

Molecular properties of the boron trimer obtained by combined Hartree-Fock and density-functional calculations

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Hartree-Fock calculations on restricted regions of the ground-state potential-energy surface of B_3 are carried out. The correlation energy is calculated by using one-body and two-body density functionals. The results obtained with all those functionals are very similar, predicting a stable molecule with a potential-energy surface that shows two minima that differ by about 1.3 eV. The present results are in good agreement with recent calculations of Hernandez and Simons [J. Chem. Phys. **94**, 2961 (1991)], who used a very different method in which correlation energy is obtained by extended multiconfiguration calculations.

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INTRODUCTION

The existence of multiple minima on the ground-state potential-energy surface (PES) of small molecules may greatly condition their thermal and spectroscopic properties. The main reason is the metastable nature of the secondary minima, such as occurs in the ozone molecule [1–3]. The secondary minimum arises from the avoided crossing between states of the same symmetry, and often the difference in energy between the absolute and the secondary minimum is very small (of the order of 1 eV). Moreover, the barrier connecting both minima lies only a few tenths of an electron volt above the second minimum. Obviously it is very difficult to obtain this information via experiment and hence theoretical calculations are needed. This class of calculations requires very expensive configuration-interactions (CI's) to obtain results that very often are not of sufficient reliability; therefore, a comparison between outputs of several different approaches is needed to reach a reliable conclusion [3]. A procedure consisting of combining a Hartree-Fock (HF) or minimal CI with the calculation of the correlation energy by means of a density functional (DF) has been shown to be an economical and accurate alternative to the traditional and very expensive methods of quantum chemistry [4–6]. Although the boron trimer has not been spectroscopically observed, some theoretical calculations indicate that this molecule is stable and that, in the ground state, it has two minima [7–9]. Recently Hernandez and Simons have studied the ground and excited states of the boron trimer [9]. They carried out complete active-space self-consistent field (CASSCF) calculations

obtaining, among other results, the following. (i) The dissociation energy of B_3 into B_2 and B in their ground states is $D_e = 4.96$ eV. The authors speculate that, due to the known limitations of the CASSCF calculations, the obtained dissociation energy is too small and the actual value must be about 5.60 eV. (ii) The CASSCF ionization potential is 8.74 eV, but the authors estimate that there is an error due to an unbalanced correlation energy, so that the actual value must have an upper limit of 9.5 eV. (iii) There are two minima connected by a saddle point. The absolute minimum corresponds to the three atoms spatially arranged as an equilateral triangle, the second minimum shows a linear geometry and the saddle point corresponds to an isosceles triangle. The bond lengths and angles obtained in Ref. [9] are shown in Tables I–III.

The most striking result of Ref. [9] is the second minimum having a well of only 0.08 eV. This value is very small for making any assessment that the secondary minimum must play an important role in the photochemistry of B_3 . Further and elaborate calculations are needed to attain confidence in such a conclusion. Here we show results of calculations performed by combining HF and DF methods to obtain the energy of the molecule and the fragments.

CALCULATIONS

We concentrate on three aspects of the ground-state PES of the boron trimer, which are the absolute minimum ($1^2A'_1$), the secondary minimum ($1^2\Pi_u$), and the saddle point connecting them (1^2A_1). To obtain the

TABLE I. Molecular properties of the boron trimer in its ground state ($1^2A'_1$).

Method	HF	PF	BF	CSF	MSF	Ref. [9]
r_e (Å)	1.58	1.55	1.54	1.54	1.54	1.59
θ_e (deg)	60	60	60	60	60	60
D_e (eV)	3.91	5.60	5.37	5.24	5.93	4.96
IP (eV)	8.65	9.55	9.33	9.31	9.23	8.74

TABLE II. Molecular properties of the boron trimer in its secondary minimum ($1^2\Pi_u$).

Method	HF	PF	BF	CSF	MSF	Ref. [9]
r_e (Å)	1.54	1.52	1.51	1.51	1.53	1.56
θ_e (deg)	180	180	180	180	180	180
ΔE (eV)	0.50	1.40	1.36	1.11	1.22	1.89

ionization potential (IP) and the dissociation energy of B_3 , calculations of the ground state of the B_3 ion ($1^1A_1'$) and of the B_2 molecule and B atom are also needed. The equilibrium geometries of all the molecules involved in the calculations are obtained by searching in the regions of the PES where the minima likes lie [9]. In these regions of the PES there are no serious deformations of the molecules in respect to their minimum-energy configurations, hence mixing of electronic configurations is not needed for a reasonable description of the electronic structure, and the HF method suffices for building the one- and two-body densities needed for the DF calculations. In Ref. [9] a 45-function basis set was used for the boron trimer (15 contracted Gaussians, including d -type functions, per atom) [10]. This is a basis of sufficient quality to accurately reproduce the properties of the B_2 molecule. Here we adopt the 6-311G** basis set of Ref. [11] having 19 contracted Gaussians per atom and also including d -type functions; this is a larger basis set than that of Ref. [9]. Density functionals are less sensible than HF and CI calculations to changes in the basis set, and in fact the 6-311G** is a very good basis set for this class of calculations. Correlation energy has been obtained by numerically integrating the DF equations, having the outputs an error less than $1 \mu\text{hartree}$.

In calculating the correlation energy, four functionals have been used. Two of them are typical DF's that include gradient correction (GCDF) and are that of Perdew (PF) [12], and of Becke (BF) [13]. The other two are the functional of Colle and Salvetti (CS) [14], characterized by having a dependence on the two-body density matrix, and the functional of Moscardó and San-Fabián (MSF) [15], written in terms of the two-body density. For the present problem, as the zero-order wave function is HF, the MSF is exactly a functional of the one-body density

(see Ref. [15]).

Results for the B_3 molecule are collected in Tables I–III. The resulting geometries are very similar to those of Ref. [9] and in agreement with our previous results on diatomic molecules [6]. The effect of the correlation energy is a small decrease of the bond lengths as compared to those obtained with the HF method. The maximum deviation in the values of the bond lengths r_e and bond angles θ_e of Tables I–III as compared to results of Ref. [9] is only 3%. The values obtained with GCDF, BF, CS, and MSF functionals for the ionization energy of the ground state are all very similar, being very close to the limit suggested in Ref. [9] (9.5 eV).

The dissociation energy D_e for the reaction $B_3(1^2A_1') \longrightarrow B_2(1^3\Sigma_g^-) + B(^2P)$ is in good agreement with the estimate of 5.6 eV of Ref. [9], greatly improving the HF results and also those from CI calculations. Our results predict that the second minimum has a well depth in the range 0.12–0.23 eV, in reasonable agreement with Ref. [9] (0.08 eV). The stabilizing effect of the correlation energy is greater for the absolute minimum than for both the secondary minimum and the saddle point, being in the range 0.6–0.9 eV. In view of the similarity between our results and those of Ref. [9], obtained by means of very different methods, it seems reasonable to assess that the boron trimer is a stable molecule having two minima in its ground-state PES and with the characteristics shown by the DF results of Tables I–III.

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TABLE III. Molecular properties of the boron trimer in its saddle point (1^2A_1).

Method	HF	PF	BF	CSF	MSF	Ref. [9]
r (Å)	1.56	1.52	1.51	1.52	1.51	1.56
θ (deg)	121	121	120	120	121	123
ΔE (eV)	0.72	1.54	1.48	1.27	1.45	1.97

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