Direct Calculation of Natural Orbitals of Two-Electron Systems

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A new method is proposed, which allows for the determination of the ground state energy and the natural orbitals (NO's) of a two-electron system directly and simultaneously. The basis for this calculation is a system of integrodifferential-equations, which defines those NO's.

1. Introduction

Natural orbitals of two-electron systems are of new interest since they have been used successfully in the PNO–CI-procedure [1]. As is wellknown, the definition and the first evaluation of the NO's goes back to Löwdin [2]. Thereafter several indirect and direct methods, i.e. methods with or without knowledge of the wavefunction, for the calculation of the NO's have been given, cf. [3], [4], [5], [6] and others.

In this paper a new method is proposed, which allows to calculate the NO's immediately from the system of integrodifferential equations defining the NO's. The basic idea is the use of a gradient method to minimize a certain quadratic functional in a Hilbertspace. It is shown that the solution of this “Extremal problem” is equivalent to the determination of the NO's.

Remark: The method was developed to determine natural nuclear and electronic orbitals (“non-Born-Oppenheimer orbitals”) directly; this will be shown in a subsequent paper. Such orbitals were proposed by Bishop and Cheung [7] and calculated by an indirect procedure, requiring the knowledge of the complete wavefunction.

2. The Calculation of the NO’s

The Hamiltonian \( H \) of a two-electron system may be given in the usual form

\[
H = h(1) + h(2) + g(1, 2)
\]

with the well known NO-expansion of the (singlet) ground-state eigenfunction \( \psi \) as

\[
\psi(1, 2) = \sum_i c_i \chi_i(1) \chi_i(2), \quad (\chi_i | \chi_j) = \delta_{ij}. 
\]

Independent variation [3] of the energy

\[
E = 2 \sum_{i=1}^n c_i^2 h_{ii} + \sum_{i,j} c_i c_j K_{ij},
\]

\[
h_{ij} = (\chi_i | h \chi_i), \quad K_{ij} = (\chi_i | g \chi_j)
\]

with respect to the \( \chi_j = \chi_j^{(n)} \) and the \( c_i = c_i^{(n)} \) limited to a \( n \)-dimensional subspace yields the system of integrodifferential equations

\[
c_i^2 h_{ii} + \sum_{j=1}^n c_i c_j K_{ij} = \sum_{j=1}^n \lambda_{ij} \chi_j, \quad (i = 1, \ldots, n),
\]

\[
2 c_i h_{ii} + \sum_{j=1}^n c_j K_{ij} = E c_i,
\]

\[
(\chi_i | \chi_j) = \delta_{ij}, \quad (i, j = 1, \ldots, n)
\]

with the usual definition of the exchange operator

\[
K_{ij} = (\int \chi_i(2) g(1, 2) \chi_j(2) d\tau_2) \chi_i(1)
\]

and the Lagrange parameter \( \lambda_{ij} = \lambda_{ji} \).

There are as many equations as unknowns, namely \( 2n \) for the \( \chi_i \) and \( c_i \); for the \( \frac{1}{2}(n^2 + n) \) Lagrange parameter \( \lambda_{ij} \) there is exactly the same number of constraints – cf. (3) – from the orthonormality of the NO's \( \chi_i \).

The solution of the system is obtained by a two step iteration procedure, decoupling the system partially. Equation (2) is used to determine \( E \) and the \( c_i \); the \( \chi_i \) are obtained from (1) under the constraints (3). The method is demonstrated for the case \( n = 2 \); an extension for \( n > 2 \) is performed analogously.

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Expansion and approximation of the $\chi_l$ with respect to the complete orthonormal system $\{\Phi_k\}$

$$\chi_l = \sum_{k=1}^{m} a_k^{l} \Phi_k, \quad (\Phi_j | \Phi_k) = \delta_{jk}$$
yields the matrix formulation of the system of integrodifferential equations above:

$$F^1_{\chi_1} = \lambda_{11} \chi_1 + \lambda_{12} \chi_2, \quad (\chi_l | \chi_l) = \delta_{ij},$$

$$F^2_{\chi_2} = \lambda_{12} \chi_1 + \lambda_{22} \chi_2, \quad (i, j = 1, 2), \quad (4)$$

$$Ac = Ec \quad (5)$$

with

$$F^i_{jk} = (\Phi_j | F^i \Phi_k),$$

$$F^i = c_i^2 h + c_i c_j K_1 + c_i c_j K_2, \quad (i = 1, 2),$$

$$A = \begin{pmatrix} 2h_{11} + K_1 & K_{12} \\ K_{12} & 2h_{22} + K_{22} \end{pmatrix},$$

$$c = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$
Table 1. Values of $E$, $F$, $a_i$, and $s_{ij}$ for three NO’s in a.u.

<table>
<thead>
<tr>
<th>$E$</th>
<th>$F$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.87886947</td>
<td>-0.94597377</td>
<td>0.99782</td>
<td>-0.06555</td>
<td>-0.00812</td>
</tr>
</tbody>
</table>


d and the integrals ($\eta = 2.5$) taken from Davis [8]. In addition to the values of the $c_i$’s, $\chi_i$’s and $E$ for \( n = 3 \) the minimal value of $F$ and the Lagrange-parameter $\lambda_{ij}$ with

$$\lambda_{ij} = \left(\chi_i / F / \chi_j\right), \quad (i, j = 1, 2, 3)$$

are calculated.

The convergence of the gradient method is rapid, only a few (about 8) iterations are required. Convergence problems as mentioned e.g. in [5] do not occur.

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