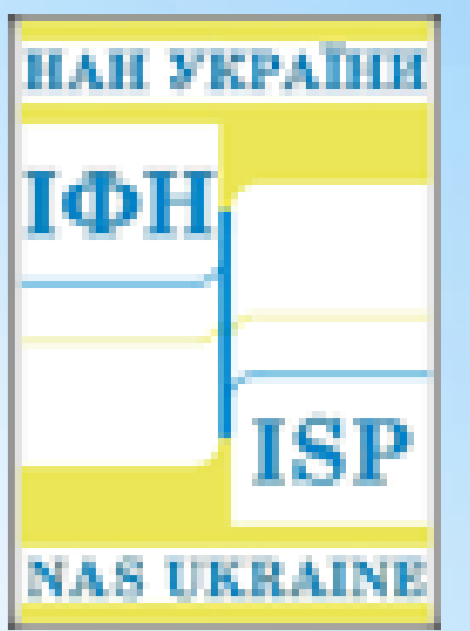


Two-electron systems in two-dimensional heterostructures with ion-covalent bond



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INTRODUCTION

The unique properties of two-dimensional (2D) materials such as graphene [1] and materials with a structure similar to graphene [2] cause interest in connection with the possibility of applying such materials in quantum electronics, semiconductor technique and quantum computing systems. The study of impurity centers in such materials is one of the fundamental areas of modern nanoscience. The paper presents the calculation of the energy of singlet and triplet states of two-electron systems such as exchange-coupled pairs of shallow hydrogen-like impurities and D-centers in 2D graphene-like structures with ion-covalent bond. The calculations were carried out by the variational method with using the Gaussian system of functions. Similar functions were previously used to calculate the energy of the singlet and triplet states of the 2D hydrogen molecule [3]. The parameters of the electron-phonon coupling were determined using the dielectric characteristics calculated in [2] with using the modified method of binding orbitals of binary 2D $A_N B_{8-N}$ compounds.

BASIC RELATIOS

We consider two D^0 centers in the phonon field of a 2D crystal. The energy E_{12} of the ground state of the considered system has the form:

$$E_{12} = \langle \Phi_{12} | H_{12} | \Phi_{12} \rangle$$

$$H_{12} = -\frac{1}{2}(\Delta_1 + \Delta_2) + H_C + H_{2e-f} + H_f$$

$$H_{2e-f} = \sum_k V_k \left\{ \left[\exp(-ikr_1) + \exp(-ikr_2) \right] a_k^+ + H.c. \right\}$$

$$H_f = \sum_k \hbar \omega_k a_k^+ a_k \quad \eta = \varepsilon_\infty / \varepsilon_0, \quad V_k = \sqrt{\frac{2\pi\alpha}{Sk}}$$

$$\alpha = \frac{1}{\hbar\omega} \frac{e_0^2}{2\varepsilon_\infty} (1-\eta) \cdot \left(\frac{2m^* \omega}{\hbar} \right)^{1/2}, \quad \tilde{E}_h = \frac{e_0^4 m_{ef}}{\hbar^2 \varepsilon_\infty^2}$$

$$H_C = -\eta Z (1/r_{a1} + 1/r_{b1} + 1/r_{a2} + 1/r_{b2} - 1/R_{12}) + 1/r_{12}$$

$$\Phi_{12} = \Psi_{12} \exp(-S_1 - S_2), \quad S_1 = \sum_k f_k (a_k^+ - a_k)$$

$$S_2 = \sum_{k,j} g_k (r_1, r_2) \exp(-ikr_j) a_k^+ + H.c.$$

$$g_k = \varphi_k (\exp(-ikr_1) + \exp(-ikr_2))$$

The electron WF is determined by:

$$\Psi_{12} \equiv \Psi_{12}(r_1, r_2, r_{12}).$$

TWO-CENTER BIPOLARON

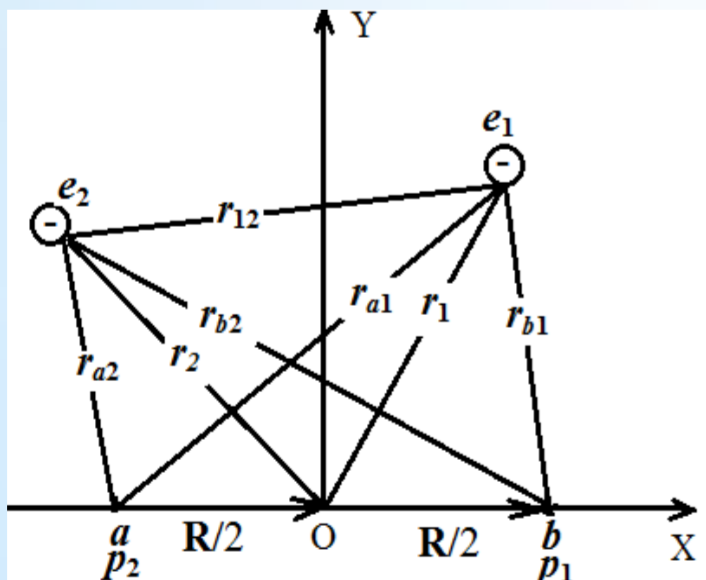


Fig. 1. Two center coordinates system.

$$\Psi_{12} = \sum_{i=1}^N (1 + P_{12}) C_i \exp(-a_i r_{a1}^2 - 2a_{2i} (r_{a1} \cdot r_{b2}) - a_{3i} r_{b2}^2), \quad (3)$$

The strong coupling energy of BP in a 2D crystal is

$$E_{12} = \min_{\{C_i, a_{1i}, a_{2i}, a_{3i}\}} \{J_{12}\}, \quad J_{12} = \frac{T_{12}}{N_{12}} + \frac{V_C}{N_{12}} + \frac{V_f}{N_{12}^2}, \quad (4)$$

where the first, second and third terms of the left part eq. (4) for J_{12} , correspond to the kinetic energy, the Coulomb energy, the total contribution of the phonon field and electron-phonon interaction, respectively; N_{12} - is the normalization integral:

$$N_{12} = \langle \Psi_{12} | \Psi_{12} \rangle$$

2D Hydrogen atom

$$\Psi_{ex}(r) = \left(\frac{8}{\pi} \right)^{1/2} \alpha \exp(-2\alpha r),$$

$$\Psi(r) = \frac{1}{\sqrt{N(C, a)}} \sum_{i=1}^n C_i \exp(-a_i r^2),$$

Table I. Parameters of the approximate WF 2D H

n	C_i	a_i
1	1	$1.03139 \cdot 10^5$
2	2.357667	$9.96784 \cdot 10^3$
3	$4.182117 \cdot 10^1$	7.54247
4	$1.041053 \cdot 10^1$	0.33655
5	$5.214417 \cdot 10^1$	2.54461
6	9.249844	$3.38236 \cdot 10^2$
7	4.867695	$1.60521 \cdot 10^3$
8	$2.754942 \cdot 10^1$	$2.41163 \cdot 10^1$
9	$4.101679 \cdot 10^1$	0.91133
10	$1.648679 \cdot 10^1$	$8.48389 \cdot 10^1$

Table II. Approximate $\Psi(r)$ and exact $\Psi_{ex}(r)$ values of the WF of a 2D H

N_e	r	$\Psi(r)$	$\Psi_{ex}(r) (\alpha=1)$
1	0	1.593303	1.595769
2	0.5	0.587129	0.587051
3	1	0.215924	0.215964
4	1.5	$7.954769 \cdot 10^{-2}$	$7.944867 \cdot 10^{-2}$
5	2	$2.912527 \cdot 10^{-2}$	$2.922753 \cdot 10^{-2}$
6	2.5	$1.084476 \cdot 10^{-2}$	$1.075221 \cdot 10^{-2}$
7	3	$3.964019 \cdot 10^{-3}$	$3.955516 \cdot 10^{-3}$

$$E_{ex} = -2E_h, \quad E_H(\Psi) = -1.9999762E_h$$

INTERMEDIATE COUPLING

$$J_{12i} = \frac{2T_{12}}{N_{12}} + \frac{2\alpha V_C}{(1-\eta)N_{12}} + \frac{2\alpha V_{ph}}{(1-\eta)N_{12}^2} + \delta J_{2i}, \quad (5)$$

$$E_2 = \min \{J_{12i}\}$$

Table III. Material parameters

Crystal	m_e/m_0	ε_0	ε_∞	$\hbar\omega$ meV	α	R
GaAs	0.063	12.1	10.64	35.0	0.056	0.164
CdTe	0.096	9.6	7.21	21.08	0.272	0.675
CdS	0.155	8.42	5.27	38.0	0.529	0.783
ZnSe	0.16	8.66	5.9	31.4	0.45	0.924
AgBr	0.22	10.6	4.68	15.4	1.64	1.68
AgCl	0.3	9.5	3.99	24.4	1.9	1.9
CdF ₂	0.283	7.78	2.4	50.0	2.53	1.274

Table IV. Results of calculations in 2D systems of the ground-state energies of D^0 and D^- - centers, E^0 , and E^- , respectively. Binding energies are denoted E_b . All energies are in units of $\hbar\omega$

Crystal	a	R	$-E^-$	$-E^0$	E_b^-	E_b^0	E_b^-/E_b^0
GaAs	0.0556	0.164	0.9227	0.7592	0.0761	0.6718	0.1133
CdTe	0.272	0.673	4.1522	3.3628	0.3622	2.9355	0.1234
CdS	0.529	0.783	5.9049	4.5496	0.5244	3.7189	0.1410
ZnSe	0.45	0.925	6.2828	4.9512	0.6247	4.2443	0.1472
AgBr	1.64	1.68	5.637	3.817	0.180	2.177	0.083
AgCl	1.9	1.9	19.046	13.079	3.3909	10.503	0.3229
AgBr	1.64	1.68	5.637	3.817	0.180	2.177	0.083
AgCl	1.9	1.9	6.634	4.482	0.261	2.582	0.101
AgCl	1.9	1.9	22.911	15.586	4.3405	12.602	0.3444
CdF ₂	2.53	1.274	24.233	14.911	5.3475	10.937	0.4889

The values highlighted in yellow correspond to three-dimensional crystals.

$$\text{in 2D systems: } E_b^-/E_b^0 = 0.11992$$

$$\text{in 3D systems: } E_b^-/E_b^0 = 0.055502$$

$$E_b^- = E^0 + E_p - E^-, \quad E_b^0 = E_p - E_b^0, \quad E_p \cong -\frac{\pi\alpha}{2}$$

For all the parameters given in the Table IV, the polaron energy calculated using the Buimistrov-Pekar method is $E_p = -\pi\alpha/2$ (weak electron-phonon coupling), which is typical for crystals with a ion-covalent bond, when the covalent component of the bond predominates and the conditions for polaron self-trapping are not fulfilled.

The R parameter in Table III determines the ratio of the effective Rydberg to the energy of longitudinal optical phonons:

$$R = \frac{Ry^*}{\hbar\omega} = m^* e^4 / (2\varepsilon_0^2 \hbar^3 \omega) = \alpha^2 \eta^2 / (1-\eta)^2$$

Exchange-Coupled Pairs of Paramagnetic Centers in 2D Crystals

The energy of exchange-coupled pairs in covalent 2D crystals can be determined based on the calculation of the energy of a 2D hydrogen molecule [3]. To calculate the value of the effective Rydberg, one should use the crystal parameters. In the case when the crystal has an addition of ionic bonds, the calculations should be performed taking into account the electron-phonon interaction with l optical phonons.

Table V. Lists the energy calculations for singlet and triplet exchange-coupled pairs of shallow hydrogen-like centers in 2D crystals, as well as various contributions to the total energy (designations T_2 , V_C , V_f and V_{fi} correspond to the first, second, third and fourth terms in equation (5).

	S	$-E_2$	T_2	$-V_C$	$-V_f$	$-V_{fi}$	R_m
AgBr	0	36.343	37.466	35.654	33.902	4.2538	0.2081
	1	20.395	23.691	27.185	13.308	13.308	
AgCl	0	43.348	45.290	40.894	43.093	4.6508	0.1785
	1	23.948	29.038	31.846	17.148	3.9916	
CdF ₂	0	43.519	41.199	22.942	54.511	7.2650	0.2209
	1	24.85	25.481	22.650	21.787	5.8945	

Table VI. Lists the energy calculations for singlet ($S=0$) and triplet ($S=1$) states of 2D shallow helium-like centers ($Z=2$) in crystals, as well as various contributions to the total energy E_2 .

Crystal	S	$-E_2$	T_2	$-V_C$	$-V_f$	$-V_{fi}$
AgBr	0	61.204	62.103	80.233	42.631	0.4436
	1	41.106	38.816	62.604	16.033	1.2843
AgCl	0	71.739	70.6252	89.380	52.509	0.4755
	1	45.8396	35.2214	64.4784	14.1375	2.4451
CdF ₂	0	62.364	60.936	57.088	65.550	0.6620
	1	41.073	37.551	51.863	24.8199	1.94151

Table VI shows the energy of the helium-like center. These values correspond to the limiting value of an exchange-coupled pair energy at a distance between the Coulomb centers $R_{12}=0$, without taking into account the energy of the Coulomb centers repulsion. As an example, crystals with a fairly significant ionic value ($1 < \alpha < 2$, $0.3 < \eta < 0.5$). The R_m is the equilibrium distance between Coulomb for the singlet term.

CONCLUSIONS

In crystals with parameters characterizing the intermediate electron-phonon coupling ($1 < \alpha < 2$, $0.06 < \eta < 0.9$), accounting for the interaction of electrons with optical phonons leads to a significant decrease in the energy of the ground state and a significant increase in the binding energy of two-electron centers. For exchange-coupled pairs of impurity centers, the phonon component of the Heisenberg exchange has an antiferromagnetic character and is comparable in magnitude to the energy of the Coulomb exchange interaction calculated without taking into account the polaron component of the energy. One-electron WF $\Psi(r)$ can be used to construct two-electron functions of the singlet and triplet states in the framework of the Heitler-London and the molecular orbital methods.

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