Optimize energy in the space of natural orbitals

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A Lagrange function is proposed to optimize the energy directly in the space of natural orbitals. The idea is to build the constraint on the off-diagonal elements of the one-matrix into the function. We demonstrate the method for the system of three electrons in six orbitals. The method provides an alternative to the reduced density matrix functional.

The one-particle reduced density matrix is defined as

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_{ij} \gamma_{ij}\phi_i^*(\mathbf{x})\phi_j(\mathbf{x}')$$
$$\gamma_{ij} = \langle\Psi|a_i^\dagger a_j|\Psi\rangle \quad (1)$$

where $a_i^\dagger$ and a_j are the creation and annihilation operators. It has a spectral expansion

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_i n_i\chi_i^*(\mathbf{x})\chi_i(\mathbf{x}') \quad (2)$$

The eigenvectors $\{\chi_i\}$ are called the natural orbitals, and the eigenvalues $\{n_i\}$ are their occupation numbers.

In the bases of natural orbitals, the energy corresponding to a CI wave function $\Psi = \sum_k c_k\Psi_k$ has the form

$$E = Z + \sum_i n_i h_{ii} + \tfrac{1}{2}\sum_{ijkl}\Gamma_{ij,kl}\langle ij|kl\rangle \quad (3)$$

where Z is the nuclear energy, h_{ii} are the one-electron integrals, and $\langle ij|kl\rangle$ are the two-electron integrals.

$\Gamma_{ij,kl}$ are the matrix elements of the two-particle reduced density matrix. In the reduced density matrix functional theory, one tries to model $\Gamma_{ij,kl}$ as a functional of γ_{ij} or $\{n_i,\chi_i\}$. While the exact reduced density matrix functional is difficult to derive, one can always define a Lagrange function

$$\begin{aligned} L = {} & Z + \sum_i n_i h_{ii} + \tfrac{1}{2}\sum_{ijkl}\Gamma_{ij,kl}\langle ij|kl\rangle \\ & + \lambda(\sum_i c_i^2 - 1) + \sum_{i\neq j}\lambda_{ij}\gamma_{ij} \\ & + \sum_{ij}\Lambda_{ij}((\chi_i,\chi_j) - \delta_{ij}) \end{aligned} \quad (4)$$

Here, $\sum_i c_i^2 - 1$ constrain the normalization of the wave function, othonormal relations of the natural orbitals are constrained by Λ_{ij}, and the off-diagonal elements of one-matrix are constrained to $\gamma_{ij} = 0$. The variational parameters are CI coefficients c_i, Lagrangian multipliers, and the expansion coefficients contained in the molecular natural orbitals as a linear combination of atomic orbitals (basis functions), $\chi_i(x) = \sum_m c_{im}\phi_m(x)$. For calculations in real space, both the one-matrix and the overlap matrix $S_{ij} = (\chi_i,\chi_j)$ are symmetric, the indexes for λ_{ij} can be reduced to $i < j$, and Λ_{ij} can also be redued to $i \leqslant j$. One may choose to optimize the CI coefficients c_i and the orbital expansion coefficients c_{im} separately, as in the multi-configuration self-consistent method(MCSCF), we can also solve all the varational paramenters simultaneously using a nonlinear algorithm such as the "Trust region" method.

For the system of three electrons in six orbitals, the full CI wave function is 20 configurations,

$$\begin{aligned} \Psi = {} & c_1|123| + c_2|124| + c_3|125| + c_4|126| + c_5|134| \\ & + c_6|135| + c_7|136| + c_8|145| + c_9|146| + c_{10}|156| \\ & + c_{11}|234| + c_{12}|235| + c_{13}|236| + c_{14}|245| \\ & + c_{15}|246| + c_{16}|256| + c_{17}|345| + c_{18}|346| \\ & + c_{19}|356| + c_{20}|456| \end{aligned} \quad (5)$$

Here, $|123|$ etc. are normalized Slate determinant. Applying the $a_i^\dagger a_j$ to the full CI wave function, one obtains the off-diagonal elements γ_{ij},

$$\begin{aligned} \gamma_{12} &= c_5c_{11} + c_6c_{12} + c_7c_{13} + c_8c_{14} + c_9c_{15} + c_{10}c_{16} \\ \gamma_{13} &= -c_2c_{11} - c_3c_{12} - c_4c_{13} + c_8c_{17} + c_9c_{18} + c_{10}c_{19} \\ \gamma_{14} &= c_1c_{11} - c_3c_{14} - c_4c_{15} - c_6c_{17} - c_7c_{18} + c_{10}c_{20} \\ \gamma_{15} &= c_1c_{12} + c_2c_{14} - c_4c_{16} + c_5c_{17} - c_7c_{19} - c_9c_{20} \\ \gamma_{16} &= c_1c_{13} + c_2c_{15} + c_3c_{16} + c_5c_{18} + c_6c_{19} + c_8c_{20} \\ \gamma_{23} &= c_2c_5 + c_3c_6 + c_4c_7 + c_{14}c_{17} + c_{15}c_{18} + c_{16}c_{19} \\ \gamma_{24} &= -c_1c_5 + c_3c_8 + c_4c_9 - c_{12}c_{17} - c_{13}c_{18} + c_{16}c_{20} \\ \gamma_{25} &= -c_1c_6 - c_2c_8 + c_4c_{10} + c_{11}c_{17} - c_{13}c_{19} - c_{15}c_{20} \\ \gamma_{26} &= -c_1c_7 - c_2c_9 - c_3c_{10} + c_{11}c_{18} + c_{12}c_{19} + c_{14}c_{20} \\ \gamma_{34} &= c_1c_2 + c_6c_8 + c_7c_9 + c_{12}c_{14} + c_{13}c_{15} + c_{19}c_{20} \\ \gamma_{35} &= c_1c_3 - c_5c_8 + c_7c_{10} - c_{11}c_{14} + c_{13}c_{16} - c_{18}c_{20} \\ \gamma_{36} &= c_1c_4 - c_5c_9 - c_6c_{10} - c_{11}c_{15} - c_{12}c_{16} + c_{17}c_{20} \\ \gamma_{45} &= c_2c_3 + c_5c_6 + c_9c_{10} + c_{11}c_{12} + c_{15}c_{16} + c_{18}c_{19} \\ \gamma_{46} &= c_2c_4 + c_5c_7 - c_8c_{10} + c_{11}c_{13} - c_{14}c_{16} - c_{17}c_{19} \\ \gamma_{56} &= c_3c_4 + c_6c_7 + c_8c_9 + c_{12}c_{13} + c_{14}c_{15} + c_{17}c_{18} \end{aligned} \quad (6)$$

and the diagonal elements $\gamma_{ii} = n_i$

$$\begin{aligned} n_1 &= c_1^2 + c_2^2 + c_3^2 + c_4^2 + c_5^2 + c_6^2 + c_7^2 + c_8^2 + c_9^2 + c_{10}^2 \\ n_2 &= c_1^2 + c_2^2 + c_3^2 + c_4^2 + c_{11}^2 + c_{12}^2 + c_{13}^2 + c_{14}^2 + c_{15}^2 + c_{16}^2 \\ n_3 &= c_1^2 + c_5^2 + c_6^2 + c_7^2 + c_{11}^2 + c_{12}^2 + c_{13}^2 + c_{17}^2 + c_{18}^2 + c_{19}^2 \\ n_4 &= c_2^2 + c_5^2 + c_8^2 + c_9^2 + c_{11}^2 + c_{14}^2 + c_{15}^2 + c_{17}^2 + c_{18}^2 + c_{20}^2 \\ n_5 &= c_3^2 + c_6^2 + c_8^2 + c_{10}^2 + c_{12}^2 + c_{14}^2 + c_{16}^2 + c_{17}^2 + c_{19}^2 + c_{20}^2 \\ n_6 &= c_4^2 + c_7^2 + c_9^2 + c_{10}^2 + c_{13}^2 + c_{15}^2 + c_{16}^2 + c_{18}^2 + c_{19}^2 \\ & + c_{20}^2 \end{aligned} \quad (7)$$

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Using the Laplace theorem for decomposition of determinant, the wave function reduce to

$$\Psi = \sum_i \frac{1}{\sqrt{3}} g_i \chi_i \tag{8}$$

where

$$\begin{aligned}
g_1 &= c_1|23| + c_2|24| + c_3|25| + c_4|26| + c_5|34| \\
&\quad + c_6|35| + c_7|36| + c_8|45| + c_9|46| + c_{10}|56| \\
g_2 &= -c_1|13| - c_2|14| - c_3|15| - c_4|16| + c_{11}|34| \\
&\quad + c_{12}|35| + c_{13}|36| + c_{14}|45| + c_{15}|46| + c_{16}|56| \\
g_3 &= c_1|12| - c_5|14| - c_6|15| - c_7|16| - c_{11}|24| \\
&\quad - c_{12}|25| - c_{13}|26| + c_{17}|45| + c_{18}|46| + c_{19}|56| \\
g_4 &= c_2|12| + c_5|13| - c_8|15| - c_9|16| + c_{11}|23| \\
&\quad - c_{14}|25| - c_{15}|26| - c_{17}|35| - c_{18}|36| + c_{20}|56| \\
g_5 &= c_3|12| + c_6|13| + c_8|14| - c_{10}|16| + c_{12}|23| \\
&\quad + c_{14}|24| - c_{16}|26| + c_{17}|34| - c_{19}|36| - c_{20}|46| \\
g_6 &= c_4|12| + c_7|13| + c_9|14| + c_{10}|15| + c_{13}|23| \\
&\quad + c_{15}|24| + c_{16}|25| + c_{18}|34| + c_{19}|35| + c_{20}|45|
\end{aligned} \tag{9}$$

Here $|ij| = \frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1))$ are the normalized two-electron Slater determinants. It can be shown that the inner product of g_i satisfies $(g_i, g_j) = \gamma_{ij}$. So when the off-diagonal elements of γ_{ij} are zero, g_i are othogonal to each other. The normalized vectors $g_i/\sqrt{n_i}$ form the eigenvectors of the two-matrix, which can be proved by

$$\begin{aligned}
\Gamma(x_1, x_2; x_1', x_2') &= \binom{3}{2} \int \Psi(123)^* \Psi(1'2'3) dx_3 \\
&= \sum_i g_i^*(x_1, x_2) g_i(x_1', x_2') \\
&= \sum_i n_i \frac{g_i^*(x_1, x_2)}{\sqrt{n_i}} \frac{g_i(x_1', x_2')}{\sqrt{n_i}}
\end{aligned} \tag{10}$$

The energy then reduces to

$$E = Z + \sum_i h_{ii} n_i + \sum_i \langle g_i | g_i \rangle \tag{11}$$

The Euler equations for the CI coefficients can be reduced from $\partial L_1/\partial c_i = 0$. For example, $\partial L_1/\partial c_1 = 0$ leads to

$$\begin{aligned}
&c_1(h_{11} + h_{22} + h_{33}) + \langle |23||g_1\rangle - \langle |13||g_2\rangle + \langle |12||g_3\rangle \\
&+ \lambda c_1 + \lambda_{14} c_{11} + \lambda_{15} c_{12} + \lambda_{16} c_{13} - \lambda_{24} c_5 \\
&- \lambda_{25} c_6 - \lambda_{26} c_7 + \lambda_{34} c_2 + \lambda_{35} c_3 + \lambda_{36} c_4 = 0
\end{aligned} \tag{12}$$

For the 3-6 system, there are 20 equations from $\partial L_1/\partial c_i = 0$, one equation for normalization, and 15 equations for off-diagonal elements $\gamma_{ij} = 0$, 36 equations from $\partial L_2/\partial c_{im} = 0$ and 21 equations from $\partial L_2/\partial \Lambda_{ij} = 0$. The derivatives can be obtained by symbolic manipulation using the Mathematica software. Altogether there are 93 equations to be solved simultaneously.

As a test, we calculate the system of three H atoms located on the corners of an arbitrary triangle. For example, we let the atoms localte at (-0.5, 0), (0.5, 0), and $(0.1, \sqrt{3}/2)$ (in Å), respectively. The 6-31G basis set is selected. Table 1 shows the CI coefficients. It is to be noted that only 8 configurations survive with nonzero CI coefficients. From the CI coefficients, one obtains n_1=0.999584404958494, n_2=0.999505521653916, n_3=0.999435179299455, n_4=0.000564820700546, n_5=0.000494478346084, n_6=0.000415595041506, which confirms Borland and Dennis's conditions: $n_1 + n_6 = 1, n_2 + n_5 = 1, n_3 + n_4 = 1, n_5 + n_6 - n_4 \geq 0$.

Table I. CI coefficients obtained by the Lagrange method for H_3 with a geometry speficied in the text.

c_1	0.999631233129409
c_2	-0.000004308460053
c_3	-0.000000000000000
c_4	-0.000000000000000
c_5	-0.000000000000000
c_6	0.000005050534641
c_7	0.000000000000000
c_8	0.017938859122051
c_9	-0.000000000000000
c_{10}	-0.000000000000000
c_{11}	0.000000000000000
c_{12}	-0.000000000000000
c_{13}	-0.000005770289517
c_{14}	0.000000000000000
c_{15}	-0.015585870339354
c_{16}	-0.000000000000000
c_{17}	0.000000000000000
c_{18}	-0.000000000000000
c_{19}	0.013136856276450
c_{20}	0.000314103719736