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Configuration Interaction: Molecular Orbitals for Accurate Calculations on Diatomics

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A procedure is developed to construct an optimum set of molecular orbitals (MO's) to be used in large scale configuration interaction expansion for diatomics. The set is optimum in the sense that a significant energy improvement can be obtained for a relatively short wavefunction expansion. Application of this methodology to the ground state of the LiH molecule gave an energy of −8.06345 a.u. for an expansion with 1852 terms obtained from a set with 16σ-, 12π-, and 6δ-type MO's.

Key words: Configuration interaction – Molecular orbitals – Lithium hydride.

1. Introduction

The virtual Self-Consistent Field-Linear Combination of Atomic Orbitals (SCF-LCAO) Molecular Orbitals (MO's), although known for quite some time as not good correlating orbitals, have been used in several configuration interaction [1] studies. Schemes to transform these virtual orbitals to increase their effectiveness have also been discussed in the literature [2]. Of these, the Iterative Approximate Natural Orbitals (IANO's) procedure, as developed by Bender and Davidson [3], seems to have been the most successful. A scheme that also uses this iterative approach but employs first-order perturbation theory (of the wavefunction) to construct approximate CI expansions is discussed by Jafri and Whitten [4]. It is worth-recalling that Bender and Davidson's IANO's approach involves the substitution of the starting set of MO's by Natural Orbitals (NO's), but they go through a large CI calculation before using the NO's, so if the starting MO set is not of "good quality" the iterative process will cause a minimum of improvement or none at all. In fact, studies by Thunemann [5] et al. have also shown the possibility of the calculation getting worse after the iteration.

Recently, Ermler and McLean [6] stressed the "critical importance of the use of adequate one-particle basis sets to provide the starting point for any *ab-initio* method", and in this connection we can notice that in several CI studies reported in the literature, the number of Slater-type functions (STF's), some of the exponents in these functions (for extended basis sets), and the number of MO's used have some arbitrariness in their choice. Clearly, a blind choice in the number of MO's can lead to the construction of maybe an unnecessarily large formula tape for the CI matrix elements.

In this paper, we propose a procedure in which the size of the MO set and consequently the size of the formula tape are not established at the outset of the calculation, but are determined after a series of small CI calculations giving enough information about the importance of the different natural orbital types that are being selected to make up the working MO set. Since the CI expansions during this stage are very small, we also have the possibility of experimenting with the orbital exponents and/or increasing the number of STF's for each MO type.

2. Procedure

Our scheme is a normal CI approach organized in such a way that all the two-electrons integrals can be computed and transformed according to their symmetry types. Having the orbitals grouped according to their symmetry, we carry out small CI calculations within each group in such a way that, besides the occupied MO's, only σ-MO's are used as virtual orbitals in one set of calculation, then π-MO's only, and then δ-MO's only. These small CI expansions in each group correspond, in one case, to the freezing of the core electrons, and in a second case to the freezing of the valence electrons. For each one of these expansions the first-order density matrix is generated and the corresponding NO's computed. The MO's for each expansion within a given symmetry type of virtual orbitals are ordered according to their occupation numbers, and those with occupation numbers below a specified threshold neglected. At this stage we expect to obtain an indication of the importance of a given NO by the magnitude of its occupation number. The next step consists of merging the selected NO's into a single set. This new set will consist of the occupied SCF orbitals and the virtual NO's grouped in decreasing value of their occupation numbers. If the number of selected NO's in this new set exceeds the number of MO's in the original set, we take this information as an indication that the original set should be augmented by this extra number of MO's. This, of course, implies a corresponding increase in the number of STF's.

The generation of an additional number of MO's and/or a variation in the exponents of the added STF's makes this procedure clearly dependent on the efficiency of the routines that calculates the two-electron integrals. In this respect we "armed" ourselves by transforming the efficient "in-core" diatomic integral routine DERIC developed many years ago by Hagstrom [7], into an "out-of-core" disk-file oriented package [8] whose efficiency becomes greater the larger the number of integrals being calculated, specially with the new computers with array processing hardware. As to the two-electron integral transformation, since we have all the integrals grouped according to their symmetry type, this step is not time consuming. Once this selection procedure has been conducted for each symmetry type of MO's, they are combined into a single set with which a large scale CI is carried out. The final CI expansion besides all singles and doubles also includes some selected triples and quadruples; this selection procedure is discussed in the next section.

3. Results and Discussion

The ideas put forth in Sect. 2 were tested in the calculation of the ground state energy of the lithium hydride (LiH) molecule. Representative calculations on this molecule are collected in Table 1; they all employed Slater type functions (STF's). The STF's used in this work are those given in Table 2. The exponents for the $nl\sigma$ functions are those given by Cade and Huo [9]. For the $nl\pi$ functions we started with the nine exponents given by Bender and Davidson [3], and then, after experimenting with them, the set given in Table 2 was generated. The exponents in parentheses were added to augment Bender and Davidson's modified set of $nl\pi$ functions. The exponents for the $nl\delta$ functions are also the ones given by Bender and Davidson, they were changed also, but no significant

Table 1. Representative studies[†] of the ground state of the LiH molecule; $R = 3.015$ bohr

(AO's/MO's)[a]	Number of terms	−Energy (Hartree)
(12-4/16)[b]	1	7.98731
(12-4, 6-3, 4-2, 1-1/not reported)[c]	939	8.0606
Hylleraas-type[d]	119	8.0630
(15-7, 8-4, 4-3/not reported)[e]	6514	8.0640
CEPA[f]	non-variational	8.0660
(12-4/16)	435	8.03262
(12-4, 6-3/16, 9)	606	8.06011
(12-4, 6-3, 4-2/16, 9, 6)	684	8.06165
(12-4, 6-3, 4-2/16, 9, 6)	684	8.06166
(12-4, 6-3, 4-2/16, 9, 6)	1517	8.06206
(12-4, 8-4, 4-2/16, 12, 6)	813	8.06265
(12-4, 8-4, 4-2/16, 12, 6)	1852	8.06317
(12-4, 8-4, 4-2/16, 12, 6)	1852	8.06347
"experimental"		8.0704[b]

[†] See text for explanation on the unreferenced results.
[a] Ref. [14]; [b] Ref. [9]; [c] Ref. [3]; [d] Ref. [15]; [e] Ref. [11]; [f] Ref. [16].

Table 2. Orbital exponents for the Slater type functions

	Lithium	Hydrogen
1*s*	4.699, 2.52117	1.56567, 0.88775
2*s*	1.200, 0.79722	2.200
3*s*	2.750	
$2p\sigma$	2.750, 1.200, 0.73691	1.37646
$3p\sigma$	3.200	
$3d\sigma$	1.200, 0.64232	
$4f\sigma$	0.92480	
$2p\pi$	4.789, 2.600, (1.274)	1.000, (0.600)
$3d\pi$	5.500, 3.000, (1.274)	1.200
$4f\pi$	7.200, 4.789	1.622
$3d\delta$	6.3852, 1.6984	2.1626
$4f\delta$	6.3852, 1.6984	2.1626

improvement was obtained. The starting MO's comprised the 1σ, 2σ and 3σ orbitals given by Cade and Huo and the remaining ones were generated by Schmidt orthonormalization, with the order of orthonormalization being that of the atomic functions given in Table 2. The orbitals centered on the hydrogen atom follow the ones centered on the lithium atom.

In Table 1 the results of this work are compared with previous calculations. Although the basis set preparatory stage had indicated that the π-MO's set should contain more than the nine functions as we originally started, the decision was made to carry out a series of calculations with this smaller basis set to better assess the improvement in subsequent results. First of all, we can notice that from an all σ-MO's, singles and doubles, 435-term CI, an all σ-, and π-MO's 606-term CI, and finally from a 684-term CI with 16σ, 9π, 6δ MO's, the correlation energy recovered (0.07434 a.u.) can be partitioned into the following contributions: 0.04531 a.u. from σ-MO's, 0.02749 a.u. from π-MO's, and 0.00154 a.u. from δ-MO's, which amounts to 60.9%, 37.0% and 2.1% respectively of the total recovered. Before working with the larger set we tried to improve this energy first by an iterative process like Bender and Davidson's approach, and second by the inclusion of selected triples and quadruples. With just one iteration the energy lowered by 1.0×10^{-5} a.u., a small improvement. As to the triples and quadruples their generation was done as single and double excitations from a reference set of seven configurations which, based on the magnitude of their coefficients, were selected as most important. For a final expansion with 1517 terms the energy obtained, -8.06206 a.u., is just 4.0×10^{-4} a.u. below the all singles and doubles value, and in our opinion reflects a deficiency in the one-particle basis.

The larger atomic basis set essentially contains three more STF's, and the improvement obtained from this addition is evident in Table 1. The correlation energy now recovered is 0.0754 a.u. (90.7%) and the total energy for an all singles and doubles 813-term CI is −8.06265 a.u. Note that this number is below the one from the previous calculation which had also included selected triples and quadruples. It is important to point out that to test the accuracy of our results for the all singles and doubles CI's we verified the invariance of the energy upon a transformation among the set of virtual orbitals [10].

In going beyond the singles and doubles level, the generation of triples and quadruples was done as single and double excitations from a reference set of 25 configurations with the constraint that these excitations would involve only the first few most important natural orbitals of each symmetry type. This constraint, although logical was also done to keep the expansion within the present limits of our computer codes. Also, due to computer time availability we did not calculate part of the matrix elements in the symbolic matrix, that is, every matrix element resultant from a triply or a quadruply excited configuration and a singly or doubly excited configuration whose coefficient in the all singles and doubles CI was less than $|1.0\times10^{-4}|$ was set equal to zero. Also, in the triples and quadruples block only the diagonal elements were kept. The results obtained, −8.06265 a.u. and −8.06317 a.u., respectively, represent a considerable improvement over the value −8.0606 a.u. obtained by Bender and Davidson with an atomic basis of almost equal size. Next, using the IANO's approach an attempt was made to improve the best value we had obtained so far. With one iteration the energy lowered to −8.06347 a.u.

The significance of the approach used in this work can be better evaluated if these results are compared with the ones reported by Langhoff and Chong [11]. Using an atomic basis with 22 $nl\sigma$, 12 $nl\pi$ and 7 $nl\delta$ STF's they generated a CI expansion with 6514 terms giving an energy of −8.0640 a.u. More recently, using the orbital exponents given by Langhoff and Chong [11], with the exception of the $4f\delta$ STO on the hydrogen, Partridge and Langhoff [12] obtained an energy of −8.06385 a.u. for an interatomic distance of 3.00 bohr. Clearly, for an almost equal energy, we have achieved a considerable compaction in the wavefunction. This result certainly shows the importance of adequately constructing the one-particle basis. A careful natural orbital study of the first row atoms in the manner done by Bunge [13] would certainly be useful in this regard, especially in the construction of the MO's to describe the core correlation.

In connection with this work, a study is now under progress to determine for the few electrons diatomics an optimum size set of MO's that guarantees the attainability of the all singles and doubles energy limit before going to triple and quadruple excitations.

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