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1992 J. Phys.: Condens. Matter 4 5863

(http://iopscience.iop.org/0953-8984/4/27/005)

J. Phys.: Condens. Matter 4 (1992) 5863–5872. Printed in the UK

Surface exciton in polyatomic polar crystals

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Received 25 September 1991, in final form 15 January 1992

Abstract. In this paper, some properties of a surface exciton in polyatomic polar crystals are studied. Effective Hamiltonians in the ground state of the surface exciton for both strong-coupling and weak-coupling polyatomic polar crystals are obtained by the method of a linear combination operator and simple unitary transformation. The effective mass of a strong-coupling surface exciton is derived using a Lagrange multiplier method. The self-trapping energy and effective potential of the surface exciton could be written as a series in α_s^{-1}, the first term being proportional to α_s, the coupling constant. The self-trapping energy and effective potential contain an extra contribution due to crossed terms between the different phonon branches. For a surface Wannier exciton the increasing part of the effective mass is proportional to α_s.

1. Introduction

Since Haken [1] studied the exciton in polar crystals for the first time, many researchers have discussed the exciton but many of them mainly concentrated their attention on the weak- and intermediate-coupling cases. In early 1976, Huybrechts [2] proposed a linear combination operator method by which a strong-coupling polaron could be studied. Gu and Zhang [3] discussed the internal motion of the strong-coupling exciton in polar crystals using the method advanced by Huybrechts.

The properties of the exciton in the surface layer of crystals influence the optical properties of the crystals very markedly. Most polar crystals are diatomic and cubic and their crystal structure belongs to NaCl, CsCl or ZnS type. In these crystals there is one mode of the longitudinal optical (LO) phonon. The properties of crystals having only one LO phonon branch have been studied by a great variety of techniques. However, a large number of polar crystals, with several atoms per unit cell, have more than one LO phonon branch. For example, in CuO_2 [4] there are two LO phonon modes. SiO_2, $GaAs_{1-x}P_x$ and a large number of perovskites [5] ($SrTiO_3$, $BaTiO_3$, $LiNbO_3$, etc) have more than two modes. In recent years the polaron problem with many LO phonon branches has been studied [4–6]. However, the exciton in polyatomic polar crystals has not been investigated so far. I [7, 8] calculated the ground-state energy of the exciton in polyatomic polar crystals by means of the perturbation method and the effective Hamiltonian of the strong-coupling exciton in polyatomic polar crystals using a linear combination operator method. In this paper, some properties of the surface exciton in polyatomic polar crystals are studied by the method of a linear combination operator and a simple unitary transformation.

2. Hamiltonian

Theoretical results [9] show that the surface layer of crystals may be regarded as pure 2D crystals if the distance from the surface is smaller than the radius of polarons. The effect of bulk phonons can be neglected, while the surface phonons are taken into account in the surface layer. In the case of many LO phonon branches, the total Hamiltonian of the surface exciton in polyatomic polar crystals can be written as

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^* \rho} + \sum_{Q,i} \hbar\omega_{si} a_{Qi}^+ a_{Qi} + \sum_{Q,i}\left(\frac{C_{Qi}}{Q^{1/2}} a_{Qi} \exp(\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{R})\,\xi_Q + \mathrm{HC}\right) \tag{1a}$$

$$C_{Qi} = 2\pi \mathrm{i} e\,(\hbar\omega_{si}/4\pi A\varepsilon)^{1/2} \tag{1b}$$

$$\xi_Q = \exp(-\mathrm{i}\beta_1 \boldsymbol{Q}\cdot\boldsymbol{\rho}) - \exp(\mathrm{i}\beta_2 \boldsymbol{Q}\cdot\boldsymbol{\rho}) \tag{1c}$$

$$1/\varepsilon = 1/\varepsilon_\infty^* - 1/\varepsilon_0^* \qquad \varepsilon_0^* = (\varepsilon_0 + 1)/2 \qquad \varepsilon_\infty^* = (\varepsilon_\infty + 1)/2 \tag{1d}$$

where M, μ, R and ρ are the mass centre mass, reduced mass, 2D mass centre coordinate and relative coordinate, respectively. a_{Qi}^+ and a_{Qi} are the creation and annihilation operators of the ith LO mode surface phonon with wavevector $\boldsymbol{Q}$. β_1 and β_2 are the fraction of the mass of electron and hole. $\boldsymbol{Q}$ is the 2D wavevector of the surface phonon. ε_∞ is the optical dielectric constant. ε_0 is the static dielectric constant. ω_{si} is the LO surface phonon frequency of the ith branch.

We introduce the creation and annihilation operators B^+ and B for the mass centre momentum $\boldsymbol{P}$ and mass centre coordinate $\boldsymbol{R}$ by

$$P_j = (M\hbar\lambda/2)^{1/2}\,(B_j + B_j^+) \tag{2a}$$

$$j = x, y$$

$$R_j = \mathrm{i}(\hbar/2M\lambda)^{1/2}\,(B_j - B_j^+) \tag{2b}$$

$$(B_i, B_j^+) = \delta_{ij} \tag{2c}$$

where λ is a variational parameter. Substituting (2a)–(2c) into (1a) and carrying out the unitary transformation

$$\mathcal{H} = U_2^{-1} U_1^{-1} H U_1 U_2 \tag{3}$$

where

$$U_1 = \exp\left(-\mathrm{i}a \sum_{Q,i} a_{Qi}^+ a_{Qi} \boldsymbol{Q}\cdot\boldsymbol{R}\right) \tag{4a}$$

$$U_2 = \exp\left(\sum_{Q,i} (a_{Q,i}^+ f_{Qi} - a_{Qi} f_{Qi}^*)\right). \tag{4b}$$

f_{Qi} and f_{Qi}^* are variational parameters. a is a parameter characterizing the coupling strength proposed by Huybrechts. $a = 1$ corresponds to the weak-coupling limit and $a = 0$ to the strong-coupling limit. Then (1a) can be rewritten as

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} + \frac{\hbar\lambda}{2}\left(\sum_j B_j^+ B_j + 1\right) + \frac{\hbar\lambda}{4}\sum_j (B_j^+ B_j^+ + B_j B_j) - a\hbar\left(\frac{\hbar\lambda}{2M}\right)^{1/2} \sum_{Q,i} (a_{Qi}^+ + f_{Qi}^*)(a_{Qi} + f_{Qi}) \sum_j Q_j (B_j^+ + B_j)$$

$$+\sum_{Q,i}\left(\hbar\omega_{si}+\frac{a^2\hbar^2Q^2}{2M}\right)(a_{Qi}^{+}+f_{Qi}^{*})(a_{Qi}+f_{Qi})$$

$$+\sum_{Q,i}\left\{\frac{C_{Qi}^{*}}{Q^{1/2}}\xi_Q^{*}(a_{Qi}^{+}+f_{Qi}^{*})\exp\left((1-a)^2\frac{\hbar Q^2}{4M\lambda}\right)\right.$$

$$\times\exp\left[-(1-a)\left(\frac{\hbar}{2M\lambda}\right)^{1/2}\sum_j Q_jB_j^{+}\right]$$

$$\left.\times\exp\left((1-a)\left(\frac{\hbar}{2M\lambda}\right)^{1/2}\sum_j Q_jB_j\right)+\mathrm{HC}\right\}$$

$$+\frac{a^2\hbar^2}{2M}\sum_{\substack{Q,Q'\\ i,i'}}\boldsymbol{Q}\cdot\boldsymbol{Q}'(a_{Qi}^{+}+f_{Qi}^{*})(a_{Q'i'}^{+}+f_{Q'i'}^{*})(a_{Qi}+f_{Qi})(a_{Q'i'}+f_{Q'i'})$$

$$-\frac{\hbar^2}{2\mu}\sum_{\substack{Q,Q'\\ i,i'}}(\nabla_\rho f_{Qi}\cdot\nabla_\rho f_{Q'i'}a_{Qi}^{+}a_{Q'i'}^{+}+\nabla_\rho f_{Qi}^{*}\cdot\nabla_\rho f_{Q'i'}^{*}a_{Qi}a_{Q'i'})$$

$$+\frac{\hbar^2}{\mu}\sum_{\substack{Q,Q'\\ i,i'}}\nabla_\rho f_{Qi}\cdot\nabla_\rho f_{Q'i'}^{*}a_{Qi}^{+}a_{Q'i'}+\frac{\hbar^2}{2\mu}\sum_{Q,i}|\nabla_\rho f_{Qi}|^2$$

$$-\frac{\hbar^2}{2\mu}\sum_{Q,i}(a_{Qi}^{+}\nabla_\rho f_{Qi}-a_{Qi}\nabla_\rho f_{Qi}^{*})\cdot\nabla_\rho-\frac{\hbar^2}{2\mu}\sum_{Q,i}(a_{Qi}^{+}\nabla_\rho^2 f_{Qi}-a_{Qi}\nabla_\rho^2 f_{Qi}^{*}).\quad(5)$$

The ground-state wavefunction of the system is $\Phi=\varphi(\rho)|0\rangle$ where $\varphi(\rho)$ is the wavefunction which describes the internal motion of an exciton. $|0\rangle$ is the zero phonon state, which satisfies

$$B_i|0\rangle=a_{Qi}|0\rangle=0.\quad(6)$$

Then the upper limit of the ground-state energy is obtained by minimizing the expectational value $E(\lambda)$:

$$E(\lambda)=\langle\Phi|\mathcal{H}|\Phi\rangle=\langle\varphi(\rho)|F(\lambda)|\varphi(\rho)\rangle\quad(7a)$$

$$H_{\mathrm{eff}}=\min F(\lambda)\quad(7b)$$

where H_{eff} is called the effective Hamiltonian.

Inserting (6) into (7*a*) we get

$$F(\lambda)=-\frac{\hbar^2}{2\mu}\nabla_\rho^2-\frac{e^2}{\varepsilon_\infty^{*}\rho}+\frac{1}{2}\hbar\lambda-\sum_{Q,i}\frac{|C_{Qi}|^2|\xi_Q|^2}{(\hbar\omega_{si}+a^2\hbar^2Q^2/2M)Q}\exp\left(-(1-a)^2\frac{\hbar Q^2}{2M\lambda}\right)$$

$$+\frac{\hbar^2}{2\mu}\sum_{Q,i}\frac{|C_{Qi}|^2|\nabla_\rho\xi_Q|^2}{(\hbar\omega_{si}+a^2\hbar^2Q^2/2M)^2Q}\exp\left(-(1-a)^2\frac{\hbar Q^2}{2M\lambda}\right).\quad(8)$$

We now discuss the two limits of strong coupling and weak coupling.

3. Weak- and strong-coupling limits

3.1. Weak coupling

In the unitary transformation, U_1 with $a = 1$ corresponds to the weak-coupling limit. Replacing Σ_Q by $(S/4\pi^2)\int_0^\infty\int_0^{2\pi} Q\,\mathrm{d}Q\,\mathrm{d}\varphi$, although the calculation is straightforward. Equation (8) can be written as

$$F(\lambda) = \frac{\hbar\lambda}{2} - \frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^* \rho} - \sum_i \alpha_{si}\hbar\omega_{si}[\pi - 2L(\rho)]$$

$$+ \sum_i \alpha_{si}\hbar\omega_{si}\left(\frac{\pi\beta}{2} + L(\rho) + \rho\frac{\mathrm{d}}{\mathrm{d}\rho}L(\rho)\right) \tag{9a}$$

where

$$L(\rho) = \int_0^{\pi/2} \exp(-u_{si}\rho\cos\varphi)\,\mathrm{d}\varphi \tag{9b}$$

$$\beta = (\beta_1^2 + \beta_2^2)/2\beta_1\beta_2 \qquad u_{si} = (2M\omega_{si}/\hbar)^{1/2}. \tag{9c}$$

Since each term is independent of λ except the first term, we have

$$\lambda = 0.$$

Finally we can obtain

$$H_{\mathrm{eff}} = -(\hbar^2/2\mu)\nabla_\rho^2 - E_{\mathrm{tr}} + V_{\mathrm{eff}}(\rho) \tag{10a}$$

$$E_{\mathrm{tr}} = \sum_i \frac{\pi\alpha_{si}\hbar\omega_{si}}{2}(2-\beta) \tag{10b}$$

$$V_{\mathrm{eff}} = -\frac{e^2}{\varepsilon_\infty^*\rho} + \sum_i \alpha_{si}\hbar\omega_{si}\left(3 + \rho\frac{\mathrm{d}}{\mathrm{d}\rho}\right)L(\rho). \tag{10c}$$

E_{tr} is the self-trapping energy and V_{eff} is the effective potential.

3.2. Strong coupling

In the unitary transformation, U_1 with $a = 0$ corresponds to the strong-coupling limit. Equation (8) can be written as

$$F(\lambda) = -\frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} + \tfrac{1}{2}\hbar\lambda - \sum_{Q,i}\frac{|C_{Qi}|^2|\xi_Q|^2}{\hbar\omega_{si}Q}\exp\left(-\frac{\hbar Q^2}{2M\lambda}\right)$$

$$+ \frac{\hbar^2}{2\mu}\sum_{Q,i}\frac{|C_{Qi}|^2|\nabla_\rho\xi_Q|^2}{(\hbar\omega_{si})^2 Q}\exp\left(-\frac{\hbar Q^2}{2M\lambda}\right). \tag{11}$$

The final two terms in $F(\lambda)$ can be calculated by replacing the summation with integration we have

$$F(\lambda) = \frac{\hbar\lambda}{2} - \frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} - \sum_i \alpha_{si}\hbar\omega_{si}\left(\frac{\lambda\pi}{\omega_{si}}\right)^{1/2}\left(1 - \frac{2}{\pi}K(\rho)\right)$$

$$+ \sum_i \sqrt{\pi}\alpha_{si}\hbar\omega_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}\left[\tfrac{1}{2}\beta + \frac{1}{\pi}\left(1 + \rho\frac{\mathrm{d}}{\mathrm{d}\rho}\right)K(\rho)\right] \tag{12a}$$

$$K(\rho) = \int_0^{\pi/2} \exp\left(-\frac{\lambda}{4\omega_{si}} u_{si}^2 \rho^2 \cos^2\varphi\right) d\varphi. \tag{12b}$$

For a strong-coupling surface Wannier exciton ($\exp(-\lambda u_{si}^2\rho^2/4\omega_{si}) \ll 1$), $F(\lambda)$ can be approximately written as

$$F(\lambda) = \frac{\hbar\lambda}{2} - \frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} - \sum_i \alpha_{si}\hbar\omega_{si}\left(\frac{\lambda\pi}{\omega_{si}}\right)^{1/2} + \sum_i \frac{\sqrt{\pi}}{2}\alpha_{si}\hbar\omega_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}\beta. \tag{13}$$

Performing the variation in (13) with respect to λ, we get

$$\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\lambda + \frac{2}{3\beta\sqrt{\pi}}\sqrt{\lambda} - \frac{2}{3\beta}\sum_i \alpha_{si}\sqrt{\omega_{si}} = 0. \tag{14}$$

The solution can be written as

$$\sqrt{\lambda} = -1\Big/3\beta\sqrt{\pi}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}} + \sqrt{\frac{2}{3\beta}}\left(\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\Big/\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\right)^{1/2}\left(1 + 1\Big/6\beta\pi\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\right)^{1/2}. \tag{15a}$$

For the strong-coupling case,

$$1\Big/6\beta\pi\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}} \ll 1.$$

(15*a*) can be expanded as

$$\sqrt{\lambda} = \sqrt{\frac{2}{3\beta}}\left(\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\Big/\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\right)^{1/2}\left(1 - 1\Big/\sqrt{6\beta\pi}\left(\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\right)^{1/2} + 1\Big/12\pi\beta\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}} + \dots\right). \tag{15b}$$

Substituting (15*b*) into (12*a*), we have

$$H_{\mathrm{eff}} = -(\hbar^2/2\mu)\nabla_\rho^2 - E_{\mathrm{tr}} + V_{\mathrm{eff}}(\rho) \tag{16a}$$

$$E_{\mathrm{tr}} = \tfrac{2}{3}\sqrt{\frac{2\pi}{3\beta}}\sum_i \alpha_{si}\hbar\omega_{si} + \sqrt{\frac{2\pi}{3\beta}}\sum_{i\neq j}\hbar\left(\alpha_{si}^{1/2}\alpha_{sj}^{1/2}\omega_{si}^{3/4}\omega_{sj}^{1/4} - \tfrac{1}{3}\frac{\alpha_{sj}^{3/2}\omega_{sj}^{3/4}\omega_{si}^{1/4}}{\alpha_{si}^{1/2}}\right) - \frac{\hbar}{3\beta}\sum_i \omega_{si} - \frac{\hbar}{3\beta}\sum_{i\neq j}\alpha_{sj}\alpha_{si}^{-1}\omega_{sj}^{1/2}\omega_{si}^{1/2} + \frac{1}{3\beta\sqrt{6\pi\beta}}\sum_i \frac{\hbar\omega_{si}}{\alpha_{si}} + \frac{\hbar}{6\beta\sqrt{6\pi\beta}}\sum_{i\neq j}\left(\frac{\omega_{si}^{5/4}}{\alpha_{si}^{1/2}\alpha_{sj}^{1/2}\omega_{sj}^{1/4}} + \frac{\alpha_{sj}^{1/2}\omega_{si}^{3/4}\omega_{sj}^{1/4}}{\alpha_{si}^{3/2}}\right) + \dots \tag{16b}$$

$$V_{\rm eff}(\rho) = -\frac{e^2}{\varepsilon_\infty^* \rho} + \frac{2}{3\beta}\sqrt{\frac{2}{3\pi\beta}}\sum_i \alpha_{si}\hbar\omega_{si}\left((1+3\beta) + \rho\frac{d}{d\rho}\right)K(\rho)$$

$$+ 2\sqrt{\frac{2}{3\pi\beta}}\sum_{i\neq j}\hbar\alpha_{si}^{1/2}\alpha_{sj}^{1/2}\omega_{si}^{3/4}\omega_{sj}^{1/4}K(\rho)$$

$$+ \frac{2}{3\beta}\sqrt{\frac{2}{3\pi\beta}}\sum_{i\neq j}\hbar\alpha_{si}^{-1/2}\alpha_{sj}^{3/2}\omega_{si}^{1/4}\omega_{sj}^{3/4}\left(1 + \rho\frac{d}{d\rho}\right)K(\rho)$$

$$- \frac{2}{3\pi\beta^2}\left(\sum_i \hbar\omega_{si} + \sum_{i\neq j}\hbar\alpha_{sj}\omega_{sj}^{1/2}\alpha_{si}^{-1}\omega_{si}^{1/2}\right)\left[\left(1 + 3\beta^2\sqrt{\frac{2\pi}{3\beta}}\right) + \rho\frac{d}{d\rho}\right]K(\rho)$$

$$+ \frac{1}{2\pi\beta^2}\sqrt{\frac{2}{3\pi\beta}}\sum_i \frac{\hbar\omega_{si}}{\alpha_{si}}\left[\left(1 + \frac{\beta}{3}\right) + \rho\frac{d}{d\rho}\right]K(\rho)$$

$$+ \frac{\hbar}{6\pi\beta}\sqrt{\frac{2}{3\pi\beta}}\sum_{i\neq j}\frac{\omega_{si}^{5/4}}{\alpha_{si}^{1/2}\alpha_{sj}^{1/2}\omega_{sj}^{1/4}}K(\rho)$$

$$+ \frac{\hbar}{2\pi\beta^2}\sqrt{\frac{2}{3\pi\beta}}\sum_{i\neq j}\frac{\alpha_{sj}^{1/2}\omega_{si}^{3/4}\omega_{sj}^{1/4}}{\alpha_{si}^{3/2}}\left(1 + \rho\frac{d}{d\rho}\right)K(\rho) + \ldots \quad (16c)$$

The first term in equation (16*a*) is the kinetic energy of the surface exciton internal motion. The second term is the self-trapping energy of the surface exciton, which is induced by the interaction of the electron and hole in the exciton with the LO phonon. The third term is the effective interaction potential energy between the electron and hole.

4. Effective mass

To obtain the surface exciton mass, the minimization of the energy should be performed by constraining the total momentum operator $\boldsymbol{P}$. This operator may be written as

$$\boldsymbol{P} = \boldsymbol{p} + \sum_{Q,i}\hbar Q a_{Qi}^+ a_{Qi}. \quad (17)$$

We now replace one of equations (2) by

$$P_j = (M\hbar\lambda/2)^{1/2}(B_j + B_j^+ + P_{0j}) \quad (18)$$

where $\boldsymbol{P}_0$ is an extra variational parameter. Carrying out the unitary transformation,

$$U = \exp\sum_{Q,i}(a_{Qi}^+ f_{Qi} + a_{Qi} f_{Qi}^*). \quad (19)$$

The expectation value of $U^{-1}(H - \boldsymbol{u}\cdot\boldsymbol{p})U$ for the ground state $|0\rangle$, where $\boldsymbol{u}$ is a Lagrange multiplier and will be in due course identified as the velocity of the surface exciton, is

$$F(\lambda, f_{Qi}, p_0, u) \equiv \langle 0|U^{-1}(H - u\cdot p)U|0\rangle$$
$$= -\frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} + \tfrac{1}{2}\hbar\lambda + \tfrac{1}{4}\hbar\lambda\rho_0^2 - \left(\frac{M\hbar\lambda}{2}\right)^{1/2} u\cdot p_0$$
$$+ \sum_{Q,i}\hbar\omega_{si}|f_{Qi}|^2 + \sum_{Q,i}\left[\frac{C_{Qi}}{Q^{1/2}}\xi_Q f_{Qi}^* \exp\left(-\frac{\hbar Q^2}{4M\lambda}\right) + \text{HC}\right]$$
$$+ \frac{\hbar^2}{2\mu}\sum_{Q,i}|\nabla_\rho f_{Qi}|^2 - \sum_{Q,i}\hbar Q\cdot u|f_{Qi}|^2. \tag{20}$$

Performing the variation in equation (20) with respect to f_{Qi} and P_0 yields

$$f_{Qi} = -[C_{Qi}^*\xi_Q^*/(\hbar\omega_{si} - \hbar Q\cdot u)Q^{1/2}]\exp(-\hbar Q^2/4M\lambda) \tag{21a}$$
$$P_0 = (2M/\hbar\lambda)^{1/2}u. \tag{21b}$$

Replacing the summation with integration and up to second order in the velocity u, we get

$$F(\lambda) = -\frac{\hbar^2}{2\mu}\nabla_\rho^2 - \frac{e^2}{\varepsilon_\infty^*\rho} + \tfrac{1}{2}\hbar\lambda - \tfrac{1}{2}Mu^2 - \sum_i \alpha_{si}\hbar\omega_{si}\sqrt{\frac{\pi\lambda}{\omega_{si}}}\left(1 - \frac{2}{\pi}K(\rho)\right)$$
$$- \frac{Mu^2}{2}\sum_i\sqrt{\pi}\alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2} + \tfrac{9}{4}\sqrt{\pi}Mu^2\sum_i\alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{5/2}\beta$$
$$- \frac{4Mu^2}{\sqrt{\pi}}\sum_i\frac{\alpha_{si}}{u_{si}^2}\left(\frac{\lambda}{\omega_{si}}\right)^{1/2}(1 - 2\sin^2\varphi_1)\frac{d^2}{d\rho^2}K(\rho)$$
$$+ \frac{2Mu^2}{\sqrt{\pi}}\sum_i\alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}\sin^2\varphi_1\left(1 + \rho\frac{d}{d\rho}\right)K(\rho)$$
$$+ \sum_i\sqrt{\pi}\alpha_{si}\hbar\omega_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}\left[\frac{\beta}{2} + \frac{1}{\pi}\left(1 + \rho\frac{d}{d\rho}\right)K(\rho)\right]$$
$$+ \frac{3Mu^2}{\sqrt{\pi}}\sum_i\alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{5/2}\sin^2\varphi_1\left(\rho^2\frac{d^2}{d\rho^2} + 5\rho\frac{d}{d\rho} + 3\right)K(\rho)$$
$$- \frac{6Mu^2}{\sqrt{\pi}}\sum_i\frac{\alpha_{si}}{u_{si}^2}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}(1 - 2\sin^2\varphi_1)\left(\rho\frac{d^3}{d\rho^3} + 3\frac{d^2}{d\rho^2}\right)K(\rho). \tag{22}$$

φ_1 in (22) is the angle between ρ and u.

For the strong-coupling surface Wannier exciton the variational parameter λ, which is the same as equation (15*b*), can be obtained by the variational method. Finally, using the variational quantities f_{Qi}, P_0 and λ determined through equations (21) and (15*b*), we obtain the effective Hamiltonian of the surface exciton:

$$H_{\text{eff}} = -(\hbar^2/2\mu)\nabla_\rho^2 + P^2/2M^* - E_{\text{tr}} + V_{\text{eff}}(\rho) \tag{23}$$

where E_{tr} and $V_{\text{eff}}(\rho)$ are the same as (16*b*) and (16*c*).

For the momentum expectation value we find

$$\bar{p} = \langle 0|U^{-1}pU|0\rangle = M\Big[1 + \sum_i \sqrt{\pi}\,\alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2} + \frac{8}{\sqrt{\pi}}\sum_i \frac{\alpha_{si}}{u_{si}^2}\left(\frac{\lambda}{\omega_{si}}\right)^{1/2}(1-2\sin^2\varphi_1)\frac{d^2}{d\rho^2}K(\rho) - \frac{4}{\sqrt{\pi}}\sum_i \alpha_{si}\left(\frac{\lambda}{\omega_{si}}\right)^{3/2}\sin^2\varphi_1\left(1+\rho\frac{d}{d\rho}\right)K(\rho)\Big]u = M^*u. \tag{24}$$

The Lagrange multiplier u is indeed the surface exciton velocity, and the surface exciton mass is therefore given by

$$\begin{aligned}M^* = M\Big\{&1 + 8\sqrt{\frac{2}{3\pi\beta}}\sum_i \frac{\alpha_{si}^{1/2}}{u_{si}^2\omega_{si}^{1/4}}\sum_j \alpha_{sj}^{1/2}\omega_{sj}^{1/4}\Big[1 - 1\Big/\sqrt{6\pi\beta}\Big(\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i \frac{\alpha_{si}}{\sqrt{\omega_{si}}}\Big)^{1/2} \\ &+ 1\Big/12\pi\beta\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i\frac{\alpha_{si}}{\sqrt{\omega_{si}}} + \dots\Big](1-2\sin^2\varphi_1)\frac{d^2}{d\rho^2}K(\rho) \\ &+ \sqrt{\pi}\left(\frac{2}{3\beta}\right)^{3/2}\Big(\sum_j \alpha_{sj}^{3/2}\omega_{sj}^{3/4}\Big/\sum_i \alpha_{si}^{1/2}\omega_{si}^{3/4}\Big) \\ &\times\Big[1 - 1\Big/\sqrt{6\pi\beta}\Big(\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i\frac{\alpha_{si}}{\sqrt{\omega_{si}}}\Big)^{1/2} \\ &+ 1\Big/12\pi\beta\sum_j \alpha_{sj}\sqrt{\omega_{sj}}\sum_i\frac{\alpha_{si}}{\sqrt{\omega_{si}}} + \dots\Big]^3 \\ &\times\Big(1 - \frac{4}{\pi}\sin^2\varphi_1\Big(1+\rho\frac{d}{d\rho}\Big)K(\rho)\Big)\Big\}.\end{aligned} \tag{25}$$

5. Results and discussion

The problem of the polaron in strong-coupling polar crystals is complicated, and even more so in strong-coupling polyatomic polar crystals. Naturally, the exciton problem in strong-coupling polyatomic polar crystals is still more difficult. An effective Hamiltonian of the ground state of the surface exciton in both strong-coupling and weak-coupling polyatomic crystals and an effective mass of the surface exciton in strong-coupling polyatomic crystals have been derived using the method of a linear combination operator and simple unitary transformation and Lagrange multiplier.

From (10*b*) and (10*c*) one can see that many LO phonon branches in polyatomic polar crystals influence both the self-trapping energy and the effective potential of the surface exciton. If the interaction between the different branches of virtual phonons with different wavevectors emitted by the surface exciton in the recoil effect is neglected, the effects of different branches of LO phonon–surface exciton coupling on both the self-trapping energy and the effective potential of the surface exciton are independent of each other. It is interesting that the effects of interaction of different branches of LO phonons and the surface exciton on the effective potential of the surface exciton is only felt by the final term of the potential and not by the Coulomb potential.

The self-trapping energy (10*b*) depends not only on the surface exciton–phonon interaction, but also on the relative magnitudes of the electron and hole masses. What is more interesting is the influence of the lattice vibration on the self-trapping. The energy of the surface exciton is changed owing to the action of the lattice vibration on the surface exciton. The value of the surface exciton energy is lowered because of the action of the lattice vibration when the electron and hole masses are not equal, i.e. the self-trapping energy is

$$\sum_i \frac{\pi \alpha_{si} \hbar \omega_{si}}{2} \left(2 - \frac{\beta_1^2 + \beta_2^2}{2\beta_1\beta_2}\right). \tag{26}$$

Equation (26) shows further that, when the mass difference between the electron and the hole is not too large, E_{tr} can be larger than zero, and the surface exciton may be self-trapped in the range $0.2113 < \beta_1 < 0.7886$. Otherwise, when the mass difference between the electron and the hole is large, the surface exciton may not be self-trapped in the range $\beta_1 < 0.2113$ or $\beta_1 > 0.7886$. Under these circumstances, the energy of the surface exciton is not reduced; on the contrary, because of the action of the lattice vibration it rises. Thus the surface exciton will not be self-trapped, when the electron-to-hole mass ratio μ_e/μ_h is in the range $\mu_e/\mu_h < 0.268$ or $\mu_e/\mu_h > 3.732$, whereas the surface exciton is self-trapped when the electron-to-hole mass ratio is in the range $0.268 < \mu_e/\mu_h < 3.732$, i.e. the self-trapping condition for the surface exciton depends critically on the electron-to-hole mass ratio, because the strength of the interaction of the electron and the hole with the lattice depends on the electron-to-hole mass ratio. The induced self-trapping energy also depends on this ratio.

In strong-coupling polyatomic polar crystals, the self-trapping energy (16*b*) and the effective potential (16*c*) of a surface Wannier exciton can be written as a series in α_s^{-1}, the first term being proportional to α_s, the coupling constant of the surface exciton–phonon. Not only does the self-trapping energy (16*b*) and the effective potential (16*c*) include the coupling contribution between the electron–hole and the different LO phonon branches, but also there exists an extra contribution due to crossed terms between the different branches and the different wavevector virtual phonon, which is emitted via the excitonic recoil.

For the surface Wannier exciton, one can omit, in the screening potential (16*c*) induced by the interaction of the electron–hole with the LO phonons due to the ionic polarization, the included $K(\rho)$ and $(\mathrm{d}/\mathrm{d}\rho)K(\rho)$ terms, which are obtained via numerical calculation, so that only the first term remains. If the effective electron–hole potential in strong-coupling polyatomic polar crystals can be described simply by $-e^2/\varepsilon_\infty^* \rho$, more satisfactory results may be obtained.

The effective mass of the surface exciton in strong-coupling polyatomic polar crystals is obtained by the Lagrange multiplier method. From (25), one can see that the effective mass M^* does depend on the exciton-surface optical phonon parameter α_s, the electron–hole distance ρ and the electron-to-hole mass ratio. For the surface Wannier exciton in strong-coupling polyatomic polar crystals the included $K(\rho)$, $\rho(\mathrm{d}/\mathrm{d}\rho)K(\rho)$ and $(\mathrm{d}^2/\mathrm{d}\rho^2)K(\rho)$ terms can be omitted, and we have

$$M^* = M\left[1 + \sqrt{\pi}\left(\frac{2}{3\beta}\right)^{3/2}\left(\sum_j \alpha_{sj}^{3/2}\omega_{sj}^{3/4} \Big/ \sum_i \alpha_{si}^{1/2}\omega_{si}^{3/4}\right)\right]. \tag{27}$$

From (27), one can see that for the surface Wannier exciton in polyatomic polar crystals the increasing part of the effective mass is proportional to α_s because of the strong coupling between the electron–hole and the surface optical phonon.

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