

## Importance of correlation in LiBO

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The ground state energies of linear isomers LiBO and LiOB have been computed using the SCF, CASSCF and CI approximations. The changes in relative energies of both isomers due to various approximations are attributed to a different description of partial occupancies of the virtual  $\pi$ -orbitals in the multiconfigurational approaches. The ordering scheme is developed for both virtual canonical SCF and secondary CASSCF orbitals for use in the restricted CI calculations. An extrapolation procedure is proposed for better estimates of the correlation energy. Under the proper treatment of correlation, the energy of LiBO is lower than the energy of LiOB.

**Key words:** Electronic correlation—LiBO

### 1. Introduction

Recent *ab initio* studies on the minimum energy path for the rearrangement LiBO  $\rightarrow$  LiOB [1] demonstrated an unexpected dependence of critical points of the ground state potential energy surface on the electronic wavefunction quality. Within the SCF approximation the energies of linear species LiOB were lower than those of linear LiBO, while the most reliable approaches of the multiconfigurational CASSCF method led to the opposite order. The changes in relative energies of both linear species due to different approximations amounted to 10 kcal/mol. Moreover, various choices of an active space in the CASSCF method resulted in contradictory conclusions even on the geometry of the system.

These results seem to be unusual for a closed shell molecule in its ground state with a strong dominance of the Hartree-Fock electronic configuration in the wavefunction.

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In the present study we have intended to clarify the reasons for disagreements in relative stability of linear isomers LiOB and LiBO, obtained in different approximations. For this purpose we have compared their energies calculated with the SCF, CASSCF and CI methods and estimated with a newly proposed extrapolation procedure.

## 2. Computational aspects

The equilibrium geometry parameters for linear isomers LiOB and LiBO have been calculated in [1] with the SCF approximation using a double zeta plus polarization (DZP) basis set. All the calculations of the present study employed these internuclear distances.

The SCF and CI problems were treated with the SPUSH program system described in [2]. In the CI approach all single and double excitations were generated from the reference set of configurations within the chosen set of active MO's, and the secular equations were solved for selected by an energy criterion dominant configurations. The following symbols are used in this paper to specify an approach:

$$\text{CI/SCF (or CI/CASSCF)} \quad \psi_1^2 \psi_2^2 \cdots (\tilde{\psi}_1 \tilde{\psi}_2 \cdots \tilde{\psi}_n)^N$$

which notify that the MO's optimized with the SCF (or CASSCF) procedure are employed to expand the CI wavefunction in such a manner that the orbitals  $\psi_1, \psi_2, \dots$  are kept doubly occupied while the remaining  $N$  electrons are allowed to occupy the active orbitals  $\tilde{\psi}_1, \tilde{\psi}_2, \dots, \tilde{\psi}_n$  in generating single and double excitations from the reference set.

The success of the CI calculations restricted by the total number  $n$  of active orbitals largely depends on a method of deciding which virtual (or secondary) orbitals should be neglected. We here propose an ordering and selecting scheme, described in the following section, for the virtual canonical Hartree-Fock orbitals or the secondary CASSCF orbitals which is more general than the method of Cooper and Ponder, used previously for ordering the modified virtual orbitals [3, 4]. We also propose an extrapolation procedure which permits to take into account contributions to the energy from the entire orbital space. Following this procedure, we are able to cover a considerable part of the correlation energy (up to 90% according to our experience with the BH molecule where the direct comparison with the full CI result is possible).

The CASSCF program described in [5] was modified to be consistent with the SPUSH integral package. The notation of a particular approach:

$$\text{CASSCF-}n/N \quad \varphi_1^2 \varphi_2^2 \cdots (\tilde{\varphi}_1 \cdots \tilde{\varphi}_n)^N$$

(the same as in [1]) indicates that the MO's  $\varphi_1, \varphi_2, \dots$  are inactive, the MO's  $\tilde{\varphi}_1, \dots, \tilde{\varphi}_n$  are active, and all the configurations arising from the distribution of  $N$  electrons among  $\tilde{\varphi}_1, \dots, \tilde{\varphi}_n$  are taken into account.

The  $C_{2v}$  subgroup of the full  $C_{\infty v}$  point group was used in calculations of linear species.

The computations were performed using the  $(9s5p)$  basis set contracted to  $(3s2p)$  [6]. The bond functions  $1s, 2p$  with the exponents 1.0 were added at the geometrical center of the BO fragment to simulate polarization effects.

With this basis set, all the results of [1] crucial for the present study were reproduced. Namely, the SCF energy of LiOB was lower than that of LiBO by 6.0 kcal/mol (the corresponding value in [1] was 2.6 with the DZP basis and 9.8 with the DZ basis), while the CASSCF-8/10 energy of LiBO was lower by 5.1 kcal/mol (in [1] the corresponding value was 8.0 with the DZP basis).

### 3. The ordering of virtual SCF or secondary CASSCF orbitals

The problem of the ordering of unoccupied MO's naturally arises in restricted CI calculations either with canonical or modified SCF virtual orbitals. Cooper and Pounder [3] suggested the ordering scheme based on the quantities

$$E^*(p) = \sum_a \frac{|\langle \psi_0 | H | \psi_{aa}^{pp} \rangle|^2}{E_o - E_{aa}^{pp}}$$

where "p" refers to virtual orbitals, "a" to doubly occupied orbitals occurred in the wavefunction  $\psi_0$ ,  $\psi_{aa}^{pp}$  and  $E_{aa}^{pp}$  denote the doubly substituted wavefunction and the corresponding mean energy.

In the present work we applied another criterion, namely, the energy lowering  $\delta_p$  resulting from all possible excitations to a given virtual or secondary orbital  $\varphi_p$  for a given reference wavefunction.

In the case of Hartree-Fock virtual orbitals the reference wavefunction for LiBO/LiOB was  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$ ,  $E_{\text{SCF}}$  being the corresponding energy, and  $\delta_p$  was defined as  $E_p - E_{\text{SCF}}$ , where  $E_p$  was an energy corresponding to the multiconfigurational CI wavefunction

$$1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 1\pi \varphi_p)^{10}$$

with overall distributions of 10 electrons among 5 orbitals. The excitations from the core  $1\sigma, 2\sigma, 3\sigma$  -MO's seem unnecessary in this case.

The next step in improving the SCF wavefunction is to optimize one more orbital in each symmetry species. For LiBO/LiOB we naturally arrive to the approximation denoted as CASSCF-8/10

$$1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 1\pi 2\pi)^{10}.$$

For technical reasons we had to simplify the ordering procedure for the secondary CASSCF orbitals, and the quantities  $\delta_p$  were defined as  $E_p - E_{\text{CASSCF}}$ , where  $E_{\text{CASSCF}}$  referred to the multiconfigurational wavefunction  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 (6\sigma 7\sigma 1\pi 2\pi)^6$ , and  $E_p$  to the wavefunction

**Table 1.** Total energies of LiBO and LiOB (in a.u.)

Approximation	$E_{\text{LiBO}}$	$E_{\text{LiOB}}$
SCF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$	-107.04928	-107.05882
CI/SCF $\epsilon$ $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$	-107.06851	-107.07372
CI/SCF $\delta$ $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$	-107.09745	-107.14585
CASSCF-8/10 $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 1\pi 2\pi)^{10}$	-107.16480	-107.15666
CI/CASSCF $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$	-107.17797	-107.17507
$E = E_{\text{CASSCF}} - \sum_p \delta_p$ ( $\varphi_p = 8\sigma, 3\pi, 4\pi$ )	-107.17678	-107.17361
Extrapolation: $E = E_{\text{CASSCF}} - \sum_{\text{all } p} \delta_p$	-107.18660	-107.18011

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 (6\sigma 7\sigma 1\pi 2\pi \varphi_p)^6$ . The proposed ordering scheme is more general than that used in [3, 4], and allows one to select the most efficient virtual or secondary orbitals for restricted CI calculations.

Table 1 demonstrates the efficiency of the ordering and selection method. In all CI calculations 3 core orbitals were kept doubly occupied, and all single and double excitations were allowed among five  $\sigma$ -type and four  $\pi$ -type orbitals with respect to the only reference Hartree-Fock configuration. The symbol SCF $\epsilon$  denotes the set of SCF orbitals ordered by orbital energies, and SCF $\delta$  – the set ordered by means of  $\delta$ -values (the orbitals themselves are distinguished by a tilde). Obviously, the SCF $\delta$  set is preferable, however, its efficiency is different for both isomers. In the case of CASSCF orbitals the ordering by  $\delta$ -values is a natural way to select the required number of secondary orbitals for the subsequent CI calculations.

With the CASSCF orbitals we have tested the additivity of the  $\delta$ -values. First of all, we note that the sum of  $\delta_p$ , corresponding to the secondary MO's added to the MO's already present in the active space (here  $8\sigma$ ,  $3\pi$  and  $4\pi$ ), gives together with the reference energy a good estimate for the corresponding CI energy. Therefore it is reasonable to form an extrapolation method summing up all the  $\delta$ -contributions with the reference energy. This procedure allows one to thereby take into account the contributions from the entire orbital space. The reliability of the proposed extrapolation method was confirmed in our studies on BH, where the results were compared with the results of the full CI calculations.

#### 4. The LiBO and LiOB energies

In order to characterize a particular calculation we introduce two quantities:  $E_c$ , which is a part of the correlation energy of LiBO or LiOB obtained as an energy lowering with respect to the corresponding SCF value, and  $\Delta E$ , which is an energy of LiBO with respect to LiOB.

Table 2 reproduces some results of [1], which stimulated the present study. Two items need an explanation: why CASSCF approaches with the distribution of 10 electrons over 7–9 active orbitals favored LiBO by contrast with the SCF approximation, and why the distribution of 8 electrons over 6 or 9 orbitals resulted in the opposite conclusion.

**Table 2.** Energies of linear LiBO and LiOB according to [1]

Approximation, basis	Energy (kcal/mol)			
	$E_c(\text{LiBO})$	$E_c(\text{LiOB})$	$\Delta E$	
SCF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$	DZ	0	0	+9.7
CASSCF-7/10 $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 1\pi 2\pi)^{10}$	DZ	47.6	36.2	-1.7
SCF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$	DZP	0	0	+2.6
CASSCF-8/10 $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 1\pi 2\pi)^{10}$	DZP	72.6	62.0	-8.0
CASSCF-9/10 $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi)^{10}$	DZP	91.8	84.2	-5.0
CASSCF-9/8 $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 (5\sigma 6\sigma 7\sigma 8\sigma 9\sigma 1\pi 2\pi)^8$	DZP	81.3	87.4	+8.7
CASSCF-6/8 $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 (5\sigma 6\sigma 7\sigma 8\sigma 1\pi)^8$	DZP	14.9	18.6	+6.2 <sup>a</sup>

<sup>a</sup> The energy minimum corresponds to a nonlinear configuration

**Table 3.** Relative energies of LiBO and LiOB according to the present study

Approximation	Energy (kcal/mol)		
	$E_c(\text{LiBO})$	$E_c(\text{LiOB})$	$\Delta E$
SCF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$	0	0	+6.0
CI/SCF $\epsilon$ $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$	12.1	9.4	+3.3
CI/SCF $\delta$ $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$	30.2	54.6	+30.4
CASSCF-8/10 $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 1\pi 2\pi)^{10}$	72.4	61.4	-5.1
CI/CASSCF $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$ 1 reference configuration	80.7	72.9	-1.8
CI/CASSCF $1\sigma^2 2\sigma^2 3\sigma^2 (4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi 2\pi 3\pi 4\pi)^{10}$ 4 reference configurations	83.2	74.5	-2.7
Extrapolation based on the CASSCF orbitals	86.2	76.1	-4.1
CI/CASSCF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 (5\sigma 6\sigma 7\sigma 8\sigma 9\sigma 1\pi 2\pi 3\pi 4\pi)^8$	71.1	69.3	+4.2

Table 3 contains the results obtained in the present work. The new versions for the wavefunction compared to the previous study [1] were those for CI approaches with the MO's optimizes either with the SCF or CASSCF method.

The population analysis of the active MO's of the CASSCF-8/10 wavefunction shows considerable occupancies of the  $2\pi$ -orbitals, which are remarkably different for LiOB (0.064) and LiBO (0.092), while occupancies of the  $7\sigma$ -MO are practically the same (0.019 for LiOB and 0.021 for LiBO). Therefore, the large population of the  $2\pi$ -orbital (unoccupied in the SCF wavefunction) is mainly responsible for large correlation corrections in this molecule. Taking into account that the population of  $2\pi$  is almost twice as large in LiBO as in LiOB, the higher stability of LiBO in the multiconfigurational approaches are explainable.

For these reasons, the version in [1] denoted as CASSCF-6/8 (cf. Table 2) was inappropriate and its conclusions were wrong.

Considerable occupancies of the  $2\pi$  MO were also reflected by the relatively high weights of the corresponding configurations associated with the excitations  $1\pi^2 \rightarrow 2\pi^2$  in the multiconfigurational wavefunctions. Therefore, the reference set

for CI calculations should include at least 4 configurations with the  $\pi$ -part  $1\pi_x^2 1\pi_y^2$ ,  $2\pi_x^2 1\pi_y^2$ ,  $1\pi_x^2 2\pi_y^2$ ,  $1\pi_x 2\pi_x 1\pi_y 2\pi_y$ .

The CASSCF-9/8 result of [1] and the CI/CASSCF calculation of the present study with the  $4\sigma$  - MO kept doubly occupied in all configurations clearly indicate the importance of excitations from this orbital - including it into the inactive space reduces the calculated fraction of the correlation energy and changes the energy balance towards LiOB.

We believe that the most reliable conclusion on the relative energies of LiBO and LiOB is that of the proposed extrapolation procedure based on the CASSCF-8/10 MO's resulting in a higher stability of LiBO by about 4 kcal/mol.

## 5. Conclusion

The results of the present study strengthen the conclusions on the role of correlation corrections in LiBO formulated in [1] and remove some ambiguities noticed in [1]. This molecule presents an interesting example of the system in which the correlation effects associated with a partial population of the virtual SCF MO's are crucial even for geometry predictions. The single-configurational SCF approximation is inappropriate in this case, since the correlation corrections are an order larger than the energy differences of various geometries, and the correlation corrections themselves are geometry dependent. Under the proper treatment of correlation LiBO is more stable than LiOB.

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