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On the Thermodynamic V-Representability of One-Particle Density Matrices

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We consider thermodynamically V-representable one-matrices, i.e., one-particle density matrices that are obtained by reducing the Gibbs grand canonical density matrix of a quantum mechanical many-particle system subject to a suitable external potential v, and show them to obey an inequality lower bounding their eigenvalues in terms of those of the one-particle kinetic energy operator. The result imposes a severe constraint on the asymptotic behavior of the eigenvalues of any one-matrix to be V-representable. For noninteracting particles, the corresponding upper bound is also proven, implying that a one-matrix can be interactionlessly V-representable for at most one temperature. We expect the upper bound to be valid more generally, as is illustrated by a model of coupled harmonic oscillators where the V-representable one-matrices can be explicitly calculated, and discuss its implications for certain aspects of density-matrix functional theory.

KEY WORDS: Density functional theory; Hohenberg–Kohn theorem; V-representability; inverse problems; reduced density matrices.

1. INTRODUCTION

As shown by Hohenberg and Kohn,[1] the external potential of a one-species quantum mechanical many-particle system is, up to an additive constant, uniquely determined by the ground-state particle density, provided that the kinetic and interaction parts of the Hamiltonian are kept fixed. Thus, the "Schrödinger map"—leading in the usual way, via solution of the N-particle Schrödinger equation and subsequent $(N-1)$-fold spatial integration, from the external one-particle potential to the ground-state particle density—can in principle be inverted. Associated with this rather

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formidable inverse problem, and a prerequisite for its solution, is the question of "V-representability"[(2–7)]: Given a nonnegative real function ρ on $\mathbb{R}^3$ with $\int \rho \, d^3x < \infty$, how is one to tell whether there exists a potential v such that ρ is realized as the actual particle density in the ground state of the many-particle system under consideration, subject to the external potential v? An answer to the latter question would at least yield a characterization of the *domain of definition* of the Hohenberg–Kohn inverse map. Since the Hohenberg–Kohn theorem has been extended, by Mermin,[(8)] to nonzero temperatures, the same question may be asked with regard to the particle density of the system in thermal equilibrium at temperature T and is referred to, then, as the question of *thermodynamic* V-representability.

For the purpose of including *nonlocal* external potentials, Gilbert[(9)] and Donnelly and Parr[(10)] have rephrased the problem, and established a theorem analogous to the Hohenberg–Kohn theorem, in terms of one-particle density matrices (or "one-matrices" for short) in lieu of particle densities. Since one-matrices are one reduction step less removed from the full grand canonical many-particle density matrix than are particle densities, the problem of the V-representability of one-matrices might conceivably be somewhat less intricate than the V-representability problem of the original Hohenberg–Kohn theory. In what follows, we derive a necessary condition for a one-matrix to be thermodynamically V-representable.

2. THERMODYNAMIC V-REPRESENTABILITY OF ONE-MATRICES

In order to make our notion of V-representability precise, we have to specify the class of external potentials v that will be admitted. What is usually done in this regard[(4)] is to allow all $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$.[2] The rationale behind this restriction is as follows.

(i) One is interested in external potentials v and particle densities ρ such that $\int \rho v \, d^3x$ is well defined, which suggests that the spaces for the v and for the ρ be chosen dual to each other.

(ii) One is interested in one-particle densities ρ that result from N-particle wave functions Ψ with finite kinetic energy expectation value $t(\Psi) = (\Psi, \mathbf{T}\Psi)$, and because of Lieb's inequality $\int [\nabla(\rho_\Psi^{1/2})]^2 \, d^3x \leqslant t(\Psi)$ (cf. ref. 4, Theorem 1.1), this requires $\rho^{1/2}$ to lie in the Sobolev space $H^1(\mathbb{R}^3)$ of functions f on $\mathbb{R}^3$ which have the property that both f and ∇f (in the distribution sense) are square integrable. By Sobolev's inequality [ref. 4, Eq. (1.10); ref. 11], $\rho^{1/2} \in H^1(\mathbb{R}^3)$ in turn implies $\rho \in L^3(\mathbb{R}^3) \cap$

[2] I.e., all v that may be decomposed as a sum $v = v_1 + v_2$ with $v_1 \in L^{3/2}(\mathbb{R}^3)$ and $v_2 \in L^\infty(\mathbb{R}^3)$.

$L^1(\mathbb{R}^3)$, which is just the dual space to the space $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ proposed by Lieb[(4)] for the class of admitted external potentials v.

Our class of potentials differs from this choice in three separate aspects.

First, we shall restrict most of our discussion to many-particle systems which are confined to a bounded region $\Omega \subset \mathbb{R}^3$, with Dirichlet boundary conditions at the walls. Although this is not the only way of holding many particles together,[3] it is a rather natural condition to impose in the case of nonzero temperatures in that

(i) it corresponds to the grand canonical point of view in thermodynamics, where one studies systems at given values of temperature, volume, and chemical potential;

(ii) it guarantees that the many-particle kinetic energy operator $\mathbf{T}$, *by itself*, has the property that $\exp(-\beta\mathbf{T})$ exists as a trace-class operator for $\beta > 0$, which makes it possible to use Kato-type perturbation theory around $\mathbf{T}$; and

(iii) it allows us to introduce purely repulsive interactions (chosen with the case of electrons particularly in mind) without complicating the choice of the class of admitted external potentials by the requirement that they be strong enough to ensure, in the presence of the given repulsive interparticle forces, the thermodynamic stability of our one-species system in infinite space.

With the confinement taken care of by the boundary conditions, the remaining external potential's only purpose is to produce the spatial inhomogeneity encoded in the one-matrix considered, whenever possible. As a further consequence, restrictions which control the potentials at infinity become redundant, and Lieb's requirement for v would, in our case, simply amount to demanding that $v \in L^{3/2}(\Omega)$.

Second, since we are studying one-particle density matrices γ rather than particle densities ρ, the external potentials which we admit form a class of linear operators $\mathbf{v}$, to be specified further below, on the one-particle Hilbert space $L^2(\Omega)$. Thus we include, besides local potentials of a certain kind, also a class of *nonlocal* potentials. In this way, our class of external potentials extends beyond any set of potentials defined as real functions.

Third, the condition which we shall impose on our external potentials—being motivated by the technical requirements of Kato-type operator perturbation theory—is different, mathematically, from the condition adopted in the work referred to above.[(4)] This turns out to be an advantage in

[3] See also the model of coupled oscillators treated in Section 5 below, where we explicitly deal with a thermodynamic system in infinite space.

the sense that our subclass of local potentials, i.e., of those admitted one-particle operators $\mathbf{v}$ which are diagonal in the x representation, is in fact even somewhat wider than $L^{3/2}(\Omega)$.

We shall formulate our general many-particle Hamiltonian for the case of fermions, because they are what density functional theory is usually applied to in practice. (There is, however, no difficulty in treating other statistics, and we shall in fact have occasion to discuss a model of bosons in Section 4, and a case of Boltzmann statistics in Section 5.) We take our particles to be spinless in order to keep the notation as simple as possible (again, there is no difficulty of principle involved in including spin).

Let $-\mathbf{\Delta}_\Omega$ denote the negative Laplace operator on Ω appropriate for Dirichlet boundary conditions,[12] i.e., the Friedrichs extension of the negative Laplace operator defined on $C_0^\infty(\Omega)$. From it, the many-fermion kinetic energy operator is obtained by the usual prescription: Given any closed linear operator $\mathbf{A}$ on $L^2(\Omega)$ with domain $\mathscr{D}(\mathbf{A})$ and form domain $\mathscr{Q}(\mathbf{A})$, we follow Cycon *et al.*[13] in writing $d\Lambda^n(\mathbf{A})$ for the associated n-fermion operator, i.e., for the closed linear operator on the space $\Lambda^n L^2(\Omega)$ of conjugate-linear antisymmetric n-forms defined on the core $\mathscr{D}(\mathbf{A}) \wedge \mathscr{D}(\mathbf{A}) \wedge \cdots \wedge \mathscr{D}(\mathbf{A})$ (n times) by

$$d\Lambda^n(\mathbf{A})(\varphi_1 \wedge \varphi_2 \wedge \cdots \wedge \varphi_n) = \sum_{i=1}^{n} \varphi_1 \wedge \cdots \wedge \varphi_{i-1} \wedge (\mathbf{A}\varphi_i) \wedge \varphi_{i+1} \wedge \cdots \wedge \varphi_n \tag{1a}$$

where $\wedge$ stands for the exterior product of antisymmetric forms. The corresponding operator on the fermion-Fock space $\Lambda^* L^2(\Omega)$ will be denoted by $d\Lambda^*(\mathbf{A})$ and is defined as the direct sum

$$d\Lambda^*(\mathbf{A}) = \bigoplus_{n=0}^{\infty} d\Lambda^n(\mathbf{A}) \tag{1b}$$

The kinetic energy operator on fermion-Fock space is thus $d\Lambda^*(-\mathbf{\Delta}_\Omega)$. (We use units such that $\hbar = 2m = 1$.)

As interaction operator $\mathbf{W}$ we choose the direct sum

$$\mathbf{W} = \bigoplus_{n=0}^{\infty} \mathbf{W}^{(n)} \tag{2}$$

of maximal multiplication operators $\mathbf{W}^{(n)}$ on $\Lambda^n L^2(\Omega)$ which multiply by $\sum_{1 \leqslant i<j \leqslant n} w(x_i - x_j)$, where $w \in L^2(\Omega')$ is a *nonnegative* real function.[4] This

[4] Here, Ω' denotes the set of all vectors $x' = x_1 - x_2$ with $x_1 \in \Omega$, $x_2 \in \Omega$.

class of interactions is large enough to include the Coulomb interaction $w(x) = 1/|x|$, while at the same time keeping each $\mathbf{W}^{(n)}$ infinitesimally operator-bounded (or "Kato-tiny")[14] with respect to the kinetic energy in the sense that, for any $\varepsilon > 0$, there exists $b_\varepsilon \in \mathbb{R}$ such that

$$\|\mathbf{W}^{(n)}\Psi\| \leqslant \varepsilon \, \|d\Lambda^n(-\mathbf{\Delta}_\Omega)\,\Psi\| + b_\varepsilon \, \|\Psi\|, \qquad \forall \Psi \in \mathscr{D}(d\Lambda^n(-\mathbf{\Delta}_\Omega)) \tag{3}$$

Hence

$$\mathbf{H}_0 = [d\Lambda^*(-\mathbf{\Delta}_\Omega) + \mathbf{W}]^\sim \tag{4}$$

where the tilde denotes operator closure, is a self-adjoint operator which is nonnegative (because of $w \geqslant 0$) and has the property that $\exp(-\beta\mathbf{H}_0)$ is of trace class for all $\beta > 0$ (ref. 15, Section X.2; ref. 16, Section VIII.10).

While the kinetic and interaction parts of the Hamiltonian are to be kept fixed, the external potential is meant to vary over a suitable class of one-particle operators $\mathbf{v}$. Ideally, this class should comprise, loosely speaking, all $\mathbf{v}$ which lead to a many-particle Hamiltonian $\mathbf{H}_\mathbf{v}$ (i.e., $\mathbf{H}_0$ "plus" the many-particle operator associated with the potential $\mathbf{v}$) that can be meaningfully defined as a self-adjoint operator on a suitable domain dense in $\Lambda^* L^2(\Omega)$ such that $\exp(-\beta\mathbf{H}_\mathbf{v})$ exists as a trace-class operator for $\beta > 0$. (Otherwise, there would be no Schrödinger map to which the Hohenberg–Kohn–Mermin inverse map could be inverse). Obviously, therefore, the class of potentials that can be admitted depends on the mathematical techniques available for assuring the properties required for $\mathbf{H}_\mathbf{v}$. If this control is to be achieved by Kato-type perturbation theory "around" $\mathbf{H}_0$, one is led to restrict the admitted external potentials to those symmetric operators $\mathbf{v}$ with $\mathscr{Q}(\mathbf{v}) \supseteq \mathscr{Q}(-\mathbf{\Delta}_\Omega)$ which are "infinitesimally form bounded"[15] with respect to $-\mathbf{\Delta}_\Omega$, i.e., we demand that, for any $\varepsilon > 0$, there exists $c_\varepsilon \in \mathbb{R}$ such that

$$|(\psi, \mathbf{v}\psi)| \leqslant \varepsilon(\psi, -\mathbf{\Delta}_\Omega\psi) + c_\varepsilon(\psi, \psi), \qquad \forall \psi \in \mathscr{Q}(-\mathbf{\Delta}_\Omega) \tag{5}$$

Then, $d\Lambda^*(\mathbf{v})$ is infinitesimally form bounded with respect to $\mathbf{H}_0$, and we can define $\mathbf{H}_\mathbf{v}$ as the self-adjoint operator associated, by Kato's first representation theorem (ref. 14, p. 322; see also ref. 17), with the closed symmetric form $(\Phi, \mathbf{H}_0\Psi) + (\Phi, d\Lambda^*(\mathbf{v})\,\Psi)$ on $\mathscr{Q}(\mathbf{H}_0)$, so that $\exp(-\beta\mathbf{H}_\mathbf{v})$, too, is of trace class for all $\beta > 0$. Similarly, we write $\mathbf{h}_\mathbf{v}$ for the self-adjoint operator associated with $(\varphi, -\mathbf{\Delta}_\Omega\psi) + (\varphi, \mathbf{v}\psi)$ on $\mathscr{Q}(-\mathbf{\Delta}_\Omega)$.

Although termed "infinitesimal," the form boundedness in condition (5) constitutes a fairly wide class of potentials and allows for quite strong singularities. In particular, as stated earlier, all $L^{3/2}(\Omega)$ functions, interpreted as multiplication operators, satisfy condition (5).[14] As a consequence, the local potentials are permitted to be as singular as

$$v(x) \sim \frac{1}{|x - x_0|^{2-\varepsilon}}, \qquad \varepsilon > 0$$

i.e., considerably more singular than the Coulomb potential. Any model of electrons in the presence of fixed nuclei, for instance, would thus be included. The class of so-called Rollnik potentials,[18] i.e., the class of all v for which

$$\int_\Omega \int_\Omega \frac{|v(x)|\,|v(y)|}{|x-y|}\, d^3x\, d^3y < \infty$$

which is also frequently considered when the construction of Hamiltonians as quadratic forms is discussed, equally satisfies (5). What cannot be handled along the lines of the present approach, on the other hand, are singularities of δ-type distributions: they are definitely excluded.[5]

Finally, let

$$\mathbf{N} = \bigoplus_{n=0}^{\infty} n \mathbf{1}_{\Lambda^n L^2(\Omega)} \tag{6}$$

denote the particle number operator. Then

$$\mathbf{H}_{\mathrm{v}} - \mu \mathbf{N} = \mathbf{H}_{\mathrm{v} - \mu \mathbf{1}_{L^2(\Omega)}} \tag{7}$$

is self-adjoint on $\mathscr{D}(\mathbf{H}_{\mathrm{v}})$ for all real μ, and $\exp[-\beta(\mathbf{H}_{\mathrm{v}} - \mu\mathbf{N})]$ is of trace class for all $\mu \in \mathbb{R}$ and all $\beta > 0$, so that the grand canonical density matrix

$$\Xi^{(\mathrm{v})}_{\beta,\mu} = \frac{\exp[-\beta(\mathbf{H}_{\mathrm{v}} - \mu\mathbf{N})]}{\mathrm{Tr}\{\exp[-\beta(\mathbf{H}_{\mathrm{v}} - \mu\mathbf{N})]\}} \tag{8}$$

and the grand thermodynamic potential

$$Y(\beta, \mu; \mathrm{v}) = -\beta^{-1} \ln(\mathrm{Tr}\{\exp[-\beta(\mathbf{H}_{\mathrm{v}} - \mu\mathbf{N})]\}) \tag{9}$$

exist and are finite for all $\mu \in \mathbb{R}$ and all $\beta > 0$.

We are now in a position to introduce the notion of V-representability.

[5] The inclusion of δ-type singularities, of interest from the point of view of certain many-electron *models* such as the Kronig–Penney model, would substantially alter the notion of V-representability that is being discussed; see, e.g., Chayes *et al.*,[7] who argue that some of the "counterexamples" of Englisch and Englisch[5] of non-V-representable densities might become V-representable if sufficiently singular potentials, such as δ-type distributions, were to be admitted.

Definition 1. The partial trace map $\Pi\colon \mathfrak{Q} \to \mathfrak{P}$ is defined on

$$\mathfrak{Q} = \{\mathbf{\Gamma} \in \mathscr{I}_1(\Lambda^* L^2(\Omega)) \mid \mathbf{\Gamma} \geqslant 0, \operatorname{Tr}\{\mathbf{\Gamma}\} = 1, \operatorname{Tr}\{\mathbf{\Gamma}^{1/2}\mathbf{N}\mathbf{\Gamma}^{1/2}\} < \infty\}$$

onto

$$\mathfrak{P} = \{\gamma \in \mathscr{I}_1(L^2(\Omega)) \mid \mathbf{0} \leqslant \gamma \leqslant \mathbf{1}\}$$

by

$$(\varphi, \Pi(\mathbf{\Gamma})\psi) = \sum_{n=1}^{\infty} \sum_{i_2 < \cdots < i_n} (\varphi \wedge \chi_{i_2} \wedge \cdots \wedge \chi_{i_n}, (\mathbf{\Gamma} \upharpoonright_{\Lambda^n L^2(\Omega)} \psi) \wedge \chi_{i_2} \wedge \cdots \wedge \chi_{i_n}) \tag{10}$$

where $\upharpoonright$ means restriction, $\mathscr{I}_1(\mathfrak{h})$ denotes the trace class of linear operators on the Hilbert space $\mathfrak{h}$, and $\{\chi_i\}_{i=1}^{\infty}$ is any complete orthonormal set in $L^2(\Omega)$. We say that $\gamma \in \mathfrak{P}$ is (thermodynamically) V-representable for an inverse temperature $\beta > 0$ if there exists an infinitesimally $(-\mathbf{\Delta}_\Omega)$-form bounded symmetric operator $\mathbf{v}$ on $L^2(\Omega)$ such that for some value of μ

$$\gamma = \Pi(\mathbf{\Xi}^{(\mathbf{v})}_{\beta,\mu}) \tag{11}$$

Obviously, in view of (7), if γ is V-representable for an inverse temperature β at the chemical potential μ by some $\mathbf{v}$, it is also V-representable, for the same β, at any other (allowed) value μ' of the chemical potential by the simple shift $\mathbf{v}' = \mathbf{v} + (\mu' - \mu)\,\mathbf{1}_{L^2(\Omega)}$. This makes it possible to speak of V-representability without reference to the chemical potential, except for noting that it is the difference $\mathbf{v} - \mu \mathbf{1}_{L^2(\Omega)}$ which is determined uniquely by a V-representable γ, so that such γ *does* determine $\mathbf{v}$ completely (and not just up to an additive constant) as soon as the chemical potential μ is specified.

Any V-representable $\gamma = \Pi(\mathbf{\Xi}^{(\mathbf{v})}_{\beta,\mu})$ must satisfy some obvious requirements, such as

$$\operatorname{Tr}\{\gamma^{1/2}(-\mathbf{\Delta}_\Omega)\gamma^{1/2}\} \leqslant \operatorname{Tr}\{\mathbf{\Xi}^{(\mathbf{v})1/2}_{\beta,\mu}\mathbf{H}_0\mathbf{\Xi}^{(\mathbf{v})1/2}_{\beta,\mu}\} < \infty$$

and, by the Klein–Delbrück–Molière inequality [see ref. 19, inequality (3.18)],

$$S(\gamma) \leqslant \beta \operatorname{Tr}\{\gamma^{1/2}(-\mathbf{\Delta}_\Omega)\gamma^{1/2}\} + \operatorname{Tr}\{\gamma\} \ln \frac{\operatorname{Tr}\{\exp[-\beta(-\mathbf{\Delta}_\Omega)]\}}{\operatorname{Tr}\{\gamma\}} < \infty$$

where $S(\gamma) = -\operatorname{Tr}\{\gamma \ln(\gamma)\}$ is the entropy of γ. Apart from these rather weak requirements which follow immediately from our basic assumptions, no further properties which would provide a more specific characterization of V-representable one-matrices seem to be known. Ideally, one would wish for a criterion which would allow one to decide, for every $\gamma \in \mathfrak{P}$ and on the basis of properties exhibited by γ alone, whether γ is V-representable or not and, if it is, for what temperature(s). This is the problem of thermodynamic V-representability of one-matrices. For want of such a criterion, we prove, in the next section, a necessary condition for V-representability which, though elementary, hitherto seems to have gone unnoticed.

3. AN INEQUALITY FOR V-REPRESENTABLE ONE-MATRICES

Our results rest on the following theorem.

Theorem 1. Let $\gamma \in \mathfrak{P}$ be V-representable, as in (11), for inverse temperature β. Then

$$-\beta^{-1} \ln(\gamma) \leqslant \mathbf{h}_{\mathbf{v}} - (Y(\beta, \mu; \mathbf{v}) + \mu)\, \mathbf{1}_{L^2(\Omega)} \tag{12}$$

and for all $\varphi \in \mathscr{D}(-\Delta_\Omega)$ with $\|\varphi\| = 1$

$$(\varphi, \gamma\varphi) > e^{\beta(Y(\beta, \mu; \mathbf{v}) + \mu)} \exp[-\beta(\varphi, \mathbf{h}_v \varphi)] \tag{13}$$

Proof. Since $\Xi^{(\mathbf{v})}_{\beta,\mu}$ is positive, omitting all terms with $n \geqslant 2$ from

$$(\varphi, \gamma\varphi) = \sum_{n=1}^{\infty} \sum_{i_2 < \cdots < i_n} (\varphi \wedge \chi_{i_2} \wedge \cdots \wedge \chi_{i_n}, (\Xi^{(\mathbf{v})}_{\beta,\mu} \restriction_{\Lambda^n L^2(\Omega)} \varphi) \wedge \chi_{i_2} \wedge \cdots \wedge \chi_{i_n})$$

gives the lower bound

$$(\varphi, \gamma\varphi) > (\varphi, \Xi^{(\mathbf{v})}_{\beta,\mu} \restriction_{L^2(\Omega)} \varphi) = e^{\beta(Y(\beta, \mu; \mathbf{v}) + \mu)} (\varphi, \exp(-\beta \mathbf{h}_{\mathbf{v}})\, \varphi) \tag{14}$$

for all $\varphi \in L^2(\Omega)$ with $\|\varphi\| \neq 0$, so that

$$\gamma > e^{\beta(Y(\beta, \mu; \mathbf{v})} \exp(-\beta \mathbf{h}_{\mathbf{v}}) \tag{15}$$

Inequality (12) now follows with the operator monotonicity of the logarithm on $(0, \infty)$ [ref. 20, Theorem 2.5, and ref. 21; the logarithm may be taken since (15), of course, implies $\gamma > \mathbf{0}$]. Inequality (13) is obtained from (14) by an application of Jensen's inequality [see ref. 19, Inequality (3.7)] to $(\varphi, \exp(-\beta \mathbf{h}_{\mathbf{v}})\, \varphi)$.

At first sight, inequalities (12), (13), and (15) appear to be of little value, since the bounds they offer still depend on the exact grand potential

$Y(\beta, \mu; \mathbf{v})$ which is, in general, unknown. This circumstance does indeed preclude any explicit numerical evaluation of the bounds in the form given above. Although the Golden–Thompson inequality (ref. 12, p. 320) allows for $Y(\beta, \mu; \mathbf{v})$ to be bounded below by the grand potential $Y^{(0)}(\beta, \mu; \mathbf{v})$ of the corresponding interactionless system, this would be of no help either, since $Y^{(0)}(\beta, \mu; \mathbf{v})$ would still depend on the unknown external potential operator $\mathbf{v}$ that represents γ and could, in turn, only be lower bounded if the appropriate constant c_ε of Eq. (5) were available.

Nonetheless, the inequalities derived above provide valuable information on V-representable one-matrices, and inequality (12) does in fact yield a rather stringent condition which every one-matrix, in order to be V-representable, must fulfill. The point is this: Since the operators on either side of (12) have pure point spectra, bounded from below and without accumulation points or infinite multiplicities (below infinity), their eigenvalues can be arranged in increasing order. While, in this order, the eigenvalues of $\mathbf{h}_\mathbf{v}$ go to $+\infty$, the unknown term $-(Y(\beta, \mu; \mathbf{v}) + \mu)$ stays constant and hence becomes more and more negligible, so that asymptotic properties of γ may be established without knowledge of the exact $Y(\beta, \mu; \mathbf{v})$.

We can make the argument precise in the following manner: For any self-adjoint operator $\mathbf{A}$ with pure point spectrum which is bounded from below and does not have an accumulation of eigenvalues at the infimum of its spectrum, we can use the min-max principle[12] to define *the* νth *eigenvalue from below* of $\mathbf{A}$ as

$$\lambda_\nu(\mathbf{A}) = \sup_{\varphi_1, \ldots, \varphi_{\nu-1}} \inf_{\psi \in \mathscr{Q}(\mathbf{A}),\ \|\psi\| = 1,\ \psi \perp \varphi_1, \ldots, \varphi_{\nu-1}} \{(\psi, \mathbf{A}\psi)\} \tag{16}$$

Likewise, for any self-adjoint operator $\mathbf{B}$ with pure point spectrum which is bounded from above and does not have an accumulation of eigenvalues at the supremum of its spectrum, we can define *the* νth *eigenvalue from above* of $\mathbf{B}$ as

$$\lambda'_\nu(\mathbf{B}) = -\lambda_\nu(-\mathbf{B}) \tag{16'}$$

With this notation, we may formulate our conclusion as follows.

Corollary 1. If $\gamma \in \mathfrak{P}$ is V-representable, then for any $\varepsilon > 0$ there exists $C_\varepsilon > 0$ (allowed to depend on γ) such that for all $\nu \in \mathbb{N}$

$$\lambda'_\nu(\gamma) \geqslant C_\varepsilon \exp[-\beta(1+\varepsilon)\, \lambda_\nu(-\mathbf{\Delta}_\Omega)] \tag{17}$$

Proof. Using (16) with $\mathbf{A} = -\beta^{-1} \ln(\gamma)$, we conclude from inequality (12) and from the infinitesimal form boundedness of $\mathbf{v}$, inequality (5), that

$$
\begin{aligned}
&-\beta^{-1}\ln[\lambda'_\nu(\gamma)] \\
&\quad= \lambda_\nu(-\beta^{-1}\ln(\gamma)) \\
&\quad= \sup_{\varphi_1,\ldots,\varphi_{\nu-1}} \inf_{\psi\in\mathscr{D}(-\ln(\gamma)),\, \|\psi\|=1,\, \psi\perp\varphi_1,\ldots,\varphi_{\nu-1}} \{(\psi, -\beta^{-1}\ln(\gamma)\,\psi)\} \\
&\quad\leqslant \sup_{\varphi_1,\ldots,\varphi_{\nu-1}} \inf_{\psi\in\mathscr{D}(-\Delta_\Omega),\, \|\psi\|=1,\, \psi\perp\varphi_1,\ldots,\varphi_{\nu-1}} \{(\psi, \mathbf{h}_\mathbf{v}\psi) - Y(\beta,\mu;\mathbf{v}) - \mu\} \\
&\quad\leqslant \sup_{\varphi_1,\ldots,\varphi_{\nu-1}} \inf_{\psi\in\mathscr{D}(-\Delta_\Omega),\, \|\psi\|=1,\, \psi\perp\varphi_1,\ldots,\varphi_{\nu-1}} \{(1+\varepsilon)(\psi, -\Delta_\Omega\psi) \\
&\qquad + c_\varepsilon - Y(\beta,\mu;\mathbf{v}) - \mu\} \\
&\quad= (1+\varepsilon)\,\lambda_\nu(-\Delta_\Omega) + c_\varepsilon - Y(\beta,\mu;\mathbf{v}) - \mu
\end{aligned}
$$

Letting $C_\varepsilon = \exp\{-\beta[c_\varepsilon - Y(\beta,\mu;\mathbf{v}) - \mu]\}$, we obtain inequality (17).

Inequality (17) places a serious constraint on the spectral properties of any V-representable one-matrix γ in that it limits, in an analytically well-specified manner, the rate at which the eigenvalues of γ, when arranged in decreasing order and repeated according to multiplicity, are allowed to go to zero. This has a number of important consequences, both for practical applications and for our insight into the nature of the V-representability problem.

(i) One consequence of inequality (17) which is of considerable practical importance is that no one-particle density operator γ of finite rank can be V-representable, for whatever temperature. This implies that approximations constructed from a finite one-particle basis never can produce V-representable γ's. Nor can V-representable γ's be obtained by reducing higher-order density operators of finite rank since, according to a theorem by Ruskai (ref. 22, Theorem 4.1), such a procedure necessarily leads to finite-rank one-matrices.

(ii) A second important feature of Corollary 1 is that it refers to the entire *infinite* sequence of eigenvalues of γ, not just to individual eigenvalues. For *finitely* many eigenvalues of γ (as long as they are all positive) a C_ε can always be found, for any $\beta > 0$ and $\varepsilon > 0$, such that inequality (17) is satisfied. Thus, inequality (17) does not lend itself easily as a test which would allow one to accept or discard possible candidates for V-representable one-matrices in situations where the eigenvalues of the one-matrices to be tested are only numerically known. Rather, inequality (17) may be looked upon as an indication of how one-matrices must be constructed in the first place if they are to stand a chance of being V-representable.

(iii) One rather subtle aspect of inequality (17) is that arbitrarily small eigenvalues of γ still have a fundamental effect upon its V-representability, even though their inclusion makes negligible contributions to the energy and to the entropy. A similar complication has been observed in the N-representability problem of two-particle density matrices.[22]

To make the bound in Corollary 1 more explicit, let us denote by $\mathscr{C}$ the largest cube inside Ω and by L the side length of $\mathscr{C}$. Then

$$\lambda_\nu(-\Delta_\Omega) \leqslant \lambda_\nu(-\Delta_{\mathscr{C}}) = \left(\frac{\pi}{L}\right)^2 (n_{\nu,x}^2 + n_{\nu,y}^2 + n_{\nu,z}^2)$$

where $(n_{\nu,x}, n_{\nu,y}, n_{\nu,z})$ are the integer quantum numbers of an eigenfunction of $-\Delta_{\mathscr{C}}$ belonging to $\lambda_\nu(-\Delta_{\mathscr{C}})$. Since, asymptotically,

$$\lambda_\nu(-\Delta_{\mathscr{C}}) \sim \frac{1}{L^2} (6\pi^2 \nu)^{2/3} \qquad \text{as} \quad \nu \to \infty$$

we have the following results.

Corollary 2.

(i) No $\gamma \in \mathfrak{P}$ whose eigenvalues $\lambda'_\nu(\gamma)$ go to zero as fast as $\exp(-\alpha \nu^\tau)$ with $\tau > 2/3$ and $\alpha > 0$, or faster, can be V-representable for any $\beta > 0$.

(ii) No $\gamma \in \mathfrak{P}$ whose eigenvalues $\lambda'_\nu(\gamma)$ go to zero as fast as $\exp(-\alpha \nu^{2/3})$ with $\alpha > 0$, or faster, can be V-representable for any $\beta < \alpha L^2/(6\pi^2)^{2/3}$.

It is tempting to speculate whether V-representability of one-matrices also implies an *upper* bound analogous to (17): Does there, for every V-representable $\gamma \in \mathfrak{P}$ and every $\varepsilon > 0$, exist C'_ε (allowed to depend on γ) such that, for all $\nu \in \mathbb{N}$,

$$\lambda'_\nu(\gamma) \leqslant C'_\varepsilon \exp[-\beta(1-\varepsilon)\, \lambda_\nu(-\Delta_\Omega)] \; ? \tag{18}$$

On a heuristic level, there are two arguments which could induce one to believe that, under the assumptions introduced earlier, inequality (18) might hold. One is that, because of the assumed positivity of the interaction $\mathbf{W}$, the exponent $-\beta(\mathbf{H}_\nu - \mu\mathbf{N})$ in (8) is bounded *above* by the corresponding expression without interactions. Since, however, exp is not an operator monotone function, there is no direct way of exploiting the positivity of $\mathbf{W}$. The second reason arguing in favor of (18) is that, on each $\Lambda^n L^2(\Omega)$, the interaction as introduced in Section 2 is infinitesimally operator bounded with respect to the kinetic energy [see inequality (3)], which suggests that it ought to be possible to obtain estimates for the γ-eigenvalues of the interacting system in terms of those of the noninteracting system.

To illustrate our point we present, in the two sections to follow, two examples where we have succeeded in rigorously establishing the validity of inequality (18) or of a variant thereof [see inequality (26) below]. The first example is the system of noninteracting fermions or bosons, which turns out to be not quite as trivial as might be thought. The second is a model of harmonic oscillators with harmonic couplings. This latter example fails to comply with the conditions laid down in Section 2 in several aspects. In particular, the interaction $\mathbf{W}^{(n)}$ is in this case not operator bounded, nor even form bounded, with respect to the kinetic energy. Nevertheless, the harmonic oscillator model appears to us worth mentioning, especially since it shows that at least inequality (26), the inequality playing the role of (18) in the context of the oscillator model, is violated even for certain positive $\mathbf{W}$. Although outside the setting provided by the conditions of Section 2, the model may thus serve as a caution against the naive belief that positivity of $\mathbf{W}$ by itself, without some additional restriction requiring that $\mathbf{W}$ be in some sense "small," might be enough for (18) to be valid.

4. NONINTERACTING PARTICLES

In the case of noninteracting fermions or bosons, the Hohenberg–Kohn–Mermin (HKM) inverse map is immediately obtained as an explicit formula expressing the representing one-particle potential operator $\mathbf{v}(\gamma)$ in terms of the one-matrix γ whenever the latter is V-representable for a given temperature. Still, the conditions which are necessary and sufficient for V-representability in the precise sense discussed here—and, hence, the characterization of the domain of definition of the HKM inverse map which they provide—turn out to be rather subtle even in this seemingly trivial situation.

For fermions ($\eta = -1$) or bosons ($\eta = +1$) with $w(x) \equiv 0$, a one-matrix γ which is V-representable at inverse temperature β obeys

$$\gamma = \{\exp[\beta(\mathbf{h}_{\mathbf{v}} - \mu \mathbf{1}_{L^2(\Omega)})] - \eta \mathbf{1}_{L^2(\Omega)}\}^{-1} \tag{19}$$

which may be solved for $\mathbf{h}_{\mathbf{v}}$ to give

$$\mathbf{h}_{\mathbf{v}} = \beta^{-1} \ln(\gamma^{-1} + \eta \mathbf{1}_{L^2(\Omega)}) + \mu \mathbf{1}_{L^2(\Omega)} \tag{20}$$

Hence, V-representability of γ is equivalent to the existence of an infinitesimally $(-\Delta_\Omega)$-form bounded potential operator $\mathbf{v}(\gamma)$ such that the operator $\mathbf{h}_{\mathbf{v}}$, as defined by (20), is the operator associated with the form

$$(\varphi, \mathbf{h}_{\mathbf{v}} \psi) = (\varphi, -\Delta_\Omega \psi) + (\varphi, \mathbf{v}(\gamma)\, \psi), \qquad \varphi, \psi \in \mathscr{Q}(-\Delta_\Omega) \tag{21}$$

by Kato's first representation theorem.[14,17] For this to be the case, it is necessary and sufficient that $\mathbf{h}_{\mathbf{v}}$ have the same form domain as $-\Delta_\Omega$ and that $(\psi, \mathbf{h}_{\mathbf{v}} \psi) - (\psi, -\Delta_\Omega \psi)$ satisfy the inequality (5) for $(\psi, \mathbf{v}\psi)$. Since by inequality (15) any V-representable one-matrix γ must be strictly positive, we have the following result.

Theorem 2. A $\gamma \in \mathfrak{P}$ is interactionlessly V-representable for inverse temperature β if, and only if:

(i) γ is strictly positive.

(ii) $\mathscr{Q}(\ln[\gamma^{-1} + \eta \mathbf{1}_{L^2(\Omega)}]) = \mathscr{Q}(-\mathbf{\Delta}_\Omega)$.

(iii) $\forall \varepsilon > 0$, $\exists c_\varepsilon \in \mathbb{R}$ such that

$$\begin{aligned}(1-\varepsilon)(\psi, -\mathbf{\Delta}_\Omega \psi) - c_\varepsilon(\psi, \psi) &\leqslant \beta^{-1}(\psi, \ln[\gamma^{-1} + \eta \mathbf{1}_{L^2(\Omega)}]\, \psi)\\ &\leqslant (1+\varepsilon)(\psi, -\mathbf{\Delta}_\Omega \psi) + c_\varepsilon(\psi, \psi), \qquad \forall \psi \in \mathscr{Q}(-\mathbf{\Delta}_\Omega)\end{aligned}$$

If conditions (i)–(iii) are satisfied, the representing external potential operator $\mathbf{v}(\gamma)$ is expressed, in the sense of the addition of forms, by

$$\mathbf{v}(\gamma) = \beta^{-1} \ln(\gamma^{-1} + \eta \mathbf{1}_{L^2(\Omega)}) + \mu \mathbf{1}_{L^2(\Omega)} - (-\mathbf{\Delta}_\Omega) \tag{22}$$

Since $\mathscr{Q}(-\mathbf{\Delta}_\Omega)$ is known to be the Sobolev space $H_0^1(\Omega)$,(12),6 and the form domain of $\ln[\gamma^{-1} + \eta \mathbf{1}_{L^2(\Omega)}]$ may, like the form itself, be expressed in terms of the eigenvalues and eigenfunctions of γ, a more explicit version of the above result may be noted as follows.

Corollary 3. Let $\gamma \in \mathfrak{P}$ be strictly positive and $\{\chi_\nu\}_1^\infty$ be a complete orthonormal system of eigenfunctions of γ with χ_ν belonging to eigenvalue $\lambda'_\nu(\gamma)$. Then the following two conditions are, together, necessary and sufficient for γ to be interactionlessly V-representable for inverse temperature β:

(i) $\forall \psi \in L^2(\Omega)$,

$$\sum_{\nu=1}^{\infty} \left\{ |(\chi_\nu, \psi)|^2 \ln\{[\lambda'_\nu(\gamma)]^{-1} + \eta\right\} < \infty \Rightarrow \psi \in H_0^1(\Omega)$$

(ii) $\forall \varepsilon > 0$, $\exists c_\varepsilon \in \mathbb{R}$ such that

$$\begin{aligned}(1-\varepsilon)(\psi, -\mathbf{\Delta}_\Omega \psi) - c_\varepsilon(\psi, \psi) &\leqslant \beta^{-1} \sum_{\nu=1}^{\infty} \left\{ |(\chi_\nu, \psi)|^2 \ln\{[\lambda'_\nu(\gamma)]^{-1} + \eta\} \right\}\\ &\leqslant (1+\varepsilon)(\psi, -\mathbf{\Delta}_\Omega \psi) + c_\varepsilon(\psi, \psi), \qquad \forall \psi \in H_0^1(\Omega)\end{aligned}$$

[6] $H_0^1(\Omega)$ consists of all complex-valued functions ψ on Ω which, together with their derivative in the distribution sense $\nabla\psi$, are square-integrable over Ω and go to zero at the boundary of Ω.

In particular, condition (i) implies that all eigenfunctions χ_ν of γ must be in $H_0^1(\Omega)$.

Although Equation (22) and Corollary 3 represent explicit solutions for the HKM inverse map and V-representability problem, respectively, extracting the information which they contain remains a fairly complicated task. In particular, it appears extremely hard to verify whether the conditions (i) and (ii) of Corollary 3 are, in any given instance, fulfilled or not.

In order to connect the foregoing results with the conjectured inequality (18), we note that (19) implies

$$\lambda'_\nu(\gamma) = (\exp\{\beta[\lambda_\nu(\mathbf{h}_\mathbf{v}) - \mu]\} - \eta)^{-1} \tag{23}$$

On the other hand, the infinitesimal form boundedness (5) of $\mathbf{v}$ implies

$$(1-\varepsilon)(\psi, -\Delta_\Omega\psi) - c_\varepsilon(\psi, \psi) \leqslant (\psi, \mathbf{h}_\mathbf{v}\psi) \leqslant (1+\varepsilon)(\psi, -\Delta_\Omega\psi) + c_\varepsilon(\psi, \psi)$$

for all $\psi \in \mathscr{Q}(-\Delta_\Omega)$. Taking the infimum over $\psi \in \mathscr{Q}(-\Delta_\Omega)$ with $\|\psi\| = 1$ and $\psi \perp \varphi_1, ..., \varphi_{\nu-1}$ and then the supremum over $\varphi_1, ..., \varphi_{\nu-1} \in L^2(\Omega)$ yields

$$(1-\varepsilon)\,\lambda_\nu(-\Delta_\Omega) - c_\varepsilon \leqslant \lambda_\nu(\mathbf{h}_\mathbf{v}) \leqslant (1+\varepsilon)\,\lambda_\nu(-\Delta_\Omega) + c_\varepsilon \tag{24}$$

We conclude that inequality (18) is satisfied for any $\varepsilon > 0$ with $C'_\varepsilon = \{\exp[-\beta(c_\varepsilon + \mu)] - (1+\eta)/2\}^{-1}$ [for bosons, we restrict μ to values $\mu < -c_\varepsilon$ so as to ensure the positivity of the right-hand side of (23)].

Now assume γ to be V-representable for the two inverse temperatures $\beta < \beta'$ with potentials $\mathbf{v}$ and $\mathbf{v}'$ relative to the same μ. Then we have, according to (23),

$$\beta[\lambda_\nu(\mathbf{h}_\mathbf{v}) - \mu] = \ln[\lambda'_\nu(\gamma)^{-1} + \eta] = \beta'[\lambda_\nu(\mathbf{h}_{\mathbf{v}'}) - \mu]$$

Choosing $\varepsilon < (\beta' - \beta)/(\beta' + \beta)$, we obtain from (24)

$$\beta'[(1-\varepsilon)\,\lambda_\nu(-\Delta_\Omega) - c'_\varepsilon - \mu] \leqslant \beta[(1+\varepsilon)\,\lambda_\nu(-\Delta_\Omega) + c_\varepsilon - \mu]$$

or

$$\vartheta\lambda_\nu(-\Delta_\Omega) \leqslant \beta c_\varepsilon + \beta' c'_\varepsilon + (\beta' - \beta)\,\mu$$

with $\vartheta = \beta'(1-\varepsilon) - \beta(1+\varepsilon) > 0$, which contradicts the fact that $\lambda_\nu(-\Delta_\Omega) \to \infty$ as $\nu \to \infty$. This proves the following result.

Corollary 4. Any one-matrix $\gamma \in \mathfrak{P}$ can be interactionlessly V-representable for at most one temperature $T = (k_B\beta)^{-1}$.

We shall return to this result in Section 6, where we discuss it with regard to the general nature of the HKM inverse problem and also with regard to the use of extended functionals in density matrix functional theory at nonzero temperatures. Before doing so, however, we want to show that the result is not restricted to the interactionless case.

5. COUPLED HARMONIC OSCILLATORS

Consider the n-particle harmonic oscillator Hamiltonian

$$\mathbf{H}^{(n)} = \sum_{i=1}^{n} \mathbf{h}_0^{(i)} + \frac{\kappa}{2} \sum_{i,j=1}^{n} (x_i - x_j)^2 \tag{25a}$$

with

$$\mathbf{h}_0^{(i)} = -\Delta_x^{(i)} + x_i^2 \tag{25b}$$

which is essentially self-adjoint on $C_0^\infty(\mathbb{R}^{3n})$ (we take $x_i \in \mathbb{R}^3$ for $i = 1,..., n$). For simplicity, we regard this model not in fermion-Fock space, but in the n-particle Hilbert space without symmetry constraint, $L^2(\mathbb{R}^{3n})$. In studying this model, we further deviate from the setting of Section 2 in that the interaction of (25) fails to be Kato-tiny in the sense of (3), and that the external potential fails to satisfy condition (5). Moreover, by fixing the external potential, we limit ourselves to exactly one V-representable one-matrix, $\gamma_{n,\beta}(\kappa)$, for any three given values of $\beta \geq 0$, $n \in \mathbb{N}$, and $\kappa > -n^{-1}$. Our purpose is to investigate whether or not the eigenvalues of $\gamma_{n,\beta}(\kappa)$ satisfy the inequality

$$\lambda'_\nu(\gamma_{n,\beta}(\kappa)) \leq C'_\varepsilon \exp[-\beta(1-\varepsilon)\, \lambda_\nu(\mathbf{h}_0)] \tag{26}$$

which here takes the place of inequality (18).

With the aid of the orthogonal coordinate transformation

$$x_k = \frac{1}{\sqrt{n}} \xi_1 - \left(\frac{k-1}{k}\right)^{1/2} \xi_k + \sum_{j=k+1}^{n} \frac{1}{[j(j-1)]^{1/2}} \xi_j, \qquad k = 1,..., n \tag{27}$$

the Hamiltonian (25) is decoupled to

$$\mathbf{H}^{(n)} = \sum_{i=1}^{n} (-\Delta_\xi^{(i)}) + \xi_1^2 + (1 + n\kappa) \sum_{j=2}^{n} \xi_j^2 \tag{28}$$

and the integral kernel for the statistical operator

$$\Xi_{\beta,\kappa}^{(n)} = \frac{\exp(-\beta \mathbf{H}^{(n)})}{\mathrm{Tr}\{\exp(-\beta \mathbf{H}^{(n)})\}}$$

is easily calculated in terms of the ξ_j. The partial trace is then performed by reverting, with the aid of (27), to the original coordinates x_j and by integrating over $x_2,..., x_n$. The result, for $\kappa > -n^{-1}$, is found to be the integral kernel of the operator

$$\gamma_{n,\beta}(\kappa) = \frac{\exp(-\bar{\beta}\bar{\mathbf{h}})}{\mathrm{Tr}\{\exp(-\bar{\beta}\bar{\mathbf{h}})\}} \tag{29}$$

where

$$\bar{\mathbf{h}} = -\Delta_x + \bar{\omega}^2 x^2 \tag{30}$$

$$\bar{\omega} = \left[\hat{\kappa}_n \frac{\coth(\beta) + (n-1)\,\hat{\kappa}_n \coth(\beta\hat{\kappa}_n)}{\hat{\kappa}_n \coth(\beta) + (n-1)\coth(\beta\hat{\kappa}_n)}\right]^{1/2} \tag{31}$$

and

$$\tanh(\bar{\beta}\bar{\omega}) = n\hat{\kappa}_n^{1/2}\,[\hat{\kappa}_n \coth^2(\beta) + (n-1)^2\,\hat{\kappa}_n \coth^2(\beta\hat{\kappa}_n) + (n-1)(1+\hat{\kappa}_n^2)\coth(\beta)\coth(\beta\hat{\kappa}_n)]^{-1/2} \tag{32}$$

with $\hat{\kappa}_n = (1+n\kappa)^{1/2}$. It follows that the eigenvalues $\lambda'_\nu(\gamma_{n,\beta}(\kappa))$ satisfy inequality (26) for all $\varepsilon > 0$ if, an only if,

$$\bar{\beta}\bar{\omega} \geqslant \beta \tag{33}$$

which (for $n \geqslant 2$) is in turn equivalent to

$$f_n(\beta, \kappa) = \frac{2 + n\kappa + n(\kappa^2 + 4n\kappa + 4)^{1/2}}{2(n+1)(1+n\kappa)^{1/2}} \tanh(\beta)\coth[\beta(1+n\kappa)^{1/2}] \leqslant 1 \tag{34}$$

Now for any fixed $\beta > 0$, there is a $\kappa_\beta^{(n)} > 0$ such that $f_n(\beta, \kappa) \leqslant 1$ for $0 \leqslant \kappa \leqslant \kappa_\beta^{(n)}$ and $f_n(\beta, \kappa) > 1$ for $\kappa > \kappa_\beta^{(n)}$. This shows that the upper bound (26) cannot hold for arbitrary positive interactions—at least as far as V-representability in $L^2(\mathbb{R}^{3n})$ or in Boltzmann–Fock space is concerned—but may hold if the interaction is positive and small in some sense, as it does in this example for coupling constants κ with $0 \leqslant \kappa \leqslant \kappa_\beta^{(n)}$.

6. CONSEQUENCES FOR DENSITY FUNCTIONAL THEORY

Generally speaking, the HKM inverse problem appears more complicated than the ground-state inverse problem of the original Hohenberg–Kohn theory, in that it represents a kind of simultaneous inverse problem in potential and temperature: Given $\gamma \in \mathfrak{P}$, one is to establish for what value (or values) of T, if at all, γ is V-representable, and one is then to construct a representing external potential operator $\mathbf{v}(\gamma)$ for every temperature T for which this is possible. While the inversion for $\mathbf{v}$ is known to be unique (once the chemical potential is fixed) by Mermin's theorem,[8] the situation has hitherto, at least to our knowledge, remained entirely unresolved as far as the inversion for T is concerned.

To this problem, the results presented above give at least a partial answer. For in those cases where inequality (18) is valid, we can conclude from (17) and (18) that a given one-matrix cannot be V-representable for more than one value of β. The proof is just the same as in Section 4. Thus, for the class of interactions for which (18) obtains—shown to be nonempty by the examples given in Sections 4 and 5 above—the T-inversion in the HKM inverse problem is unique, too. In the case of these interactions there is associated, with every V-representable one-matrix γ not only a unique representing external potential operator $\mathbf{v}(\gamma)$ (relative to the chemical potential chosen), but also a unique "representation temperature" $T(\gamma)$. Moreover, $T(\gamma)$ can be explicitly expressed, since from (17) and (18) it follows that

$$T(\gamma) = \frac{1}{k_{\mathrm{B}}} \lim_{\nu \to \infty} \frac{\lambda_\nu(-\Delta_\Omega)}{-\ln[\lambda'_\nu(\gamma)]} \tag{35}$$

Hence the T-inversion can actually be performed in these cases.

Equation (35) is a rather curious formula, in that it reveals that $T(\gamma)$ depends on the extreme tail of the sequence of eigenvalues of γ, a feature already noted above with regard to inequality (17). This trait makes the formula (35) extremely awkward from a numericist's point of view and may be regarded as one more indication of the highly delicate nature of the HKM inverse problem.

The limit in (35) will, as a rule, fail to exist for one-matrices γ that are not V-representable.[7] As a consequence, the unique relationship furnished by (35) between a one-matrix γ and an associated temperature $T(\gamma)$ will be lost as soon as one steps outside of the domain of V-representable γ-matrices, and will hence not be available in the context of functionals that extend the original "Mermin functional"

$$G^{(\mathrm{M})}_{\beta,\mu}[\gamma] := Y(\beta, \mu; \mathbf{v}(\gamma)) - \mathrm{Tr}\{\gamma^{1/2}\mathbf{v}(\gamma)\,\gamma^{1/2}\} \tag{36}$$

[7] This does not mean to say, however, that the existence of the limit ensures V-representability. As shown for the interactionless case in Corollary 3, the requirements for γ to be V-representable not only refer to the eigenvalues, but also to the eigenfunctions of γ.

beyond its original domain of definition. An extension of this kind is obtained, in analogy to similar constructions by Levy[2] and Lieb[4] for the ground-state functional, by defining, for $\gamma \in \mathfrak{P}$,

$$G_{\beta,\mu}[\gamma] = \inf\{\mathrm{Tr}[\boldsymbol{\Gamma}^{1/2}(\mathbf{H}_0 - \mu\mathbf{N})\,\boldsymbol{\Gamma}^{1/2} + \beta^{-1}\boldsymbol{\Gamma}\ln\boldsymbol{\Gamma}]\mid \boldsymbol{\Gamma}\in\mathfrak{D},\ \Pi(\boldsymbol{\Gamma}) = \gamma\} \quad (37)$$

and has the attractive feature that

$$Y(\beta, \mu; \mathbf{v}) = \min\{G_{\beta,\mu}[\gamma] + \mathrm{Tr}[\gamma^{1/2}\mathbf{v}\gamma^{1/2}]\mid \gamma\in\mathfrak{P}\} \quad (38)$$

There is, however, no way of using (35) to eliminate the T dependence on the right-hand side of (37), for the reasons mentioned.

7. CONCLUSION

Under the assumptions specified in Section 2, every V-representable one-particle density matrix is subject to the "spectral constraint" of Corollary 1 as expressed in inequality (17). This result has important consequences both for practical applications, where it has to be respected in any attempted construction of one-matrices that are intended to be V-representable, and for the more fundamental theoretical questions associated with the Hohenberg–Kohn–Mermin inverse problem.

The corresponding upper bound (18) has so far only been established for noninteracting particles, and for a rather special model of harmonically coupled harmonic oscillators. However, we believe it to be valid in greater generality and want to draw attention to the important task of identifying a useful class of interaction potentials for which inequality (18) can be proven, the case of greatest interest being, of course, the Coulomb interaction. Any success in that direction would contribute toward clarifying the extent of the Hohenberg–Kohn–Mermin inverse problem, by showing the T-inversion to be unique.

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