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Changchun Institute of Physics, Academia Sinica, Changchun[1)]

The Behaviour of Excitons near the Interface of a Polar Crystal

By

QU ZHE and PAN JIN-SHENG

Since the seventies, there have been many works to discuss the behaviour of the Mott-Wannier exciton near the interface of a layer structure /1 to 4/. In this note, we shall consider the similar problem by using the method developed in/5/.

Suppose a piece of polar crystal is filled in the space z > 0 and another piece of non-polar material contacts with it at z = 0. Assume that the exciton may be regarded as a surface electron polaron and hole polaron interacting with each other. Then, in the centre-of-mass frame, the Hamiltonian for such a system can be written as

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + \hbar\omega_s \sum_{\vec{Q}} a^+_Q a_Q + \hbar\omega_v \sum_{\vec{q}} a^+_q a_q + \left[\sum_{\vec{Q}} V^*_Q a^+_Q \exp(-i\vec{Q}\cdot\vec{R}_{\parallel} - QR_z) + \text{c.c.}\right] +$$
$$+ \left\{\sum_{\vec{q}} V^*_q a^+_q \left[\exp(-i\vec{q}\cdot\vec{R}) - \exp(-i\vec{q}_{\parallel}\cdot\vec{R}_{\parallel} - q_{\parallel}R_z)\right] + \text{c.c.}\right\} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\infty 1} r_{\parallel}} +$$
$$+ \frac{(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})e^2}{4\pi\varepsilon_0\varepsilon_{\infty 1}(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})}\left[\frac{1}{2R_z} - \frac{1}{(4R_z^2 + r_{\parallel}^2)^{1/2}}\right], \quad (1)$$

where we have implicitly taken the electron and hole being on the same X-Y plane, and $M = (m_1^* + m_2^*)$, M_1^* and m_2^* are the band mass of the electron and the hole, μ the reduced mass, and $\vec{R}$ the centre-of-mass coordinate of the exciton. ω_v and ω_s are, respectively, the bulk LO-phonon and the surface LO-phonon frequency without considering dispersion. ε_0 is the static dielectric constant, $\varepsilon_{\infty 1}$ the high-frequency dielectric constant of the polar crystal, $\varepsilon_{\infty 2}$ that of the non-polar material, and

$$|V^*_Q|^2 = \frac{2\pi\alpha_s(\hbar\omega_s)^2}{L^2 Q\beta_s}\left|\exp\left(-i\frac{m_1^*}{M}\vec{Q}\cdot\vec{r}_{\parallel}\right) - \exp\left(i\frac{m_2^*}{M}\vec{Q}\cdot\vec{r}_{\parallel}\right)\right|^2, \quad \beta_s = \left(\frac{2\mu\omega_s}{\hbar}\right)^{1/2}, \quad (2a)$$

$$|V^*_q|^2 = \frac{4\pi\alpha(\hbar\omega_v)^2}{L^3 q^2\beta_v}\left|\exp\left(-i\frac{m_1^*}{M}\vec{q}_{\parallel}\cdot\vec{r}_{\parallel}\right) - \exp\left(i\frac{m_2^*}{M}\vec{q}_{\parallel}\cdot\vec{r}_{\parallel}\right)\right|^2, \quad \beta_v = \left(\frac{2\mu\omega_v}{\hbar}\right)^{1/2}, \quad (2b)$$

where α_s and α are, respectively, the Fröhlich coupling constants of the surface LO-phonon and the bulk LO-phonon with the quasi-particle having the re-

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1) Changchun, Jiliu, People's Republic of China.

duced mass μ . They are defined by /6/

$$\alpha_s = \frac{e^2\beta_s}{\hbar\omega_s}\left(\frac{1}{\varepsilon_{\infty 1}+\varepsilon_{\infty 2}} - \frac{1}{\varepsilon_0+\varepsilon_{\infty 2}}\right) , \quad \alpha = \frac{e^2\beta_v}{2\hbar\omega_v}\left(\frac{1}{\varepsilon_{\infty 1}} - \frac{1}{\varepsilon_0}\right) . \tag{3}$$

For the centre-of-mass motion parallel to the X-Y plane, analogous to /7, 8/ we introduce the following unitary transformation:

$$U_1 = \exp\left(-i\sum_{\vec{Q}}\vec{R}_\parallel\cdot\vec{Q}\,a_Q^+a_Q - i\sum_{\vec{q}}\vec{R}\cdot\vec{q}\,a_q^+a_q\right), \quad U_2 = \exp\left[\sum_{\vec{Q}}(a_Q^+f_Q - a_Q f_Q^*) + \sum_{\vec{q}}(a_q^+f_q - a_q f_q^*)\right]. \tag{4}$$

Here f_q, f_q^*, f_Q, f_Q^* are variational functions. In addition, we also introduce the Boson creation and annihilation operators to represent the momentum and position coordinates ($\vec{P}$, $\vec{R}$)

$$P_j = (M_\parallel\,\hbar\,\lambda/2)^{1/2}(b_j^+ + b_j + P_{oj}) , \quad R_j = i(\hbar/2M_\parallel\lambda)^{1/2}(b_j - b_j^+) , \tag{5}$$

where j refers to X and Y direction. λ and P_{oj} are the variational parameters. If the vacuum state of the phonon and interface exciton is described by $|0\rangle$, we have

$$b_j|0\rangle = a_q|0\rangle = a_Q|0\rangle = 0 . \tag{6}$$

In the processes of variation, the system must be constrained by the conservation of the total momentum. In the adiabatic approximation, the momentum in z-direction may be regarded as a parameter. So it is only constrained by the total momentum parallel to the X-Y plane:

$$\vec{P}_{\parallel\,t} = \vec{P}_\parallel + \sum_{\vec{q}}\hbar\,\vec{q}\,a_q^+a_q + \sum_{\vec{Q}}\hbar\vec{Q}\,a_Q^+a_Q . \tag{7}$$

Applying the unitary transformation (4) to the above expression gives

$$\vec{\mathcal{P}}_\parallel = \langle 0|(U_1U_2)^{-1}\vec{P}_{\parallel\,t}(U_1U_2)|0\rangle = (M\,\hbar\lambda/2)^{1/2}\vec{P}_{0\parallel} . \tag{8}$$

Choosing an arbitrary multiplier u we finally have

$$F(f_q, f_q^*, f_Q, f_Q^*, \vec{P}_0, \vec{u}_\parallel, \lambda) = \bar{H}_0 - \vec{u}_\parallel\cdot\vec{\mathcal{P}}_\parallel , \tag{9}$$

where $\bar{H}_0$ is obtained from (1) by appling (4) and considering (5), (6). From the extreme condition $\partial F/\partial f_q = \partial F/\partial f_q^* = \partial F/\partial f_Q = \partial F/\partial f_Q^* = 0$, we can obtain these functions. Then, inserting them into (9) and expanding them up to the second-order term $\vec{P}_o$, the extreme condition $\partial F/\partial\vec{P}_o = 0$ gives $\vec{P}_o$. Then, from (8), we have

$$\vec{\mathcal{P}}_\parallel = M_\parallel\left[1 - (f_1+f_2)(2\,\hbar^2/M_\parallel)\right]^{-1}\vec{u}_\parallel ,$$

$$f_1 = \frac{8\pi}{L^2\beta_v}\frac{\varepsilon_o\,\varepsilon_{\infty 1}\alpha(\hbar\omega_v)^2}{(\varepsilon_o+\varepsilon_{\infty 2})(\varepsilon_{\infty 1}+\varepsilon_{\infty 2})}\frac{\omega_s}{\omega_v}\sum_{\vec{Q}}\frac{Q(\vec{P}_o\cdot\vec{Q}/P_oQ)^2\exp(-2QR_z)\langle\varphi|1-\cos(\vec{Q}\cdot\vec{r})|\varphi\rangle}{\left[\hbar\omega_s+(\hbar^2Q^2/2M_\parallel)\right]^3},$$

$$f_2 = \frac{8\pi\alpha}{L\,\beta_v}(\hbar\omega_v)^2\sum_{\vec{q}}\frac{q_\parallel(\vec{P}_o\cdot\vec{q}_\parallel/P_oq_\parallel)^2\left[1-\exp(-2q_\parallel R_z)\right]\langle\varphi|\,1-\cos(\vec{q}_\parallel\cdot\vec{r}_\parallel)\,|\varphi\rangle}{\left[\hbar\omega_v+(\hbar^2q_\parallel^2/2M_\parallel)\right]^3}.$$

Here we have used $\langle\varphi\left|\exp(i\,m\,\vec{q}_\parallel\vec{r}_\parallel/M_\parallel)-\exp(-i\,m\,\vec{q}_\parallel\cdot\vec{r}_\parallel/M_\parallel)\right|^2\varphi\rangle$ to substitute for $\left|\exp(i\,m\,\vec{q}_\parallel\cdot\vec{r}_\parallel/M_\parallel)-\exp(-i\,m\,\vec{q}_\parallel\cdot\vec{r}_\parallel/M_\parallel)\right|^2$. This is equivalent to have taken the average over φ before minimizing F with respect to $\vec{P}_o$. It is evident from the structure of this expression that $\vec{u}_\parallel$ has the meaning of the velocity which may be interpreted as the average translation velocity of the interface exciton in the X-Y plane, and the factor before $\vec{u}_\parallel$ can be interpreted as the effective mass of the interface exciton. Evidently, $M_\parallel^*$ will become smaller and smaller with the increase in R_z. On the other hand, if we use the trial function $\varphi=\varrho\exp(-\varrho r_\parallel/2)$, from the calculated value of ϱ given in Fig. 3 for different $\varepsilon_{\infty 2}$, one can see that, at a certain value of $R'_{z'}$. $M_\parallel^*$ will decrease with the increase of the dielectric constant $\varepsilon_{\infty 2}$. Using f_q, f_q^*, f_Q, f_Q^*, and $\vec{P}_o$ obtained above we finally have for the Hamiltonian at $R_z\to 0$

$$H_o=\frac{\mathcal{P}_\parallel^2}{2M^*}+\frac{p^2}{2\mu}-\frac{e^2}{2\pi\varepsilon_o(\varepsilon_{\infty 1}+\varepsilon_{\infty 2})r_\parallel}+\frac{(\varepsilon_{\infty 1}-\varepsilon_{\infty 2})e^2}{8\pi\varepsilon_o\varepsilon_{\infty 1}(\varepsilon_{\infty 1}+\varepsilon_{\infty 2})R_z}-\frac{2\,\varepsilon_o\varepsilon_{\infty 1}\alpha\hbar\omega_s}{(\varepsilon_o+\varepsilon_{\infty 2})(\varepsilon_{\infty 1}+\varepsilon_{\infty 2})}\left(\frac{\pi}{2}-I_1\right), \qquad (10)$$

where $I_1=\int_0^{\pi/2}\exp(r_\parallel\beta_v\cos\Theta)d\Theta$. The term being dependent of R_z may be regarded as parameter, and the rest presents a two-dimensional hydrogen-like atom and an interaction term with surface phonon. Thus, we use the plane hydrogen-like function $\varphi=\varrho\exp(-\varrho r_\parallel/2)$ and substitute it into (10). We can obtain the energy which is shown in Fig. 1 (on the left side of the arrow A), and for examining the effect of the image potential, the same result but not containing the term $1/R_z$ is also given in Fig. 2 (on the left side of the arrow A).

On the contrary, when $R_z\gg r_\parallel$, the Hamiltonian becomes

$$H_o=\frac{\mathcal{P}_\parallel^2}{2M_\parallel^*}+\frac{p^2}{2\mu}-\frac{e^2}{4\pi\varepsilon_o\varepsilon_{\infty 1}r_\parallel}-\alpha\hbar\omega_v\left(\frac{\pi}{2}-I_1\right) \qquad (11)$$

which is that of a two-dimensional hydrogen-like atom and an interaction term with bulk phonon. The energy is represented in Fig. 1 and 2 (on the right side of the arrow B).

For $R_z \approx r_{\parallel}$, the case is more complex but the procedure of calculation is the same as before. Using the trial function $\varphi = \varrho \exp(-\varrho r_{\parallel}/2)$, the ground state energy is obtained to be

$$E_o = \frac{\hbar^2 \beta_v^2 \varrho'^2}{8\mu} + \frac{\varphi_{\parallel}^2}{2M_{\parallel}^*} - \frac{e^2 \beta_v \varrho'}{4\pi \varepsilon_o \varepsilon_{\infty 1}} + \frac{(\varepsilon_{\infty 1} - \varepsilon_{\infty 2}) e^2 \beta_v}{8\pi \varepsilon_o \varepsilon_{\infty 1}(\varepsilon_{\infty 1} + \varepsilon_{\infty 2}) R'_z} - \alpha \hbar \omega_v \left(\frac{\pi}{2} - A(2R'_z)\right) -$$
$$- \frac{e^2(\varepsilon_{\infty 1} - \varepsilon_{\infty 2}) \beta_v \varrho'^2}{4\pi \varepsilon_o \varepsilon_{\infty 1}(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})} \left\{ -2R'_z + R'_z \pi \left[H_1(2R'_z \varrho') - Y_1(2R'_z \varrho') \right] \right\} +$$
$$+ \alpha \hbar \omega_v (I_3 - I_4) - \frac{2 \varepsilon_o \varepsilon_{\infty 1} \alpha \hbar \omega_s}{(\varepsilon_o + \varepsilon_{\infty 2})(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})} \left[A(2R'_z) - I_4 \right], \tag{12}$$

$$I_3 = \int_0^{\pi/2} \left[\varrho'^2 / (\varrho' + \cos\Theta)^2 \right] d\Theta , \quad I_4 = \int_0^{\infty} \frac{\varrho'^3}{(1 + x^2)(\varrho'^2 + x^2)} \exp(-2xR'_z) dx; \varrho' = \varrho/\beta_v ,$$
$$R'_z = R_z \beta_v .$$

$$A(x) = \mathrm{Ci}(x)\sin(x) - \mathrm{Si}(x)\cos(x), \quad \mathrm{Ci}(x) = \int_x^{\infty} (\cos(t)/t) dt , \quad \mathrm{Si}(x) = \int_x^{\infty} (\sin(t)/t) dt .$$

H_o and H_1, Y_o and Y_1 are the zeroth- and first-order Struve and Neumann functions, respectively. From the condition $\partial E_o / \partial \varrho' = 0$ we obtain the equation determining ϱ' which we have solved numerically as a function of R'_z. The result is shown in Fig. 3. Then substituting ϱ' obtained into (12), we have the ground state energy as shown in Fig. 1 (the parts between the arrows A and B).

From these figures we come to the following conclusions:

1. When the non-polar material is vacuum, i.e. $\varepsilon_{\infty 2} = 1$, the image action makes the energy increase with decrease of the distance from the interface. Thus, near the interface, there is no exciton. This layer is called the absolute dead layer for the exciton. However, the lower energy state is more stationary. Thus the real dead layer should be such one beyond which the energy begins to approach a constant value. From Fig. 1 one can see that for a material such as GaAs the real thickness of this layer is about 4 to 5 $R_z \approx 40$ nm.

2. From Fig. 1 one can see that there exists a certain critical value $(\varepsilon_{\infty 2})_{min}$, as soon as $\varepsilon_{\infty 2} \geqq (\varepsilon_{\infty 2})_{min}$ the dead layer disappears.

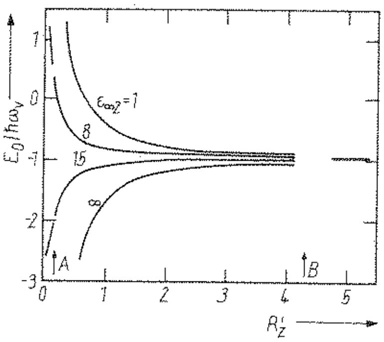

Fig. 1. The ground state energy of exciton

3. When the non-polar material is metal, i.e. $\varepsilon_{\infty 2} = \infty$ as shown in Fig. 3 and 2, $\varrho' \rightarrow 0$; $E_o \rightarrow 0$. It means that within a certain range, it is not possible for the exciton to exist, either. However, this layer is not the dead layer. This is because the attraction of the electron and hole in the exciton is weakened by the screening effect of the metal. Thus an exciton is dissociated into an electron and a hole. This phenomenon is quite similar to a phase transition from the exciton to free electron and free hole, i.e. near the interface, a semiconductor would be changed to a conductor, or an exciton dielectric would be changed to an electron-hole plasma.

4. Near the interface, if the existence of the exciton is possible, the energy would be much lower than that in the bulk. From (11) we can see that this energy is independent of the choice of the non-polar material. So no matter what material contacts with the polar material, as long as the distance from the interface is large enough, the energy would approach the same value. If we take the energy which begins to become an invariant value as the ground state energy of the interface exciton, it is about 1 $\hbar\omega_v$ which is lower than the corresponding value (0.3 $\hbar\omega_v$) of the bulk exciton.

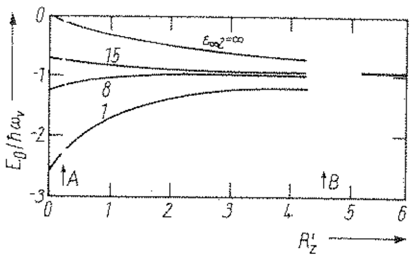

Fig. 2. The ground state energy not containing the term $\sim e^2/R'_z$

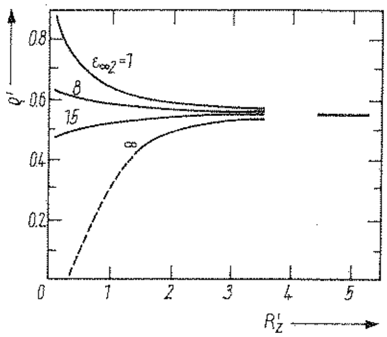

Fig. 3. ϱ' as a function of R'_z

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