Commentationes

Preliminary Calculations on Excited States
of the Oxygen Molecule

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It is well known that the energy interval separating $^3\Sigma_u^-$ and $^3\Sigma_u^+$ states of O_2, as given by the conventional ASMO method, is too large. In order to resolve this difficulty, removal of the equivalence restrictions usually employed in the orbital theory is proposed. Thus the orbital exponent of one antibonding π_g MO is allowed to take a different value from the other π_g's. Variational calculations show that the resulting outermost orbital is much more diffuse than the others. This model of a single diffuse orbital brings about a considerable energy lowering for the $^3\Sigma_u^-$ state and thus the agreement of the $^3\Sigma_u^- - {}^3\Sigma_u^+$ interval with experiment is improved.

Die konventionelle ASMO-Theorie liefert bekanntlich eine viel zu große Differenz der Terme $^3\Sigma_u^-$ und $^3\Sigma_u^+$ von O_2, weswegen der Vorschlag gemacht wird, die üblicherweise vorgenommene Äquivalenz-Einschränkung fallen zu lassen. Der Orbital-Exponent eines lockernden MO's kann von dem der übrigen π_g's abweichen. Rechnungen zeigen, daß das äußerste MO viel diffuser als die anderen ist und daß die Energie des $^3\Sigma_u^-$-Zustandes beträchtlich erniedrigt wird.

La séparation entre les états $^3\Sigma_u^-$ et $^3\Sigma_u^+$ de O_2 donnée par la méthode ASMO conventionnelle est connue pour être trop grande. Afin de résoudre cette difficulté la levée des restrictions d'équivalence ordinairement utilisées est proposée. Ainsi l'exposant orbital d'une des orbitales moléculaires antiliantes π_g peut prendre une valeur différente de celui de l'autre orbitale antiliante π_g. Des calculs variationnels montrent que l'orbitale la plus haute ainsi obtenue est beaucoup plus diffuse que les autres. Ceci a pour effet de diminuer considérablement l'énergie de l'état $^3\Sigma_u^-$, améliorant la séparation entre les états $^3\Sigma_u^-$ et $^3\Sigma_u^+$.

1. Introduction

In describing excited electronic states of molecules by the molecular orbital method, we usually start from an electron configuration in which one or more electrons are moved from occupied molecular orbitals to unoccupied molecular orbitals. Quite often these molecular orbitals (MO's) are approximated as linear combinations of atomic orbitals (LCAO). In conventional calculations, the basic atomic orbitals are restricted to those which are occupied in the ground state of the free atom and their functional forms are determined before the calculation starts.

It is well known that for some excited states the conventional calculation fails signally. For example, the computed value of the singlet-triplet separation of the B_{1u} state of the ethylene molecule is 8.4 eV while the observed value is 3.0 eV, and the theoretical estimate of the $^3\Sigma_u^- - {}^3\Sigma_u^+$ interval of the oxygen molecule is 9.8 eV while the observed one is 2.0 eV.

Several attempts have been made to meet the difficulty [1–7], among which Huzinaga's approach [7] is probably the closest to the conventional molecular orbital scheme. The point in his method is to use different orbital exponents for the bonding and antibonding LACO MO's. These were used as variational parameters for each state. He applied the method to C_2H_4. An appreciable lowering of the energy of the singlet B_{1u} state was obtained and thus the agreement with experiment was improved. One somewhat disturbing fact in his calculation is that the optimum orbital exponent of the antibonding MO for the singlet B_{1u} state is as small as 0.4. That of the bonding MO in the same state is 1.4 and the Slater value is 1.625.

In this paper, we first apply Huzinaga's method to the lower electronic states of oxygen (Section 2). The result is disappointing since for all the states whose energies were computed, the addoption of separate orbital exponents for bonding and antibonding MO's yielded very little energy lowering.

Thus Huzinaga's method is successful for C_2H_4 and unsuccessful for O_2. This leads us to try removing a widely employed but arbitrary restriction in the orbital theory. This restriction is to use one and the same one-electron space function for a particular symmetry type. For an atom, this means that the radial function is determined by the principal quantum number n and the azimuthal quantum number l and is independent of the magnetic quantum number m and the spin m_s. The restriction is sometimes referred to as the "equivalence restrictions" [8, 9].

In the case of O_2, the removal of this restriction for the antibonding π orbital turns out to be quite effective in lowering the energy of $^3\Sigma_u^-$ (Section 3). As a result, the energy separation of $^3\Sigma_u^-$ and $^3\Sigma_u^+$ becomes smaller and the agreement with experiment is improved.

Although the numerical calculations reported in this paper are limited and thus of preliminary character, there seems to be little doubt that the removal of the equivalence restriction can have significant effects on calculated energies of some excited states of a molecule.

2. Use of Separate Orbital Exponents for Bonding and Antibonding MO's

In this work, the oxygen molecule is treated as a π-electron system in which six π-electrons are moving in a field of a σ-core. The latter consists of two oxygen nuclei each with two $1s$, two $2s$ and one $2p\sigma$ electrons. The simplest approximation is employed for the σ-core; namely the σ charge cloud is approximated as the sum of two O^{+++} ions and the exchange interaction between σ and π electrons is neglected. The effective Hamiltonian operator $\mathscr{H}^\pi$ for the six π electrons then can be wirtten as

$$\mathscr{H}^\pi(1, 2, \ldots, 6) = \sum_{i=1}^{6} f^\pi(i) + \sum_{i<j}^{6} \frac{1}{r_{ij}},$$

$$f^\pi(1) = -\tfrac{1}{2}\Delta_1 + v_a(1) + v_b(1),$$

$$v_a(1) = -\frac{8}{r_{a1}} + \int \frac{1}{r_{12}} \{2|1s_a(2)|^2 + 2|2s_a(2)|^2 + |2p\sigma_a(2)|^2\} \, dv_2,$$

and we have a similar expression for $v_b(1)$. Atomic units are used in the above formulae.

The atomic orbitals are of the Slater type except for $2s$ which is orthogonalized to $1s$:

$$2s = \frac{1}{\sqrt{1-(1s|2s')^2}} \{2s' - (1s|2s')\,1s\},$$

where $2s'$ is the ordinary Slater $2s$ orbital:

$$2s' = \sqrt{\frac{\delta^5}{3\pi}}\, r \exp(-\delta r)$$

and $(1s|2s')$ is the overlap integral between AO's $1s$ and $2s'$.

A π-electron configuration is specified by an assignment of the six π-electrons to two pairs of doubly degenerate MO's, namely π_u and π_g:

$$\pi_u = \frac{1}{\sqrt{2\{1+(\pi_a|\pi_b)\}}}\,(\pi_a + \pi_b),$$

$$\pi_g = \frac{1}{\sqrt{2\{(1-(\pi_a|\pi_b))\}}}\,(\pi_a - \pi_b).$$

It should be remembered that different orbital exponents δ_u and δ_g are used for π_u and π_g. The resulting three configurations are

$$A\colon (\pi_u)^4\,(\pi_g)^2; \quad B\colon (\pi_u)^3\,(\pi_g)^3; \quad C\colon (\pi_u)^2\,(\pi_g)^4.$$
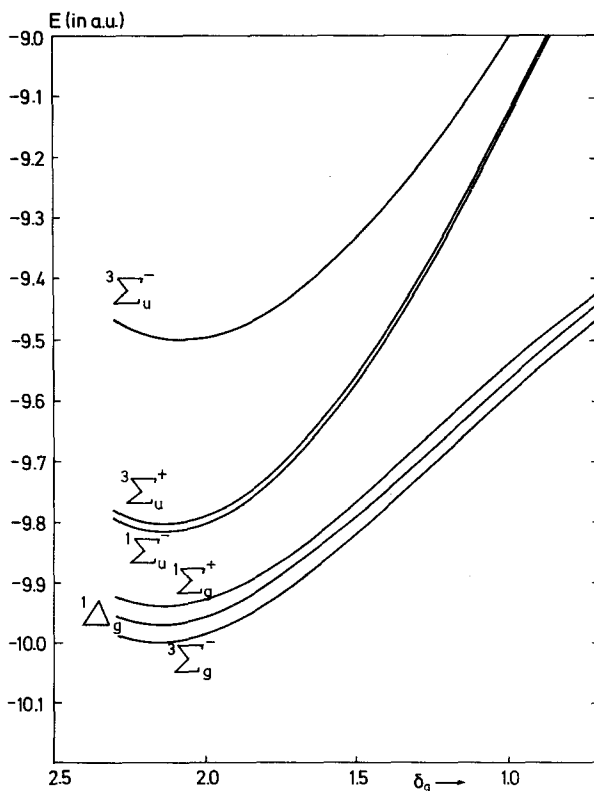

Fig. 1. Energy versus orbital exponent δ_g of antibonding MO's ($\delta_u = 2.1$)

From these configurations, we can construct 6-electron wave functions with proper symmetry of $D_{\infty h}$ and proper total spin and component of spin about the the internuclear axis. One each of such functions with $^1\Sigma_g^+$, $^1\Delta_g$, $^3\Sigma_g^-$ are obtained from the configurations A and C, and $^1\Delta_u$, $^3\Delta_u$, $^1\Sigma_u^+$, $^1\Sigma_u^-$, $^3\Sigma_u^+$, $^3\Sigma_u^-$ are from B. The explicit forms of the wave functions and the matrix elements of the Hamiltonian with respect to these orbitals can be found in Ref. [1] and will not be reproduced here.

The energies are computed for the six states $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^3\Sigma_u^+$, $^3\Sigma_u^-$ for which observed values are available. For the sake of simplicity, the orbital exponents for $1s$, $2s$, $2p\sigma$ are fixed at the Slater value for all calculations reported in this paper:

$$\delta_{1s} = 7.7$$
$$\delta_{2s} = \delta_{2p\sigma} = 2.275.$$

The internuclear distance is also fixed at the equilibrium value of 1.20741 Å, then the energies of the states are functions of two parameters δ_u and δ_g. For each of the three values of δ_u, 2.275, 2.1 and 1.925, δ_g is varied. The resultant energy levels for $\delta_u = 2.1$ are shown in Fig. 1. This value of δ_u gives lower energies for all levels than the other two. The figure shows that all levels have a minimum near $\delta_g = \delta_u = 2.1$.

We have to conclude then, that the use of separate orbital exponents for π_u and π_g, which was very successful in treating the π-electronic levels of C_2H_4 does not improve the conventional calculation for the case of O_2 and no significant improvement on the crucial $^3\Sigma_u^- - 3\Sigma_u^+$ separation is produced by this device.

3. Use of Different Orbital Exponents within Antibonding MO Shell

The same method has been applied to C_2H_4 successfully [7] and has failed here for O_2. What is the cause of this difference? The simplest difference between the π-electron systems of C_2H_4 and O_2 is that the former has only two π-electrons while the latter has six. This means that in lower excited states of C_2H_4, there is only one electron in the antibonding π_g orbital while, in the excited configuration B of O_2, there are three in π_g. The adoption of a smaller orbital exponent for π_g reduces interelectronic repulsions but at the same time raises one-electron energies considerably. This observation led us to trial calculations in which the orbital exponent of one π_g is taken to be different from the other π_g's.

It should be remembered that there is no *a priori* reason why we should use the same space orbital twice (or more in case of degeneracy) in describing an electronic structure of an atom or a molecule. Instead, by the original Hartree Fock approximation the π-electron configuration B of O_2 is expected to be

$$(\pi_u)(\pi_u^{\rm I})(\pi_u^{\rm II})(\pi_g^{\rm III})(\pi_g^{\rm IV})(\pi_g^{\rm V}), \qquad (3.1)$$

rather than the usual $(\pi_u)^3 (\pi_g)^3$. The latter is obtained only when we impose the so-called "equivalence restrictions" [8].

The configuration (3.1) is much too general for computational facilities available to us so we restrict ourselves to the case in which the orbital exponent of only one antibonding π_g is taken to be different from the other π_g's and the bonding

π_u orbitals. A common orbital exponent is used for the latter. The electron configurations to be considered are then

$$A' \quad (\pi_u)^4 \ (\pi_g) \ (\pi'_g);$$

$$B' \quad (\pi_u)^3 \ (\pi_g)^2 \ (\pi'_g);$$

$$C' \quad (\pi_u)^2 \ (\pi_g)^3 \ (\pi'_g).$$

Since there are two or more open shells in these configurations, a number of wave functions can be constructed for a given spin and space symmetry. In constructing these basic symmetry-adapted wave functions, there is arbitrariness in the choice of spin functions. An example of explicit forms of these wave functions is given in Appendix. The result of a configuration interaction calculation (CI)[1] within a given symmetry type is, however, independent of a specific choice of these spin functions.

Numerical calculations were carried out under the same assumptions about the σ-core and about the atomic orbitals as in the previous section. The energies are thus functions of two parameters $\delta_u = \delta_g$ and δ'_g. For each of two values of $\delta_u = \delta_g$, i.e. 2.275 and 2.1, δ'_g is varied. The value of 2.275 gives lower energies than the other and the energy levels for $\delta_u = \delta_g = 2.275$ are illustrated in Fig. 2.

In marked contrast to the energy levels in Fig. 1, those in Fig. 2 become a minimum for a value of δ'_g which is much smaller than $\delta_u = \delta_g$. In other words, the adoption of a model of a single diffuse orbital brings about sizable energy lowering for all the states. The energy lowering is particularly big for the $^3\Sigma_u^-$ state and thus the agreement of the calculated $^3\Sigma_u^- - {}^3\Sigma_u^+$ separation with experiment is improved. The optimum value is 0.25 for $^3\Sigma_u^-$ and is about 0.9 for all other states. Calculated excitation energies are illustrated and compared with observed values in Fig. 3.

The overall agreement with experiment of the present calculation is not good. The calculated excitation energies are too small. However, let us concentrate our attention on the $^3\Sigma_u^- - {}^3\Sigma_u^+$ interval. It should be recalled that we cannot make a reasonable estimate of this interval by the conventional ASMO LCAO method in which the same (and very limited number of) atomic orbitals are used for the two states. This was pointed out by Moffitt in 1951 [1] and was identified by him as one of the most important reasons for the failure of the conventional ASMO method. We find that, as far as this interval is concerned, the present calculation gives a much better value than the conventional ASMO calculation with π-electron CI and even better than the more extended CI calculation which involves some σ-excited configurations as well [10]. A modified atomic orbital calculation [4] which is characterized by the use of different orbital exponents for a neutral atom and for its ions gives better overall agreement than the present calculation. However, the $^3\Sigma_u^- - {}^3\Sigma_u^+$ intervals calculated by these two methods are almost the same. As these two methods start from different forms of the orbital theory, namely MO and AO or valence bond approximations, and as a number of simplifications and approximations are involved in the modified AO calculation, the relation between them, if there is any, is not clear.

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[1] In the valence bond terminology, the procedure is nothing but resonance between various structures.
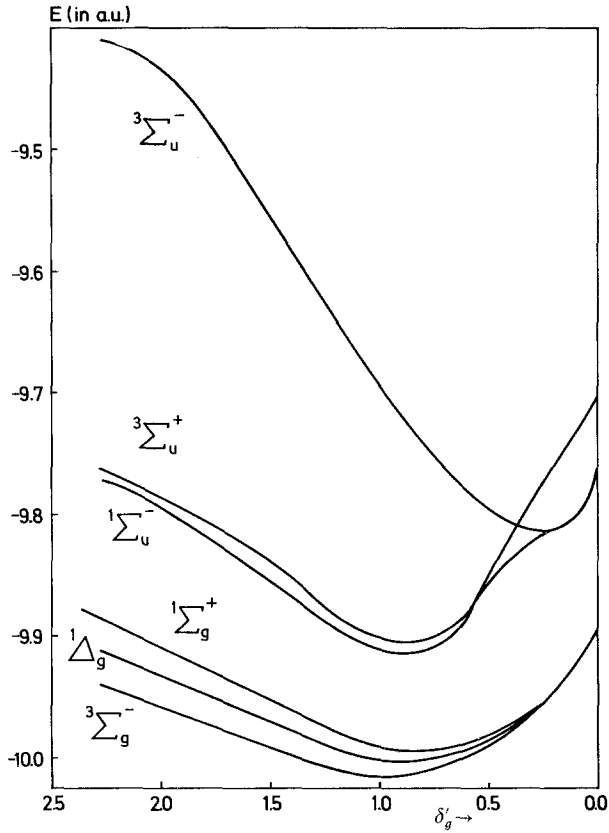
Fig. 2. Energy versus orbital exponent δ'_g of an outermost antibonding MO ($\delta_u = \delta_g = 2.275$)
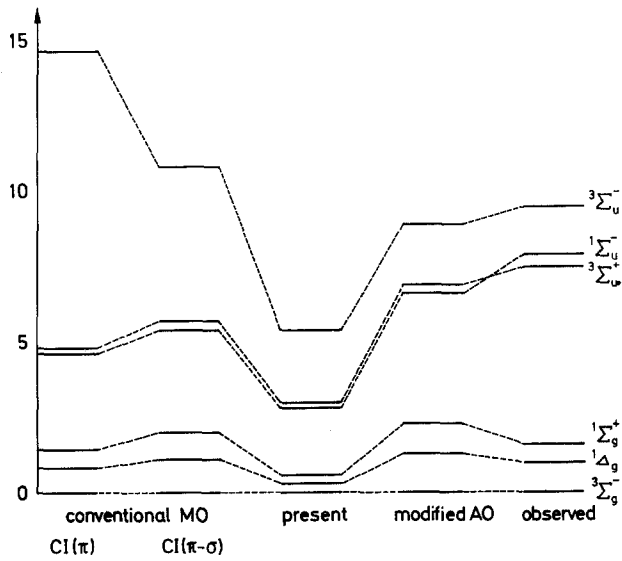

Fig. 3. Excitation energies of O_2 (in eV)

4. Conclusions

The calculations which have been reported in this paper are definitely of preliminary character and there is much room for improvement. For example, in the calculations $\sigma - \pi$ exchange interaction is neglected and in fact the σ-charge cloud is treated very approximately. Nevertheless, the authors feel that the model of one diffuse electron which resulted from the present variational calculations reflects what is happening in electronic structures of molecules. Degrees of diffuseness of this outermost electron would depend on the states and the difference between them could be important for explaining excitation energies of a molecule. At least, there seems to be little doubt that the removal of the equivalence restrictions in the Hartree-Fock theory should be considered seriously for atoms and molecules, particularly in their excited states [2].

Appendix

Symmetry-adapted wave functions from the configurations A', B' and C'

Configuration A' $(\pi_u)^4 \pi_g \pi_g'$

	Space part	Spin part	Reflection[a]
$^3\Sigma_g^-$:	$\pi_u^+ \pi_u^+ \pi_u^- \pi_u^- \pi_g^+ \pi_g^-{}'$	Θ_1^t	$-$
$^1\Delta_g$:	$\pi_u^+ \pi_u^+ \pi_u^- \pi_u^- \pi_g^+ \pi_g^+{}'$	Θ_1^s	
$^1\Sigma_g^+$:	$\pi_u^+ \pi_u^+ \pi_u^- \pi_u^- \pi_g^+ \pi_g^-{}'$	Θ_1^s	$+$

Configuration B' $(\pi_u)^3 (\pi_g)^2 \pi_g'$

$^1\Sigma_u^-$:	$\pi_u^+ \pi_u^+ \pi_g^- \pi_g^- \pi_u^- \pi_g^+{}'$	Θ_1^s	$-$
$^1\Sigma_u^-$:	$\pi_u^+ \pi_u^+ \pi_u^- \pi_g^+ \pi_g^- \pi_g^-{}'$	Θ_2^s	$-$
$^1\Sigma_u^-$:	the same as above	Θ_3^s	$-$
$^3\Sigma_u^\pm$:	$\pi_u^+ \pi_u^+ \pi_g^- \pi_g^- \pi_u^- \pi_g^+{}'$	Θ_1^t	$\pm$
$^3\Sigma_u^\pm$:	$\pi_u^+ \pi_u^+ \pi_u^- \pi_g^+ \pi_g^- \pi_g^-{}'$	Θ_2^t	$\pm$
$^3\Sigma_u^\pm$:	the same as above	Θ_3^t	$\pm$
$^3\Sigma_u^\pm$:	the same as above	Θ_4^t	$\pm$

[a] The notation means

$$\Phi(^3\Sigma_g^-, A') = N \mathscr{A}\{(\pi_u^+ \pi_u^+ \pi_u^- \pi_u^- \pi_g^+ \pi_g^-{}' \Theta_1^t) - \sigma_v(\pi_u^+ \pi_u^+ \pi_u^- \pi_u^- \pi_g^+ \pi_g^-{}' \Theta_1^t)\},$$

where $\mathscr{A}$ and σ_v are the antisymmetrizer and the reflection operator through a plane containing the molecular axis, respectively and N is a normalization constant.

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[2] The removal of the equivalence restrictions also ensures that an upper bound of the Hartree Fock energy of an N electron system is that of the corresponding $N - 1$ electron system since the limit $\delta_g' \to 0$ leads to a Slater determinant of an $N - 1$ electron system [11].

Configuration C' $(\pi_u)^2 (\pi_g)^3 \pi_g'$

$^3\Sigma_g^-$:	$\pi_u^+ \pi_u^+ \pi_g^- \pi_g^- \pi_g^+ \pi_g^{-\prime}$	Θ_1^t	—
$^3\Sigma_g^-$:	$\pi_g^+ \pi_g^+ \pi_u^+ \pi_u^- \pi_g^- \pi_g^{-\prime}$	Θ_2^t	—
$^3\Sigma_g^-$:	the same as above	Θ_3^t	—
$^3\Sigma_g^-$:	the same as above	Θ_4^t	—
$^1\Delta_g$:	$\pi_u^+ \pi_u^+ \pi_g^- \pi_g^- \pi_g^+ \pi_g^{+\prime}$	Θ_1^s	
$^1\Delta_g$:	$\pi_u^+ \pi_u^+ \pi_g^+ \pi_g^+ \pi_g^- \pi_g^{-\prime}$	Θ_1^s	
$^1\Delta_g$:	$\pi_g^+ \pi_g^+ \pi_u^+ \pi_u^- \pi_g^- \pi_g^{+\prime}$	Θ_2^s	
$^1\Delta_g$:	the same as above	Θ_3^s	
$^1\Sigma_g^+$:	$\pi_u^+ \pi_u^+ \pi_g^- \pi_g^- \pi_g^+ \pi_g^{-\prime}$	Θ_1^s	+
$^1\Sigma_g^+$:	$\pi_g^+ \pi_g^+ \pi_u^+ \pi_u^- \pi_g^- \pi_g^{-\prime}$	Θ_2^s	+
$^1\Sigma_g^+$:	the same as above	Θ_3^s	+

$$\Theta_1^s = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 \alpha_3 \beta_4)(\alpha_5 \beta_6 - \beta_5 \alpha_6)$$

$$\Theta_2^s = \frac{1}{2} (\alpha_1 \beta_2)(\alpha_3 \alpha_4 \beta_5 \beta_6 - \alpha_3 \beta_4 \alpha_5 \beta_6 - \beta_3 \alpha_4 \beta_5 \alpha_6 + \beta_3 \beta_4 \alpha_5 \alpha_6)$$

$$\Theta_3^s = \frac{1}{\sqrt{8}} (\alpha_1 \beta_2)(\alpha_3 \alpha_4 \beta_5 \beta_6 + \alpha_3 \beta_4 \alpha_5 \beta_6 - 2\alpha_3 \beta_4 \beta_5 \alpha_6 - 2\beta_3 \alpha_4 \alpha_5 \beta_6$$
$$+ \beta_3 \alpha_4 \beta_5 \alpha_6 + \beta_3 \beta_4 \alpha_5 \alpha_6)$$

$$\Theta_1^t = \alpha_1 \beta_2 \alpha_3 \beta_4 \alpha_5 \alpha_6$$

$$\Theta_2^t = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 \alpha_3 \alpha_4)(\alpha_5 \beta_6 - \beta_5 \alpha_6)$$

$$\Theta_3^t = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2)(\alpha_3 \beta_4 - \beta_3 \alpha_4)(\alpha_5 \alpha_6)$$

$$\Theta_4^t = \frac{1}{2} (\alpha_1 \beta_2)(\alpha_3 \alpha_4 \alpha_5 \beta_6 + \alpha_3 \alpha_4 \beta_5 \alpha_6 - \alpha_3 \beta_4 \alpha_5 \alpha_6 - \beta_3 \alpha_4 \alpha_5 \alpha_6)$$

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