\ \gamma < N$. We shall find a trace class operator $\sigma \ge 0$ such that for

$$\gamma_\varepsilon = (1 - \varepsilon\|\sigma\|)\gamma + \varepsilon\sigma$$

and all sufficiently small $\varepsilon > 0$,

$$\widehat{\mathcal{E}}^M(\gamma_\varepsilon) < \widehat{\mathcal{E}}^M(\gamma).$$

In fact, the factor $(1 - \varepsilon\|\sigma\|)$ guarantees that $0 \le \gamma_\varepsilon \le 1$ for $0 < \varepsilon \le \|\sigma\|^{-1}$. If $\mathrm{tr}\ \gamma < N$, then $\mathrm{tr}\ \gamma_\varepsilon < N$ for

$$\varepsilon < \frac{N - \mathrm{tr}\ \gamma}{\big|\|\sigma\|\ \mathrm{tr}\ \gamma - \mathrm{tr}\ \sigma\big|},$$

and this leads to a contradiction because γ was supposed to be a minimizer.

To prove $\widehat{\mathcal{E}}^M(\gamma_\varepsilon) < \widehat{\mathcal{E}}^M(\gamma)$, we use convexity of the homogeneous terms in the functional $\widehat{\mathcal{E}}^M$ and expand the repulsion term explicitly. We begin with

$$\begin{aligned}\frac{1}{2}\operatorname{tr}(-\nabla^2\gamma_\varepsilon) &= \frac{1}{2}\operatorname{tr}\Big((-\nabla^2)\big[(1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma\big]\Big)\\ &\le \frac{1}{2}\operatorname{tr}(-\nabla^2\gamma)-\varepsilon\|\sigma\|\frac{1}{2}\operatorname{tr}(-\nabla^2\gamma)+\varepsilon\frac{1}{2}\operatorname{tr}(-\nabla^2\sigma).\end{aligned} \tag{6.1}$$

Moreover,

$$\begin{aligned}-\int V_c\rho_{\gamma_\varepsilon}\mathrm{d}\mathbf{r} &= -\int V_c(\mathbf{r})\big[(1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma\big](\mathbf{r})\mathrm{d}\mathbf{r}\\ &= -\int V_c(\mathbf{r})\gamma(\mathbf{r})\mathrm{d}\mathbf{r}+\varepsilon\|\sigma\|\int V_c(\mathbf{r})\gamma(\mathbf{r})\mathrm{d}\mathbf{r}-\varepsilon\int V_c(\mathbf{r})\sigma(\mathbf{r})\mathrm{d}\mathbf{r};\end{aligned} \tag{6.2}$$

$$\begin{aligned}D(\rho_{\gamma_\varepsilon},\rho_{\gamma_\varepsilon}) &= \frac{1}{2}\iint\frac{\big[(1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma\big](\mathbf{r})\big[(1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma\big](\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\ &= D(\rho_\gamma,\rho_\gamma)+\varepsilon\frac{1}{2}\iint\frac{\gamma(\mathbf{r})\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'+\varepsilon\frac{1}{2}\iint\frac{\gamma(\mathbf{r}')\sigma(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\ &\quad -\varepsilon\|\sigma\|\frac{1}{2}\iint\frac{\gamma(\mathbf{r})\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'-\varepsilon\|\sigma\|\frac{1}{2}\iint\frac{\gamma(\mathbf{r})\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\ &\quad \varepsilon^2D(\rho_\sigma-\|\sigma\|\rho_\gamma,\rho_\sigma-\|\sigma\|\rho_\gamma);\end{aligned} \tag{6.3}$$

$$\begin{aligned}-X(\gamma_\varepsilon^{1/2}) &= -\frac{1}{2}\iint\frac{(1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\ &= -X(\gamma^{1/2})+\varepsilon\|\sigma\|X(\gamma^{1/2})-\varepsilon X(\sigma^{1/2});\end{aligned} \tag{6.4}$$

In this way,

$$\begin{aligned}\frac{1}{8}\operatorname{tr}\,\gamma_\varepsilon &= \frac{1}{8}\int\big((1-\varepsilon\|\sigma\|)\gamma+\varepsilon\sigma\big)\mathrm{d}\mathbf{r}\\ &= \frac{1}{8}\operatorname{tr}\,\gamma-\varepsilon\|\sigma\|\frac{1}{8}\operatorname{tr}\,\gamma+\varepsilon\frac{1}{8}\operatorname{tr}\,\sigma.\end{aligned} \tag{6.5}$$

Collecting all the formulas above we arrive at

$$\widehat{\mathcal{E}}^M(\gamma_\varepsilon) \leq \widehat{\mathcal{E}}^M(\gamma)+\varepsilon\big(\,\mathrm{tr}\,(-\frac{\nabla^2}{2}-\varphi_\gamma+\frac{1}{8})\sigma-X(\sigma^{1/2})\big)-\varepsilon A_1+\varepsilon^2 A_2 \quad (6.6)$$

where

$$\varphi_\gamma(\mathbf{r}) = V_c(\mathbf{r}) - \int \frac{\rho_\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}',$$

$$A_1 = \|\sigma\|\Big(\widehat{\mathcal{E}}^M(\gamma) + D(\rho_\gamma,\rho_\gamma)\Big),$$

$$A_2 = D(\rho_\sigma - \|\sigma\|\rho_\gamma, \rho_\sigma - \|\sigma\|\rho_\gamma).$$

We proceed as we did in the proof of Proposition 4.1, letting $\sigma = \sigma_L$, where

$$\sigma_L^{1/2}(\mathbf{x},\mathbf{x}') = L^{-3/2}\chi(\mathbf{r}/L)g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}'/L)q^{-1/2}\delta_{\sigma,\sigma'}.$$

Here $g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{r}'|}$ and χ is a smooth function satisfying $\|\chi\|_4^4 = 1, \chi \geq 0$.

Asymptotically, as $|\mathbf{r}| \to \infty$,

$$\begin{aligned}\varphi_\gamma(\mathbf{r}) &= V_c(\mathbf{r}) - \int \frac{\rho_\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' \\ &\to \frac{Z}{|\mathbf{r}|} - \frac{\mathrm{tr}\ \gamma}{|\mathbf{r}|} = (Z - \mathrm{tr}\ \gamma)|\mathbf{r}|^{-1} > 0\end{aligned}$$

since $Z - \mathrm{tr}\ \gamma > 0$ by our assumption. Similar to the proof of Proposition 4.1, we find that

$$\mathrm{tr}\,(-\nabla^2\sigma_L) \to 2X(\sigma_L^{1/2}) - \frac{1}{4}\,\mathrm{tr}\,(\sigma_L),$$

$$\mathrm{tr}\,(-\varphi_\gamma\sigma_L) \to -\iint (Z - \mathrm{tr}\ \gamma)|\mathbf{r}|^{-1}\sigma_L \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.$$

Thus

$$\begin{aligned}
& \operatorname{tr}(-\frac{\nabla^2}{2}\sigma_L) + \operatorname{tr}(-\varphi_\gamma \sigma_L) + \frac{1}{8}\operatorname{tr}(\sigma_L) - X(\sigma_L^{1/2}) \\
\to \quad & X(\sigma_L^{1/2}) - \frac{1}{8}\operatorname{tr}(\sigma_L) - \iint (Z - \operatorname{tr}\,\gamma)|\mathbf{r}|^{-1}\sigma_L \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' + \frac{1}{8}\operatorname{tr}(\sigma_L) - X(\sigma_L^{1/2}) \\
= \quad & -\iint (Z - \operatorname{tr}\,\gamma)|\mathbf{r}|^{-1}\sigma_L \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
= \quad & -\iint (Z - \operatorname{tr}\,\gamma)|\mathbf{r}|^{-1} L^{-3}\chi^2(\frac{\mathbf{r}}{L}) g(\mathbf{r}-\mathbf{r}')^2 \chi^2(\frac{\mathbf{r}'}{L}) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
\to \quad & -\frac{Z - \operatorname{tr}\,\gamma}{L} \int |\mathbf{z}|^{-1}\chi(\mathbf{z})^4 \mathrm{d}\mathbf{z}
\end{aligned}$$

by using again the formula $L^3 \int g^2(L(\mathbf{r}-\mathbf{r}'))\chi^2(\mathbf{r}')\mathrm{d}\mathbf{r}' \;\to\; \chi^2(\mathbf{r})$, as $L \to \infty$ and substituting $\mathbf{z}$ for $\frac{\mathbf{r}}{L}$, $\mathbf{z}'$ for $\frac{\mathbf{r}'}{L}$.

From the proof of Proposition 4.1 and Lemma 5.1, it follows that $D(\rho_{\sigma_L}, \rho_{\sigma_L}) = \mathcal{O}(L^{-1})$ and $\|\sigma_L\| = \mathcal{O}(L^{-3})$, the latter is seen as follows.

indeed

$$
\begin{aligned}
\|\sigma_L\|_1 &= \iint |\sigma_L^{1/2}(\mathbf{x},\mathbf{x}')|^2 \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \iint \chi_L^2(\mathbf{r}) g(\mathbf{r}-\mathbf{r}')^2 \chi_L^2(\mathbf{r}') q^{-1} \delta_{\sigma,\sigma'} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \Sigma_{\sigma=\sigma'=1}^2 \iint \chi_L^2(\mathbf{r}) g(\mathbf{r}-\mathbf{r}')^2 \chi_L^2(\mathbf{r}') 2^{-1} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \int \chi_L^2(\mathbf{r}) \Big(\int g(\mathbf{r}-\mathbf{r}')^2 \chi_L^2(\mathbf{r}') \mathrm{d}\mathbf{r}' \Big) \mathrm{d}\mathbf{r} \\
&= \int \widehat{\chi_L^2}(\mathbf{p}) \widehat{g^2 * \chi_L^2}(\mathbf{p}) \mathrm{d}\mathbf{p} \\
&= (2\pi)^{3/2} \int \widehat{\chi_L^2}(\mathbf{p}) \widehat{g^2}(\mathbf{p}) \widehat{\chi_L^2}(\mathbf{p}) \mathrm{d}\mathbf{p} \\
&\leq (2\pi)^{3/2} \|\widehat{g^2}\|_\infty \int \widehat{\chi_L^2}(\mathbf{p}) \widehat{\chi_L^2}(\mathbf{p}) \mathrm{d}\mathbf{p} \\
&= (2\pi)^{3/2} \|\widehat{g^2}\|_\infty \int \chi_L^2(\mathbf{r}) \chi_L^2(\mathbf{r}) \mathrm{d}\mathbf{r} \quad (\textit{Plancherel theorem}) \\
&= (2\pi)^{3/2} \|\widehat{g^2}\|_\infty \int L^{-3} \chi^4(\mathbf{r}/L) \mathrm{d}\mathbf{r} \\
&= L^{-3} (2\pi)^{3/2} \|\widehat{g^2}\|_\infty \|\chi\|_4^4 \\
&= \mathcal{O}(L^{-3})
\end{aligned}
$$

since $\|\chi\|_4^4 = N$ and

$$
\widehat{g^2}(\mathbf{p}) = \frac{2^{5/2}}{\pi^{3/2}} \frac{1}{(4+|\mathbf{p}|^2)^2}
$$

as given before are bounded. This implies that $A_1 = \mathcal{O}(L^{-3})$ and $A_2 = \mathcal{O}(L^{-1})$. Then $\widehat{\mathcal{E}}^M(\gamma_\varepsilon) < \widehat{\mathcal{E}}^M(\gamma)$ follows naturally if we choose L large enough and ε being tiny. $\square$

7. Further Properties

Recall that

$$E^M(N) = \inf\{\mathcal{E}^M(\gamma)|0 \le \gamma \le 1, \text{tr } \gamma = N\}.$$

We will see in Proposition 7.1 that this energy $E^M(N)$ is closely related to $\widehat{E}^M_{\le}(N)$.

7.1. **Properties of the minimal energy.**

Proposition 7.1. *For any $Z > 0$ and $N > 0$ one has*

$$E^M(N) = \widehat{E}^M_{\le}(N) - N/8.$$

Proof. First, notice that

$$\begin{aligned}
\widehat{E}^M_{\le}(N) &= \inf\{\widehat{\mathcal{E}}^M(\gamma)|\ 0 \le \gamma \le 1, \text{tr } \gamma \le N\} \\
&= \inf\{\mathcal{E}^M(\gamma) + \frac{1}{8}\text{tr } \gamma|\ 0 \le \gamma \le 1, \text{tr } \gamma \le N\} \\
&\le \inf\{\mathcal{E}^M(\gamma) + \frac{1}{8}\text{tr } \gamma|\ 0 \le \gamma \le 1, \text{tr } \gamma = N\} \\
&= \inf\{\mathcal{E}^M(\gamma)|\ 0 \le \gamma \le 1, \text{tr } \gamma \le N\} + \frac{1}{8}N \\
&= E^M(N) + \frac{1}{8}N. \qquad (7.1)
\end{aligned}$$

Then let $\gamma' = \gamma + \delta\gamma$, such that $\delta > 0, \text{tr } \gamma = N, \text{tr } \gamma' = N'$. If we can show that

$$\mathcal{E}^M(\gamma') \ge \mathcal{E}^M(\gamma) - \frac{\delta N}{8}, \qquad (7.2)$$

then

$$\widehat{\mathcal{E}}^M(\gamma') \geq \mathcal{E}^M(\gamma) + \frac{N}{8}, \tag{7.3}$$

indeed,

$$\begin{aligned} \widehat{\mathcal{E}}^M(\gamma') &= \mathcal{E}^M(\gamma') + \frac{1}{8}\operatorname{tr}\gamma' \\ &\geq \mathcal{E}^M(\gamma) - \frac{\delta N}{8} + \frac{N}{8} + \frac{\delta N}{8} \\ &= \mathcal{E}^M(\gamma) + \frac{N}{8}. \end{aligned} \tag{7.4}$$

Since (7.3) should hold for all such γ' and γ, we have

$$\widehat{E}^M_{\leq}(N') \geq E^M(N) + \frac{1}{8}N. \tag{7.5}$$

Hence

$$E^M(N) + \frac{1}{8}N \leq \widehat{E}^M_{\leq}(N') \leq E^M(N') + \frac{1}{8}N',$$

i.e.,

$$E^M(N) + \frac{1}{8}N \leq \widehat{E}^M_{\leq}(N+\delta N) \leq E^M(N+\delta N) + \frac{1}{8}N + \frac{\delta}{8}N.$$

Let $\delta N \to 0$, we conclude that $\widehat{E}^M_{\leq}(N) = E^M(N) + \frac{1}{8}N$.

Now it remains to show that (7.2) holds. Insert $\gamma' = \gamma + \delta\gamma$ into the Müller energy functional and expand explicitly, we have

$$\mathcal{E}^M(\gamma') = \mathcal{E}^M(\gamma) + \delta\Big[\frac{1}{2}\operatorname{tr}(-\nabla^2\gamma) + D(\rho_\gamma,\rho_\gamma) - X(\gamma^{1/2})\Big] + \delta^2 D(\rho_\gamma,\rho_\gamma). \tag{7.6}$$

With (4.3) and Lemma 9.1, one can conclude that

$$\mathcal{E}^M(\gamma') \geq \mathcal{E}^M(\gamma) - \frac{\delta N}{8}.$$

□

Proposition 7.2. *For any* $Z > 0$*, the energies* $\widehat{E}^M_{\leq}(N)$ *and* $E^M(N)$ *are convex functions of* N*. They are strictly convex for* $0 < N \leq Z$*.*

Proof. By Proposition 7.1 it suffices to consider $\widehat{E}^M_{\leq}(N)$. Let $N = \lambda N_1 + \mu N_2$ where $\lambda + \mu = 1, N_1 < N < N_2 \leq Z$. That $\widehat{E}^M_{\leq}(N)$ are convex functions of N means that $\widehat{E}^M_{\leq}(N) \leq \lambda \widehat{E}^M_{\leq}(N_1) + \mu \widehat{E}^M_{\leq}(N_2)$, i.e.,

$$\inf\{\widehat{\mathcal{E}}^M(\gamma); \mathrm{tr}\ \gamma \leq N\} \leq \lambda \inf\{\widehat{\mathcal{E}}^M(\gamma); \mathrm{tr}\ \gamma \leq N_1\} + \mu \inf\{\widehat{\mathcal{E}}^M(\gamma); \mathrm{tr}\ \gamma \leq N_2\}. \tag{7.7}$$

If γ_1, γ_2 are the minimizer of $\widehat{E}^M(N_1)$ and $\widehat{E}^M(N_2)$ respectively, write $\gamma = \lambda\gamma_1 + \mu\gamma_2$, then $\mathrm{tr}\ \gamma = N$, but γ is not necessarily a minimizer of $\widehat{E}^M(N)$. However, in Section 9.3 we have proved that $\mathcal{E}^M(\gamma)$ is a convex functional of γ:

$$\mathcal{E}^M(\gamma) \leq \lambda \mathcal{E}^M(\gamma_1) + \mu \mathcal{E}^M(\gamma_2),$$

thus we have

$$\widehat{\mathcal{E}}^M(\gamma) \leq \lambda \widehat{\mathcal{E}}^M(\gamma_1) + \mu \widehat{\mathcal{E}}^M(\gamma_2),$$

and it follows that

$$\begin{aligned} \widehat{E}^M_{\leq}(N) = \widehat{E}^M(N) \leq \widehat{\mathcal{E}}^M(\gamma) &\leq \lambda \widehat{E}^M(N_1) + \mu \widehat{E}^M(N_2) \\ &= \lambda \widehat{E}^M_{\leq}(N_1) + \mu \widehat{E}^M_{\leq}(N_2). \end{aligned}$$

It gives the convexity of $\widehat{E}^M_{\leq}(\gamma)$.

To see the strict convexity we consider the minimizers γ_1 and γ_2 which have different traces due to the theorem 3.4. We claim the densities ρ_{γ_1} and ρ_{γ_2} are different.

In fact, if $\rho_{\gamma_1}(\mathbf{r}) = \rho_{\gamma_2}(\mathbf{r})$, i.e.,

$$\sum_{\sigma} \gamma_1(\mathbf{x}, \mathbf{x}) = \sum_{\sigma} \gamma_2(\mathbf{x}, \mathbf{x}),$$

then

$$\text{tr } \gamma_1 = \int \gamma_1(\mathbf{x}, \mathbf{x}) \mathrm{d}\mathbf{x} = \int \gamma_2(\mathbf{x}, \mathbf{x}) \mathrm{d}\mathbf{x} = \text{tr } \gamma_2,$$

this ruins the condition that tr $\gamma_1 \neq$ tr γ_2. Hence by the positive properties of the Coulomb energy ([24, Theorem 9..8]) we conclude that

$$D(\lambda\rho_{\gamma_1} + \mu\rho_{\gamma_2}, \lambda\rho_{\gamma_1} + \mu\rho_{\gamma_2}) < \lambda D(\rho_{\gamma_1}, \rho_{\gamma_1}) + \mu D(\rho_{\gamma_2}, \rho_{\gamma_2}).$$

This leads to

$$\widehat{E}^M_{\leq}(N) = \widehat{E}^M(N) < \lambda \widehat{E}^M_{\leq}(N_1) + \mu \widehat{E}^M_{\leq}(N_2).$$

□

In Theorem 3.3 we have conclude that the energy $\widehat{E}^M_{\leq}(N) < 0$ for all $N > 0, Z > 0$. Now we will show in the following proposition that the energy is bounded from below uniformly in N for fixed Z.

Proposition 7.3. *There is a constant $C > 0$ such that for all $Z > 0$ and $N > 0$, $\widehat{E}^M_{\leq}(N) \geq -CZ^3$.*

Proof. First, we consider the atomic case with a nucleus of charge Z located at the origin $\mathbf{R} = 0$.

Recall the formulas:

$$\widehat{\mathcal{E}}^M(\gamma) = \mathcal{E}^M(\gamma) + \frac{1}{8}\operatorname{tr}\gamma,$$

$$\mathcal{E}^M(\gamma) = \frac{1}{2}\operatorname{tr}(-\nabla^2\gamma) - \int_{\mathbb{R}^3}\frac{Z\rho_\gamma(\mathbf{r})}{|\mathbf{r}-\mathbf{R_j}|}\mathrm{d}\mathbf{r} + D(\rho_\gamma,\rho_\gamma) - \frac{1}{2}\iint\frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}',$$

$$\gamma(\mathbf{x},\mathbf{x}) = \int|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}'.$$

And let $\psi(\mathbf{x},\mathbf{x}') = \gamma^{1/2}(\mathbf{x},\mathbf{x}')$ in $L^2(\mathbb{R}^6)$. We are going to check several facts below.

Fact 1 (Symmetry)

$$\widehat{\mathcal{E}}^M(\gamma) = \frac{1}{2}\langle\psi| - \frac{1}{2}\nabla^2_{\mathbf{r}} - \frac{1}{2}\nabla^2_{\mathbf{r}'} - \frac{Z}{|\mathbf{r}|} - \frac{Z}{|\mathbf{r}'|} - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4}|\psi\rangle + D(\rho_\gamma,\rho_\gamma). \tag{7.8}$$

Verification. Firstly, consider about the kinetic energy:

$$\begin{aligned}
\operatorname{tr}(-\nabla^2_{\mathbf{r}}\gamma) &= \frac{1}{2}\big(\operatorname{tr}(-\nabla^2_{\mathbf{r}}\gamma) + \operatorname{tr}(-\nabla^2_{\mathbf{r}'}\gamma)\big)\\
&= \frac{1}{2}\Big(\iint(-\nabla^2_{\mathbf{r}}\gamma)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \iint(-\nabla^2_{\mathbf{r}'}\gamma)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\Big)\\
&= \frac{1}{2}\Big(\iint(-\nabla^2_{\mathbf{r}}|\psi|^2)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' + \iint(-\nabla^2_{\mathbf{r}'}|\psi|^2)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\Big)\\
&= \langle\psi| - \frac{1}{2}\nabla^2_{\mathbf{r}}|\psi\rangle + \langle\psi| - \frac{1}{2}\nabla^2_{\mathbf{r}'}|\psi\rangle.
\end{aligned}$$

Then for the attraction term

$$\begin{aligned}\frac{1}{2}\int_{\mathbb{R}^3}\frac{Z\rho_\gamma(\mathbf{r})}{|\mathbf{r}|}\mathrm{d}\mathbf{x} &= \frac{1}{2}\int_{\mathbb{R}^3}\frac{Z}{|\mathbf{r}|}\gamma(\mathbf{x},\mathbf{x}')\mathrm{d}\mathbf{x}\\ &= \frac{1}{2}\int_{\mathbb{R}^3}\frac{Z}{|\mathbf{r}|}\left(\int_{\mathbb{R}^3}|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}'\right)\mathrm{d}\mathbf{x}\\ &= \frac{1}{2}\iint\frac{Z|\psi(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}|}\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{x}\\ &= \frac{1}{2}\langle\psi|\frac{Z}{|\mathbf{r}|}|\psi\rangle.\end{aligned}$$

Moreover, we have

$$\frac{1}{2}\iint\frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' = \frac{1}{2}\langle\psi|\frac{1}{|\mathbf{r}-\mathbf{r}'|}|\psi\rangle.$$

At last the assertion follows immediately. □

Fact 2. (Positive Definiteness)

$$D(\rho_\gamma,\rho_\gamma)+D(\sigma_Z,\sigma_Z)\geq 2D(\rho_\gamma,\sigma_Z) \tag{7.9}$$

for any σ_Z.

Verification. We use the positive definiteness of the Coulomb kernel.

$$\begin{aligned}D(\rho_\gamma,\rho_\gamma)+D(\sigma_Z,\sigma_Z)-2D(\rho_\gamma,\sigma_Z) &= \frac{1}{2}\iint\frac{(\rho_\gamma+\sigma_Z)(\mathbf{r})(\rho_\gamma+\sigma_Z)(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\ &= D(\rho_\gamma+\sigma_Z,\rho_\gamma+\sigma_Z)\geq 0 \quad \Box\end{aligned}$$

Fact 3.

$$D(\rho_\gamma,\sigma_Z)=\frac{1}{2}\langle\psi|\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'|\psi\rangle. \tag{7.10}$$

Verification. Direct calculation leads to the assertion.

$$\begin{aligned}
\frac{1}{2}\langle\psi|\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'|\psi\rangle &= \frac{1}{2}\iint|\psi(\mathbf{x},\mathbf{x}')|^2\Big(\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \\
&= \frac{1}{2}\int\Big(\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\Big)\Big(\int|\psi(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}'\Big)\mathrm{d}\mathbf{x} \\
&= \frac{1}{2}\int\Big(\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\Big)\gamma(\mathbf{x},\mathbf{x})\mathrm{d}\mathbf{x} \\
&= \frac{1}{2}\int\Big(\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\Big)\Sigma_\sigma\gamma(\mathbf{r},\mathbf{r})\mathrm{d}\mathbf{r} \\
&= \frac{1}{2}\iint\frac{\sigma_Z(\mathbf{r}')\rho_\gamma(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r} \\
&= D(\rho_\gamma,\sigma_Z). \qquad \square
\end{aligned}$$

From Facts (7.8)-(7.10) we conclude that

$$\begin{aligned}
\widehat{\mathcal{E}}^M(\gamma) &= \frac{1}{2}\langle\psi|-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{1}{2}\nabla_{\mathbf{r}'}^2-\frac{Z}{|\mathbf{r}|}-\frac{Z}{|\mathbf{r}'|}-\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{4}|\psi\rangle+D(\rho_\gamma,\rho_\gamma) \\
&\geq \frac{1}{2}\langle\psi|-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{1}{2}\nabla_{\mathbf{r}'}^2-\frac{Z}{|\mathbf{r}|}-\frac{Z}{|\mathbf{r}'|}-\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{4}|\psi\rangle+2D(\rho_\gamma,\sigma_Z) \\
&\quad -D(\sigma_Z,\sigma_Z) \\
&= \frac{1}{2}\langle\psi|-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{1}{2}\nabla_{\mathbf{r}'}^2-\frac{Z}{|\mathbf{r}|}+\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'-\frac{Z}{|\mathbf{r}'|}+\int\frac{\sigma_Z(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r} \\
&\quad -\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{4}|\psi\rangle-D(\sigma_Z,\sigma_Z) \\
&= \frac{1}{2}\langle\psi|-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{1}{2}\nabla_{\mathbf{r}'}^2-V_Z(\mathbf{r})-V_Z(\mathbf{r}')-\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{4}|\psi\rangle-D(\sigma_Z,\sigma_Z)
\end{aligned}$$

where

$$V_Z(\mathbf{r})=\frac{Z}{|\mathbf{r}|}-\int\frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'.$$

We shall choose σ_Z in such a way that

$$-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{1}{2}\nabla_{\mathbf{r}'}^2-V_Z(\mathbf{r})-V_Z(\mathbf{r}')-\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{4}\geq 0,$$

and this leads to

$$\widehat{\mathcal{E}}^M(\gamma) \geq -D(\sigma_Z, \sigma_Z).$$

In this case we shall choose σ_Z of the form

$$\sigma_Z(\mathbf{r}) = Z^4\sigma(Z\mathbf{r})$$

for some fixed σ, which yields $D(\sigma_Z, \sigma_Z) = Z^3 D(\sigma, \sigma)$:

$$\begin{aligned} D(\sigma_Z, \sigma_Z) &= \frac{1}{2}\iint \frac{\sigma_Z(\mathbf{r})\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \frac{1}{2}\iint \frac{Z^4\sigma(Z\mathbf{r})Z^4\sigma(Z\mathbf{r})Z}{Z|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \frac{1}{2}\iint \frac{Z^3\sigma(Z\mathbf{r})\sigma(Z\mathbf{r})}{|Z\mathbf{r}-Z\mathbf{r}'|}\mathrm{d}(Z\mathbf{r})\mathrm{d}(Z\mathbf{r}') \\ &= Z^3 D(\sigma, \sigma). \end{aligned}$$

To prove that

$$-\frac{1}{2}\nabla^2_{\mathbf{r}} - \frac{1}{2}\nabla^2_{\mathbf{r}'} - V_Z(\mathbf{r}) - V_Z(\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4} \geq 0,$$

we make an orthogonal change of variables:

$$\begin{pmatrix} \mathbf{s} \\ \mathbf{t} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \mathbf{r} \\ \mathbf{r}' \end{pmatrix} \, or \, \begin{cases} \mathbf{s} = \frac{\mathbf{r}-\mathbf{r}'}{\sqrt{2}} \\ \mathbf{t} = \frac{\mathbf{r}+\mathbf{r}'}{\sqrt{2}} \end{cases}$$

Then

$$\begin{aligned}
& -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2}\nabla_{\mathbf{r}'}^2 - V_Z(\mathbf{r}) - V_Z(\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4} \\
= & -\frac{1}{4}\nabla_{\mathbf{s}}^2 - \frac{1}{2}\nabla_{\mathbf{st}} - \frac{1}{4}\nabla_{\mathbf{t}}^2 - \frac{1}{4}\nabla_{\mathbf{s}}^2 + \frac{1}{2}\nabla_{\mathbf{st}} - \frac{1}{4}\nabla_{\mathbf{t}}^2 \\
& -V_Z(\frac{\mathbf{s}+\mathbf{t}}{\sqrt{2}}) - V_Z(\frac{\mathbf{t}-\mathbf{s}}{\sqrt{2}}) - \frac{1}{\sqrt{2}|\mathbf{s}|} + \frac{1}{4} \\
= & \Big(-\frac{1}{2}\nabla_{\mathbf{ss}} - \frac{1}{\sqrt{2}|\mathbf{s}|} + \frac{1}{4}\Big) + \frac{1}{4}\Big(-\nabla_{\mathbf{tt}} - 4V_Z(\frac{\mathbf{s}+\mathbf{t}}{\sqrt{2}})\Big) \\
& +\frac{1}{4}\Big(-\nabla_{\mathbf{tt}} - 4V_Z(\frac{\mathbf{t}-\mathbf{s}}{\sqrt{2}})\Big).
\end{aligned}$$

Recall the ground state energy of the hydrogen atom (see (4.2)): $-\nabla^2 - \frac{z}{|\mathbf{r}|} + \frac{z^2}{4} \geq 0$, from which it follows that $\Big(-\frac{1}{2}\nabla_{\mathbf{ss}} - \frac{1}{\sqrt{2}|\mathbf{s}|} + \frac{1}{4}\Big) \geq 0$. Hence it suffices to choose σ such that the operator

$$-\nabla_{\mathbf{tt}} - 4V_Z(\frac{\mathbf{t}+\mathbf{a}}{\sqrt{2}}) \geq 0 \tag{7.11}$$

for any $\mathbf{a} \in \mathbb{R}^3$. Note that with $V(\mathbf{r}) = \frac{1}{|\mathbf{r}|} - \int \frac{\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'$ we deduce that

$$V_Z(\mathbf{r}) = \frac{Z}{|\mathbf{r}|} - \int \frac{\sigma_Z(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' = \frac{Z^2}{|Z\mathbf{r}|} - Z^2\int \frac{\sigma(Z\mathbf{r}')}{|Z\mathbf{r}-Z\mathbf{r}'|}\mathrm{d}(Z\mathbf{r}') = Z^2V(Z\mathbf{r}).$$

Let $\xi = \frac{Z(\mathbf{t}+\mathbf{a})}{\sqrt{2}}$, then $\nabla_{\mathbf{t}} = \nabla_{\xi}\cdot\frac{Z}{\sqrt{2}}$, $\nabla_{\mathbf{tt}} = \nabla_{\xi\xi}\cdot\frac{Z^2}{2}$. Thus if (7.11) holds,

$$0 \leq -\nabla_{\mathbf{tt}} - 4V_Z(\frac{\mathbf{t}+\mathbf{a}}{\sqrt{2}}) = -\nabla_{\mathbf{tt}} - 4Z^2V(\frac{Z(\mathbf{t}+\mathbf{a})}{\sqrt{2}}) = -\nabla_{\xi\xi}\cdot\frac{Z^2}{2} - 4Z^2V(\xi),$$

Therefore what remains to be proved is that $-\nabla_{\xi\xi} - 8V(\xi) \geq 0$. For this purpose we choose σ a non-negative, spherically symmetric function with $\int \sigma(\mathbf{r})\mathrm{d}\mathbf{r} = 1$ and with support in $\{|\mathbf{r}| \leq 1/32\}$. By Theorem 9.7(in "Analysis" written by Lieb & Loss), we have $V(\mathbf{r}) = 0$ for $|\mathbf{r}| \geq 1/32$, and for $|\mathbf{r}| \leq 1/32$ one has $8V(\mathbf{r}) \leq 1/(4|\mathbf{r}|^2)$. Next I shall apply the so-called Newton's Theorem.

First we see that

$$\begin{aligned} V(\mathbf{r}) &= |\mathbf{r}|^{-1} - \int |\mathbf{r}-\mathbf{r}'|^{-1}\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \int (|\mathbf{r}|^{-1} - |\mathbf{r}-\mathbf{r}'|^{-1})\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \int (\frac{|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|}{|\mathbf{r}||\mathbf{r}-\mathbf{r}'|})\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}'. \end{aligned} \tag{7.12}$$

Let μ_+, μ_-be the positive measures on $\mathbb{R}^3$ such that

$$\mathrm{d}\mu_+ = \frac{\mathbf{1} + |\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|}{2}\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}', \tag{7.13}$$

$$\mathrm{d}\mu_- = \frac{-\mathbf{1} + |\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|}{2}\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}'. \tag{7.14}$$

Then

$$\mathrm{d}\mu = \mathrm{d}\mu_+ - \mathrm{d}\mu_- = \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}',$$

$$\mathrm{d}\nu = \mathrm{d}\mu_+ + \mathrm{d}\mu_- = (|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|)\sigma(\mathbf{r}')\mathrm{d}\mathbf{r}'.$$

Hence when $|\mathbf{r}| \geq 1/32$, by the Newton theorem [24, Theorem 9.7],

$$V(\mathbf{r}) = \int \left(\frac{|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|}{|\mathbf{r}||\mathbf{r}-\mathbf{r}'|}\sigma(\mathbf{r}')\right)\mathrm{d}\mathbf{r}' = 0 \cdot \int \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}'.$$

For $|\mathbf{r}| < 1/32$, however,

$$\begin{aligned} V(\mathbf{r}) &= \int \left(\frac{|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}|}{|\mathbf{r}||\mathbf{r}-\mathbf{r}'|} \right) \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \int \frac{1}{|\mathbf{r}||\mathbf{r}-\mathbf{r}'|} \Big(|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}| \Big) \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \int \frac{1}{|\mathbf{r}||\mathbf{r}-\mathbf{r}'|} \mathrm{d}\nu \\ &\le \frac{1}{|\mathbf{r}|^2} \int \Big(|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}| \Big) \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &\le \frac{1}{|\mathbf{r}|^2} \cdot \frac{1}{32} \int \sigma(\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \frac{1}{32|\mathbf{r}|^2}. \end{aligned}$$

with an observation that $|\mathbf{r}-\mathbf{r}'| - |\mathbf{r}| \le 1/32$ when both $\mathbf{r}$ and $\mathbf{r}'$ are inside the ball with radius $1/32$. Consequently, by the Hardy's inequality (see Lemma 9.6)

$$-\nabla^2 \ge \frac{1}{4|\mathbf{r}|^2},$$

we conclude that $-\nabla_{\xi\xi} - 8V(\xi) \ge 0$. This completes the proof in the atomic case.

In the molecular case we recall that we are not taking into account the nuclear repulsion U, which is fixed, and this means that we freely locate the nuclei so that minimizing the energy $\widehat{E}^M(N)$. We assert that the best choice of the R_j is one in which they are all equal and, by translation invariance, this common point can be the origin. The problem thus reduces to the atomic case with a nucleus whose charge is the total charge Z. □

7.2. **Properties of the Minimizer.**

Proposition 7.4. *Let* γ *be a minimizer of*

$$\widehat{E}^M_{\leq} = \inf_{\gamma}\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \text{tr}\ \gamma \leq N\}$$

and let $M_\gamma = \{\mathbf{r} : \rho_\gamma(\mathbf{r}) > 0\}$. *Then the null-space of the spin-summed density matrix,* $\mathcal{N}(\text{tr}_\sigma \gamma)$, *coincides with the set of* $L^2(\mathbb{R}^3)$ *functions that vanish identically on* $M_{\mathbf{r}}$.

Proof. Write $\rho_\gamma(\mathbf{r}) = \Sigma_\sigma \gamma(\mathbf{r}, \sigma; \mathbf{r}, \sigma) = \Sigma_\sigma \Sigma_j \lambda_j \psi(\mathbf{r})\psi(\mathbf{r})^*$ and $(\text{tr}_\sigma \gamma)(\mathbf{r}, \mathbf{r}') = \Sigma_\sigma \Sigma_j \lambda_j \psi_j(\mathbf{r})\psi_j(\mathbf{r}')^*$ with $\psi_j(\mathbf{r})$ orthonormal and $0 < \lambda_j \leq q$. And we can see $\mathbb{R}^3 \setminus M_\gamma = \cap_j \{\mathbf{r} : \psi_j(\mathbf{r}) = 0\}$. These reveal another explanation of this proposition that if $\text{tr}_\sigma \gamma$ has a zero eigenvalue then the eigenfunction vanishes wherever the density ρ_γ is non-zero. Meanwhile, if $\rho_\gamma > 0$ almost everywhere then the so-called eigenfunction vanishes almost everywhere in $\mathbb{R}^3$, so 0 could not be an eigenvalue of the spin-summed density matrix $\text{tr}_\sigma \gamma$. Now we prove the proposition. If $\varphi = 0$ a.e. on M_γ then

$$\begin{aligned}(\text{tr}_\sigma \gamma)\varphi &= \int \Sigma_j \lambda_j \psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* \varphi(\mathbf{r}')\text{d}\mathbf{r}' \\ &= \int_{M_\gamma} \Sigma_j \lambda_j \psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* \varphi(\mathbf{r}')\text{d}\mathbf{r}' + \int_{\mathbb{R}^3 \setminus M_\gamma} \Sigma_j \lambda_j \psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* \varphi(\mathbf{r}')\text{d}\mathbf{r}' \\ &\equiv 0.\end{aligned}$$

Conversely, let $\varphi \in \mathcal{N}(\text{tr}_\sigma \gamma)$, That is

$$(\text{tr}_\sigma \gamma)\varphi = \int \Sigma_j \lambda_j \psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* \varphi(\mathbf{r}')\text{d}\mathbf{r}' \equiv 0.$$

Thus $\psi_j \perp \varphi$. Moreover, $(|\varphi\rangle\langle\varphi|) \perp (|\psi_j\rangle\langle\psi_j|)$. We conclude from this that

$$\mathrm{tr}\,(|\varphi\rangle\langle\varphi| - |\psi_j\rangle\langle\psi_j|) = \mathrm{tr}\,(|\varphi\rangle\langle\varphi|) - \mathrm{tr}\,(|\psi_j\rangle\langle\psi_j|) = 1 - 1 = 0$$

Then consider

$$\begin{aligned}
\gamma_\varepsilon &= \mathrm{tr}_\sigma\,\gamma + \varepsilon(|\varphi\rangle\langle\varphi| - |\psi_1\rangle\langle\psi_1|) \\
&= \Sigma_{j=1}^{\infty}\lambda_j\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* + \varepsilon\varphi(\mathbf{r})\varphi(\mathbf{r}')^* - \varepsilon\psi_1(\mathbf{r})\psi_1(\mathbf{r}')^* \\
&= \Sigma_{j=2}^{\infty}\lambda_j\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* + \varepsilon\varphi(\mathbf{r})\varphi(\mathbf{r}')^* + (\lambda_1 - \varepsilon)\psi_1(\mathbf{r})\psi_1(\mathbf{r}')^* \\
.
\end{aligned}$$

One has tr $\gamma_\varepsilon =$ tr $\gamma \leq N, 0 \leq \gamma_\varepsilon \leq 1$ for $0 \leq \varepsilon \leq \lambda_1$. And

$$\begin{aligned}
\gamma_\varepsilon^{1/2} &= \Sigma_{j=2}^{\infty}\sqrt{\lambda_j}\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* + \sqrt{\varepsilon}\varphi(\mathbf{r})\varphi(\mathbf{r}')^* + \sqrt{\lambda_1 - \varepsilon}\psi_1(\mathbf{r})\psi_1(\mathbf{r}')^* \\
&= \Sigma_{j=1}^{\infty}\sqrt{\lambda_j}\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* + \sqrt{\varepsilon}\varphi(\mathbf{r})\varphi(\mathbf{r}')^* + (\sqrt{\lambda_1 - \varepsilon} - \sqrt{\lambda_1})\psi_1(\mathbf{r})\psi_1(\mathbf{r}')^* \\
&= (\mathrm{tr}_\sigma\,\gamma)^{1/2} + \sqrt{\varepsilon}|\varphi\rangle\langle\varphi| + \big(\sqrt{\lambda_1 - \varepsilon} - \sqrt{\lambda_1}\big)|\psi_1\rangle\langle\psi_1|.
\end{aligned}$$

It follows from convexity that minimizing $\widehat{\mathcal{E}}^M$ for density matrices $0 \leq \gamma \leq 1$ with q spin states is equivalent to minimizing under the condition

$0 \le \gamma \le q$ without spin. We calculate directly as follows:

$$
\begin{aligned}
&\operatorname{tr}(-\nabla_{\mathbf{r}}^2\gamma_\varepsilon)\\
&= \iint (-\nabla_{\mathbf{r}}^2\gamma_\varepsilon)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \int (-\nabla_{\mathbf{r}}^2)\Big(\int \big(\Sigma_{j=1}^{\infty}\lambda_j\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^* + \varepsilon\varphi(\mathbf{r})\varphi(\mathbf{r}')^* - \varepsilon\psi_1(\mathbf{r})\psi_1(\mathbf{r}')^*\big)\mathrm{d}\mathbf{r}'\Big)\mathrm{d}\mathbf{r}\\
&= \operatorname{tr}(-\nabla_{\mathbf{r}}^2\gamma) - \varepsilon\iint \big(\varphi''(\mathbf{r})\varphi(\mathbf{r}')^* - \psi_1''(\mathbf{r})\psi_1(\mathbf{r}')^*\big)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \operatorname{tr}(-\nabla_{\mathbf{r}}^2\gamma) + \mathcal{O}(\varepsilon),
\end{aligned}
$$

since $\varphi, \psi_1 \in L^2$.

$$
\begin{aligned}
&\int V_c(\mathbf{r})\rho_{\gamma_\varepsilon}(\mathbf{r})\mathrm{d}\mathbf{r}\\
&= \int V_c \int \gamma_\varepsilon(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}\\
&= \int V_c\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + \varepsilon\iint V_c\big(\varphi(\mathbf{r})\varphi(\mathbf{r}')^* - \psi_1(\mathbf{r})\psi_1(\mathbf{r}')^*\big)\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}\\
&= \int V_c\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + \mathcal{O}(\varepsilon).
\end{aligned}
$$

$$
\begin{aligned}
&D(\rho_{\gamma_\varepsilon}, \rho_{\gamma_\varepsilon})\\
&= \frac{1}{2}\iint \frac{\rho_{\gamma_\varepsilon}(\mathbf{r})\rho_{\gamma_\varepsilon}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \frac{1}{2}\iint \frac{\gamma_\varepsilon(\mathbf{r},\mathbf{r})\gamma_\varepsilon(\mathbf{r}',\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}\Big\{\int \big(\operatorname{tr}_\sigma \gamma(\mathbf{r},\mathbf{r}') + \varepsilon(|\varphi\rangle\langle\varphi| - |\psi_1\rangle\langle\psi_1|)\big)\mathrm{d}\mathbf{r}'\Big\}\\
&\qquad \Big\{\int \big(\operatorname{tr}_\sigma \gamma(\mathbf{r},\mathbf{r}') + \varepsilon(|\varphi\rangle\langle\varphi| - |\psi_1\rangle\langle\psi_1|)\big)\mathrm{d}\mathbf{r}\Big\}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' + \mathcal{O}(\varepsilon).
\end{aligned}
$$

For exchange energy, we have

$$
\begin{aligned}
&X(\gamma_\varepsilon^{1/2})\\
&= \frac{1}{2}\iint \frac{|\gamma_\varepsilon^{1/2}|^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}\Big\{(\mathrm{tr}_\sigma\,\gamma)+\varepsilon(|\varphi\rangle\langle\varphi|)^2+(2\lambda_1-\varepsilon-2\sqrt{\lambda_1^2-\varepsilon\lambda_1})(|\psi\rangle\langle\psi|)^2\\
&\quad +2(\mathrm{tr}_\sigma\,\gamma)^{1/2}(\sqrt{\lambda_1-\varepsilon}-\sqrt{\lambda_1})|\psi\rangle\langle\psi|+2\sqrt{\varepsilon}|\varphi\rangle\langle\varphi|(\mathrm{tr}_\sigma\,\gamma)^{1/2}\Big\}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\
&= \frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}(\mathrm{tr}_\sigma\,\gamma)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'+\frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}2\sqrt{\varepsilon}|\varphi\rangle\langle\varphi|(\mathrm{tr}_\sigma\,\gamma)^{1/2}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'+\mathcal{O}(\varepsilon)\\
&= \frac{1}{2}\iint |\mathbf{r}-\mathbf{r}'|^{-1}(\gamma^{1/2})^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'+\sqrt{\varepsilon}\iint |\mathbf{r}-\mathbf{r}'|^{-1}|\varphi\rangle\langle\varphi|\gamma^{1/2}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'+\mathcal{O}(\varepsilon)
\end{aligned}
$$

Hence we conclude that

$$E_{\leq}^{M}(N)\leq\widehat{\mathcal{E}}^{M}(\gamma_\varepsilon)=\widehat{\mathcal{E}}^{M}(\gamma)-\sqrt{\varepsilon}C(\varphi)+\mathcal{O}(\varepsilon),$$

where

$$
\begin{aligned}
C(\varphi) &= \iint |\mathbf{r}-\mathbf{r}'|^{-1}|\varphi\rangle\langle\varphi|\gamma^{1/2}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\
&= \iint \frac{\varphi(\mathbf{r})^*\Sigma_j\sqrt{\lambda_j}\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^*\varphi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\
&= \Sigma_j\sqrt{\lambda_j}\iint \frac{\varphi(\mathbf{r})^*\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^*\varphi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\
&\geq 0.
\end{aligned}
$$

Since γ is a minimizer, one has $C(\varphi)=0$, which by the positive definiteness of the Coulomb kernel means $\varphi\psi_j^*=0$ a.e.for all j. It follows that $\varphi=0$ a.e. on M_γ. □

At the other end of the spectrum of γ, we comment on the eigenvalue 1 of the minimizer. Consider the minimization problem

$$\widehat{E}_{\leq}^{boson} = \inf\{\widehat{\mathcal{E}}^M(\gamma) : \gamma \geq 0, \mathrm{tr}\ \gamma \leq N\}.$$

This energy can be interpreted as the ground state energy of N bosons in the Müller model. Clearly, $\widehat{E}_{\leq}^{boson} \leq \widehat{E}_{\leq}^{M}$ with equality for $N \leq 1$. This is because tr $\gamma = \Sigma_j \langle \psi_j, \gamma\psi_j \rangle \leq 1$ with $\Sigma_j \langle \psi_j, \psi_j \rangle = 1$ leading to $\|\gamma\| \leq 1$. We will see in the next proposition, however, for the large valued of N, they are different values.

Proposition 7.5. *Assume that $\widehat{E}_{\leq}^{boson}(N) < \widehat{E}_{\leq}^{M}(N)$ for some N and Z. Then any minimizer γ of $\widehat{E}_{\leq}^{M} = \inf_\gamma\{\widehat{\mathcal{E}}^M(\gamma) : 0 \leq \gamma \leq 1, \mathrm{tr}\ \gamma \leq N\}$ has at least one eigenvalue 1.*

Proof. Assume that $\gamma < 1$. Let γ_b denote a minimizer for $\widehat{E}_{\leq}^{boson}(N)$. Then

$$\gamma_\varepsilon = (1-\varepsilon)\gamma + \varepsilon\gamma_b$$

satisfies tr $\gamma_\varepsilon \leq N$ and $0 \leq \gamma_\varepsilon \leq 1$ for sufficiently small $\varepsilon > 0$. Moreover, by the convexity of $\widehat{\mathcal{E}}^M(\gamma)$ with respect to (Section 9.3),

$$\begin{aligned} \widehat{\mathcal{E}}^M(\gamma_\varepsilon) &\leq (1-\varepsilon)\widehat{\mathcal{E}}^M(\gamma) + \varepsilon\widehat{\mathcal{E}}^M(\gamma_b) \\ &= (1-\varepsilon)\widehat{E}_{\leq}^{M}(N) + \varepsilon\widehat{E}_{\leq}^{boson}(N) \\ &< \widehat{E}_{\leq}^{M}(N) \end{aligned}$$

contradicting the fact that γ is a minimizer. □

7.3. **Virial Theorem.**

Proposition 7.6. *(Virial Theorem)Let $K = 1$(i.e., consider an atom) and let γ be a minimizer for $\widehat{E}^M_\leq(N)$. Then*

$$2\,\mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma) = \mathrm{tr}\,(\frac{Z}{|\mathbf{r}|}\gamma) - D(\rho_\gamma, \rho_\gamma) + X(\gamma^{1/2}).$$

Proof. For any $\lambda > 0$ the density matrix γ_λ defined by

$$\gamma_\lambda(\mathbf{x}, \mathbf{x}') = \lambda^3\gamma(\lambda\mathbf{r}, \sigma; \lambda\mathbf{r}', \sigma')$$

is unitarily equivalent to γ, i.e., $\|\gamma\| = \|\gamma_\lambda\|$, and hence satisfies $0 \leq \gamma_\lambda \leq 1$ and $\mathrm{tr}\ \gamma_\lambda = \mathrm{tr}\ \gamma \leq N$. Therefore, the functional

$$\begin{aligned}\widehat{\mathcal{E}}^M(\gamma_\lambda) &= \mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma_\lambda) - \mathrm{tr}\,(Z|\mathbf{r}|^{-1}\gamma_\lambda) + \frac{1}{8}\,\mathrm{tr}\ \gamma_\lambda + D(\rho_{\gamma_\lambda}, \rho_{\gamma_\lambda}) - X(\gamma_\lambda^{1/2}) \\ &= \lambda^2\,\mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma) - \lambda\,\mathrm{tr}\,(Z|\mathbf{r}|^{-1}\gamma) + \frac{1}{8}\,\mathrm{tr}\ \gamma + \lambda D(\rho_\gamma, \rho_\gamma) - \lambda X(\gamma^{1/2})\end{aligned}$$

has a minimum at $\lambda = 1$ whence γ is a minimizer for $\widehat{E}^M_\leq(N)$. So differentiate the functional above with respect to λ:

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\widehat{\mathcal{E}}^M(\gamma_\lambda)\bigg|_{\lambda=1} = 2\,\mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma) - \mathrm{tr}\,(Z|\mathbf{r}|^{-1}\gamma) + D(\rho_\gamma, \rho_\gamma) - X(\gamma^{1/2}) = 0.$$

The assertion follows immediately. □

8. The Müller's functional as a lower bound to quantum mechanics

We are going to show in this section that the Müller energy $E^M(N)$ without the addition of N/8 is a lower bound to the true Schrödinger energy when $N = 2$, with arbitrarily many nuclei.

Consider the N-particle Hamiltonian

$$H = \Sigma_j(-\frac{1}{2}\nabla_j^2 - V_c(\mathbf{r}_j)) + R$$

in either the symmetric or the anti-symmetric N-fold tensor product of $L^2(\mathbb{R}^3, \mathbb{C}^q)$, where $V_c(\mathbf{r}) = \Sigma_{i=1}^K \frac{Z_i}{|\mathbf{r}-\mathbf{R_i}|}$ and $R = \Sigma_{1\leq i<j\leq N}|\mathbf{r_i} - \mathbf{r_j}|^{-1}$. We recall that the one particle density matrix γ_ψ for a symmetric or the anti-symmetric ψ is defined by

$$\gamma_\psi(\mathbf{x}, \mathbf{x}') = N\int \psi(\mathbf{x}, \mathbf{x_2}, ..., \mathbf{x_N})\psi(\mathbf{x}', \mathbf{x_2}, ..., \mathbf{x_N})^* \mathrm{d}\mathbf{x_2}\cdots \mathrm{d}\mathbf{x_N}$$

Proposition 8.1. *Assume that $N = 2$. Then for any symmetric or anti-symmetric normalized ψ,*

$$\langle\psi|H|\psi\rangle \geq \mathcal{E}^M(\gamma_\psi).$$

Proof. In this case,

$$H = \Sigma_{j=1}^2(-\frac{1}{2}\nabla_j^2 - V_c(\mathbf{r}_j)) + \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|},$$

and

$$\gamma_\psi(\mathbf{x}, \mathbf{x}') = 2\int \psi(\mathbf{x}, \mathbf{x_2})\psi(\mathbf{x}', \mathbf{x_2})^* \mathrm{d}\mathbf{x_2}$$

Then

$$\begin{aligned}
\langle\psi| -\frac{1}{2}\nabla_1^2|\psi\rangle &= \iint(-\frac{1}{2}\nabla_1^2)|\psi(\mathbf{x_1},\mathbf{x_2})|^2\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} \\
&= \int(-\frac{1}{2}\nabla^2)\Big(\int|\psi(\mathbf{x_1},\mathbf{x_2})|^2\mathrm{d}\mathbf{x_2}\Big)\mathrm{d}\mathbf{x_1} \\
&= \frac{1}{2}\int(-\frac{1}{2}\nabla^2)\gamma_\psi(\mathbf{x_1},\mathbf{x_1})\mathrm{d}\mathbf{x_1} \\
&= \frac{1}{2}\,\mathrm{tr}\,(-\frac{1}{2}\nabla^2\gamma_\psi),
\end{aligned}$$

$$\begin{aligned}
\langle\psi| -V_c(\mathbf{r_1})|\psi\rangle &= \iint\big(-V_c(\mathbf{r_1})\big)|\psi(\mathbf{x_1},\mathbf{x_2})|^2\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} \\
&= \int\big(-V_c(\mathbf{r_1})\big)\int|\psi(\mathbf{x_1},\mathbf{x_2})|^2\mathrm{d}\mathbf{x_2}\mathrm{d}\mathbf{x_1} \\
&= \frac{1}{2}\int\big(-V_c(\mathbf{r_1})\big)\gamma_\psi(\mathbf{x_1},\mathbf{x_1})\mathrm{d}\mathbf{x_1} \\
&= \frac{1}{2}\,\mathrm{tr}\,(-V_c(\mathbf{r_1})\gamma_\psi).
\end{aligned}$$

So we can see that $\langle\psi|\Sigma_{j=1}^2(-\frac{1}{2}\nabla_j^2 - V_c(\mathbf{r}_j))|\psi\rangle = \mathrm{tr}\,[(-\frac{1}{2}\nabla^2 - V_c(\mathbf{r}))\gamma_\psi]$.

Thus we just have to prove

$$\langle\psi|\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}|\psi\rangle \geq D(\rho_{\gamma_\psi},\rho_{\gamma_\psi}) - X(\gamma_\psi^{1/2}).$$

For the Coulomb repulsion term,

$$\begin{aligned}
D(\rho_{\gamma_\psi},\rho_{\gamma_\psi}) &= \frac{1}{2}\iint\frac{\rho_{\gamma_\psi}(\mathbf{r})\rho_{\gamma_\psi}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \frac{1}{2}\iint\frac{\Sigma_\sigma\gamma_\psi(\mathbf{r},\mathbf{r})\Sigma'_\sigma\gamma_\psi(\mathbf{r}',\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \frac{1}{2}\iint\frac{\gamma_\psi(\mathbf{x},\mathbf{x})\gamma_\psi(\mathbf{x}',\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'.
\end{aligned}$$

For the exchange energy,

$$X(\gamma_\psi^{1/2}) = \iint \frac{|\gamma_\psi^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'.$$

What we are going to prove is simply

$$\begin{aligned}&\iint \frac{|\psi(\mathbf{x_1},\mathbf{x_2})|^2}{|\mathbf{r_1}-\mathbf{r_2}|}\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} + \iint \frac{|\gamma_\psi^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\ \geq\ & \frac{1}{2}\iint \frac{\gamma_\psi(\mathbf{x},\mathbf{x})\gamma_\psi(\mathbf{x}',\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'.\end{aligned}$$

Applying the representation of Coulomb Kernel in Lemma 2.1

$$|\mathbf{r}-\mathbf{r}'|^{-1} = \frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{\mathbf{z},r}(\mathbf{r})\chi_{\mathbf{z},r}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}r}{r^5}.$$

and the Fubini's theorem to the formula above, we have for any characteristic function $\chi(\mathbf{r})$ of a ball (or, more generally, for any real-valued function χ)

$$\begin{aligned}&2\iint \chi(\mathbf{r_1})|\psi(\mathbf{x_1},\mathbf{x_2})|^2\chi(\mathbf{r_2})\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} + \iint \chi(\mathbf{r})|\gamma_\psi^{1/2}(\mathbf{x},\mathbf{x}')|^2\chi(\mathbf{r})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\ \geq\ & \left(\int \chi(\mathbf{r})\gamma_\psi(\mathbf{x},\mathbf{x})\mathrm{d}\mathbf{x}\right)^2.\end{aligned}$$

Introducing Ψ as an operator in $L^2(\mathbb{R}^3)$ with kernel $\sqrt{2}\psi(\mathbf{x},\mathbf{x}')$, that is for all $\varphi \in L^2$,

$$\Psi\varphi = \sqrt{2}\int \psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}',$$

So

$$\begin{aligned}\langle\varphi,\Psi\varphi\rangle &= \int\overline{\varphi(\mathbf{x})}\Big(\sqrt{2}\int\psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\Big)\mathrm{d}\mathbf{x}\\ &= \int\Big(\sqrt{2}\int\overline{\varphi(\mathbf{x})}\psi(\mathbf{x},\mathbf{x}')\mathrm{d}\mathbf{x}\Big)\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\\ &= \int\overline{\Big(\sqrt{2}\int\overline{\psi(\mathbf{x},\mathbf{x}')}\varphi(\mathbf{x})\mathrm{d}\mathbf{x}\Big)}\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'.\end{aligned}$$

Since $\langle\varphi,\Psi\varphi\rangle=\langle\Psi^*\varphi,\varphi\rangle$, Ψ^* is an operator such that

$$\Psi^*\varphi=\sqrt{2}\int\overline{\psi(\mathbf{x},\mathbf{x}')}\varphi(\mathbf{x})\mathrm{d}\mathbf{x}.$$

moreover,

$$\begin{aligned}\Psi\Psi^*\varphi &= \int 2\psi(\mathbf{x},\mathbf{x_2})\int\overline{\psi(\mathbf{x}',\mathbf{x_2})}\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{x_2}\\ &= \int\Big(2\int\psi(\mathbf{x},\mathbf{x_2})\overline{\psi(\mathbf{x}',\mathbf{x_2})}\mathrm{d}\mathbf{x_2}\Big)\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\\ &= \int\gamma_\psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'.\end{aligned}$$

This means $\Psi\Psi^*=\gamma_\psi$. And $2\iint\chi(\mathbf{r_1})|\psi(\mathbf{x_1},\mathbf{x_2})|^2\chi(\mathbf{r_2})\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} = 2\iint\chi(\mathbf{r_1})\overline{\psi(\mathbf{x_1},\mathbf{x_2})}\psi(\mathbf{x_1},\mathbf{x_2})\chi(\mathbf{r_2})\mathrm{d}\mathbf{x_1}\mathrm{d}\mathbf{x_2} = \mathrm{tr}\ \chi\Psi^*\chi\Psi$, so that what we want to prove reduces to the inequality that

$$\mathrm{tr}\ \chi\Psi^*\chi\Psi+\mathrm{tr}\ \chi\gamma_\psi^{1/2}\chi\gamma_\psi^{1/2}\geq(\mathrm{tr}\ \chi\gamma_\psi)^2.$$

We have mentioned that $\Psi\Psi^*=\gamma_\psi$, so $\Psi=\gamma_\psi^{1/2}\mathcal{V}$ for a partial isometry $\mathcal{V}$, such that $\Psi\Psi^*=\gamma_\psi^{1/2}\mathcal{V}\mathcal{V}^*\gamma_\psi^{1/2}=\gamma_\psi$. Since ψ is (anti-)symmetric, $\Psi^*\Psi=\mathcal{C}\gamma_\psi\mathcal{C}$, where $\mathcal{C}$ denotes complex conjugation. This can be obtained by direct calculation as below,

$$\begin{aligned}\Psi^*\Psi\varphi &= \Psi^*(\sqrt{2}\int \psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}') \\ &= 2\int \overline{\psi(\mathbf{x},\mathbf{x}'')}\int \psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{x} \\ &= 2\iint \overline{\psi(\mathbf{x},\mathbf{x}'')}\psi(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{x},\end{aligned}$$

and

$$\begin{aligned}\mathcal{C}\gamma_\psi\mathcal{C}\varphi &= \mathcal{C}(\int \gamma_\psi(\mathbf{x},\mathbf{x}')\overline{\varphi(\mathbf{x}')}\mathrm{d}\mathbf{x}') \\ &= \mathcal{C}(2\iint \psi(\mathbf{x},\mathbf{x}'')\overline{\psi(\mathbf{x}',\mathbf{x}'')}\mathrm{d}\mathbf{x}''\overline{\varphi(\mathbf{x}')}\mathrm{d}\mathbf{x}') \\ &= 2\iint \overline{\psi(\mathbf{x},\mathbf{x}'')}\psi(\mathbf{x}',\mathbf{x}'')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{x}' \\ &= 2\iint \overline{\psi(\mathbf{x},\mathbf{x}'')}\psi(\mathbf{x}',\mathbf{x}'')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{x}' \\ &= 2\iint \overline{\psi(\mathbf{x}'',\mathbf{x})}\psi(\mathbf{x}'',\mathbf{x}')\varphi(\mathbf{x}')\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{x}'' \\ &\quad (whenever\ \psi\ is\ symmetric\ or\ anti-symmetric\ )\end{aligned}$$

Hence,

$$\Psi^*\Psi = \mathcal{V}^*\gamma_\psi^{1/2}\gamma_\psi^{1/2}\mathcal{V} = \mathcal{V}^*\gamma_\psi\mathcal{V} = \mathcal{C}\gamma_\psi\mathcal{C}.$$

Since the square root is uniquely defined [25, Theorem 9.4-2],

$$\mathcal{V}^*\gamma_\psi^{1/2}\mathcal{V} = \mathcal{C}\gamma_\psi^{1/2}\mathcal{C}.$$

Write $\delta = \gamma_\psi^{1/2}$, and consider the quadratic form

$$Q(X,Y) = \frac{1}{4}(2\,\mathrm{tr}\ X^*\delta Y\delta + \mathrm{tr}\ X^*\delta\mathcal{V}Y\mathcal{V}^*\delta + \mathrm{tr}\ \mathcal{V}X^*\mathcal{V}^*\delta Y\delta).$$

Here we consider this quadratic form on the real vector space of real operators, i.e., operators assigning a $L^2(\mathbb{R}^3)$-function a real value, in other words, $\mathcal{C}X\mathcal{C} = X$. Note that

$$\begin{aligned} Q(X,X) &= \frac{1}{4}(2\,\mathrm{tr}\ X^*\delta X\delta + \mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta + \mathrm{tr}\ \mathcal{V}X^*\mathcal{V}^*\delta X\delta) \\ &= \frac{1}{2}(\mathrm{tr}\ X^*\delta X\delta + \mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta), \end{aligned}$$

since $\mathrm{tr}\ \mathcal{V}X^*\mathcal{V}^*\delta X\delta = \mathrm{tr}\ \delta\mathcal{V}X^*\mathcal{V}^*\delta X = \mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta$, and that, by Schwarz's inequality,

$$(\mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta)^2 \leq (\mathrm{tr}\ X^*\delta X\delta)(\mathrm{tr}\ \mathcal{V}X^*\mathcal{V}^*\delta\mathcal{V}X\mathcal{V}^*\delta)$$

Since $\mathcal{V}^*\delta\mathcal{V} = \mathcal{C}\delta\mathcal{C}$ and $\mathcal{C}X\mathcal{C} = X$, the inequality above can be written as

$$(\mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta)^2 \leq (\mathrm{tr}\ X^*\delta X\delta)^2,$$

so that

$$|\,\mathrm{tr}\ X^*\delta\mathcal{V}X\mathcal{V}^*\delta| \leq \mathrm{tr}\ X^*\delta X\delta.$$

From this we can conclude that $Q(X,X) \geq 0$. Since that $Q(X,Y)$ is a positive semi-definite sesquilinear form, according [1, Theorem (41.14)], $Q(X,Y)$ satisfies $(Q(X,Y))^2 \leq Q(X,X)Q(Y,Y)$. In particular, $(Q(\chi,\mathbf{1}))^2 \leq Q(\chi,\chi)Q(\mathbf{1},\mathbf{1})$. In this case,

$$Q(\chi,\mathbf{1}) = \frac{1}{4}(2\,\mathrm{tr}\ \chi\delta^2 + \mathrm{tr}\ \chi\delta^2 + \mathrm{tr}\ \chi\delta^2) = \mathrm{tr}\ \chi\delta^2 = \mathrm{tr}\ \chi\gamma_\psi,$$

$$
\begin{aligned}
Q(\chi,\chi) &= \frac{1}{2}(\mathrm{tr}\ \chi\delta\chi\delta + \mathrm{tr}\ \chi\delta\mathcal{V}\chi\mathcal{V}^*\delta) \\
&= \frac{1}{2}(\mathrm{tr}\ \chi\delta\chi\delta + \mathrm{tr}\ \chi\Psi\chi\Psi^*),
\end{aligned}
$$

and

$$
Q(\mathbf{1},\mathbf{1}) = \mathrm{tr}\ \gamma_\psi = 2.
$$

This is exactly what we want. □

9. Appendix

9.1. Some Lemmas.

Lemma 9.1. ([24, Theorem9.8]) If $\rho_\gamma(\mathbf{r}) : \mathbb{R}^n \to \mathbb{C}$ satisfies $D(|\rho_\gamma|, |\rho_\gamma|) < \infty$, then

$$D(\rho_\gamma, \rho_\gamma) \geqslant 0. \tag{9.1}$$

Proof. Since one can easily consider the real and imaginary parts separately, it suffices to assume that ρ_γ is real valued. Let $h \in C_c^\infty(\mathbb{R}^n)$ with $h(\mathbf{r}) \geq 0$ for all $\mathbf{r}$ and with h spherically symmetric, i.e., $h(\mathbf{r}) = h(\mathbf{r}')$ when $|\mathbf{r}| = |\mathbf{r}'|$, especially $h(\mathbf{r}) = h(-\mathbf{r})$ for all $\mathbf{r} \in \mathbb{R}^n$. Let $k(\mathbf{r}) := (h * h)(\mathbf{r}) = K(|\mathbf{r}|)$ where

$$(h * h)(\mathbf{r}) = \int_{\mathbb{R}^n} h(\mathbf{r} - \mathbf{r}')h(\mathbf{r}')\mathrm{d}\mathbf{r}'.$$

By multiplying h by a suitable constant, we can assume henceforth that

$$\int_0^\infty t^{n-3}K(t)\mathrm{d}t = \frac{1}{2}.$$

Now one can calculate

$$\begin{aligned} I(r) : &= \int_0^\infty t^{n-3}k(t\mathbf{r})\mathrm{d}t \\ &= \int_0^\infty \frac{t^{n-3}}{|\mathbf{r}|^{n-3}}K(t)|\mathbf{r}|^{-1}\mathrm{d}t \quad (\textit{scaling } t \longmapsto t|\mathbf{r}|^{-1}) \\ &= |\mathbf{r}|^{2-n}\int_0^\infty t^{n-3}K(t)\mathrm{d}t \\ &= \frac{1}{2}|\mathbf{r}|^{2-n}. \end{aligned}$$

However,

$$\begin{aligned} I(\mathbf{r}-\mathbf{r}') &= \int_0^\infty t^{n-3}k(t(\mathbf{r}-\mathbf{r}'))\mathrm{d}t \\ &= \int_0^\infty t^{n-3}\Big(\int_{\mathbb{R}^n} h(t\mathbf{r}-t\mathbf{s})h(t\mathbf{s}-t\mathbf{r}')\mathrm{d}(t\mathbf{s}-t\mathbf{r}')\Big)\mathrm{d}t \\ &= \int_0^\infty t^{n-3}\Big(\int_{\mathbb{R}^n} h(t(\mathbf{r}-\mathbf{s}))h(t(\mathbf{s}-\mathbf{r}'))t^n\mathrm{d}\mathbf{s}\Big)\mathrm{d}t \\ &= \int_0^\infty t^{2n-3}\int_{\mathbb{R}^n} h(t(\mathbf{s}-\mathbf{r}))h(t(\mathbf{s}-\mathbf{r}'))\mathrm{d}\mathbf{s}\mathrm{d}t. \end{aligned}$$

Finally, as we have defined in (1.9),

$$\begin{aligned} D(\rho_\gamma(\mathbf{r}),\rho_\gamma(\mathbf{r})) &= \frac{1}{2}\int_{\mathbb{R}^n}\int_{\mathbb{R}^n}\frac{\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{n-2}}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \int_{\mathbb{R}^n}\int_{\mathbb{R}^n}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')I(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \int_{\mathbb{R}^n}\int_{\mathbb{R}^n}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')\Big[\int_0^\infty t^{2n-3}\int_{\mathbb{R}^n} h(t(\mathbf{s}-\mathbf{r}))h(t(\mathbf{s}-\mathbf{r}'))\mathrm{d}\mathbf{s}\mathrm{d}t\Big]\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \int_0^\infty t^{-3}\int_{\mathbb{R}^n}\Big[t^n\int_{\mathbb{R}^n}\rho_\gamma(\mathbf{r})h(t(\mathbf{s}-\mathbf{r}))\mathrm{d}\mathbf{r}\Big]\Big[t^n\int_{\mathbb{R}^n}\rho_\gamma(\mathbf{r}')h(t(\mathbf{s}-\mathbf{r}'))\mathrm{d}\mathbf{r}'\Big] \\ &= \int_0^\infty t^{-3}\int_{\mathbb{R}^n}\Big[t^n\int_{\mathbb{R}^n}\rho_\gamma(\mathbf{r})h(t(\mathbf{s}-\mathbf{r}))\mathrm{d}\mathbf{r}\Big]^2\mathrm{d}\mathbf{s} \end{aligned}$$

It follows that

$$D(\rho_\gamma(\mathbf{r}),\rho_\gamma(\mathbf{r})) \geq 0. \tag{9.2}$$

□

Lemma 9.2. *(Transforms of Symmetrical Functions in three dimensions) For any symmetrical functions $h(\mathbf{r})$, i.e., $h(\mathbf{r}) = h(r)$, in which $|\mathbf{r}| = r$,*

$$\int_{\mathbb{R}^3} e^{-i\mathbf{k}\cdot\mathbf{r}}h(\mathbf{r})\mathrm{d}\mathbf{r} = \frac{1}{k}\int_0^\infty 4\pi r h(r)\sin(kr)\mathrm{d}r,$$

where $|\mathbf{k}| = k$.

Proof. Initiating a spherical polar co-ordinates systems (r, θ, φ). Then we have

$$\mathrm{d}\mathbf{r} = r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi,$$

$$\mathbf{k}\cdot\mathbf{r} = kr\cos\theta.$$

So that if $h(\mathbf{r}) = h(r)$ then

$$\begin{aligned}\int_{\mathbb{R}^3} e^{-i\mathbf{k}\cdot\mathbf{r}} h(\mathbf{r})\mathrm{d}\mathbf{r} &= \int_0^\infty \mathrm{d}r \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi \Big(e^{-ikr\cos\theta} h(r) r^2 \sin\theta \Big) \\ &= \int_0^\infty 2\pi r^2 h(r)\mathrm{d}r \int_{-1}^1 e^{ikr(-\cos\theta)} \mathrm{d}(-\cos\theta) \\ &= \int_0^\infty 2\pi r^2 h(r)\mathrm{d}r \int_{-1}^1 e^{ikr\eta}\mathrm{d}\eta \\ &= \frac{1}{k}\int_0^\infty 4\pi r h(r)\sin(kr)\mathrm{d}r.\end{aligned}$$

□

Next Lemma is given in [30, Lemma 3.1], now we give a detailed proof.

Lemma 9.3. *(IMS localization formula) Let* $\{J_a\}_{a=0}^k$ *be any smooth partition of unity with* $J_1, ...J_k \in \mathbb{C}_0^\infty$ *normalized by* $\Sigma_{a=0}^k J_a^2 = 1$. *Let* V *be any potential so that the form sum* $H = -\triangle + V$ *has form domain* $Q(H_0)\bigcap Q(V_+)$, *here* $H_0 = -\triangle$. *Then*

$$H = \Sigma_{a=0}^k J_a H J_a - \Sigma_{a=0}^k (\nabla J_a)^2.$$

Proof. In one hand, by the definition of commutator, one has

$$[J_a, [J_a, H]] = [J_a, J_a H - H J_a] = J_a^2 H - 2J_a H J_a + H J_a^2.$$

In the other hand, as for the Hamiltonian $H = -\nabla^2 + V$, and for any function $\Psi \in L^2$, we have

$$\begin{aligned}
[J_a, H]\Psi &= (J_a H - H J_a)\Psi \\
&= (J_a(-\nabla^2 + V) - (-\nabla^2 + V)J_a)\Psi \\
&= J_a(-\nabla^2\Psi) + \nabla^2(J_a\Psi) \\
&= J_a(-\nabla^2\Psi) + (\nabla^2 J_a)\Psi + J_a(\nabla^2\Psi) + 2\nabla J_a \nabla\Psi \\
&= (\nabla^2 J_a)\Psi + 2\nabla J_a \nabla\Psi.
\end{aligned}$$

So $[J_a, H] = \nabla^2 J_a + 2\nabla J_a \nabla$, then

$$\begin{aligned}
[J_a, [J_a, H]]\Psi &= [J_a, \nabla^2 J_a + 2\nabla J_a \nabla]\Psi \\
&= J_a(\nabla^2 J_a)\Psi + 2J_a \nabla J_a \nabla\Psi - (\nabla^2 J_a)J_a\Psi - 2\nabla J_a \nabla(J_a\Psi) \\
&= 2J_a \nabla J_a \nabla\Psi - 2(\nabla J_a)^2\Psi - 2(\nabla J_a)J_a(\nabla\Psi) \\
&= -2(\nabla J_a)^2\Psi,
\end{aligned}$$

which means $[J_a, [J_a, H]] = -2(\nabla J_a)^2$. Combining these two respects we have

$$J_a^2 H - 2J_a H J_a + H J_a^2 = -2(\nabla J_a)^2.$$

Summation on a we conclude that

$$H = \Sigma_0^k J_a H J_a - \Sigma_0^k (\nabla J_a)^2.$$

$\square$

Lemma 9.4. *Let* $g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2} e^{-|\mathbf{r}-\mathbf{r}'|}$ *and* $\chi(\mathbf{r})$ *be any smooth function on* $\mathbb{R}^3$. *Then*

$$\begin{aligned}&\mathrm{tr}\,(-\nabla_{\mathbf{r}}^2\gamma)\\ &= \iint \Big(|\chi(\mathbf{r})|^2|\chi(\mathbf{r}')|^2(-\nabla_{\mathbf{r}}^2 g(\mathbf{r}-\mathbf{r}'))g(\mathbf{r}-\mathbf{r}') - |\nabla\chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2\Big)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.\end{aligned}$$

Proof. Assume $q = 2$.

$$\begin{aligned}\mathrm{tr}\,(-\nabla_{\mathbf{r}}^2\gamma) &= \mathrm{tr}\,\big((1-\nabla_{\mathbf{r}}^2)\gamma - \gamma\big)\\ &= \mathrm{tr}\,(1-\nabla_{\mathbf{r}}^2)\gamma - tr\gamma\\ &= \iint \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\Big(|\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 + |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\Big) - \iint \gamma(\mathbf{x},\mathbf{x}')\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\ &= \iint |\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\\ &= \Sigma_{\sigma=1}^2\Sigma_{\sigma'=2}^2 \iint |\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\end{aligned}$$

Now let's see $\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')$:

$$\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}') = \big(\nabla\chi^*(\mathbf{r})\big)g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}')q^{-1/2}\delta_{\sigma,\sigma'} + \chi^*(\mathbf{r})\big(\nabla_{\mathbf{r}} g(\mathbf{r}-\mathbf{r}')\big)\chi(\mathbf{r}')q^{-1/2}\delta_{\sigma,\sigma'}.$$

So

$$
\begin{aligned}
& |\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 \\
= & |\nabla\chi^*(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'} + |\chi^*(\mathbf{r})|^2|\chi(\mathbf{r}')|^2|\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'} \\
& +2\big(\nabla\chi^*(\mathbf{r})\big)\big(\chi^*(\mathbf{r})\big)\big(\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')\big)g(\mathbf{r}-\mathbf{r}')|\chi(\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'}.
\end{aligned}
$$

Then in the second term, we integral by parts:

$$
\begin{aligned}
& \iint |\chi^*(\mathbf{r})|^2|\chi(\mathbf{r}')|^2|\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
= & q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\bigg(\int |\chi^*(\mathbf{r})|^2\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}\bigg)\mathrm{d}\mathbf{r}' \\
= & q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\bigg(\int |\chi^*(\mathbf{r})|^2\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')\mathrm{d}(g(\mathbf{r}-\mathbf{r}'))\bigg)\mathrm{d}\mathbf{r}' \\
= & q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\bigg(g(\mathbf{r}-\mathbf{r}')(\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}'))|\chi^*(\mathbf{r})|^2\bigg|_{|\mathbf{r}|\to\infty}\bigg)\mathrm{d}\mathbf{r}' \\
& -q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\bigg(\int g(\mathbf{r}-\mathbf{r}')2|\chi^*(\mathbf{r})||\nabla_{\mathbf{r}}\chi^*(\mathbf{r})|\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}\bigg)\mathrm{d}\mathbf{r}' \\
& -q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\bigg(\int g(\mathbf{r}-\mathbf{r}')|\chi^*(\mathbf{r})|^2\nabla_{\mathbf{r}}^2 g(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}\bigg)\mathrm{d}\mathbf{r}'
\end{aligned}
$$

For the boundary term, we have that

$$
g(\mathbf{r}-\mathbf{r}')(\nabla_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}'))|\chi^*(\mathbf{r})|^2\bigg|_{|\mathbf{r}|\to\infty} = 0,
$$

since $g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{r}'|} = 0$ as $\mathbf{r} \to \infty$, remember that $\mathbf{r}'$ is any fixed number. Hence

$$\begin{aligned}
\mathrm{tr}\,(-\nabla^2_{\mathbf{r}}\gamma) &= \Sigma^2_{\sigma=1}\Sigma^2_{\sigma'=2}\iint |\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\
&= \Sigma^2_{\sigma=1}\Sigma^2_{\sigma'=2}\Big[\iint |\nabla\chi^*(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'} \\
&\quad + q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\Big(\int g(\mathbf{r}-\mathbf{r}')|\chi^*(\mathbf{r})|^2(-\nabla^2_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}'))\mathrm{d}\mathbf{r}\Big)\mathrm{d}\mathbf{r}'\Big] \\
&= \Sigma^2_{\sigma=\sigma'=1}\Big[\iint |\nabla\chi^*(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2 q^{-1}\delta_{\sigma,\sigma'} \\
&\quad + q^{-1}\delta_{\sigma,\sigma'}\int |\chi(\mathbf{r}')|^2\Big(\int g(\mathbf{r}-\mathbf{r}')|\chi^*(\mathbf{r})|^2(-\nabla^2_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}'))\mathrm{d}\mathbf{r}\Big)\mathrm{d}\mathbf{r}'\Big] \\
&= \iint \Big(|\nabla\chi^*(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2 \\
&\quad + |\chi(\mathbf{r}')|^2|\chi^*(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')(-\nabla^2_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}'))\Big)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.
\end{aligned}$$

□

Lemma 9.5. ([25, Theorem 2.5]) (approximate identities) Let $f(x)$ be a piecewise continuous function such that $\int_{-\infty}^{\infty}|f(x)|\mathrm{d}x < \infty$ and $\int_{\infty}^{\infty} f(x)\mathrm{d}x = 1$. We write $f_a(x) = af(ax)$. Then as $a \to \infty$

$$f_a(x) = af(ax) \to \delta(x).$$

Proof. The idea is that , as $a \to \infty$, $f_a(x)$ becomes a narrow pulse, with its height growing at the same rate that its width shrinks, the integral of f_a remains equal to 1. Take any test function φ, and take $\varepsilon > 0$. Choose $\delta > 0$ so that $|\varphi(x) - \varphi(0)| < \varepsilon$ for $|x| < \delta$. Choose M so that

$\left(\int_{-\infty}^{M}+\int_{M}^{\infty}\right)|f(x)|\mathrm{dx}<\varepsilon$. Finally take any $a>M/\delta$, let K_1 denote the fixed value $\int_{-\infty}^{\infty}|f(x)|\mathrm{d}x<\infty$ and let K_2 denote $\max\{|\varphi(\mathrm{x})|,\mathrm{x}\in\mathbb{R}\}$. Then $af(ax)\to\delta(x)$ in the sense of distribution. Indeed,

$$\begin{aligned}
\left|\langle T_{af(ax)},\varphi\rangle-\langle\delta,\varphi\rangle\right| &= \left|\int_{-\infty}^{\infty}af(ax)\varphi(x)\mathrm{dx}-\varphi(0)\right| \\
&\overset{u=ax}{=} \left|\int_{-\infty}^{\infty}f(u)[\varphi(u/a)-\varphi(0)]\mathrm{du}\right| \\
&\le \left|\int_{-M}^{M}f(u)[\varphi(u/a)-\varphi(0)]\mathrm{du}\right| \\
&\quad +\left|\left(\int_{-\infty}^{M}+\int_{M}^{\infty}\right)f(u)[\varphi(u/a)-\varphi(0)]\mathrm{du}\right| \\
&\le \left(\int_{-\infty}^{\infty}|f(u)|\mathrm{du}\right)\max\{|\varphi(\mathrm{u/a})-\varphi(0)|\} \\
&\quad +\left[\left(\int_{-\infty}^{-M}+\int_{M}^{\infty}\right)|f(u)|\mathrm{du}\right]\left(\max\{|\varphi(\mathrm{u/a})-\varphi(0)|\}\right) \\
&\le K_1\varepsilon+2K_2\varepsilon.
\end{aligned}$$

□

9.2. **Hardy's inequality.**

Lemma 9.6. (Hardy's inequality) For $F(\mathbf{r})\in\mathbf{H_0^1}(\mathbb{R}^\mathbf{3})$,

$$\int_{\mathbb{R}^3}\frac{|F|^2}{|\mathbf{r}|^2}\mathrm{d}\mathbf{r}\le\mathbf{4}\int_{\mathbb{R}^\mathbf{3}}|\nabla F|^2\mathrm{d}\mathbf{r}.$$

Proof. First we state the classical Hardy's inequality in one dimensional which presented by Hardy ([12, Theorem 327]) in 1920 and give its brief proof.

Claim. If $p>1, f(x)\ge 0,$ *and* $F(x)=\int_0^x f(t)\mathrm{dt},$ *where* $f(x)$ *is an* *integrable function on $\mathbb{R}$. Then*

$$\int_0^\infty \left(\frac{F}{x}\right)^p \mathrm{d}x \le \left(\frac{p}{p-1}\right)^p \int_0^\infty f^p \mathrm{d}x,$$

the equality holds for $f \equiv 0$.

Verification. For $0 < \varepsilon < X$,

$$\begin{aligned}\int_\varepsilon^X \left(\frac{F}{x}\right)^p \mathrm{d}x &= -\frac{1}{p-1}\int_\varepsilon^X F^p \mathrm{d}x^{1-p} \\ &= \frac{F(\varepsilon)^p\varepsilon^{1-p}}{p-1} - \frac{F(X)^p X^{1-p}}{p-1} + \frac{p}{p-1}\int_\varepsilon^X x^{1-p}F^{p-1}\cdot f\mathrm{d}x\end{aligned}$$

Let $\varepsilon \to 0, X \to \infty$, then $F(\varepsilon) \to 0, 0 \le F(X) < \infty$, so that

$$\int_0^\infty \left(\frac{F}{x}\right)^p \mathrm{d}x \le \frac{p}{p-1}\int_0^\infty x^{1-p}F^{p-1}\cdot f\mathrm{d}x.$$

By Hölder inequality,

$$\begin{aligned}\int_0^\infty (F/x)^p \mathrm{d}x &\le \frac{p}{p-1}\int_0^\infty x^{1-p}F^{p-1}\cdot f\mathrm{d}x \\ &\le \frac{p}{p-1}\Big(\int_0^\infty [(F/x)^{p-1}]^\alpha \mathrm{d}x\Big)^{\frac{1}{\alpha}}\Big(\int_0^\infty f^p\mathrm{d}x\Big)^{\frac{1}{p}} \\ &\quad (\frac{1}{\alpha}+\frac{1}{p}=1) \\ &= \frac{p}{p-1}\Big(\int_0^\infty (F/x)^p \mathrm{d}x\Big)^{\frac{1}{\alpha}}\Big(\int_0^\infty f^p\mathrm{d}x\Big)^{\frac{1}{p}}.\end{aligned}$$

Note that $\int_0^\infty (F/x)^p \mathrm{d}x \ge 0$, it follows that

$$\Big(\int_0^\infty (F/x)^p \mathrm{d}x\Big)^{\frac{1}{p}} \le \frac{p}{p-1}\Big(\int_0^\infty f^p\mathrm{d}x\Big)^{\frac{1}{p}},$$

which is exactly what we want:

$$\int_0^\infty (F/x)^p \mathrm{d}x \le \left(\frac{p}{p-1}\right)^p \int_0^\infty f^p\mathrm{d}x.$$

Next turn back to the case of 3-dimensional. The proof presented here is from B. Simon [32]. In this case, note that

$$\nabla_{\mathbf{r}}(r^{1/2}F) = r^{1/2}\nabla_{\mathbf{r}}F + \frac{1}{2}r^{-1/2}\frac{\mathbf{r}}{r}F = r^{1/2}\nabla_{\mathbf{r}}F + \frac{1}{2}r^{-3/2}\mathbf{r}F$$

So

$$\begin{aligned}
|\nabla_{\mathbf{r}}F|^2 &= |r^{-1/2}\nabla_{\mathbf{r}}(r^{1/2}F) - \frac{1}{2}r^{-2}\mathbf{r}F|^2 \\
&\geq r^{-1}|\nabla_{\mathbf{r}}(r^{1/2}F)|^2 - r^{-3/2}F|\nabla_{\mathbf{r}}(r^{1/2}F)| + \frac{1}{4}r^{-2}|F|^2 \\
&\geq \frac{1}{4}r^{-2}|F|^2 - r^{-3/2}F\nabla_r(r^{1/2}F) \\
&= \frac{1}{4}r^{-2}|F|^2 - \frac{1}{2}r^{-2}\nabla_r(r|F|^2),
\end{aligned}$$

where

$$-\frac{1}{r^{3/2}}F\nabla_r(r^{1/2}F) = -\frac{1}{2r^2}2(r^{1/2}F)\nabla_r(r^{1/2}F) = -\frac{1}{2r^2}\nabla_r(r|F|^2)$$

in the last equality.

Now integrate on the whole space, we have

$$\begin{aligned}
\int_{\mathbb{R}^3}|\nabla_{\mathbf{r}}F|^2\mathrm{d}\mathbf{r} &\geq \int_{\mathbb{R}^3}\frac{1}{4}r^{-2}|F|^2\mathrm{d}\mathbf{r} - \mathbf{\frac{1}{2}}\int_{\mathbb{R}^3} r^{-2}\nabla_r(r|F|^2)\mathrm{d}\mathbf{r} \\
&= \int_{\mathbb{R}^3}\frac{1}{4}r^{-2}|F|^2\mathrm{d}\mathbf{r} - \mathbf{\frac{1}{2}}\int_{\mathbf{0}}^{\infty}\frac{\mathbf{1}}{r^2}\nabla_r\left(\int_{\mathbf{S^2}}(r|F|^2)\mathrm{d}\Omega\right)\mathrm{r}^2\mathrm{dr} \\
&= \int_{\mathbb{R}^3}\frac{1}{4}r^{-2}|F|^2\mathrm{d}\mathbf{r} - \mathbf{\frac{1}{2}}\left(\int_{\mathbf{S^2}}(r|F|^2)\mathrm{d}\Omega\right)\Big|_0^{\infty} \\
&= \int_{\mathbb{R}^3}\frac{1}{4}r^{-2}|F|^2\mathrm{d}\mathbf{r}.
\end{aligned}$$

□

9.3. **The convexity of $\mathcal{E}^M$ with respect to γ.** The convexity of $\mathcal{E}^M(\gamma)$ is not at all obvious. By the linearity of the trace operator and the laplacian and the linearity of $\rho_\gamma(\mathbf{r})$ with respect to γ, we can see the convexity of the first two terms in the expression

$$\mathcal{E}^M(\gamma) = \frac{1}{2}\operatorname{tr}(-\nabla^2\gamma) - \int_{\mathbb{R}^3} V_c(\mathbf{r})\rho_\gamma(\mathbf{r})\mathrm{d}\mathbf{r} + \mathrm{D}(\rho_\gamma, \rho_\gamma) - \mathrm{X}(\gamma^{1/2}).$$

And the strict convexity of the term $D(\rho_\gamma, \rho_\gamma)$ is shown by E.H.Lieb [24, Theorem 9.8]. Thus it remains to show the convexity of the term $-X(\gamma^{1/2})$, in other words, the concavity of the functional $X(\gamma^{1/2})$. Towards this end, we firstly introduce a theorem given by E.H.Lieb in [22].

Theorem 9.7. *Let K be a linear operator (not necessarily bounded) on some certain Hilbert space $\mathcal{H}$. Let T, H be positive operators on $\mathcal{H}$, and let $\lambda, 0 < \lambda < 1$ be given. Form the convex combination,*

$$G = \lambda T + (1-\lambda)H.$$

Let p and r be given positive real numbers with $p + r = s \leq 1$. If $M := G^{p/2}KG^{r/2}$ has an extension to $\mathfrak{S}^2$(Hilbert-Schmidt operator ideal), then (1) $T^{p/2}KT^{r/2}$ and $H^{p/2}KH^{r/2}$ have extensions to $\mathfrak{S}^2(\mathcal{H})$; (2) $G \mapsto \operatorname{tr}(G^{r/2}K^\dagger G^p K G^{r/2})$ is concave, i.e.,

$$\operatorname{tr}(G^{r/2}K^\dagger G^p K G^{r/2}) \geq \lambda \operatorname{tr}(T^{r/2}K^\dagger T^p K T^{r/2}) + (1-\lambda)\operatorname{tr}(H^{r/2}K^\dagger H^p K H^{r/2}).$$

Corollary 9.8. *Let γ be the density operator, then $\gamma \mapsto \mathrm{tr}\,(\gamma^{1/2}K^\dagger\gamma^{1/2}K)$ is concave for any fixed function K.*

Proof. Let $r = 1/2, p = 1/2$, and let $G = \gamma$ in the above theorem, we can conclude that $\gamma \mapsto \mathrm{tr}\,(\gamma^{1/4}K^\dagger\gamma^{1/2}K\gamma^{1/4})$ is concave. Since γ is bounded, $\mathrm{tr}\,(\gamma^{1/4}K^\dagger\gamma^{1/2}K\gamma^{1/4}) = \mathrm{tr}\,(\gamma^{1/2}K^\dagger\gamma^{1/2}K)$ according to B. Simon [29, Theorem 3.1] □

Corollary 9.9. *$X(\gamma^{1/2})$ is concave with respect to γ.*

Proof. As shown in Lemma 2.1, $|\mathbf{r}-\mathbf{r}'|^{-1}$ can be written as

$$|\mathbf{r}-\mathbf{r}'|^{-1} = \frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} \chi_{B(\mathbf{z},l)}(\mathbf{r})\chi_{B(\mathbf{z},l)}(\mathbf{r}')\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5}.$$

Then

$$X(\gamma^{1/2}) = \frac{1}{2\pi}\int_0^\infty \int_{\mathbb{R}^3} \mathrm{tr}\,(\gamma^{1/2}\chi_{B(\mathbf{z},l)}\gamma^{1/2}\chi_{B(\mathbf{z},l)})\mathrm{d}\mathbf{z}\frac{\mathrm{d}l}{l^5}.$$

The concavity follows from the concavity of the map $\gamma \mapsto \mathrm{tr}\,(\gamma^{1/2}K^\dagger\gamma^{1/2}K)$ immediately. □

9.4. strictly convexity of $\mathcal{E}^M$ with respect to ρ.

Theorem 9.10. *(strictly convexity of $\mathcal{E}^M$ with respect to ρ) For $0 < \lambda < 1$, $\rho_1 \neq \rho_2$,*

$$\mathcal{E}^M(\lambda\rho_1 + (1-\lambda)\rho_2) < \lambda\mathcal{E}^M(\rho_1) + (1-\lambda)\mathcal{E}^M(\rho_2). \tag{9.3}$$

Proof. Given a ρ_0 such that $\mathcal{E}^M(\rho_0) = E^M(\lambda N_1 + (1-\lambda)N_2)$, i.e.,

$$\int \rho_0 = \lambda N_1 + (1-\lambda)N_2.$$

Then we can find $\rho_1,\ \rho_2$ such that $\rho_0 = \lambda\rho_1 + (1-\lambda)\rho_2$, and

$$\int \rho_1 = N_1, \quad \int \rho_2 = N_2.$$

Next, apply Proposition 7.2 directly, we have

$$\mathcal{E}^M(\lambda\rho_1 + (1-\lambda)\rho_2) < \lambda\mathcal{E}^M(\rho_1) + (1-\lambda)\mathcal{E}^M(\rho_2)$$

Indeed,

$$\begin{aligned}\mathcal{E}^M(\lambda\rho_1 + (1-\lambda)\rho_2) &= E^M(\lambda N_1 + (1-\lambda)N_2) \\ &< \lambda E^M(N_1) + (1-\lambda)E^M(N_2) \\ &\leq \lambda\mathcal{E}^M(\rho_1) + (1-\lambda)\mathcal{E}^M(\rho_2).\end{aligned}$$

□

After identifying the strictly convexity of $\mathcal{E}^M$ w.r.t. ρ, we consider the uniqueness of ρ.

Suppose γ_1, γ_2 are two different minimizers of constraint problem $E^M_{\leq N}$, tr $\gamma_1 =$ tr $\gamma_2 = N$, let ρ_1, ρ_2 be corresponding densities.

Assume $\rho_1 \neq \rho_2$. Then by the convexity of $\mathcal{E}^M$ w.r.t. ρ, we have

$$\begin{aligned}\mathcal{E}^M(\lambda\rho_1 + (1-\lambda)\rho_2) &< \lambda\mathcal{E}^M(\rho_1) + (1-\lambda)\mathcal{E}^M(\rho_2) \\ &= \lambda E^M(N) + (1-\lambda)E^M(N) \\ &= E^M(N).\end{aligned}$$

On the left hand side, however, $\mathcal{E}^M(\lambda\rho_1 + (1-\lambda)\rho_2) \geq E^M(N)$. This is a contradiction. Hence $\rho_1 = \rho_2$.

9.5. **Compactness of** $(-\nabla^2+1)^{-1/2}V(-\nabla^2+1)^{-1/2}$ **for** $V \in L^{3/2}$**.**

Definition 9.11. A function $V(\mathbf{x}), \mathbf{x} \in \mathbb{R}^3$ is said to be of Rollnik class if

$$\|V\|_{\mathcal{R}}^2 := \iint \frac{|V(\mathbf{x})||V(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|^2} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y} < \infty.$$

We write $V \in \mathcal{R}$ briefly.

Lemma 9.12. *(Hardy-Littlewood-Sobolev inequality)*

Let $p, r > 1$ and $0 < \lambda < n$ with $\frac{1}{p} + \frac{\lambda}{n} + \frac{1}{r} = 2$. Let $f \in L^p(\mathbb{R}^n)$ and $h \in L^r(\mathbb{R}^n)$. Then there exists a constant $C(n, \lambda, p)$, independent of f and h, such that

$$\iint \frac{|f(\mathbf{x})||h(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|^\lambda} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y} \leq \mathrm{C(n, \lambda, p)\|f\|_p\|h\|_r}.$$

Proof. The proof of this lemma, we refer the reader to [24] and [28]. $\square$

Corollary 9.13. *If $V \in L^{3/2}$, then $V \in \mathcal{R}$.*

Proof. Applying Hardy-Littlewood-Sobolev inequality to V, let $n = 3, p = 3/2, r = 3/2, \lambda = 2$. Then

$$\iint \frac{|V(\mathbf{x})||V(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|^{\lambda}} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y} \leq \mathrm{C(n,\lambda,p)}\|\mathrm{V}\|^2_{\mathrm{L}^{3/2}} < \infty.$$

□

We write the Fourier transform of a function f as $\hat{f} = \mathcal{F}f$ and the inverse $\check{f} = \mathcal{F}^{-1}f$. Let $H_0 = -\nabla^2$, we now turn to computing explicit formulas for $(H_0+1)^{-1/2}V(H_0+1)^{-1/2}, V \in \mathcal{R}$. Since $H_0 = \mathcal{F}^{-1}p^2\mathcal{F}, f(H_0) = \mathcal{F}^{-1}f(p^2)\mathcal{F}$ where f is any bounded measurable function [32, Section IX.7], $(H_0+1)^{-1/2}$ can be expressed in terms of multiplication operator: $(H_0+1)^{-1/2} = \mathcal{F}^{-1}(p^2+1)^{-1/2}\mathcal{F}$.

Lemma 9.14. *The operator* $(H_0+1)^{-1/2}V(H_0+1)^{-1/2}, V \in \mathcal{R}$ *has an integral kernel of the form*

$$\frac{\widehat{V}(p-q)}{(q^2+1)^{1/2}(p^2+1)^{1/2}}$$

in momentum space.

Proof. Let $\phi \in \mathrm{Ran}\,(H_0)$, we have

$$\begin{aligned}
& \langle \phi, (H_0+1)^{-1/2} V (H_0+1)^{-1/2} \phi \rangle \\
= & \langle \phi, \big(\mathcal{F}^{-1/2}(q^2+1)^{-1}\mathcal{F}\big) V \big(\mathcal{F}^{-1/2}(p^2+1)^{-1}\mathcal{F}\big)\phi \rangle \\
= & \langle \mathcal{F}\phi, (q^2+1)^{-1/2}\mathcal{F}\big(V\mathcal{F}^{-1}(p^2+1)^{-1/2}\widehat{\phi}\big)\rangle \\
= & \langle \widehat{\phi}, (q^2+1)^{-1/2}\widehat{V} * (p^2+1)^{-1/2}\widehat{\phi}\rangle \\
= & \langle \widehat{\phi}, \frac{\widehat{V}(p-q)}{(q^2+1)^{1/2}(p^2+1)^{1/2}}\widehat{\phi}\rangle
\end{aligned}$$

□

Theorem 9.15. $(H_0+1)^{-1/2}V(H_0+1)^{-1/2}$ *is a Hilbert-Schmidt operator.*

Proof. Let $A = (H_0+1)^{-1/2}V(H_0+1)^{-1/2}, U = \widehat{V}$. Let $\tilde{\tau} = \mathrm{tr}\,(AA^*)$. To prove that A is a Hilbert-Schmidt operator, it is equivalent to prove that $\tilde{\tau} < \infty$. We express $\tilde{\tau}$ in the momentum space as

$$\begin{aligned}
\tilde{\tau} &= \mathrm{tr}\,(AA^*) \\
&= \iint \frac{|\widehat{V}(p-q)|^2}{(p^2+1)(q^2+1)}\mathrm{dpdq} \\
&= \iint \frac{|U(p-q)|^2}{(p^2+1)(q^2+1)}\mathrm{dpdq} \\
&= \int |U(s)|^2 \mathrm{ds} \times \int \frac{1}{(\mathrm{p}^2+1)((\mathrm{p}-\mathrm{s})^2+1)}\mathrm{dp} \qquad (9.4) \\
&= \pi^3 \int \frac{|U(s)|^2}{s}\mathrm{ds}
\end{aligned}$$

The p integral in (9.4) can be calculated by Feynman's method It remains to show that

$$\tilde{\tau} = \pi^3 \int \frac{|U(s)|^2}{s} \mathrm{ds} \tag{9.5}$$

exists. In [27], the author pointed that if local potential

$$\int_{\mathbb{R}^3} |V(\mathbf{r})| \mathrm{d}\mathbf{r} < \infty \tag{9.6}$$

then $U(s)$ is finite for all p, and the integral (9.5) will then exist if

$$U(s) = \mathcal{O}(|s|^{-1-\varepsilon}) \tag{9.7}$$

as $|s| \to \infty$. And (9.7) will hold if

$$V(\mathbf{r}) = \mathcal{O}(|\mathbf{r}|^{-2+\varepsilon}). \tag{9.8}$$

as $|\mathbf{r}| \to \infty$. And the inequality (9.6) will hold if $V(\mathbf{r})$ is finite for all finite $\mathbf{r}$, satisfies (9.8), and if

$$V(\mathbf{r}) = \mathcal{O}(|\mathbf{r}|^{-3-\varepsilon}). \tag{9.9}$$

as $|\mathbf{r}| \to \infty$. Since $V \in \mathcal{R}$ gives V is locally L^1 ([28, Theorem I.7]). Antonio claimed in [4, 10.22] that if $V \in L^1 \cap \mathcal{R}$, (9.5) exists. □

9.6. **Grümm's convergence theorem on $\mathfrak{S}^p$ and its application.** For the completeness, we introduce Grümm's convergence theorem here, readers can also find more details in [29].

Lemma 9.16. *Let A_n, A, B be bounded operators on a Hilbert space H, with $B^* = B > 0$. Suppose that $|A_n| \leq B$ and $|A_n^*| \leq B$ for all n, $|A| \leq B$, $|A^*| \leq B$, and that $A_n \to A$ weakly. If $p < \infty$ and $B \in \mathfrak{S}^p$, then $\|A - A_n\|_p \to 0$.*

Proof. Fix $\varepsilon > 0$. We can find a finite rank projection P so that for $Q = 1 - P$, we have that

$$\|QBQ\|_p < \varepsilon.$$

For instance, by choosing P to be the projection onto the span of the first few eigenvectors of B in the canonical expansion. Thus for n large,

$$\|Q|A_n|Q\|_p \leq \varepsilon,$$

since $|A_n| \leq B$. So

$$\||A_n|^{1/2}Q\|_{2p}^2 \leq \varepsilon$$

and likewise

$$\||A_n^*|^{1/2}Q\|_{2p}^2 \leq \varepsilon.$$

Using Hölder's inequality, we have $\|A_nQ\|_p \leq \||A_n|^{1/2}\|_{2p}\||A_n|^{1/2}Q\|_{2p}$. Indeed,

$$\begin{aligned}\|A_nQ\|_p &= \left(\int |A_nQ|^p\right)^{1/p} \\ &= \left(\int |A_n|^{p/2}|A_n|^{p/2}|Q|^p\right)^{1/p} \\ &\leq \left(\int |A_n|^p\right)^{1/2p}\left(\int |A_n|^p|Q|^{2p}\right)^{1/2p} \\ &= \||A_n|^{1/2}\|_{2p}\||A_n|^{1/2}Q\|_{2p}.\end{aligned}$$

Moreover, since $|A_n| < B$,

$$\|A_nQ\|_p \leq \||A_n|^{1/2}\|_{2p}\||A_n|^{1/2}Q\|_{2p} \leq \|B\|_p^{1/2}\varepsilon^{1/2}.$$

Similarly, for $\|QA_nP\|_p$, we have

$$\|QA_nP\|_p = \|QA_n(1-Q)\|_p \leq \|QA_n\|_p = \|A_n^*Q\|_p \leq \|B\|_p^{1/2}\varepsilon^{1/2}.$$

Finally, look at $\|A - A_n\|_p$. Using triangular inequality, we come out with

$$\|A - A_n\|_p \leq 4\varepsilon^{1/2}\|B\|_p^{1/2} + \|P(A - A_n)P\|_p.$$

In fact,

$$\begin{aligned}\|A - A_n\|_p &= \|(P+Q)(A-A_n)(P+Q)\|_p \\ &\leq \|P(A-A_n)P\|_p + \|PAQ + QAP - PA_nQ - QAnP\|_p \\ &\quad +\|QAQ\|_p + \|QA_nQ\|_p \\ &\leq 4\varepsilon^{1/2}\|B\|_p^{1/2} + \|P(A-A_n)P\|_p.\end{aligned}$$

Since P is finite rank,

$$\|P(A-A_n)P\|_p \to 0 \; as \; n \to \infty$$

in light of the weak convergence of A_n. Hence $\lim \|A - A_n\|_p \leq 4\varepsilon^{1/2}\|B\|_p^{1/2}$. Since ε is arbitrary and $\|B\|_p < \infty$, $\|A - A_n\|_p \to 0$ as $n \to \infty$. □

Lemma 9.17. *Fix $p < \infty$. Suppose that $A_n \to A$, $|A_n| \to |A|$, and $|A_n^*| \to |A^*|$ all weakly, and that $\|A_n\|_p \to \|A\|_p$. Then $\|A_n - A\|_p \to 0$.*

Proof. Without loss of generality, suppose $\|A\|_p = \|A_n\|_p = 1$. Fix $\varepsilon > 0$. Find a finite-dimensional projection P so that $\|P|A|P\|_p \geq 1-\varepsilon$ and $\|P|A^*|P\|_p \geq 1-\varepsilon$. For instance, P can be the projection onto the span of the first few eigenvectors for $|A|$ and for $|A^*|$.

By the weak convergence of A_n, we can find such N that for all $n > N$, $\|P|A_n|P\| \geq 1-2\varepsilon$ and $\|P|A_n^*|P\| \geq 1-2\varepsilon$. In the other hand, according [29, Theorem 1.20], for Q=1-P,

$$\|Q|A_n|Q\| \leq \big(1-(1-2\varepsilon)^p\big)^{1/p}.$$

Similarly, $\|Q|A_n^*|Q\| \leq \big(1-(1-2\varepsilon)^p\big)^{1/p}$. Then just repeat the proof of Lemma 9.16 above and reach the conclusion. □

Theorem 9.18. *(Grümm's convergence theorem on $\mathfrak{G}^p$)*

Fix $p < \infty$. Let $A \in \mathfrak{G}^p$. Suppose that $A_n \to A$ and $A_n^* \to A^*$ in the strong operator topology and that $\|A_n\|_p \to \|A\|_p$. Then $\|A_n - A\|_p \to 0$.

Proof. Firstly, we claim that $A_n^*A_n \to A^*A$ in the strong operator topology. Indeed, for an arbitrary $\varphi \in \mathcal{H}$,

$$\|(A_n^*A_n - A^*A)\varphi\|_p \leq \|(A_n^* - A^*)A_n\varphi\|_p + \|A^*(A_n - A)\varphi\|_p.$$

The first term on the right hand side can be arbitrarily small because of the strong operator convergence of A_n^* to A^*, and the second term on the right hand side can be arbitrarily small because of the strong operator convergence of A_n to A and the linearity of the operator A^*. Besides, since $\sqrt{\cdot}$ and $(\cdot)^\alpha,\ \alpha \in \mathbb{R}$ are strongly continuous,

$$|A_n| = \sqrt{A_n^*A_n} \to \sqrt{A^*A} = |A| \ \ \textit{strongly}$$

and therefore

$$|A_n|^\alpha \to |A|^\alpha \ \ \textit{strongly for} \alpha \in \mathbb{R}.$$

Likewise, we have $|A_n^*| \to |A^*|,\ |A_n^*|^\alpha \to |A^*|^\alpha$. Finally applying 9.17 leads to the conclusion. □

Remark 9.19. ($A \to |A|^{1/2}$ is continuous between $\mathfrak{G}^1$ and $\mathfrak{G}^2$)

If $A_n \to A$ in $\mathfrak{G}^1$, i.e., $\|A_n\|_1 \to \|A\|_1$, then by the same argument in 9.18, $|A_n|^{1/2} \to |A|^{1/2}$ strongly. Since $\||A_n|^{1/2}\|_2 = \|A_n\|_1^{1/2}$ and $\||A|^{1/2}\|_2 = \|A\|_1^{1/2}$, $\||A_n|^{1/2}\|_2 \to \||A|^{1/2}\|_2$. Now by Grümm's theorem 9.18, $|A_n|^{1/2}$ converges to $|A|^{1/2}$.

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