

where $f(\omega)$ is the Fermi function, and the Green function has the value

$$G(\omega) = \frac{(2\lambda/\pi)\{ \omega[S_{\uparrow}(\omega) + S_{\downarrow}(\omega)] - 8\lambda^2 S_{\uparrow}(\omega)S_{\downarrow}(\omega) \}}{[\omega - 4\lambda^2 S_{\uparrow}(\omega)][\omega - 4\lambda^2 S_{\downarrow}(\omega)] - \frac{1}{4}U^2}, \quad (6)$$

where

$$S_m(\omega) \equiv \frac{1}{N} \sum_k \frac{\omega V_k^2}{\omega^2 - \epsilon_{km}^2}. \quad (7)$$

The transport properties are obtainable from the equations of motion:

$$\langle\langle c_{km} | c_{k'm}^* \rangle\rangle = \frac{\delta_{k,k'}}{2\pi} \frac{1}{\omega - \epsilon_k} + \frac{\lambda^2}{N} \frac{V_k}{\omega - \epsilon_k} G_{adm}(\omega) \frac{V_{k'}}{\omega - \epsilon_{k'}}. \quad (8)$$

The transport lifetime is

$$\tau_{km}^{-1} \propto 2 \operatorname{Im} G_{adm}(\epsilon_k), \quad (9)$$

where

$$G_{adm}(\omega) = \langle\langle c_{dm}^* + c_{dm} | c_{dm}^* + c_{dm} \rangle\rangle. \quad (10)$$

An evaluation of these transport properties (in which we *do* find a low- T "Kondo effect") will be given elsewhere.⁵

We conclude the present work by a comparison of the free energies F of \mathcal{K} and F_A and \mathcal{K}_A . As we may use the eigenstates of our model for a variational evaluation of \mathcal{K}_A , we can obtain $F(\lambda) > F_A(2\lambda)$. On the other hand, $F(2\lambda) < F_A(2\lambda)$. Combining these,

$$F(\lambda) < F_A(\lambda) < F(\frac{1}{2}\lambda). \quad (11)$$

In the limit $T=0$ we see that these inequalities also hold for the respective ground-state energies. As the upper and lower bounds differ by $O(\lambda^2)$, F_A becomes adequately circumscribed in the weak-coupling limit ($\lambda^2 \rightarrow 0$).

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⁴See the discussion in E. Lieb and D. Mattis, *Mathematical Physics in One Dimension* (Academic, New York, 1966).

⁵I am presently studying the paramagnetic susceptibility by this method, as well as the interaction between two impurities and the transport properties of my model (to be published).

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Ground-State Energy of an Exciton-Donor Complex Calculated in a "Two-Polaron Model"*

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The ground-state energy of an exciton bound to ionized donors in III-V and II-VI compounds is calculated with the electron-phonon coupling taken into account. Results for thirteen crystals are in very good agreement with the available experimental data.

Though exciton theory has considerably improved the understanding of the luminescence spectra in the band-edge region, a further extended theory had to be developed for the interpretation of certain lines beneath free exciton lines. Led by a proposal of Lampert,¹ bound ex-

citons have thus been intensively investigated during the last years, as reviewed by Thomas,² Johnson,³ Halsted,⁴ and Reynolds, Litton, and Collins.⁵ As in the case of a free exciton, however, the electron-phonon coupling has to be taken into account for a precise calculation of

TABLE I. Ground-state energy of an exciton-donor complex (in meV).

	Sharma and Rodriguez ^a	Present work	Expt.
GaAs	5.9	6.15	6.1 ^b
CdTe	No binding	14.6	14.0 ^c
CdS	23.6	34.0	32.2 ^d
ZnO	39.0	70.2	68.0 ^e

^aSee Ref. 7.^bM. A. Gilleo, P. T. Bailey, and D. E. Hill, *Phys. Rev.* **174**, 898 (1968).^cG. Babonas and A. Sileika, *Phys. Status Solidi* **42**, 577 (1970).^dD. G. Thomas and J. J. Hopfield, *Phys. Rev.* **128**, 2135 (1962).^eD. C. Reynolds, C. W. Litton, and T. C. Collins, *Phys. Rev.* **140**, A1726 (1965).

the binding energies. We report here the influence of this interaction on the ground-state energy of an exciton bound to an ionized donor.

In the frame of the effective-mass approximation, this complex can be treated in correspondence to the H_2^+ molecule for the hole mass m_2^* being very large compared with the electron mass m_1^* ,^{1,6} while the influence of the crystal surroundings is then taken into account by a static screening of the Coulomb interactions. To take the finite hole mass into consideration, one

$$H = H_1 + H_2 + H_{12} + H_F + H_{1F} + H_{2F} + H_{DF} + H_{1L} + H_{2D};$$

$$H_1 = -(\hbar^2/2m_1^*)\Delta_1, \quad H_F = \sum_{\vec{q}} \hbar\omega_{LO} b_{\vec{q}}^\dagger b_{\vec{q}}, \quad H_{12} = -e^2/\epsilon_\infty r_{12}, \quad (1)$$

$$H_{1F} = (-1)^{l+1} \sum_{\vec{q}} [V_{\vec{q}} b_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}_1) + \text{c.c.}], \quad H_{1D} = (-1)^l e^2/\epsilon_\infty r_1,$$

where

$$V_{\vec{q}} = -i(2\pi e^2 \hbar\omega_{LO}/q^2 V \epsilon^*)^{1/2}, \quad (2)$$

$$1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_0, \quad (3)$$

and $l=1$ or 2 ; r_1 , r_2 , and r_{12} are the donor-electron, donor-hole, and electron-hole distances, respectively. By the canonical transformation¹⁰

$$a_{\vec{q}} = b_{\vec{q}} - V_{\vec{q}}^\dagger / \hbar\omega_{LO}, \quad (4)$$

Eq. (1) is reduced to

$$H = -\frac{\hbar^2}{2m_1^*} \Delta_1 - \frac{\hbar^2}{2m_2^*} \Delta_2 - \frac{e^2}{\epsilon_0 r_1} + \frac{e^2}{\epsilon_0 r_2} - \frac{e^2}{\epsilon_\infty r_{12}} + \sum_{\vec{q}} \hbar\omega_{LO} a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{\vec{q}} [V_{\vec{q}} a_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}_1) - V_{\vec{q}}^\dagger a_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}_2) + \text{c.c.}] + \text{const.} \quad (5)$$

Following the treatment of Haken¹¹ for the free-exciton case, we use the polaron function of Lee, Low, and Pines¹² to eliminate the phonon-field operators. This procedure has already been used by Schröder and Birman.¹³ In this approximation the effective Hamiltonian for the electron and hole is then given

TABLE II. Calculated ground-state energy W of an exciton-donor complex in III-V compounds (in meV).

	InSb	InP	GaAs	GaP	AlSb	GaSb
σ	0.04	0.18	0.11	0.18	0.12	0.16
W	0.7	6.8	6.15	22.8	12.8	2.7

has to include dynamical effects of both effective-mass particles. On this basis Sharma and Rodriguez⁷ carried out a variational calculation and showed the ground-state energy [in units of the donor energy E_D^H (hydrogen model)] to be a monotonic function of $\sigma = m_1^*/m_2^*$. They found that for a complex to be stable, σ should not exceed $\sigma_c = 0.2$. Skettrup, Suffczynski, and Gorzkowski⁸ found $\sigma_c = 0.426$ by an improved variational treatment. These results agree in part with experimental data, but only if the free exciton energy is fitted to its experimental value,⁹ which is not consistent with the theory used.

We think the effective-mass approximation to be rather reliable in this complex controlled by long-range Coulomb forces, and the static deformation of the lattice by the defect to be negligible. But the use of a static screening seems rather unjustified for complexes with a ground-state energy of the order of the LO phonon.

Describing the electron-phonon coupling by an operator due to Fröhlich,⁹ we get for the Hamiltonian of the problem

TABLE III. Calculated ground-state energy W of an exciton-donor complex in II-VI compounds (in meV).

	CdS ^a	CdSe ^a	CdTe ^b	ZnS ^a	ZnSe ^b	ZnTe ^b	ZnO ^a
σ	0.17	0.24	0.27	0.47	0.28	0.15	0.13
W	34.0	26.5	14.6	77.1	37.1	13.0	70.2

^aHexagonal modification.^bCubic modification.

by

$$H_{\text{eff}} = -\frac{\hbar^2}{2m_1^{**}} \Delta_1 - \frac{\hbar^2}{2m_2^{**}} \Delta_2 - \frac{e^2}{\epsilon_0 r_1} + \frac{e^2}{\epsilon_0 r_2} - \frac{e^2}{r_{12}} \left\{ \frac{1}{\epsilon_0} + \frac{1}{2\epsilon^*} \left[\exp(-r_{12}/R_1) + \exp(-r_{12}/R_2) \right] \right\}. \quad (6)$$

Here

$$R_i = \hbar(2m_i^{**}\hbar\omega_{\text{LO}})^{-1/2} \quad (7)$$

is approximately the polaron radius, and

$$m_i^{**} = m_i^* \left(1 + \frac{1}{6} \alpha_i\right) \quad (8)$$

is the effective polaron mass with

$$\alpha_i = (e^2/\hbar\epsilon^*)(m_i^*/2\hbar\omega_{\text{LO}})^{1/2}. \quad (9)$$

Two corrections have been made to the Hamiltonian (6). (1) The renormalization (8) of the self-energies is only correct for a large exciton radius, whereas for a small radius and a partial cancelation of the phonon clouds the band mass should be used instead. This has been considered by Mahanti and Varma,¹⁴ who introduced an interpolation scheme between the two values. In our calculation we use the band mass for $r_{12} < R_{1,2}$ and the polaron mass for $r_{12} > R_{1,2}$. This correction is found to be very important. (2) The anisotropic crystals are described approximately by an effective isotropic Hamiltonian in the usual way.¹⁵

The remaining three-body problem is then solved by a variational *Ansatz* proposed by James and Coolidge.¹⁶ In our theory the ground-state energy W is no longer simply a function of σ and E_D^{H} alone. Additionally, we found it necessary to reexamine the stability condition⁷ of the complex,

$$W - E_D > 0,$$

which is based on the assumption that for a given crystal $E_D/E_{\text{ex}} > 1$ (E_{ex} is the exciton binding energy), whereas this ratio is now approximately given by

$$E_D/E_{\text{ex}} = (1 + \sigma)(\epsilon_{\text{eff}}/\epsilon_0)^2$$

(where ϵ_{eff} is the renormalized dielectric constant), which may be greater or less than 1.

Our results compared with experimental data

are given in Table I. The very good agreement seems to justify the approximation used. Tables II and III summarize our results for III-V and II-VI compounds, which may be helpful for identification of lines in future.

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