

# On the Jahn–Teller Origin of the Phosphorus Molecule $P_4$ Activation by One- and Two-Electron Reduction

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## Abstract

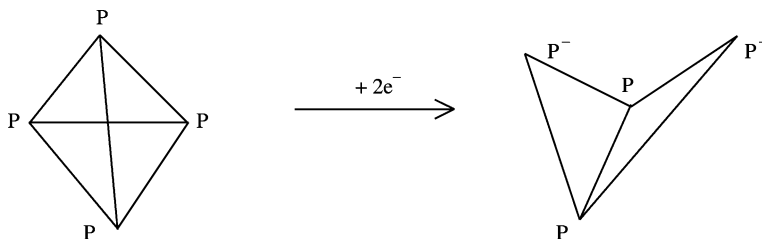
The quantum chemical calculations of the tetra-phosphorus  $P_4^q$  were carried out with values of charge  $q = 0, -1, -2$ . It is shown that the electronic system of the  $P_4$  molecule has equal P–P bond orders. The neutral phosphorus molecule is stable under the reduction of the symmetry from  $T_d$  to  $C_{2v}$  or  $C_{3v}$ . Unlike the neutral molecule, the electronic states of the reduced forms of the  $P_4$  molecule ( $^2T_1(P_4^-)$ ,  $^1T_1(P_4^{2-})$  or  $^3T_1(P_4^{2-})$ ) are degenerated in the  $T_d$  geometry. Due to the orbital degeneracy of the electronic states, the reduced forms of the phosphorus molecules  $P_4^-$  and  $P_4^{2-}$  are unstable with the lowering of the symmetry from  $T_d$  to  $C_{2v}$  or  $C_{3v}$  with unsymmetrical changes of the bond order values. On the other hand, the Jahn–Teller effect destabilizes the tetrahedral geometry of the nuclear system, resulting in the bond order's changes too. Thus the phosphorous molecule in the reduced forms is *activated* due to degeneracy of the electronic orbitals and to vibronic instability. The energy of such a type of activation of the *free* phosphorous molecule is estimated as 60–120 kcal/mol.

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## 1. INTRODUCTION

White phosphorus is the principal source in the manufacture of organophosphorus compounds, pesticides, detergents, etc. Most of the industrial processes in the production of these compounds are based on the oxidation of the phosphorus in the presence of chlorine. Such kinds of processes are accompanied by formation of the hydrochloric acid, which has a negative effect on the surrounding environment. This ecological problem demands the production of the organophosphorus compounds in chlorine-free conditions. Previously it has been established [1–5] that safe chlorine-free processes could be developed utilizing d metals. These compounds activate the  $P_4$  molecule by oxidation or reduction. A qualitative explanation of how the  $P_4$  activation occurs, follows from numerous experimental data. It is generally assumed that in many chemical processes with white phosphorus the tetrahedron  $P_4$  is opened to form the *butterfly* geometry (the P–P bond(s) cleavage) by  $2e^-$ -reduction [1] (Scheme 1).



**Scheme 1.**

To find such effective compounds in activation processes by reduction (or oxidation), it is necessary to study in detail these processes and the *activation* mechanism. This can be done on the basis of the quantum chemical calculations only, which reveal the effects that take place when the phosphorus molecule is changed.

In this article for the simulation of the phosphorus molecule in coordinated states the quantum chemical calculations of  $P_4^q$  were carried out with values of charge  $q = 0, -1, -2$ . Special attention is given to the instabilities of the electronic and nuclear subsystems with the possible reduction of symmetry, resulting in the breaking of the chemical bonds in the tetrahedral phosphorus molecule. Results are analyzed using vibronic theory.

## 2. COMPUTATIONAL METHODS

Calculations of the electronic structure of the phosphorus molecule were carried out by *ab initio* MO LCAO Hartree–Fock–Roothaan SCF method in the restricted (RHF), restricted-open (ROHF) or unrestricted Hartree–Fock (UHF)

approximations. The STO-6G atomic functions were used. To obtain better (more exact) relative positions of the ground and excited many-electron states, the interaction of the 75 many-electron configurations (CI) was taken into consideration. Numerical calculations were performed using the GAMESS program [6]. For ROHF and RHF in the CI method, the 26 mono-electronic states are considered as frozen. The quantum chemical calculations were carried out with and without the d functions of the P atoms.

### 3. ELECTRONIC STRUCTURE OF THE $P_4^q$ ( $q = 0, -1, -2$ ) MOLECULAR SYSTEMS

To optimize the geometry of the  $P_4$  molecule with different charges the calculations of the electronic structure were performed using two methods: the optimization algorithm of the GAMESS program and by changing the P–P distances while the total energy did not reach the minimal value. In both cases the results are very close to each other. In this article the results obtained with the second type of optimization are used.

Studies of the electronic structure of the  $P_4^q$  molecular system were performed in the  $T_d$  symmetry in all charge states (for  $P_4^{2-}$  both in the singlet state with total spin value  $S = 0$  and in the triplet one with  $S = 1$ ). To study any possible instability of the electronic system to the lowering of symmetry in the fixed  $T_d$  configuration of the nuclear subsystem, the calculations were performed using the following three variants:

- (a) when both electronic and nuclear subsystems have the same  $T_d$  symmetry;
- (b) when the phosphorus nuclei form the  $T_d$  configuration, but the electronic subsystem has symmetry  $C_{2v}$ ;
- (c) when the electronic subsystem has symmetry  $C_{3v}$  and the phosphorus nuclei are in the  $T_d$  configuration.

The values of the total energies in atomic units of energy (a.u.e.), calculated in the above-mentioned conditions, are presented in Table 1. It is seen that the P–P distances ( $R_{P-P}$ ), obtained after optimization of the neutral molecule of the phosphorus (neglecting the d-orbital), are very close to the experimental value of 2.21 Å [7].

The detailed analysis of the results shows that the main properties of the  $P_4^q$  electronic structure are qualitatively independent of the P–P distance. So in the case (a) the order of the energy of the mono-electronics levels and the distribution of the electrons on energetic levels (Table 2) are similar to that presented in Fig. 1 for the experimental distance  $R_{P-P}^{\text{exp}}$ .

Similar diagrams and tables for the above cases (b) and (c) (when the symmetry of the electronic subsystem is  $C_{2v}$  or  $C_{3v}$ , but in the high symmetrical  $T_d$  nuclear configuration) are given in Figs 2 and 3 and Tables 3 and 4.

**Table 1.** The total energies of  $P_4^q$  ( $q = 0, -1, -2$ ) in the optimized geometry

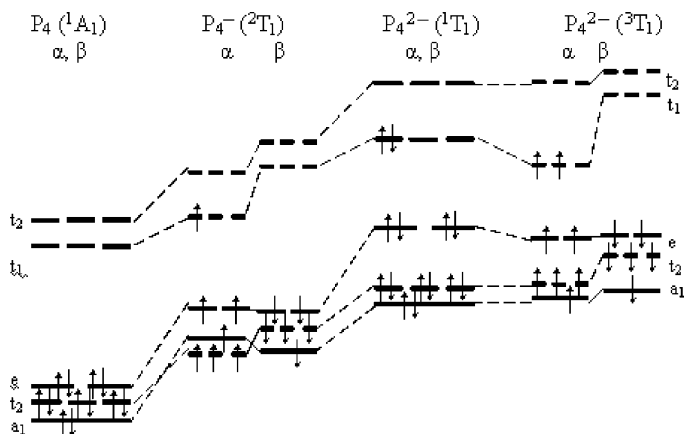
Systems	Symm.	Without d functions			With d functions		
		$R_{P-P}$ (Å)	$E_{\text{tot}} + 1358$ (a.u.e.)	$E_{\text{tot}} + 1358$ (a.u.e.) $R_{P-P} = 2.21$ Å	$R_{P-P}$ (Å)	$E_{\text{tot}} + 1358$ (a.u.e.)	$E_{\text{tot}} + 1358$ (a.u.e.) $R_{P-P} = 2.21$ Å
$P_4$	$T_d$	2.26	-0.483	-0.472	2.14	-0.721	-0.712
	$C_{2v}$	2.30	-0.485	-0.472	2.15	-0.721	-0.711
	$C_{3v}$	2.31	-0.483	-0.472	2.23	-0.721	-0.711
	<b><math>T_d, C_{2v}, C_{3v}</math></b>	2.25	-0.387	-0.384	2.11	-0.663	-0.643
$P_4^-$	$T_d$	2.36	-0.353	-0.321	2.29	-0.503	-
	$C_{2v}$	2.36	-0.354	-	2.18	-0.540	-0.538
	$C_{3v}$	2.36	-0.357	-0.321	2.29	-0.540	-
	<b><math>T_d</math></b>	2.51	-0.145	0.115	2.44	-0.257	-0.102
	<b><math>C_{2v}</math></b>	2.27	-0.263	-0.249	2.18	-0.486	-0.483
	<b><math>C_{3v}</math></b>	2.32	-0.730	-0.047	2.23	-0.480	0.684
$P_4^{2-}; S = 0$	$T_d$	2.45	0.011	0.085	2.38	-0.061	-0.033
	$C_{2v}$	2.41	0.009	0.078	2.27	-0.131	-0.125
	$C_{3v}$	2.44	0.014	0.096	2.28	-0.124	-0.890
	<b><math>T_d</math></b>	2.65	0.233	0.907	2.60	0.176	0.684
	<b><math>C_{2v}</math></b>	2.41	0.132	0.185	2.26	-0.027	-0.024
	<b><math>C_{3v}</math></b>	2.40	0.132	-	2.25	-0.027	-
$P_4^{2-}; S = 1$	$T_d$	2.44	0.000	0.069	-	-	-
	$C_{2v}$	2.43	0.004	-	2.29	-0.137	-0.131
	$C_{3v}$	2.43	0.004	0.069	2.27	-0.134	-
	<b><math>T_d</math></b>	2.61	0.107	0.628	2.57	0.045	0.451
	<b><math>C_{2v}</math></b>	2.40	0.082	0.141	2.24	-0.086	-0.080
	<b><math>C_{3v}</math></b>	2.32	0.091	0.134	2.29	-0.085	-0.085

The bold (normal) notation of symmetry is used for the calculations performed in the UHF (RHF or ROHF) approximation.

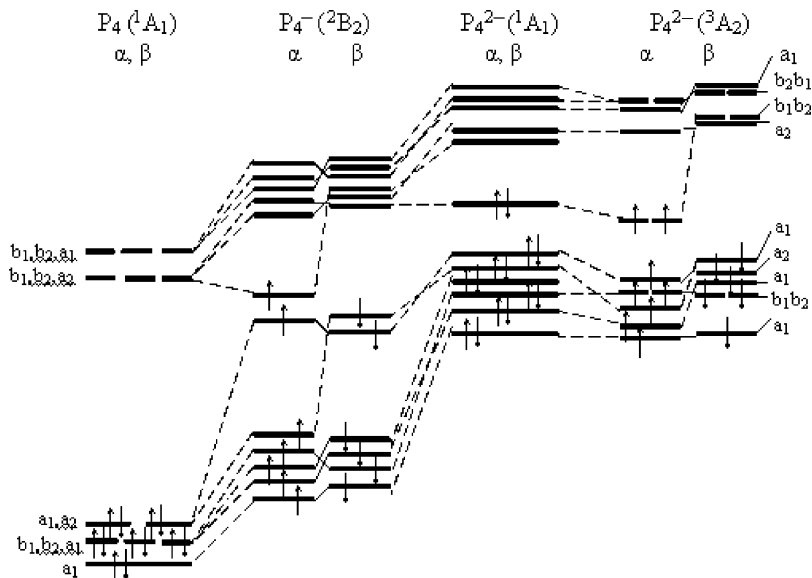
**Table 2.** The values of the one-electron energies for  $P_4^q$  ( $q = 0, -1, -2$ ) in  $T_d$  symmetry at  $R_{P-P} = 2.21$  Å

Irreduc. repres.	$P_4$ ( ${}^1A_1$ )	$P_4^-$ ( ${}^2T_1$ )		$P_4^{2-}$ ( ${}^1T_1$ )	$P_4^{2-}$ ( ${}^3T_1$ )	
	$\alpha, \beta$	$\alpha$	$\beta$	$\alpha, \beta$	$\alpha$	$\beta$
$t_2$	0.276	0.451	0.547	0.722	0.741	0.783
$t_1$	0.187	<b>0.290</b>	0.463	<b>0.568</b>	<b>0.469</b>	0.711
$e$	- <b>0.314</b>	- <b>0.029</b>	- <b>0.045</b>	<b>0.237</b>	<b>0.210</b>	<b>0.212</b>
$t_2$	- <b>0.349</b>	- <b>0.161</b>	- <b>0.102</b>	<b>0.096</b>	<b>0.075</b>	<b>0.157</b>
$a_1$	- <b>0.419</b>	- <b>0.154</b>	- <b>0.190</b>	<b>0.073</b>	<b>0.056</b>	<b>0.071</b>

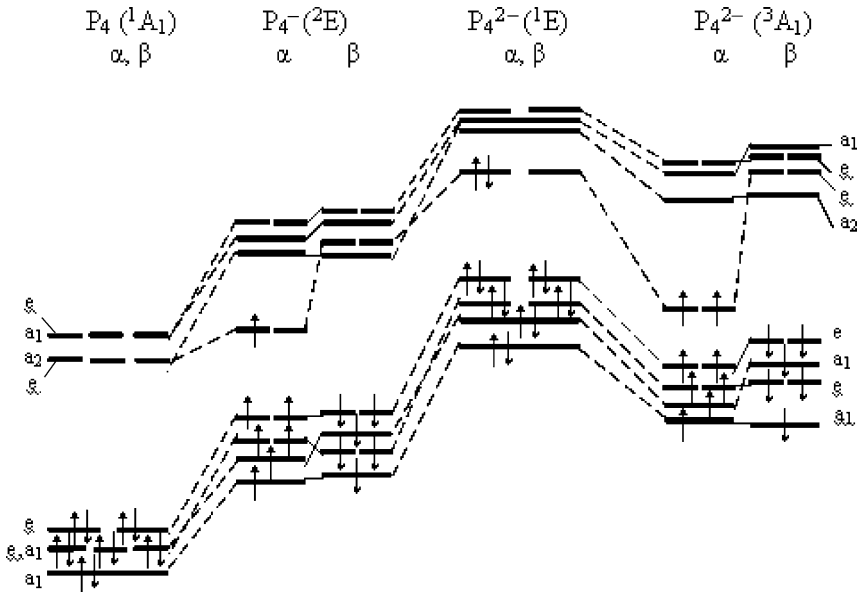
Bold numbers correspond to the populated one-electron levels.



**Fig. 1.** The correlation diagram of the one-electron levels in active zone for  $P_4^q$  ( $q = 0, -1, -2$ ) in  $T_d$  symmetry at  $R_{P-P} = 2.21 \text{ \AA}$ .



**Fig. 2.** The correlation diagram of the one-electron levels in the active zone for  $P_4^q$  ( $q = 0, -1, -2$ ) in  $C_{2v}$  symmetry at  $R_{P-P} = 2.21 \text{ \AA}$ . Numerical values of the one-electron energies are given in [Table 3](#).



**Fig. 3.** The correlation diagram of the one-electron levels in the active zone for  $P_4^q$  ( $q = 0, -1, -2$ ) in  $C_{3v}$  symmetry at  $R_{p-p} = 2.21 \text{ \AA}$ . Numerical values of the one-electron energies are given in Table 4.

**Table 3.** The values of the one-electron energies for  $P_4^q$  ( $q = 0, -1, -2$ ) in the  $C_{2v}$  symmetry at  $R_{p-p} = 2.21 \text{ \AA}$  (for Fig. 2)

Irreduc. Repres.	$P_4 (^1A_1)$	$P_4^- (^2B_2)$		$P_4^{2-} (^1A_1)$	$P_4^{2-} (^3A_2)$	
	$\alpha, \beta$	$\alpha$	$\beta$	$\alpha, \beta$	$\alpha$	$\beta$
$b_1, b_2, a_1$	0.276	$b_1$ 0.527 $a_1$ 0.514 $b_2$ 0.512	0.543 $b_2$ 0.541 $a_1$ 0.531 $b_1$	0.781 $b_2$ 0.774 $b_1$ 0.769 $a_1$	$b_2$ 0.762 $b_1$ 0.762 $a_1$ 0.760	0.805 $a_1$ 0.796 $b_1$ 0.796 $b_2$
$b_1, b_2, a_2$	0.187	$b_1$ 0.430 $a_2$ 0.420 $b_2$ <b>0.134</b>	0.481 $b_2$ 0.445 $a_2$ 0.431 $b_1$	0.677 $a_2$ 0.674 $b_2$ <b>0.433</b> $b_1$	$a_2$ 0.653 $b_2$ <b>0.374</b> $b_1$ <b>0.374</b>	0.726 $b_2$ 0.726 $b_1$ 0.702 $a_2$
$a_1, a_2$	- <b>0.314</b>	$a_2$ - <b>0.075</b> $a_1$ - <b>0.089</b>	- <b>0.041</b> $a_1$ - <b>0.058</b> $a_2$	<b>0.180</b> $a_2$ <b>0.167</b> $a_1$	$a_2$ <b>0.168</b> $b_1$ <b>0.119</b>	<b>0.223</b> $a_1$ <b>0.198</b> $a_2$
$b_1, a_1, b_2$	- <b>0.349</b>	$b_1$ - <b>0.106</b> $b_2$ - <b>0.126</b> $a_1$ - <b>0.146</b>	- <b>0.088</b> $b_2$ - <b>0.095</b> $a_1$ - <b>0.107</b> $b_1$	<b>0.137</b> $b_2$ <b>0.133</b> $b_1$ <b>0.130</b> $a_1$	$b_2$ <b>0.119</b> $a_1$ <b>0.116</b> $a_1$ <b>0.078</b>	<b>0.169</b> $a_1$ <b>0.154</b> $b_2$ <b>0.154</b> $b_1$
$a_1$	- <b>0.419</b>	$a_1$ - <b>0.183</b>	- <b>0.175</b> $a_1$	<b>0.060</b> $a_1$	$a_1$ <b>0.053</b>	<b>0.072</b> $a_1$

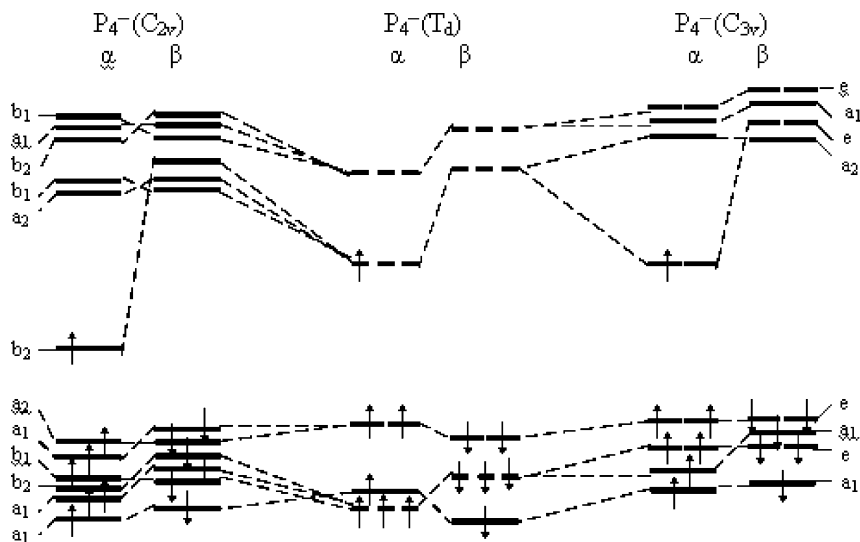
The bold numbers correspond to the populated levels.

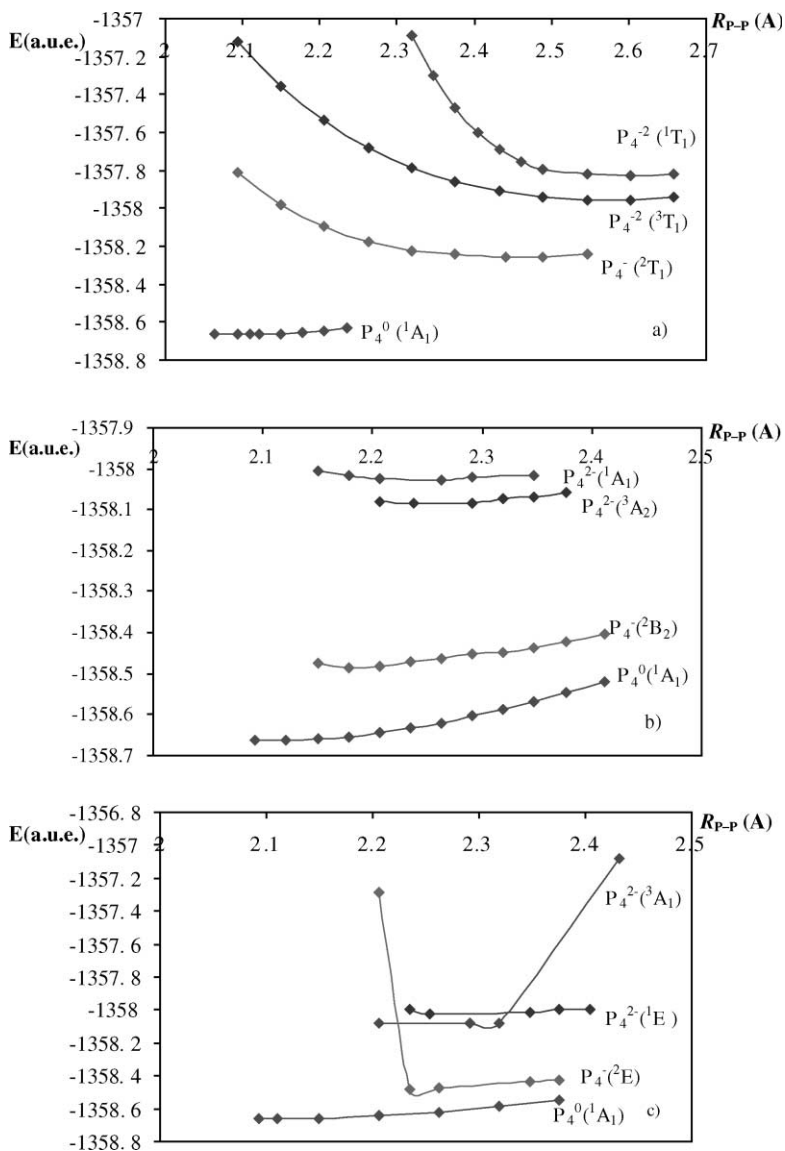
**Table 4.** The values of the one-electron energies for P<sub>4</sub><sup>q</sup> (*q* = 0, −1, −2) in C<sub>3v</sub> symmetry at R<sub>P–P</sub> = 2.21 Å (for Fig. 3)

Irreduc. Repres.	P <sub>4</sub> ( <sup>1</sup> A <sub>1</sub> )	P <sub>4</sub> <sup>−</sup> ( <sup>2</sup> E)		P <sub>4</sub> <sup>2−</sup> ( <sup>1</sup> E)	P <sub>4</sub> <sup>2−</sup> ( <sup>3</sup> A <sub>1</sub> )	
	α, β	α	β	α, β	α	β
<i>e</i>	0.276	0.582	0.606	0.962	0.761	0.797
<i>a</i> <sub>1</sub>	0.276	0.555	0.597	0.870	0.750	0.802
<i>a</i> <sub>2</sub>	0.187	0.529	0.505	0.898	0.661	0.684
<i>e</i>	0.187	<b>0.293</b>	0.531	<b>0.658</b>	<b>0.373</b>	0.735
<i>e</i>	<b>−0.314</b>	<b>−0.010</b>	<b>0.001</b>	<b>0.392</b>	<b>0.147</b>	<b>0.212</b>
<i>e</i>	<b>−0.349</b>	<b>−0.069</b>	<b>−0.046</b>	<b>0.327</b>	<b>0.101</b>	<b>0.148</b>
<i>a</i> <sub>1</sub>	<b>−0.349</b>	<b>−0.093</b>	<b>−0.028</b>	<b>0.313</b>	<b>0.093</b>	<b>0.171</b>
<i>a</i> <sub>1</sub>	<b>−0.419</b>	<b>−0.130</b>	<b>−0.117</b>	<b>0.255</b>	<b>0.055</b>	<b>0.070</b>

The bold numbers correspond to the populated levels.

For further discussion the correlation diagram of the one-electron levels in the active zone for P<sub>4</sub><sup>1−</sup> in T<sub>d</sub>, C<sub>2v</sub> and C<sub>3v</sub> symmetry at R<sub>P–P</sub> = 2.21 Å are given in Fig. 4. In addition, the dependencies of the total energies of P<sub>4</sub><sup>q</sup> in function of the P–P distance are represented in Fig. 5.

**Fig. 4.** The correlation diagram of the one-electron levels for P<sub>4</sub><sup>−</sup> in T<sub>d</sub>, C<sub>2v</sub>, C<sub>3v</sub> symmetry at R<sub>P–P</sub> = 2.21 Å.



**Fig. 5.** Dependencies of total energies on the P–P distance in symmetry: (a)  $T_d$ , (b)  $C_{2v}$ , (c)  $C_{3v}$ .

#### 4. DISCUSSION OF THE RESULTS

The results of the quantum chemical calculations, which were carried out for the phosphorus neutral molecule in  $T_d$  symmetry, are in good agreement with the



experimental data and earlier quantum chemical calculations [7]. A comparison of the results for the P<sub>4</sub> molecule is presented in Table 5. It can be seen that the optimal values of the P–P distances obtained in this work are close to experimental data and, in general, all the results score better when neglecting the phosphorus d orbitals.

One of the most important qualitative results is probably the effect of orbital degeneracy on the multielectronic states of the P<sub>4</sub> molecule in the reduced forms (see Figs 1, 4, and 5). In the ROHF approximation the degenerated many-electronic wave functions of the P<sub>4</sub><sup>−</sup> ground states can be presented as follows:

$$\begin{aligned}\Psi_{xz}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1xz})^1| \\ \Psi_{yz}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1yz})^1| \\ \Psi_{xy}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1xy})^1|\end{aligned}\quad (1)$$

where  $N$  is the number of electrons in the system and the one-electron MOs (see Fig. 6).

$$\begin{aligned}2t_{1xz} &= 0.437(P_{1x} + P_{1z} + P_{2x} - P_{2z} - P_{3x} - P_{3z} - P_{4x} + P_{4z}) \\ 2t_{1yz} &= 0.437(P_{1y} - P_{1z} + P_{2y} + P_{2z} - P_{3y} - P_{3z} - P_{4y} + P_{4z}) \\ 2t_{1xy} &= 0.437(P_{1x} + P_{1y} - P_{2x} - P_{2y} - P_{3x} - P_{3y} - P_{4x} + P_{4y})\end{aligned}\quad (2)$$

are the HOMOs in the many-electron degenerated wave functions; the  $P_{\gamma x}$ ,  $P_{\gamma y}$  and  $P_{\gamma z}$  are the 3p-functions of the  $\gamma$ th phosphorus atom.

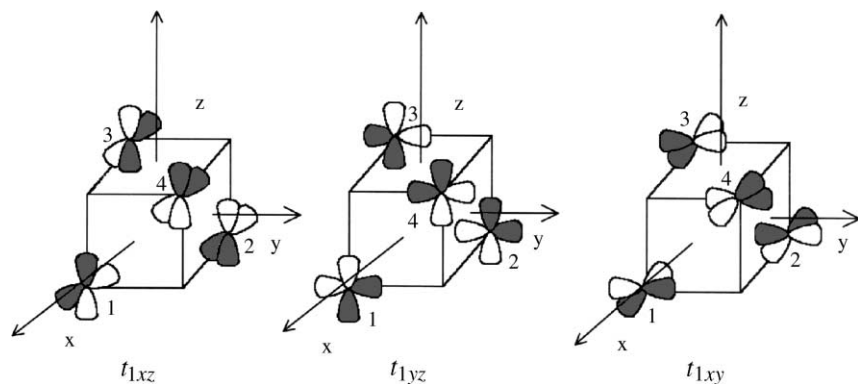
To study the possible lowering of the symmetry of the electronic system, which can improve the results in accordance with the Löwdin dilemma [8], the P<sub>4</sub><sup>q</sup> systems were considered in the above (b) and (c) cases. From the data of Table 1 it can be

**Table 5.** Orbital one-electron energies (in a.u.e.) for the P<sub>4</sub> molecule

	Exper. data	NOCOR without d-funct. <sup>a</sup>	NOCOR with d-funct. <sup>a</sup>	RHF without d-funct.	RHF with d-funct.	UHF without d-funct.	UHF with d-funct.
$R_{P-P}$ (Å)	2.21	2.38	–	2.26	2.14	2.25	2.11
$2e$	−0.357	−0.357	−0.333	−0.333	−0.326	−0.334	−0.330
				<b>−0.343</b>	<b>−0.314</b>	<b>−0.343</b>	<b>−0.314</b>
$6t_2$	−0.384	−0.359	−0.361	−0.361	−0.356	−0.362	−0.359
				<b>−0.367</b>	<b>−0.349</b>	<b>−0.367</b>	<b>−0.349</b>
$5a_1$	−0.421	−0.396	−0.419	−0.413	−0.434	−0.414	−0.439
				<b>−0.422</b>	<b>−0.419</b>	<b>−0.422</b>	<b>−0.419</b>

The orbital energies for the experimental P–P distance of 2.21 Å are presented as bold characters.

<sup>a</sup>Neglect of the core orbital (NOCOR) calculations [7].



**Fig. 6.** The triples degenerate MOs ( $2t_{1xz}$ ,  $2t_{1yz}$ ,  $2t_{1xy}$ ) of the  $P_4^-$  anion.

seen that an artificial lowering of the electronic subsystem symmetry of the neutral  $P_4$  molecule from  $T_d$  to  $C_{2v}$  or  $C_{3v}$  does not change essentially the values of the total energy contrary to the Löwdin dilemma prediction [8]. It is not the case, when the reduced forms of the  $P_4$  molecule ( $P_4^{1-}$  and  $P_4^{2-}$ ) are considered. In case (a), the symmetry of every degenerate state (see equation (1) and Fig. 6) for the  $P_4^-$  anion is lower than the supposed symmetry  $T_d$  of the  $P_4^-$  and  $P_4$  systems. This can be seen by the calculations of the bond orders  $P_{\mu\nu}^\kappa$

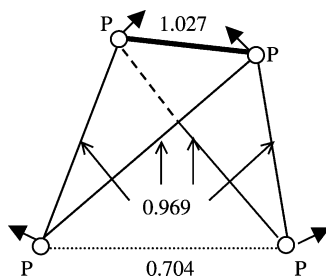
$$P_{\mu\nu}^\kappa = \sum_{i(\text{populated})} C_{i\mu}^\kappa C_{i\nu}^\kappa \quad \kappa = \alpha, \beta \quad (3)$$

where  $C_{i\mu}^\kappa$  are the coefficients in the  $i$ th MO LCAO populated by the electron with the projection  $\kappa = \alpha, \beta$  of the spin. In the MO LCAO approximation, all of the physical mean values can be expressed using  $P_{\mu\nu}^\kappa$ .

It can be easily seen that the contributions of closed shells ( $(1a_1)^2 \cdots (6t_2)^6 \times (5a_1)^2 (2e)^4$ ) are equal in all degenerated states (1). The differences in bond orders in the states (1) are due to the differences in the coefficients in the HOMO LCAO: ( $2t_{1xz}$ ,  $2t_{1yz}$ ,  $2t_{1xy}$ ) (equation (2)). The results of the bond orders  $P_{\mu\nu} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta$  calculations for the  $P_4$ ,  $P_4^-$  (in the state  $\Psi_{xz}(T_1)$ ),  $P_4^{2-}$  (in the singlet state) and  $P_4^{2-}$  (in the triplet state) are given in Table 6. It follows from these data that the tetrahedral  $P_4^q$  molecule in the reduced form with  $q = -1$  or  $-2$ , being in one of the orbitally triple degenerated states ( ${}^2T_1(P_4^-)$ ,  ${}^1T_1(P_4^{2-})$  or  ${}^3T_1(P_4^{2-})$ ), has non-equal bond orders. The lowering of the electronic subsystem symmetry in these cases is accompanied by the stronger polarization of the electronic system, the lowering of the HOMO levels and total energies (see the correlation of the mono electronic levels in Fig. 4 for  $P_4^-$  and by changing of the bond orders (Table 6). It should be noted that in case (b) (energetically more preferable lowering of symmetry to  $C_{2v}$ ) one of the bonds is weakened exactly as in Scheme 1.

**Table 6.** The values of bond orders  $P_{\mu\nu}$  for  $P_4^q$  ( $q = 0, -1, -2$ ) in the nuclear configuration with  $T_d$  symmetry at  $R_{P-P} = 2.21 \text{ \AA}$ 

Symmetry	Bond order	$P_4$	$P_4^-$	$P_4^{2-}$	$P_4^{2-}$
$T_d$	$P_{12}, P_{34}$	1.011	0.867	0.750	0.865
	$P_{13}, P_{24}$		0.995	1.037	0.895
	$P_{14}, P_{23}$		0.867	0.750	0.895
$C_{2v}$	$P_{12}$	1.011	1.027	1.046	0.709
	$P_{\mu\nu}$ ( $\mu = 1, 2; \nu = 3, 4$ )		0.969	0.910	0.954
	$P_{34}$		0.704	0.536	0.709
$C_{3v}$	$P_{12}, P_{13}$	1.011	0.929	0.898	0.745
	$P_{14}$		0.907	0.642	0.745
	$P_{23}$		1.024	1.046	0.961
	$P_{34}, P_{24}$		0.899	0.965	0.961

**Fig. 7.** The bond orders for  $P_4^-$  in the  $C_{2v}$  symmetry and one of the Jahn–Teller active distortions.

At the same time, as it is known, the molecular systems in the degenerated states are dynamically unstable with respect to symmetry distortions due to the Jahn–Teller effect [9]. Such kinds of distortions are expected both in the electronic and nuclear subsystems (vibronic instability). The Jahn–Teller effect destabilizes the tetrahedral geometry of the nuclear system, which results in the bond order's changes too. In particular, according to the theory of the Jahn–Teller effect [9] the tetrahedral molecular systems in the  ${}^2T_1(P_4^-)$ ,  ${}^1T_2(P_4^{2-})$  or  ${}^3T_1(P_4^{2-})$  states are dynamically unstable to the  $e$ - and  $t_2$ -type nuclear distortions, one of which is presented in Fig. 7.<sup>1</sup> Evidently such a kind of distortion to the *butterfly* geometry

<sup>1</sup> General considerations of the butterfly geometry (opening ( $C_{2v}$ )) of the 62-electron tetra nuclear metal clusters are given in Ref. [10] by solving the  $(T_1 + T_2) \times (e + t_2)$  Jahn–Teller problem.

contributes to the further weakening of one of the P–P bonds (*activation* of the reduced phosphorus molecule).

## 5. CONCLUSIONS

Results discussed above show that the theoretical value of the total energy and the geometric parameters for the P<sub>4</sub> molecule in the ground <sup>1</sup>A<sub>1</sub> state does not depend essentially on the approximations used in the calculations. The P–P distances ( $R_{P-P}$ ) are very close to the experimental value of 2.21 Å, possessed by the free molecule P<sub>4</sub>. The P<sub>4</sub> molecule has equal P–P bond orders and it is stable under the reduction of the symmetry from  $T_d$  to  $C_{2v}$  or  $C_{3v}$ .

Unlike the neutral molecule, the electronic states of the reduced forms of the P<sub>4</sub> (P<sub>4</sub><sup>-</sup> and P<sub>4</sub><sup>2-</sup>) in the  $T_d$  geometry are degenerated (<sup>2</sup>T<sub>1</sub>(P<sub>4</sub><sup>-</sup>), <sup>1</sup>T<sub>1</sub>(P<sub>4</sub><sup>2-</sup>) or <sup>3</sup>T<sub>1</sub>(P<sub>4</sub><sup>2-</sup>)). Due to the orbital degeneracy, the equivalence of the P–P bonds in all of the degenerated states is broken, the values of the bond order become different, their electronic and nuclear subsystems are vibronically unstable, and the molecule is *activated*. Thus the *activation* (breaking of the equivalence and cleavage of the bonds) of the phosphorous molecule in the reduced anionic forms is due to the electronic orbital degeneracy and to the vibronic instability. The energies of such a type of phosphorus activation can be estimated as the differences of the phosphorus molecule energies in the reduced and neutral forms. In accordance with data from [Table 1](#) the energies of the one- and two-electron *activation* of the phosphorus molecule are equal to ~60–120 kcal/mol.

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