数理解析研究所講究録
第 1565 巻 2007 年 86-92

Stability of Formation of Large Bipolaron

岡山大学大学院自然科学研究科　廣川 真男 (Masao HIROKAWA)
The Graduate School of Natural Science and Technology,
Okayama University

1 Introduction

This is a brief report on the results in [1].

Let us consider two electrons coupled with longitudinal optical (LO) phonons in a 3-dimensional crystal now. Then, in general, an electron is dressed in a phonon cloud because of the electron-phonon interaction. The dressed electron is the so-called *polaron* [2, 3]. If the Coulomb repulsion between the two electrons is strong enough, the two electrons are so far away from each other that each electron dresses itself in an individual phonon cloud. Thus, there is no exchange of phonons between the two. On the other hand, if the distance between the two electrons is so short that a common phonon cloud grasps both electrons, then the phonon-exchange takes place. In this case, there is a possibility that attraction appears between them and thus we can expect that they are bound to each other. The bound two polarons is called a *bipolaron* [4, 5, 6, 7, 8, 9]. We consider the tug of war between the two electrons.

The total Hamiltonian $H_{\rm BP}$ of bipolaron we consider is given by

$$H_{\rm BP} = H_{\text{el-el}} + H_{\rm ph} + H_{\text{el-ph}}, \tag{1.1}$$

where

$$H_{\text{el-el}} = \sum_{j=1,2} \frac{1}{2m} p_j^2 + \frac{U}{|x_1 - x_2|}, \tag{1.2}$$

$$H_{\rm ph} = \sum_k \hbar\omega_k a_k^\dagger a_k, \tag{1.3}$$

$$H_{\text{el-ph}} = \sum_{j=1,2} \sum_k \left\{ V_k e^{ik\cdot x_j} a_k + V_k^* e^{-ik\cdot x_j} a_k^\dagger \right\}. \tag{1.4}$$

In Eq.(1.2), x_j and p_j denote the position and momentum operators of the jth electron ($j = 1, 2$) of mass m, respectively, so $p_j = -i\hbar\nabla_{x_j}$. The symbol U stands for the strength of the Coulomb repulsion, so $U \equiv e^2/\epsilon_\infty$ for the electric charge e and the optic dielectric constant ϵ_∞. In Eq.(1.3), a_k and $a_k^\dagger$ are the annihilation and creation operators, respectively, of the LO phonon with the momentum $\hbar k$. Since phonons are bosons, a_k and $a_k^\dagger$ satisfy the canonical commutation relation. We can set the dispersion relation ω_k as $\omega_k = \omega_{\rm LO}$ because the LO phonons can be assumed to be dispersionless. In Eq.(1.4), V_k is defined by $V_k := -i\hbar\omega_{\rm LO}\left(4\pi\alpha r_{\rm fp}/k^2V\right)^{1/2}$ for the crystal volume V and the free polaron radius $r_{\rm fp} \equiv (\hbar/2m\omega_{\rm LO})^{1/2}$. The dimensionless electron-phonon coupling constant is

$$\alpha := \frac{1}{\hbar\omega_{\rm LO}}\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{1}{r_{\rm fp}}, \tag{1.5}$$

where ϵ_0 is the static dielectric constant. We define the ionicity η of the crystal by $\eta := \epsilon_\infty/\epsilon_0$, so $0 < \eta < 1$. Then, the strength of the Coulomb repulsion is rewritten as $U = \sqrt{2}\,\alpha/(1-\eta)$. We note the wave vector k in $\sum_k$ runs over the first Brillouin zone because we consider the two-body system of large polarons.

From now on, we use the natural units $\hbar = m = \omega_{\rm LO} = 1$ in this report. Using the well-known conversion of sums to integrals, we estimate $\sum_k |V_k|^2$ at $\sqrt{2}\,\alpha K/\pi$, where K means the radius of a sphere of the first Brillouin zone. Using the approximation of the Fourier expansion, $V/(4\pi|x|) \approx \sum_k e^{ik\cdot x}/k^2$, we have

$$\sum_k |V_k|^2 e^{ik\cdot x} \approx \frac{\alpha}{\sqrt{2}\,|x|}. \tag{1.6}$$

We often use this approximation (1.6).

In this report we say $H_{\rm BP}$ *has a ground state* if $H_{\rm BP}$ has an eigenvector of which eigenenergy is the lowest point spectrum of $H_{\rm BP}$. We note $H_{\rm BP}$ has translation invariance. Thus, to give a possibility that $H_{\rm BP}$ has a ground state, we put a device in the interaction Hamiltonian:

$$H_{\text{el-ph}}(\rho) = \rho(x_1+x_2)\sum_{j=1,2}\sum_k\left\{V_k e^{ik\cdot x_j}a_k + V_k^* e^{-ik\cdot x_j}a_k^\dagger\right\}.$$

where $\rho(x)$ is a function satisfying $0 \le \rho(x) \le 1$. We employ $H_{\text{el-ph}}(\rho)$ in $H_{\rm BP}$ instead of $H_{\text{el-ph}}$:

$$H_{\rm BP} = H_{\text{el-el}} + H_{\rm ph} + H_{\text{el-ph}}(\rho).$$

For instance, we define $\rho(x)$ so that $\rho(x) = 0$ outside the crystal and $\rho(x) = 1$ inside the crystal. We can also define $\rho(x)$ by $\rho(x) \equiv \rho_Q(x)$, where $\rho_Q(x) := 1$ if $x = 2Q$; $\rho_Q(x) := 0$ if $x \ne 2Q$. For $\rho(x) \equiv 1$ the Hamiltonian $H_{\text{el-el}} + H_{\rm ph} + H_{\text{el-ph}}(\rho)$ becomes the original $H_{\rm BP}$.

2 Spatial Localization in Weak-Coupling Regime

We define a positive constant $E_{\mathrm{w}}(\alpha)$ by

$$E_{\mathrm{w}}(\alpha) := 4\sum_{k}|V_k|^2 = \frac{4\sqrt{2}\,\alpha}{\pi}K = \frac{8\sqrt{2}\,\alpha}{\Lambda} \tag{2.1}$$

for every $\alpha > 0$, where Λ is a wave length defined by $\Lambda := 2\pi/K$.

When H_{BP} has a ground state Ψ_0, we define the distance $d_{\mathrm{BP}}(\Psi_0)$ between the two electrons in bipolaron by

$$d_{\mathrm{BP}}(\Psi_0) := \langle\Psi_0|\Psi_0\rangle^{-1}\langle\Psi_0||x_1 - x_2||\Psi_0\rangle. \tag{2.2}$$

We say that *the relative motion of the bipolaron in a bound state* Ψ_n *is spatially localized in the closed ball* $\overline{B}(r)$ if $d_{\mathrm{BP}}(\Psi_0) \leq r$.

Using and developing Lieb's idea [10], we can show that *the relative motion of the bipolaron in a ground state is not spatially localized in* $\overline{B}(r)$, *provided that the ground state exists under the condition:*

$$E_{\mathrm{w}}(\alpha) < \frac{U}{r} \qquad \left(\text{i.e., } 0 \leq 1 - \frac{\Lambda}{8r} < \eta\right). \tag{2.3}$$

3 Bipolaron Formation

We consider the original H_{BP} (i.e., in the case $\rho(x) \equiv 1$) in the strong-coupling regime in this section. We derive two effective Hamiltonians from H_{BP} by modifying Bogolubovs' method [11], which is similar to Adamowski's [5] and ours [12].

We find a canonical transformation U_θ with the parameter $\theta \geq 0$ so that $H_{\mathrm{BP}}(\theta) := U_\theta^* H_{\mathrm{BP}} U_\theta = H_{\mathrm{eff}}(\theta) + H_{\mathrm{ph}} + H_{\text{el-ph}}(\theta) + \Sigma_\theta$, where $H_{\mathrm{eff}}(\theta)$ is an effective Hamiltonian in quantum mechanics, and Σ_θ a divergent energy as $\theta \to \infty$. Then, we make the effective Hamiltonian $H_{\mathrm{eff}}(\theta)$ should have an attractive potential $V(\theta)$ from the phonon field as $H_{\mathrm{eff}}(\theta) = H_{\text{el-el}} + V(\theta)$. By the help of this extra attractive potential $V(\theta)$, we expect a critical point θ_c so that the Hamiltonian $H_{\mathrm{eff}}(\theta)$ itself or the Hamiltonian $H_{\mathrm{eff}}^{\mathrm{rel}}(\theta)$ for the relative motion of $H_{\mathrm{eff}}(\theta)$ has a ground state if $\theta > \theta_c$. On the other hand, it has no ground state if $\theta < \theta_c$.

We can show that *the approximation (1.6) yields an effective Hamiltonian describing balanced state [1] in quantum mechanics:*

$$H_{\mathrm{eff}}(\theta) = H_{\text{el-el}} + V(\theta) = \frac{1}{2}p_1^2 + \frac{1}{2}p_2^2 + \frac{U(\theta)}{|x_1 - x_2|} \tag{3.1}$$

with

$$U(\theta) = U - \sqrt{2}\,\alpha\theta = \sqrt{2}\,\alpha\left(\frac{1}{1-\eta} - \theta\right). \tag{3.2}$$

Clearly $\theta_c = 1/(1-\eta)$.

Let c_* be an arbitrary constant so that $0 < c_* < 1$. We set $c_{\rm BP}$ as:

$$c_{\rm BP} := \frac{2}{5}\left(c_* - \frac{1}{\theta(1-\eta)}\right)^2. \tag{3.3}$$

Then, the effective Hamiltonian $H_{\rm eff}(\theta)$ in Eq.(3.1) leads us to *an upper bound to $E_{\rm BP}$ as:*

$$E_{\rm BP} \le -\,c_{\rm BP}\alpha^2\theta^2 + \frac{\sqrt{2}\,\alpha\theta}{\pi}\left(4K + \frac{K^3}{3}\right), \tag{3.4}$$

provided that

$$1 - \frac{1}{c_*\theta} > \eta. \tag{3.5}$$

We note that the condition (3.5) prohibits us from taking the limit $\theta \to 0$ in the inequality (3.4) because

$$\theta > \frac{1}{c_*(1-\eta)} > \frac{1}{1-\eta}.$$

We can also show that *a lower bound to $E_{\rm BP}$ as:*

$$E_{\rm BP} \ge \left(\inf_{\varphi} \mathcal{E}_\theta(\varphi)\right)\alpha^2\theta^2 - |1 - \frac{1}{\theta}|\frac{4\sqrt{2}\,\alpha\theta}{\pi}K. \tag{3.6}$$

where

$$\begin{aligned}\mathcal{E}_\theta(\varphi) \ := \ & \frac{1}{2}\int\!\!\int d^3x_1 d^3x_2\left[\left|\nabla_{x_1}\varphi(x_1,x_2)\right|^2 + \left|\nabla_{x_2}\varphi(x_1,x_2)\right|^2 + \frac{2\sqrt{2}}{\theta(1-\eta)}\frac{|\varphi(x_1,x_2)|^2}{|x_1-x_2|}\right] \\ & -\frac{1}{\sqrt{2}}\int\!\!\int d^3x_1 d^3x_2 \int\!\!\int d^3y_1 d^3y_2 \sum_{j,j'=1,2}\frac{\left|\varphi(x_1,x_2)\right|^2\left|\varphi(y_1,y_2)\right|^2}{|x_j - y_{j'}|}\end{aligned} \tag{3.7}$$

is an energy functional describing unbalanced state [1] and $\inf_\varphi \mathcal{E}_\theta(\varphi) < 0$.

We can obtain another effective Hamiltonian. *The approximation (1.6) yields another effective Hamiltonian describing unbalanced state [1] in quantum mechanics:*

$$H_{\rm eff}(\theta) = \alpha^2\theta^2\left[\sum_{j=1,2}\frac{1}{2}p_j^2 - \sqrt{2}\sum_{j=1,2}\frac{1}{|x_j|} + \frac{\sqrt{2}}{\theta(1-\eta)|x_1-x_2|}\right]. \tag{3.8}$$

Then, the transformed total Hamiltonian $H_{\rm BP}[\theta]$ is approximated as:

$$\begin{aligned} H_{\rm BP}[\theta] &\approx H_{\rm eff}(\theta) + H_{\rm ph} \\ &+ \sum_{j=1.2}\sum_{k}\left\{V_k\left(e^{ik\cdot x_j/\alpha\theta} - \theta\right)a_k + V_k^*\left(e^{-ik\cdot x_j/\alpha\theta} - \theta\right)a_k^\dagger\right\} + \Sigma_\theta, \end{aligned} \tag{3.9}$$

where $H_{\rm eff}(\theta)$ is given by Eq.(3.8) and $\Sigma_\theta := \theta E_{\rm w}(\alpha)/4$. Here the approximation (1.6) breaks the translation invariance in the original Hamiltonian $H_{\rm BP}$.

Let $E_{\rm s}(\alpha)$ be

$$E_{\rm s}(\alpha) := \left(\frac{2\sqrt{2}}{r} - \frac{1}{r^2} - 1\right)\alpha\theta \tag{3.10}$$

now. Then, *the effective Hamiltonian $H_{\rm eff}(\theta)$ in Eq.(3.8) has a ground state if there is an $r > 0$ so that*

$$\frac{U}{r} < E_{\rm s}(\alpha). \tag{3.11}$$

Then, we have $\theta_c \le 1/(2-\sqrt{2})(1-\eta)$. The condition (3.11) puts restrictions on θ, η and r. *The sufficient condition for the inequality (3.11) is:*

$$1 - \frac{1+\sqrt{2}}{\sqrt{2}\,\theta} > \eta. \tag{3.12}$$

and

$$R_{\theta.\eta} - \sqrt{{R_{\theta.\eta}}^2 - 1} < r < R_{\theta.\eta} + \sqrt{{R_{\theta.\eta}}^2 - 1}, \tag{3.13}$$

where

$$R_{\theta.\eta} := \sqrt{2}\left(1 - \frac{1}{2\theta(1-\eta)}\right).$$

(i.e., $\theta \approx \infty$), $0.585 \le r/r_{\rm fp} \le 3.415$.

4 Spatial Localization in Strong-Coupling Regime

In this section we deal with the approximated $H_{\rm BP}[\theta]$ given in Eq.(3.9). When a ground state Ψ_0 of $H_{\rm BP}[\theta]$ exists, we define the radius $u_{\rm BP}(\Psi_0)$ of the sphere in which the two electron lives by

$$u_{\rm BP}(\Psi_0) := \max_{j=1,2}\left\{\langle\Psi_0|\Psi_0\rangle^{-1}\langle\Psi_0||x_j||\Psi_0\rangle\right\}. \tag{4.1}$$

Then, we can show that *if the bipolaron has a ground state Ψ_0, then there is a relation:*

$$u_{\mathrm{BP}}(\Psi_0) \geq \frac{1}{\sqrt{2}}\left\{1+\left(1+\frac{3\theta}{4}\right)\frac{E_{\mathrm{w}}(\alpha)}{\alpha_\theta^2}\right\}^{-1}\left(\frac{1}{\theta(1-\eta)}-2\right). \tag{4.2}$$

Thus, even if η approaches 1, $\theta > 0$ in the strong-coupling regime works to prevent its size from growing. This is a noticeable difference from the case of the weak-coupling regime.

5 Positive Binding Energy

We obtain a sufficient condition for the binding energy being positive.

Let $\mathcal{E}_{\mathrm{P}}(\psi)$ be the Pekar functional [13, 14, 15, 16, 17] for single polaron, i.e.,

$$\mathcal{E}_{\mathrm{P}}(\psi) := \frac{1}{2}\int d^3x|\nabla_x\psi(x)|^2 - \frac{1}{\sqrt{2}}\int\int d^3xd^3y\,\frac{|\psi(x)|^2|\psi(y)|^2}{|x-y|}.$$

Lieb [15] proved that there is a unique and smooth minimizing $\psi(x)$ in $c_{\mathrm{SP}} := -\inf_{\psi,\langle\langle\psi\rangle\rangle=1}\mathcal{E}_{\mathrm{P}}(\psi)$ up to translations. Then, according to the estimate of c_{SP} by Miyake [14] and by Gerlach and Löwen [17],

$$c_{\mathrm{SP}} = 0.108513\cdots.$$

Then, *if c_*, θ, and η satisfy $c_{\mathrm{BP}} > 2c_{\mathrm{SP}}$, then the binding energy is positive, i.e.,*

$$E_{\mathrm{BP}} < 2E_{\mathrm{SP}} \tag{5.1}$$

for sufficiently large $\theta > 0$ with the condition (3.5). Thus, we note that $0 < c_{\mathrm{BP}} \leq 0.4$ and $\lim_{c_*\to 1,\theta\to\infty} = 0.4$ under the condition (3.5).

According to the recent result of study [18], we might be able to choose $-\inf_{\varphi,\langle\langle\psi\rangle\rangle=1}\mathcal{E}_\theta(\varphi)$ as c_{BP} (i.e., $-c_{\mathrm{BP}} = \inf_\varphi \mathcal{E}_\theta(\varphi)$) so that $2E_{\mathrm{SP}} - E_{\mathrm{BP}} = -(2c_{\mathrm{SP}} - c_{\mathrm{BP}})\alpha_\theta^2 > 0$ for sufficiently large $\theta > 0$, where E_{SP} is the ground state energy of the single polaron [19].

参考文献

[1] M. Hirokawa, arXiv:cond-mat/0606095.

[2] H. Fröhlich, H. Pelzer, and S. Zienau, Philos. Mag. **41**, 221 (1950).

[3] H. Fröhlich, Adv. Phys. **3**, 325 (1954).

[4] D. Emin, Phys. Rev. Lett. **62**, 1544 (1989); D. Emin and M. S. Hillery, Phys. Rev. B **39**, 6575 (1989).

[5] J. Adamowski, Phys. Rev. B **39**, 3649 (1989).

[6] F. Bassani, M. Geddo, G. Iadonisi, and D. Ninno, Phys. Rev. B **43**, 5296 (1991).

[7] G. Verbist, F. M. Peeters, and J. T. Devreese, Phys. Rev. B **43**, 2712 (1991).

[8] G. Verbist, A. Smondyrev, F. M. Peeters, and J. T. Devreese, Phys. Rev. B **45**, 5262 (1992).

[9] A. S. Alexandrov and S. N. Mott, *Polarons & Bipolarons* (World Scientific, Singapore, 1995).

[10] E. H. Lieb, Phys. Rev. Lett. **52**, 315 (1984); Phys. Rev. A **29**, 3018 (1984).

[11] N. N. Bogolubov and N. N. Bogolubov, Jr., *Polaron Theory: Model Problems* (Gordon and Breach Science Publishers, 2000).

[12] M. Hirokawa, F. Hiroshima, and H. Spohn, Adv. Math. **191**, 339 (2005).

[13] S. I. Pekar, *Issledovaniya po Elektronnoy Teorii Kristallov* (Gosud. Izd. Techn. — Teor. Literatury, Moscow, 1951).

[14] S. J. Miyake, J. Phys. Soc. Jpn. **38**, 181 (1975); *ibid.* **41**, 747 (1976).

[15] E. H. Lieb, Stud. Appl. Math. **57**, 93 (1977).

[16] H. Spohn, J. Phys. A **19**, 533 (1986); Phys. Rev. B **33**, 8906 (1986); Ann. Phys. **175**, 278 (1987); J. Phys. A **21**, 1199 (1988).

[17] B. Gerlach and H. Löwen, Rev. Mod. Phys. **63**, 63 (1991).

[18] T. Miyao and H. Spohn, (preprint, 2006).

[19] E. H. Lieb and L. E. Thomas, Commun. Math. Phys. **183**, 511 (1997); *ibid.* **188**, 499 (1997).