Three-particle charged electron-hole complexes in semiconductors

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The variational method is used to calculate the dependence of the binding energy of three-particle electron-hole complexes in semiconductors on the mass ratio. The stability of these complexes is considered.

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At low temperatures ~10°K, nonequilibrium carriers –electrons (e) and holes (h) excited optically in semiconductors—become bound to one another, forming a system of excitons eh.[1] The pair interaction between excitons produces biexcitons e_2h_2.[2-5] Thermal dissociation of some excitons produces free electrons and holes.[6,7] At high excitation rates, condensation may take place and electron-hole drops may be formed; these drops were predicted theoretically by Keldysh[1] and observed experimentally in[8-11] and elsewhere.

The gaseous phase of an exciton system consists of eh, e_2h_2, e, h and it resembles a partly ionized plasma. It is natural to assume that three-particle charged complexes e_2h and eh_2 also form in such a system. We shall calculate the binding energies of such complexes for different values of the particle masses.[1)] We shall calculate the binding energies of such complexes for different values of the particle masses.[1)] We shall calculate the binding energies by the variational method using the scalar effective mass approximation; we shall ignore spin and consider spherical constant-energy surfaces. It is convenient to consider separately systems of the H^- and H_2^+ types.

SYSTEMS OF H^- TYPE

A system of this kind consists of one heavy charged particle and two light charged particles of the opposite sign. We shall denote the heavy-particle mass by m_h and the masses of the light particles by m_e. The Schrödinger equation can be expressed in the form[12]

$$\left\{\frac{1}{2}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2}+\frac{\partial^2}{\partial \mathbf{r}_2^2}\right)+\sigma\left[\frac{1}{2}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2}+\frac{\partial^2}{\partial \mathbf{r}_2^2}\right)+\frac{\partial^2}{\partial \mathbf{r}_1 \partial \mathbf{r}_2}\right]+E-V\right\}U=0, \quad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radius vectors drawn from the heavy particle to the light particles; $\sigma = m_e/m_h$; V is the potential energy of the Coulomb interaction of the charges; E is the required eigenvalue. Equation (1) is in atomic units and the unit of energy is $m_e e^4/\hbar^2$. A three-parameter wave function will be used in the calculations:

$$U=(1+c_1u+c_2t^2)e^{-s/2}. \quad (2)$$

The three coordinates defining the distance will be the two "elliptic coordinates" and the distance between the particles:

$$s=r_1+r_2, \quad t=r_1-r_2, \quad u=|\mathbf{r}_1-\mathbf{r}_2|.$$

The expression (2) depends explicitly on two parameters c_1 and c_2; the third parameter occurs in s, t, and u as a scale factor and the effects of its variation can be studied analytically.[12] The calculated values of the binding energy $J(\sigma) = E(\sigma) - 0.5$ are:

σ:	0	0.2	0.4	0.6	0.8	1.0	2.5
$J(\sigma)$:	0.0253	0.0171	0.0127	0.0100	0.0083	0.0071	0.0035

SYSTEMS OF H_2^+ TYPE

When σ increases to >1, a system of the H^- type transforms to one of the H_2^+ type (to within the sign of the particle charges), which is composed of one light particle and two heavy particles. We shall denote the masses of the heavy particles again by m_h and the mass of the light particle by m_e, and we shall rewrite the Schrödinger equation in the form

$$\left[\frac{1}{2}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2}+\frac{\partial^2}{\partial \mathbf{r}_2^2}\right)+\frac{\partial^2}{\partial \mathbf{r}_1 \partial \mathbf{r}_2}+\frac{\sigma}{2}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2}+\frac{\partial^2}{\partial \mathbf{r}_2^2}\right)+E-V\right]U=0, \quad (3)$$

where the unit of energy is, as in Eq. (1), the ratio $m_e e^4/\hbar^2$. A test variational wave function should allow for the presence of two heavy centers. Therefore, instead of Eq. (2), we shall use the function

$$U=(1+c_2t^2)\exp\left(\frac{\beta u-s}{2}\right)u^{\alpha/2} \quad (4)$$

with the parameters c_2, β, and α (the fourth parameter is a scale factor). Calculations of the binding energy give:

σ:	0	0.1	0.2	0.3	0.6	1.0
$J(\sigma)$:	0.1025	0.0470	0.0320	0.0243	0.0143	0.0068

At low values of $\sigma > 0$, the variational calculations are difficult but we can use the harmonic approximation

$$J(\sigma)=0.1025-0.222\sqrt{\sigma}. \quad (5)$$

The coefficients can be found from the experimental values of the binding energy and vibrational quanta of the H_2^+ molecule.[13] The reliability of Eq. (5) is confirmed by the data for the neutral hydrogen molecule because it is found that the expression $J(\sigma) = 0.174 - 0.407\sqrt{\sigma}$ describes excellently the binding energies[13] of the molecules of all three hydrogen isotopes. The anharmonicity appears for $\sigma > 10^{-2}$.

In Fig. 1, the range $0 \le \sigma \le 1$ corresponds to the range $1 \le \sigma < \infty$ in Fig. 2, and conversely. The binding energies are related by the factor σ. Figures 1 and 2 are plotted on the assumption that $m_e < m_h$. If we consider the case $m_e > m_h$, we find that the binding energy of e_2h should be obtained from Fig. 2 and the binding energy of eh_2 from Fig. 1. In this case, σ is understood to be the ratio m_h/m_e and the unit of energy is $m_h e^4/\hbar^4$.

DISCUSSION

The results obtained demonstrate the stability of three-particle electron-hole complexes throughout the range $0 \le \sigma < \infty$. This result can also be obtained in its general form by applying to such bound states the approach used in[14] for biexcitons. For example, in the case of the e_2h system, we find that $J(0) > 0$ is the binding energy of H^- and $J(\infty) = +0$ coincides with the bind-

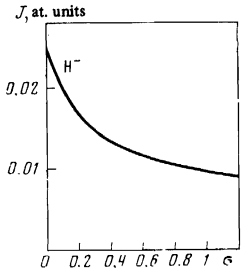

FIG. 1

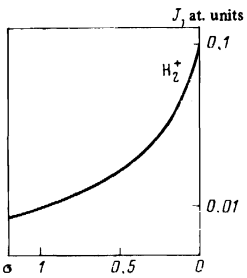

FIG. 2

FIG. 1. Dependence of the binding energy J of a three-particle complex (eeh) with one heavy and two light particles (system of the H^- type) on the mass ratio $\sigma=m_e/m_h$.

FIG. 2. Dependence of the binding energy J of a three-particle complex (ehh) with two heavy particles and one light particle (system of the H_2^+ type) on the mass ratio $\sigma=m_e/m_h$.

ing energy of H_2^+ measured in units of $m_h e^4/\hbar^2$. On the other hand, the conclusion drawn by analogy with[14] shows that $dJ(\sigma)/d\sigma < 0$ throughout the range $0 \leq \sigma < \infty$. Hence, it follows that $J(\sigma) > 0$ for all values of σ. Consequently, the conclusion of stability applies within the approximation (1) or (3).

The function (4) gives better values of the binding energy for $\sigma < 0.97$ and the function (2) for $\sigma > 0.97$ (on the scale for H_2^+). The recommended binding energies for the systems of the H^- and H^+ types are plotted in Figs. 1 and 2. The values in the range $\sigma \sim 1$ are obtained by interpolation of the results found with the aid of Eqs. (2) and (4). The interpolation is carried out so as to satisfy always $dJ(\sigma)/d\sigma < 0$.

The precision of the calculated values of J can be estimated by comparison with the results available for certain values of σ obtained using a large number of variational parameters. Thus, a 444-parameter calculation[15] gives 0.0276 for the binding energy of H^-. If $\sigma = 1$, a 6-parameter function[16] gives 0.0075. Thus, we may assume that our values of J are accurate to within about 10%, which is quite satisfactory in view of the number of indeterminacies encountered in the treatment of excitons in semiconductors.

We are only concerned with the ground states of e_2h and eh_2. Excited states of excitons have been observed experimentally[9] and we cannot exclude the possibility of their existence also in the case of three-particle complexes, particularly for systems of the H_2^+ type.

Estimates indicated that, at high excitation rates, the concentrations of e_2h and eh_2 may be comparable with the concentrations of other components. The problem of the composition of an exciton plasma in various semiconductors deserves a separate study.

Even larger (12-particle) complexes have been investigated (see, for example,[17]). The bound nature of such complexes is attributed to specific effects arising from the nature of the energy band structure. Many-particle complexes (clusters) may also appear because of pretransition phenomena[18] associated with phase transformations.[1 8-11] Such clusters are physical; they may be neutral or charged and they form close to the phase equilibrium line. The position of this line is discussed in[6,7,10,11,19]. Chemical and physical clusters in a nonideal plasma are discussed in[20] and some of the ideas put forward there can be also extended to an exciton plasma.

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[1)]These complexes were mentioned in a list of many-particle bound states which could exist, in principle, in semiconductors [3].

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