

# Energy of Chemical Bonds and Spatial Energy Principles of the Hybridization of Atom Orbitals

G. A. Korablev,<sup>1</sup> G. E. Zaikov<sup>2</sup>

<sup>1</sup>Basic Research–Educational Center of Chemical Physics and Mesoscopy, Udmurt Research Center, Ural Division, Russian Academy of Sciences, Izhevsk, Russia

<sup>2</sup>Institute of Biochemical Physics After N. M. Emanuel, Russian Academy of Sciences, 4 Kosygina Street, Moscow 119991, Russia

Received 22 September 2005; accepted 5 January 2006

DOI 10.1002/app.24213

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Methods for the evaluation of energy directness of atom orbital hybridization and the calculation of the energy of chemical bonds in simple and complex structures are proposed on the basis of the application of the spatial energy parameter concept. Appropriate calculations and comparisons for 68 compounds were made. The calcu-

lation results agreed with the experimental data. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2101–2107, 2006

**Key words:** spatial-energy parameter; hybridization; bond energy

## INTRODUCTION

Bond energy is a direct measure of chemical bond strength. Its value is determined by the work necessary to destroy the bond between the atoms of a molecular structure (or the gain of energy in the formation process of this structure from atoms). If the molecule contains two or more similar bonds, the breakoff energy of this bond differs from its average energy (by all bonds).

The values of the bond energy of the electrons of free atoms are calculated by quantum–mechanical methods via the wave functions.<sup>1</sup> However, their practical application for the determination of the energy values of interatomic bonds of actual structures produces significant difficulties because the values of electron bond energy in these structures depend on the changes in the electron and nucleus configuration of the systems, especially during the hybridization of atom orbitals. The prognostic evaluation of such processes is still not properly developed.

Therefore, the main computational method for determining the values of chemical bond energy is the use of corresponding thermochemical values (enthalpies of the formation of reaction products and the initial molecule).

It is of interest in both the theoretical and practical senses to arrange a more direct dependence between

the character of changes in the initial energy characteristics of an atom and the value of its chemical bond energy.

In this respect, it is important to experimentally study the electron spectra of different (not only molecular) structures by means of X-ray electron spectroscopy, which allows one to estimate the electron bond energies in complex systems.<sup>2</sup>

In this research, we attempted to estimate the energy of chemical bonds on the basis of the initial spatial energy characteristics of free atoms with the help of the concept of the spatial energy parameter ( $P$ ), taking into consideration their changes during the hybridization of atom orbitals.

## Method substantiation

The analysis of various physicochemical macroprocesses and microprocesses results in the conclusion that, in many cases, the inverse values of kinetic or energy parameters of subsystems are added when the resulting interaction of atom–molecular structures is estimated. Therefore, the tabulated (initial) values of  $P$ s can be calculated on the basis of the principle of the addition of inverse values of energy components of free atom systems:<sup>3</sup>

$$\frac{1}{P_0} = \frac{1}{q^2} + \frac{1}{(wrn)_i} \quad (1)$$

$$P_E = \frac{\sum P_0}{R} \quad (2)$$

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

TABLE I  
P Parameters of Atoms Calculated via the Bond Energy of the Electrons

Atom I	Valence electrons 2	$w$ (eV) 3	$r_i$ (Å) 4	$q_0^2$ (eV Å) 5	$P_0$ (eV Å) 6	$R$ (Å) 7	$P_0/R$ (cV) 8	$\kappa$ 9	$P_E/\kappa$ 10	$r_1$ (Å) 11	$P_0/r_1$ (eV) 12
H	1s <sup>1</sup>	13.595	0.5295	14.394	4.7985	0.5295	9.0624	1	9.0624	1.36	3.528
C	2p <sup>1</sup>	11.792	0.596	35.395	5.8680	0.77	7.6208	1	7.6208	2.60	2.2569
	2p <sup>2</sup>	11.792	0.596	35.395	10.061	0.77	13.066	2	6.533	2.60	3.8696
	2p <sub>r</sub> <sup>3</sup>				13.213						
	2p <sub>r</sub> <sup>1</sup>				4.4044						
	2s <sub>r</sub> <sup>1</sup>	19.201	0.620	37.240	9.0209	0.77	11.715	1	11.715	2.60	3.470
	2s <sub>r</sub> <sup>2</sup>				14.524	0.77	18.862			2.60	5.5862
	2s <sub>r</sub> <sup>1</sup> + 2p <sub>r</sub> <sup>3</sup>				22.234	0.772	28.801	4	7.2003		
	2s <sub>r</sub> <sup>1</sup> + 2p <sub>r</sub> <sup>2</sup>				19.082	0.710	26.876	3	8.9587		
	2s <sub>r</sub> <sup>1</sup> + 2p <sub>r</sub> <sup>1</sup>				13.425						
	2s <sub>r</sub> <sup>2</sup> + 2p <sub>r</sub> <sup>2</sup>				24.585	0.710	34.627	4	8.657		
N	2p <sup>1</sup>	15.445	0.4875	52.912	6.5916	0.71	9.2839			2.60	9.456
	2p <sup>2</sup>				11.723					0.20	122.9
	2p <sup>3</sup>				15.830	0.71	22.296	3	5.2767	1.48	10.696
	2p <sub>r</sub> <sup>4</sup>				19.193	0.55	34.896	3	11.632		
	2p <sub>r</sub> <sup>5</sup>				21.966	0.55	39.938	5	7.9876		
	2s <sub>r</sub> <sup>1</sup>	25.724	0.521	53.283	10.709	0.71	15.083				
	2s <sub>r</sub> <sup>2</sup>	25.724	0.521	53.283	17.833	0.71	25.117				
	2s <sub>r</sub> <sup>2</sup> + 2p <sub>r</sub> <sup>3</sup>				33.663	0.71	47.413	5	9.4826	1.48	22.745
	2p <sup>1</sup>	17.195	0.4135	71.383	6.4663	0.66	9.7979				
	2p <sup>2</sup>	17.195	0.4135	71.383	11.858	0.66	17.967	2	8.9835	1.36	8.7191
O	2p <sup>4</sup>	17.195	0.4135	71.383	20.338	0.66	30.815	4		1.36	14.954
	2s <sup>1</sup>	33.859	0.450	72.620	12.594	0.66	19.082				
	2s <sup>2</sup>	33.859	0.450	72.620	21.466	0.66	32.524				
	2s <sup>2</sup> + 2p <sup>4</sup>				41.804	0.66	63.339			1.36	30.738
						0.59	70.854				
Si	3p <sup>1</sup>	8.0848	1.068	29.377	6.6732	1.17	5.7036	4			
						1.34	4.990				
	3p <sup>2</sup>				10.876	1.34	8.1164	4			
						1.17	9.2974	4			
	3p <sub>r</sub> <sup>3</sup>				13.766	1.11	12.402	4			
						1.34	10.723				
	3s <sup>1</sup>	14.690	0.904	38.462	9.8716	1.17	8.4373	4			
						1.34	7.3669				
	3s <sup>2</sup>				15.711	1.17	13.428	4			
	3s <sup>2</sup> + 3p <sub>r</sub> <sup>2</sup>				26.587	1.11	23.952	4	5.988	0.39	68.172
Ge	3s <sup>1</sup> + 3p <sub>r</sub> <sup>3</sup>	7.8190	1.090	41.372	23.638	1.11	21.295	4	5.3238		
	4p <sup>1</sup>				7.0669	1.24	5.6991				
						1.39	5.0841				
	4p <sup>2</sup>				12.072	1.24	9.7355				
						1.39	8.6649			0.65	18.572
	4p <sup>3</sup>				15.803						
	4s <sup>1</sup>	15.059	0.886	58.223	10.855	1.24	8.7540				
						1.39	7.8094				
	4s <sup>2</sup>				18.298	1.24	14.756				
	4s <sup>2</sup> + 4p <sup>2</sup>				30.370	1.24	24.492		69.023	0.44	
F	4s <sup>1</sup> + 4p <sup>3</sup>				26.658						
	2p <sup>1</sup>	19.864	0.3595	93.625	6.6350	0.64	10.367			1.33	4.9887
	2p <sup>3</sup>				17.433	0.64					
	2p <sup>5</sup>				25.648	0.64	40.388			1.33	19.435
	2s <sup>1</sup>	42.792	0.396	94.641	14.375	0.64	22.461				
	2s <sup>2</sup>				24.961	0.64	39.002				
	2s <sup>1</sup> + 2p <sup>3</sup>				31.808	0.64	49.700	4	12.425		
2s <sup>2</sup> + 2p <sup>5</sup>				50.809	0.64	79.388			1.33	38.202	

TABLE I Continued

Atom I	Valence electrons 2	$w$ (eV) 3	$r_i$ (Å) 4	$q_0^2$ (eV Å) 5	$P_0$ (eV Å) 6	$R$ (Å) 7	$P_0/R$ (cV) 8	$\kappa$ 9	$P_E/\kappa$ 10	$r_I$ (Å) 11	$P_0/r_I$ (eV) 12				
Sn	5p <sup>1</sup>	7.2124	1.240	47.714	7.5313	1.42	5.3037								
							1.58	4.7666							
	5p <sup>2</sup>							13.0091	1.42	9.1613			1.02	12.754	
										1.58	8.2336				
	5p <sup>3</sup> <sub>r</sub>								17.173	1.42	12.094				
	5s <sup>1</sup>					12.965	1.027	65.062	11.053	1.42	7.7838				
						1.58	6.9956								
	5s <sup>2</sup>				18.896	1.42	13.307								
						1.58	11.959								
	5p <sup>2</sup> + 5s <sup>2</sup>				26.427	1.42	18.611		0.67		38.443				
						1.58	16.726		0.67						
Cl	3p <sup>1</sup>	13.780	0.7235	59.844	8.5461	1.00	8.5461		1.81	4.7216					
	3p <sup>3</sup>						19.943								
	3p <sup>5</sup>						27.196	1.00	27.196						
	3s <sup>1</sup>					29.196	0.660	79.928	15.526	1.00	15.526				
	3s <sup>2</sup>					29.196	0.660	79.928	26.002						
	3s <sup>1</sup> + 3p <sup>3</sup>								35.468	1.00	35.468	4	8.867		
Br	3s <sup>2</sup> + 3p <sup>5</sup>				53.198	1.00	53.198		1.81	29.391					
	4p <sup>1</sup>	12.438	0.8425	73.346	9.1690	1.14	8.0430		1.96	4.6781					
	4p <sup>3</sup>				22.005	1.14									
	4p <sup>5</sup>				30.563		26.809								
	4s <sup>1</sup>	27.013	0.730	100.21	16.477		14.454								
	4s <sup>2</sup>				28.300		24.825								
I	4s <sup>1</sup> + 4p <sup>3</sup>				38.462	1.14	33.739	4	8.4348						
	4s <sup>2</sup> + 4p <sup>5</sup>				58.863		51.634		(0.39)	150.93					
	5p <sup>1</sup>	10.971	1.0215	77.651	9.7936	1.35	7.2545		2.20	4.4516					
	5p <sup>3</sup>				23.462	1.35	13.739	3	4.580						
	5p <sup>5</sup>				32.548		24.109								
	5s <sup>1</sup>	22.345	0.876	103.44	16.459		12.192								
	5s <sup>2</sup>				28.400		21.037								
	5s <sup>2</sup> + 5p <sup>5</sup>				60.948		45.147		0.50	121.90					

where  $w_i$  is the bond energy of electrons;<sup>1</sup>  $r_i$  is the orbital radius of the  $i$  orbital;<sup>4</sup>  $n_i$  is the number of electrons in the given orbital;  $q = Z^*/n^*$ , where  $Z^*$  and  $n^*$  are the nucleus effective charge and effective main quantum number, respectively;<sup>5,6</sup> and  $R$  is the dimensional characteristics of the atom bond.

Values of tabulated atomic P-parameter ( $P_0$ ) are constant for electrons of the  $i$  orbital of the given atom.

As described in ref. 3,  $P_E$  is a parameter that numerically equals the energy of the valence electrons in an atom static model, which is a direct characteristic of electron density inside the atom at a given distance from the nucleus and, therefore, can be used to estimate the kinetics of chemical reactions and chemical bond energy of structures.

$P_0$  and  $P_E$  of free atoms were calculated with eqs. (1) and (2), the results of which are given in Table I. For the hydrogen atom, the value of the Bohr radius of the hydrogen atom was equal to 0.529 Å; for some cases, the ionic radius ( $r_I = 1.36$  Å) was used as the main dimensional characteristic.

All atoms, covalent radii, and  $r_I$  values were taken basically according to Belov–Bokii. For C, N, and O atoms, the possibility of changing covalent radii, de-

pending on the bond repetition factor, was also taken into consideration. For the same elements, the average statistical values of  $P$  were given as  $P_E/K$ , which assumed the possibility for further calculation of the average value of bond energy.

### Spatial energy principles of hybridization

Hybridization refers to the mixing of atom orbitals of different types of a given atom in one molecular (or atom) orbital. Hybridization principles are well-developed in accordance with the experimental data in the frames of general theories of valence bonding and molecular orbitals.

However, the sources of energy directedness of hybridization processes have to be further investigated and discussed.

The authors of ref. 1 made a conclusion based on the analysis of multiple computational and experimental data in which the most valence-active were the orbitals with minimum values of  $P_0$ . We applied this principle to the hybridization of atom orbitals to the example of carbon and nitrogen atoms.

TABLE II  
Computation of Bond Energy Taking into Account the Hybridization of Atom Orbitals

Structure 1	Bond 2	Hybridization 3	Orbitals 4	$P_0'$ (eVÅ)	$\Sigma P_0'$ (eVÅ)	$R_k$ $= d/2$ (Å)	$P_E'$ (eV)	$(N/\kappa)_1$ 9	$P_E''$ (eV) 10	$(N/\kappa)_2$ 11	$P_C$ (eV) 12	$E$ (kJ/mol)	
												Calcd 13	Found 14
Diamond	$\sigma$	$sp^3$	$2s^1$	9.0209	22.234	0.772	28.801	1/4	28.801	1/4	3.600	347.5	347.3
	C—C		$2p_r^3$	13.213									
Graphite (1)	$\sigma$	$sp^2$	$2s^1$	9.0209	19.082	0.710	26.876	1/3	26.876	1/3	4.479	432.4	418.7–460.6
	C—C		$2p^2$	10.061									
Graphite (2)	$\sigma$	$s^2p^2$	$2s^2$	14.524	24.585	0.710	34.627	1/4	34.627	1/4	4.3283	417.8	418.7
	C—C		$2p^2$	10.061									
Carbyne (—C≡C—) <sub>m</sub>	Single	$sp$	$2s^1$	9.0209	13.425*	0.6895	9.7365	1/4	9.7365	1/4	1.2170	117.5	108.9
			$2p_r^1$	4.4044	*1/2								
Ethylene H <sub>2</sub> C=CH <sub>2</sub>	$\sigma$	$sp^2$	$2s^1$	9.0209	19.082	0.665	28.695	2/4	28.695	2/4	3.587	346.2	347
	C—C		$2p^2$	10.061									
Acetylene HC≡CH	$\sigma$	$sp$	$2s^1$	9.0209	13.425	0.601	22.375	3/4	22.375	3/4	8.391	807.6	782
	C—C		$2p_t^1$	4.4044									
Methane (1) CH <sub>4</sub>	$\pi$	$sp^3$	$2s^1$	4.4044	8.8088	0.601	14.657	1/4	14.657	1/4	1.832	176.8	
	C—C		$2p_r^1$	4.4044									
	$\sigma + \pi$											984.4	962.3
	$\sigma$				9.0209	22.234	0.546	40.722	1/4	$\frac{4.7985}{0.546}$	1/1	4.716	455.3
Methane (2)	C—H		$2p_r^3$	13.213									
	C—H		$2s^2$	14.524	24.585	0.77	31.929	1/4	9.0624	1/1	4.243	409.6	410
			$2p^2$	10.061									
Ethane H <sub>3</sub> C—CH <sub>3</sub>	$\sigma$	$sp^3$	$2s^1$	9.0209	22.234	0.772	28.819	1/4	28.819	1/4	3.6024	347.7	345.6
	C—C		$2p_r^3$	13.213									
Nitrogen N <sub>2</sub>	N—N	—	$2p^1$	6.5916	13.183	0.71	18.658	1/3	18.658	1/3	3.095	298.7	318
			$2p^1$	6.5916									
	N=N		$2p^2$	11.723	23.446	0.63	37.216	1/3	37.216	1/3	6.2026	598.7	586
N <sub>2</sub> N≡N	$\sigma$	$sp$	$2p^2$	11.723									
	N—N		$2p_r^4$	19.193	19.193	0.55	34.896	1/3	34.896	1/3	5.8161	561.4	543.4
	$2\pi$		$2p_r^5$	21.966	21.966	0.55	39.938	1/5	39.938	1/5	3.9938	385.5	
Silicon Si <sub>2</sub> →2Si	$\sigma + \pi$	$s^2 p^2$	$3s^2$	15.711	26.587	1.11	23.952	1/4	23.952	1/4	2.994	289	946.9 305 ± 3
	$\sigma$		$3p^2$	10.876									309.6 ± 13
SiH <sub>4</sub>	Si—H	$sp^3$	$3p_r^3$	13.766	13.766	1.34	10.273	1/3	10.273	1/3	1.712	165.3	176
			$3s^1$	9.8716	23.638	0.738	32.030	1/4	9.0624	1/1	4.251	410.3	395
Germanium Ge <sub>2</sub> →2Ge	Ge—Ge	$sp^3$	$3p_r^3$	13.766									
	$\sigma$		$4s^1$	10.855	26.658	1.22	21.851	1/4	21.851	1/4	2.7314	263.6	273
Tin Sn <sub>2</sub> →2Sn		$5p_r^3$	$4p_r^3$	15.803	15.803	1.39	11.369	1/3	11.369	1/3	1.895	183	278 ± 13
			$4p_r^3$	15.803	15.803	1.39	11.369	1/3	11.369	1/3	1.895	183	168
			$5p_r^3$	17.173	17.173	1.42	12.094	1/3	12.094	1/3	2.016	194.6	192.5 ± 16.7
Sn(II)	Sn—Sn	$p^2$	$5p^2$	13.009	13.009	1.63	7.981	1/2	7.981	1/2	1.995	192.6	192.5
Sn(IV)	Sn—Sn	$s^2p^2$	$5p^2$	13.009	26.427	1.58	16.726	1/4	16.726	1/4	2.098	202.5	192.5
			$5s^2$	18.896									
HF	$\sigma$	$sp^2$	$2s^1$	14.375	31.808	0.64	49.700	1/4	4.79851/0.438	1/1	5.822	562	566
	F—H		$2p^3$	17.433					0.438				
HCl	$\sigma$	$sp^2$	$3s^1$	15.526	35.468	1.00	35.468	1/4	4.7985/0.529	1/1	4.482	432.6	427.8
	Cl—H		$3p^2$	19.943					0.529				
HBr	$\sigma$	$sp^2$	$4s^1$	16.477	38.462	1.14	33.734	1/4	4.7985/0.704	1/1	3.769	363.9	362.5
	Br—H		$4p^3$	22.005					0.704				
HI	I—H	$p^3$	$5p^3$	23.462	23.462	1.35	17.379	1/3	4.7985/0.8045	1/1	2.94	283.7	294.6

$P_0'$ , tabulated atomic P-parameter of the given atom;  $R_k$ , cation radius;  $d$ , bond length.

### Carbon ( $2s^22p^2$ )

As shown in Table I, the maximum value of  $P_0$  of the  $2p^2$  orbital was 10.061 eV Å, but the minimum value of  $P_0$  of the  $2s^1$  orbital was smaller (9.029 eV Å). This means that the  $2s^1$  orbital was more valence-active than the  $2p^2$

orbital. This conditioned their hybridization. The calculation, according to eq. (1), produced a value of  $P_0$  of the  $2p^3$  (hybridized) orbital equal to 13.213 eV Å. This was much smaller than  $P_0$  of the  $2s^2$  orbital (14.524 eV Å). Therefore, only the following hybridization options

TABLE III  
 $D_0$  (kJ/mol) Values of the Diatomic Molecules

Structure	First atom				Second atom					$D_0$	
	Orbitals	$N/\kappa$	$P_E$ (eV)	$P_{E\frac{N}{\kappa}}$	Orbitals	$N/\kappa$	$P_E$ (eV)	$P_{E\frac{N}{\kappa}}$	$P_C$ (eV)	Calcd	Found
1	2	3	4	5	6	7	8	9	10	11	12
CCl	2p <sup>1</sup>	1/1	7.6208	7.6208	3p <sup>1</sup>	1/1	8.5461	8.5461	4.0209	388.9	393.3
CBr	2p <sup>1</sup>	1/1	7.6208	7.6208	4p <sup>1</sup>	1/1	8.0430	8.0430	3.9130	377.7	364
CJ	2p <sup>1</sup>	1/1	7.6208	7.6208	5p <sup>1</sup>	1/1	7.2545	7.2545	2.2523	217.4	209.2
CN	2p <sup>2</sup>	2/2	13.066	13.066	2s <sup>2</sup> 2p <sup>3</sup>	2/5	47.413	18.965	7.7358	746.7	755.6
CN	2p <sup>2</sup>	2/2	14.581	14.581	2p <sup>3</sup>	2/3	25.127	16.751	7.796	752.5	755.6
C—O	2p <sup>2</sup>	1/2	13.066	6.533	2p <sup>2</sup>	1/2	17.967	8.984	3.782	365	356
NO	2p <sup>1</sup>	1/1	9.2839	9.2839	2p <sup>2</sup>	2/2	20.048	20.048	6.346	612.5	626.8
CH	2p <sup>2</sup>	1/2	13.066	6.533	1s <sup>1</sup>	1/1	9.066	9.066	3.7969	366.5	333 ± 1
OH	2p <sup>2</sup>	1/2	17.967	8.9835	1s <sup>1</sup>	1/1	9.066	9.066	4.5118	435.5	423.7
CIF	3s <sup>2</sup> 3p <sup>5</sup>	1/7	29.391 <sup>a</sup>	4.1987	2s <sup>2</sup> 2p <sup>5</sup>	1/7	38.202 <sup>a</sup>	5.4574	2.5579	246.9	229.1
CIO	3s <sup>2</sup> 3p <sup>5</sup>	1/7	29.391 <sup>a</sup>	4.1987	2p <sup>2</sup>	2/2	8.7191 <sup>a</sup>	8.7191	2.8337	273.5	264
CIO	3p <sup>1</sup>	1/1	4.7216 <sup>a</sup>	4.7216	2s <sup>2</sup> 2p <sup>4</sup>	1/6	30.738 <sup>a</sup>	5.123	2.450	237.2	264
FO	2p <sup>1</sup>	1/1	4.9887 <sup>a</sup>	4.9887	2p <sup>2</sup>	1/2	8.7191 <sup>a</sup>	4.3596	2.327	224.6	219.2
NF	2p <sup>3</sup>	1/3	10.696 <sup>a</sup>	3.5653	2p <sup>1</sup>	1/7	38.202 <sup>a</sup>	5.4574	2.486	239.5	298.9
NCL	2p <sup>3</sup>	1/3	22.296	7.432	3p <sup>1</sup>	1/1	8.5461	8.5461	3.9751	383.7	384.9
H <sub>2</sub>	1s <sup>1</sup>	1/1	9.0624	9.0624	1s <sup>1</sup>	1/1	9.066	9.066	4.533	437.5	432.2
Li <sub>2</sub>	2s <sup>1</sup>	1/1	2.2419	2.2419	2s <sup>1</sup>	1/1	2.2419	2.2419	1.121	108.2	98.99
B <sub>2</sub>	2p <sup>1</sup>	1/1	5.4885	5.4885	2p <sup>1</sup>	1/1	5.4885	5.4885	2.744	264.9	276 ± 21
C—C	2p <sup>1</sup>	1/1	7.6208	7.6208	2p <sup>1</sup>	1/1	7.6208	7.6208	3.810	367.8	376.7
C=C	2p <sup>1</sup>	2/2	13.066	13.066	2p <sup>2</sup>	2/2	13.066	13.066	6.533	630.6	611
N—N	2p <sup>3</sup>	1/3	10.696 <sup>a</sup>	3.5653	2p <sup>3</sup>	1/3	10.696 <sup>a</sup>	3.5653	1.783	172.1	161
N=N	2s <sup>2</sup> 2p <sup>3</sup>	2/5	22.745 <sup>a</sup>	9.098	2s <sup>2</sup> 2p <sup>3</sup>	2/5	22.745 <sup>a</sup>	9.098	4.549	439	418
O—O	2p <sup>2</sup>	1/2	8.7191	4.3596	2p <sup>2</sup>	1/2	8.7191	4.3596	2.1798	210.4	213.4
O=O	2s <sup>2</sup> 2p <sup>4</sup>	2/6	30.738 <sup>a</sup>	10.246	2s <sup>2</sup> 2p <sup>4</sup>	2/6	30.738 <sup>a</sup>	10.246	5.123	494.5	498.3

<sup>a</sup> Calculations of  $P_E$  are given with  $r_1$  based on the equation  $P_E = \Sigma P_0/r_1$ .

could occur:  $2p^3 + 2s^1$ ,  $2p^2 + 2s^1$ , and  $2p^1 + 2s^1$ ; this corresponded to single, double, and triple bonds of hybridization of the  $sp^3$ ,  $sp^2$ , and  $sp$  types.

#### Nitrogen ( $2s^2 2p^3$ )

$P_0$  of the  $2p^3$  orbital was 15.830 eV Å, and  $P_0$  of the  $2s^1$  orbital was 10.709 eV Å. Therefore, they were hybridized with the formation of the  $2p_1^4$  hybridized orbital responsible for  $\sigma$ -bond  $sp$  hybridization, where  $P_0 = 19.193$  eV Å. However, this was still greater than  $P_0$  of the  $2s^2$  orbitals (17.833 eV Å). That is, the hybridization process continued due to the  $2s^2$  orbital with the formation of the  $2p_1^5$  orbital ( $P_0 = 21.966$  eV Å) responsible for the  $2\pi$ -bond of  $s$ - $p$  hybridization.

There are main hybridization options for orbitals in carbon and nitrogen atoms in this approach. Less possible are metastable states with the hybridization of the  $2s^2 + 2p^2$  type with carbon and the  $2s^2 + 2p^3$  of nitrogen.

The initial hybridization principle was applied to the analysis of the energy directedness of mixing of atom orbitals for some other structures (Table II). The computational values of  $P_0$  of the hybridized orbitals were further used to determine bond energies ( $E$ ). In the supposition of pair interatomic interaction, the

structural  $P_C$  parameter was calculated<sup>1,7</sup> following the principle of the addition of inverse values of initial values of  $P$  and, in this case, based on the following equation:

$$\frac{1}{E} = \frac{1}{P_C} = \frac{1}{\left(P_{E\frac{N}{K}}\right)_1} + \frac{1}{\left(P_{E\frac{N}{K}}\right)_2} \quad (3)$$

where  $N$  is the coefficient of the bond repetition factor and  $K$  usually equals the number of registered atom valence electrons. The half internuclear distance was frequently used as  $R$  for binary bonds. The same was true for the hydrogen atom in halogen-hydrogen.

The corresponding calculations for several structures are given in Table II. As shown in Table II,  $K$  in the crystalline carbon structures observed was equal to the coordination number. For the  $\sigma$ -bond of nitrogen,  $K = 3$ ; this corresponded to the number of valence electrons of the  $2p^3$  orbital:  $K_1 = n_1 = 3$ .

The comparison of computational values with the experimental data by bond energy<sup>8</sup> given in Table II characterizes rather the high efficiency of this method. Usually, the ratio error does not exceed 0.1% and is not more than 5% in other cases.

TABLE IV  
*E* (kJ/mol) Values of Bond Breakoff in Complex Structures

No.	Reaction 1	Bond breakoff 2	First atom			Second atom			E	
			Orbitals 3	<i>N</i> / <i>κ</i> 4	$P_E$ (eV) $P_1$ 5	Orbitals 6	<i>N</i> / <i>κ</i> 7	$P_E$ (eV) 8	Calcd 9	Found 10
1	CH <sub>2</sub> =CH + H									430 ± 12.6
2	CH <sub>3</sub> =CH <sub>2</sub> + H									457 ± 12.6 >434.8
3	CH <sub>4</sub> =CH <sub>3</sub> + H	C—H	2s <sup>2</sup> 2p <sup>2</sup>	1/4	7.982	1s <sup>1</sup>	1/1	9.0624	409.7	435 ± 4.2
4	C <sub>2</sub> H <sub>4</sub> =C <sub>2</sub> H <sub>3</sub> + H									438.9
5	C <sub>2</sub> H <sub>6</sub> =C <sub>2</sub> H <sub>5</sub> + H							10.426	436.4	445.2
6	C <sub>6</sub> H <sub>6</sub> =C <sub>6</sub> H <sub>5</sub> + H									457.3
7	CH <sub>2</sub> =CH + H	C—H	2p <sup>2</sup>	1/2	6.533	1s <sup>1</sup>	1/1	9.0624	366.5	338.9
8	CH <sub>4</sub> =CH <sub>2</sub> + H <sub>2</sub>	C—(H <sub>2</sub> )	2p <sup>2</sup>	1/2	6.533	1s <sup>1</sup>	2 · 1/1	2 · 9.0624	463.6	364 432.6
9	C <sub>2</sub> H <sub>5</sub> =CH <sub>3</sub> + CH <sub>2</sub>									416.7 ± 8.4
10	C <sub>2</sub> H <sub>6</sub> =2CH <sub>3</sub>	C—C	2s <sup>2</sup> 2p <sup>2</sup>	1/4	7.982	2s <sup>2</sup> 2p <sup>2</sup>	1/4	7.982	385.2	372.4
11	C <sub>3</sub> H <sub>8</sub> =C <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub>									380.7
12	O <sub>2</sub> =O + O	O=O	2p <sup>2</sup>	2/2	17.967	2p <sup>2</sup>	2/2	17.967		—
13	CH <sub>3</sub> O · OH=CH <sub>3</sub> O + OH	—O—O—	2p <sup>4</sup>	1/4	14.954 <sup>a</sup>	2p <sup>4</sup>	1/4	14.954 <sup>a</sup>	180.4	181.5 ± 19
14	H <sub>2</sub> O <sub>2</sub> =2OH	—O—O—	2p <sup>2</sup>	1/2	8.7192	2p <sup>2</sup>	1/2	8.7192	210.4	231.8 ± 2.5
15	H <sub>2</sub> O <sub>2</sub> =2OH	(OH)—(OH)			4.5118			4.5118	217.8	231.8 ± 2.5
16	N <sub>2</sub> =2N	N—N	2s <sup>2</sup> 2p <sup>3</sup>	1/5	22.745	2s <sup>2</sup> 2p <sup>3</sup>	1/5	22.745	219.5	—
17	N <sub>2</sub> H <sub>2</sub> =NH + NH	N=N	2s <sup>2</sup> 2p <sup>3</sup>	2/5	22.745 <sub>5</sub> <sup>2</sup>	2s <sup>2</sup> 2p <sup>3</sup>	2/5	8.898 <sup>a</sup>	439.1	472.8 ± 33.5
					= 8.898 <sup>a</sup>					
18	NH <sub>2</sub> =N + H <sub>2</sub>	N=N	2p <sup>3</sup>	2/3	10.696 <sup>a</sup>	1s <sup>1</sup>	1/1	9.0624	( <i>P</i> <sub>1</sub> = 5.118 eV)	—
19	N <sub>2</sub> H <sub>4</sub> = 2(NH <sub>2</sub> )	(NH <sub>2</sub> )—(NH <sub>2</sub> )			5.118 <sup>a</sup>			5.118 <sup>a</sup>	247	252.7 ± 16.7
20	CH <sub>3</sub> NHNH <sub>2</sub> =CH <sub>3</sub> NH + NH <sub>2</sub>	N—N	2p <sup>3</sup>	1/3	10.696 <sup>a</sup>	2P <sup>3</sup>	1/3	10.696 <sup>a</sup>	172.1	175.7
		N—N	2s <sup>2</sup> 2p <sup>3</sup>	1/5	22.745 <sup>a</sup>	2S <sup>2</sup> 2P <sup>3</sup>	1/5	22.745 <sup>a</sup>	219.5	217 ± 4
21	NO <sub>2</sub> =NO + O	(=N=O)—O	2s <sup>2</sup> 2p <sup>3</sup>	—	4.4525	2P <sup>2</sup>	2/2	8.7191 <sup>a</sup>	284.5	305.9
22	N <sub>2</sub> O=NO + N	N—O	2p <sup>1</sup>	1/1	9.2839	2P <sup>1</sup>	1/1	9.7979	460.2	481.8
23	N <sub>2</sub> O=(N <sub>2</sub> ) + O	(N <sub>2</sub> )=O	—	—	22.745 <sup>a</sup>	—	—	8.7191 <sup>a</sup>	172.5	167.4
24	NO <sub>2</sub> =N + O <sub>2</sub>	(N)—(O <sub>2</sub> )	2s <sup>2</sup> 2p <sup>2</sup>	1/5	9.4826	—	—	8.9835	445.3	439.3

<sup>a</sup> Calculations of  $P_E$  were done with  $r_1$ .

Also, the given model mainly confirmed the approved conclusions and results of the corresponding computational methods of bond energies as applicable to certain structures, the list of which in this article is limited only by the authors' interests.

#### Calculation of chemical bond energy via the average values of $p_0$

The application of methods of valence bonding and molecular orbitals to complex structures meets significant difficulties with regard to the prediction of hybridization energy directedness and the type of bonds being formed. Let us consider several opportunities of with  $P_0$  method. It is practical to apply eq. (3) to calculate the energy of chemical bonds, where  $K$  usually equals the number of registered valence electrons and  $P_E$  ( $N/K$ ) has a physical sense of the averaged energy of the spatial energy parameter falling on one valence electron of registered orbitals. However, for complex structures,  $P$  ( $N/K$ ) is averaged by all of the main valence orbitals.

Let us first approve such an approach for binary molecules. For binary molecules, the dissociation en-

ergy ( $D_0$ ) corresponds to the value of chemical bond energy:  $D_0 = E$ .

The results of the calculation of  $D_0$  by eq. (3) given in Table III showed that  $P_C = D_0$ . For some molecules containing F, N, and O, the values of  $r_1$  (in Table III marked with a superscript *a*) were used to register the ionic character of the bond in the process of  $P_E$  calculation. For molecules C<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, the calculations were done by divisible bonds. In other cases, the average values of bond energy were calculated. The computational data were not in conflict with the experimental data.<sup>8</sup>

With a similar computation of average values of bond energy in complex structures, the average values of  $P_E$  (taken from Table I) were also considered but with valence sublevels taken into account (Table IV). In these cases,  $P_C = E$  (bond energy).

Also, in most cases, due to the influence of all of the valence electrons of atoms, it was possible for the first approximation to be limited with the estimation of interaction only between basic bond atoms (e.g., C—H in hydrocarbon structures). To a greater extent, this

refers to hydrocarbon organic structures. However, for nitrogen oxides and hydrides, more accurate results were obtained with preliminary calculations of the  $P_C$  values of the reaction intermediate products with eq. (3).

Then,  $E$  was calculated according to the following equation:

$$\frac{1}{\bar{E}} = \frac{1}{P_{C1}} + \frac{1}{P_{C2}} \quad (4)$$

where  $P_{C1}$  and  $P_{C2}$  are the  $P_C$  values of complex structure parameters.

Calculations based on eqs. (3) and (4) are given in Tables III and IV. In some cases, the results of the calculations of bond energy for fragments of  $\text{NH}_2$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$  that were introduced into other complex structures are given. The deviations of the computational data from the experimental ones<sup>8</sup> did not exceed 10% for complex structures.

### CONCLUSIONS

1. The energy of chemical bonds in simple and complex structures could be satisfactorily deter-

mined by means of the  $P$  method on the basis of the initial spatial energy characteristics of free atoms with the hybridization of their atom orbitals taken into account.

2. The proposed method for the estimation of the energy directedness of mixing atom orbitals agreed with the experimental data.

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