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Iterative Natural Orbitals for Configuration Interaction Using Perturbation Theory

Jawed A. Jafri

Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973, USA

Jerry L. Whitten

Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, N.Y. 11794, USA

Approximate natural orbitals are determined iteratively from CI expansions constructed using first-order perturbation theory in order to investigate the possibility of eliminating the complete transformation of MO integrals on each iteration. Results on LiH and H_2O are compared with fully variationally determined NO's to assess questions of convergence.

Key words: Natural orbitals for CI, iterative ~ - Configuration interaction, iterative NO's for ~

1. Introduction

The method of configuration interaction (CI) provides a well-defined variational procedure for including electronic correlation in many electron systems. Its difficulty lies in the rapid increase in the number of molecular orbital integrals and the number of configurations with an increase in the number of molecular orbitals. Two simplifying steps are usually taken: 1) The set of molecular orbitals is kept small, and 2) only the more important configurations are retained in the expansion.

The set of molecular orbitals is generally obtained from some reference calculation, such as a single or multideterminant SCF treatment to determine the primary orbitals, and a transformation of the remainder of the virtual orbitals to increase their individual effectiveness and thereby to enhance convergence of the CI expansion, e.g., see exchange maximizations or positive ion optimization transformations [1, 2].

Another type of transformation, *in situ* in the CI procedure, involves the use of natural orbitals to construct the configurations; see discussions of convergence and reviews of the general theory by Löwdin [3], Kutzelnigg [4], Davidson [5], Bender [6], and Schaefer [7]. One way to proceed, discussed by Bender and Davidson [8], is to determine approximate natural orbitals by the diagonalization of the first-order density matrix constructed from a given CI wave function.

Refinements can be accomplished iteratively in the Bender and Davidson scheme [8]. Here, an initial CI wave function is chosen by some method and natural orbitals are constructed from that wave function by setting up and diagonalizing the density matrix. The natural orbitals thus obtained are used to generate configurations in the next iteration, a new CI wave function is constructed from these configurations and is used subsequently to set up the first-order density matrix and to obtain new natural orbitals. The process is repeated until energy convergence is achieved, and the density matrix remains sufficiently close to a diagonal form. The difficulty in the iterative technique for large systems is the transformation of integrals after each step, and thus a rigorous execution of the prescription becomes very time consuming.

In this paper we consider a simplification of the problem of determining approximate natural orbitals iteratively from CI expansions. The idea is very simple: in all intermediate constructions, a precise variational treatment is abandoned in favor of using first-order perturbation theory (of the wave function) to construct approximate CI expansions [9]. These expansions are used to generate the density matrices which are then diagonalized to determine natural orbitals. This means that the types of matrix elements which appear are well defined and require only a small subset of the total number of MO integrals for their construction. Algorithms are available for the generation of a subset of MO integrals without requiring a transformation of all MO integrals. Finally in the last iteration, the CI problem is treated in a fully variational and conventional manner. Closely related work is due to Siu and Hayes [9] who also used first-order perturbation theory to treat CI expansions to determine approximate natural orbitals which are then used to generate final CI expansions, and by Hay [10] using the B_k method of Shavitt [11] to determine approximate MO's. The present work can be regarded as an iterative application of the Siu and Hayes scheme. See also work on the determination of pseudo-NO's (or pair-NO's) using perturbation theory by Meyer[12], and Ahlrichs and Driessler [13].

The molecules LiH and H_2O are used for illustration and calculated natural orbitals and energies are compared with results from variational CI treatments.

2. Theory

The first-order density matrix for a given antisymmetric wave function ψ is defined as

$$\gamma(1'|1) = N \int \psi^*(1', 2, 3, \ldots N)\psi(1, 2, 3, \ldots N) dx_2, dx_3, \ldots dx_N.$$

For a configuration interaction wave function (normalized)

$$\psi = \sum_k C_k \psi_k$$

where a single set of orthonormal spin orbitals, $\{u_i\}$, is used to construct Slater determinants,

$$\psi_k(1, 2, \ldots N) = (N!)^{-1/2} \mathscr{A} (u_1^k(1) u_2^k(2) \ldots u_N^k(N))$$

$$\gamma(1'|1) = \sum_k \sum_l C_k^* C_l \int \psi_k^*(1', 2, \ldots N) \psi_l(1, 2, \ldots N) dx_2, dx_3 \ldots dx_N.$$

Diagonalization of the Hermitian matrix γ can be accomplished by a unitary transformation, $S^{\dagger}\gamma S = n$ (diagonal matrix), and a new set of spin orbitals χ_i (called natural spin orbitals) can be defined by

$$\chi_i = \sum_m u_m S_{mi}$$

such that

$$\gamma(1'|1) = \sum_k n_k \chi_k^*(1')\chi_k(1)$$

where the occupation numbers, n_k, satisfy $0 \leqslant n_k \leqslant 1$ and $\Sigma_k n_k = N$.

If the molecular orbitals are expanded in terms of a basis $\{f_k\}$

$$u_i = \sum_k a_{ik} f_k$$

the natural orbitals can be expressed as

$$\chi_i = \sum_m \sum_k a_{mk} s_{mi} f_k .$$

In the present iterative scheme, we proceed as follows.

1) A choice of an initial set of molecular orbitals. Generally for the ground state these are taken to be the occupied SCF orbitals plus virtual orbitals. The latter could first be transformed to enhance convergence, e.g., by exchange maximization with the occupied set.
2) The construction of a set of configurations by promotion from the occupied to unoccupied set, including all single excitations plus selected multiple excitations. The zeroth-order description may contain several determinants in which case excitations would be performed from the major determinants.
3) Approximate solution of the mixing of configurations problem using perturbation theory (first order in the wave function).
4) Construction of the first-order density matrix and its diagonalization.
5) Repetition of the procedure using the natural orbitals as the set of molecular orbitals in 1) until the energies and orbitals converge. In the last iteration the CI problem is treated variationally.

As noted earlier, the procedure outlined is essentially that of Bender and Davidson except for the use of perturbation theory for the intermediate iterations.

The CI expansion is of the form

$$\psi = \psi^0 + \sum_{i>m} C_i \psi_i$$

where ψ^0 is a multideterminant function

$$\psi^0 = \sum_{i=1}^{m} d_i \psi_i$$

constructed from the important contributors to the state of interest. In the present case ψ^0 consists of the single determinant ground state SCF solution plus other determinants which interact strongly with the SCF solution. All single excitations are included; these configurations which can significantly affect the first-order density matrix do not interact directly with the SCF solution (Brillouin's theorem), but enter through their mixing with double excitation configurations. All other configurations were generated and selected using the procedure discussed by Whitten and Hackmeyer [14]. In this procedure a configuration is retained in the CI expansion if and only if its interaction with the zeroth-order description of the state exceeds a specified threshold, δ,

$$\frac{|\langle \psi^0 | H | \psi_k \rangle|^2}{E_k - E^0} > \delta$$

Coefficients d_i can be obtained from a simple variational calculation as in the present work, or from perturbation theory. Coefficients C_i are obtained from first-order perturbation theory, and as such are the approximate solutions of the variational secular equations,

$$C_i = \frac{\langle \psi - C_i\psi_i | H | \psi_i \rangle}{E - E_i} \approx \frac{\langle \psi^0 | H | \psi_i \rangle}{E - E_i}$$

where $E_i = \langle \psi_i | H | \psi_i \rangle$, and $E = \langle \psi^0 | H | \psi^0 \rangle$, or E could be taken as the energy of the CI expansion as in the Brillouin-Wigner theory. For $E = \langle \psi^0 | H | \psi^0 \rangle$, it should be noted that the determination of ψ does not require computation of all of the elements of the Hamiltonian matrix, and thus not all integrals over molecular orbitals are needed.

3. Results and Discussion

Calculations were performed on the LiH and H_2O molecules using the basis set and geometry given in Table 1 where the SCF results are also reported. Natural orbitals were computed using two different techniques:

a) The iterative natural orbital scheme proposed by Bender and Davidson using the occupied and all virtual orbitals from the SCF treatment of the ground state. A variational CI calculation was carried out on each iteration, selecting approximately 200 to 300 configurations for each iteration as determined using an interaction threshold, δ. Four to six iterations were required to achieve convergence for LiH and H_2O, respectively.

b) The iterative natural orbital scheme based on wave functions calculated using first-order perturbation theory for the wave-function, as discussed in the previous section. The same set of occupied and virtual orbitals as in 1) was used. Iterations were performed and the number of configurations was kept between 200 and 300 by using an appropriate interaction threshold. Variational CI calculations were then performed using the orbitals from the last iteration.

For comparison with the iterative natural orbital calculations, a conventional CI calculation was carried out based on the ground state SCF molecular orbitals. In the natural orbital and conventional CI calculations all single excitations from the doubly occupied ground state MO's were included.

The ground state SCF energy for LiH obtained in this study reported in Table 1 is slightly higher than that obtained by Bender and Davidson since the basis set employed here is not as large. Since the aim of the present work is the illustration of the technique, no effort was made to improve the basis set to achieve a lower energy. In addition,

Table 1. SCF total enegry and orbital energies of LiH and H_2O. Calculations are for the ground state equilibrium geometry

LiH[a]	Total energy: −7.97968 a.u.			
	Nuclear repulsion: 0.99502 a.u.			Electronic energy: −8.97470 a.u.
Orbital energies:	−2.4397	0.397	0.980	1.507
	−0.2955	0.455	0.980	⋮
	0.046	0.764	1.483	3.071
	0.397	0.764	1.483	49.328
H_2O[b]	Total energy: −76.04264 a.u.			
	Nuclear repulsion: 9.18711 a.u.			Electronic energy: −85.22975 a.u.
Orbital energies:	−20.5534	0.265	0.869	1.425
	−1.3458	0.348	1.127	1.454
	−0.7128	0.638	1.189	⋮
	−0.5789	0.780	1.345	3.608
	−0.5028	0.809	1.392	45.134

[a] Coordinates: Li(0, 0, 0), H(0, 0, 3.015), in a.u.
Basis: 18 basis function groups.
Li s_1, s_2, s_3, s_4 (10 Gaussians/4 groups):
p_1, p_2 (2 Gaussians/2 groups, x, y, z/exponents 0.5, 1.0).
H s_1, s_2 (4 Gaussians/2 groups)
p_1, p_2 (2 Gaussigns/2 groups, x, y, z/exponents 0.2, 0.4)
Basis group exponents and coefficients are given in Ref. [14].

[b] Coordinates O(0, 0, 0), H(0, ± 1.431, 1.109), in a.u.
Basis: 23 basis function groups.
O s_1, s_2, s_3 (9 Gaussians/3 groups); p_1, p_2 (5 Gaussians/2 groups)
d_1, d_2 (2 Gaussians/2 groups/exponents 1.322, 0.3917)
H s_1, s_2 (4 Gaussians/2 groups)
p_1 (2 Gaussians/1 group, y, z)
Basis group exponents and coefficients are given in Ref. [15].

the choice of p basis, while suitable for introducing σ polarization, is appropriate only for correlation of the valence shell. The results of iterative natural orbital calculations are reported in Table 2. In the case of the variational CI calculations, two series of calculations are reported: series A, in which single excitations and double excitations of the type $a^2 \rightarrow b^2$ only are included; series B, in which all single excitations and multiple excitations which satisfy an interaction threshold $\delta > 5 \times 10^{-7}$ a.u. are included. Rapid convergence of the energy to the limiting value occurs in all calculations. However, it is noted that the small CI expansion (series A) shows a significant error compared to the larger CI expansion (series B). This demonstrates the fact that natural orbitals cannot be relied on to enhance convergence to such an extent that a very small CI expansion of this type would closely approximate a larger CI expansion.

For the iterative natural orbital calculations based on perturbation theory, series C in Table 2, the same type of excitations and threshold values were used as in the variational calculations (B). In order to illustrate the convergence, $\langle\psi|H|\psi\rangle$ energies are reported using *the wave function* determined by first-order perturbation theory. Again rapid convergence of the energy is noted. The second entry for iteration five, (−9.02803), is determined using the natural orbitals from iteration four, an independent generation of 350 configurations using $\delta = 5 \times 10^{-7}$ a.u., followed by a fully variational determination

Table 2. Iterative natural orbitals CI calculations on LiH. Variational CI energy calculations (accurate matrix diagonalization) and energies evaluated using wave functions obtained by first-order perturbation theory are reported for each iteration. Natural orbitals obtained on each iteration are used to construct CI expansions for the next iteration. The number of determinants in each calculation is denoted by N

	Variational Calculations				Perturbation Theory	
Iteration	N	(A)[a] Electronic Energy	N	(B)[b] Electronic Energy	N	(C)[c] Electronic Energy
1 (SCF MO's)	10	−8.98570	239	−9.02756	208	−8.99215
2	38	−9.00563	202	−9.02782	182	−9.02108
3	38	−9.00568	335	−9.02815	266	−9.02130
4	38	−9.00575	364	−9.02817	314	−9.02157
5	38	−9.00575	369	−9.02826	360	−9.02157
					(350)	(−9.02803)[d]

[a] Series A calculations include all single excitations and double excitations, $a^2 \rightarrow b^2$, from orbitals 1 and 2 to orbitals 3–10 of Table 1.

[b] Series B calculations include all single excitations, and multiple excitations from the zeroth-order 38 determinant CI wave function, ψ^0, of series A, for an interaction threshold $\delta = 5 \times 10^{-7}$ a.u. (see text).

[c] Series C calculations include all single excitations, and multiple excitations from the zeroth-order CI wave function, ψ^0, for an interaction threshold $\delta = 5 \times 10^{-7}$ a.u.

[d] Variational determination of the energy and coefficients of the CI expansion using the NO's of iteration 4.

of the energy and coefficients of the CI expansion. This result is in very good agreement with the variational determination of NO's, differing by only 2×10^{-4} a.u.

Similarly, for the water molecule, NO's were obtained iteratively using energy variational and perturbation theory techniques, and comparisons of the two methods of calculation are reported in Table 3. Since the electron pairs are separated in H_2O, the molecule affords a better test of the iterative procedures than does LiH. The procedures followed are the same as described for LiH except in reporting the results of the perturbation theory method the energy values correspond to a variational determination of energies and coefficients of the CI expansion. The determination of NO's for the next iteration in the perturbation theory procedure is, as before, using first-order perturbation theory to determine the CI expansion. In the generation of configurations, only those determinants with an interaction with the ground state determinant, ψ^0, satisfying $\delta = 2 \times 10^{-4}$ were retained in the calculation. On successive iterations, it is therefore possible to have a variation in the total number of determinants in the CI expansion, and for both series of calculations the variation is between 187 and 212 determinants. In the first four iterations of Table 3, results are reported for the 160 determinants with the largest interaction with ψ^0, and in iterations five and six, both the 160 determinant result and the result including all determinants are reported. Comparing either series gives a measure of the convergence. For the variational calculations, approximately six iterations are required to achieve a difference in energy on successive iterations of 3×10^{-4} a.u. The perturbation theory series was carried out for only five iterations and

Table 3. Iterative natural orbitals CI calculations on H_2O. Variational CI energy calculations (accurate matrix diagonalization) and energies evaluated using wave functions obtained by first-order perturbation theory are reported for each iteration. Natural orbitals obtained on each iteration are used to construct CI expansions for the next iteration. The number of determinants in each calculation is denoted by N

	Variational Calculations[a]		Perturbation Theory[a]	
Iteration	N	(B) Electronic Energy	N	(C) Electronic[b] Energy
1 (SCF MO's)	160	−85.36127	160	−85.36127
2	160	−85.38721	160	−85.37852
3	160	−85.39059	160	−85.39239
4	160	−85.39497	160	−85.39271
5	160	−85.39671	160	−85.39237
	187	−85.40188	205	−85.39938
6	160	−85.39791		
	187	−85.40222		

[a] Calculations include all single excitations, and multiple excitations from the single determinant ground state wave function, ψ^0, for an interaction threshold $\delta = 2 \times 10^{-4}$ a.u. (see text). Unless otherwise indicated, the 160 determinants with the largest interaction with ψ^0 were used in the CI, the other entires, 187 and 205, correspond to the total number of determinants generated for the interaction threshold δ.

[b] Energies reported are for a variational determination of the energy and coefficients, but the coefficients used to construct NO's for the next iteration are from perturbation theory.

comparing the fifth iterations shows an energy 3 x 10^{-3} a.u. higher than the variational result. Thus, in both approaches, energy convergence does occur, but the rate of convergence is significantly slower than in LiH.

In applications, the point of view expressed in the present work would involve carrying out a sequence of iterations without computation of $\langle\psi|H|\psi\rangle$ since such an evaluation would require the same matrix elements as a fully variational iterative approach. The convergence would then be tested by performing variational CI calculations starting with the natural orbital basis determined from perturbation theory.

As a side issue, the natural orbitals from the final iteration of the variational (B) and perturbation theory (C) calculations are used to generate CI expansions of different size as determined by the choice of interaction threshold δ. The results are compared in Table 4 with CI expansions produced using occupied and virtual (not transformed) SCF MO's. The latter energies are seen to lag considerably behind the CI energies obtained using NO's until small thresholds, hence relatively large CI expansions, are produced, see Table 4; similar results are reported in Ref. [9].

These results suggest several conclusions which are likely closer to being generally applicable than to being limited to only the present example. First, a relatively modest size CI expansion based on NO's can be much inferior to a significantly larger CI based on either NO's or SCF MO's. On the other hand, comparing relatively small CI expansions using NO's and SCF MO's, the former is expected to be superior. This simply

Table 4. Comparison of CI calculations using natural orbitals with CI calculations using SCF molecular orbitals. Natural orbitals were taken from the final iteration of the variational and perturbation theory calculations on LiH and H_2O, see Tables 2 and 3

	Energies (a.u.)		
Number of Determinants[a]	SCF MO's	NO's (Variational Calc.)	NO's (Perturbation Theory)
LiH			
17[b]	−9.00215	−9.02155	−9.02157
65[c]	−9.00669	−9.02315	−9.02289
50[d]	−8.99064	-	−9.02587
350[e]	−9.02756	−9.02826	−9.02803
H_2O			
80	−85.35448	−85.39249	−85.38643
160	−85.38732	−85.41032	−85.40646
320	−85.41373	−85.42039	−85.42075
480	−85.42343	−85.42587	−85.42719
	−85.42943 (854)[f]	−85.42984 (678)[g]	

[a] For LiH the number of individual determinants in the CI is given, and for H_2O the totals are for the number of determinant pairs, $\varphi_k \pm \bar{\varphi}_k$, where $\bar{\varphi}_k$ corresponds to a change of all spins of φ_k, see Ref. [14].

[b] Double excitations, $a^2 \rightarrow b^2$, from orbitals 1 and 2 to orbitals 3–10.

[c] All single and double excitations, $a^2 \rightarrow b^2$, from orbitals 1 and 2 to orbitals 3–18.

[d, e, f, g] Single and multiple excitations which satisfy an interaction threshold: (d) $\delta = 5 \times 10^{-5}$, (e) $\delta = 5 \times 10^{-7}$, (f) $\delta = 5 \times 10^{-6}$, (g) $\delta = 1 \times 10^{-5}$.

reflects the desirability of transforming the virtual SCF MO's prior to performing CI expansions. The present results provide no information on the best type of transformation, however. NO's are superior to no transformation, but on the basis of other work one would expect the use of positive ion or exchange maximized virtual orbitals to lead also to considerable improvement of the convergence. Finally the large CI expansions produce nearly equivalent results, de-emphasizing a special efficacy attributed to NO's, providing the organization of the generation of configurations is properly treated to allow multiple excitations to occur from the major contributing configurations of the state of interest. For further discussion of these conclusions see the comprehensive work of I. Shavitt [16].

Of course, another sense in which to view the perturbation scheme is not as a method for determining precise NO's, but instead simply as a practical device for performing virtual orbital transformations prior to large-scale configuration interaction; here one would imagine carrying out for example only one or a very few iterations to determine the NO basis. This point of view is the same as advocated by Siu and Hayes in their perturbation theory studies [9]. See also a recent study of the convergence of natural orbital procedures by Thunemann *et al.* [17] in which the choice of configuration space is found to be much more important than the attainment of strict NO convergence.

As a final remark, in problems in which the entire MO basis is to be used to construct configurations, we have found no practical advantage in using NO's if one is prepared to go to large CI expansions; indeed, the NO computations are more lengthy than the use of SCF MO's. However, in problems in which one seeks to reduce the size of the MO basis, an approximate determination of NO's using perturbation theory can lead to a useful practical procedure for performing the transformation of virtual orbitals.

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