Multiexciton molecules in the hexaborides

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We investigate multiexciton bound states in a semiconducting phase of divalent hexaborides. Due to three degenerate valleys in both the conduction and valence bands the binding energy of a 6-exciton molecule is greatly enhanced by the shell effect. The ground state energies of multiexciton molecules are calculated using the density functional formalism. We also show that charged impurities stabilize multiexciton complexes leading to condensation of localized excitons. These complexes can act as nucleation centers of local moments.

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I. INTRODUCTION

The recent discovery of unusual high-temperature weak ferromagnetism in lightly doped divalent hexaborides, CaB$_6$, SrB$_6$, BaB$_6$, has raised the need to understand the properties of these compounds in a broader perspective. The unique features of the novel type of ferromagnetism in Ca$_{1-x}$La$_x$B$_6$ are (i) there are no partially filled d- or f-orbitals, (ii) magnetism appears only at finite doping $0 < x < 2\%$, and (iii) tiny magnetic moments ($\sim 0.1\mu_B$ per doped electron) are very robust and develop at temperatures as high as 600–1000 K. All these features are consistently explained by ferromagnetism of a doped excitonic insulator. Thus, not only is the magnetic phase quite unusual, but also the undoped stoichiometric hexaborides may also exhibit a novel type of ground state — a condensate of bound electron-hole pairs or excitons. The theory of excitonic insulators has been developed long time ago, see [3]. However, divalent hexaborides seem to be the first experimental realization of an excitonic insulator made possible by their unique band structure. Band structure calculations predict a small overlap of valence and conduction bands at the $\Delta$ symmetry related nonequivalent $X$ points in the cubic Brillouin zone. There is a certain ambiguity both from theoretical and experimental points of view regarding whether the stoichiometric divalent hexaborides have a small band overlap or a small band gap. Precise treatment of correlation effects in electron-hole plasma beyond the standard approximations of band structure calculations predicts a first order transition from a semiconductor to a semimetal under pressure. Therefore, stoichiometric hexaborides may be on a semiconducting side of the phase diagram close to the first order metal-insulator transition.

Motivated by the unique band structure with equal number of degenerate valleys in conduction and valence bands with different symmetries, we investigate here the formation of multiexciton molecules and complexes in these materials, assuming that there is a finite band gap between conduction and valence bands. In the effective mass approximation the valley index appears as an extra quantum number. By analogy with nuclei we expect a shell structure of the single particle orbits where six electrons and six holes with different spin and valley quantum numbers can occupy the lowest shell. Hence, the 6-exciton molecule is expected to be the most stable configuration.

Binding energy calculations of several excitons have been reported in the late seventies for multiexciton complexes bound to impurities in Si and Ge [1,2]. It was recognized that Hartree-Fock calculations do not work for multiexciton complexes because the main contribution to binding energy comes from correlation effects and that the density functional formalism provides a useful tool to include such correlation effects. In this paper we consider both multiexciton molecules and multiexciton complexes bound to impurities and calculate their binding energies within the framework of the density functional theory. The Kohn-Sham equations are single particle Schrödinger equations for electrons and holes moving in a self-consistent potential. These equations connect the density functional formalism to the shell model of multiexciton complexes and molecules [1].

The binding energies of exciton molecules provide information on whether a Bose gas of multiexciton molecules is stabilized between semiconducting and semimetallic phases when the band gap is varied from positive to negative values. In the previous study by two of us [3] an intermediate phase of a free exciton gas stabilized by intervalley scattering processes was considered. Binding of several excitons is an alternative mechanism for appearance of an intermediate phase between a semiconductor and a semimetal. The binding energy per electron-hole pair in the molecule has to be compared to the minimal ground state energy of the electron-hole liquid, which according to Ref. [3] is $E_{g,x}^{\text{min}} = -1.55E_x$. As another application of our results we suggest that the formation of multiexciton complexes near donor impurities (e.g., La-substitutions) can be a source of local magnetic moments, which appear in a semiconducting state. Such moments
could explain the unusual NMR relaxation rate measurements in the hexaborides \[13\].

II. METHOD

We use the effective mass approximation considering electrons near minima in the conduction band and holes near the maxima of the valence band as oppositely charged quasiparticles with anisotropic effective masses which interact via a screened Coulomb potential \(V(r) = e_1 e_2 / r\), \(\epsilon\) being the static dielectric constant. For CaB\(_6\) the principal values of the effective mass tensor in units of the bare electron mass are given by \(m_{e}^{||} = 0.504\), \(m_{e}^{\perp} = 0.212\) (conduction band) and \(m_{h}^{||} = 2.17\), \(m_{h}^{\perp} = 0.206\) (valence band). The model Hamiltonian is

\[
\hat{H} = \hat{T} + \hat{U},
\]

\[
\hat{T} = \sum_{\lambda} \int dr \Psi_{\lambda}^{\dagger}(r) K_{\lambda} \Psi_{\lambda}(r),
\]

\[
\hat{U} = \frac{1}{2} \sum_{\lambda,\lambda'} \int dr dr' \Psi_{\lambda}^{\dagger}(r) V_{\lambda,\lambda'} \Psi_{\lambda'}(r') \Psi_{\lambda}(r),
\]

where \(\lambda = (\kappa, \nu, \sigma)\) with \(\kappa = e, h\); \(\nu = 1, 2, 3\) is the valley index; \(\sigma = \pm\) is the spin index; and \(q_{\lambda}\) is +\(e\) for positively charged holes and \(-e\) for negatively charged electrons. The kinetic energy operator \(K_{\lambda}\) for one valley is

\[
K_{(\kappa,1,\sigma)} = - \frac{h^2}{2 m_{e}^{\kappa} \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)} + \frac{1}{m_{e}^{\perp} \frac{\partial^2}{\partial x^2}}.
\]

The expressions for the valleys 2 and 3 are obtained by cyclic permutations of \(x, y\) and \(z\). We investigate the ground state energy of this Hamiltonian for a given number of electrons and holes. To treat this problem we use the density functional formalism which is presented in the next section. In the following all equations are written in dimensionless variables. A natural set of units is the excitonic Rydberg for the energy scale \(E_x = \mu e^4 / 2h^2 c^2\) and the excitonic Bohr radius for the length scale \(\alpha_x = h^2 \epsilon / \mu e^2\), where \(\mu = m_{oe} m_{oh} / (m_{oe} + m_{oh})\). The reduced mass \(\mu\) is determined by optical masses where \(3/m_{oe} = 2/m_{e}^{\perp} + 1/m_{e}^{||}\).

The density functional theory \[14\] expresses the ground state energy in terms of electron and hole densities only and when applied to the Hamiltonian \[\hat{H}\] it gives:

\[
E[n_{\lambda}(r)] = T[n_{\lambda}(r)] + E_{xc}[n_{\lambda}(r)]
\]

\[
+ \frac{1}{2} \sum_{\lambda,\lambda'} q_{\lambda} q_{\lambda'} \int dr dr' \frac{n_{\lambda}(r)n_{\lambda'}(r')}{|r-r'|},
\]

\[
n_{\lambda}(r)\text{ is the density of the component } \lambda \text{ [see Eq. (3)]. The Coulomb energy is split into a direct Hartree term and an exchange-correlation term. The exchange-correlation energy is considered in the local density approximation which can be expressed as follows:}
\]

\[
E_{xc}[n_{\lambda}(r)] \approx \int dr \epsilon_{xc}[n_{\lambda}(r)] \sum_{\lambda} n_{\lambda}(r). \tag{4}
\]

\(\epsilon_{xc}\) is obtained from the ground state energy calculations of a uniform neutral plasma with \(\text{equal}\) electron and hole densities. In our case charge neutrality can be locally broken due to different electron and hole masses. However, because of a strong Coulomb interaction the two densities differ only slightly and, therefore, it is reasonable to calculate \(\epsilon_{xc}\) substituting an averaged pair density

\[
n_{e-h}(r) = \frac{1}{2} \sum_{\nu,\sigma} [n_{e,\nu,\sigma}(r) + n_{h,\nu,\sigma}(r)]. \tag{5}
\]

Vashishta and Kalia \[13\] have shown that the exchange-correlation energy of a homogeneous electron-hole liquid is nearly independent of several band characteristics of semiconductors, such as valley degeneracy, effect of anisotropy, and electron-hole mass ratio. The reason is that the anisotropic contribution from the exchange energy cancels out the contribution of the correlation energy for these band characteristics. Vashishta and Kalia further fitted \(\epsilon_{xc}\) from their self-consistent calculations to a simple analytic expression

\[
\epsilon_{xc}(r_s) = \frac{a + br_s}{c + dr_s + r_s^2}, \tag{6}
\]

where \(a = -4.8316, b = -5.0879, c = 0.0152, d = 3.0426,\) and \(r_s = (3/4\pi a_n^{e-h})^*\) is the dimensionless distance between carriers.

The densities in Eq. (3) are related to the solution of the Kohn-Sham equations \[16\] which are self-consistent one-particle Schrödinger equations:

\[
\left[-\mu \hat{K}_\lambda + V_\lambda(n_{\lambda}(r))\right] \psi_{\lambda}(r) = \epsilon_{\lambda i} \psi_{\lambda i}(r), \tag{7}
\]

\[
V_\lambda = q_{\lambda} \int dr' \sum_{\nu,\sigma} q_{\lambda'} n_{\lambda'}(r') + \frac{1}{2} \phi_{xc}[n_{e-h}(r)],
\]

\[
\phi_{xc}[n] = \frac{d(n_{xc}[n])}{dn}, \tag{8}
\]

\[
n_{\lambda}(r) = \sum_{i=1}^{N_{\lambda}} |\psi_{\lambda i}(r)|^2.
\]

The sum of the eigenvalues \(\epsilon_{\lambda i}\) over all occupied states \((\lambda, i)\) does not give the energy of the molecule but it can be directly related to it by:

\[
E = \sum_{\lambda,i} \epsilon_{\lambda i} - \frac{1}{2} \sum_{\lambda,\lambda',\nu,\sigma} q_{\lambda} q_{\lambda'} \int dr dr' \frac{n_{\lambda}(r)n_{\lambda'}(r')}{|r-r'|} + \int dr \left\{ \epsilon_{xc}[n_{e-h}(r)] - \phi_{xc}[n_{e-h}(r)] \right\} n_{e-h}(r). \tag{8}
\]
An approximate solutions to the Kohn-Sham equations can be obtained by using a variational ansatz for $\psi_{\lambda i}$ and minimizing the energy (9). Alternatively, one can choose to solve the Kohn-Sham equations directly imposing a self-consistency requirement. We calculate a few simple cases in both ways and then resort to a variational approach in more complicated situations.

III. BINDING ENERGY CALCULATION FOR MULTIEXCITON MOLECULES

A. Isotropic and equal electron and hole masses

For isotropic masses ($m^e_0 = m^h_0 \equiv m_e$), we use the spherical symmetry of the ground state wave function and the effective potential $V(r)$:

$$
\psi_{\lambda,nl,m}(r) = R_{\lambda,nl}(r) Y_{lm}(\theta, \phi).
$$

(9)

Defining $\sigma_{e-h} = m_e/m_h$ and $R_{\lambda,nl}(r) = \chi_{\lambda,nl}(r)/r$, we obtain the $l = 0$ Kohn-Sham equations for electrons and holes:

$$
\begin{align*}
-\frac{1}{1 + \sigma_{e-h}} \frac{d^2}{dr^2} + V_e \chi_{e,n0}(r) &= \epsilon_{e,n0} \chi_{e,n0}(r), \\
-\frac{\sigma_{e-h}}{1 + \sigma_{e-h}} \frac{d^2}{dr^2} + V_h \chi_{h,n0}(r) &= \epsilon_{h,n0} \chi_{h,n0}(r).
\end{align*}
$$

(10)

The two equations differ only in the kinetic energy term because of unequal electron and hole masses. In this subsection we consider the case of equal masses $\sigma_{e-h} = 1$. Then, we have only one Kohn-Sham equation to solve. This equation gives the same density profiles for electrons and holes and, therefore, the direct Hartree term vanishes identically. The self-consistent solution of the Kohn-Sham equation for the lowest eigenvalue is shown in Fig. 1 for a molecule formed of 6 electron-hole pairs.

For the variational solution of the Kohn-Sham equations we take the trial functions to be of ‘Fermi-Dirac’ type:

$$
\begin{align*}
1s \text{ states}: \quad & R_{1s}(r) = \frac{n_1}{1 + \exp(-r/r_1)}, \\
2s \text{ states}: \quad & R_{2s}(r) = \frac{n_2(1 - br)}{1 + \exp(-r/r_2)}.
\end{align*}
$$

(11)

Here, $r_1, \rho_1, r_2, \rho_2$ are variational parameters and $n_1, n_2$ are normalization constants. The choice of the 1s wave-function is specially suited for large exciton molecules, which are described by a ‘droplet’ model: the density is constant up to $r_1$ and then drops to zero in a surface layer of width $\rho_1$. The results of the two methods for different molecule sizes are summarized in Table I.

The variational and exact solutions of the Kohn-Sham equation are in a very good agreement. The difference in energies does not exceed 0.5% for all molecule sizes. This agreement is not only achieved in the binding energies but also in the wave-functions. The comparison of the electron-hole pair densities is plotted in Fig. 2 for a molecule formed of six electron-hole pairs. For small $r$ the variational trial functions have a linear behavior which explains the small difference at the center of the molecule between the exact solution and the variational solution. The third column of Table I is a measure for the stability of the molecule against dissociation into the next smaller molecule and one free exciton. We see that only the 5- and the 6-pairs molecules are stable against this dissociation. The 6 electron-hole pairs molecule is in a state where all single particle states of the lowest shell are filled up. This represents the most stable configuration. The energy gain of 24% of $E_x$ per one e-h pair in a 6-exciton molecule is much higher than a binding energy of an ordinary bi-exciton molecule for nondegenerate bands, which is only 1.7% of $E_x$. If we go to larger molecules shell effects appear. The extra energy cost which is needed to put a further electron into the 2s shell favors clearly the 6 electron-hole molecule. Shell effects appear also if the radii of different molecules are compared. Surprisingly, the radius gets smaller when we are filling up the 1s shell. This feature was also found by Wünsche and co-workers [12]. The radius of the molecule shows a sharp increase if a further electron-hole pair in the 2s shell is added.

The calculated binding energies have to be compared to the ground state energy of the metallic electron-hole liquid. The ground state energy $E_{g.s.}(r_s)$ was calculated in the RPA approximation in Ref. [8] with $E_{g.s.}^{\text{min}} = -1.55E_x$ at $r_s = 0.92$. The ansatz (9) gives a close value $E_{g.s.}^{\text{V}} = -1.6E_x$, which is reached at the density $r_s \approx 1.0$. Both these values are lower than the maximum gain from formation of a 6-exciton molecule which indicates that in the chosen approximation there is no intermediate phase of a dilute Bose gas of exciton molecules.

Although it is difficult to give an exact criterion for the applicability of the density functional approach to multiexciton molecules, it is expected that the theory works best at high densities, i.e. for large molecules. Further, these densities have to be compared to the density for which the ground state energy per pair for an electron-hole liquid is minimal $r_s = 0.92$. We expect that in the limit of large $N$, the density at the center of the molecule approaches this value. For a finite number of electron-hole pairs the density at the center will be higher than $r_s \approx 0.9$, since we must include a surface tension which increases the density. To see if such a picture of an electron-hole droplet is correct, we split the binding energy $E_B$ into a bulk and a surface term:

$$
E_B = E_{\text{bulk}} + E_{\text{surf}}.
$$

(12)

We approximate the density by a uniform spherical density of radius $r_M$. Then the bulk energy can be deter-
The surface energy is proportional to $r_M^2$:

$$E_{\text{bulk}} = NE_{\text{g.s.}}[r_s(r_M)],$$

$$E_{\text{surf}} = 4\pi r_M^2 S.$$  \hspace{1cm} (13)

Table [I] presents the surface tension $S$ evaluated for different molecules. If an electron-hole droplet consideration of an exciton molecule is correct, then $S$ should be a constant. From table [I] we can see that this is true for molecules formed of 5–7 electron-hole pairs but it fails for smaller molecules.

**B. Effect of electron-to-hole mass ratio**

In this subsection we lift the approximation of equal electron and hole masses but continue to replace the effective mass tensors by isotropic optical masses. The numerical procedure of solution of the coupled K-S equations (10) was found to be unstable. In view of the results of the previous section, we expect, however, to obtain accurate results using again ‘Fermi-Dirac’-type variational wave-functions, but this time with different adjustable parameters for electron and holes. Our calculations are limited to the most stable molecule formed of six electron-hole pairs. We have varied $\sigma_{e-h}$ from 1 to 0.1. The results are plotted in Fig. 3 and further details are presented shown in table III. The total energy of the 6-exciton molecule is lowered only by an amount of 0.23 $E_x$ or 4% if $\sigma_{e-h}$ varies from 1 to 0.1. For CaB$_6$ the ratio of electron and hole optical masses is $\sigma_{e-h} = 0.89$. For this value of $\sigma_{e-h}$ the electron and hole densities will be only slightly different and there is nearly no change in the binding energy $E_B$.

We can check validity of the obtained results by comparing them to the exact analytic criteria which have been derived in Ref. [7] for the problem of a bi-exciton molecule. Frequently these criteria are not satisfied by variational solutions. To check them we evaluate the energy functional (3) in the ground state and take it to be a function of $\sigma_{e-h}$: $E(\sigma_{e-h})$. From the form of the Hamiltonian (1) it can be shown [17] that $[\partial E(\sigma_{e-h})/\partial \sigma_{e-h}]_{\sigma_{e-h}=1} = 0$ and that $E(\sigma_{e-h})$ has to be a concave and monotonically increasing function of $\sigma_{e-h}$. We see in Fig. 3 that these two criteria are satisfied by our solution, which further supports validity of the obtained results.

**C. Effect of mass anisotropy**

According to the results of the previous subsection the binding energy changes only very little for unequal electron and hole masses. Therefore, for simplicity we assume that electron and hole dispersion are described by the *same* anisotropic mass tensors. Otherwise, one has to deal with too many variational parameters. As in the previous section we limit our calculations to the 6-exciton molecule. We define the reduced masses $1/m^\perp = 1/m_{e}^\perp + 1/m_{h}^\perp$ and $1/m^\parallel = 1/m_{e}^\parallel + 1/m_{h}^\parallel$ and the ratio between the components of the reduced mass tensor $\sigma_a = m^\perp/m^\parallel$, with $m^\perp < m^\parallel$ or $\sigma_a < 1$.

The variational trial functions are taken to be again ‘Fermi-Dirac’-type, but now we use functions with a cylindrical symmetry. In different valleys the wave-functions are different. For the first valley they are defined as

$$\psi_{\kappa,1}(r) = \frac{n_0}{1 + \exp \left( \frac{\sqrt{d_\perp^2 + d_\parallel^2} - \rho}{\sigma_a} \right)}.$$  \hspace{1cm} (14)

$n_0$ is the normalization constant and $d_\perp$, $d_\parallel$ and $\rho$ are the three variational parameters. The wave-functions for particles in the other valleys are obtained by cyclical permutations of $x$, $y$ and $z$ in analogy with the kinetic energy operator $K_\lambda$. This implies that the total density distribution is not spherically symmetric but is a superposition of three ellipsoidal distributions along the coordinate axes.

The results of the minimization of the energy functional (3) are presented in table [V] for $0.2 < \sigma_a < 1$. Varying $\sigma_a$ in this range produces an increase in the binding energy of 0.51 $E_x$ or 6%. For CaB$_6$ the mass ratio is 0.255, which corresponds to an energy of 7.81 $E_x$ and thus to an increase in binding by 5%. Thus, mass anisotropy has a somewhat stronger effect on binding energies of multiexciton molecules in the hexaborides than electron-to-hole mass ratio, though both effects give only small corrections to the simplest model with equal and isotropic masses.

**IV. EXCITON COMPLEXES BOUND TO IMPURITIES**

It is well known that excitons in semiconductors are attracted to charged donor or acceptor impurities [11–12]. We investigate here the case of a monovalent donor impurity, which models the effect of La$^{3+}$-substitution in divalent-metal hexaborides CaB$_6$ and SrB$_6$. We add an external Coulomb potential to the Hamiltonian (4):

$$\hat{V} = \sum_\lambda d\psi_\lambda^\dagger(r) V_\lambda \psi_\lambda(r), \quad \hat{V}_\lambda = \frac{e\lambda}{\epsilon r}$$  \hspace{1cm} (15)

and assume equal and isotropic electron and hole masses. (In this case there is an obvious symmetry between donors and acceptors.) At low impurity concentrations the electrons and holes are completely localized at a single impurity. The impurity adds a heavy center to the molecule. Therefore we choose the variational wave-functions in the hydrogenic form:
$$R_e(r) = \frac{1}{\sqrt{\pi} r_e^3} e^{-\frac{r}{r_e}},$$
$$R_h(r) = \frac{1}{\sqrt{3\pi} r_h} e^{-\frac{r}{r_h}},$$
(16)

with electrons and holes occupying s-wave and p-wave orbitals, respectively, near a positively charged donor. The results for the binding energies of multie exciton complexes are presented in table V. The second column shows the total energy of a complex $-E_B$, which includes one extra electron in addition to $N$ electron-hole pairs. All complexes with $N > 1$ are stable against dissociation into a next smaller complex and a free exciton, since $|E_B(N + 1) - E_B(N)| > E_x$. To compare the energy gain from a formation of a multie exciton complex to the energy gain in a dense electron-hole plasma we need to subtract from $E_B$ the energy of a donor with a single electron, which is approximately $2E_x$. The third column shows that excitons gain the most of energy in a 5-exciton complex, which is again consistent with a filled shell argument. The energy gain per one exciton in a 5-exciton complex exceeds the energy gain in a 6-exciton molecule. Hence, upon decreasing the band gap charged impurities will work as nucleation centers for electron-hole droplets and localized excitons will appear before condensation of multie exciton molecules in the bulk of a semiconductor.

The maximum possible energy gain per exciton in the 5-exciton complex $\Delta E = 1.38E_x$ is still below the energy gain in a dense electron-hole plasma $|E_{g,min}| = 1.55E_x$. Effective mass calculations have also been done for divalent donors (acceptors) with 4 excitons being attracted, but we did not find any additional energy lowering for them. This result means that the direct first-order transition occurs under pressure without an intermediate excitonic phase. However, the two numbers are now closer to each other. In such a case so-called central cell corrections to the effective mass approximation, which have been estimated in Ref. [8] as $\Delta E_{c.c.} \sim 0.2E_x$ for a single exciton, can be sufficient to increase the energy gain per one exciton in a donor complex compared to the energy density in a bulk e-h plasma. As a result, an intermediate state of localized excitons may appear under pressure. These localized exciton complexes bound to charged impurities carry uncompensated spin-$1/2$, as suggested by the shell scenario. It is an interesting problem to understand whether such an intermediate phase can be responsible for the unusual relaxation effects in the hexaborides [13].

Usually, in lightly doped semiconductors (e.g. P in Si) localized donor electrons develop antiferromagnetic correlations between nearest-neighbor donors. This can be understood in the following way. For two donor atoms, which appear to be neighbors, the electronic hydrogen-type orbitals hybridize forming a lower bonding orbital and an upper antibonding orbital, similar to a hydrogen molecule. The two extra electrons will go to the non-degenerate bonding orbital and the Pauli principle requires them to have opposite spins. We suggest that the opposite sign ferromagnetic correlations will develop in a localized excitonic phase of doped hexaborides. Their origin is in additional multivalley degeneracy of electrons and holes in the hexaborides. The bonding orbitals for two nearest-neighbor donors have six-fold total degeneracy. We expect that in such a case only 4 excitons will be attracted to such a double center complex in order to fill the bonding electron orbitals. The total spin of a double-impurity complex (0 or 1) comes from a partially filled hole shell (two ‘holes’ in the hole shell). In the case of degenerate orbitals the Hund’s rule plays the major role and produces parallel alignment of spins of the two ‘holes.’ Similar scenario applies also to divalent donors or acceptors. (In the case of the hexaborides, Ca- or Sr-vacancies can play a role of divalent acceptors.) Localized moments produced in this way could be a source of the unusually fast NMR-relaxation observed experimentally [13] and lead to significant sample-to-sample variations of ferromagnetic moments in Ca$_{1-x}$La$_x$B$_6$ [13].

Estimation of the Hund’s splitting in multie exciton complexes is an interesting open question. Note, that ordinary semiconductors, like Si or Ge, also have a multivalley structure of the conduction band. The degeneracy of donor orbitals in these cases is partially lifted by anisotropic central cell corrections, which select a nondegenerate lowest level and, hence, suppress ferromagnetic correlations. This effect might be present in multie exciton complexes as well. However, the difference between the two cases is in the shells which produce the total spin. In the multie exciton complexes bound to a donor, uncompensated spin is formed in the p-wave hole shell. Wavefunctions for these states vanish at the origin Eq. (14) and have a small probability in the central cell. Therefore, the states in the hole shell are better described in the effective mass theory than states in the electron shell and their splitting must be less significant.

V. CONCLUSIONS

We have shown that the multivalley degeneracy which is present in both the conduction and the valence bands of the hexaboride materials leads to a number of peculiar effects: (i) 6-exciton molecules are stabilized due to the shell effect. Their binding energies are comparable to the exciton binding energy in contrast to a weak binding energy of a bi-exciton molecule. The energetics of the multiexciton complexes is rather insensitive to the details of the band structure: electron-to-hole mass ratio and anisotropy in the effective mass tensors. (ii) Multiexciton complexes are attracted to charged impurities. They have a larger energy gain per one electron-hole pair than a 6-exciton molecule. Therefore, upon decreasing a semiconducting gap excitons will first condense at donors
and acceptors producing an intermediate phase of localized excitons. Though, the energy of this phase lies somewhat higher than the energy gain in a dense electron-hole plasma, localized excitons can be further stabilized by central cell effects or appear as a metastable phase at the first-order transition between a semiconducting and a semimetallic state. (iii) Uncompensated spins on multiexciton complexes show a tendency towards ferromagnetic correlations, which is again a multivalley effect. Our theoretical results indicate that a semiconducting phase of divalent hexaborides must have a number of interesting physical properties. Further experiments at ambient and applied pressure can shed more light on their relevance to the physics of hexaborides.

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### TABLE I. The binding energies $E_B$ of molecules consisting of $N$ excitons for isotropic and equal $e$ and $h$ masses.

| Method           | $N$ | $-E_B$ | $-E_B/6$ | $r_M$ | $r_s(0)$ | $n_1$ | $n_2$ | $n_3$ |
|------------------|-----|--------|----------|-------|----------|-------|-------|-------|
| Variational      | 7   | 7.90   | 1.13     | 2.10  | 0.80     | 1.2   | 0.79  | 2.1   | 1.19  |
| Self-consistent  | 6   | 7.32   | 1.24     | 1.65  | 1.83     | 1.4   | 0.72  | -     | -     |
|                  | 5   | 5.77   | 1.15     | 1.73  | 1.91     | 1.4   | 0.77  | -     | -     |
|                  | 4   | 4.24   | 1.06     | 1.78  | 1.00     | 1.4   | 0.80  | -     | -     |
|                  | 3   | 3.86   | 0.95     | 1.87  | 1.04     | 1.4   | 0.86  | -     | -     |
|                  | 2   | 7.92   | 1.13     | 2.05  | 0.83     | -     | -     | -     | -     |

### TABLE II. The surface tension for exciton molecules of different sizes.

| $4\pi S$ | 0.75 | 0.79 | 0.77 | 0.66 | 0.49 |
|----------|------|------|------|------|------|

### TABLE III. The binding energy of a 6-exciton molecule for different values of the electron-hole mass ratio $\sigma_{e-h}$.

| $\sigma_{e-h}$ | $-E_B$ | $-E_B/6$ | $r_e$ | $r_h$ | $n_e$ | $n_h$ |
|----------------|--------|----------|-------|-------|-------|-------|
| 1.0            | 7.42   | 1.24     | 1.40  | 0.72  | 1.40  | 0.72  |
| 0.9            | 7.43   | 1.24     | 1.30  | 0.75  | 1.34  | 0.73  |
| 0.8            | 7.43   | 1.24     | 1.32  | 0.75  | 1.36  | 0.72  |
| 0.7            | 7.43   | 1.24     | 1.28  | 0.79  | 1.34  | 0.71  |
| 0.6            | 7.45   | 1.24     | 1.30  | 0.77  | 1.30  | 0.70  |
| 0.5            | 7.46   | 1.24     | 1.28  | 0.76  | 1.36  | 0.69  |
| 0.4            | 7.48   | 1.25     | 1.28  | 0.76  | 1.38  | 0.67  |
| 0.3            | 7.52   | 1.25     | 1.28  | 0.76  | 1.38  | 0.65  |
| 0.2            | 7.57   | 1.26     | 1.30  | 0.74  | 1.38  | 0.62  |
| 0.1            | 7.65   | 1.28     | 1.28  | 0.74  | 1.42  | 0.58  |

$r_e$, $r_h$, $n_e$, $n_h$ are the optimal values of the variational parameters.
TABLE IV. The binding energy of a 6-exciton molecule for different values of the anisotropy parameter $\sigma_a$. $\bar{d}_||$, $\bar{d}_\perp$ and $\bar{\rho}$ are the values of the variational parameters.

| $\sigma_a$ | $-E_B$ | $-E_B/6$ | $\bar{d}_||$ | $\bar{d}_\perp$ | $\bar{\rho}$ |
|-----------|--------|---------|-------------|--------------|-------------|
| 0.1       | 7.42   | 1.24    | 0.52        | 0.52         | 1.94        |
| 0.9       | 7.43   | 1.24    | 0.52        | 0.55         | 1.78        |
| 0.8       | 7.44   | 1.24    | 0.49        | 0.56         | 1.78        |
| 0.7       | 7.45   | 1.24    | 0.47        | 0.57         | 1.76        |
| 0.6       | 7.49   | 1.25    | 0.43        | 0.58         | 1.76        |
| 0.5       | 7.54   | 1.26    | 0.40        | 0.59         | 1.73        |
| 0.4       | 7.61   | 1.27    | 0.35        | 0.59         | 1.73        |
| 0.3       | 7.73   | 1.29    | 0.30        | 0.60         | 1.69        |
| 0.255     | 7.81   | 1.30    | 0.27        | 0.60         | 1.66        |
| 0.2       | 7.93   | 1.32    | 0.23        | 0.61         | 1.62        |

TABLE V. The binding energies for different multiexciton complexes. $\bar{\tau}_e$, $\bar{\tau}_h$ are the values of the variational parameters for which the energy is minimized.

| $N$ | $-E_B$ | $-(E_B + 2)/N$ | $\bar{\tau}_e$ | $\bar{\tau}_h$ |
|-----|-------|----------------|----------------|----------------|
| 5   | 8.91  | 1.38           | 0.90           | 0.62           |
| 4   | 7.21  | 1.30           | 0.89           | 0.64           |
| 3   | 5.62  | 1.21           | 0.87           | 0.66           |
| 2   | 4.17  | 1.09           | 0.82           | 0.69           |
| 1   | 2.86  | 0.86           | 0.73           | 0.74           |

FIG. 1. The self-consistent numerical $1s$ solution of the Kohn-Sham equation for a molecule formed of six electron-hole pairs. The resulting effective potential is presented on the bottom panel and the lowest eigenvalue is shown by a horizontal line.

FIG. 2. The electron-hole pair densities profiles for numerical (solid line) and variational (dashed line) solutions of the Kohn-Sham equations. The results are for the most stable 6-exciton molecule.

FIG. 3. The binding energy of a 6-exciton molecule versus the electron-to-hole mass ratio $\sigma_{e-h}$.