Direct Calculation of Natural Orbitals of Two-Electron Systems

Heinz Kleindienst and Kai Rossen

Institut für Physikalische Chemie, Lehrstuhl I, Universität Düsseldorf

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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

$$H = h(1) + h(2) + g(1, 2)$$

Reprint requests to Prof. Dr. H. Kleindienst, Institut für Physikalische Chemie I, Universität Düsseldorf, Universitätsstraße 1, D-4000 Düsseldorf.

with the well known NO-expansion of the (singlet) ground-state eigenfunction ψ 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

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

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

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

$$c_i^2 h \chi_i + \sum_{j=1}^n c_i c_j K_j \chi_i = \sum_{j=1}^n \lambda_{ij} \chi_j, \quad (i = 1, \dots, n), \quad (1)$$

$$2 c_i h_{ii} + \sum_{j=1}^n c_j K_{ij} = E c_i, \quad (2)$$

$$(\chi_i | \chi_j) = \delta_{ij}, \quad (i, j = 1, \dots, n) \quad (3)$$

with the usual definition of the exchange operator

$$K_j \chi_i(1) = (\int \chi_i(2) g(1, 2) \chi_j(2) d\tau_2) \chi_j(1)$$

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

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

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

$$\chi_i = \sum_{k=1}^m a_k^i \Phi_k, \quad (\Phi_j | \Phi_k) = \delta_{jk}$$

yields the matrixformulation of the system of integrodifferential equations above:

$$\begin{aligned} F^1 \chi_1 &= \lambda_{11} \chi_1 + \lambda_{12} \chi_2, \quad (\chi_i | \chi_j) = \delta_{ij}, \\ F^2 \chi_2 &= \lambda_{12} \chi_1 + \lambda_{22} \chi_2, \quad (i, j = 1, 2), \end{aligned} \quad (4)$$

$$A c = E c \quad (5)$$

with

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

$$F^i = c_1^2 h + c_1 c_1 K_1 + c_1 c_2 K_2, \quad (i = 1, 2),$$

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

$$c = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

With known values for the c_i and χ_i from a former iteration cycle the matrix A is estimated first, then E and new c_i are obtained from (5) by matrix diagonalization. With these new c_i but the old χ_i the matrices F^1 and F^2 are constructed.

New χ_i , i.e. new a_k^i , are obtained from the minimum of the quadratic form

$$\begin{aligned} F(\chi_1, \chi_2) &= (\chi_1 | F^1 \chi_1) + (\chi_2 | F^2 \chi_2) \\ &= \sum_{j,k=1}^m (F_{jk}^1 a_j^1 a_k^1 + F_{jk}^2 a_j^2 a_k^2), \end{aligned} \quad (6)$$

$$\begin{aligned} g_1 &= (\chi_1 | \chi_1) - 1 = 0, & g_3 &= (\chi_1 | \chi_2) = 0, \\ g_2 &= (\chi_2 | \chi_2) - 1 = 0, \end{aligned} \quad (7)$$

This statement follows from the fact that the determination of the χ_i from (4) is equivalent to the calculation of the minimum of the quadratic functional (6) under the constraints (7) in a $2m$ -dimensional Hilbert space. The introduction of a $2m$ -dimensional space is necessary because there are $2m$ independent variables a_i^1 and a_i^2 ($i = 1, \dots, m$) in the quadratic functional $F(\chi_1, \chi_2)$ of (6). The equivalence follows from the Euler-equations

$$\nabla F + \mu_1 \nabla g_1 + \mu_2 \nabla g_2 + \mu_3 \nabla g_3 = 0 \quad (8)$$

of the given variational problem: $\min F$ under $g_k = 0$. Equation (8) written out in full is

$$\begin{aligned} 2F^1 \chi_1 + 2\mu_1 \chi_1 + \mu_3 \chi_2 &= 0, \\ 2F^2 \chi_2 + \mu_3 \chi_1 + 2\mu_2 \chi_2 &= 0. \end{aligned} \quad (9)$$

The equivalence of (6)–(7) with (4)–(5) is given directly by (9) with

$$\mu_1 = -\lambda_{11}, \quad \mu_2 = -\lambda_{22}, \quad \mu_3 = -2\lambda_{12}.$$

For the calculation of the minimum of F under the constraints $g_k = 0$ we take advantage of the fact that the gradient ∇F is orthogonal to the tangent plane of the directions allowed by the constraints, i.e.

$$(\nabla F | \nabla g_k) = 0, \quad (k = 1, 2, 3). \quad (10)$$

The direction $z = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}$ orthogonal to the gradients of the constraints is given by

$$\begin{aligned} z_1 &= F^1 \chi_1 - (\chi_1 | F^1 \chi_1) \chi_1 \\ &\quad - \frac{1}{2} [(\chi_2 | F^1 \chi_1) + (\chi_1 | F^2 \chi_2)] \chi_2, \\ z_2 &= F^2 \chi_2 - (\chi_2 | F^2 \chi_2) \chi_2 \\ &\quad - \frac{1}{2} [(\chi_2 | F^1 \chi_1) + (\chi_1 | F^2 \chi_2)] \chi_1. \end{aligned} \quad (11)$$

This is easily verified by $(z | \nabla g_k) = 0$.

With $y_i(t) = \chi_i(t) + t z_i$, ($i = 1, 2$), $t \in \mathbb{R}$ the gradient $F(y_1(t), y_2(t))$ is varied until F is stationary, i.e. t is determined from

$$(\nabla F | z) = 0. \quad (12)$$

This yields

$$t = - \frac{(z_1 | F^1 \chi_1) + (z_2 | F^2 \chi_2)}{(z_1 | F^1 z_1) + (z_2 | F^2 z_2)}.$$

The $y_i(t)$ obtained from stationary F are orthonormalized and the whole process is performed until self consistence is reached.

For this usually good converging iteration process starting values of c_i and χ_i are needed. Because the system of integrodifferential equations for $n = 1, 2, \dots$ is solved successively we get a good approximation with $\chi_1 = \chi_{\text{HF}}$ for $n = 1$. In the case $n = 2$ we choose $c_1 < 1$, $c_2 > 0$ and $c_1^2 + c_2^2 = 1$ without further restrictions. An approximation for χ_2 is obtained from

$$F^2 \chi_2 = \lambda_{12} \chi_1 + \lambda_{22} \chi_2$$

with $\lambda_{12} = 0$, which now is of the Hartree-Fock type.

Table 1. Values of E , F , λ_{ij} and a_k^l for three NO's in a.u.

$E = -2.87886947$ $F = -0.94597377$					
$c_1 = 0.99782$		$c_2 = -0.06555$		$c_3 = -0.00812$	
$\chi_1:$	0.93463 -0.00612	-0.32385 0.00199	0.13740 -0.00072	-0.04861 0.00022	0.01729 -0.00007
$\chi_2:$	0.35429 0.01618	0.81928 -0.00497	-0.43565 0.00330	0.10008 -0.00063	-0.05606 0.00079
$\chi_3:$	-0.02596 0.12098	-0.46433 0.03037	-0.85520 0.02262	0.18170 -0.01811	0.05406 -0.00488
$\lambda_{11} =$	-0.93306	$\lambda_{12} =$	-0.02126	$\lambda_{13} =$	0.00028
$\lambda_{22} =$	-0.012413	$\lambda_{23} =$	-0.00068	$\lambda_{33} =$	-0.00051

3. Discussion of the Result

The method was tested for the He-atom in the radial-limit-approximation, with the basis ($m = 10$)

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

$$\lambda_{ij} = (\chi_i | F^j \chi_j), \quad (i, j = 1, 2, 3)$$

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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