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. . . .

\[ \gamma(r, r') \Gamma_2(r_1, r_2; r'_1, r'_2) \Gamma_3(r_1, r_2, r_3; r'_1, r'_2, r'_3) \Gamma_4 \text{ full-CI} \]

\[ \rho_2(r, r') \rho_3(r_1, r_2, r_3) \rho_4(r_1, \ldots r_4) \rho_N = |\Psi|^2 \]

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:

$$E_{\text{g.s.}}[v;N] = \min_{N\text{-representable } f(\tau)} E_{v,N}[f]$$
The variational principle follows directly from the variational principle for the wave function:

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

or density matrix

\[
E_{\text{g.s.}}[\nu; N] = \min_{\text{all } N\text{-fermion density matrices}} \hat{\text{Tr}} \left[ \hat{H}_{\nu,N} \Gamma_N \right]
\]

This means that:

\[
E_{\text{g.s.}}[\nu; N] = \min_{\text{all } f(\tau) \text{ that correspond to a system containing } N \text{ fermions}} E_{\nu,N}[f]
\]

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.,

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

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:

$$\min_{f(\tau)} E_{v,N}[f] \ll E_{\text{g.s.}}[v;N] = \min_{f(\tau) \in \mathcal{N}_N} E_{v,N}[f]$$
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 $x_1$ and $x_2$. It is related to the structure factor in X-ray/neutron scattering.

$$
\rho_2(x_1,x_2) \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \sum_{j \neq i} \delta(r_i - x_1) \delta(r_j - x_2) \right| \Psi \right\rangle
$$

$$
= \text{Tr} \left[ \left( \sum_{i=1}^{N} \sum_{j \neq i} \delta(r_i - x_1) \delta(r_j - x_2) \right) \Gamma_N \right]
$$

Simple Properties of the pair density:

- **normalization**
  $$
  N(N-1) = \int \int \rho_2(x_1,x_2) \, dx_1 \, dx_2
  $$

- **nonnegativity**
  $$
  0 \leq \rho_2(x_1,x_2)
  $$

- **symmetry**
  $$
  \rho_2(x_1,x_2) = \rho_2(x_2,x_1)
  $$
Hohenberg-Kohn-Ziesche Theorem: $\rho_2 \rightarrow$ all observable properties, including the energy and its components.

\[
V_{ee}[\rho_2] = \frac{1}{2} \iint \frac{\rho_2(x_1, x_2)}{|x_1 - x_2|} \, dx_1 \, dx_2
\]

\[
V_{ne}[\rho_2] = \frac{1}{2} \iint \rho_2(x_1, x_2) \left( \frac{v(x_1) + v(x_2)}{N - 1} \right) \, dx_1 \, dx_2
\]

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

Variational Principle for the pair density:

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

**N-representability problem:** We must restrict the variational principle to $\rho_2(x_1, x_2)$ 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.)

The Classical $N$-body Structure Problem

**Given:** A potential representing the interaction between any pair of particles inside a system, $V(x_1, x_2)$.

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

$$E_{N}^{Cl}[V] = \min_{x_i} \sum_{i=1}^{N} \sum_{j \neq i} V(x_i, x_j)$$

Clearly

$$E_{N}^{Cl}[V] \leq \left\langle \Psi \left| \sum_{i=1}^{N} \sum_{j \neq i} V(r_i, r_j) \right| \Psi \right\rangle.$$ 

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

$$E_{N}^{Cl}[V] \leq \int \int \rho_2(x_1, x_2) V(x_1, x_2) \, dx_1 \, dx_2$$

This is the only $N$-representability constraint on $\rho_2$. 
For every $N$-representable $\rho_2(x_1, x_2)$ and any $V(x_1, x_2)$, 

$$E_{N}^{Cl}[V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2)\,dx_1dx_2$$

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

$$E_{N}^{Cl}[V] = \inf_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2)V(x_1, x_2)\,dx_1dx_2.$$ 

because:

$$E_{N}^{Cl}[V] = \min \sum_{x_i} \sum_{j \neq i} V(r_i, r_j)$$

$$= \inf \sum_{x_i, x_j = x_k \text{ is}} \sum_{i = 1}^{N} \sum_{j \neq i} V(r_i, r_j)$$

$$= \inf \text{Tr} \left[ \left( \sum_{i = 1}^{N} \sum_{j \neq i} V(r_i, r_j) \right) \Gamma_N \right]$$

The solution usually looks like $\Psi = \lim_{\varepsilon \to 0^+} \mathcal{A} \left( \varepsilon^{3/2} \prod_{j=1}^{N} e^{-\frac{(r_j - r^\text{min})^2}{2\varepsilon}} \sigma(j) \right)$. 
For every \( N \)-representable \( \rho_2(x_1, x_2) \) and any \( V(x_1, x_2) \),
\[
E_{N}^{Cl}[V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2)dx_1dx_2
\]
In fact, as long as \( V(x_1, x_2) \) is continuous,
\[
E_{N}^{Cl}[V] = \inf_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2)V(x_1, x_2)dx_1dx_2.
\]

**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
\[
E_{N}^{Cl}[V] > \iint \rho_2(x_1, x_2)V(x_1, x_2)dx_1dx_2
\]

**Known:** The set of \( N \)-representable \( \rho_2 \) is a convex set. (This follows directly from the definition,
\[
\rho_2(x_1, x_2) = \text{Tr} \left[ \left( \sum_{i=1}^{N} \sum_{j \neq i} \delta(r_i - x_1) \delta(r_j - x_2) \right) \Gamma_N \right] = \text{Tr} \left[ \hat{L}_{\rho_2} \Gamma_N \right]
\]
If \( \rho^{(a)}_2 \) and \( \rho^{(b)}_2 \) are \( N \)-representable, then convex sums are also:
\[
t\rho^{(a)}_2 + (1-t)\rho^{(b)}_2 = \text{Tr} \left[ \hat{L}_{\rho_2} \left\{ t\Gamma_N^{(a)} + (1-t)\Gamma_N^{(b)} \right\} \right]
\]
**Hahn-Banach Separation Theorem:** Given two disjoint convex sets, $S_1$ and $S_2$, there exists a hyperplane that separates the sets. For sets of pair densities:

$$
\int \ldots \int \rho_2(r_1, r_2)w(r_1, r_2) dr_1 dr_2 \begin{cases} 
\geq Q & \rho_k \in S_1 \\
\leq Q & \rho_k \in S_2
\end{cases}
$$

If the distance between $S_1$ and $S_2$ 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, $N_N$; choose the second convex set to be a non-$N$-representable pair density, $\tilde{\rho}_2$. 

\[ \int \rho_2(\vec{r}_1, \vec{r}_2)w(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \geq E_N^c[w] \]

\[ \int \rho_2(\vec{r}_1, \vec{r}_2)w(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \leq E_N^c[w] \]
For every \( N \)-representable \( \rho_2(x_1, x_2) \) and any \( V(x_1, x_2) \),
\[
E_N^{CI} [V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2) \, dx_1 \, dx_2
\]
In fact, as long as \( V(x_1, x_2) \) is continuous,
\[
E_N^{CI} [V] = \inf_{N\text{-representable } \rho_2} \iint \rho_2(x_1, x_2)V(x_1, x_2) \, dx_1 \, dx_2.
\]

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

**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
\[
E_N^{CI} [V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2) \, dx_1 \, dx_2
\]
for every possible \( V(x_1, x_2) \).
Consequences

**N-representable pair densities are nonnegative:**

Suppose that \( \tilde{\rho}_2 (x_1, x_2) \) is negative in the region \( \Omega \). Choose

\[
w_\Omega (r_1, r_2) = \begin{cases} 
0 & (r_1, r_2) \notin \Omega \\
1 & (r_1, r_2) \in \Omega
\end{cases}
\]

Then \( E^{CI}_N [w] = 0 \). But \( \iint \tilde{\rho}_2 (x_1, x_2) w(x_1, x_2) dx_1 dx_2 < 0 \).

**Normalization:**

Choose \( w_{+1} (x_1, x_2) = 1 \); then

\[
\iint \rho_2 (x_1, x_2) dx_1 dx_2 \geq E^{CI}_N [w_{+1}] = \sum_{i=1}^{N} \sum_{j \neq i} 1 = \frac{N!}{(N - 2)!}
\]

Choose \( w_{-1} (x_1, x_2) = -1 \); then

\[
-\iint \rho_2 (x_1, x_2) dx_1 dx_2 \geq E^{CI}_N [w_{+1}] = \sum_{i=1}^{N} \sum_{j \neq i} -1 = -\frac{N!}{(N - 2)!}
\]

So \( N(N-1) \geq \iint \rho_2 (x_1, x_2) dx_1 dx_2 \geq N(N-1) \).
Generalized Davidson Constraint:

Choosing:

\[ w(r_1, r_2) = f(r_1) \cdot f(r_2) + \frac{|f(r_1)|^2 + |f(r_2)|^2}{2(N-1)} \]

then

\[ E_{N}^{\text{Cl}}[w] = \min_{x_i} \left( \sum_{i=1}^{N} f(r_i) \right)^2 \geq 0 \]

This implies that

\[ \int \int \rho_2(r_1, r_2)(f(r_1) \cdot f(r_2)) \, dr_1 \, dr_2 \geq -\int |f(r_1)|^2 \rho_1(r_1) \, dr_1 \]

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 \( V(x_1, x_2) \),
\[
E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2)\,dx_1dx_2
\]

**THEOREM:** The pair density \( \rho_2(x_1, x_2) \) is \( N \)-representable, if and only if
\[
E_N^{Cl}[V] \leq \iint \rho_2(x_1, x_2)V(x_1, x_2)\,dx_1dx_2
\]
for every \( V(x_1, x_2) \). Here the “classical” \( N \)-body energy is defined by
\[
E_N^{Cl}[V] \equiv \min_x \sum_{i=1}^{N} \sum_{j \neq i} V(x_i, x_j)
\]
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

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

for every $V(x_1, x_2)$.

Thus:

$$E_{\text{g.s.}}[\nu, N] = \min_{\text{N-representable } \rho_2} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

$$= \min_{\{\rho_2 \mid \forall w(r_1, r_2), \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$

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:

$$E_{\text{g.s.}}[\nu, N; w] \geq \min_{\{\rho_2 \mid \langle \rho_2 w \rangle \geq E_N^{Cl}[w]\}} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2]$$
So we have a lower bound:

\[ E_{g.s.}[v, N; w] \geq \min_{\rho_2} \left\{ T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \right\} \]

\( \{\rho_2|\langle\rho_2 w\rangle \geq E_N^{cl}[w]\} \)

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.

\[ E_{g.s.}[v, N] \geq \max_w \min_{\rho_2} \left\{ T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \right\} \]

\( \{\rho_2|\langle\rho_2 w\rangle \geq E_N^{cl}[w]\} \)

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

\[ E_{g.s.}[v, N] = \max_w \min_{\rho_2} \left\{ T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \right\} \]

\( \{\rho_2|\langle\rho_2 w\rangle \geq E_N^{cl}[w]\} \)
**Theorem:** This construction produces the exact ground-state energy. That is,

\[
E_{\text{g.s.}}[\nu, N] = \max_w \min_{\rho_2} \left\{ T[\rho_2] + V_{\text{ne}}[\rho_2] + V_{\text{ee}}[\rho_2] \right\} \quad \{\rho_2 | \langle \rho_2 w \rangle \geq E_{\text{g.s.}}^C[w]\}
\]

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

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

**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,

\[
\mathcal{L}_N = \left\{ \rho_2 | E_{\nu,N}[\rho_2] \leq E_{\text{g.s.}}[\nu, N] \right\}
\]

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

\[
E_{\nu,N}[t\rho_2^{(a)} + (1-t)\rho_2^{(b)}] \leq t \cdot E_{\nu,N}[\rho_2^{(a)}] + (1-t) E_{\nu,N}[\rho_2^{(b)}] 
\leq E_{\text{g.s.}}[\nu, N]
\]

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:

$$E_{g.s.}[\nu, N] = \max_{\rho_2} \min_{w} \left \{ \rho_2 \mid \langle \rho_2, w \rangle \geq E_{N}^{C_l}[w] \right \}$$

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

$$\int_{\rho_2 \in \mathcal{N}_N} \rho_2 (x_1, x_2) w(x_1, x_2) dx_1 dx_2 \geq E_{N}^{C_l}[w] > \int_{\tilde{\rho}_2 \in \mathcal{L}_N} \tilde{\rho}_2 (x_1, x_2) w(x_1, x_2) dx_1 dx_2$$
Theorem: The exact ground-state energy is obtained by the max-min prob:

\[
E_{g.s.}[\nu, N] = \max_{w} \min_{\rho_2} T[\rho_2] + V_{ne}[\rho_2] + V_{ee}[\rho_2] \quad \text{s.t.} \quad \langle \rho_2 w \rangle \geq E_N^{cl}[w]
\]
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.

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

$$\Gamma_N = \sum_i w_i \Psi^*(r_1, \ldots, r_N) \Psi(r_1, \ldots, r_N)$$

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

**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.:

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

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

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

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

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.

\[
F\left[ tf^{(a)} + (1-t) f^{(b)} \right] = \sup_{\hat{h}} \left( \min_{\Gamma_N} \text{Tr} \left[ \hat{H}_{v,N} \Gamma_N \right] - \left\{ \hat{h} \left| tf^{(a)} + (1-t) f^{(b)} \right. \right\} \right)
\]

\[
= \sup_{\hat{h}} \left( \left( t + (1-t) \right) \min_{\Gamma_N} \text{Tr} \left[ \hat{H}_{v,N} \Gamma_N \right] \right)
\]

\[
= \sup_{\hat{h}} \left( t \min_{\Gamma_N} \text{Tr} \left[ \hat{H}_{v,N} \Gamma_N \right] - t \left\{ \hat{h} \left| f^{(a)} \right. \right\} \right)
\]

\[
\leq \sup_{\hat{h}} \left( t \min_{\Gamma_N} \text{Tr} \left[ \hat{H}_{v,N} \Gamma_N \right] - t \left\{ \hat{h} \left| f^{(a)} \right. \right\} \right)
\]

\[
+ \sup_{\hat{h}} \left( (1-t) \min_{\Gamma_N} \text{Tr} \left[ \hat{H}_{v,N} \Gamma_N \right] - (1-t) \left\{ \hat{h} \left| f^{(b)} \right. \right\} \right)
\]

\[
\leq t \cdot F\left[ f^{(a)} \right] + (1-t) F\left[ f^{(b)} \right]
\]
**Theorem:** \( f(\tau) \) is \( N \)-representable if and only if
\[
\{ \hat{h} \mid f \} \geq E_N^{\text{partial}} [\hat{h}]
\]

Here
\[
E_N^{\text{partial}} [\hat{h}] = \min_{\Gamma_N} \left\{ \hat{h} \mid \text{Tr} \left[ \hat{L}_f \Gamma_N \right] \right\}
\]

**Proof:**
If \( f(\tau) \) is \( N \)-representable, then clearly
\[
\{ \hat{h} \mid f \} \geq \min_{\Gamma_N} \left\{ \hat{h} \mid \text{Tr} \left[ \hat{L}_f \Gamma_N \right] \right\} = E_N^{\text{partial}} [\hat{h}]
\]

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
\[
E_{g.s.}[v, N] = \max_{\hat{h}} \min_{\hat{f}} \left\{ F[f] + \langle \hat{h} \cdot f \rangle \right\}
\]

\[
\text{subject to } \langle \hat{h}f \rangle \geq E_N^{\text{partial}} [\hat{h}]
\]
The 2-electron reduced density matrix

Variational Principle:

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

\[ \]

\[ * \text{ In practice, it is more convenient to consider any pair density that corresponds to an ensemble average of fermionic wave functions.} \]
• 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, $\hat{\Gamma}$ is (ensemble) $N$-representable if and only if

\[
\min_{\mathbf{g}_s} n \mathbf{e} \leq \mathbf{E} \Gamma \geq \Gamma + \Gamma + \Gamma
\]

for every Hamiltonian.

• Equivalently, if $\hat{\Gamma}$ is not $N$-representable, there exists some system with

\[
\min_{\mathbf{g}_s} n \mathbf{e} < \mathbf{E} \Gamma
\]

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 \( \hat{H} \) 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 as the ground-state energy of the independent particle model with Hamiltonian .
Theorem (Garrod and Percus): is (ensemble) $N$-representable if

and only if

for every .
If we choose just one , then

Assertion:
The exact ground-state energy is obtained by

The maximizing 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 \( E_v \) as the ground-state energy of the classical structure problem with energy.
Theorem: \( \rho \) is (ensemble) \( N \)-representable if and only if

\[
\min_{v, v} v \rho \geq \int_{x, x} x \quad \text{for every } \rho. \]

This constraint merely implies that \( \rho \geq x \). If \( \rho < x \) at some point, then one can obtain a contradiction by letting \( v \to \infty \) at that point, while it stays the same elsewhere.

The exact ground-state energy is obtained from

Assertion:
The exact ground-state energy is obtained by
Maximizing $v$ ensures that the energy of the system does not get “too low.” Except for a constant shift, the maximizing $v$ is a representation of the local energy, $E_x$, of the system since requiring

is sufficient to enforce the variational principle.
The Pair Density, Revisited

For a Hamiltonian of the form

\[ H = \sum_{i,j} v_{ij} \rho_{ij} \]

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

\[ E = \int \rho(x) \cdot \left( -\nabla^2 + v_N + T \right) \rho(x) \ dx \]

The variational principle is:

Define \( E_N \) 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 ensures that the energy of the system does not get “too low.” Except for a constant shift, the maximizing is a representation of the pairwise interaction energy, .

Sketch of Proof

Step 1. can be chosen to be convex.

Proof: 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 is the sum of a linear functional and a convex functional, it is convex.
Step 3. The set of all $\rho_{xx}$ 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 $\rho_{xx}$ 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.
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As an adolescent I aspired to lasting fame,
I craved factual certainty, and I thirsted
for a meaningful vision of human life—so I
became a scientist. This is like becoming
an archbishop so you can meet girls.

Matt Cartmill