# Generalized density-functional theory: Conquering the *N*-representability problem with exact functionals for the electron pair density and the second-order reduced density matrix

PAUL W AYERS[1]* and MEL LEVY[2]*

[1]Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada
[2]Department of Physics, North Carolina A&T University; Greensboro NC 27411, USA and
Department of Chemistry, Tulane University, New Orleans, LA 70118, USA
e-mail: ayers@mcmaster.ca; mflevy@neat.edu

**Abstract.** Using the constrained search and Legendre-transform formalisms, one can derive "generalized" density-functional theories, in which the fundamental variable is either the electron pair density or the second-order reduced density matrix. In both approaches, the *N*-representability problem is solved by the functional, and the variational principle is with respect to all pair densities (density matrices) that are nonnegative and appropriately normalized. The Legendre-transform formulation provides a lower bound on the constrained-search functional. Noting that experience in density-functional and density-matrix theories suggests that it is easier to approximate functionals than it is to approximate the set of *N*-representable densities sheds some light on the significance of this work.

**Keywords.** Density-functional theory; *N*-representability problem; electron pair density.

## 1. Historical perspective

Among the most fundamental equations in all of chemistry is the variational principle for the ground state energy, which states that if we minimize the expectation value of the *N*-electron Hamiltonian,

$$\hat{H}[v,N] \equiv \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} + v(\boldsymbol{r}_i) + \sum_{j=1}^{i-1}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\right) \qquad (1)$$

with respect to all antisymmetric and normalized wave functions, we obtain the ground state energy

$$E_{v,N}^{g.s.} \equiv \min_{\substack{\text{antisymettric } \Psi \\ \langle \Psi|\Psi\rangle=1}} \langle \Psi | \hat{H}[v,N] | \Psi \rangle. \qquad (2)$$

This equation is the foundation for most of quantum chemistry. Unfortunately, because the wave function depends on $3N$ spatial coordinates, methods based directly on (2) tend to suffer from the curse of dimension – computational costs grow exponentially with increasing numbers of electrons.

This motivates work that uses simpler quantities than the many-electron wave function to describe molecular systems. Arguably the first work along these lines was that of Thomas and Fermi, way back in the 1920's.[1,2] Work on simpler alternatives to the Schrödinger equation received sustained attention starting in the mid-1950's, when work on the second-order reduced density matrix[3,4] began to appear. For an ensemble composed of the wave functions $\{\Psi_i\}$ with weights that satisfy,

$$0 \le w_i \le 1,$$
$$\sum_i w_i = 1, \qquad (3)$$

the *N*-electron density matrix is defined as

$$\Gamma_N(\boldsymbol{r}_1, \dots \boldsymbol{r}_N; \boldsymbol{r}_1', \dots \boldsymbol{r}_N')$$
$$\equiv \sum_i w_i \Psi_i(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)\Psi_i^*(\boldsymbol{r}_1', \dots \boldsymbol{r}_N'), \qquad (4)$$

and the second-order reduced density matrix is, in turn, defined as

$$\Gamma_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')$$
$$\equiv (N)(N-1)\int \cdots \int \Gamma_N(\boldsymbol{r}_1 \dots \boldsymbol{r}_N; \boldsymbol{r}_1', \boldsymbol{r}_2', \boldsymbol{r}_3 \dots \boldsymbol{r}_N)\mathrm{d}\boldsymbol{r}_3 \dots \mathrm{d}\boldsymbol{r}_N. \qquad (5)$$

*For correspondence

The second-order reduced density matrix is interesting because we can express the exact electronic energy in terms of the second-order reduced density matrix. Specifically,

$$E[\Gamma_2, v] = \frac{1}{2(N-1)} \langle \boldsymbol{d}(\boldsymbol{r}_1 - \boldsymbol{r}_1')\boldsymbol{d}(\boldsymbol{r}_2 - \boldsymbol{r}_2') \\ \times \left\{ \left[ \begin{array}{c} \dfrac{\nabla_1' \cdot \nabla_1}{2} + \dfrac{\nabla_2' \cdot \nabla_2}{2} \\ +v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2) \\ +\dfrac{N-1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \end{array} \right] \Gamma_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') \right\} \rangle, \quad (6)$$

where the integration is with respect to all the arguments of the density matrix. Equation (6) is often written in terms of the reduced Hamiltonian operator,

$$\hat{K}_2[v, N] \equiv \frac{1}{2(N-1)} \left( \begin{array}{c} \dfrac{\nabla_1' \cdot \nabla_1}{2} + \dfrac{\nabla_2' \cdot \nabla_2}{2} \\ +\dfrac{\left( \begin{array}{c} v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2) \\ +v(\boldsymbol{r}_1') + v(\boldsymbol{r}_2') \end{array} \right)}{2} \\ +\dfrac{N-1}{2|\boldsymbol{r}_1' - \boldsymbol{r}_2'|} + \dfrac{N-1}{2|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \end{array} \right), \quad (7)$$

as

$$E_{v,N}[\Gamma_2] = \text{Tr}[\hat{K}_2 \Gamma_2], \quad (8)$$

where the trace notation means "evaluate $\hat{K}_2 \Gamma_2$, remove the primes, and then integrate with respect to the unprimed variables."

Research into density-matrix theories slowed (though there has been a recent resurgence) when it was observed that the naïve variational procedure – minimize (8) with respect to all positive-semidefinite $\Gamma_2$ that are appropriate normalized – gives results that are far lower than the true ground state energy. The problem is that not every positive-semidefinite $\Gamma_2$ satisfying the normalization constraint

$$\text{Tr}[\Gamma_2] = N(N-1), \quad (9)$$

corresponds to an ensemble of antisymmetric and normalized wave functions. That is, some "reasonable" density matrices cannot be written in the form

of (5). Since the variational principle for the wave function (or the $N$-electron density matrix) is restricted to antisymmetric and normalized wave functions, the variational principle for $\Gamma_2$ must be restricted to those density matrices that can be expressed in the form of (5). Such $\Gamma_2$ are said to be $N$-representable.[5,6] (More precisely, such $\Gamma_2$ are said to be ensemble $N$-representable. Pure-state $N$-representable $\Gamma_2$ are expressed in the form of (5), but only one of the weighting factors in (4) is nonzero.)

The true ground-state energy, then, can be written as

$$E_{v,N}^{g.s.} = \underbrace{\min}_{\Gamma_2 \in \mathbf{N}(N)} E_{\boldsymbol{n},N}[\Gamma_2], \quad (10)$$

where $\mathbf{N}(N)$ denotes the set of $N$-representable density matrices. Though the exact form of the $N$-representability constraints is known,[6] it is not computationally useful. Computational treatments based on approximate implementations of (10) are extremely demanding and, as of this writing, usually are not competitive with other methods of similar computational cost.[7–10] In approaches based on $\Gamma_2$, we trade the daunting problem of representing a high-dimensional wave function with the daunting problem of characterizing the set of $N$-representable $\Gamma_2$. (However, in contrast to density-functional theory, the exact energy functional for $\Gamma_2$ is known in a computationally practical form, (8).)

The next milestone along this chain of research appeared in the mid-1960's, when Hohenberg and Kohn[11] showed that the ground state electron density,

$$\boldsymbol{r}(\boldsymbol{r}_1) \equiv \frac{1}{N-1} \int \Gamma_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2) \mathrm{d}\boldsymbol{r}_2 \quad (11)$$

determines every property of an electronic system. Specifically, the Hohenberg–Kohn functional is[11,12]

$$F^{HK}[\boldsymbol{r}] = E_{v,N}^{g.s.} - \int \boldsymbol{r}(\boldsymbol{r})v(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \quad (12)$$

in terms of which

$$E_{v,N}^{g.s.} = \underbrace{\min}_{\substack{\langle \boldsymbol{r}(\boldsymbol{r}) \rangle = N \\ \boldsymbol{r}(\boldsymbol{r}) \geq 0}} F^{HK}[\boldsymbol{r}] + \int \boldsymbol{r}(\boldsymbol{r})v(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \quad (13)$$

That is, one can minimize the energy functional,

$$E_{v,N}^{HK}[\mathbf{r}] \equiv F^{HK}[\mathbf{r}] + \int \mathbf{r}(\mathbf{r})v(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{14}$$

subject to the constraint that the electron density is positive and appropriately normalized. There is no *N*-representability problem here, because every electron density that is nonnegative and normalized is *N*-representable.[13,14] There is a well-known problem with the variational principle, however, which is that $F^{HK}[\mathbf{r}]$ is only defined for electron densities that are the ground state for some local external potential (cf. (12)). This is termed the *v*-representability problem.

Solutions to the *v*-representability problem can be achieved by constrained search,[15]

$$F^{constr.\,srch.}[\mathbf{r}] = \underbrace{\min}_{\Psi \rightarrow \mathbf{r}(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \tag{15}$$

or the generalized Legendre transform,[16]

$$F^{Legendre}[\mathbf{r}] = \underbrace{\sup}_{v(\mathbf{r})} (E_{v,N}^{g.s.} - \int \mathbf{r}(\mathbf{r})v(\mathbf{r})). \tag{16}$$

Equation (15) indicates that $F^{constr.srch.}[\mathbf{r}]$ is defined by minimizing the expectation value of the sum of the kinetic energy and electron-electron repulsion energy operators with respect to all antisymmetric and normalized wave functions that are associated with the electron density of interest. Equation (16) indicates that you find the maximum (the supremum is a mathematical generalization of the concept of a maximum) of the difference of the total energy and the electron-external potential energy over all possible choices of the external potential. One has that[17,18]

$$F^{Legendre}[\mathbf{r}] \leq F^{constr.\,srch.}[\mathbf{r}] \tag{17}$$

with equality only when the density is pure-state *v*-representable (in which case both functions equal $F^{HK}[\mathbf{r}]$).

One reason density-functional theory is so useful is because there is no *N*-representability problem. Neither do we have the problem of representing a function that depends on a large number of variables: the electron density depends on only three coordinates. Unlike theories based on the wave function or the second-order reduced density matrix, however, the energy functional is not known in a practical form for computational applications. Density-functional

theory is applied much more widely than theories based on $\Gamma_2$, suggesting that the problem of approximating energy functionals is "easier" than approximately accounting for *N*-representability.

Moving forward another decade, Gilbert,[13] Donnelly and Parr,[19,20] and Levy[15] laid the foundations for theories based on the first-order reduced density matrix,

$$\Gamma_1(\mathbf{r}_1, \mathbf{r}_1') \equiv \frac{1}{N-1} \int \Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2)\mathrm{d}\mathbf{r}_2. \tag{18}$$

It is important to note that the ensemble-*N*-representability conditions for the $\Gamma_1$ are known (though the pure-state conditions do not seem to be known).[5,6] Unlike the electron density, the kinetic energy can be computed exactly from the first-order reduced density matrix. Like the electron density, however, the electron-electron repulsion energy needs to be approximated. The exact electron-electron repulsion energy functional can be constructed by constrained search[15] or Legendre transform[16] and, again,

$$V_{ee}^{Legendre}[\Gamma_1] \leq V_{ee}^{constr.\,srch}[\Gamma_1]. \tag{19}$$

Though neither of these exact functionals takes a computationally practical form, the properties of the exact functionals are useful for constraining the form of the approximate functionals used in practical applications.

Recent years have seen a resurgence of interest in theories based on the first-order reduced density matrix and some very promising numerical results have been obtained.[21–36] Again we have traded the problems of high-dimensionality (wave-function theory) and the *N*-representability problem ($\Gamma_2$-theory) for the problem of approximating a functional and, again, the result seems to be a computationally tractable theory.

In the mid-1990's, Ziesche completed this family of theories by formulating the energy as a functional of the electron pair density,[37,38]

$$\mathbf{r}_2(\mathbf{r}_1, \mathbf{r}_2) = \Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2). \tag{20}$$

(Prescient early work was performed by Weinhold, Wilson, and Davidson in the late 1960's.[39–41]) For the pair density, the electron-electron repulsion energy functional is known exactly in explicit form

$$V_{ee}[\mathbf{r}_2] = \frac{1}{2} \iint \frac{\mathbf{r}_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \tag{21}$$

**Table 1.** Summary of different computational approaches to the molecular electronic structure problem.

Where a single fundamental variable has more than one entry, this indicates the existence of two alternative approaches. Shaded entries constitute contributions from this work. The entries are ordered according to the chronology in the introductory section of the paper.

| Type of theory | Fundamental variable | Dimensionality | $N$-representability problem? | Functional approximation problem? |
|---|---|---|---|---|
| Wave-function | $\Psi(r_1,...r_N)$ | $3N$ | No | No |
| Density-matrix | $\Gamma_2(r_1,r_2;r_1',r_2')$ | 12 | Yes | No |
| | | | No | Yes |
| Density-functional | $r(r)$ | 3 | No | Yes |
| Natural-orbital | $\Gamma_1(r_1,r_1')$ | 6 | No | Yes |
| Pair-density functional | $r_2(r_1,r_2)$ | 6 | Yes | Yes |
| | | | No | Yes |

but no explicit exact expression for the kinetic energy functional is known.[37,42,43] Worse still, $r_2(r_1,r_2)$ suffers from the $N$-representability problem too![44–46] Thus, while the "curse of dimension" that afflicts computational methods based on the wave function has been avoided, theories based on the electron pair density suffer from both an $N$-representability problem *and* the functional approximation problem. This perhaps explains why, despite great current interest in the electron pair density,[42,54] no variational calculations using the electron pair density have been reported.

The goal of this paper is to show that matters are not quite so bad as this. We can "combine" the problem of the unknown kinetic energy functional, $T[r_2]$, with the $N$-representability problem by defining functionals, $T[r_2]$, that are "big enough" for non-$N$-representable electron pair densities to ensure that minimizing the energy functional

$$E_{v,N}[r_2] \equiv T[r_2] + V_{ee}[r_2]$$
$$+ \iint r_2(r_1,r_2)\left(\frac{v(r_1)+v(r_2)}{2(N-1)}\right)dr_1dr_2. \quad (22)$$

with respect to all nonnegative and appropriately normalized electron pair densities gives the correct answer, i.e.

$$E_{v,N}^{g.s.} = \min_{\substack{\langle r_2 \rangle = N(N-1) \\ r_1(r_1,r_2) \geq 0}} (T[r_2] + V_{ee}[r_2] + \int r(r)v(r)dr).$$
$$(23)$$

Unsurprisingly, this goal can be achieved using the Legendre-transform (§2.1) or constrained-search

(§2.2) formulation. (As might be expected, the Legendre transform is a lower bound on the constrained-search functional.) Section 3 sketches how our results can be extended to the second-order reduced density matrix. Our intent, here, is to give an overview of the state of the theory, stressing the links between different approaches. (See table 1 for a graphical representation.) Except as required to establish the plausibility of our results, the proofs (none of which are very hard) are omitted. More detailed analyses will be published separately.[43,55]

## 2. Conquering the $N$-representability problem for the electron pair density

### 2.1 *Legendre-transform approach*

The desired variational principle for the energy is

$$E_{v,N}^{g.s.} \leq T[r_2] + V_{ee}[r_2]$$
$$+ \iint r_2(r_1,r_2)\left(\frac{v(r_1)+v(r_2)}{2(N-1)}\right)dr_1dr_2. \quad (24)$$

This is equivalent to desiring that

$$T[r_2] \geq E_{v,N} - V_{ee}[r_2]$$
$$- \iint r_2(r_1,r_2)\left(\frac{v(r_1)+v(r_2)}{2(N-1)}\right)dr_1dr_2 \quad (25)$$

for every external potential $v(r)$, with the equality only holding when $r_2(r_1,r_2)$ is a ground state for this external potential. To achieve this, we maximize the right-hand side of (25) with respect to the external

potential. (However, due to mathematical considerations, we need to actually take the supremum.) Our Legendre transform function is then

$$
\begin{aligned}
T^{Legendre}[\boldsymbol{r}_2] \\
= \sup_{v(\boldsymbol{r})} \left( \begin{array}{l} E_{v,N}^{g.s.} - V_{ee}[\boldsymbol{r}_2] \\ -\iint \boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\left(\dfrac{v(\boldsymbol{r}_1)+v(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2 \end{array} \right) \\
= \sup_{v(\boldsymbol{r})} (E_{v,N}^{g.s.} - \int \boldsymbol{r}[\boldsymbol{r}_2;\boldsymbol{r}]v(\boldsymbol{r})\mathrm{d}\boldsymbol{r}) - V_{ee}[\boldsymbol{r}_2].
\end{aligned}
\tag{26}
$$

Here, $\boldsymbol{r}[\boldsymbol{r}_2;\boldsymbol{r}]$ is the electron density associated with the pair density of interest.

By construction, $T^{Legendre}[\boldsymbol{r}_2]$ satisfies the variational principal for any nonnegative and normalized $\boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$. Comparing (16) and (26), it is clear that $T^{Legendre}[\boldsymbol{r}_2]=F^{Legendre}[\boldsymbol{r}[\boldsymbol{r}_2]]-V_{ee}[\boldsymbol{r}_2]$. A constrained-search analogue is $T[\boldsymbol{r}_2]=F^{constr.srch}[\boldsymbol{r}[\boldsymbol{r}_2]]-V_{ee}[\boldsymbol{r}_2]$. Further, $V_{ee}[\Gamma_1]=F[\boldsymbol{r}[\Gamma_1]]-T[\Gamma_1]$ is the corresponding electron-electron repulsion energy functional of the first-order reduced density matrix, $\Gamma_1(\boldsymbol{r},\boldsymbol{r}_1')$.

Every other functional that satisfies the variational principle, (24), will be greater than or equal to $T^{Legendre}[\boldsymbol{r}_2]$. That is, among all functionals that do not suffer from the *N*-representability problem, $T^{Legendre}[\boldsymbol{r}_2]$ is the "smallest possible" exact functional. To derive this, merely suppose that $T^{<}[\boldsymbol{r}_2]$ is smaller than $T^{Legendre}[\boldsymbol{r}_2]$ for some pair density, $\boldsymbol{r}_2^{<}(\boldsymbol{r}_1,\boldsymbol{r}_2)$. Using the definition, (26), there exists some external potential, $v^{<}(\boldsymbol{r})$, such that

$$
T^{<}[\boldsymbol{r}_2^{<}] < E_{v^{<},N}^{g.s.} - V_{ee}[\boldsymbol{r}_2]
$$

$$
-\iint \boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\left(\frac{v^{<}(\boldsymbol{r}_1)+v^{<}(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2.
\tag{27}
$$

Then

$$
E_{v^{<},N}^{g.s.} > T^{<}[\boldsymbol{r}_2^{<}] + V_{ee}[\boldsymbol{r}_2]
$$

$$
+\iint \boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\left(\frac{v^{<}(\boldsymbol{r}_1)+v^{<}(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2,
\tag{28}
$$

which violates the variational principle.

## 2.2 *A constrained-search approach*

Define

$$
W[\boldsymbol{r}_2] \equiv \min_{\Psi \to \boldsymbol{r}[\boldsymbol{r}_2]} |\langle\Psi|\hat{V}_{ee}|\Psi\rangle - V_{ee}[\boldsymbol{r}_2]|,
\tag{29}
$$

where the minimization runs over all normalized antisymmetric wave functions that are associated with the electron density,

$$
\boldsymbol{r}[\boldsymbol{r}_2,\boldsymbol{r}_1] = \frac{1}{N-1}\int \boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_2.
\tag{30}
$$

The requirement that the electron density be *N*-representable forces the electron pair density to be nonnegative and normalized to *N(N–1)*, but nothing else is required. Note that $W[\boldsymbol{r}_2]$ is greater than or equal to zero for non-*N*-representable pair densities and equal to zero for pair densities that are pure-state *N*-representable.

A wave function that minimizes (29) is denoted

$$
\Psi_{\min}[\boldsymbol{r}_2] \equiv \arg \min_{\Psi \to \boldsymbol{r}[\boldsymbol{r}_2]} |\langle\Psi|\hat{V}_{ee}|\Psi\rangle - V_{ee}[\boldsymbol{r}_2]|.
\tag{31}
$$

If more than one wave function minimizes (29), choose the $\Psi$ whose pair density resembles $\boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ most closely. The wave function in (31) is obviously associated with an *N*-representable pair density, denoted

$$
\boldsymbol{r}_2[\Psi_{\min}] \equiv N(N-1)
$$

$$
\times \int\cdots\int \Psi_{\min}(\boldsymbol{r}_1,...,\boldsymbol{r}_N)\Psi_{\min}^{*}(\boldsymbol{r}_1,...,\boldsymbol{r}_N)\mathrm{d}\boldsymbol{r}_3...\mathrm{d}\boldsymbol{r}_N.
\tag{32}
$$

Now, we define

$$
T^{constr.srch.}[\boldsymbol{r}_2]
$$

$$
\equiv \min_{\Psi \to \boldsymbol{r}_2[\Psi_{\min}]} (\langle\Psi|\hat{T}|\Psi\rangle + W[\boldsymbol{r}_2]
$$

$$
+ c_{\boldsymbol{r}_2}\iint |\boldsymbol{r}_2[\Psi_{\min};\boldsymbol{r}_1,\boldsymbol{r}_2] - \boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)|\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2.
\tag{33}
$$

The coefficient, $c_{\boldsymbol{r}_2}$, of the last term in (33) should be chosen to maintain consistency of units. $c_{\boldsymbol{r}_2}$ can be any positive real number, since the last term, like $W[\boldsymbol{r}_2]$, is identically zero for *N*-representable pair densities.[56] When $\boldsymbol{r}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is *N*-representable, (33)

becomes the direct analogue[37] of the density-functional theory constrained-search expression. The wave function that minimizes (33) is denoted $\Psi^{const.srch.}[\boldsymbol{r}_2]$; note that the pair density of $\Psi^{const.srch.}[\boldsymbol{r}_2]$ is $\boldsymbol{r}_2[\Psi_{min}]$ whenever $\boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is not $N$-representable. When $\boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is not $N$-representable, then

$$T^{constr.\,srch.}[\boldsymbol{r}_2] + V_{ee}[\boldsymbol{r}_2] + \int \boldsymbol{r}[\boldsymbol{r}_2, \boldsymbol{r}]v(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$
$$\geq \langle \Psi^{constr.srch.} | \hat{T} | \Psi^{constr.srch.} \rangle$$
$$+ V_{ee}[\boldsymbol{r}_2[\Psi_{min}]] + \int \boldsymbol{r}[\boldsymbol{r}_2, \boldsymbol{r}]v(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$
$$= \langle \Psi^{constr.srch.} | \hat{H} | [v, N] | \Psi^{constr.srch.} \rangle. \quad (34)$$

Thus, the "penalty functional" in (29) is large enough to ensure that the pair density that minimizes the energy is $N$-representable. Using $T^{constr.srch}[\boldsymbol{r}_2]$ as the energy functional in (23), it is clear that the ground state energy and pair density are determined by minimizing

$$E_{v,N}^{constr.srch.}[\boldsymbol{r}_2] \equiv T^{constr.srch.}[\boldsymbol{r}_2] + V_{ee}[\boldsymbol{r}_2]$$
$$+ \iint \boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\left(\frac{v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2, \quad (35)$$

with respect to all pair densities that are positive and appropriately normalized.

Based on the discussion in the previous section, it is apparent that

$$T^{Legendre}[\boldsymbol{r}_2] \leq T^{constr.\,srch.}[\boldsymbol{r}_2], \quad (36)$$

and that both functionals are equal to the Hohenberg–Kohn-type functional

$$T^{HK}[\boldsymbol{r}_2] = E_{v,N}^{g.s.} - V_{ee}[\boldsymbol{r}_2]$$
$$- \iint \boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\left(\frac{v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2, \quad (37)$$

for electron pair densities that are $v$-representable. (That is, $T^{Legendre}[\boldsymbol{r}_2] = T^{constr.srch.}[\boldsymbol{r}_2] = T^{HK}[\boldsymbol{r}_2]$ whenever there exists a $v(\boldsymbol{r})$ for which $\boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the ground state electron pair density.)

In density-functional theory, the constrained-search for the wave function can be replaced by the constrained-search for the ensemble[57]

$$F^{ensemble}[\boldsymbol{r}] = \min_{\Gamma_N \rightarrow \boldsymbol{r}} \; \mathrm{Tr}[(\hat{T} + \hat{V}_{ee})\Gamma_N]. \quad (38)$$

It is interesting to note that $F^{Legendre}[\boldsymbol{r}] = F^{ensemble}[\boldsymbol{r}]$.[16] One can also generalize the constrained search for the electron pair density to ensembles. If one does so, then the constrained-search and Legendre-transform functionals are identical for ensemble-$v$-representable density matrices.

The key result of this section should be reiterated. Minimizing the energy functional

$$E_{v,N}[\boldsymbol{r}_2] \equiv T[\boldsymbol{r}_2] + V_{ee}[\boldsymbol{r}_2]$$
$$+ \iint \boldsymbol{r}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\left(\frac{v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2)}{2(N-1)}\right)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2 \quad (39)$$

with respect to nonnegative and normalized electron pair densities gives the correct ground state energy, if one uses either (26) or (33) as the definition of the kinetic energy functional. This is analogous to the situation in density functional theory: the $N$-representability problem has been replaced with the problem of constructing accurate approximations to the specified functionals.

## 3. Conquering the $N$-representability problem for the second-order reduced density matrix

The significance of the results in the previous section is that they convert the $N$-representability problem (which seems difficult to address in practical computations) to the problem of functional approximation (which, as is attested to by the great success of density-functional theory and the burgeoning interested in theories based on the first-order reduced matrix, is less problematic in practical computations). This suggests that it would be useful to replace the $N$-representability problem for the second-order reduced density-matrix with the problem of constructing accurate approximations to some predefined functional. Just as before, there is a Legendre-transform functional,

$$Q^{Legendre}[\Gamma_2] = \sup_{v(\boldsymbol{r})} \; (E_{v,N}^{g.s.} - \mathrm{Tr}[\hat{K}_2[v]\Gamma_2]), \quad (40)$$

in terms of which the variational principle may be stated

$$E_{v,N}^{g.s.} = \min_{\Gamma_2} \; (\mathrm{Tr}[\hat{K}_2[v]\Gamma_2] + Q^{Legendre}[\Gamma_2]). \quad (41)$$

For $N$-representable $\Gamma_2$, it is clear that $Q^{Legendre}[\Gamma_2] = F^{Legendre}[\rho[[\Gamma_2]] - T[\Gamma_2] - V_{ee}[\Gamma_2] \leq 0$, where $\boldsymbol{r}[\Gamma_2; \boldsymbol{r}]$ is the electron density associated with the density-matrix. The equality holds when $\boldsymbol{r}[\Gamma_2; \boldsymbol{r}]$ is $v$-representable. Even though $Q^{Legendre}[\Gamma_2] \leq 0$ for $N$-representable $\Gamma_2$, $Q^{Legendre}[\Gamma_2]$ will positive for some (and perhaps most) non-$N$-representable density matrices.

A constrained-search analogue to (40) is $Q[\boldsymbol{r}_2] = F^{constr.srch}[\boldsymbol{r}[\boldsymbol{r}_2] - T[\Gamma_2] - V_{ee}[\Gamma_2]$.

There is another constrained-search approach. Denote the sum of the kinetic and electron-electron repulsion energies as

$$G[\Gamma_2] = \frac{1}{2(N-1)}\left\langle \boldsymbol{d}(\boldsymbol{r}_1 - \boldsymbol{r}_1')\boldsymbol{d}(\boldsymbol{r}_2 - \boldsymbol{r}_2')\right.$$
$$\left. \times \left\{\left[\frac{\nabla_1' \cdot \nabla_1}{2} + \frac{\nabla_2' \cdot \nabla_2}{2} + \frac{N-1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\right]\Gamma_2\left(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2'\right)\right\}\right\rangle. \tag{42}$$

Next, define the constrained-search functional as

$$Q^{constr.srch.}[\Gamma_2]$$
$$\equiv \underset{\Psi \to \boldsymbol{r}[\Gamma_2]}{\min}\left(\begin{array}{l}|\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle - G[\Gamma_2]| \\ + c_{\Gamma_2}\,\|\,\Psi; \boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2'] - \Gamma_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')\|\end{array}\right). \tag{43}$$

In the last term, $\Gamma_2[\Psi; \boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2']$ denotes the density matrix that corresponds to the wave function $\Psi$. Analogous to the situation in (33) $c_{\Gamma_2}$ is a positive real number that maintains consistency of units.[58] The minimization in (43) can only be performed if $\boldsymbol{r}[\Gamma_2]$ is $N$-representable; this means that $\Gamma_2$ must be an appropriately normalized positive semidefinite density matrix. (The requirement that the density matrix be positive semidefinite may be simply imposed by adopting the ansatz $\Gamma_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') =$

$$\iint (A(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{x}_1, \boldsymbol{x}_2))^* A(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') d\boldsymbol{x}_1 d\boldsymbol{x}_2.)$$

Defining

$$F[\Gamma_2] \equiv G[\Gamma_2] + Q^{constr.srch.}[\Gamma_2], \tag{44}$$

it follows, by the same argument used in §2.2, that the ground state energy and density matrix can be found using the variational principle:

$$E_{v,N}^{g.s.} = \underset{\Gamma_2}{\min}\ \left(F[\Gamma_2] + \int \boldsymbol{r}[\Gamma_2; \boldsymbol{r}]v(\boldsymbol{r})d\boldsymbol{r}\right)$$
$$= \underset{\Gamma_2}{\min}\ (\mathrm{Tr}[\hat{K}_2[v]\,\Gamma_2] + Q^{constr.srch}[\Gamma_2]). \tag{45}$$

Note that the $G$ component of $F$ does not have to be approximated and that $Q^{constr.srch.}[\Gamma_2]$ is greater than or equal to zero. That is,

$$0 \leq Q^{constr.srch.}[\Gamma_2] \tag{46}$$

with equality holding for all pure-state $N$-representable density matrices.

Corresponding to (17), (19), and (36), we have that

$$Q^{Legendre}[\Gamma_2] \leq Q^{constr.srch.}[\Gamma_2] \tag{47}$$

with both functionals equal to zero for all $v$-representable density matrices. The nonnegativity of $Q^{constr.srch}[\Gamma_2]$ should be useful for constructing approximations.

## 4. Summary

When solving the Schrödinger equations computationally, one encounters costs that grow exponentially as the number of electrons increases. This curse of dimension can be avoided by considering a "reduced" function – e.g., the second-order reduced density matrix, the first-order reduced density matrix, the electron density, or the electron pair density – to be the fundamental descriptor of the chemical system. Unfortunately, for the second-order reduced density matrix and the electron pair density, the naïve variational approach to the electronic structure problem does not work because of the $N$-representability problem. The difficulty of the $N$-representability problem can be contrasted to the great success in density-functional theory (and the lesser, but still impressive, successes in theories based on the first-order density matrix), where there is no $N$-representability problem but, instead, one needs to approximate the exact energy functionals. This motivates the present work, in which the $N$-representability problem is "converted" into a functional approximation problem by using the Legendre transform and constrained search to define exact functionals that are free from the $N$-representability problem. In each case, one simply minimizes the energy functional ((39) for the electron pair density; either (41) or (45) for the second-order reduced density matrix) with respect to objects that are appropriately normalized and positive semidefinite. We hope that the present functionals will prove as useful for further developments of density-matrix and electron-pair-density functional theories as their analogues have been in density-functional theory.

## Acknowledgement

## References

1. Thomas L H 1927 *Proc. Cambr. Philos. Soc.* **23** 542
2. Fermi E 1928 *Z. Phys.* **48** 73
3. Lowdin P-O 1955 *Phys. Rev.* **97** 1474
4. Mayer J E 1955 *Phys. Rev.* **100** 1580
5. Coleman J 1963 *Rev. Mod. Phys.* **35** 668
6. Garrod C and Percus J K 1964 *J. Math. Phys.* **5** 1756
7. Zhao Z J, Braams B J, Fukuda M, Overton M L and Percus J K 2004 *J. Chem. Phys.* **120** 2095
8. Mazziotti D A 2002 *Phys. Rev.* **A65** art-062511
9. Mazziotti D A 2004 *Phys. Rev. Lett.* **93**
10. Mazziotti D A 2004 *J. Chem. Phys.* **121** 10957
11. Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864–B871
12. Freed K F and Levy M 1982 *J. Chem. Phys.* **77** 396
13. Gilbert T L 1975 *Phys. Rev.* **B12** 2111
14. Harriman J E 1981 *Phys. Rev.* **A24** 680
15. Levy M 1979 *Proc. Natl. Acad. Sci. USA* **76** 6062
16. Lieb E H 1988 *Int. J. Quantum Chem.* **24** 243
17. Lieb E H 1985 *NATO ASI Ser.* **B123** 31
18. Levy M and Perdew J P 1985 *NATO ASI Ser.* **B123** 11
19. Donnelly R A and Parr R G 1978 *J. Chem. Phys.* **69** 4431
20. Donnelly R A 1979 *J. Chem. Phys.* **71** 2874
21. Mazziotti D A 2001 *J. Chem. Phys.* **115** 8305
22. Mazziotti D A 2001 *Chem. Phys. Lett.* **338** 323
23. Cioslowski J and Lopez-Boada R 1998 *J. Chem. Phys.* **109** 4156
24. Buijse M A and Baerends E J 2002 *Mol. Phys.* **100** 401
25. Cioslowski J, Ziesche P and Pernal K 2001 *J. Chem. Phys.* **115** 8725
26. Yasuda K 2001 *Phys. Rev.* **A6303** art-032517
27. Yasuda K 2002 *Phys. Rev. Lett.* **8805** art-053001
28. Cioslowski J and Pernal K 2002 *J. Chem. Phys.* **117** 67
29. Holas A 1999 *Phys. Rev.* **A59** 3454
30. Csanyi G, Goedecker S and Arias T A 2002 *Phys. Rev.* **A65** art-032510
31. Staroverov V N and Scuseria G E 2002 *J. Chem. Phys.* **117** 2489
32. Cioslowski J, Pernal K and Ziesche P 2002 *J. Chem. Phys.* **117** 9560
33. Ziesche P 2002 *Int. J. Quantum Chem.* **90** 342
34. Herbert J M and Harriman J E 2002 *Int. J. Quantum Chem.* **90** 355
35. Cohen A J and Baerends E J 2002 *Chem. Phys. Lett.* **364** 409
36. Goedecker S and Umrigar C J 1998 *Phys. Rev. Lett.* **81** 866
37. Ziesche P 1994 *Phys. Lett.* **A195** 213
38. Ziesche P 1996 *Int. J. Quantum Chem.* **60** 149
39. Weinhold F and Wilson E B 1968 *Reduced density matrices with applications to chemical and physical systems; Queen's papers in pure and applied mathematics* (Kingston, Ontario: Queen's University)
40. Weinhold F and Wilson E B 1967 *J. Chem. Phys.* **47** 2298
41. Davidson E R 1970 *Phys. Rev.* **A1** 30
42. Ayers P W 2005 *J. Math. Phys.* **46** 062107
43. Ayers P W, Golden S and Levy M 2005 *J. Chem. Phys.* (accepted)
44. Davidson E R 1995 *Chem. Phys. Lett.* **246** 209
45. Samvelyan S K 1997 *Int. J. Quantum Chem.* **65** 127
46. Pistol M E 2004 *Chem. Phys. Lett.* **400** 548
47. Levy M and Ziesche P 2001 *J. Chem. Phys.* **115** 9110
48. Nagy A 2002 *Phys. Rev.* **A66** art-022505
49. Furche F 2004 *Phys. Rev.* **A70**
50. Nagy A and Amovilli C 2004 *J. Chem. Phys.* **121** 6640
51. Hsu J Y 2003 *Phys. Rev. Lett.* **91** 133001
52. Hsu J Y, Lin C H and Cheng C Y 2005 *Phys. Rev.* **A71** 052502
53. Gonis A, Schulthess T C, Turchi P E A and Vanek J 1997 *Phys. Rev.* **B56** 9335
54. Gonis A, Schulthess T C, Vanek J and Turchi P E A 1996 *Phys. Rev. Lett.* **77** 2981
55. Levy M and Ayers P W 2005 *J. Chem. Phys.* (in preparation)
56. The last term in (33) in strictly positive for non-*N*-representable pair densities. This eliminates the problem of 'false' pair densities. (Without the last term, the variational principle in (35) might give the right energy, but have a minimizing pair density that is non-*N*-representable.)
57. Valone S M 1980 *J. Chem. Phys.* **73** 4653
58. The norm in (43) can be chosen in any reasonable way; possibilities include the Frobenius

$$\| \Gamma_2[\Psi;r_1,r_2;r_1',r_2'] - \Gamma_2(r_1,r_2;r_1',r_2') \|_F = \sqrt{\iint | \Gamma_2[\Psi;r_1,r_2;r_1',r_2'] - \Gamma_2(r_1,r_2;r_1',r_2') |^2 \, dr_1 dr_2 dr_1' dr_2'}$$

and $L^2$ norms,

$$\| \Gamma_2[\Psi;r_1,r_2;r_1',r_2'] - \Gamma_2(r_1,r_2;r_1',r_2') \|_2 = \underset{\{y(r_1,r_2)\}}{\sup} \frac{\iint y^*(r_1',r_2')(\Gamma_2[\Psi;r_1,r_2;r_1',r_2'] - \Gamma_2(r_1,r_2;r_1',r_2'))y(r_1,r_2) dr_1 dr_2 dr_1' dr_2'}{\langle y(r_1,r_2) | y(r_1,r_2) \rangle}.$$