Theoret. chim. Acta (Berl.) 30, 209—216 (1973)

Commentationes

The Use of Average Natural Orbitals for Configuration Interaction Calculations on the Boron Hydride Molecule

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Received July 24, 1972/January 29, 1973

The use of average natural orbitals is compared to some better known methods of performing limited and restricted CI calculations. It is found that a moderately extensive restricted valence shell CI computation using a subset of these orbitals is an efficient and accurate method for the calculation of state wavefunctions. Total and electronic excitation energies have been calculated for the BH molecule.

Die Verwendung von gemittelten natürlichen Orbitalen wird mit einigen besser bekannten Methoden beschränkter CI-Rechnungen verglichen. Man findet, daß eine eingeschränkte Valenzschalen-CI-Rechnung von mäßigem Umfang mit einer Untermenge der genannten Orbitale eine leistungsfähige und genaue Methode zur Berechnung der Wellenfunktion eines Zustandes darstellt. Die Gesamtenergien und elektronische Anregungsenergien wurden für das BH-Molekül berechnet.

Key words: Average natural orbitals – Excitation energies of BH

Introduction

The computation of accurate electron excitation energies can be an expensive task since it usually requires extensive calculations to be repeated for each state of interest. Efficiency is therefore a more important criterion for such calculations than for those in which properties of only one state are determined. This paper illustrates a method which combines accuracy with efficiency and compares the results obtained for BH with those obtained from some well known CI methods.

Results and Discussion

Choice of Atomic Orbitals

Since most sets of atomic orbitals quoted in the literature have been optimized for ground state wave functions only, our set of orbitals includes additional ones chosen for the more diffuse excited states. The core of this set of atomic orbitals for BH is a so-called "double zeta" set of contracted gaussian orbitals. These orbitals (Boron s_1, s_2, s_3, s_4, p_1, p_2 and Hydrogen s_1 plus the first gaussian orbital of s_2, shown in Table 1) are taken from published works.

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Table 1. Contracted gaussian function basis set for BH

Atom	Type	Exponent	Coefficient
Boron	s_1	10411.559	0.00602874
		1576.1919	0.03414955
		361.66537	0.21343952
		98.726437	0.81532002
	s_2	31.781408	0.14008659
		10.842225	0.32796748
		4.9774725	0.43910393
		1.5888265	0.21500160
	s_3	2.8590772	−0.10128056
		0.35556953	0.50247350
		0.14972248	0.56801575
	s_4	0.07433206	0.91758759
		0.03701718	0.08939910
	s_5	0.1	1.0
	s_6	0.0556	0.82613835
		0.0185	0.20653459
	p_1	26.8281	0.00918291
		5.81572	0.06903735
		1.63092	0.29193173
		0.54881	0.74403225
	p_2	0.204009	0.61097738
		0.0822550	0.40114602
		0.0356435	0.06767884
	p_3	0.2415	1.0
Hydrogen	s_1	19.24060	0.32828011
		2.89915	0.23120807
		0.65341	0.81723826
	s_2	0.17758	0.92065144
		0.05	0.10229460
	s_3	0.1	1.0
	p_1	0.5	1.0

The orbitals centred on the Boron nucleus are those of Huzinaga [1] while those on Hydrogen are from Basch *et al.* [2].

These orbitals are augmented with orbitals which increase electron density in the bonding region of the molecule rather than with orbitals optimized for improved ground state energy. This latter approach invariably leads to orbitals highly localized on the atomic nucleus; i.e. to better representation of the Boron 1s cusp. The maximum density of the radial part of a gaussian orbital is related to the value of the exponent, α, by the relationship

$$\alpha = \frac{n-1}{2r^2}$$

For an s-type gaussian orbital ($n=1$) the maximum is always at $r=0$ and so exponents were selected which came between those of the two most diffuse orbitals in the double zeta set. For p-type gaussian orbitals ($n=2$) on Boron the value of r in the above expression was set at the position of the second maximum of the numerical Hartree-Fock 2s orbital [3]. This value ($r=1.439$ bohr) yields an exponent of 0.2415. An exponent of 0.5 was arbitrarily chosen for the p-type gaussian orbital on H atom which places the maximum density at $r=1$ bohr from the H nucleus or slightly less than the mid-point of the BH axis. The full set of atomic orbitals used consists of 21 contracted gaussian orbitals; 6 s-type and 3 sets of p-type orbitals on Boron and 3 s-type and 1 set of p-type orbitals on Hydrogen (Table 1).

SCF *Calculations*

An SCF calculation was performed on BH using the above set of atomic orbitals for a nuclear separation of 2.3291 bohr. This calculation may be compared with two published ones. Cade and Huo [4] using a large set of Slater orbitals obtained an energy of -25.1314 hartree. This energy is taken to be the Hartree-Fock limit for BH. Kaufman and Burnelle [5] using a large set of gaussian orbitals obtained -25.1298 hartree. In spite of the fact that the augmenting orbitals used in this work were not chosen on an energy lowering criterion, quite a good energy is obtained. This energy, -25.1196 hartree, is only 0.0118 hartree above the Hartree-Fock limit.

Just as the ground state wavefunction may be approximated by a single configuration, the excited state wavefunctions may be also. These configurations are constructed by replacing one of the occupied orbitals in the SCF ground state wavefunction with one of the virtual orbitals. First, however, it must be pointed out that since BH belongs to the $C_{\infty v}$ space point group, the SCF ground state wavefunction has the form

$$\mathscr{A}\,\sigma_1(1)\,\sigma_1(2)\,\sigma_2(3)\,\sigma_2(4)\,\sigma_3(5)\,\sigma_3(6)$$

(where σ_1 is an orbital which transforms according to the Σ^+ irreducible representation). The SCF calculation involves only atomic orbitals of σ symmetry and so results in SCF orbitals of σ symmetry only. Orbitals of π symmetry were formed by symmetrically orthonormalizing [6] atomic orbitals of π symmetry. Thus the $A^1\pi$ single configuration wavefunction formed by replacing one of the σ orbitals by a π virtual orbital which is an orthonormalized symmetry adapted orbital is too poor to be used for the calculation of transition energy.

The $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition energy is calculated to be 0.246 hartree compared to an experimental value of 0.238 hartree [7]. The observed $C^1\Sigma^+$ state wavefunction cannot be approximated by the virtual orbital technique since it has no single principle configuration but rather a combination of two configurations involving double substitutions by orbitals of π symmetry.

CI *Calculations*

All CI calculations were performed by making substitutions for the orbitals of the valence electrons only. We are calling this a *valence shell* CI. The calculation is a *full* valence shell CI when all possible substitutions of the valence orbitals by all combinations of virtual orbitals are included in the wavefunction. We refer to a full *double* valence shell CI when only the configurations formed by single and double replacements of the four valence orbitals are included in the wavefunction. The term *restricted* valence shell CI refers to a calculation where all possible substitutions of the valence orbitals are made from a subset of the virtual orbitals. Finally a *limited* valence shell CI is one in which a subset of the configurations of a full valence shell CI are used. (The full double valence shell CI and the restricted valence shell CI are particular examples of a limited valence shell CI).

The partitioning of the CI calculation into *core* and *valence shell* is after Miller and Ruedenberg [8] and is based on the postulate that the core electrons are relatively unaffected by the molecular environment. The core correlation energy can therefore be treated as a constant quantity and attention confined to the valence electrons only. They calculate the total correlation energy and the core correlation energy of BH to be 0.152 hartree and 0.039 hartree respectively, leaving a valence shell correlation energy of 0.113 hartree.

Full Double Valence Shell CI *Calculations*

A full double valence shell CI calculation was performed for each of the five lowest singlet electronic states of BH at a separation of 2.3291 bohr. The ${}^1\Sigma^+$ wavefunctions included 253 configurations while the ${}^1\Pi$ wavefunction included 376 configurations. Only the $X^1\Sigma^+$ and the $A^1\Pi$ states are represented accurately since higher state wavefunctions have important terms which involve higher than double replacement. The energies obtained were -25.1706 hartree and -25.0503 hartree respectively, yielding a transition energy of 0.1202 hartree (experimental, 0.105 hartree [7]). The ground state energy represents an improvement of 0.0510 hartree over the SCF result. This corresponds to a recovery of 45% of the valence shell correlation energy.

These wavefunctions cannot be improved simply by performing a full valence shell CI calculation since this would involve 3526 ${}^1\Sigma^+$ and 3410 ${}^1\Pi$ configurations. A working maximum for the present computer program is 2500 configurations; hence we turned our attention to several forms of restricted and limited valence shell CI methods.

Restricted Valence Shell CI *Calculations*

The first attempt was to restrict the substituting orbitals to a subset of the virtual orbitals choosing those with lowest orbital energy[1]. This subset included 5 virtual orbitals of σ symmetry and 4 of π symmetry. The ground state wavefunction includes 622 configurations and yields an energy of -25.1443 hartree. This corresponds to a lowering of only 0.0247 hartree or 22% of the valence shell correlation energy. In addition, a similar calculation for the $A\,{}^1\Pi$ state (588 configurations) leads to a predicted $A^1\Pi \leftarrow X^1\Sigma^+$ transition energy of 0.210 hartree!

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[1] Strictly speaking the term "orbital energy" applies only to the SCF orbitals. In the case of the orthonormalized symmetry orbitals, the value calculated in the same manner as an orbital energy is used; i.e. the term orbital energy is used for the diagonal Lagrangian multiplier of any orbital when substituted into the SCF equation. This is reasonable in the sense that increasing orbital energies are obtained as the number of nodes in the orbital increases, as found for SCF orbitals.

It is obvious that this is an extremely poor method of extending a calculation. This conclusion is extremely relevant considering that restriction of substituting orbitals in this way is a relatively common practice.

Limited Valence Shell CI *Calculations*

The next procedures that were considered limit the configurations rather than restricting the orbitals. In the first case, the sums of the orbital energies of the orbitals in each configuration were listed and those with the lowest sums selected. It is felt that this is justified on the grounds that this would rank the configurations in a similar manner to toal energy.

Two limited valence shell CI calculations were made, one for the $X^1\Sigma^+$ state and one for the $A^1\Pi$ state, both at 2.3291 bohr and both limited to 2000 configurations. The energies obtained were -25.1828 hartree and -25.0700 hartree respectively. The $A^1\Pi \leftarrow X^1\Sigma^+$ transition energy is predicted almost exactly equal to experimental while the ground state energy represents a lowering of 0.0632 hartree or 56% of the valence shell correlation energy.

Since this size of calculation is unsuitable for a series of calculations, the number of configurations was further limited to 700 by the same method and new calculations performed. The ground state energy, -25.1765 hartree, is only slightly below that for the full double valence shell CI calculation. The transition energy between the two states, 0.1215 hartree, is also similar to the full double valence shell CI calculation. This demonstrates the limitation of this simple procedure.

The use of Perturbation Theory for limiting configurations has already been described [9]. This theory was applied to the two sets of 2000 configurations discussed above in order to limit the wavefunctions to the most significant 748 $^1\Sigma^+$

Table 2. Molecular state energies of BH

Calculation	Energy (hartree)		
	$X^1\Sigma^+$	$A^1\Pi$	ΔE
Full double valence shell CI[a]	-25.1706	-25.0503	0.1202
Restricted valence shell CI[b]	-25.1443	-24.9341	0.2102
Limited valence shell[c]			
A	-25.1828	-25.0700	0.1127
B	-25.1765	-25.0549	0.1215
C	-25.1824	-25.0695	0.1128
Experimental transition energy [7]			0.105

[a] 253 $^1\Sigma^+$ and 376 $^1\Pi$ configurations.

[b] Basis orbitals restricted to 12 virtual orbitals with lowest orbital energy; 622 $^1\Sigma^+$ and 588 $^1\Pi$ configurations.

[c] Full valence shell CI restricted as follows:

A. 2000 configurations of each symmetry selected on sum of orbital energies of orbitals in each configuration.

B. 700 configurations selected as for *A*,

C. 748 $^1\Sigma^+$ and 740 $^1\Pi$ configurations selected by perturbation theory.

and 740 $^1\Pi$ configurations. The energies obtained, -25.1824 hartree and -25.0695 hartree for the $X^1\Sigma^+$ and $A^1\Pi$ states respectively, are virtually identical to the calculations with 2000 configurations. This is a significant demonstration of the applicability of perturbation theory for this type of problem.

The various energies obtained in the above calculations are summarized in Table 2.

Natural Orbital Calculations

The full double valence shell CI wavefunctions discussed above were analyzed in terms of their natural orbitals. When the NO are put in order of increasing occupation number, the first twelve include 8 of σ and 4 of π symmetry as for the 12 orbitals ranked by orbital energy previously. These 12 NO were selected for restricted valence shell CI calculations. The results of these calculations as given in columns 1 and 3 of Table 3, are essentially the same as for the 2000 configuration calculation described above. In fact, the slight difference in the $A^1\Pi$ energy is such that the transition energy agrees better with the experimental value. The calculations involved 622 $^1\Sigma^+$ and 588 $^1\Pi$ configurations respectively.

Table 3. Total and transition energies[a] for states of BH calculated with NO and ANO[b]

Quantity	$X^1\Sigma^+$(NO)	$X^1\Sigma^+$(ANO)	$A^1\Pi$(NO)	$C^1\Delta$(ANO)	$B^1\Sigma^+$(ANO)	$C^1\Sigma$(ANO)
Total energy	-25.1827	-25.1802	-25.0710	-24.9534	-24.9600	-24.9177
Transition energy	–	–	0.1083	0.2268	0.2203	0.2625
Experimental transition energy [11]			0.105	0.211	0.238	0.252

[a] In hartree.

[b] Restricted valence shell CI using 12 NO or ANO from full double valence shell CI wavefunctions. The NO or ANO with highest occupancy numbers were chosen resulting in 622 $^1\Sigma^+$ and 588 $^1\Pi$ configurations.

Average Natural Orbital Calculations

The use of NO also requires separate calculations to be performed for each state of interest. Therefore, in order to look at values predicted for several states, the use of average natural orbitals (ANO) was investigated. The ANO are calculated in the same manner as NO except that the one particle density matrices of the wavefunctions in question are first averaged and then the resultant matrix is diagonalized.

Each state has a one particle density matrix $\boldsymbol{P}_1^{(i)}$ which may be diagonalized to give the NO $\{\chi^i\}$:

$$\begin{array}{cccc} \boldsymbol{P}_1^{(0)} & \boldsymbol{P}_1^{(1)} & \boldsymbol{P}_1^{(2)} \ldots & \boldsymbol{P}_1^{(n)} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \{\chi^0\} & \{\chi^1\} & \{\chi^2\} \ldots & \{\chi^n\} \end{array}$$

Each set of NO $\{\chi^i\}$ is an orthonormal set but the sets are not orthogonal to each other. Since the individual density matrices, $\boldsymbol{P}_1^{(i)}$ are all hermitian, their average $\boldsymbol{P}_1^A$, where

$$\boldsymbol{P}_1^A = \frac{\boldsymbol{P}_1^{(0)} + \boldsymbol{P}_1^{(1)} + \boldsymbol{P}_1^{(2)} \ldots \boldsymbol{P}_1^{(n)}}{n+1}$$

must also be hermitian and can be diagonalized. The diagonalization of $\boldsymbol{P}_1^A$ yields $\{\bar{\chi}\}$ the "average" NO or ANO.

The ANO resulting from the averaged density matrix of the full double valence shell CI wavefunctions of each of five singlet states of BH (three $^1\Sigma^+$ and two components of the $C^1\Delta$ state) were formed. The restricted valence shell CI calculation using the 12 ANO with highest occupation numbers was then performed. These 12 ANO also include eight of σ and four of π symmetry and so yield 622 configurations of $^1\Sigma$ symmetry and 588 of $^1\Pi$ symmetry. The wavefunctions for five states together with total energy were obtained from this calculation. These results are included in columns 2, 4, 5 and 6 of Table 3. The ground state energy is only 0.0025 hartree higher than from the NO calculation indicating that the loss in absolute accuracy is very slight. The electronic transition energies are all close to experimental values. The energies of the $C^1\Delta$ and $B^1\Sigma^+$ are calculated very close together and occur intermediate to the experimental values for the two states. More extensive calculations, to be published separately, have indicated that the reason for this is that configurations involving substitutions by orbitals of δ symmetry are important for accurate representation of these two states. There were no orbitals of this symmetry resulting from our atomic orbital basis.

Conclusion

The use of a subset of ANO formed by averaging the density matrices of a set wavefunctions resulting from intermediate calculations (in this case limiting the configuration to double substitutions) as basis orbitals for a more extensive calculation (restricted valence shell CI) yielding several state wavefunctions at one time has been found to yield results comparable in accuracy other sophisticated CI procedures. The intrinsic efficiency of this method, however, suggests that it is more suitable for the calculations of multiple state wavefunction of molecules.

Acknowledgements. The financial support of the National Research Council of Canada are gratefully acknowledged. One of us (SAH) would like to thank the Province of Ontario and the National Research Council of Canada for Graduate Fellowships.

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