

# Variational Approaches to the N-representability Problem

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*I consider it useless and tedious to represent what exists, because nothing that exists satisfies me. Nature is ugly, and I prefer the monsters of my fancy to what is positively trivial.*

Charles Baudelaire  
“Salon of 1859” §3  
Curiosités Esthétiques (1868)

# I. Motivation

## Density Functional Theory isn't *really* a black box:

- Problems with systems with strong static correlation. (E.g., systems where the single determinantal reference is poor.)
- Problems with systems where long-range correlation is important (i.e., the exchange-correlation hole is not very localized.) (E.g., van der Waals forces, multi-center bonding, associative transition states, . . . .)
- Semi-ab initio functionals can fail when describing “unconventional” chemistry, e.g., highly charged systems.
- In general, existing functionals are not “systematically improvable.”
- **Good News:** Existing Density-Functionals are quite accurate for thermodynamic properties and (in most cases) chemical dynamics.
- **Good News:** When DFT works, the accuracy/computational cost ratio of density-functional theory far exceeds that of most other methods.

**Can we “improve” DFT without using wave-function-based methods?**

Past the density, but not yet to the wave function. . . .

$\gamma(\mathbf{r}, \mathbf{r}')$   $\Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$   $\Gamma_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3)$   $\Gamma_4$  full-CI

$\rho(\mathbf{r})$   $\rho_2(\mathbf{r}, \mathbf{r}')$   $\rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$   $\rho_4(\mathbf{r}_1, \dots, \mathbf{r}_4)$   $\rho_N = |\Psi|^2$   $\Psi$

HF, CIS CCSD, etc. CCSDT, etc. CCSDTQ, etc. full-CI

Baerends, Buijse, Cioslowski, Coleman, Davidson, Donnelly, Garrod, Goedecker  
Levy, Mazziotti, Parr, Percus, Umrigar, Valdemoro...

Davidson, Furche, Levy, Nagy, Pistol, Samvelyan, Weinhold, Wilson, Ziesche...

“classic” quantum chemistry

“Polydensity” alternative: Gori-Giorgi, Percus, Savin.

# Outline of the Remainder of the Talk

- II. The  $N$ -representability Problem
- III. The  $N$ -representability problem: Special Case; electron pair density.
- IV. Variational approaches to the  $N$ -representability problem: Special Case; electron pair density.
- V. Variational Approaches: General Case.
- VI. Specific Variational Approaches: Density Matrices, etc..
- VII. Algorithmic Considerations
- VIII. The  $N$ -representability Problem, Revisited

## II. The $N$ -representability Problem

**Given:** A descriptor,  $f(\tau)$ , which contains enough information to describe a molecular electronic system.

**There exists:** An energy function,  $E_{v,N}[f]$ , that depends only on the descriptor and the identity of the system (as encapsulated by the external potential,  $v(r)$ , and the number of electrons,  $N$ ).

**There exists:** A variational principle for the ground-state energy, namely:

$$E_{g.s.}[v;N] = \min_{N\text{-representable } f(\tau)} E_{v,N}[f]$$

The variational principle follows directly from the variational principle for the wave function:

$$E_{g.s.} [v; N] = \underbrace{\min}_{\substack{\text{all appropriately antisymmetric} \\ N\text{-fermion wavefunctions}}} \frac{\langle \Psi | \hat{H}_{v,N} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

or density matrix

$$E_{g.s.} [v; N] = \underbrace{\min}_{\substack{\text{all } N\text{-fermion} \\ \text{density matrices}}} \hat{\text{Tr}} \left[ \hat{H}_{v,N} \Gamma_N \right]$$

This means that:

$$E_{g.s.} [v; N] = \underbrace{\min}_{\substack{\text{all } f(\tau) \text{ that correspond to a} \\ \text{system containing } N \text{ fermions}}} E_{v,N} [f]$$

If  $f(\tau)$  corresponds to a system of  $N$  fermions, then it is said to be  $N$ -representable.

**Definition:** The descriptor,  $f(\tau)$ , is said to be  $N$ -representable if and only if it corresponds to a system of  $N$ -fermions. Therefore, if  $f(\tau)$  is  $N$ -representable, then there exists some fermionic  $N$ -electron density matrix,  $\Gamma_N$ , that is consistent with  $f(\tau)$ . I.e.,

$$f(\tau) \text{ is } N\text{-representable} \leftrightarrow (\exists \Gamma_N \ni \Gamma_N \text{ yields } f(\tau))$$

**Notation:**  $\mathcal{N}_N$  denotes the set of  $N$ -representable  $f(\tau)$ .

**The  $N$ -representability problem:** Find a way to constrain the variational principle so that the correct ground-state energy is obtained:

$$\underbrace{\min}_{f(\tau)} E_{v,N} [f] \ll E_{g.s.} [v; N] = \underbrace{\min}_{f(\tau) \in \mathcal{N}_N} E_{v,N} [f]$$

*All ... popularization involves a putting of the complex into the simple, but such a move is instantly deconstructive. For if the complex can be put into the simple, then it cannot be as complex as it seemed in the first place; and if the simple can be an adequate medium of such complexity, then it cannot after all be as simple as all that.*

**Terry Eagleton**  
**Against the Grain**



### III. Variational Approaches to the $N$ -representability problem: Special Case; electron pair density.

The pair density is the probability of observing an electron at  $\mathbf{x}_1$  and  $\mathbf{x}_2$ . It is related to the structure factor in X-ray/neutron scattering.

$$\begin{aligned}\rho_2(\mathbf{x}_1, \mathbf{x}_2) &\equiv \left\langle \Psi \left| \sum_{i=1}^N \sum_{j \neq i} \delta(\mathbf{r}_i - \mathbf{x}_1) \delta(\mathbf{r}_j - \mathbf{x}_2) \right| \Psi \right\rangle \\ &= \text{Tr} \left[ \left( \sum_{i=1}^N \sum_{j \neq i} \delta(\mathbf{r}_i - \mathbf{x}_1) \delta(\mathbf{r}_j - \mathbf{x}_2) \right) \Gamma_N \right]\end{aligned}$$

**Simple Properties of the pair density:**

- normalization

$$N(N-1) = \iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

- nonnegativity

$$0 \leq \rho_2(\mathbf{x}_1, \mathbf{x}_2)$$

- symmetry

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho_2(\mathbf{x}_2, \mathbf{x}_1)$$

**Hohenberg-Kohn-Ziesche Theorem:**  $\rho_2 \rightarrow$  all observable properties, including the energy and its components.

$$V_{ee}[\rho_2] = \frac{1}{2} \iint \frac{\rho_2(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_1 d\mathbf{x}_2$$

$$V_{ne}[\rho_2] = \frac{1}{2} \iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) \left( \frac{v(\mathbf{x}_1) + v(\mathbf{x}_2)}{N-1} \right) d\mathbf{x}_1 d\mathbf{x}_2$$

**The Kinetic energy functional is not known exactly.** Approximations are available. (Furche, Levy, March, Nagy, ...\*)

**Variational Principle for the pair density:**

$$E_{g.s.}[v, N] = \underbrace{\min}_{N\text{-representable } \rho_2} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

**N-representability problem:** We *must* restrict the variational principle to  $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$  that correspond to  $N$ -fermion systems. (If one fails to do this, there will always exist 2-body Hamiltonians for which the error from the variational calculation is arbitrarily large.)

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\* *J. Math. Phys.* **46**, 062107 (2005); Ayers & Levy *Chem. Phys. Lett.* **415**, 211 (2005).

# The Classical N-body Structure Problem

**Given:** A potential representing the interaction between any pair of particles inside a system,  $V(\mathbf{x}_1, \mathbf{x}_2)$ .

**Classical N-body structure problem:** Find the best (lowest-energy) configuration of N-classical particles interacting with this potential.

$$E_N^{Cl}[V] \equiv \min_{\mathbf{x}_i} \sum_{i=1}^N \sum_{j \neq i} V(\mathbf{x}_i, \mathbf{x}_j)$$

Clearly

$$E_N^{Cl}[V] \leq \left\langle \Psi \left| \sum_{i=1}^N \sum_{j \neq i} V(\mathbf{r}_i, \mathbf{r}_j) \right| \Psi \right\rangle.$$

so: For **every** N-representable  $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$  and **any**  $V(\mathbf{x}_1, \mathbf{x}_2)$ ,

$$E_N^{Cl}[V] \leq \iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) V(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

This is the only N-representability constraint on  $\rho_2$ .

For every  $N$ -representable  $\rho_2(x_1, x_2)$  and any  $V(x_1, x_2)$ ,

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

In fact, as long as  $V(x_1, x_2)$  is continuous,

$$E_N^{Cl}[V] = \underbrace{\inf}_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2.$$

because:

$$\begin{aligned} E_N^{Cl}[V] &= \min_{\mathbf{x}_i} \sum_{i=1}^N \sum_{j \neq i} V(\mathbf{r}_i, \mathbf{r}_j) \\ &= \underbrace{\inf}_{\left\{ \mathbf{x}_i \mid \begin{array}{l} \mathbf{x}_i = \mathbf{x}_j = \mathbf{x}_k \text{ is} \\ \text{never true} \end{array} \right\}} \sum_{i=1}^N \sum_{j \neq i} V(\mathbf{r}_i, \mathbf{r}_j) \\ &= \underbrace{\inf}_{\Gamma_N} \text{Tr} \left[ \left( \sum_{i=1}^N \sum_{j \neq i} V(\mathbf{r}_i, \mathbf{r}_j) \right) \Gamma_N \right] \end{aligned}$$

The solution usually looks like  $\Psi = \lim_{\varepsilon \rightarrow 0^+} \mathcal{A} \left( (\varepsilon \sqrt{2\pi})^{-3N/2} \prod_{j=1}^N e^{-\frac{|r_j - r_j^{\min}|^2}{2\varepsilon}} \sigma(j) \right).$

For every  $N$ -representable  $\rho_2(x_1, x_2)$  and any  $V(x_1, x_2)$ ,

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

In fact, as long as  $V(x_1, x_2)$  is continuous,

$$E_N^{Cl}[V] = \inf_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2.$$

**THEOREM:** For any  $\tilde{\rho}_2(x_1, x_2)$  that is not  $N$ -representable, there exists a  $V(x_1, x_2)$  such that

$$E_N^{Cl}[V] > \iint \tilde{\rho}_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

**Known:** The set of  $N$ -representable  $\rho_2$  is a convex set. (This follows directly from the definition,

$$\rho_2(x_1, x_2) = \text{Tr} \left[ \left( \sum_{i=1}^N \sum_{j \neq i} \delta(\mathbf{r}_i - \mathbf{x}_1) \delta(\mathbf{r}_j - \mathbf{x}_2) \right) \Gamma_N \right] = \text{Tr} \left[ \hat{L}_{\rho_2} \Gamma_N \right]$$

If  $\rho_2^{(a)}$  and  $\rho_2^{(b)}$  are  $N$ -representable, then convex sums are also:

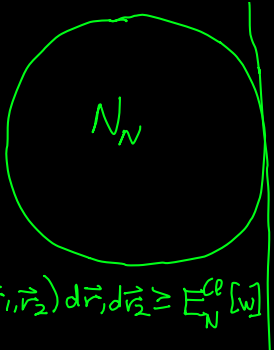
$$t\rho_2^{(a)} + (1-t)\rho_2^{(b)} = \text{Tr} \left[ \hat{L}_{\rho_2} \left\{ t\Gamma_N^{(a)} + (1-t)\Gamma_N^{(b)} \right\} \right]$$

Hahn-Banach Separation Theorem: Given two disjoint convex sets,  $\mathcal{S}_1$  and  $\mathcal{S}_2$ , there exists a hyperplane that separates the sets. For sets of pair densities:

$$\int \cdots \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \begin{cases} \geq Q & \rho_k \in \mathcal{S}_1 \\ \leq Q & \rho_k \in \mathcal{S}_2 \end{cases}$$

If the distance between  $\mathcal{S}_1$  and  $\mathcal{S}_2$  is greater than zero, then the “ $\leq$ ” and “ $\geq$ ” can be replaced by strict inequalities.

Choose the first convex set to be the set of  $N$ -representable pair densities,  $\mathcal{N}_N$ ; choose the second convex set to be a non- $N$ -representable pair density,  $\tilde{\rho}_2$



$$\bullet \tilde{\rho}_2(\mathbf{r}_1, \mathbf{r}_2)$$

$$\int \rho_2(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \geq E_N^{\text{cl}}[w]$$

$$\int \rho_2(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 < E_N^{\text{cl}}[w]$$

For every  $N$ -representable  $\rho_2(x_1, x_2)$  and any  $V(x_1, x_2)$ ,

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

In fact, as long as  $V(x_1, x_2)$  is continuous,

$$E_N^{Cl}[V] = \inf_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2.$$

**THEOREM:** For any  $\tilde{\rho}_2(x_1, x_2)$  that is not  $N$ -representable, there exists a  $V(x_1, x_2)$  such that

$$E_N^{Cl}[V] > \iint \tilde{\rho}_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

**Proof:**

If  $\tilde{\rho}_2(x_1, x_2)$  is not  $N$ -representable, then it follows from the Hahn-Banach separation theorem that there exists a potential for which this is true.

**This means that  $\rho_2(x_1, x_2)$  is  $N$ -representable if and only if**

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

**for every possible  $V(x_1, x_2)$ .**

# Consequences

## N-representable pair densities are nonnegative:

Suppose that  $\tilde{\rho}_2(\mathbf{x}_1, \mathbf{x}_2)$  is negative in the region  $\Omega$ . Choose

$$w_\Omega(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} 0 & (\mathbf{r}_1, \mathbf{r}_2) \notin \Omega \\ 1 & (\mathbf{r}_1, \mathbf{r}_2) \in \Omega \end{cases}$$

Then  $E_N^{Cl}[w] = 0$ . But  $\iint \tilde{\rho}_2(\mathbf{x}_1, \mathbf{x}_2) w(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 < 0$ .

## Normalization:

Choose  $w_{+1}(\mathbf{x}_1, \mathbf{x}_2) = 1$ ; then

$$\iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \geq E_N^{Cl}[w_{+1}] = \sum_{i=1}^N \sum_{j \neq i}^N 1 = \frac{N!}{(N-2)!}$$

Choose  $w_{-1}(\mathbf{x}_1, \mathbf{x}_2) = -1$ ; then

$$-\iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \geq E_N^{Cl}[w_{-1}] = \sum_{i=1}^N \sum_{j \neq i}^N -1 = -\frac{N!}{(N-2)!}$$

So  $N(N-1) \geq \iint \rho_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \geq N(N-1)$ .



## Generalized Davidson Constraint:

Choosing:

$$w(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{f}(\mathbf{r}_1) \cdot \mathbf{f}(\mathbf{r}_2) + \frac{|\mathbf{f}(\mathbf{r}_1)|^2 + |\mathbf{f}(\mathbf{r}_2)|^2}{2(N-1)}$$

then

$$E_N^{Cl}[w] = \underbrace{\min}_{x_i} \left( \sum_{i=1}^N \mathbf{f}(\mathbf{r}_i) \right)^2 \geq 0$$

This implies that

$$\iint \rho_2(\mathbf{r}_1, \mathbf{r}_2) (\mathbf{f}(\mathbf{r}_1) \cdot \mathbf{f}(\mathbf{r}_2)) d\mathbf{r}_1 d\mathbf{r}_2 \geq - \int |\mathbf{f}(\mathbf{r}_1)|^2 \rho_1(\mathbf{r}_1) d\mathbf{r}_1$$

There are other similar arguments for all other previously known  $N$ -representability constraints on the pair density.

*It is the last lesson of modern science,  
that the highest simplicity of structure  
is produced, not by few elements, but by  
the highest complexity.*

Ralph Waldo Emerson

For every  $N$ -representable  $\rho_2(x_1, x_2)$  and any  $V(x_1, x_2)$ ,

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

**THEOREM:** The pair density  $\rho_2(x_1, x_2)$  is  $N$ -representable, if and only if

$$E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

for every  $V(x_1, x_2)$ . Here the “classical”  $N$ -body energy is defined by

$$E_N^{Cl}[V] \equiv \underbrace{\min}_{x_i} \sum_{i=1}^N \sum_{j \neq i} V(x_i, x_j)$$

**This is not a practical solution because it requires us to solve every possible classical many-body problem. This is very hard.**

## IV. Variational approaches to the $N$ -representability problem: Special Case; electron pair density.

**THEOREM:** The pair density  $\rho_2(x_1, x_2)$  is  $N$ -representable, if and only if

$$E_N^{CI}[V] \leq \iint \rho_2(x_1, x_2) V(x_1, x_2) dx_1 dx_2$$

for every  $V(x_1, x_2)$ .

**Thus:**

$$\begin{aligned} E_{g.s.}[v, N] &= \min_{N\text{-representable } \rho_2} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \\ &= \min_{\{\rho_2 | \forall w(r_1, r_2), \langle \rho_2 w \rangle \geq E_N^{CI}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \end{aligned}$$

This is not very practical; but if we constrained this result using only one  $w(r_1, r_2)$ , then that would be more acceptable. Then:

$$E_{g.s.}[v, N; w] \geq \min_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{CI}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

So we have a lower bound:

$$E_{g.s.}[\nu, N; w] \geq \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

We would like for this lower bound to be as tight as possible. This suggests that we maximize over all the potentials, obtaining the tightest possible lower bound for a “simple” constrained variational principle.

$$E_{g.s.}[\nu, N] \geq \underbrace{\max}_w \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

**Theorem:** This construction produces the exact ground-state energy. That is,

$$E_{g.s.}[\nu, N] = \underbrace{\max}_w \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

**Theorem:** This construction produces the exact ground-state energy. That is,

$$E_{g.s.}[v, N] = \underbrace{\max}_w \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{CI}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

**Known:** The energy is a convex functional of the pair density. That is, for any two pair densities, we have that

$$E_{v,N} \left[ t\rho_2^{(a)} + (1-t)\rho_2^{(b)} \right] \leq t \cdot E_{v,N} \left[ \rho_2^{(a)} \right] + (1-t) E_{v,N} \left[ \rho_2^{(b)} \right]$$

**Implication:** This means that the set of pair densities whose energy is too small is convex. Let  $\mathcal{L}_N$  denote the set of density matrices with energy lower than the true ground-state energy,

$$\mathcal{L}_N = \left\{ \rho_2 \mid E_{v,N}[\rho_2] \leq E_{g.s.}[v, N] \right\}$$

$\mathcal{L}_N$  is convex because if  $\rho_2^{(a)}$  and  $\rho_2^{(b)}$  are both in  $\mathcal{L}_N$ , then

$$\begin{aligned} E_{v,N} \left[ t\rho_2^{(a)} + (1-t)\rho_2^{(b)} \right] &\leq t \cdot E_{v,N} \left[ \rho_2^{(a)} \right] + (1-t) E_{v,N} \left[ \rho_2^{(b)} \right] \\ &\leq E_{g.s.}[v, N] \end{aligned}$$

Which implies that  $t\rho_2^{(a)} + (1-t)\rho_2^{(b)} \in \mathcal{L}_N$ .

**Theorem:** The exact ground-state energy is obtained by the max-min prob:

$$E_{g.s.}[\nu, N] = \underbrace{\max}_w \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

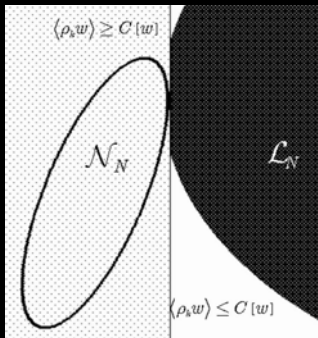
**Known:** The set of pair densities with “too low” energy is convex.

**Known:** The set of  $N$ -representable pair densities is convex.

**Known:** These two sets do not intersect because every  $N$ -representable pair density has energy greater than or equal to the true energy.

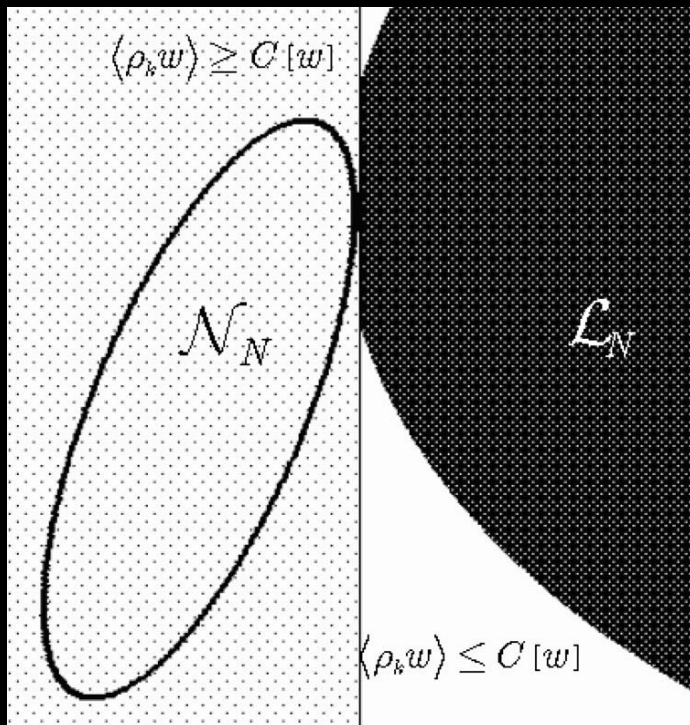
**Implication:** There exists some potential,  $w(x_1, x_2)$ , that separates these sets. I.e., there exists a  $w(x_1, x_2)$  such that

$$\underbrace{\int_{\rho_2 \in \mathcal{N}_N} \rho_2(x_1, x_2) w(x_1, x_2) dx_1 dx_2}_{\rho_2 \in \mathcal{N}_N} \geq E_N^{Cl}[w] > \underbrace{\int_{\tilde{\rho}_2 \in \mathcal{L}_N} \tilde{\rho}_2(x_1, x_2) w(x_1, x_2) dx_1 dx_2}_{\tilde{\rho}_2 \in \mathcal{L}_N}$$



**Theorem:** The exact ground-state energy is obtained by the max-min prob:

$$E_{g.s.}[v, N] = \underbrace{\max}_w \underbrace{\min}_{\{\rho_2 | \langle \rho_2 w \rangle \geq E_N^C[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$





## V. Variational Approaches: General Case.

**Given:** A descriptor that determines all properties of any molecular system. It is assumed that this is a “reduced” descriptor (i.e., less complex than the  $N$ -electron wavefunction) and that it is a *linear* functional of the  $N$ -electron density matrix.

$$f(\tau) = \text{Tr}[\hat{L}_f \Gamma_N]$$

$$\Gamma_N = \sum_i w_i \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$$0 \leq w_i \leq 1; \quad \sum_i w_i = 1$$

**Implication:** Because  $f(\tau) = \text{Tr}[\hat{L}_f \Gamma_N]$ , the set of  $N$ -representable  $f(\tau)$  is a closed, convex set.

**Given:** It is assumed that some portion of the energy can be evaluated exactly in terms of this descriptor. This portion of the energy is denoted

$$W = \{\hat{h} | f\}$$

**Theorem:** The remainder of the energy,  $F[f]$ , can be exactly represented by a convex functional.

**Proof:**

Let  $F[f]$  denote the Legendre transform functional. I.e.:

$$F[f] = \sup_{\hat{h}} \left( \underbrace{\min}_{\Gamma_N} \text{Tr} [\hat{H}_{v,N} \Gamma_N] - \{\hat{h}|f\} \right)$$

**1. This functional is exact.** For a specific choice,  $\hat{h}_0$ ,

$$F[f] \geq \left( \underbrace{\min}_{\Gamma_N} \text{Tr} [\hat{H}_{v,N} \Gamma_N] - \{\hat{h}_0|f\} \right)$$

$$F[f] + \{\hat{h}_0|f\} \geq \underbrace{\min}_{\Gamma_N} \text{Tr} [\hat{H}_{v,N} \Gamma_N] = E_{g.s.}[v, N]$$

If  $\hat{h}_0$  is associated with a maximum, then the energy is exact. Otherwise one has the variational principle.

## 2. This functional is convex.

$$\begin{aligned}
F\left[tf^{(a)} + (1-t)f^{(b)}\right] &= \sup_{\hat{h}} \left( \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] - \left\{\hat{h}\left|tf^{(a)} + (1-t)f^{(b)}\right.\right\} \right) \\
&= \sup_{\hat{h}} \left( \begin{aligned} &\left( (t + (1-t)) \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] \right) \\ &- t\left\{\hat{h}\left|f^{(a)}\right.\right\} - (1-t)\left\{\hat{h}\left|f^{(b)}\right.\right\} \end{aligned} \right) \\
&= \sup_{\hat{h}} \left( \begin{aligned} &t \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] - t\left\{\hat{h}\left|f^{(a)}\right.\right\} \\ &(1-t) \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] - (1-t)\left\{\hat{h}\left|f^{(b)}\right.\right\} \end{aligned} \right) \\
&\leq \sup_{\hat{h}} \left( t \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] - t\left\{\hat{h}\left|f^{(a)}\right.\right\} \right) \\
&\quad + \sup_{\hat{h}} \left( (1-t) \underbrace{\min}_{\Gamma_N} \text{Tr}\left[\hat{H}_{v,N}\Gamma_N\right] - (1-t)\left\{\hat{h}\left|f^{(b)}\right.\right\} \right) \\
&\leq t \cdot F\left[f^{(a)}\right] + (1-t)F\left[f^{(b)}\right]
\end{aligned}$$

**Theorem:**  $f(\tau)$  is  $N$ -representable if and only if

$$\langle \hat{h} | f \rangle \geq E_N^{partial} [\hat{h}]$$

Here

$$E_N^{partial} [\hat{h}] = \min_{\Gamma_N} \langle \hat{h} | \text{Tr} [\hat{L}_f \Gamma_N] \rangle$$

**Proof:**

If  $f(\tau)$  is  $N$ -representable, then clearly

$$\langle \hat{h} | f \rangle \geq \min_{\Gamma_N} \langle \hat{h} | \text{Tr} [\hat{L}_f \Gamma_N] \rangle = E_N^{partial} [\hat{h}]$$

If  $\tilde{f}(\tau)$  is not  $N$ -representable then because  $\mathcal{N}_N$  is a convex set, we can use the Hahn-Banach separation theorem to obtain the proof.

**Theorem:** The exact ground-state energy can be obtained using

$$E_{g.s.} [v, N] = \max_{\hat{h}} \min_{\langle \hat{h} | f \rangle \geq E_N^{partial} [\hat{h}]} F[f] + \langle \hat{h} \cdot f \rangle$$

# The 2-electron reduced density matrix

## Variational Principle:

***N*-representability problem:** We *must* restrict the variational principle to that correspond to antisymmetric wavefunctions.\* (If one fails to do this, there will always exist 2-body Hamiltonians for which the error from the variational calculation is arbitrarily large.)

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\* In practice, it is more convenient to consider any pair density that corresponds to an ensemble average of fermionic wave functions.

- the only density matrices that cause problems are those that give too small an energy for some Hamiltonian.
  - non- $N$ -representable density matrices with energies that are too high could be ignored.
- 
- This condition is actually identical to the  $N$ -representability condition. That is,  $\rho$  is (ensemble)  $N$ -representable if and only if
 

for every Hamiltonian.
  - Equivalently, if  $\rho$  is not  $N$ -representable, there exists some system with

One can make the error arbitrarily large by scaling the Hamiltonian.

- Actually, we can get the right energy if we only ensure that the energy is greater than the ground-state energy for the specific system of interest. That is, if we require

For the system of interest, then we clearly can't get too low an energy.

- This gives the variational principle:
  
- For an arbitrarily Hamiltonian, though,

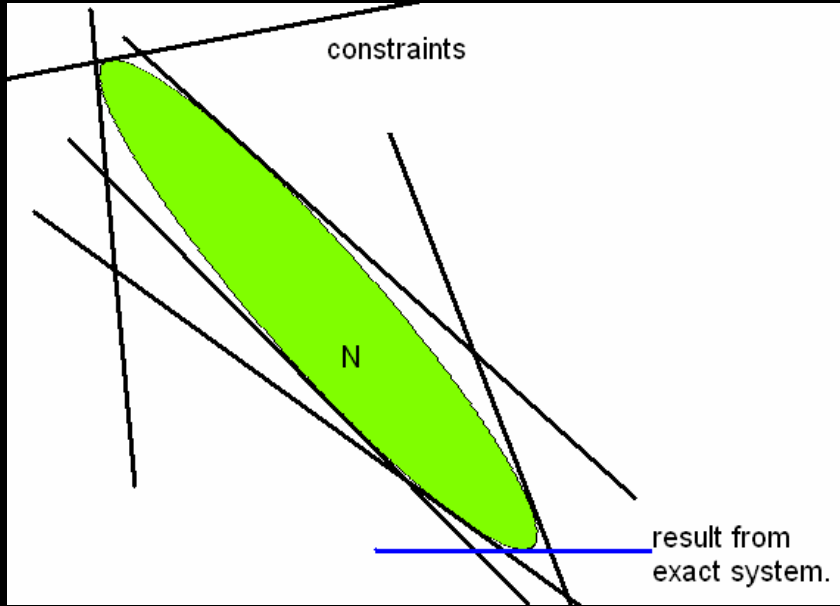
Since

but, in general,

the ground-state energy is obtained by

The maximizing is the energy operator for the system.

This is *not* a practical procedure—one has to solve the many-fermion problem many times to do the outer maximization. It is better to just solve it once, outright.



**Proof by picture**





# One-Electron Density Matrix

For a Hamiltonian of the form

The energy can be written in terms of the first-order density matrix as:

The variational principle is:

Define  $E_0$  as the ground-state energy of the independent particle model with Hamiltonian  $H_0$ .

**Theorem (Garrod and Percus):**  
and only if

is (ensemble)  $N$ -representable if

for every .

If we choose just one  $\psi$ , then

**Assertion:**

**The exact ground-state energy is obtained by**

**The maximizing  $\psi$  is an interesting choice for the one-electron Hamiltonian in the mean-field model, because it represents a “one-electron energy operator” for the system.**

**One-Electron Density**

For a Hamiltonian of the form

The energy can be written in terms of the electron density as:

The variational principle is:

Define  $E_{cl}$  as the ground-state energy of the classical structure problem with energy

**Theorem:**  $\rho$  is (ensemble)  $N$ -representable if and only if

for every  $\mu$ .

This constraint merely implies that  $\rho$  is  $N$ -representable. If  $\rho$  is not  $N$ -representable, then one can obtain a contradiction by letting  $\rho$  be  $N$ -representable at some point, while it stays the same elsewhere.  $\rho$  is not  $N$ -representable at that point.

**The exact ground-state energy is obtained from**

**Assertion:**

**The exact ground-state energy is obtained by**

**Maximizing  $\langle H \rangle$  ensures that the energy of the system does not get “too low.” Except for a constant shift, the maximizing  $\langle H \rangle$  is a representation of the local energy,  $E_{\text{local}}$ , of the system since requiring**

**is sufficient to enforce the variational principle.**

# The Pair Density, Revisited

For a Hamiltonian of the form

The energy can be written in terms of the pair density as:

The variational principle is:

Define  $E_{\text{pair}}$  as the ground-state energy of the classical structure problem with 2-body interaction potentials



**Assertion:**

**The exact ground-state energy is obtained by**

**Maximizing  $\mathcal{E}(\{\lambda_{ij}\})$  ensures that the energy of the system does not get “too low.” Except for a constant shift, the maximimizing  $\mathcal{E}(\{\lambda_{ij}\})$  is a representation of the pairwise interaction energy,  $E_{int} = \sum_{i,j} \lambda_{ij} \sigma_i \sigma_j$ .**

### **Sketch of Proof**

**Step 1.**  $\mathcal{E}(\{\lambda_{ij}\})$  can be chosen to be convex.

**Proof:**

$\mathcal{E}(\{\lambda_{ij}\})$  can be constructed using the Legendre-transform formalism,

This formalism always gives convex functionals.

**Step 2.** The energy functional can be chosen to be convex.

**Proof:**

Since  $\mathcal{E}$  is the sum of a linear functional and a convex functional, it is convex.

**Step 3.** The set of all  $\rho$  that give too small an energy is an open, convex set.

**Proof:**

The energy is a convex functional. For any convex functional, the set of arguments for which the function is less than or equal to some value is convex.

**Step 4.** The set of all  $N$ -representable  $\rho$  is closed and convex.

**Proof:**

The proof is a standard exercise, and follows from the fact any ensemble- $N$ -representable pair density can be written as

**Step 5.** The sets of  $N$ -representable pair densities and pair densities with too low an energy do not intersect.

**Proof:**

and so no  $N$ -representable is in

**Step 6.** There must exist some such that

For all and in .

**Proof:**

This is the so-called geometric Hahn-Banach Theorem.

**Step 7.** The “constant of separation” in this result is , the solution to the classical structure problem.

**Proof:** A bit complicated; it is the Banach-space analogue of the “polar cone theorem” used by Garrod and Percus.

