Theoret. chim. Acta (Berl.) 17, 259—263 (1970)

Application of the Extended Geminal Theory to the BH Molecule

P. J. Gagnon and D. P. Chong

Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada

Received October 14, 1969

Extended geminal theory is applied to the ground state of BH at $R = 2.329$ bohr. It is found that the inclusion of only "one-electron transfer" configurations leads to a lowering in the energy of ~ 0.01 hartree, compared to the antisymmetrized geminal product wavefunction. This improvement is $> 90\%$ of that achieved by a full configuration-interaction wavefunction. A "contracted" double-zeta basis set is also found to be quite good.

Die erweiterte Geminaltheorie wird auf den Grundzustand des BH für $R = 2{,}329$ Bohr angewendet. Es wird gefunden, daß der Einschluß von nur „Ein-Elektron-Transfer"-Konfigurationen zu einer Energieerniedrigung von $\sim 0{,}01$ Hartree, verglichen mit der antisymmetrisierten Geminal-Produkt-Wellenfunktion, führt. Diese Verbesserung beträgt mehr als 90% gegenüber dem Wert, der mit einer vollen CI-Funktion erreicht wird. Ein „kontrahierter" doppelt-zeta-Basis-Satz liefert ebenfalls gute Ergebnisse.

La théorie des géminales généralisée est appliquée à l'état fondamental de BH pour $R = 2{,}329$ bohr. On trouve que l'introduction des seules configurations à «un transfert d'électron» conduit à un abaissement de l'énergie de $\sim 0{,}01$ hartree, par rapport à celle correspondant à un simple produit antisymmétrisé de géminales. Cette amélioration est supérieure à 90% de celle obtenue par I.C. complète. Une base double zèta «contractée» s'avère aussi fort bonne.

1. Introduction

The use of a geminal function to describe each electron pair in a molecule is conceptually attractive to many chemists. (See, for example, Refs. [1, 2].) On the other hand, the computational procedure has also been clearly presented [3, 4]. Recently, Kapuy [5] developed the extended geminal theory which goes beyond the best antisymmetrized geminal product (AGP) wavefunction. In his application to *trans*-butadiene, Kapuy [6] assumed σ-π separability and used second-order perturbation theory as well as the Goeppert-Mayer and Sklar Hamiltonian.

In this paper, we wish to report extended geminal calculations on the $^1\Sigma^+$ ground state of BH at an internuclear separation of 2.329 bohrs. By choosing the BH molecule and four simple basis sets, we can study the effects of basis sets and of inclusion of only "one-electron transfer" configurations, without Kapuy's approximations. However, we do use a Born-Oppenheimer spinless Hamiltonian and very small basis sets.

2. Calculations and Results

Basis Sets

Only four orbitals are used: k ($1s$ on B), s ($2s$ on B), σ ($2p\sigma$ on B), and h ($1s$ on H). In basis set I, the orbitals on boron are the single-zeta Slater-type orbitals of Clementi and Raimondi [7], but the orbital exponent ζ of h is optimized to give the lowest energy for the AGP function. Set II is like set I, but s has been Schmidt orthogonalized to k. In set III, $\zeta(h)=1$ and the orbitals on boron are "contractions" of the double-zeta set of Clementi [8, 9], that is, with fixed linear coefficients [9]. Basis set IV is identical to set III with the exception of h, the exponent of which is optimized as in set I.

Antisymmetrized Geminal Product

First, two hybrids are formed from s and σ:

$$b=\alpha s+(1-\alpha^2)^{1/2}\,\sigma\,, \tag{1}$$

$$n=(1-\alpha^2)^{1/2}\,s-\alpha\sigma\,, \tag{2}$$

where the hybridization parameter α is also optimized to give the best energy for the AGP wavefunction.

Next, the orbitals k, b, n, and h are transformed by a symmetric $\boldsymbol{T}$ into orthonormal K, B, N, and H.

Then, the geminals for the core and lone pairs are simply

$$\phi_1=(K\bar{K})\,, \tag{3}$$

$$\phi_2=(N\bar{N})\,, \tag{4}$$

where the symbols represent the usual Slater determinants. The bond pair is described by

$$\phi_3=C_1(B\bar{B})+C_2[(B\bar{H})+(H\bar{B})]+C_3(H\bar{H})\,. \tag{5}$$

Finally, the AGP function is simply

$$\Psi_{\text{AGP}}=\mathscr{A}\,\phi_1(1,2)\,\phi_2(3,4)\,\phi_3(5,6)\,. \tag{6}$$

For our example, this Ψ_{AGP} is equivalent to a 3-term limited configuration-interaction (CI) wavefunction with the configurations

$$\psi_1=(K\bar{K}N\bar{N}B\bar{H})+(K\bar{K}N\bar{N}H\bar{B})\,, \tag{7}$$

$$\psi_2=(K\bar{K}N\bar{N}B\bar{B})\,, \tag{8}$$

$$\psi_3=(K\bar{K}N\bar{N}H\bar{H})\,. \tag{9}$$

One-Electron Transfer

For *trans*-butadiene, Kapuy [6] found that the most important corrections to the energy of Ψ_{AGP} come from "one-electron transfer" configurations. In the present study therefore, only these configurations are included in the extended geminal calculations labelled G + 1 (geminals plus one-electron transfer configurations).

For our simple example, Ψ_{G+1} is equivalent to a 7-term limited CI wavefunction with the configurations ψ_1, ψ_2, and ψ_3 plus

$$\psi_4 = (K\bar{K}H\bar{H}N\bar{B}) + (K\bar{K}H\bar{H}B\bar{N}), \tag{10}$$

$$\psi_5 = (K\bar{K}B\bar{B}N\bar{H}) + (K\bar{K}B\bar{B}H\bar{N}), \tag{11}$$

$$\psi_6 = (N\bar{N}B\bar{B}K\bar{H}) + (N\bar{N}B\bar{B}H\bar{K}), \tag{12}$$

$$\psi_7 = (N\bar{N}H\bar{H}K\bar{B}) + (N\bar{N}H\bar{H}B\bar{K}). \tag{13}$$

Full Configuration Interaction

Because of our small basis sets, full CI calculations can be easily performed. In addition to ψ_1 to ψ_7, the only other configurations in Ψ_{CI} are

$$\psi_8 = (KKB\bar{B}H\bar{H}), \tag{14}$$

$$\psi_9 = (N\bar{N}B\bar{B}H\bar{H}), \tag{15}$$

$$\psi_{10} = (B\bar{B}H\bar{H}K\bar{N}) + (B\bar{B}H\bar{H}N\bar{K}). \tag{16}$$

These correspond to "two-electron transfer" configurations in the language of extended geminal theory [5, 6]. For our example, Ψ_{CI} is equivalent to Ψ_{G+1+2}.

Results

The results of AGP, G + 1 and full CI calculations with the four basis sets are summarized in the Table. The difference E(AGP) − E(CI) is the maximum improvement on E(AGP) we can get for the particular basis set; and f represents the fraction of this maximum improvement when we include only "one-electron transfer" configurations.

Table. *Summary of results. The four basis sets are described in the text. The energies for Ψ_{AGP}, Ψ_{G+1}, and Ψ_{CI} are in atomic units. The fraction f is defined as* [E(AGP) − E(G + 1)]/[E(AGP) − E(CI)]

Basis set	I	II	III	IV
$\zeta(H)$[a]	1.26	1.31	(1.0)	1.362
α[a]	0.47	0.50	0.52	0.507
E(AGP)	−25.07331	−25.07601	−25.06673	−25.10324
E(G + 1)	−25.08589	−25.08541	−25.08971	−25.11575
E(CI)	−25.08683	−25.08627	−25.09116	−25.11634
f	0.930	0.916	0.941	0.955

[a] Optimized for minimum E(AGP), except the value in parentheses.

3. Discussion

Although our CI energy from basis set IV is quite respectable compared to other calculations on BH (see compendia by Cade and Huo [10] and by Krauss [11]), the purpose of the present study is not to obtain an excellent wavefunction and energy for the system[1]. Thus, we have used small basis sets and very little non-linear optimization in order to save computer time.

The main objective of this work is to support Kapuy's extended geminal theory with a better example. This is achieved by the fact that the fraction f in the Table is over 0.9 with all four basis sets used. The implication here is that, when one uses more extended basis sets and full CI becomes unmanageable, the extended geminal wavefunction Ψ_{G+1}, including only "one-electron transfer" configurations, may do quite well.

A by-product of the present study is also quite interesting. The results in the Table show that the double-zeta basis set of Clementi [8, 9], even with "contraction" (that is, with fixed linear coefficients [9]) and without further exponent optimization, is capable of giving significant improvement over a single-zeta basis set. For example, a full CI with an optimized single-zeta set gives an energy of -25.09034 for BH [13] compared to our -25.11634. This means that, for some systems, contracted double-zeta basis sets may be more economical as well as capable of giving lower energies.

For the limited basis sets used, we can see an approximate one-to-one correspondence with the molecular orbital (MO) CI treatment of BH. From ϕ_3, one can thus obtain two natural orbitals which correspond to 2σ and 4σ, and the orbitals K and N roughly represent 1σ and 3σ respectively. In terms of such MO interpretation, several points may be noted: (a) Our AGP wavefunction in Eq. (6) is an approximate MOCI-ansatz which provides correlation correction to the $(2\sigma)^2$ pair. (b) The ansatz in Eq. (6) does not contain correlation correction to the $(1\sigma)^2$ or $(3\sigma)^2$ pair. (c) The configurations ψ_4 and ψ_5 contribute to the correlation correction for the $(2\sigma 3\sigma)$ pair; and ψ_6 and ψ_7, for the $(1\sigma 2\sigma)$ pair. (d) A full MOCI calculation is manageable; besides the ground state configuration, it involves six doubly excited configurations and three relatively unimportant singly excited ones [13]. However, when one uses more general AGP wavefunctions with larger basis sets, points (b) and (d) are no longer valid, and the AGP and G+1 approaches may be useful alternatives to the more familiar MO and MOCI treatments respectively.

Acknowledgement. We are grateful to the National Research Council of Canada for financial support.

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Professor D. P. Chong
Department of Chemistry
University of British Columbia
Vancouver 8, B.C., Canada