# Direct variation of the second-order reduced density matrix and positive semidefinite programming

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## 1  Introduction

The basic equation for chemistry is known and it is called the Schrödinger equation, however, it is also known that the Schödinger equation is too difficult to solve [1]. This is a motivation for direct determination of the second-order reduced density matrix (2-RDM) [2] instead of solving the Schödinger equation, since it is much simpler than wavefunction by following reasons: (i) we can calculate the total energy and all physical proprieties without approximation by the 2-RDM (ii) the number of variables is *always four* regardless how many electrons exist in the system, and We hope we can construct wave mechanics without waves, and much simpler.

One major obstacle for the RDM method that the 2-RDM should satisfy the $N$-representability condition, that trial 2-RDM should have its parent wavefunction, otherwise, it is non-physical. It is not understood very much in two ways: approximate or complete solution to the $N$-representability is not very well understood, and how to do practical and systematic calculation had been unknown. There are some early attempts, but faded away.

In 2001, interest returned to the RDM method when Nakata *et al.* [3] formulated the problem as a primal semidefinite programming problem. They performed a direct variational calculation of the 2-RDM employing the $P$, $Q$ and $G$ conditions using the well-established semidefinite programming solver known as SemiDefinite Programming Algorithm (SDPA) [4]. This approach was applied to many few electron atoms and molecules. Their results using the $P$, $Q$, and $G$ conditions were very encouraging; yielding around 100 to 130% of correlation energy as well as being able to produce the dissociation curve of the nitrogen dimer in good agreement with fullCI. Zhao *et al.* included the $T1$ and $T2$ conditions in addition to the $P$, $Q$ and $G$ conditions in this approach for their calculations on small molecules [5]. The accuracy of their results are comparable to coupled-cluster singles and doubles with perturbative triples (CCSD(T)) at equilibrium geometries. The calculated correlation energies range typically from 100 to 101%. Mazziotti confirmed the findings of Nakata *et al.* [3] and Zhao *et al.* [5], by applying these conditions to larger systems. He accomplished this by implementing a semidefinite programming solver [6]. Mazziotti *et al.*'s thorough study of these $N$-representability conditions was important to establish the validity of the approach.

In this paper, we present summary of our research.

## 2  The Reduced-Density Matrix Method

### 2.1  The Schrodinger equation in Chemistry

The *ground state energy* calculation of a non-relativistic and time-independent, $N$-electron molecular system under the Born-Oppenheimer approximation is the most important problem It can be obtained as the lowest eigenvalue $E$ of the electronic Schrödinger equation:

$$H\Psi(\boldsymbol{z}) = E\Psi(\boldsymbol{z}).$$

The Hamiltonian in second quantized form is expressed as follows:

$$H = \sum_{ij} v_j^i a_i^\dagger a_j + \frac{1}{2}\sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1},$$

where $a^\dagger$ and $a$ are creation and annihilation operators, and where $v_j^i$ and $w_{k\ell}^{ij}$ are one- and two-particle terms are calculated as follows:

$$v_j^i = \int \psi_i^*(\boldsymbol{z})\left(-\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{r_A}\right)\psi_j(\boldsymbol{z})d\boldsymbol{z},$$

$$w_{k\ell}^{ij} = \int \psi_i^*(\boldsymbol{z_1})\psi_j^*(\boldsymbol{z_2})\left(\frac{1}{|\boldsymbol{z_1}-\boldsymbol{z_2}|}\right)\psi_\ell(\boldsymbol{z_1})\psi_k(\boldsymbol{z_2})d\boldsymbol{z_1}d\boldsymbol{z_2}.$$

in which $Z_A$ is the atomic number of the nucleus $A$, $r_{iA}$ is the distance between the electron $i$ and nucleus $A$, and $r_{ij}$ is the distance between two distinct electrons and $\{\psi_i\}_{i=1}^\infty$ is the one-particle complete orthnormal system. We usually choose finite subset from $\{\psi_i\}_{i=1}^\infty$, and it is called "basis set".

### 2.2  The reduced density matrix and variatioanl method

The definition of 1- and 2-RDM in the second-quantized versions are following:

$$\gamma_j^i = \sum_p t_p \langle\Psi_p|a_i^\dagger a_j|\Psi_p\rangle,$$

$$\Gamma_{k\ell}^{ij} = \frac{1}{2}\sum_p t_p \langle\Psi_p|a_i^\dagger a_j^\dagger a_\ell a_k|\Psi_p\rangle,$$

where $D = \sum_p t_p|\Psi_p\rangle\langle\Psi_p|, t_p \geq 0, \sum_p t_p = 1$.

The ground state energy $E_{\min}$ can be calculated by minimizing the total energy over 1- and 2-RDMs.

$$E_{\min} = \min \sum_p t_p \langle\Psi_p|H|\Psi_p\rangle$$

$$= \min\{\sum_{ij} v_j^i \gamma_j^i + \sum_{ijk\ell} w_{k\ell}^{ij}\Gamma_{k\ell}^{ij}\}.$$

## 2.3 $N$-representability condition and the RDM method

$N$-representability condition on 1- and 2-RDMs is first coined by Coleman, that whether trial 1- or 2-RDM has its $N$-particle ancestor wavefunction.

$$\Gamma \to D.$$

If there are, then $N$-representable, and no, then non $N$-representable. The variational determination of 2-RDM can be formulated using $\mathcal{E}^N$, a complete set of $N$-presentable RDMs like folows.

$$E_{\min} = \min_{\Gamma \in \mathcal{E}^N} \{ \sum_{ij} v_j^i \gamma_j^i + \sum_{ijk\ell} w_{k\ell}^{ij} \Gamma_{k\ell}^{ij} \}.$$

Since practical complete $N$-representability condition on 2-RDM is not accessible, we need practical condition on 1- and 2-RDMs. For 1-RDM, practical complete condition is known: if eigenvalue of 1-RDM (occupation number by natural orbital) are lie in $[0, 1]$, then it is $N$-representable, but for 2-RDM, such condition is not known, and we only know that some *necessary* conditions like $P$, $Q$, $G$, $T1$ and $T2'$ conditions. Explicit form of these conditions can be found in literature [5]. These necessary conditions states that $P$-matrix, $Q$-matrix, $G$-matrix, etc. are all positive semidefinite; eigenvalues of these matrices are larger than or equal to zero. Moreover, complete $N$-representability condition of 1-RDM can be restated as: given 1-RDM is $N$-representable if and only if $\gamma$ and $I - \gamma$ are positive semidifinite, where $I$ is an identity matrix.

Finally, the ground state problme using the 2-RDM as a basic variable can be formulated as:

$$\tilde{E}_{\min} = \min_{\Gamma \in \tilde{\mathcal{E}}^N} \{ \sum_{ij} v_j^i \gamma_j^i + \sum_{ijk\ell} w_{k\ell}^{ij} \Gamma_{k\ell}^{ij} \}. \tag{1}$$

where $\tilde{\mathcal{E}}^N$ is approximately $N$-representable 2-RDM which satisfies *necessary* condition:

$$\tilde{\mathcal{E}}^N = \{ \Gamma | \Gamma \text{ satisfies } P, Q, G, T1 \text{ and } T2' \text{ conditions} \}.$$

We refer such varational method as the "the RDM method".

## 2.4 Positive semidefinite programming

The definition of the standard type semidefinite programming is given by folloiwng:

$$(P) \quad \min : \Sigma_{k=1}^m c_k x_k$$
$$\text{s.t.} : \boldsymbol{X} = \Sigma_{k=1}^m \boldsymbol{F}_k x_k - \boldsymbol{F}_0, \boldsymbol{X} \succeq \boldsymbol{O},$$

where the symbol $\mathbb{S}^n$ is the space of $n \times n$ symmetric matrices. The Lagrangian dual $(D)$ of the problem $(P)$ can be derived as:

$$(D) \quad \max : \boldsymbol{F}_0 \bullet \boldsymbol{Y}$$
$$\text{s.t.} : \boldsymbol{F}_k \bullet \boldsymbol{Y} = c_k \ (k = 1, \dots, m)$$
$$\boldsymbol{Y} \succeq \boldsymbol{O}.$$

We can formulate the RDM method as the standard type semidefinite programming of huge size [3, 5]. We can use one of the implementations as a black box solver.

Table 1. Ground state energies (in differences from that of full CI) calculated by the RDM method imposing the $P$, $Q$, $G$, $T1$, $T2'$ conditions from SDPARA 7.3.2, and those obtained by CCSD(T), and Hartree-Fock. The last column shows the full CI energies. The correlation energies (0% for Hartree-Fock and 100% for full CI) in percentage are also shown in the second row.

| system | state | basis | $N$ | $\Delta E_{PQGT1T2'}$ | $\Delta E_{CCSD(T)}$ | $\Delta E_{HF}$ | $E_{FCI}$ |
|---|---|---|---|---|---|---|---|
| $NH_2^-$ | $^1A_1$ | 28 | 10 (5) | +0.000 63 | +0.008 74 | +0.141 98 | −55.624 71 |
| | | | | 100.4 | 99.55 | 100 | 0 |
| $CH_2$ | $^1A_1$ | 28 | 8 (4) | +0.000 59 | +0.005 80 | +0.100 67 | −38.962 24 |
| | | | | 100.4 | 99.42 | 100 | 0 |
| $NH_3$ | $^1A_1$ | 30 | 10 (5) | +0.000 49 | +0.007 46 | +0.128 75 | −56.304 89 |
| | | | | 100.4 | 99.62 | 100 | 0 |
| $CH_3$ | $^2A_2''$ | 30 | 9 (5) | +0.000 31 | +0.004 01 | +0.094 54 | −39.644 14 |
| | | | | 100.3 | 99.67 | 100 | 0 |
| $C_2$ | $^1\Sigma_g^+$ | 36 | 12 (6) 1 | +0.000 39 | +0.055 98 | +0.285 66 | −75.642 11 |
| | | | | 101.2 | 99.86 | 100 | 0 |

## 3 Results and Conclusion

We showed the outline of the RDM method with applications to molecular systems. Some feature of this method are: (i) it is an *ab initio* method, which is rigorously the same as the Schrödinger equation for the ground state; (ii) the number of variables is always four, regardless of the size of the system. The major obstacle for this method is the fundamentally difficulty of obtaining the complete $N$-representability conditions for the 2-RDM; therefore we used approximate ones: $P$, $Q$, $G$, $T1$ and $T2'$. The considered problem becomes a semidefinite programming problem and we presented results for $NH_2^-$, $CH_2$, $NH_3$, $C_2$, $CH_3$, in Table 1 using a supercomputer with a highly efficient semidefinite programming solver, SDPARA. We obtained fairly good energies comprable to CCSD(T).

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