Direct Determination of Pair Natural Orbitals

A New Method to Solve the Multi-Configuration Hartree-Fock Problem for Two-Electron Wave Functions

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A method is proposed to solve the two-electron Schrödinger equation by a rapidly converging iterative procedure. The wavefunction is obtained in terms of its NO's. The special features of the present method are:

1. Each iteration requires only the computational equivalent of a conventional Hartree-Fock iteration.

2. Within each iteration we improve simultaneously the NO's, the CI expansion coefficients and the total energy.

3. The construction of a CI matrix is never required.

We further propose simplified NO-equations the solution of which requires a small fraction of computertime only. As examples of the efficiency of these methods we report applications to the $1\,^1S$ state of He, the $1\,^1\Sigma_g^+$, $1\,^3\Sigma_u^+$ states of H_2, and IEPA, PNO-CI, and CEPA type computations on CH_4.

Key words: Pseudo natural orbitals – Pair natural orbitals

1. Introduction

It is well known that the configuration interaction (CI) expansion of a two-electron wave function $\Psi(1, 2)$ has optimal convergence properties if it is based on the natural orbitals (NO) φ_i of $\Psi[1, 2]$. This makes the NO's most suited for a CI treatment of two-electron systems. The NO's of a two-electron function which describes the behaviour of a pair of electrons of an n-electron system for $n > 2$, which will be denoted PNO's[1] in this paper, have furthermore been used with advantage in the treatment of n-electron systems. This advantage is quite obvious for the independent pair approximation (IEPA) [3, 4]. In the IEPA-PNO method [5] as well as in the related PNO-CI and CEPA schemes [6, 7] one approximates the treatment of an n-electron system by a series of two-

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[1] PNO's (Pseudo Natural Orbitals) were introduced by Edmiston and Krauss [8] as approximations to the NO's of the n-electron wavefunction with the idea of improving the rate of convergence of a CI computation. In context with the IEPA, CEPA or PNO-CI [6, 7] one considers, however, an individual set of PNO's for each pair of electrons and in this case it may be more appropriate to speak of Pair-NO's.

electron computations which are most conveniently performed in using the PNO's of the corresponding pair function. Edmiston and Krauss [8] further utilized PNO's to improve the rate of convergence of the n-electron CI calculation. This idea has since proved fruitful in a number of CI calculations (see e.g. Refs. [9, 10]).

In this work we present an efficient method for a direct determination of PNO's which actually requires less amount of computational work than a conventional Hartree-Fock (HF) computation within the same basis set. This method furthermore yields automatically the CI coefficients and the total energy of the PNO-CI wavefunction of the corresponding two-electron system and makes superfluous a final CI computation. We also present a simplification of the corresponding PNO-equations which yields good approximations to the exact PNO's (a loss of less than 1% of correlation energy) and requires little computational effort, roughly 3–5 matrix diagonalizations and matrix transformations. Examples of the effenciency of the present method and comparison with other approaches for a direct determination of PNO's are included.

2. Method

Our aim is to solve a two-electron Schrödinger equation

$$H\Psi = (h(1) + h(2) + g(1, 2))\, \Psi(1, 2) = E\Psi(1, 2) \tag{1}$$

for the spinless two-electron function Ψ. In the absence of magnetic fields, Ψ and the NO's φ_i of Ψ can always be chosen as real functions (the extension to complex Ψ or φ_i is no problem, however) and the NO expansion of Ψ then reads:

$$\text{(singlet case)} \quad \Psi(1, 2) = \sum_i d_i \varphi_i(1)\, \varphi_i(2) \tag{2}$$

$$\text{with} \qquad \langle \varphi_i | \varphi_j \rangle = \delta_{ij} \tag{3}$$

$$\text{(triplet case)} \quad \Psi(1, 2) = \sum_i d_i [\varphi_i(1)\, \varphi_i^|(2) - \varphi_i^|(1)\, \varphi_i(2)] \tag{4}$$

$$\text{with} \qquad \langle \varphi_i | \varphi_j \rangle = \langle \varphi_i^| | \varphi_j^| \rangle = \delta_{ij} \text{ and } \langle \varphi_i^| | \varphi_j \rangle = 0. \tag{5}$$

[Subsequently we drop the argument and simply write $\varphi_i \varphi_j$ instead of $\varphi_i(1)\, \varphi_j(2)$.]

In the case of a true two-electron system h is simply the one-electron part of the total Hamiltonian, whereas h is an effective one-electron operator if we are dealing with the PNO's of an n-electron system for $n > 2$ (see e.g. Refs. [5, 11]).

In order to solve Eqs. (1), (2) or (1), (4) under the constraints (3) or (5), respectively, we use an iterative procedure. Let Ψ_0 be an approximation to the exact wavefunction built from approximate NO's $\tilde{\varphi}_i$ with approximate CI coefficients $\tilde{d}_i$. We now improve Ψ_0 by performing a CI with the trial function

$$\tilde{\Psi} = \Psi_0 + \sum_{i,j} c_{ij} \tilde{\varphi}_i \tilde{\varphi}_j. \tag{6}$$

As the $\varphi_i \varphi_j$ form a linearly independent basis set the c_{ij} are uniquely determined by $\tilde{\Psi}$ and Ψ_0. If $\tilde{\Psi}$ is determined only up to an arbitrary normalization constant, then the c_{ij} depend, of course, on $\langle \tilde{\Psi} | \tilde{\Psi} \rangle$.

The basic idea is now to introduce some simplifications into the CI equations for the trial function $\tilde{\Psi}$ in order to obtain a simple system of equations for the c_{ij}. After the c_{ij} are determined one transformes $\tilde{\Psi}$ into its PNO expansion and uses this improved $\tilde{\Psi}$ as a new approximation $\Psi_0 = \tilde{\Psi}$. Since the CI equation for (6) is solved only approximately, an iterative procedure is necessary to obtain the exact d_i and φ_i. This procedure usually converges within 7 iterations.

It furthermore has to be shown that the wavefunction and energy obtained in this way solve the Schrödinger equation (1), i.e. that the approximations introduced do not affect the converged solutions Ψ and E.

3. Approximate Equations for c_{ij}

Variation of the expectation value of the trial function as given in Eq. (6)

$$
E = \frac{\langle \tilde{\Psi} |H| \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} = \Big[\langle \Psi_0 |H| \Psi_0 \rangle + 2 \sum_{i,j} c_{ij} \langle \Psi_0 |H| \tilde{\varphi}_i \tilde{\varphi}_j \rangle
$$
$$
+ \sum_{i,j,k,l,} c_{ij} c_{kl} \langle \tilde{\varphi}_i \tilde{\varphi}_j |H| \tilde{\varphi}_k \tilde{\varphi}_l \rangle \Big] \Big/ \sum_{i,j} (c_{ij} + \tilde{d}_i \delta_{ij})^2
$$

with respect to the c_{ij} leads to the following set of equations:

$$
\langle \Psi_0 |H| \tilde{\varphi}_i \tilde{\varphi}_j \rangle + \sum_{k,l} c_{kl} \langle \tilde{\varphi}_i \tilde{\varphi}_j |H| \tilde{\varphi}_k \tilde{\varphi}_l \rangle = E(c_{ij} + \langle \Psi_0 | \tilde{\varphi}_i \tilde{\varphi}_j \rangle) . \tag{7}
$$

In order to simplify Eqs. (7) we approximate the two-electron integrals $\left\langle \tilde{\varphi}_i \tilde{\varphi}_j \left| \frac{1}{r_{12}} \right| \tilde{\varphi}_k \tilde{\varphi}_l \right\rangle$ which occur in the matrix elements $\langle \tilde{\varphi}_i \tilde{\varphi}_j |H| \tilde{\varphi}_k \tilde{\varphi}_l \rangle$.

We first neglect the relatively small integrals for which $i \neq k$ and $j \neq l$. If now $i = k$ (or similarly for $j = l$) we can write

$$
\left\langle \tilde{\varphi}_i \tilde{\varphi}_j \left| \frac{1}{r_{12}} \right| \tilde{\varphi}_i \tilde{\varphi}_l \right\rangle = \langle \tilde{\varphi}_j |J_i| \tilde{\varphi}_l \rangle
$$

where J_i denotes the Coulomb potential of the charge distribution $(\varphi_i)^2$. As the PNO's are all located in the same region of space it is reasonable to assume that $J_i \approx J$ for all i, where J is an average Coulomb potential. In the actual computation we may e.g. put $J \approx J_1$ or $J \approx 1/2 \sum_i \gamma_{ii} J_i$ where γ_{ii} is the occupation number of $\tilde{\varphi}_i$. Consistent with the above considerations, we further assume that the true Coulomb type two-electron integrals can be approximated in the following way:

$$
\left\langle \tilde{\varphi}_i \tilde{\varphi}_j \left| \frac{1}{r_{12}} \right| \tilde{\varphi}_i \tilde{\varphi}_j \right\rangle \approx \langle \tilde{\varphi}_i |J| \tilde{\varphi}_i \rangle \approx q .
$$

These approximations of the two-electron integrals can be summarized in the following relationship:

$$
\left\langle \tilde{\varphi}_i \tilde{\varphi}_j \left| \frac{1}{r_{12}} \right| \tilde{\varphi}_k \tilde{\varphi}_l \right\rangle \approx \langle \tilde{\varphi}_i |J| \tilde{\varphi}_k \rangle \delta_{jl} + \langle \tilde{\varphi}_j |J| \tilde{\varphi}_l \rangle \delta_{ik} - q \delta_{ik} \delta_{jl} . \tag{8}
$$

If we insert the approximation (8) into (7) we obtain a simple matrix equation for the c_{ij} which are to be determined. If we introduce the matrices F and G (it should be noted that F_{ij} and G_{ij} are defined in terms of the approximate NO's of the respective iteration)

$$F_{ij} = \langle \tilde{\varphi}_i | h + J | \tilde{\varphi}_j \rangle , \tag{9}$$

$$G_{ij}(E) = \langle \Psi_0 | H - E | \tilde{\varphi}_i \tilde{\varphi}_j \rangle , \tag{10}$$

straightforward algebraic manipulations yield the desired matrix equation for C:

$$G(E) + CF + FC = (E + q) C . \tag{11}$$

3.1. Solution of Eq. (11)

Let us first consider Eq. (7) from which (11) was obtained. Equation (7) can be written in the form

$$\left\langle \tilde{\varphi}_i \tilde{\varphi}_j | H - E | \Psi_0 + \sum_{k,l} c_{kl} \tilde{\varphi}_k \tilde{\varphi}_l \right\rangle = 0 . \tag{7a}$$

If E is *not* an eigenvalue of H, then Eq. (7) or (7a) has the unique solution $\Sigma_{k,l} c_{kl} \tilde{\varphi}_k \tilde{\varphi}_l = - \Psi_0$, i.e. $\tilde{\Psi} = 0$. Nontrivial solutions $\tilde{\Psi} \neq 0$ exist only if E is an eigenvalue of H and in this case $\tilde{\Psi}$ is determined up to an arbitrary normalization constant. We may also consider (7a) as a system of linear equations for the c_{kl} which has to be solved under a constraint which prevents occurrence of the solution $\tilde{\Psi} = 0$, e.g.

$$\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1 , \tag{12a}$$

$$\left\langle \Psi_0 | \sum_{k,l} c_{kl} \tilde{\varphi}_k \tilde{\varphi}_l \right\rangle = 0 , \tag{12b}$$

$$c_{ij} = 0 \quad \text{for any one pair } i,j \text{ with} \quad \langle \tilde{\varphi}_i \tilde{\varphi}_j | \Psi_0 \rangle \neq 0 . \tag{12c}$$

The constrained system of equations has a solution (which is now uniquely determined) only if E is an eigenvalue of H and $\tilde{\Psi}$ the corresponding eigenfunction.

We now turn to Eq. (11). Due to the approximations introduced into (7), the system of Eqs. (11) has a unique solution $C(E)$ for arbitrary E, provided $E + q \neq f_i + f_j$ [see Eq. (16) below], where f_i denotes the eigenvalues of F. Since we may consider q as a parameter at our disposal we can always fulfill this condition. We consequently cannot uniquely determine E and C from Eq. (11). In order to make a selection of the possible solutions we could impose any of the constraints (12a–c). We have found that an even simpler procedure is quite useful in practice. Since the constraint (12c) will be fulfilled approximately if the corresponding G_{ij} vanishes, as can be inferred from Eq. (11), we determine E from the requirement that $G_{ij}(E) = 0$ for the corresponding i, j. We choose $i, j = 1,1$ for the singlet and $i, j = 2,1$ for the triplet case and thus determine E from Eq. (10):

$$\begin{aligned} E \approx \tilde{E} = \langle \Psi_0 | H | \tilde{\varphi}_1 \tilde{\varphi}_1 \rangle / \langle \Psi_0 | \tilde{\varphi}_1 \tilde{\varphi}_1 \rangle \quad \text{(singlet case)} \\ E \approx \tilde{E} = \langle \Psi_0 | H | \tilde{\varphi}_2 \tilde{\varphi}_1 \rangle / \langle \Psi_0 | \tilde{\varphi}_2 \tilde{\varphi}_1 \rangle \quad \text{(triplet case)} \end{aligned} \tag{13}$$

and then solve Eq. (11) for $E = \tilde{E}$.

It should be pointed out that the approximation (8) introduced into Eq. (7) in order to arrive at (11) as well as the approximation (13) does not affect the accuracy of the PNO's and the energy E if the iterative procedure converges. Equation (11) has the solution $C = 0$ if and only if $G = 0$ which in turn is equivalent (see Eq. 10) to

$$\langle \Psi_0 | H - E | \tilde{\varphi}_i \tilde{\varphi}_j \rangle = 0 . \tag{14}$$

Since the two-electron functions $\tilde{\varphi}_i \tilde{\varphi}_j$ form a complete set in the Hilbert space of two-electron functions, Eq. (14) means that

$$H \Psi_0 = E \Psi_0$$

i.e. Ψ_0 is an eigenfunction of H with eigenvalue E.

The solution of Eq. (11) is straightforward. Let U be a unitary matrix which diagonalizes F

$$(U^+ F U)_{ij} = f_i \delta_{ij} . \tag{15}$$

We multiply (11) from the left and right by U^+ and U, respectively, and use $U^+ U = 1$ together with (15) to obtain

$$(U^+ C U)_{ij} = (U^+ G U)_{ij} / [E + q - f_i - f_j] . \tag{16}$$

The matrix C itself is then recovered from $U^+ C U$ according to

$$C = U(U^+ C U) U^+ .$$

The computational steps to be actually performed within one iteration are as follows:

1. Construct the matrix $G_{ij} = \langle \Psi_0 | H - \tilde{E} | \tilde{\varphi}_i \tilde{\varphi}_j \rangle$.

   Let us first consider the singlet case. If we insert the explicit expression (2) for Ψ_0, we get

$$G_{ij} = \langle \tilde{\varphi}_i | K + (\tilde{d}_i + \tilde{d}_j) h | \tilde{\varphi}_j \rangle - \tilde{E} \tilde{d}_i \delta_{ij} , \tag{17}$$

$$K = \sum_l \tilde{d}_l K_l , \tag{18a}$$

where K_l denotes the exchange operator of the orbital $\tilde{\varphi}_l$:

$$\langle f | K_l | g \rangle = \int f(1) \, \tilde{\varphi}_l(1) \, \frac{1}{r_{12}} \, \tilde{\varphi}_l(2) \, g(2) \, d\tau_1 \, d\tau_2 . \tag{18b}$$

In order to get K we can interchange the construction of K_l with the summation over l, i.e. we first construct the density matrix

$$P = \sum_l \tilde{d}_l |\tilde{\varphi}_l\rangle \langle \tilde{\varphi}_l| \tag{19}$$

and then compute K from the density P. The construction of K thus requires the same computational work as the construction of a single exchange operator. In the triplet case the formula for G_{ij} is

$$G_{ij} = \langle \tilde{\varphi}_i | K^- | \tilde{\varphi}_j \rangle + \langle \Psi_0 | h(1) + h(2) - \tilde{E} | \tilde{\varphi}_i \tilde{\varphi}_j \rangle , \tag{20}$$

$$K^- = \sum_l \tilde{d}_l K_l^- . \tag{21a}$$

The explicit form of the one-electron term in (20) is somewhat lengthy but easily evaluated. The operator K^- is defined by

$$\langle f|K_l^-|g\rangle = \int f(1)\,\tilde{\varphi}_l^\rceil(1)\frac{1}{r_{12}}\,\tilde{\varphi}_l(2)\,g(2)\,d\tau_1\,d\tau_2$$

$$-\int f(1)\,\tilde{\varphi}_l(1)\frac{1}{r_{12}}\,\tilde{\varphi}_l^\rceil(2)\,g(2)\,d\tau_1\,d\tau_2$$

(21 b)

[for the definition of $\varphi_l,\varphi_l^\rceil$ see (4), (5)].

K^- is constructed analogously to K, one simply has to use

$$P = \sum \tilde{d}_l\{|\tilde{\varphi}_l\rangle\langle\tilde{\varphi}_l^\rceil| - |\tilde{\varphi}_l^\rceil\rangle\langle\tilde{\varphi}_l|\}$$

instead of (19).

2. Compute $\tilde{E}$ according to Eq. (13).

In order to test convergence we also compute the variational energy $\langle E\rangle = \langle\Psi_0|H|\Psi_0\rangle$. Inserting the operators K and K^- defined in Eqs. (18) and (21) one immediately obtains for the singlet case

$$\langle E\rangle = \sum_l \langle\tilde{\varphi}_l|\tilde{d}_l K + (\tilde{d}_l)^2\,h|\tilde{\varphi}_l\rangle,$$ (22)

and for the triplet case

$$\langle E\rangle = \sum_l \{(\tilde{d}_l)^2[\langle\tilde{\varphi}_l|h|\tilde{\varphi}_l\rangle + \langle\tilde{\varphi}_l^\rceil|h|\tilde{\varphi}_l^\rceil\rangle] + \tilde{d}_l\langle\tilde{\varphi}_l|K^-|\tilde{\varphi}_l^\rceil\rangle.$$ (23)

3. After having determined K (or K^-) and $\tilde{E}$ we set up the matrices G and F and solve Eq. (11) for C, see (16). In order to dampen possible oscillations of the iterative procedure we replace c_{ij} by

$$\frac{c_{ij}}{(A+Bc_{ij}^2)^{\frac{1}{2}}}.$$

Convergence may also be improved by considering q in Eq. (16) as a parameter at our disposal. The appropriate values for A, B and q will be given in the next section.

4. We finally renormalize $\Psi_0 + \Sigma_{ij}c_{ij}\tilde{\varphi}_i\tilde{\varphi}_j$ and write this improved wavefunction in terms of its NO's.

The most time-consuming step is usually the construction of the operator K (or K^-) defined in Eqs. (18) and (21). The computational time required for this step does not depend, however, on the number of PNO's actually taken into account. Our method thus depends little on the number of PNO's considered, since it does not require to set up a CI matrix and its diagonalization.

4. Applications

We want to demonstrate the usefulness of our procedure by computations of the ground states of He (1^1S) and H_2 $(1^1\Sigma_g^+)$ as well as the $1^3\Sigma_u^+$ state of H_2. As indications for the convergence properties of our method we list in Table 1

Table 1. NO calculations on $H_2(1^1\Sigma_g^+, 1^3\Sigma_u^+)$ and $He(1^1S)$

iteration	H_2 $1^1\Sigma_g^+$ ($r = 1.4$ a.u.)			CPU-time[c] [sec]	$1^3\Sigma_u^+$ ($r = 2.0$ a.u.)			He 1^1S		
	$-\langle E \rangle$	$-\tilde{E}$	$\|C\|$		$-\langle E \rangle$	$-\tilde{E}$	$\|C\|$	$-\langle E \rangle$	$-\tilde{E}$	$\|C\|$
2[a]	1.13319703			27	0.88979048			2.85244781		
3[b]	1.17089930	1.13319	0.199722	26	0.89668344	0.88979	0.060174	2.90085557	2.85245	0.160580
4	1.17371479	1.18297	0.050976	56	0.89682319	0.89744	0.016188	2.90297593	2.90824	0.044780
5	1.17388426	1.17160	0.011483	53	0.89682392	0.89682	0.002901	2.90318169	2.90194	0.013651
6	1.17388778	1.17410	0.001651	53	0.89682393[e]	0.89683	0.002446	2.90319575	2.90344	0.003269
7	1.17388782[d]	1.17387	0.000191	53				2.90319629	2.90316	0.000592
8								2.90319630[f]	2.90320	0.000071

[a] Diagonalization of $(h + J)$; the 1ˢᵗ iteration is a diagonalization of h.
[b] In the H_2 calculations: diagonalization of $(h + J)$.
[c] UNIVAC 1108.
[d] For comparison: Ref. [14]: 1.174475.
[e] Reference [15] (NO calculation): 0.896697, Ref. [16]: 0.897064.
[f] Reference [17] (NO calculation): 2.90322, Ref. [18]: 2.90372.
For further explanations see text.

a) the approximate energy $\tilde{E}$ [see Eq. (13)],
b) the variational energy $\langle E \rangle$ [Eqs. (22), (23)], and
c) the norm of the matrix C, i.e. $\|C\| = (\Sigma_{i,j} c_{ij}^2)^{\frac{1}{2}}$.
The details of our computations are as follows:

Basis Sets and Distances

Our basis sets consist of essentially uncontracted Gaussian type functions (for the construction of d- and f-type functions see [12]).

He (1^1S), 66 groups

> $9s$ (from Ref. [13]), contracted in the manner (3, 1, 1, 1, 1, 1, 1)
> $6p$ (exponents: 17.0, 7.5, 3.2, 1.4, 0.6, 0.25)
> $4d$ (8.2, 3.5, 1.55, 0.65)
> $3f$ (5.5, 2.2, 0.9)

$H_2(1^1\Sigma_g^+)$, $r = 1.4$ a.u., 62 groups

> $7s$ (from Ref. [13]), contracted (3, 1, 1, 1, 1)
> $3p$ (3.2, 0.9, 0.3)
> $2d$ (2.4, 0.6)
> $1f$ (1.2).

$H_2(1^3\Sigma_u^+)$ $r = 2.0$ a.u., 48 groups

> $7s$ (as above)
> $3p$ (2.1, 0.6, 0.2)
> $2d$ (1.6, 0.4).

Parameters for Optimal Convergence

There are four "parameters" in our scheme that may be used for improving the rate of convergence: A, B, q and the average potential J.

We found A and B to be of minor importance. The best choice was $B = 1$, $A = \min [2, 1 + 0.2 \times (n - 1)]$, where n counts the iterations. This choice saves one iteration at best, compared to $A = 1$.

It is not worthwhile to vary q independently of J. If P denotes the density matrix used for the construction of J (of course P is dependent on the respective choice for J) we simply take $q = Tr(PJ)$. So we are left with the problem to find a judicious choice for J. In the singlet case we choose $J = J_1$ (see preceding section). In the triplet case, however, this would not be appropriate. A possible choice seems to be $J = 0.5(J_1 - K_1 + J_2 - K_2)$, where 1 and 2 denote the two strongly occupied orbitals. It turns out, however, that it is sufficient to approximate this potential by $J = 0.6 J_1$. This last potential was employed in our triplet calculation. It nevertheless should be stressed that even with the rather poor potential $J = J_1$ convergence is achieved within 13 iterations (as compared to 7 iterations with $J = 0.6 J_1$). This stability of our method with respect to variations of J bears important implications: in order to start with the NO iterations we have to know J and q beforehand, but J is dependent on the NO's. So one could argue that J had to be computed anew after each NO-iteration. Actually the following procedure suffices (see Table 1):

1st iteration: diagonalization of h,

2nd iteration: diagonalization of $(h + J)$ (Hartree-Fock like),

3rd to last iteration: NO iterations (J is kept fixed as computed in the 2nd it.).
In the calculations on H_2 we slightly changed this scheme, i.e. we did one more
diagonalization of $(h + J)$ because in this way we saved one NO-iteration.

Computer Time Requirements

Most of our calculations were done on a UNIVAC 1108. In Table 1 we list the
CPU-times for the H_2 ground state calculation.

The total CPU-time in this case consists of:

$$\text{Integral evaluation} \approx 90\%,$$

$$\text{NO construction} \approx 10\%.$$

5. Determination of Approximate PNO's

It has been shown in the preceding sections that for a two-electron system it is
not worthwhile to perform a HF computation in order to use this approximation
as a starting point for the solution of the Schrödinger equation (1). For an n-
electron system ($n > 2$) it is, however, convenient to start with a conventional
HF computation. In order to describe the behaviour of an electron pair in the field
of the remaining $(n - 2)$ electrons one has to known, at least approximately, the
field produced by these $(n - 2)$ electrons which is usually obtained by "freezing"
these electrons in their HF-MO's. If the HF-MO's are already known one can
make further simplifications which lead to a drastic reduction of the computa-
tional work required to determine good approximations to the correct PNO's.
If the PNO's are used mainly to improve the rate of convergence of a CI treatment
[8] it is anyway sufficient to have approximate solutions of the PNO equations.
Even for other kinds of computations, like e.g. a PNO-CI or CEPA treatment
[6, 7], it is generally sufficient to obtain PNO's with an accuracy that ensures
that one looses less than about 1% of the corresponding pair correlation energy.

For the determination of approximate PNO's we start from the two-electron
HF wave function

$$\psi_{HF}(1, 2) = \varphi_a(1)\, \varphi_a(2)$$

for the "closed shell" or intrapair case. In the following we restrict ourselves to
the discussion of the intrapair case since the extension to the other cases (singlet
and triplet interpair) is obvious.
The pair function Ψ is then approximated as

$$\Psi = d_0 \psi_{HF} + \sum_i d_i \varphi_i \varphi_i \tag{24}$$

with the additional constraint

$$\langle \varphi_a | \varphi_i \rangle = 0 . \tag{25}$$

Due to the constraint (25), the pair function Ψ as given in Eq. (24) cannot be an exact eigenfunction of H [i.e. we cannot fulfill the eigenvalue Eq. (1) exactly, not even in the restricted Hilbert space spanned by the actual basis set], since Ψ does not contain single substitutions. The constraint (25) guarantees that the PNO's are orthogonal to the occupied HF-MO's which facilitates considerably a subsequent n-electron CI calculation.

In order to determine the PNO's φ_i and the CI coefficients d_0 and d_i we use the iterative procedure explained in detail in the preceding sections. The constraint(25) ist most conveniently taken care of if one expands the φ_i in terms of the virtual HF-MO's.

In order to save computer time we take advantage of the fact that $d_0 \approx 1$ whereas the remaining d_i are usually small in absolute value, and approximate the matrix elements of the operators K_l for $l > 0$ in the following way:

$$\langle \tilde{\varphi}_i | K_l | \tilde{\varphi}_j \rangle = \langle \tilde{\varphi}_i | J | \tilde{\varphi}_j \rangle \, (\delta_{il} + \delta_{jl}) - q \delta_{il} \delta_{jl} \, . \tag{26}$$

We thus neglect the matrix elements $\langle \tilde{\varphi}_i | K_l | \tilde{\varphi}_j \rangle$ if i, j and l are all different and use the identity

$$\langle \tilde{\varphi}_i | K_i | \tilde{\varphi}_j \rangle = \langle \tilde{\varphi}_i | J_i | \tilde{\varphi}_j \rangle$$

together with the approximations expressed in the relationship (8). Denoting by K_0 the exchange operator of the HF-MO φ_a under consideration, we obtain the following approximation for the matrix elements of G [for the exact expression see Eq. (17)]:

$$G_{ij} \approx \langle \tilde{\varphi}_i | \tilde{d}_0 K_0 + (\tilde{d}_i + \tilde{d}_j) (h + J) | \tilde{\varphi}_j \rangle - (\tilde{E} + q) \tilde{d}_i \delta_{ij} \, . \tag{27}$$

The use of (27) reduces the determination of the PNO's by means of the iterative procedure described above, see Eqs. (9)–(13), to simple matrix algebra. We note that the operators K_0 and $J = J_0$ (Coulomb operator of φ_a) are required anyway in a subsequent n-electron CI treatment. We have already pointed out that the most tedious step of our method is the evaluation of the operator K required to construct G, see Eq. (17). It is the advantage of the approximation (27) that we do not have to evaluate a two-electron operator in each iteration since K_0 is computed only once.

In order to see the effect of the approximations expressed in Eqs. (24)–(26), we may e.g. compare the exact energy (exact within the chosen basis set) obtained for H_2 with the one computed in employing the above simplifications, see Table 2. The loss of $\approx 0.6\%$ of the corresponding correlation energy is in fact an excellent justification for our simplified method. In Table 3 we further compare our method with two other existing procedures [6, 19] for a direct determination of approximate PNO's. As the other procedures have been described and discussed in the literature we shall not comment on them.

The individual pair correlation energies computed by Meyer are between 1% and 5% poorer as compared to the present work, whereas the corresponding difference is 1.0–1.7% for the total valence shell correlation energy within the PNO-CI or CEPA. Some care is recommended, however, in comparing the results of Meyer with those obtained in this paper, since the construction of p- and d-type AO's is slightly different.

Table 2. Comparison of the exact and approximate procedure for determination of PNO's

Molecule/state	Basis set	$-(E_{exact} - E_{HF})$[a]	$-(E_{approx.} - E_{HF})$[a]	Error in %
$H_2\ 1\,^1\Sigma_g^+$	$5s, 3p$	0.0385413	0.0382775	0.7
	$5s, 3p, 2d$	0.0401115	0.0396859	1.1[b]
He $1\,^1S$	$7s, 6p$	0.0388143	0.0386421	0.45
	$7s, 6p, 4d$	0.0410352	0.0407270	0.75[b]

[a] E_{HF} means the Hartree-Fock energy within the given basis set.

[b] These relatively large errors are partly due to the fact that our program for the determination of approximate PNO's takes at most 30 NO's into account. In calculations on larger molecules this means no loss of accuracy because there is no possibility of employing such extended basis sets, i.e. in general the higher PNO's do not contribute significantly to the correlation energy. If we take into account an estimate for the importance of the higher PNO's, we arrive at an error estimate of 0.5–0.7%.

Table 3. Comparison of CH_4 valence shell correlation energies as obtained by different methods[a]

	Pair[b]	Ref. [6]	Ref. [19]	This work	Improvement in % relative to	
					[6]	[19]
Localized	bb	0.03019	0.03014	0.03045	0.9	1.0
	$bb'S$	0.00588	0.00605	0.00620	5.0	2.5
	$bb'T$	0.00989	0.01018	0.01023	3.4	0.5
	IEPA	0.21538	0.21801	0.22032	2.3	1.1
	PNO-CI	0.17890		0.18077	1.0	
	CEPA	0.18969		0.19182	1.1	
Canonical	IEPA	0.20265		0.20560	1.5	
	PNO-CI	0.18040		0.18330	1.6	
	CEPA	0.19197		0.19523	1.7	

[a] Basis set denoted A' in Ref. [6] was used, containing a total of 47 groups.

[b] bb denotes an intrabond, $bb'S$ ans T a singlet and triplet interbond correlation energy, respectively. For the precise meaning of IEPA, PNO-CI, CEPA see [6, 7],

As regards the efficiency of the respective methods we can directly compare the present one with the "one PNO at a time method" [19], since both computations were performed on the UNIVAC 1108 using double precision arithmetic. The determination of the NO's for a IEPA treatment (one intrabond and one singlet and triplet interbond case) required 14 min (CPU-time) with the "one PNO at a time" method and 2 min with the present one. These timings are valid if the operators h (in general the effective one-electron operator) and K_0 [see Eq. (27)], which are required anyway, have already been constructed. Actually, the new method yields all PNO's in the same time in which "one PNO at a time" yields about 3 PNO's.

The present work thus confirms qualitatively the statement of Meyer that his method to determine approximate PNO's guarantees an accuracy of roughly 1% in the total correlation energy.

Although a gain of $1-2\%$ of correlation energy may not be of much importance, in most applications it means a reduction of the energy error (due to the approximations made in the determination of PNO's) by roughly a factor $1/3$. This estimate is deduced from the results of Tables 2 and 3.

We therefore expect the present method to yield more consistent and reliable results.

6. Conclusions

We have developed and applied an iterative Hartree-Fock like method to solve exactly the two-electron Schrödinger equation for a given basis set without ever setting up a CI matrix. In all test cases the energy had converged to 10^{-7} a.u. within 8 iterations or even less. The most time consuming step in each iteration is the construction of the K matrix explained in Eq. (18) which is about as expensive as a conventional HF iteration within the same basis set. Our method appears to be an order of magnitude faster than any other procedure to determine directly PNO's and two-electron correlation energies. All methods proposed so far for this purpose [6, 11, 17, 20–23] require the repeated computation of the complete CI matrix in an iterative scheme. The computer time needed to set up the PNO-CI matrix is almost precisely N times as large as the time for the computation of a single exchange operator, where N is the number of PNO's taken into account (if we disregard utilization of symmetry).

Since our method requires only the equivalent of 8 HF iterations, we can hardly imagine a considerably faster procedure.

Our method to determine approximate PNO's, see Section 5, has proved useful during the last 20 months in a number of correlation energy computations of n-electron systems with the IEPA, PNO-CI, and CEPA type treatments [7, 24, 25].

References

1. Hurley, A. C., Lennard-Jones, J., Pople, J. A.: Proc. Soc. (London A **220**, 446 (1953)
2. Löwdin, P.-O., Shull, H.: Phys. Rev. **101**, 1730 (1956);
   Shull, H.: J. Chem. Phys. **30**, 1405 (1959)
3. Nesbet, R. K.: Advan. Chem. Phys. **14**, 1 (1969)
4. Sinanoğlu, O.: Advan. Chem. Phys. **14**, 237 (1969)
5. Jungen, M., Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **17**, 339 (1970)
6. Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
7. a) Ahlrichs, R., Lischka, H., Staemmler, V., Kutzelnigg, W.: J. Chem. Phys., in press
   b) Ahlrichs, R., Driessler, F., Lischka, H., Staemmler, V., Kutzelnigg, W.: J. Chem. Phys., in press
8. Edmiston, C., Krauss, M.: J. Chem. Phys. **42**, 1119 (1965); **45**, 1833 (1966)
9. Weiss, A. W.: Phys. Rev. **162**, 71 (1967)
10. Sanders, W. A., Krauss, M.: J. Res. Natl. Bur. Stand. **72** A, 85 (1968)
11. Palting, P.: Intern. J. Quantum Chem. **7**, 717 (1973)
12. Driessler, F., Ahlrichs, R.: Chem. Phys. Letters **23**, 571 (1973)
13. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)

14. Kolos, W., Wolniewicz, L.: J. Chem. Phys. **49**, 404 (1968)
15. Rothenberg, S., Davidson, E. R.: J. Chem. Phys. **45**, 2560 (1966)
16. Kolos, W., Wolniewicz, L.: J. Chem. Phys. **43**, 2499 (1965)
17. Ahlrichs, R., Kutzelnigg, W., Bingel, W. A.: Theoret. Chim. Acta (Berl.) **5**, 289 (1966)
18. Pekeris, C. L.: Phys. Rev. **112**, 1649 (1958)
19. a) Kutzelnigg, W.: Theoret. Chim. Acta (Berl.) **1**, 327 (1963)
    b) Ahlrichs, R., Kutzelnigg, W.: J. Chem. Phys. **48**, 1819 (1968)
20. Das, G., Wahl, A. C.: J. Chem. Phys. **44**, 87 (1966)
21. Sabelli, N., Hinze, J.: J. Chem. Phys. **50**, 684 (1969)
22. Reid, C. E., Öhrn, Y.: Rev. Mod. Phys. **35**, 445 (1963)
23. Grein, F., Chang, T. C.: Chem. Phys. Letters **12**, 44 (1971)
24. Ahlrichs, R.: Theoret. Chim. Acta (Berl.), in press
25. Ahlrichs, R., Keil, F.: J. Am. Chem. Soc., in press

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