Müller's exchange-correlation energy in density-matrix-functional theory

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The increasing interest in the Müller density-matrix-functional theory has led us to a systematic mathematical investigation of its properties. This functional is similar to the Hartree-Fock (HF) functional, but with a modified exchange term in which the square of the density matrix $\gamma(\mathbf{x},\mathbf{x}')$ is replaced by the square of $\gamma^{1/2}(\mathbf{x},\mathbf{x}')$. After an extensive introductory discussion of density-matrix-functional theory we show, among other things, that this functional is convex (unlike the HF functional) and that energy minimizing γ's have unique densities $\rho(\mathbf{r})$, which is a physically desirable property often absent in HF theory. We show that minimizers exist if $N \leq Z$, and derive various properties of the minimal energy and the corresponding minimizers. We also give a precise statement about the equation for the orbitals of γ, which is more complex than for HF theory. We state some open mathematical questions about the theory together with conjectured solutions.

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I. INTRODUCTION

The basic goal of density-functional theory is to express the energy of a quantum-mechanical state in terms only of its one-particle density $\rho(\mathbf{r})$ and then to minimize the resulting functional (the "density functional") with respect to $\rho(\mathbf{r})$ [under the subsidiary condition that $\int_{\mathbb{R}^3}\rho(\mathbf{r})d\mathbf{r}=N=$number of electrons] in order to calculate the ground-state energy of the system, which could be an atom or a molecule or a solid. Although the first—and by far most used and important density functional in theory, computation, and mathematical investigation of multielectron systems—is the Thomas-Fermi functional (Lenz [1]), strong interest in the subject was triggered by Hohenberg and Kohn [2]. We refer the reader interested in the recent developments to the books by Eschrig [3] and Gross and Dreizler [4] and the review [5].

While this program is possible in principal, experience has shown that it is far from easy to guess the appropriate functional—especially if one wants the functional to be universal and not simply "tuned" to the particular kind of atom or molecule under investigation. There are also pitfalls connected with the admissible class of functions to use in the variational principle [5,6].

Whereas the external potential energy can easily be expressed in terms of the one-particle density, it is not known how to express the kinetic energy and the interaction energy in terms of $\rho(\mathbf{r})$. Going from density- to density-matrix-functional theory eliminates the first problem altogether, since all expectations of one-particle operators can be expressed in term of the one-particle density matrix. The density matrix analogue of the Hohenberg-Kohn density-functional program was established by Gilbert [7]. See also [8].

The most difficult component of the density functional to estimate is the exchange-correlation energy (which we shall henceforth simply call exchange energy), and it is that energy that will concern us here. Owing to this and other difficulties, it has been the tendency recently to replace the energy as a functional of $\rho(\mathbf{r})$ by a functional of the one-body density *matrix*, $\gamma(\mathbf{x},\mathbf{x}')$. In this way it is hoped to have more flexibility and achieve, hopefully, more accurate answers.

Fermions have spin and it is convenient to 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. (In nuclear physics one sometimes considers $q=4$.) We shall, however, call the particles electrons. Similarly we write for any function f depending on space and spin variables

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

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i.e., $\int d\mathbf{x}$ indicates integration over the whole space and summation over all spin indices. This allows us to write the density matrix γ as an operator on the Hilbert space of spinors ψ for which $\int|\psi(\mathbf{x})|^2 d\mathbf{x}<\infty$. Its integral kernel is $\gamma(\mathbf{x},\mathbf{x}')$.

The Schrödinger Hamiltonian we wish to consider is

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

where

$$V_c(\mathbf{r})=\sum_{j=1}^{K}\frac{Z_j}{|\mathbf{r}-\mathbf{R}_j|} \tag{3}$$

is the Coulomb potential of $K\geq 1$ fixed nuclei acting on the N electrons. The jth nucleus has charge $+Z_j e>0$ and is located at some fixed point $\mathbf{R}_j\in\mathbb{R}^3$. We define the total nuclear charge by $Z\equiv\sum_{j=1}^{K}Z_j$. The electron-electron repulsion R is given by

$$R=\sum_{1\leq i<j\leq N}|\mathbf{r}_i-\mathbf{r}_j|^{-1}. \tag{4}$$

If one is interested in minimizing over the nuclear positions $\mathbf{R}_j$, one also has to take into account the nucleus-nucleus repulsion e^2U, of course, which is given by

$$U=\sum_{1\leq i<j\leq K}Z_iZ_j|\mathbf{R}_i-\mathbf{R}_j|^{-1}. \tag{5}$$

Since we will not be concerned with this question but rather consider the nuclei to be fixed, we will not take this term into consideration here.

A. Hartree-Fock exchange energy

The best known density-matrix-functional associated with Eq. (2) is the *Hartree-Fock* (HF) functional

$$\mathcal{E}^{\mathrm{HF}}(\gamma)=\frac{\hbar^2}{2m}\operatorname{tr}(-\nabla^2\gamma)-e^2\int_{\mathbb{R}^3}V_c(\mathbf{r})\rho_\gamma(\mathbf{r})d\mathbf{r}+e^2D(\rho_\gamma,\rho_\gamma)-e^2X(\gamma), \tag{6}$$

where $\rho_\gamma(\mathbf{r})=\sum_{\sigma=1}^{q}\gamma(\mathbf{x},\mathbf{x})=\sum_{\sigma=1}^{q}\gamma(\mathbf{r},\sigma,\mathbf{r},\sigma)$ is the particle density,

$$D(\rho,\mu)=\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(\mathbf{r})\mu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{7}$$

and where the exchange term is [note the sign in Eq. (6)]

$$X(\gamma)=\frac{1}{2}\int\int\frac{|\gamma(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'. \tag{8}$$

As is well known, this functional $\mathcal{E}^{\mathrm{HF}}$ is the expectation value of H in a determinantal wave function Ψ made of orthonormal functions φ_i,

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)=(N!)^{-1/2}\det\varphi_i(\mathbf{x}_j)\big|_{i,j=1}^{N}, \tag{9}$$

in which case

$$\gamma(\mathbf{x},\mathbf{x}')=\sum_{i=1}^{N}\varphi_i(\mathbf{x})\varphi_i(\mathbf{x}')^*. \tag{10}$$

It is also well known that *any* one-body density matrix γ for fermions always has two properties [in addition to the obvious requirement of self-adjointness, i.e., $\gamma(\mathbf{x},\mathbf{x}')=\gamma(\mathbf{x}',\mathbf{x})^*$] which are necessary and sufficient to ensure that it comes from a normalized N-body state satisfying the Pauli exclusion principle, see, e.g., [5,9]:

$$0\leq\gamma\leq 1\ \text{as an operator}\quad\text{and}\quad\operatorname{tr}\gamma=N, \tag{11}$$

where tr denotes the trace$=\int d\mathbf{x}\,\gamma(\mathbf{x},\mathbf{x})=$sum of the eigenvalues of γ. A simple consequence of Eq. (11) is that the spin-summed density matrix $(\operatorname{tr}_\sigma\gamma)(\mathbf{r},\mathbf{r}')=\sum_\sigma\gamma(\mathbf{r},\sigma,\mathbf{r}'\sigma)$, which acts on functions of space alone, satisfies

$$0\leq\operatorname{tr}_\sigma\gamma\leq q\ \text{as an operator}\quad\text{and}\quad\operatorname{tr}(\operatorname{tr}_\sigma\gamma)=N. \tag{12}$$

The HF γ in Eq. (10) has N eigenvalues equal to 1, and the rest equal to 0, but one could ignore this feature and apply Eq. (6) to any γ satisfying Eq. (11). If we do this, then we can define the HF energy (for all $N\geq 0$) by

$$E^{\mathrm{HF}}(N)=\inf_{\gamma}\{\mathcal{E}^{\mathrm{HF}}(\gamma):0\leq\gamma\leq 1,\operatorname{tr}\gamma=N\}. \tag{13}$$

[We say "infimum" in Eq. (13) instead of "minimum" because there may be no actual minimizer—as occurs when $N\gg Z=\sum_j Z_j$.] A HF energy minimizer does exist when $N<Z+1$, at least, and possibly for larger N's as well [10,11].

It is a fact [12] (see also [13]) that $E^{\mathrm{HF}}(N)$ is the infimum over all γ's of the determinantal form (10), i.e., the determinantal functions always win the competition in Eq. (13). Therefore, $E^{\mathrm{HF}}(N)\geq E_0(N)$, where $E_0(N)$ is the true ground state energy of the Hamiltonian (2).

Thus, the HF density-matrix-functional has the advantage of providing an upper bound to E_0, but it cannot do better than HF theory. We know, however, that this is often not very good, numerically, especially for dissociation energies.

Another disadvantage of $\mathcal{E}^{\mathrm{HF}}$ is that the energy minimizer γ^{HF} (if there is one) may not be unique although, in some cases, it is known to be unique (see [14] for the Dirac-Fock equations). In fact it follows from Hund's rule that in many cases the spatial part of the wave function has a nonzero angular momentum and cannot, therefore, be spherically symmetric.

A third point to note is that in HF theory the electron Coulomb repulsion is modeled by $D(\rho_\gamma,\rho_\gamma)-X(\gamma)$. This energy really should be $\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|\mathbf{r}-\mathbf{r}'|^{-1}\rho^{(2)}(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'$, however, where $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is the two-particle density, i.e., the spin summed diagonal part of the *two-particle* density matrix. In effect, one is replacing $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ by $G^{(2)}(\mathbf{r},\mathbf{r}')=\frac{1}{2}\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')-\frac{1}{2}\sum_{\sigma,\sigma'=1}^{q}|\gamma(\mathbf{x},\mathbf{x}')|^2$. It is not possible for this $G^{(2)}$ to be the two-body density of any state because that would require that $\int_{\mathbb{R}^3}G^{(2)}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=\frac{N-1}{2}\rho(\mathbf{r})$. This condition fails unless the state is a HF state [because even the total integral is wrong, namely, $\int\int G^{(2)}d\mathbf{r}d\mathbf{r}'>N(N-1)/2$ unless we have a HF state].

B. Müller's square-root exchange-correlation energy

There is an alternative to $\mathcal{E}^{\mathrm{HF}}(\gamma)$, which we will call $\mathcal{E}^{\mathrm{M}}(\gamma)$ (Müller [15]). It replaces the operator γ in $X(\gamma)$ by $\gamma^{1/2}$. This means the *operator* square root (note that γ is self-adjoint and positive as an operator, so the square root is well defined). Thus, $\gamma(\mathbf{x},\mathbf{x}')=\int d\mathbf{x}''\gamma^{1/2}(\mathbf{x},\mathbf{x}'')\gamma^{1/2}(\mathbf{x}'',\mathbf{x}')$. In terms of spectral representations, with eigenvalues λ_i and orthonormal eigenfunctions φ_i (the "natural orbitals"),

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

and

$$\gamma^{1/2}(\mathbf{x},\mathbf{x}')=\sum_{i=1}^{\infty}\lambda_i^{1/2}\varphi_i(\mathbf{x})\varphi_i(\mathbf{x}')^*. \tag{14}$$

There is no simple formula for the calculation of $\gamma^{1/2}(\mathbf{x},\mathbf{x}')$ in terms of $\gamma(\mathbf{x},\mathbf{x}')$, unfortunately, but there is an integral representation, which we shall use later.

Thus,

$$\mathcal{E}^{\mathrm{M}}(\gamma)=\frac{\hbar^2}{2m}\operatorname{tr}(-\nabla^2\gamma)-e^2\int_{\mathbb{R}^3}V_c(\mathbf{r})\rho_\gamma(\mathbf{r})d\mathbf{r}+e^2D(\rho_\gamma,\rho_\gamma)-e^2X(\gamma^{1/2}), \tag{15}$$

and

$$E^{\mathrm{M}}(N)=\inf_{\gamma}\{\mathcal{E}^{\mathrm{M}}(\gamma):0\le\gamma\le 1,\operatorname{tr}\gamma=N\}. \tag{16}$$

The functional $\mathcal{E}^{\mathrm{M}}(\gamma)$ was introduced by Müller [15] and was rederived by other methods by Buijse and Baerends [16]. A similar functional was introduced by Goedecker and Umrigar [17], the chief difference being that [17] attempts to remove an electron "self-energy" by omitting certain diagonal terms that arise when Eq. (16) is explicitly written out using the expansion of γ into its orbitals (14). In particular, quite analogous to density-functional theory, explicit corrections terms have been added to correct the overestimate of binding energies using Müller's functional (Gritsenko *et al.* [18]).

From now on we will use atomic units, i.e., $\hbar=m=e=1$. To get some idea of the magnitudes involved we can look at hydrogen. Numerical computations [[18], Fig. 6] and [[19], Fig. 3.1] suggest that $E^{\mathrm{M}}(1)\approx-0.525$. This is to be compared with the true energy, -0.5.

It might be wondered how Müller's exchange energy compares to the old Dirac $-\int\rho_\gamma(\mathbf{r})^{4/3}d\mathbf{r}$. As remarked after Lemma 2, and as found earlier by Cioslowski and Pernal [20], $X(\gamma^{1/2})$ cannot be bounded by $C\int\rho_\gamma(\mathbf{r})^{4/3}d\mathbf{r}$ for any C.

Müller [15] also considered using $\gamma^p(\mathbf{x},\mathbf{x}')\gamma^{1-p}(\mathbf{x}',\mathbf{x})$ for some $0<p<1$ in place of $|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2=\gamma^{1/2}(\mathbf{x},\mathbf{x}')\gamma^{1/2}(\mathbf{x}',\mathbf{x})$, which satisfies the integral condition stated in **A.1** below, but he decided to take $p=1/2$ because this yields the smallest value of X, and hence the largest energy. (The proof is analogous to $a^pb^{1-p}+a^{1-p}b^p\ge 2\sqrt{ab}$ for positive numbers a,b.)

Müller's functional (15) has several advantages, the first of which is as follows.

A.1. The quantity that effectively replaces $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ in the functional is now

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

and this satisfies the correct integral condition

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

On the other hand, $\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')-\Sigma_{\sigma,\sigma'=1}^{q}|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2$ is not necessarily positive as a *function* of $\mathbf{r},\mathbf{r}'$, whereas the HF choice $\rho_\gamma(\mathbf{r})\rho_\gamma(\mathbf{r}')-\Sigma_{\sigma,\sigma'=1}^{q}|\gamma(\mathbf{x},\mathbf{x}')|^2\ge 0$ (which is true for any positive semidefinite operator). This nonpositivity is a source of some annoyance. In particular, it prevents the application of a standard method [21] for proving a bound on the maximum N.

A.2. A special choice of γ is a HF type of γ, namely, one in which all the λ_i are 0 or 1. In this special case $\gamma^{1/2}=\gamma$ 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 $E^{\mathrm{M}}(N)\le E^{\mathrm{HF}}(N)$ (because, as we remarked above, the minimizers for the HF problem always have this projection property).

Later, we shall propose that the quantity $\hat{E}^{\mathrm{M}}(N)=E^{\mathrm{M}}(N)+N/8$ should be interpreted as the binding energy; it is not obvious that $\hat{E}^{\mathrm{M}}(N)$ satisfies such an inequality, however. Indeed, it does not, in general, as the hydrogen example shows $(-0.525+1/8>-0.5)$.

A.3. The original Müller functional seems to give good numerical results when few electrons are involved. Moreover, $E^{\mathrm{M}}(N)$ appears to satisfy $E^{\mathrm{M}}(N)\le E_0(N)$ for all electron numbers N, i.e., it is always a lower bound. We shall *prove* this inequality when $N=2$ in the last section. (Numerical accuracy of larger electron numbers seem to require appropriately modified functionals. We refer the reader interested on numerical results and improved density matrix functionals to the papers of Buijse and Baerends [16], Staroverov and Scuseria [22], Herbert and Harriman [23], Gritsenko *et al.* [18], Poater *et al.* [24], Lathiotakis *et al.* [25], and Helbig [19].) Since we are primarily interested in the structure of the underlying theory rather than numerical results, we concentrate on the unmodified original Müller functional despite the above mentioned numerical deficiency for large electron number. The Müller functional can be viewed as a prototype of density matrix functionals with simple structures, but which are potentially useable as the basis of more elaborate functionals, e.g., [17,18,26,27].

C. Convexity and some of its uses

A key observation about $\mathcal{E}^{\mathrm{M}}(\gamma)$ is that it is a *convex functional* of γ. This means that for all $0<\lambda<1$ and density matrices γ_1, γ_2 (not necessarily with the same trace and not necessarily satisfying $\gamma\le 1$)

$$\mathcal{E}^{\mathrm{M}}(\lambda\gamma_1+(1-\lambda)\gamma_2)\leq\lambda\mathcal{E}^{\mathrm{M}}(\gamma_1)+(1-\lambda)\mathcal{E}^{\mathrm{M}}(\gamma_2). \quad (17)$$

[Note that the convex combination $\lambda\gamma_1+(1-\lambda)\gamma_2$ satisfies the conditions in Eq. (16) if γ_1 and γ_2 both satisfy the conditions.] The convexity is a bit surprising, given the minus sign in the exchange term of $\mathcal{E}^{\mathrm{M}}$, and it will lead to several important theorems. One is that the electron *density* $\rho_\gamma(\mathbf{r})$ of the minimizer (if there is one) is the same for all minimizers with the same N, and hence that the density of an atom is always spherically symmetric. This contrasts sharply with HF theory, whose functional (6) is *not* convex, and it can contradict the original Schrödinger theory (since an atom can have a nonzero angular momentum in its ground state). Also, the Dirac estimate for the exchange energy, $-\int\rho^{4/3}$ is not convex; it is concave, in fact.

Some writers [28] regard the retention of symmetry as a desirable property for an approximate theory; one speaks of the "symmetry dilemma" of HF theory (which means that while symmetry restriction of HF orbitals improves the overall symmetry it raises the minimum energy). Müller theory has no symmetry dilemma.

From another perspective the sphericity of an atom might be seen as a drawback since real atoms sometimes have a nonzero angular momentum, and such states are not spherically symmetric. Sphericity is not a drawback, in fact, since density matrix-functional theory deals with density matrices obtained from *all* N-particle states, including mixed ones (because the only restriction we impose is that the eigenvalues of γ lie between 0 and 1, and this condition precisely defines the set of γ obtained from the set of mixed states, not the set of pure states). In the case of atoms there is always a mixed state with spherical symmetry, namely, the projection onto all the ground states, divided by the degeneracy. This is the state that one sees (in principle) when looking at an atom at zero temperature (Lüders's projection postulate [29]).

A second consequence of convexity is that the energy $E^{\mathrm{M}}(N)$ is always a convex function of N, as it is in Thomas-Fermi theory, for example [12,30]. This means that as we add one electron at a time to our molecule, the (differential) binding energy steadily decreases. Such a property is *not* known to hold for the true Schrödinger energy $E_0(N)$.

The convexity of $\mathcal{E}^{\mathrm{M}}(\gamma)$ is not at all obvious. All the terms except $-X(\gamma^{1/2})$ are clearly convex. In fact, the term $D(\rho_\gamma,\rho_\gamma)$ is *strictly* convex as a function of the density $\rho_\gamma(\mathbf{r})$ [strict inequality in Eq. (17) when $\rho_{\gamma_1}\neq\rho_{\gamma_2}$] since the Coulomb kernel $|\mathbf{r}-\mathbf{r}'|^{-1}$ is positive definite. It is this strict convexity that implies the uniqueness of $\rho_\gamma(\mathbf{r})$ when there is a minimizer.

To show convexity of $\mathcal{E}^{\mathrm{M}}(\gamma)$, therefore, we have to show concavity [like Eq. (17) but with the inequality reversed] of the functional $X(\gamma^{1/2})$. First, we write $|\mathbf{r}-\mathbf{r}'|^{-1}=\int_\Lambda B_\lambda(\mathbf{r})^* B_\lambda(\mathbf{r}')d\lambda$ where λ is in some parameter-space Λ. There are many ways to construct such a decomposition. One way is due to Fefferman and de la Llave [31], which we shall use in the following, in which the functions B_λ are all characteristic functions of balls in $\mathbb{R}^3$ and λ parametrizes their radii and centers. Another way is $|\mathbf{r}-\mathbf{r}'|^{-1}=C\int_{\mathbb{R}^3}|\mathbf{r}-\mathbf{z}|^{-2}|\mathbf{r}'-\mathbf{z}|^{-2}d\mathbf{z}$. Anyway, it suffices now to prove that $\int d\mathbf{x}d\mathbf{x}'\,\gamma^{1/2}(\mathbf{x},\mathbf{x}')B(\mathbf{r})^*\gamma^{1/2}(\mathbf{x}',\mathbf{x})B(\mathbf{r}')$ is concave in γ, for any fixed function $B(\mathbf{r})$. We can write this in abstract operator form as $\mathrm{tr}\,\gamma^{1/2}B^\dagger\gamma^{1/2}B$. The concavity of such functions of γ was proved by Wigner and Yanase [32] in connection with a study of entropy.

Convexity also holds for Müller's general p functional, which we mentioned earlier. It uses $\gamma^p(\mathbf{x},\mathbf{x}')\gamma^{1-p}(\mathbf{x}',\mathbf{x})$ in the exchange term. The fact that $\mathrm{tr}\,\gamma^p B^\dagger\gamma^{1-p}B$ is concave for all $0<p<1$ was proved in [33] and plays a role in quantum information theory [34].

Another important use of the convexity of $\mathcal{E}^{\mathrm{M}}(\gamma)$ is to significantly simplify the question of the spin dependence of $\gamma(\mathbf{r},\sigma,\mathbf{r}',\sigma')$. For concreteness, let us assume the usual case of two spin states ($q=2$), but the conclusion holds for any q. In the HF problem it is not obvious how γ should depend on σ,σ' and usually one makes some standard *a priori* assumption, such as that $\gamma^{\mathrm{HF}}(\mathbf{r},\sigma,\mathbf{r}',\sigma')=\gamma_{\uparrow,\uparrow}(\mathbf{r},\mathbf{r}',)\delta_{\sigma,\uparrow}\delta_{\sigma',\uparrow}+\gamma_{\downarrow,\downarrow}(\mathbf{r},\mathbf{r}',)\delta_{\sigma,\downarrow}\delta_{\sigma',\downarrow}$. In the Müller case this problem does not arise. Note that the functional $\mathcal{E}^{\mathrm{M}}$ is invariant under simultaneous rotation of σ and σ' in spin-space. (This means that we regard γ as a 2×2 matrix whose elements are function of $\mathbf{r},\mathbf{r}'$. The spin rotation is then just a 2×2 unitary transformation of this matrix.) If we take any $\gamma(\mathbf{r},\sigma,\mathbf{r}',\sigma')$ and average it over all such simultaneous rotations we will obtain a new $\tilde{\gamma}$ whose energy $\mathcal{E}^{\mathrm{M}}(\tilde{\gamma})$ is at least as low as that of the original γ (by convexity). But $\tilde{\gamma}$ is clearly spin-space rotation invariant, which means it must have the form

$$\tilde{\gamma}(\mathbf{r},\sigma,\mathbf{r}',\sigma')=\frac{1}{2}\hat{\gamma}(\mathbf{r},\mathbf{r}')\otimes\mathbb{I}, \quad (18)$$

where $\mathbb{I}$ is the 2×2 identity matrix. The subsidiary conditions become

$$\mathrm{tr}\,\hat{\gamma}\equiv\int\hat{\gamma}(\mathbf{r},\mathbf{r})d\mathbf{r}=N \quad \text{and} \quad 0\leq\hat{\gamma}\leq 2. \quad (19)$$

The change from 1 to 2 in Eq. (19) is to be noted. Often $\hat{\gamma}$ is called the *spin-summed density matrix*.

The conclusion is that to get the correct minimum energy one can always restrict attention to the simpler, spin-independent $\hat{\gamma}$, but with the revised conditions (19). This is a significant simplification relative to HF theory. In much of the following we utilize the formal notation $\mathbf{x}$ instead of $\mathbf{r}$, but the reader should keep in mind that one can always assume that γ has the form (18) and all spin summations become trivial.

A question will arise: Although it is possible to choose γ in the form (18), are there other possibilities? They will certainly exist if $\hat{\gamma}$ is not unique (but we conjecture that it is unique since its density is unique, as we said). Even if $\hat{\gamma}$ is unique we still might have other possibilities, however, when N is small. For example, we could take $\gamma(\mathbf{x},\mathbf{x}')=\hat{\gamma}(\mathbf{r},\mathbf{r}')\times\delta_{\sigma,\uparrow}\delta_{\sigma',\uparrow}$, but this density matrix is bounded above by 1 only if $\hat{\gamma}\leq 1$ (not ≤ 2). This situation can arise if N is small, but we expect that it does not arise when $N\gtrsim 1$. In any case, we show that, for large N and Z, $\hat{\gamma}$ has at least one maximal eigenvalue, namely 2 (see Proposition 8).

In short, it is likely that whatever the Müller functional has to say about the energy, it probably has little to say, reliably, about the spin of the ground state. Unlike HF theory, we do not have to worry about spin here. This does not mean that HF theory is necessarily better as concerns spin. Sometimes it is [35], and sometimes it is not [36].

In the atomic case $\mathcal{E}^{\mathrm{M}}(\gamma)$ is also rotationally invariant and we can apply the same logic used above for the spin to the simultaneous rotation of $\mathbf{r},\mathbf{r}'$ in $\hat{\gamma}(\mathbf{r},\mathbf{r}')$. The conclusion is that we may assume the following computationally useful representation:

$$\hat{\gamma}(\mathbf{r},\mathbf{r}') = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\gamma_\ell(r,r')Y_{\ell,m}(\theta_{\mathbf{r}})Y^*_{\ell,m}(\theta_{\mathbf{r}'}) = \frac{2\,\ell\,+1}{4\pi}\sum_{\ell=0}^{\infty}\gamma_\ell(r,r')P_\ell(\cos\Theta), \tag{20}$$

where $r=|\mathbf{r}|$, $r'=|\mathbf{r}'|$. The $Y_{\ell,m}$ are normalized spherical harmonics, $\theta_{\mathbf{r}}$ is the angle of the vector $\mathbf{r}$, etc., P_ℓ is the ℓth Legendre polynomial, and Θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. Another way to say this is that we can assume that the eigenfunctions of $\hat{\gamma}(\mathbf{r},\mathbf{r}')$ are radial functions times spherical harmonics $Y_{\ell,m}$ and that the allowed m values occur with equal weight. This observation can simplify numerical computations.

Any other symmetry can be treated in a similar way. For example, in the case of a solid there is translation invariance of the lattice of nuclei. By wrapping a large, finite piece of the lattice on a torus (periodic boundary conditions) we have a finite system with translation invariance and we can conclude, as above, that we can assume that $\hat{\gamma}(\mathbf{r},\mathbf{r}')$ is also translation invariant, which means that $\hat{\gamma}(\mathbf{r},\mathbf{r}')$, viewed as a function of $\mathbf{r}+\mathbf{r}'$ and $\mathbf{r}-\mathbf{r}'$ is periodic in the variable $\mathbf{r}+\mathbf{r}'$.

One obvious symmetry is complex conjugation $(i\to -i)$ in the absence of a magnetic field. Convexity implies that in the spin-independent formulation any minimizing γ must be real, as shown in Proposition 9 of Sec. IV B.

D. The Müller equations

If the Müller functional has a minimizing γ (with tr $\gamma=N$) then this γ satisfies an Euler equation. A minimizer does exist if $N\le Z$ as we show in Theorem 2. It is not altogether a trivial matter to write down an equation satisfied by a minimizing γ. Conversely, one can ask whether a γ that satisfies this equation is necessarily a minimizer. We partly answer these questions in several ways.

(1) Suppose that γ satisfies tr $\gamma=N$ and that γ minimizes $\mathcal{E}^{\mathrm{M}}(\gamma)$, i.e., $\mathcal{E}^{\mathrm{M}}(\gamma)=E^{\mathrm{M}}(N)$. Then we conclude (by definition of the minimum) that

$$\mathcal{E}^{\mathrm{M}}((1-t)\gamma+t\gamma') \ge \mathcal{E}^{\mathrm{M}}(\gamma) \tag{21}$$

for all admissible γ' with tr $\gamma'=N$ and for all $0\le t\le 1$. Conversely, if tr $\gamma=N$ and if Eq. (21) is true for all such γ' and for *some* $0<t\le 1$ (with t possibly depending on γ') then γ is a minimizer. Alternatively, it suffices to require that for all such γ',

$$\frac{d}{dt}\mathcal{E}^{\mathrm{M}}((1-t)\gamma+t\gamma')|_{t=0} = \lim_{t\downarrow 0}\frac{1}{t}[\mathcal{E}^{\mathrm{M}}((1-t)\gamma+t\gamma')-\mathcal{E}^{\mathrm{M}}(\gamma)] \ge 0. \tag{22}$$

To see that γ is a minimizer we exploit the convexity of the functional $\mathcal{E}^{\mathrm{M}}$, which implies that $\mathcal{E}^{\mathrm{M}}((1-t)\gamma+t\gamma') \le (1-t)\mathcal{E}^{\mathrm{M}}(\gamma)+t\mathcal{E}^{\mathrm{M}}(\gamma')$, and hence, from Eq. (21) or Eq. (22), that $\mathcal{E}^{\mathrm{M}}(\gamma)\le\mathcal{E}^{\mathrm{M}}(\gamma')$. [Note that the convexity also implies that $\mathcal{E}^{\mathrm{M}}((1-t)\gamma+t\gamma')$ is a convex function of t in the interval $[0,1]$, which, in turn, implies that the right derivative defined in Eq. (22) always exists.]

To summarize, we say that *the equation defining a minimizer is* Eq. (22) (for all γ'). To make this more explicit we have to compute the derivative in Eq. (22).

(2) The variational equations are most conveniently written down in terms of $\gamma^{1/2}$, the square root of a minimizer. In Proposition 10, we will show that $\gamma^{1/2}(\mathbf{r},\mathbf{r}')$ satisfies the following variational equation. Let φ_γ denote the effective potential $\varphi_\gamma(\mathbf{r})=V_c(\mathbf{r})-\int\rho_\gamma(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{r}'$, where $\rho_\gamma(\mathbf{r})=\Sigma_\sigma\gamma(\mathbf{x},\mathbf{x})=\Sigma_\sigma\int|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2d\mathbf{x}'$ denotes the particle density. Then

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}}-\frac{1}{2}\nabla^2_{\mathbf{r}'}-\varphi_\gamma(\mathbf{r})-\varphi_\gamma(\mathbf{r}')-\frac{1}{|\mathbf{r}-\mathbf{r}'|}-2\mu\right)\gamma^{1/2}(\mathbf{x},\mathbf{x}') = \sum_i 2e_i\psi_i(\mathbf{x})\psi_i(\mathbf{x}')^*, \tag{23}$$

where $\mu\le -1/8$, $e_i\le 0$ and $\psi_i(\mathbf{x})$ is an eigenfunction of $\gamma^{1/2}$ with eigenvalue 1, i.e., $\int\gamma^{1/2}(\mathbf{x},\mathbf{x}')\psi_i(\mathbf{x}')d\mathbf{x}'=\psi_i(\mathbf{x})$ for all i. Note that the number of ψ_i's corresponding to eigenvalue 1 is necessarily less than N.

Conversely, is it true that any $\gamma^{1/2}$ satisfying $0\le\gamma^{1/2}\le 1$ (as an operator) and $\mathrm{tr}(\gamma^{1/2})^2=\mathrm{tr}\ \gamma=N$ which is a solution to Eq. (23) under the constraints mentioned above, is a minimizer of $\mathcal{E}^{\mathrm{M}}(\gamma)$? Unfortunately, we can answer this question affirmatively only if we know that the density $\rho_\gamma(\mathbf{r})$ does not vanish on a set of positive measure. Presumably such a vanishing does not occur, but we do not know how to prove this and leave it as an open problem.

(3) As a practical matter it is the fact that γ satisfies Eq. (23) that is important because it gives us equations for the orbitals of γ. A minimizer γ can be expanded in natural orbitals $\psi_j(\mathbf{x})$ as

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_j \lambda_j\psi_j(\mathbf{x})\psi_j(\mathbf{x}')^*$$

with corresponding occupation numbers (eigenvalues) $0<\lambda_j\le 1$. Then $\gamma^{1/2}(\mathbf{x},\mathbf{x}')=\Sigma_j\lambda_j^{1/2}\psi_j(\mathbf{x})\psi_j(\mathbf{x}')^*$. Multiplying Eq. (23) by $\psi_i(\mathbf{x}')$ and integrating over $\mathbf{x}'$ yields an eigenvalue equation for the $\psi_i(\mathbf{x})$, namely

$$\left[\left(-\frac{1}{2}\nabla^2-\varphi_\gamma\right)\gamma^{1/2}+\gamma^{1/2}\left(-\frac{1}{2}\nabla^2-\varphi_\gamma\right)\right]|\psi_i\rangle - (Z_\gamma+2\mu\lambda_i^{1/2})|\psi_i\rangle = 2e_i|\psi_i\rangle. \tag{24}$$

Here, Z_γ is the operator with integral kernel

$$Z_\gamma(\mathbf{x},\mathbf{x}') = \gamma^{1/2}(\mathbf{x},\mathbf{x}')|\mathbf{r}-\mathbf{r}'|^{-1}. \tag{25}$$

Taking the product with $\langle\psi_j|$, this implies, in particular, that

$$\left\langle \psi_j \left| -\frac{1}{2}\nabla^2 - \varphi_\gamma \right| \psi_i \right\rangle - \frac{1}{\sqrt{\lambda_i}+\sqrt{\lambda_j}}\langle\psi_j|Z_\gamma|\psi_i\rangle = (\mu + e_i)\delta_{ij}. \tag{26}$$

(See also Pernal [37] who derived—although merely on a formal level—similar equations for more general functionals.)

(4) We shall show that γ has no zero eigenvalues unless the density $\rho_\gamma(\mathbf{r})$ vanishes identically on a set Ω of positive measure. We do not expect such a set to exist but we do not know how to exclude this possibility. Any nonzero, square integrable function that vanishes identically outside Ω is a zero eigenvalue eigenfunction of γ. In any case, there are no other zero eigenvalue eigenfunctions.

Hence the orbitals $\psi_j(\mathbf{x})$ form a complete set in $L^2(\mathbb{R}^3\backslash\Omega)$. Formally, we can thus rewrite Eq. (26) as an eigenvalue equation for a linear operator H_γ on $L^2(\mathbb{R}^3\backslash\Omega)$. Let

$$H_\gamma = -\frac{1}{2}\nabla^2 - \varphi_\gamma - \mathfrak{X}_\gamma, \tag{27}$$

where $\mathfrak{X}_\gamma$ is the nonlocal exchange operator with matrix elements $\langle\psi_i|\mathfrak{X}_\gamma|\psi_j\rangle = (\sqrt{\lambda_i}+\sqrt{\lambda_j})^{-1}\langle\psi_i|Z_\gamma|\psi_j\rangle$. Alternatively, one can write

$$\mathfrak{X}_\gamma = \frac{1}{\pi}\int_0^\infty \frac{1}{\gamma+s}Z_\gamma\frac{1}{\gamma+s}\sqrt{s}ds. \tag{28}$$

The variational equations are then

$$H_\gamma|\psi_j\rangle = \mu|\psi_j\rangle \tag{29}$$

for all j with $0<\lambda_j<1$, where $\mu \le -1/8$ is the chemical potential. Notice that all eigenvalues in Eq. (29) are identical, namely, μ.

In the subspace in which γ has eigenvalue 1, which can only be finite dimensional since tr $\gamma = N$, there is an orthonormal basis such that

$$H_\gamma|\psi_j\rangle = (\mu + e_j)|\psi_j\rangle \tag{30}$$

with all $e_j \le 0$. The finite collection of numbers $\mu + e_j$ constitutes all the eigenvalues of H_γ that are less than μ.

The reason we say that Eqs. (29) and (30) are formal is that the operator H_γ is only formally defined by Eq. (27). Both ∇^2 and $\mathfrak{X}_\gamma$ are unbounded operators. Their sum is defined as a quadratic form (i.e., expectation values) but this form does not uniquely define the operator sum. If we knew that there are no zero eigenvalues then the set Ω would be empty and ∇^2 would be defined as the usual Laplacian on $\mathbb{R}^3$, but if $\mathbb{R}^3\backslash\Omega$ has a boundary there are many extensions of ∇^2 with different boundary conditions, and this prevents the precise specification of Eqs. (29) and (30). There is no problem with the matrix elements in Eq. (26), however, since the ψ_i vanish on the boundary of $\mathbb{R}^3\backslash\Omega$.

On the other hand, Eq. (23), which is an equation for the *function* $\gamma^{1/2}(\mathbf{x},\mathbf{x}')$, is true on the whole space. It is not necessary to impose any boundary conditions and ∇^2 is just the usual Laplacian—whether or not the set Ω is empty.

Surely Ω is empty, in fact, and the practical quantum chemist can freely use Eqs. (29) and (30).

E. Other considerations about the Müller functional

Let us conclude this introduction with a list of other significant questions about $E^{\mathrm{M}}(N)$ and with statements about what we can prove rigorously.

Q1. If there are no nuclei at all ($K=0$), and if we try to minimize $\mathcal{E}^{\mathrm{M}}(\gamma)$ (with tr $\gamma=N$, however) it is clear that there will be no energy minimizing γ. There will, of course, be a minimizing sequence [i.e., a sequence γ_n, $n=1,2,\ldots$ such that $\mathcal{E}^{\mathrm{M}}(\gamma_n)\to E^{\mathrm{M}}(N)$ as $n\to\infty$]. Such a sequence will tend to "spread out" and get smaller and smaller as it spreads (always with tr $\gamma_n=N$). What, then, is $E^{\mathrm{M}}(N)$? We prove that it is *exactly* given by

$$E^{\mathrm{M}}(N) = -N/8 \quad \text{when all } Z_j = 0. \tag{31}$$

[If the units are included the energy is $-(me^4/8\hbar^2)N$.] A similar calculation in the context of the homogeneous electron gas was done by Cioslowski and Pernal [20].

This situation is reminiscent of Thomas-Fermi-Dirac theory [12] where, in the absence of nuclei, the energy equals $-(\text{const})N$. This negative energy comes from balancing the kinetic energy against the negative exchange. In such a case it is convenient to add $+(\text{const})\text{tr}\,\gamma$ to $\mathcal{E}^{\mathrm{M}}(\gamma)$ [with (const) $=1/8$ in our case] in order that $E^{\mathrm{M}}(N)\equiv 0$ when there are no nuclei.

Another way to say this is that the energy, $-1/8$, is the *self-energy* of a particle in this theory. It has no physical or chemical meaning but we have to pay attention to it. It is the quantity

$$\hat{E}^{\mathrm{M}}(N) = E^{\mathrm{M}}(N) + \frac{N}{8} \tag{32}$$

that might properly be regarded as the energy of N electrons in the presence of the nuclei, i.e., $-\hat{E}^{\mathrm{M}}(N)$ is the physical binding (or dissociation) energy. We do not insist on this interpretation, however. On the other hand, if we are interested in the binding energy with fixed N (e.g., the binding energy of two atoms to form a molecule) then it makes no difference whether we use the difference of $\hat{E}^{\mathrm{M}}(N)$ or $E^{\mathrm{M}}(N)$.

The motivation here is to ensure that the ground state energy of free electrons is zero. This can be compared with the formulation in [17] in which the "self-energy" correction is obtained by omitting certain diagonal terms in the energy (when the energy is written in terms of the orbitals of γ). This procedure does not have a natural physical interpretation and, more importantly, does not appear to give the zero energy condition for free electrons.

This consideration leads us to the functional

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) = \mathcal{E}^{\mathrm{M}}(\gamma) + \frac{1}{8}\,\text{tr}\,\gamma \tag{33}$$

and its corresponding infimum $\hat{E}^{\mathrm{M}}(N)$. Note that $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ is also a convex functional of γ since the new term tr $\gamma/8$ is

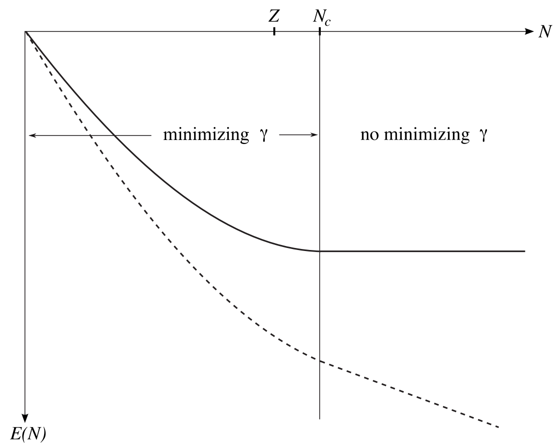

FIG. 1. Schematic diagram of the energy dependence on the particle number N. The lower, dashed curve is the Müller energy $E^{\mathrm{M}}(N)$ and the upper, solid curve is $\hat{E}^{\mathrm{M}}(N)=E^{\mathrm{M}}(N)+N/8$, in which the "self-energy" $-N/8$ has been subtracted. Beyond the value N_c each curve is linear, whereas for $N<N_c$ each is strictly convex and there is an energy minimizing density matrix.

linear, and hence convex. Likewise, $\hat{E}^{\mathrm{M}}(N)$ is a convex function of N.

Having added this term, and with nuclei present, $\hat{E}^{\mathrm{M}}(N)$ will qualitatively look like the Thomas-Fermi (TF) energy, $E^{\mathrm{TF}}(N)$. That is, $\hat{E}^{\mathrm{M}}(0)=0$ and $\hat{E}^{\mathrm{M}}(N)$ decreases monotonically, and with nondecreasing derivative, as N increases ([30], Fig. 1 of Ref. [12]). It is bounded below, that is,

$$\hat{E}^{\mathrm{M}}(N) \geq \hat{E}^{\mathrm{M}}(\infty), \tag{34}$$

where $\hat{E}^{\mathrm{M}}(\infty)$ is some finite, negative constant. We shall *prove* this here. These features are displayed schematically in Fig. 1.

There is another feature of $E^{\mathrm{TF}}(N)$ that we believe to be true for $\hat{E}^{\mathrm{M}}(N)$, but leave as an *open question*. At a certain critical value N_c of the electron number $E^{\mathrm{TF}}(N)$ stops decreasing and becomes constant for all $N \geq N_c$. When $N>N_c$ the excess charge $N-N_c$ just leaks off to infinity. In TF theory N_c is the neutrality point $Z=\Sigma Z_j$, but this need not be so in other theories. In the original Schrödinger theory (2) N_c is greater than Z for many atoms (since stable, negative ions exist) but we know it is less than $2Z+1$ [21]. In the Thomas-Fermi-Weizsäcker theory, N_c is approximately $Z+(\text{const})$ [12,38]. We do not know how to prove that there is a finite N_c for $\hat{E}^{\mathrm{M}}(N)$, but we believe there is one.

Q2. The main problem that has to be addressed is whether or not there is a γ that minimizes $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ in Eq. (16). If $N_c<\infty$ we know that there is *no* minimizer when $N>N_c$, so we obviously do not expect to prove the existence of a minimizer for all N.

The way around this problem, as used in [30], for example, is to consider the *relaxed problem*

$$\hat{E}^{\mathrm{M}}_{\leq}(N) = \inf_{\gamma}\{\hat{\mathcal{E}}^{\mathrm{M}}(\gamma): 0 \leq \gamma \leq 1, \mathrm{tr}\,\gamma \leq N\}. \tag{35}$$

The relaxation of the number condition allows electrons to move to infinity in case N is larger than the maximal number of electrons that can be bound. In Proposition 4 we show that $\hat{E}^{\mathrm{M}}_{\leq}(N)=\hat{E}^{\mathrm{M}}(N)$ for all N.

The difference is that while the $\hat{E}^{\mathrm{M}}$ problem may not have a minimizer we prove that the $\hat{E}^{\mathrm{M}}_{\leq}$ problem (35) has a minimizer for all N. The proof is more complicated in several ways than the analogous proof in TF theory [12,30]. A minimizer, which we can call $\gamma_{\leq}(N)$, will have some particle number $\mathrm{tr}\,\gamma_{\leq}(N) \equiv N_{\leq} \leq N$. It then follows from standard arguments using convexity [and strict convexity of $D(\rho,\rho)$] that the following is true, as displayed in Fig. 1.

If $N_{\leq}<N$ then $\gamma_{\leq}(N)=\gamma_{\leq}(N_{\leq})$ and $\hat{E}^{\mathrm{M}}(N)=(\text{const}) =\hat{E}^{\mathrm{M}}(N_{\leq})$, i.e., the original problem (16) has no minimizer.

If $N_{\leq}=N$ then $\gamma_{\leq}(N)$ is also a minimizer for the original problem (16). That is, the relaxed problem and the original problem give the same minimizer and the same energy. In this case, $\hat{E}^{\mathrm{M}}(N)<\hat{E}^{\mathrm{M}}(N')$ for all $N'<N$. The largest N with this property is equal to N_c.

It might occur to the reader that nothing said so far precludes the possibility that $N_c=0$, but this is not so. We prove that $N_c \geq Z$=total nuclear charge.

Q3. How many orbitals are contained in a minimizing γ? We shall prove that γ has infinitely many positive eigenvalues. This feature also holds for the full Schrödinger theory (Friesecke [39] and Lewin [40]), whereas there are only N in HF theory. We believe that γ has no zero eigenvalues (in the "spin-summed" version), but cannot prove this. In other words, we believe that the eigenfunctions belonging to the nonzero eigenvalues span Hilbert space (they form a complete set). We can, however, prove that the eigenfunctions of the spin-summed γ are a complete set on the support of $\rho_\gamma(\mathbf{r})$, namely, on the set of $\mathbf{r}\in\mathbb{R}^3$ for which $\rho_\gamma(\mathbf{r})>0$. Presumably, this is the whole of $\mathbb{R}^3$.

This introduction is long, but we hope it serves to clarify our goals and results, since the rest of the paper is unavoidably technical.

F. Open problems

For the reader's convenience we give a brief summary of some of the open problems raised by this work, some of which are discussed at various places in this paper.

(1) What is the critical value of the total electron charge, N_c, beyond which there is no energy minimizing γ and the energy $\hat{E}^{\mathrm{M}}(N)$ is constant? Is N_c finite and can one give upper and lower bounds to it? In particular is $N_c>Z$, i.e., can negative ions exist? [We prove $N_c \geq Z$ and we prove that $\hat{E}^{\mathrm{M}}(N)$ is bounded below, for all N, by a Z-dependent constant.]

(2) Is $E^{\mathrm{M}}(N) \leq$ the true Schrödinger ground state energy? (We prove this for $N=2$.) Can anything be said, in this regard, about $\hat{E}^{\mathrm{M}}(N)=E^{\mathrm{M}}(N)+N/8$?

(3) Is the spin-summed energy minimizing γ unique? [We prove that all minimizers have the same density $\rho(\mathbf{r})$, however.]

(4) Is the domain on which the unique $\rho(\mathbf{r})>0$ equal to the whole of $\mathbb{R}^3$ (except, possibly, for sets of measure zero)? If so, this would imply that the spin-summed γ does not have a zero eigenvalue.

(5) What are the qualitative properties of the density $\rho(\mathbf{r})$? How does it fall off for large $|\mathbf{r}|$? What is its behavior near the nuclei?

(6) In this theory do atoms bind to form molecules? (Recall that there is no binding in Thomas-Fermi theory [30].)

II. THE CASE $Z=0$

As noted in the Introduction the energy of *free* electrons $E^{\mathrm{M}}(N)$ is not zero but is proportional to N. To be precise, $E^{\mathrm{M}}(N)=-N/8$ (in atomic units) when there are no nuclei, and comes about from the negative exchange energy $-X(\gamma^{1/2})$. This negative energy could be $-\infty$ were it not for the positive kinetic energy, which controls it and leads to a finite result. We shall prove that the direct Coulomb repulsion term, $D(\rho_\gamma,\rho_\gamma)$ plays *no role* here because it is quadratic in γ, whereas the terms we are concerned with are homogeneous of order 1. We would get $-N/8$ even if we omitted the direct term. Similarly, the value $-N/8$ is independent of the number of spin states q. Moreover, the assumption $\gamma\leq 1$ is *not* needed in the proof.

In this section, $Z=\Sigma Z_j=0$, and we are considering the functional

$$\mathcal{E}^{\mathrm{M}}(\gamma) \equiv \operatorname{tr}\left(-\frac{1}{2}\nabla^2\gamma\right) + D(\rho_\gamma,\rho_\gamma) - X(\gamma^{1/2}), \tag{36}$$

and the minimal energy $E^{\mathrm{M}}(N)$ in Eq. (16). We also consider the relaxed energy $E^{\mathrm{M}}_{\leq}(N)$ for which, in analogy with Eq. (35), the condition $\operatorname{tr}\gamma=N$ is replaced by $\operatorname{tr}\gamma\leq N$.

We always assume that $(-\nabla^2+1)^{1/2}\gamma^{1/2}\in\mathfrak{S}^2$, the set of Hilbert-Schmidt operators, so $\operatorname{tr}((1-\nabla^2)\gamma) =\int\int d\mathbf{x}d\mathbf{x}'[|\nabla\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2+|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2]<\infty$. We use the usual notation for L^p-norms, namely,

$$\|f\|_p = \left(\int |f(\mathbf{x})|^p d\mathbf{x}\right)^{1/p} \quad \text{and} \quad \|f\|_\infty = \sup_{\mathbf{x}}\{|f(\mathbf{x})|\}.$$

Proposition 1. *If $Z=0$, then for any $N>0$,*

$$E^{\mathrm{M}}(N) = E^{\mathrm{M}}_{\leq}(N) = -N/8 \tag{37}$$

and there is no minimizing γ.

Proof. Lower bound: We use the lower semiboundedness of the hydrogenic Hamiltonian (i.e., for an imaginary nucleus with $Z=1/2$, located at $\mathbf{r}'$)

$$-\frac{1}{2}\nabla^2_{\mathbf{r}} - (2|\mathbf{r}-\mathbf{r}'|)^{-1} \geq -\frac{1}{8} \tag{38}$$

for all $\mathbf{r}'\in\mathbb{R}^3$, together with the fact that $D(\rho_\gamma,\rho_\gamma)\geq 0$ to get

$$\begin{aligned}\mathcal{E}^{\mathrm{M}}(\gamma) &\geq \frac{1}{2}\int\int\left(|\nabla_{\mathbf{r}}\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 - \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\right)d\mathbf{x}d\mathbf{x}' \\ &\geq -\frac{1}{8}\int\int|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 d\mathbf{x}d\mathbf{x}' \\ &= -\frac{1}{8}\operatorname{tr}\gamma.\end{aligned}$$

This proves the lower bound on $E^{\mathrm{M}}(N)$ and $E^{\mathrm{M}}_{\leq}(N)$.

To prove the nonexistence of a minimizer we denote by $g(\mathbf{r}-\mathbf{r}')$ the ground state of $-\nabla^2_{\mathbf{r}}-|\mathbf{r}-\mathbf{r}'|^{-1}$, i.e.,

$$g(\mathbf{r}-\mathbf{r}') = \pi^{-1/2}e^{-|\mathbf{r}-\mathbf{r}'|}, \tag{39}$$

and note that the inequality $\geq$ in Eq. (38) is strict (i.e., it is $>$), except for multiples of the function $g(\mathbf{r}-\mathbf{r}')$. Hence the above lower bound on $\mathcal{E}^{\mathrm{M}}(\gamma)$ is strict unless $\gamma^{1/2}(\mathbf{x},\mathbf{x}') =c_{\sigma\sigma'}(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')$. By self-adjointness, $c_{\sigma\sigma'}$ has to be a constant, and since $\gamma\in\mathfrak{S}^1$, the set of trace class operators, $c_{\sigma\sigma'}=0$. But this means that there exists no minimizer.

Upper bound: We define a trial density matrix γ by defining its square root:

$$\gamma^{1/2}(\mathbf{x},\mathbf{x}') = \chi(\mathbf{r})^* g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}')q^{-1/2}\delta_{\sigma,\sigma'}. \tag{40}$$

Here, g is the same as in Eq. (39) and χ is a smooth function which will be specified later. Note that this definition makes sense, since the operator whose kernel is given on the right side of Eq. (40) is non-negative. This follows from the positivity of $\hat{g}$, the Fourier transform of g, given by

$$\hat{g}(\mathbf{p}) = \frac{2^{3/2}}{\pi}\frac{1}{(1+|\mathbf{p}|^2)^2}.$$

An easy calculation shows that

$$\begin{aligned}\operatorname{tr}(-\nabla^2_{\mathbf{r}}\gamma) = \int\int &\{|\chi(\mathbf{r})|^2|\chi(\mathbf{r}')|^2[-\nabla^2_{\mathbf{r}}g(\mathbf{r}-\mathbf{r}')]g(\mathbf{r}-\mathbf{r}') \\ &+ |\nabla\chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2\}d\mathbf{r}d\mathbf{r}'.\end{aligned}$$

Using the eigenvalue equation for g one finds

$$\begin{aligned}\operatorname{tr}(-\nabla^2_{\mathbf{r}})\gamma = {}& 2X(\gamma^{1/2}) - \frac{1}{4}\operatorname{tr}\gamma \\ &+ \int\int|\nabla\chi(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi(\mathbf{r}')|^2 d\mathbf{r}d\mathbf{r}'.\end{aligned}$$

The upper bound will follow from this if we can find functions χ_L (where L is some free parameter) such that for γ_L defined via χ_L,

$$\gamma_L \leq 1, \text{ as an operator}, \quad \operatorname{tr}\gamma_L \to N, \tag{41}$$

$$\int\int|\nabla\chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2|\chi_L(\mathbf{r}')|^2 d\mathbf{r}d\mathbf{r}' \to 0,$$

$$\text{and} \quad D(\rho_{\gamma_L},\rho_{\gamma_L}) \to 0 \tag{42}$$

as $L\to\infty$. We shall choose χ_L of the form $\chi_L(\mathbf{r}) =L^{-3/4}\chi(\mathbf{r}/L)$ for a fixed smooth function $\chi\geq 0$ satisfying $\|\chi\|_4^4=N$.

We note that for any L^2 function ψ (and with $\widehat{\cdots}$ denoting the Fourier transform)

$$(\psi,\gamma_L^{1/2}\psi)=(2\pi)^{3/2}\int \hat{g}(\mathbf{p})|(\hat{\chi}_L\psi)(\mathbf{p})|^2 d\mathbf{p}$$
$$\leq (2\pi)^{3/2}\|\hat{g}\|_\infty\|\chi_L\|_\infty^2\|\psi\|_2^2,$$

which is less than or equal to $\|\psi\|_2^2$ for L large, since $\|\chi_L\|_\infty \to 0$. This implies the first condition in Eq. (41). To check the second one, we write

$$\operatorname{tr}\gamma_L=(2\pi)^{3/2}\int \widehat{(g^2)}(\mathbf{p})|\widehat{(\chi_L^2)}(\mathbf{p})|^2 d\mathbf{p}.$$

Now $|\widehat{(\chi_L^2)}(\mathbf{p})|^2=L^3|\widehat{(\chi^2)}(L\mathbf{p})|^2$, which converges to $N\delta(\mathbf{p})$ as $L\to\infty$ (recall that $\|\chi\|_4^4=N$). Therefore

$$\operatorname{tr}\gamma_L\to(2\pi)^{3/2}\widehat{(g^2)}(0)N=N.$$

To check conditions (42) we estimate (again using that $\|g\|_2=1$),

$$\int\int|\nabla\chi_L(\mathbf{r})|^2 g(\mathbf{r}-\mathbf{r}')^2\chi_L(\mathbf{r}')^2 d\mathbf{r}d\mathbf{r}'$$
$$\leq\|\chi_L\|_\infty^2\int|\nabla\chi_L(\mathbf{r})|^2 d\mathbf{r}=L^{-2}\|\chi\|_\infty^2\|\nabla\chi\|^2.$$

Moreover,

$$D(\rho_{\gamma_L},\rho_{\gamma_L})=\frac{1}{2L}\int\int\frac{\chi^2(\mathbf{r})\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')\chi^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

where $\varphi_L(\mathbf{r})=L^3\int g^2(L(\mathbf{r}-\mathbf{r}'))\chi^2(\mathbf{r}')d\mathbf{r}'$. Since $\varphi_L(\mathbf{r})\to\chi^2(\mathbf{r})$ as $L\to\infty$, we conclude that $D(\rho_{\gamma_L},\rho_{\gamma_L})=L^{-1}D[\chi^4]+o(L^{-1})$ by dominated convergence.

Hence Eq. (42) holds, and the proof is complete. ∎

Remark: One might ask whether $X(\gamma^{1/2})$ can be bounded from above in terms of the usual Dirac type estimate for the exchange energy, $\int\rho_\gamma(\mathbf{r})^{4/3}d\mathbf{r}$ (cf. [12]). However, this is not the case, as the following example shows: define γ_L, as in the proof of Proposition 1, by $\gamma_L^{1/2}(\mathbf{x},\mathbf{x}')=L^{-3/2}\chi(\mathbf{r}/L)g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}'/L)q^{-1/2}\delta_{\sigma,\sigma'}$, and carry out calculations similar to those done above. We find that

$$X(\gamma_L^{1/2})\to\|\chi\|_4^4\int\frac{|g(\mathbf{r})|^2}{2|\mathbf{r}|}d\mathbf{r},$$

$$\int\rho_{\gamma_L}(\mathbf{r})^{4/3}d\mathbf{r}\sim L^{-1}\|\chi\|_{16/3}^{16/3},$$

$$\int\rho_{\gamma_L}(\mathbf{r})dx\to\|\chi\|_4^4.$$

Hence a bound in terms of the 4/3-norm cannot hold. This example can be traced back to Cioslowski and Pernal [20].

III. MINIMIZER IN THE CASE $Z>0$

We return here, and in the remainder of this paper, to the general case in which all $Z_j>0$. We investigate the functional $\hat{\mathcal{E}}^{\mathrm{M}}$ in Eq. (33) and the corresponding relaxed minimization problem given in Eq. (35). Our goal is to show that there is an energy minimizing γ for this problem and that its trace is $\operatorname{tr}\gamma=N$ whenever $N\leq Z=\Sigma_j Z_j$. The main result of this section is contained in the following two theorems, whose elaborate proof will be given in several parts.

Theorem 1. *For any $Z>0$ and $N>0$ one has $\hat{E}_{\leq}^{\mathrm{M}}(N)<0$ and the infimum (35) is attained.*

As explained in the Introduction, we do not know how to prove that the minimizer is unique. The strict convexity of the direct energy $D(\rho_\gamma,\rho_\gamma)$, however, does imply that all minimizing γ's have the same (spin summed) density $\rho_\gamma(\mathbf{r})$.

Theorem 2. *Assume that $N\leq Z$. Then a minimizer of Eq. (35) has trace N.*

In particular, this result implies that in the original problem (16) the infimum is achieved in case $N\leq Z$. The critical number N_c mentioned in the Introduction is thus at least Z.

A. Proof of Theorem 1

By Proposition 1, the functional $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ is non-negative, if $Z=0$. By using a trial density matrix, we will first show that it assumes negative values as soon as Z is positive.

Lemma 1. *For any $Z>0$ and $N>0$ one has $\hat{E}_{\leq}^{\mathrm{M}}(N)<0$.*

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 γ_L of trial density matrices as in the proof of the upper bound in Proposition 1. Using the same estimates, we have

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_L)=-Z\operatorname{tr}|\mathbf{r}|^{-1}\gamma_L+\frac{1}{L}D[\chi^4]+o(L^{-1})\quad\text{as }L\to\infty. \tag{43}$$

Since $L^3\int g^2(L(\mathbf{r}-\mathbf{r}'))\chi^2(\mathbf{r}')d\mathbf{r}'\to\chi^2(\mathbf{r})$, we have $\operatorname{tr}|\mathbf{r}|^{-1}\gamma_L=L^{-1}\int|\mathbf{r}|^{-1}\chi^4(\mathbf{r})d\mathbf{r}+o(L^{-1})$. Hence,

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_L)=L^{-1}\left(-Z\int|\mathbf{r}|^{-1}\chi^4(\mathbf{r})d\mathbf{r}+D[\chi^4]\right)+o(L^{-1}) \tag{44}$$

as $L\to\infty$. For $Z>0$ and $N=\|\chi\|_4^4$ small enough, the term in large parentheses can clearly be made negative by an appropriate choice of χ. This shows that $\hat{E}_{\leq}^{\mathrm{M}}(N)<0$ for small N, and hence for all N. ∎

Proposition 2. *Let $Z>0$ and $N>0$. There exists a minimizing sequence γ_j for Eq. (35) which converges in $\mathfrak{S}^1$, the space of trace-class operators, i.e., there is a γ such that $\operatorname{tr}|\gamma_j-\gamma|\to0$.*

Before giving the proof of this proposition, we collect some useful auxiliary material.

Lemma 2. *For every $\varepsilon>0$*

$$\int\int_{\{|\mathbf{r}-\mathbf{r}'|<\varepsilon\}}\frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'\leq4\varepsilon\operatorname{tr}(-\nabla^2)\gamma \tag{45}$$

and

$$X(\gamma^{1/2})\leq\frac{\varepsilon}{4}\operatorname{tr}(-\nabla^2)\gamma+\frac{1}{4\varepsilon}\operatorname{tr}\gamma. \tag{46}$$

Proof. The first inequality can be easily deduced from Hardy's inequality, which states that

$$-\nabla^2 \geq \frac{1}{4|\mathbf{r}|^2}. \tag{47}$$

For the second inequality, we use the well-known expression for the ground state energy of the hydrogen atom, namely,

$$-\nabla^2 - \frac{z}{|\mathbf{r}|} \geq -\frac{z^2}{4}, \tag{48}$$

from which it follows (with $z=2/\varepsilon$) that for every $\mathbf{x}'$,

$$\frac{1}{2}\int \frac{|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x} \leq \frac{\varepsilon}{4}\int |\nabla\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 d\mathbf{x} + \frac{1}{4\varepsilon}\int |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 d\mathbf{x}. \tag{49}$$

The lemma follows by integrating over $\mathbf{x}'$. ■

Lemma 3. *Let* $\chi(\mathbf{r})$ *satisfy* $|\chi(\mathbf{r})| \leq 1$. *Then*

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

Proof. For convenience we introduce the characteristic function of a ball of radius r centered at $\mathbf{z}$,

$$B_{\mathbf{z},r}(\mathbf{r}) = \begin{cases} 1, & |\mathbf{r}-\mathbf{z}| < r \\ 0, & |\mathbf{r}-\mathbf{z}| \geq r. \end{cases} \tag{50}$$

Writing the Coulomb kernel as

$$|\mathbf{r}-\mathbf{r}'|^{-1} = \frac{1}{\pi}\int_0^\infty \int_{\mathbb{R}^3} B_{\mathbf{z},r}(\mathbf{r})B_{\mathbf{z},r}(\mathbf{r}')d\mathbf{z}\frac{dr}{r^5} \tag{51}$$

(Fefferman and de la Llave [31]), we get

$$X(\delta) = \frac{1}{2\pi}\int_0^\infty \int_{\mathbb{R}^3} \mathrm{tr}(\delta B_{\mathbf{z},r}\delta B_{\mathbf{z},r})d\mathbf{z}\frac{dr}{r^5}. \tag{52}$$

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

$$\begin{aligned}\chi^*\gamma^{1/2}\chi &= [(\chi^*\gamma^{1/2}\chi)(\chi^*\gamma^{1/2}\chi)]^{1/2} \\ &\leq (\chi^*\gamma^{1/2}\gamma^{1/2}\chi)^{1/2} \\ &= (\chi^*\gamma\chi)^{1/2}.\end{aligned}$$

Hence

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

The assertion follows now from Eq. (52). ■

Proof of Proposition 2. We choose an arbitrary minimizing sequence γ_j for Eq. (35) and, after passing to a subsequence (if necessary), assume that $\mathrm{tr}\ \gamma_j \to \tilde{N} \in [0,N]$. It follows from Eq. (46) and the hydrogen bound, $\mathrm{tr} Z_k|\mathbf{r}-\mathbf{R}_k|^{-1}\gamma \leq (Z_k\varepsilon/4Z)\mathrm{tr}(-\nabla^2)\gamma + (Z_k Z/\varepsilon)\mathrm{tr}\ \gamma$ that

$$\frac{1}{2}(1-\varepsilon)\mathrm{tr}(-\nabla^2)\gamma_j \leq \hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j) + \frac{1}{\varepsilon}(Z^2+1/4)\mathrm{tr}\ \gamma_j. \tag{53}$$

Hence the sequence $(-\nabla^2+1)^{1/2}\gamma_j(-\nabla^2+1)^{1/2}$ is bounded in $\mathfrak{S}^1$ and, by the Banach-Alaoglu theorem (see [41]) 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 compactness condition is satisfied if K is simply multiplication by some function $f \in L^p(\mathbb{R}^3)$ for some $3/2 \leq p < \infty$ (see [[42], Sec. 13.4]). In this case we have that

$$\int f(\mathbf{r})\rho_{\gamma_j}(\mathbf{r})d\mathbf{r} = \mathrm{tr}\ f\gamma_j \to \mathrm{tr}\ f\gamma = \int f(\mathbf{r})\rho_\gamma(\mathbf{r})d\mathbf{r}. \tag{54}$$

In particular, we can take f in Eq. (54) 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 $3/2 < p < 3$ and $3 < q < \infty$.

Note that $0 \leq \gamma \leq 1$ and, by the lower semicontinuity of the $\mathfrak{S}^1$-norm,

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

We claim that $\gamma \not\equiv 0$ (and hence $M > 0$). Indeed, by Proposition 1 one has $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j) \leq -\varepsilon$ for some $\varepsilon > 0$ and all sufficiently large j. Hence $\mathrm{tr}\ V_c\gamma_j \geq \varepsilon$ and by Eq. (54) also $\mathrm{tr}\ V_c\gamma \geq \varepsilon$.

Clearly, $\gamma_j \rightharpoonup \gamma$ in the sense of weak operator convergence. If $M=\tilde{N}$, then also $\mathrm{tr}\ \gamma_j \to \mathrm{tr}\ \gamma$, and thus $\gamma_j \to \gamma$ in $\mathfrak{S}^1$ (see Theorem A.6 in [43]) and we are done.

We are thus left with the case $M < \tilde{N}$. Our strategy will be to construct a minimizing sequence γ_j^0 out of the γ_j which converges to γ in $\mathfrak{S}^1$. 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 $|\mathbf{r}| \geq 2$. For fixed j, $\mathrm{tr}[\chi^0(\mathbf{r}/R)]^2\gamma_j$ is a continuous function of R which increases from 0 to $\mathrm{tr}\ \gamma_j$. If we restrict ourselves to large j, then $\mathrm{tr}\ \gamma_j > M$ and we can choose an R_j such that $\mathrm{tr}[\chi^0(\mathbf{r}/R_j)]^2\gamma_j = M$. 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 claim $R_j \to \infty$. To see this, assume the contrary, namely, that there is a subsequence that converges to some $R < \infty$. Then, for this subsequence, $\chi_j^0(\mathbf{r})^2 \to \chi^0(\mathbf{r}/R)^2$ strongly in any L^p. Since $\rho_{\gamma_j} \rightharpoonup \rho_\gamma$ weakly in L^p for $1 < p < 3$ by Eq. (54), one has

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

But, by definition, the left side is independent of j and equals $\int \chi_j^0(\mathbf{r})^2\rho_{\gamma_j}(\mathbf{r})d\mathbf{r} = M = \int \rho_\gamma(\mathbf{r})d\mathbf{r}$. This is a contradiction, since $\chi^0(\mathbf{r})^2 < 1$ almost everywhere and $\gamma \not\equiv 0$.

Therefore $\lim_{j\to\infty} R_j = \infty$. We note that $\gamma_j^0 \rightharpoonup \gamma$ in the sense of weak operator convergence. (It suffices to check the weak convergence on functions of compact support, since the γ_j^0 remain uniformly bounded.) By construction, $\mathrm{tr}\ \gamma_j^0 = \mathrm{tr}\ \gamma$, so that $\gamma_j^0 \to \gamma$ in $\mathfrak{S}^1$ (again by Theorem A.6 in [43]) and it remains to prove that γ_j^0 is a minimizing sequence.

For the kinetic energy we use the IMS formula [44]

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

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

$$\mathrm{tr}(-\nabla^2)\gamma_j=\mathrm{tr}(-\nabla^2)\gamma_j^0+\mathrm{tr}(-\nabla^2)\gamma_j^1+o(1). \tag{55}$$

For the attraction term we use again that $R_j\to\infty$, so $\mathrm{tr}|\mathbf{r}-\mathbf{R}_k|^{-1}\gamma_j^1\to 0$ and

$$\mathrm{tr}|\mathbf{r}-\mathbf{R}_k|^{-1}\gamma_j=\mathrm{tr}|\mathbf{r}-\mathbf{R}_k|^{-1}\gamma_j^0+o(1). \tag{56}$$

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

$$D(\rho_{\gamma_j},\rho_{\gamma_j})\ge D(\rho_{\gamma_j^0},\rho_{\gamma_j^0}). \tag{57}$$

Finally, we turn to the exchange term, which we write as

$$X(\gamma_j^{1/2})=X(\chi_j^0\gamma_j^{1/2}\chi_j^0)+X(\chi_j^1\gamma_j^{1/2}\chi_j^1)+2X(\chi_j^0\gamma_j^{1/2}\chi_j^1).$$

We shall show that

$$X(\gamma_j^{1/2})\le X((\gamma_j^0)^{1/2})+X((\gamma_j^1)^{1/2})+o(1). \tag{58}$$

It follows from Lemma 3 that $X(\chi_j^\nu\gamma_j^{1/2}\chi_j^\nu)\le X((\gamma_j^\nu)^{1/2})$. To show that the off-diagonal term tends to zero we decompose, for any $\varepsilon>0$,

$$X(\chi_j^0\gamma_j^{1/2}\chi_j^1)=\int\int_{\{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2\}}\frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}' +\int\int_{\{|\mathbf{r}-\mathbf{r}'|\ge\varepsilon/2\}}\frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'.$$

The term with the singularity is controlled by Eq. (45),

$$\int\int_{\{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2\}}\frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}' \le\varepsilon\,\mathrm{tr}(-\nabla^2)\chi_j^0\gamma_j^{1/2}(\chi_j^1)^2\gamma_j^{1/2}\chi_j^0\le\varepsilon\,\mathrm{tr}(-\nabla^2)\chi_j^0\gamma_j\chi_j^0.$$

This can be made arbitrarily small by choosing ε small. For j large enough, $R_j>A$ for any $A>0$. We decompose the term without singularity into two pieces,

$$\begin{aligned}
&\int\int_{\{|\mathbf{r}-\mathbf{r}'|\ge\varepsilon/2\}}\frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'\\
&\le\int\int_{\{|\mathbf{r}-\mathbf{r}'|\ge\varepsilon/2,|\mathbf{r}|\ge A\}}\frac{|\chi_j^0(\mathbf{r})\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'
+\int\int_{\{|\mathbf{r}|<A\}}\frac{|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')\chi_j^1(\mathbf{r}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'\\
&\le\varepsilon^{-1}\int\int_{\{|\mathbf{r}|\ge A\}}\chi_j^0(\mathbf{r})^2|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2d\mathbf{x}d\mathbf{x}'
+[2(R_j-A)]^{-1}\int\int|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2d\mathbf{x}d\mathbf{x}'\\
&=\varepsilon^{-1}\,\mathrm{tr}\,\chi_{\{|\mathbf{r}|\ge A\}}\gamma_j^0+[2(R_j-A)]^{-1}\,\mathrm{tr}\,\gamma_j.
\end{aligned}$$

In the next to last line we used that $|\mathbf{r}-\mathbf{r}'|\ge R_j-A$ if $|\mathbf{r}|<A$ and $\chi_j^1(\mathbf{r}')\ne 0$. Since $\gamma_j^0\to\gamma$ in $\mathfrak{S}^1$, one has $\mathrm{tr}\,\chi_{\{|\mathbf{r}|\ge A\}}\gamma_j^0\to\mathrm{tr}\,\chi_{\{|\mathbf{r}|\ge A\}}\gamma$. This can be made arbitrarily small by choosing A large. Since $R_j\to\infty$, the term $[2(R_j-A)]^{-1}\,\mathrm{tr}\,\gamma_j$ converges to 0. This proves Eq. (58).

Collecting Eqs. (55)–(58) we find that

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j)\ge\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j^0)+\left(-\frac{1}{2}\,\mathrm{tr}\,\nabla^2\gamma_j^1-X(\gamma_j^1)+\frac{1}{8}\,\mathrm{tr}\,\gamma_j^1\right)+o(1).$$

We have shown in the proof of Proposition 1 that the term in large parentheses is non-negative. Hence

$$\liminf_{j\to\infty}\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j)\ge\liminf_{j\to\infty}\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j^0),$$

which shows that γ_j^0 is a minimizing sequence. This concludes the proof. ■

Proposition 3. *Let* $\gamma_j\to\gamma$ *in* $\mathfrak{S}^1$. *Then*

$$\liminf_{j\to\infty}\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j)\ge\hat{\mathcal{E}}^{\mathrm{M}}(\gamma). \tag{59}$$

Proof. The bound (53) shows that $E=\liminf_{j\to\infty}\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j)>-\infty$. 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 $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_j)\to E$. As in the proof of Proposition 2 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. In particular, Eq. (54) holds. By weak lower semicontinuity we infer that

$$\mathrm{tr}\left(-\frac{1}{2}\nabla^2+1/8\right)\gamma\le\liminf_{j\to\infty}\mathrm{tr}\left(-\frac{1}{2}\nabla^2+1/8\right)\gamma_j. \tag{60}$$

Now we turn to the repulsion term. Since $D(\rho_{\gamma_j},\rho_{\gamma_j})$ is bounded we may, passing to a subsequence (if necessary), assume that ρ_{γ_j} converges weakly to some ρ with respect to the D-scalar product. With the help of Eq. (54) one concludes that $\rho=\rho_\gamma$. Weak lower semicontinuity with respect to the D-norm implies that

$$D(\rho_\gamma,\rho_\gamma)\le\liminf_{j\to\infty}D(\rho_{\gamma_j},\rho_{\gamma_j}). \tag{61}$$

The continuity of the attraction term follows from Eq. (54), since $|\mathbf{r}|^{-1}\in L^{3/2}+L^p$ for $p>3$, therefore

$$\lim_{j\to\infty}\mathrm{tr}\,V_c\gamma_j=\mathrm{tr}\,V_c\gamma. \tag{62}$$

Finally, we prove continuity of the exchange term. Similarly as in the proof of Proposition 2 we decompose, for any $\varepsilon>0$,

$$\begin{aligned}
&|X(\gamma_j^{1/2})-X(\gamma^{1/2})|\\
&\le\int\int_{\{|\mathbf{r}-\mathbf{r}'|<\varepsilon/2\}}\frac{|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2+|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'
+\int\int_{\{|\mathbf{r}-\mathbf{r}'|\ge\varepsilon/2\}}\frac{\left||\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2-|\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\right|}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'.
\end{aligned}$$

According to Lemma 2 the term involving the singularity is bounded by $\varepsilon\,\mathrm{tr}(-\nabla^2)(\gamma_j+\gamma)$, which can be made arbitrarily small (recall that $\mathrm{tr}[-\nabla^2(\gamma_j+\gamma)]$ is bounded). To treat the term without the singularity we use the fact that the mapping $K \mapsto |K|^{1/2}$ is continuous from $\mathfrak{S}^1$ to $\mathfrak{S}^2$ (see Example 2 after Theorem 2.21 in [43]). Hence $\gamma_j^{1/2} \to \gamma^{1/2}$ in $\mathfrak{S}^2$, and we can bound

$$\left(\int\int_{\{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2\}} \frac{\big||\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')|^2 - |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2\big|}{2|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}d\mathbf{x}'\right)^2$$
$$\leq \int\int |\gamma_j^{1/2}(\mathbf{x},\mathbf{x}') - \gamma^{1/2}(\mathbf{x},\mathbf{x}')|^2 d\mathbf{x}d\mathbf{x}'$$
$$\times \int\int_{\{|\mathbf{r}-\mathbf{r}'|\geq\varepsilon/2\}} \frac{[|\gamma_j^{1/2}(\mathbf{x},\mathbf{x}')| + |\gamma^{1/2}(\mathbf{x},\mathbf{x}')|]^2}{4|\mathbf{r}-\mathbf{r}'|^2} d\mathbf{x}'d\mathbf{x}'$$
$$\leq \|\gamma_j^{1/2} - \gamma^{1/2}\|_2^2 2\varepsilon^{-2} \operatorname{tr}(\gamma_j + \gamma).$$

The first factor tends to zero by the convergence of $\gamma_j^{1/2}$ mentioned before, and the second one remains bounded. Hence we have proved that

$$\lim_{j\to\infty} X(\gamma_j^{1/2}) = X(\gamma^{1/2}). \tag{63}$$

By collecting Eqs. (60)–(63) we arrive at Eq. (59). ■

Proof of Theorem 1. According to Proposition 2, there exists a minimizing sequence that converges strongly to some γ. By Proposition 3, this γ is a minimizer of $\hat{\mathcal{E}}^{\mathrm{M}}$. ■

B. Proof of Theorem 2

Assume that $N \leq Z$. Under this assumption we shall show that a γ minimizing $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ satisfies tr $\gamma = N$.

Assuming the contrary, we shall find a trace class operator $\sigma \geq 0$ such that for $\gamma_\varepsilon = (1-\varepsilon\|\sigma\|)\gamma + \varepsilon\sigma$ and all sufficiently small $\varepsilon > 0$,

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_\varepsilon) < \hat{\mathcal{E}}^{\mathrm{M}}(\gamma). \tag{64}$$

The factor $(1-\varepsilon\|\sigma\|)$ guarantees that $0 \leq \gamma_\varepsilon \leq 1$ for $0 < \varepsilon \leq \|\sigma\|^{-1}$. If tr $\gamma < N$, which we assume, then also tr $\gamma_\varepsilon < N$ for small ε and Eq. (64) leads to a contradiction since γ was assumed to be a minimizer.

To prove Eq. (64) we use convexity for the homogeneous terms in the functional $\hat{\mathcal{E}}^{\mathrm{M}}$ and expand the repulsion term explicitly. This leads to

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_\varepsilon) \leq \hat{\mathcal{E}}^{\mathrm{M}}(\gamma) + \varepsilon[\operatorname{tr}(-\nabla^2 - \varphi_\gamma + 1/8)\sigma - X(\sigma^{1/2})]$$
$$- \varepsilon R_1 + \varepsilon^2 R_2, \tag{65}$$

where

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

$$R_1 = \|\sigma\|[\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) + D(\rho_\gamma, \rho_\gamma)],$$

$$R_2 = D(\rho_\sigma - \|\sigma\|\rho_\gamma, \rho_\sigma - \|\sigma\|\rho_\gamma).$$

Now we proceed similarly as in the proof of Proposition 1, letting $\sigma = \sigma_L$ depend on a (large) parameter L. More precisely, we define σ_L by

$$\sigma_L^{1/2}(\mathbf{x},\mathbf{x}') = L^{-3/2}\chi(\mathbf{r}/L)g(\mathbf{r}-\mathbf{r}')\chi(\mathbf{r}'/L)q^{-1/2}\delta_{\sigma,\sigma'}, \tag{66}$$

with g as in Eq. (39) and $\chi \geq 0$ a smooth function satisfying $\|\chi\|_4^4 = 1$. Asymptotically, for large $|\mathbf{r}|$, $\varphi_\gamma(\mathbf{r}) \approx (Z - \operatorname{tr}\gamma)|\mathbf{r}|^{-1}$, which is positive by our assumption. It follows similarly to the proof of Proposition 1 that

$$\operatorname{tr}(-\nabla^2 - \varphi_\gamma + 1/8)\sigma_L - X(\sigma_L^{1/2})$$
$$= -\frac{Z - \operatorname{tr}\gamma}{L} \int |\mathbf{r}|^{-1}\chi^4(\mathbf{r})d\mathbf{r} + o(L^{-1}).$$

It remains to show that the terms R_1 and R_2 are relatively small. In the proof of Proposition 1 and in Eq. (43) we showed that $\|\sigma_L\| = O(L^{-3})$ and $D(\rho_{\sigma_L}, \rho_{\sigma_L}) = O(L^{-1})$, which implies that $R_1 = O(L^{-3})$ and $R_2 = O(L^{-1})$. We can then choose L large enough and ε small enough to conclude Eq. (64).

This finishes the proof of Theorem 2.

IV. FURTHER PROPERTIES

A. Properties of the minimal energy

Recall that $E^{\mathrm{M}}(N)$ as defined in Eq. (16) is the lowest energy of $\mathcal{E}^{\mathrm{M}}(\gamma)$ under the condition tr $\gamma = N$. This energy is closely related to $\hat{E}^{\mathrm{M}}_{\leq}(N)$ defined in Eq. (35).

Proposition 4. *For any $Z > 0$ and $N > 0$ one has* $E^{\mathrm{M}}(N) = \hat{E}^{\mathrm{M}}_{\leq}(N) - N/8$.

What this proposition really says is that $E^{\mathrm{M}}(N) + N/8$ is a monotone nondecreasing function of N. This, in turn, follows from the fact that we can always add mass δN far away from the nuclei, with an energy as close as we please to $-\delta N/8$. This was shown in the proof of Theorem 2, and we shall not repeat the argument.

Proposition 5. *For any $Z > 0$ the energies $\hat{E}^{\mathrm{M}}_{\leq}(N)$ and $E^{\mathrm{M}}(N)$ are convex functions of N. They are strictly convex for $0 < N \leq Z$.*

Proof. By Proposition 4 it suffices to consider $\hat{E}^{\mathrm{M}}_{\leq}(N)$. The convexity follows from the convexity of the functional. Moreover, from Theorem 2 we know that minimizers for $0 < N < N' \leq Z$ have different traces, and hence different densities. The *strict* convexity thus follows from the strict convexity of $D(\rho, \rho)$ in ρ. ■

We now prove that the energy is bounded from below uniformly in N for fixed Z.

Proposition 6. *There is a constant $C > 0$ (independent of N and the charges and positions of the nuclei) such that for all $Z > 0$ and $N > 0$, $\hat{E}^{\mathrm{M}}_{\leq}(N) \geq -CZ^3$.*

Remark: The proof below does *not* use the property that $\gamma \leq 1$ and this results in the exponent 3, which is not optimal in the fermionic case. Without the restriction $\gamma \leq 1$, the exponent 3 is optimal, however.

Proof. First, let us consider the atomic case with a nucleus of charge Z located at the origin $\mathbf{R} = 0$. We consider $\psi(\mathbf{x},\mathbf{x}') = \gamma^{1/2}(\mathbf{x},\mathbf{x}')$ as a wave function in $L^2(\mathbb{R}^6)$ and find after symmetrization

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) = \frac{1}{2}\left\langle \psi \left| -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2}\nabla_{\mathbf{r}'}^2 - Z|\mathbf{r}|^{-1} - Z|\mathbf{r}'|^{-1} - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4} \right| \psi \right\rangle + D(\rho_\gamma,\rho_\gamma).$$

By the positive definiteness of the Coulomb kernel, $D(\rho_\gamma,\rho_\gamma) \geq 2D(\rho_\gamma,\sigma_Z) - D(\sigma_Z,\sigma_Z)$ for any σ_Z. Hence

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) \geq \frac{1}{2}\left\langle \psi \left| -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2}\nabla_{\mathbf{r}'}^2 - V_Z(\mathbf{r}) - V_Z(\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4} \right| \psi \right\rangle - D(\sigma_Z,\sigma_Z)$$

with $V_Z(\mathbf{r}) = Z|\mathbf{r}|^{-1} - \int|\mathbf{r}-\mathbf{r}'|^{-1}\sigma_Z(\mathbf{r}')d\mathbf{r}'$. We shall choose σ_Z in such a way that

$$-\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2}\nabla_{\mathbf{r}'}^2 - V_Z(\mathbf{r}) - V_Z(\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{4} \geq 0. \quad (67)$$

From this it follows that $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) \geq -D(\sigma_Z,\sigma_Z)$. Actually, we shall choose σ_Z of the form $\sigma_Z(\mathbf{r}) = Z^4\sigma(Z\mathbf{r})$ for some fixed σ, which yields $D(\sigma_Z,\sigma_Z) = Z^3 D(\sigma,\sigma)$.

To prove Eq. (67) we make an orthogonal change of variables, $\mathbf{s} = (\mathbf{r}-\mathbf{r}')/\sqrt{2}$, $\mathbf{t} = (\mathbf{r}+\mathbf{r}')/\sqrt{2}$, so that the operator on the left side of Eq. (67) becomes

$$\left(-\frac{1}{2}\nabla_{\mathbf{s}}^2 - \frac{1}{\sqrt{2}|\mathbf{s}|} + \frac{1}{4}\right) + \frac{1}{4}\{-\nabla_{\mathbf{t}}^2 - 4V_Z[(\mathbf{t}+\mathbf{s})/\sqrt{2}]\}$$

$$+ \frac{1}{4}\{-\nabla_{\mathbf{t}}^2 - 4V_Z[(\mathbf{t}-\mathbf{s})/\sqrt{2}]\}.$$

The operator in the first set of parentheses is non-negative [see Eq. (48)]. Hence it suffices to choose σ such that the operator $-\nabla_{\mathbf{t}}^2 - 4V_Z[(\mathbf{t}+\mathbf{a})/\sqrt{2}]$ is non-negative of any $\mathbf{a} \in \mathbb{R}^3$. Note that $V_Z(\mathbf{t}) = Z^2 V(Z\mathbf{t})$ with $V(\mathbf{r}) = |\mathbf{r}|^{-1} - \int|\mathbf{r}-\mathbf{r}'|^{-1}\sigma(\mathbf{r}')d\mathbf{r}'$. After scaling and translation, we have to prove that $-\nabla_{\mathbf{r}}^2 - 8V(\mathbf{r}) \geq 0$. For this we choose σ a non-negative, spherically symmetric function with $\int\sigma dx = 1$ and with support in $\{|\mathbf{r}| \leq 1/32\}$. Then by Newton's theorem $V(\mathbf{r}) = 0$ for $|\mathbf{r}| \geq 1/32$, and for $|\mathbf{r}| \leq 1/32$ one has $8V(\mathbf{r}) \leq 1/(4|\mathbf{r}|^2)$, so $-\nabla_{\mathbf{r}}^2 - 8V(\mathbf{r}) \geq 0$ by Hardy's inequality (47). This concludes the proof in the atomic case.

In the molecular case we proceed as follows: We recall that we are not taking account of the (fixed) nuclear repulsion U, and this means that we can freely place the nuclei at locations that minimize the energy $\hat{E}^{\mathrm{M}}(N)$. We assert that the best choice of the $\mathbf{R}_j$ 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. That the optimum choice is equal $\mathbf{R}_j$ follows from the fact that for *any* γ the attractive energy for nucleus j is $-\int\rho_\gamma(\mathbf{r})|\mathbf{r}-\mathbf{R}_j|^{-1}d\mathbf{r}$ and the best possible energy is obtained by placing all the $\mathbf{R}_j$ at the point $\mathbf{R}$ that maximizes this integral. ■

B. Properties of the minimizer

Proposition 7. *Let γ be a minimizer of Eq.* (35) *and let $M_\gamma = \{\mathbf{r} : \rho_\gamma(\mathbf{r}) > 0\}$. Then the null-space of the spin-summed density matrix, $\mathcal{N}\operatorname{tr}_\sigma \gamma$, coincides with the set of $L^2(\mathbb{R}^3)$ functions that vanish identically on M_γ.*

Another way to say this is that if $\operatorname{tr}_\sigma \gamma$ has a zero eigenvalue then the eigenfunction vanishes wherever the density ρ_γ is non-zero. In particular, if $\rho_\gamma > 0$ almost everywhere then 0 is not an eigenvalue of the spin-summed density matrix $\operatorname{tr}_\sigma \gamma$.

Proof. Write $(\operatorname{tr}_\sigma \gamma)(\mathbf{r},\mathbf{r}') = \sum_j \lambda_j \psi_j(\mathbf{r})\psi(\mathbf{r}')^*$ with ψ_j orthonormal and $0 < \lambda_j \leq q$. Then $\mathbb{R}^3 \setminus M_\gamma = \cap_j\{\mathbf{r} : \psi_j(\mathbf{r}) = 0\}$, and if $\varphi = 0$ a.e. on M_γ then obviously $\gamma\varphi \equiv 0$. Conversely, let $\varphi \in \mathcal{N}\operatorname{tr}_\sigma \gamma$ and consider

$$\gamma_\varepsilon = \operatorname{tr}_\sigma \gamma + \varepsilon(|\varphi\rangle\langle\varphi| - |\psi_1\rangle\langle\psi_1|).$$

One has $\operatorname{tr}\gamma_\varepsilon = \operatorname{tr}\gamma \leq N$, $0 \leq \gamma_\varepsilon \leq 1$ for $0 \leq \varepsilon \leq \lambda_1$ and

$$\gamma_\varepsilon^{1/2} = (\operatorname{tr}_\sigma \gamma)^{1/2} + \sqrt{\varepsilon}|\varphi\rangle\langle\varphi| + (\sqrt{\lambda_1 - \varepsilon} - \sqrt{\lambda})|\psi_1\rangle\langle\psi_1|.$$

As noted in the Introduction, it follows from convexity that minimizing $\hat{\mathcal{E}}^{\mathrm{M}}$ for density matrices $0 \leq \gamma \leq 1$ with q spin states is equivalent to minimizing under the condition $0 \leq \gamma \leq q$ without spin. Hence

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

where

$$C[\varphi] = \int\int \frac{\varphi(\mathbf{r})^*\gamma^{1/2}(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$= \sum_j \sqrt{\lambda_j}\int\int \frac{\varphi(\mathbf{r})^*\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^*\varphi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \geq 0.$$

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. Hence $\varphi = 0$ 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 (35) without the constraint $\gamma \leq 1$,

$$\hat{E}_{\leq}^{\mathrm{boson}}(N) = \inf\{\hat{\mathcal{E}}^{\mathrm{M}}(\gamma) : \gamma \geq 0, \operatorname{tr}\gamma \leq N\}. \quad (68)$$

This energy can be interpreted as the ground state energy of N *bosons* in the Müller model. Obviously, $\hat{E}_{\leq}^{\mathrm{boson}}(N) \leq \hat{E}_{\leq}^{\mathrm{M}}(N)$ with equality for $N \leq 1$. For large values of N we expect them to differ, however.

Proposition 8. *Assume that $\hat{E}_{\leq}^{\mathrm{boson}}(N) < \hat{E}_{\leq}^{\mathrm{M}}(N)$ for some N and Z. Then any minimizer γ of Eq.* (35) *has at least one eigenvalue 1.*

Proof. Assume, on the contrary, that $\gamma < 1$ and let γ_b denote a minimizer for Eq. (68). (The existence is shown in the same way as in the proof of Theorem 1.) Then $\gamma_\varepsilon = (1-\varepsilon)\gamma$

$+\varepsilon\gamma_b$ satisfies tr $\gamma_\varepsilon \le N$ and $0 \le \gamma_\varepsilon \le 1$ for sufficiently small $\varepsilon > 0$. Moreover, by convexity,

$$\hat{\mathcal{E}}^{\mathrm{M}}(\gamma_\varepsilon) \le (1-\varepsilon)\hat{E}^{\mathrm{M}}_{\le}(N) + \varepsilon \hat{E}^{\mathrm{boson}}_{\le}(N) < \hat{E}^{\mathrm{M}}_{\le}(N),$$

contradicting the fact that γ is a minimizer. ■

It is not difficult to see that $\hat{E}^{\mathrm{M}}_{\le}(N) \sim N^{1/3}Z^2$ for large N and Z, while $\hat{E}^{\mathrm{boson}}_{\le}(N) \sim NZ^2$. Hence clearly $\hat{E}^{\mathrm{boson}}_{\le}(N) < \hat{E}^{\mathrm{M}}_{\le}(N)$ for large N and Z.

Lathiotakis *et al.* [45] find numerically that in fact occupation numbers that correspond to core electrons of large atoms all have the value one.

Proposition 9. *Let $\gamma(\mathbf{x},\mathbf{x}')$ be a minimizer of $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ for some N and let $\hat{\gamma}(\mathbf{r},\mathbf{r}') = \Sigma_\sigma \gamma(\mathbf{r},\sigma,\mathbf{r}',\sigma)$ be the spin-summed minimizer. Then $\hat{\gamma}(\mathbf{r},\mathbf{r}')$ is necessarily real.*

Proof. It suffices to show that $\hat{\gamma}^{1/2}$ is real. Write $\hat{\gamma}^{1/2}(\mathbf{r},\mathbf{r}') = A(\mathbf{r},\mathbf{r}') + iB(\mathbf{r},\mathbf{r}')$, where A is real and symmetric and B is real and antisymmetric, whence iB is self-adjoint. Define $\delta = A^2 - B^2$, noting that both A^2 and $-B^2$ are positive (semidefinite). The kinetic and potential energy of δ and γ are equal. Moreover, the densities $\rho_\gamma(\mathbf{r})$ and $\rho_\delta(\mathbf{r})$ are equal. Therefore, we just have to show that the exchange terms favor δ, i.e., $X(\delta^{1/2}) > X(\gamma^{1/2})$.

To prove this assertion use the concavity of $X(\cdot)$ to conclude that $X(\delta^{1/2}) \ge X(|A|) + X(|B|)$, where $|A| = \sqrt{A^2}$ and $|B| = \sqrt{B^\dagger B} = \sqrt{-B^2}$. On the other hand, $X(\gamma^{1/2}) = X(A) + X(B)$, with the obvious meaning that $X(A) = \frac{1}{2}\int |A(\mathbf{r},\mathbf{r}')|^2 |\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}'$ and similarly for $X(B)$.

To conclude the proof we have to show that $X(|A|) \ge X(A)$ and $X(|B|) > X(B)$ if $B \ne 0$. For the first, we write $A = A_+ - A_-$ and $|A| = A_+ + A_-$, where $A_\pm$ are both positive operators. Clearly, the cross term $\int A_+(\mathbf{r},\mathbf{r}')A_-(\mathbf{r}',\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}' \ge 0$ since $|\mathbf{r}-\mathbf{r}'|$ is positive definite. The same argument applies to $iB = B_+ - B_-$, but now we want to show that $\int B_+(\mathbf{r},\mathbf{r}')B_-(\mathbf{r}',\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}' > 0$ unless $B=0$.

To show this we use the fact that the positive definiteness of the Coulomb kernel implies that $\int \alpha(\mathbf{r},\mathbf{r}')\beta(\mathbf{r}',\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}'$ is (operator) monotone in α and in β. Therefore, it suffices to show positivity for selected eigenfunctions of $B_\pm$. That is, we replace $B_+(\mathbf{r},\mathbf{r}')$ by eigenfunctions $\varphi_+(\mathbf{r})\varphi_+(\mathbf{r}')^*$ and similarly we replace $B_-(\mathbf{r},\mathbf{r}')$ by $\varphi_-(\mathbf{r})\varphi_-(\mathbf{r}')^*$.

Since iB is imaginary and antisymmetric, however, its positive and negative spectra are equal, apart from sign, so $B_\pm$ have the same spectrum. Moreover, $B_\pm$ are complex conjugates of each other. Therefore, for every $\varphi_+(\mathbf{r})$ there is a $\varphi_-(\mathbf{r})$ and the two functions are complex conjugates of each other. In short, it suffices to show strict positivity of $\int \varphi(\mathbf{r})^2 [\varphi(\mathbf{r}')^*]^2 |\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}'$, but this is true as long as the function φ is not identically zero (since the Coulomb kernel is positive definite). ■

Finally, we show that a minimizer of $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$ satisfies the variational equation (23), as claimed in the Introduction.

Proposition 10. *Let γ be a minimizer of $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$. Then*

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} - \frac{1}{2}\nabla^2_{\mathbf{r}'} - \varphi_\gamma(\mathbf{r}) - \varphi_\gamma(\mathbf{r}') - \frac{1}{|\mathbf{r}-\mathbf{r}'|} - 2\mu\right)\gamma^{1/2}(\mathbf{x},\mathbf{x}') = \sum_i 2e_i \psi_i(\mathbf{x})\psi_i(\mathbf{x}')^*. \tag{69}$$

Here, $\varphi_\gamma(\mathbf{r}) = V_c(\mathbf{r}) - \int \rho_\gamma(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r}'$ denotes the effective potential, $\mu \le -1/8$ is the chemical potential, $e_i \le 0$ and the $\psi_i(\mathbf{x})$ are eigenfunctions of γ with eigenvalue 1.

Proof. Let μ be the slope of a tangent to the curve $E^{\mathrm{M}}(N)$ at N. Since $E^{\mathrm{M}}(N)$ is convex, such a tangent always exists, although it may not be unique in case the derivative of $E^{\mathrm{M}}(N)$ is discontinuous at this point.

Since γ is a minimizer of $\hat{\mathcal{E}}^{\mathrm{M}}(\gamma)$, its square root $\gamma^{1/2}$ minimizes the expression

$$\mathcal{F}(\delta) = \mathrm{tr}\left[-\frac{1}{2}\nabla^2 - V_c(\mathbf{r}) - \mu\right]\delta^2 + D(\rho_{\delta^2},\rho_{\delta^2}) - X(\delta) \tag{70}$$

among *all* δ with $0 \le \delta \le 1$, irrespective of the trace of δ^2. In fact, it is even a minimizer if one relaxes the condition $\delta \ge 0$. This follows from the fact that $X(\delta) \le X(|\delta|)$ for any self-adjoint operator δ, which was shown in the proof of Proposition 9.

Consequently, $\gamma^{1/2}$ is a minimizer of Eq. (70) subject to the constraint $-1 \le \delta \le 1$. From this we conclude that for any self-adjoint σ with finite trace such that, for small ε, $\gamma^{1/2} + \varepsilon\sigma \le 1 +$ terms of order ε^2,

$$\left.\frac{d}{d\varepsilon}\mathcal{F}(\gamma^{1/2} + \varepsilon\sigma)\right|_{\varepsilon=0} \ge 0. \tag{71}$$

The derivative can easily be calculated to be

$$\mathrm{tr}\left\{\left[\left(-\frac{1}{2}\nabla^2 - \varphi_\gamma\right)\gamma^{1/2} + \gamma^{1/2}\left(-\frac{1}{2}\nabla^2 - \varphi_\gamma\right) - Z_\gamma - 2\mu\gamma^{1/2}\right]\sigma\right\}, \tag{72}$$

where Z_γ is defined in Eq. (25). The condition on σ is that $\langle\psi_i|\sigma|\psi_i\rangle \le 0$ for all $|\psi_i\rangle$ with $\gamma|\psi_i\rangle = |\psi_i\rangle$. Hence we conclude that

$$\left(-\frac{1}{2}\nabla^2 - \varphi_\gamma\right)\gamma^{1/2} + \gamma^{1/2}\left(-\frac{1}{2}\nabla^2 - \varphi_\gamma\right) - Z_\gamma - 2\mu\gamma^{1/2} = \sum_i 2e_i|\psi_i\rangle\langle\psi_i|, \tag{73}$$

with $e_i \le 0$. ■

The variational equation (69) was obtained by varying $\gamma^{1/2}$ instead of γ. If γ does not have a zero eigenvalue (which, for a spin-invariant minimizer γ, is the case if ρ_γ does not vanish on a set of positive measure, see Proposition 7), then these variations are equivalent. Hence we conclude that Eq. (69) is actually *equivalent* to γ being a minimizer in case γ has no zero eigenvalue. (See the discussion in Sec. I D.)

C. Virial theorem

A well-known property of Coulomb systems is the virial theorem, which quantifies a relation between the kinetic and potential energies. We state it here for an atom.

Proposition 11. *Let $K=1$ (i.e., consider an atom) and let γ be a minimizer for $\hat{E}^{\mathrm{M}}_{\leq}(N)$. Then*

$$2\,\mathrm{tr}\left(-\frac{1}{2}\nabla^2\gamma\right)=\mathrm{tr}(Z|\mathbf{r}|^{-1}\gamma)-D(\rho_\gamma,\rho_\gamma)+X(\gamma^{1/2}). \quad (74)$$

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 and hence satisfies $0\leq\gamma_\lambda\leq 1$ and $\mathrm{tr}\,\gamma_\lambda=\mathrm{tr}\,\gamma\leq N$. Since γ is a minimizer, the function

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

has a minimum at $\lambda=1$. This implies the assertion. ∎

V. THE MÜLLER FUNCTIONAL AS A LOWER BOUND TO QUANTUM MECHANICS

We are able to show that the Müller energy $E^{\mathrm{M}}(N)$ (without the addition of $N/8$) is a lower bound to the true Schrödinger energy when $N=2$, but with arbitrarily many nuclei. The situation for $N>2$ is open. As we remark below, our $N=2$ proof definitely fails when $N>2$.

Consider the N-particle Hamiltonian (2) in either the symmetric or the antisymmetric N-fold tensor product of $L^2(\mathbb{R}^3,\mathbb{C}^q)$. For a symmetric or antisymmetric ψ we recall that the one-particle density matrix γ_ψ is defined by

$$\gamma_\psi(\mathbf{x},\mathbf{x}')=N\int\psi(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)\psi(\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)^*d\mathbf{x}_2\cdots d\mathbf{x}_N.$$

Proposition 12. *Assume that $N=2$. Then for any symmetric or anti-symmetric normalized ψ,*

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

Proof. Since $\langle\psi|\sum_{j=1}^2[-\frac{1}{2}\nabla_j^2-V_c(\mathbf{r}_j)]|\psi\rangle=\mathrm{tr}[-\frac{1}{2}\nabla^2-V_c(\mathbf{r})]\gamma_\psi$, we have to prove that

$$\int\frac{|\psi(\mathbf{x}_1,\mathbf{x}_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{x}_1d\mathbf{x}_2+\int\frac{|\gamma_\psi^{1/2}(\mathbf{x},\mathbf{x}')|^2}{2|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}' \geq\int\frac{\gamma_\psi(\mathbf{x}_1,\mathbf{x}_1)\gamma_\psi(\mathbf{x}_2,\mathbf{x}_2)}{2|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{x}_1d\mathbf{x}_2.$$

By Eq. (51) it suffices to prove that for any characteristic function χ of a ball (or, more generally, for any real-valued function χ)

$$2\int\chi(\mathbf{r}_1)|\psi(\mathbf{x}_1,\mathbf{x}_2)|^2\chi(\mathbf{r}_2)d\mathbf{x}_1d\mathbf{x}_2 +\int\chi(\mathbf{r})|\gamma_\psi^{1/2}(\mathbf{x},\mathbf{x}')|^2\chi(\mathbf{r}')d\mathbf{x}d\mathbf{x}' \geq\left(\int\chi(\mathbf{r})\gamma_\psi(\mathbf{x},\mathbf{x})d\mathbf{x}\right)^2. \quad (75)$$

Introducing Ψ as the (non-self-adjoint) operator in $L^2(\mathbb{R}^3)$ with kernel $\sqrt{2}\psi(\mathbf{x},\mathbf{x}')$, we can rewrite the previous inequality as

$$\mathrm{tr}\,\chi\Psi^\dagger\chi\Psi+\mathrm{tr}\,\chi\gamma_\psi^{1/2}\chi\gamma_\psi^{1/2}\geq(\mathrm{tr}\,\chi\gamma_\psi)^2. \quad (76)$$

The proof of this inequality can be found in [46]. For completeness, we present the proof here.

Note that $\Psi\Psi^\dagger=\gamma_\psi$, so $\Psi=\gamma_\psi^{1/2}\mathcal{V}$ for a partial isometry $\mathcal{V}$. Since ψ is (anti) symmetric, $\Psi^\dagger\Psi=\mathcal{C}\gamma_\psi\mathcal{C}$, where $\mathcal{C}$ denotes complex conjugation. Hence $\mathcal{V}^\dagger\gamma_\psi\mathcal{V}=\mathcal{C}\gamma_\psi\mathcal{C}$ and, since the square root is uniquely defined,

$$\mathcal{V}^\dagger\gamma_\psi^{1/2}\mathcal{V}=\mathcal{C}\gamma_\psi^{1/2}\mathcal{C}. \quad (77)$$

We write $\delta=\gamma_\psi^{1/2}$ for simplicity and consider the quadratic form

$$Q(A,C)=\frac{1}{4}(2\,\mathrm{tr}\,A^\dagger\delta C\delta+\mathrm{tr}\,A^\dagger\delta\mathcal{V}C\mathcal{V}^\dagger\delta+\mathrm{tr}\,\mathcal{V}A^\dagger\mathcal{V}^\dagger\delta C\delta).$$

We consider this quadratic form on the real vector space of *real* operators, i.e., operators satisfying

$$\mathcal{C}A\mathcal{C}=A. \quad (78)$$

Note that $Q(A,A)=\frac{1}{2}(\mathrm{tr}\,A^\dagger\delta A\delta+\mathrm{tr}\,A^\dagger\delta\mathcal{V}A\mathcal{V}^\dagger\delta)$ and that, by Schwarz's inequality,

$$(\mathrm{tr}\,A^\dagger\delta\mathcal{V}A\mathcal{V}^\dagger\delta)^2\leq(\mathrm{tr}\,A^\dagger\delta A\delta)(\mathrm{tr}\,\mathcal{V}A^\dagger\mathcal{V}^\dagger\delta\mathcal{V}A\mathcal{V}^\dagger\delta).$$

Recalling Eqs. (77) and (78) we thus see that Q is positive semidefinite. This implies in particular that $Q(\chi,1)^2\leq Q(\chi,\chi)Q(1,1)$. This is the desired inequality (76), since $Q(1,1)=\mathrm{tr}\,\gamma_\psi=2$, $Q(\chi)=\frac{1}{2}(\mathrm{tr}\,\chi\delta\chi\delta+\mathrm{tr}\,\chi\delta\mathcal{V}\chi\mathcal{V}^\dagger\delta)$ $=\frac{1}{2}(\mathrm{tr}\,\chi\delta\chi\delta+\mathrm{tr}\,\chi\Psi\chi\Psi^\dagger)$ and

$$Q(1,\chi)=\frac{1}{4}(3\,\mathrm{tr}\,\chi\delta^2+\mathrm{tr}\,\chi\mathcal{V}^\dagger\delta^2\mathcal{V})=\mathrm{tr}\,\chi\gamma_\psi.$$

Here we used Eq. (77) once more. ∎

The obvious generalization of inequality (75) to $N\geq 3$ is not true, as [47] shows. But this does not mean that the Müller energy is not a lower bound to the true energy. There is some numerical evidence for this, as mentioned in **A.3** of Sec. I B.

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