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 from

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

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

$$\Psi(1, 2) = \sum_i c_i \chi_i(1)\, \chi_i(2)\,, \quad (\chi_i \mid \chi_j) = \delta_{ij}\,.$$

Independent variation [3] of the energy

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

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

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

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

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

$$(\chi_i \mid \chi_j) = \delta_{ij}\,, \quad (i, j = 1, \ldots, n) \tag{3}$$

with the usual definition of the exchange operator

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

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 $\frac{1}{2}(n^2 + n)$ Lagrangeparameter 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.

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

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

yields the matrixformulation of the system of integrodifferential equations above:

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

$$A\,\boldsymbol{c} = E\,\boldsymbol{c} \tag{5}$$

with

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

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

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

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

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

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

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

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 $(i=1,\ldots,m)$ in the quadratic functional $F(\chi_1,\chi_2)$ of (6). The equivalence follows from the Euler-equations

$$\nabla F + \mu_1 \nabla g_1 + \mu_2 \nabla g_2 + \mu_3 \nabla g_3 = 0 \tag{8}$$

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

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

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.

$$(\nabla F \mid \nabla g_k) = 0\,, \quad (k=1,2,3)\,. \tag{10}$$

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

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

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

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

$$(\nabla F \mid z) = 0\,. \tag{12}$$

This yields

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

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 $n=1,2,\ldots$ is solved successively we get a good approximation with $\chi_1 = \chi_{\mathrm{HF}}$ 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^i for three NO's in a.u.

$E=-2.87886947$		$F=-0.94597377$			
$c_1=0.99782$		$c_2=-0.06555$		$c_3=-0.00812$	
χ_1:	0.93463	−0.32385	0.13740	−0.04861	0.01729
	−0.00612	0.00199	−0.00072	0.00022	−0.00007
χ_2:	0.35429	0.81928	−0.43565	0.10008	−0.05606
	0.01618	−0.00497	0.00330	−0.00063	0.00079
χ_3:	−0.02596	−0.46433	−0.85520	0.18170	0.05406
	0.12098	0.03037	0.02262	−0.01811	−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

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

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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