# The polaron and squeezed states



1990 J. Phys.: Condens. Matter 2 10573

(http://iopscience.iop.org/0953-8984/2/51/027)

J. Phys.: Condens. Matter 2 (1991) 10573–10579. Printed in the UK

# The polaron and squeezed states

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Received 17 May 1990, in final form 27 September 1990

**Abstract.** The structure of the phonon cloud surrounding the polaron and the ground-state energy is investigated. The proposed variational wavefunction consists of a few squeezed effective phonon modes.

## 1. Introduction

The problem of the electron–phonon interaction is still of interest owing to the polaron and exciton localization (Fischer *et al* 1989, Wagner and Köngeter 1989).

An electron in the conduction band interacting with phonons is described by the dimensionless Fröhlich-like Hamiltonian

$$H = \tfrac{1}{2}\boldsymbol{p}^2 + \sum_{\boldsymbol{k}} \omega(k) b_{\boldsymbol{k}}^{+} b_{\boldsymbol{k}} + \sum_{\boldsymbol{k}} V(k)(b_{\boldsymbol{k}}^{+} \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) + \mathrm{HC}) \tag{1}$$

where $\boldsymbol{p}$ is the momentum of the electron, $\boldsymbol{r}$ is its coordinate, $b_{\boldsymbol{k}}$ and $b_{\boldsymbol{k}}^{+}$ are the annihilation and creation operators of phonons, $\omega(k)$ is the phonon frequency and the coupling $V(k)$ is proportional to $\sqrt{\alpha}$, $\alpha$ being the coupling constant. For simplicity we set the mass $m$ of the electron equal to unity and the Planck constant $\hbar$ equal to unity. The discrete version of this Hamiltonian describes the Frenkel exciton in a molecular chain.

It is well known that the electron coordinate can be eliminated owing to the translational symmetry of (1) by the Lee–Low–Pines (1953) transformation

$$U_{\mathrm{LLP}} = \exp\Big(-\mathrm{i}\boldsymbol{r}\cdot\sum_{\boldsymbol{k}} \boldsymbol{k} b_{\boldsymbol{k}}^{+} b_{\boldsymbol{k}}\Big). \tag{2}$$

The transformed Hamiltonian

$$H(\boldsymbol{P}) = U_{\mathrm{LLP}}^{+} H U_{\mathrm{LLP}} = \frac{1}{2}\Big|\boldsymbol{P} - \sum_{\boldsymbol{k}} \boldsymbol{k} b_{\boldsymbol{k}}^{+} b_{\boldsymbol{k}}\Big|^2 + \sum_{\boldsymbol{k}} \omega(k) b_{\boldsymbol{k}}^{+} b_{\boldsymbol{k}} + \sum_{\boldsymbol{k}} [V(k) b_{\boldsymbol{k}}^{+} + \mathrm{HC}] \tag{3}$$

describes the cloud of correlated phonons which accompany the polaron with the total momentum $\boldsymbol{P}$. For the problem of an exciton in a molecular chain there is an analogous generalized Fulton–Gouterman transformation (Wagner and Köngeter 1989).

In both cases we obtain an anharmonic vibrational eigenvalue equation which is difficult to solve, especially for the coupling strength in the transition region between the weak- and strong-coupling regimes. The main advantage of this approach is the explicit translational invariance of the approximate solution.

Gross (1955), Tulub (1961) and Barentzen (1975) have presented an approximate method of the diagonalization of the effective Hamiltonian (3). Although these theories

0953-8984/90/5110573 + 07 $03.50  

yield a set of equations describing the polaron over the whole coupling range they have two disadvantages.

(i) It turns out to be impossible to solve this set of integral equations exactly.

(ii) The correlations of the phonons are taken into account only partially.

Our aim is to pick up a few relevant phonon modes which are responsible for the main features of the phonon cloud. For simplicity we shall deal only with the ground state; thus $\boldsymbol{P} = \boldsymbol{0}$. The eigenstates of the relevant Hamiltonian are to be found in the form of displaced and squeezed phonon states. Such approach was fruitfully used in tunnelling systems (Chen *et al* 1989, Jayannavar 1989).

## 2. The relevant phonon modes

Let us express the plane-wave phonon modes $b_{\boldsymbol{k}}$ in terms of the spherical wave phonon modes $B_\mu$. In general the index $\mu = (n, l, m)$ represents the three quantum numbers, i.e. the main quantum number $n$, the orbital momentum $l$ and the projection of the orbital momentum $m$:

$$b_{\boldsymbol{k}} = \sum_\mu u_\mu(\boldsymbol{k}) B_\mu. \tag{4}$$

The functions $u_\mu(\boldsymbol{k})$ form a complete orthonormal set:

$$\sum_\mu u_\mu^*(\boldsymbol{k}) u_\mu(\boldsymbol{k}') = \delta_{\boldsymbol{k},\boldsymbol{k}'} \qquad \sum_{\boldsymbol{k}} u_\mu^*(\boldsymbol{k}) u_\nu(\boldsymbol{k}) = \delta_{\mu,\nu} \tag{5}$$

to ensure the standard boson commutation relations for $B_\mu$. The Hamiltonian (3) for $\boldsymbol{P} = \boldsymbol{0}$ expressed in terms of $B_\mu^+$ and $B_\mu$ becomes

$$H = \sum_{\mu,\nu} \Omega_{\mu,\nu} B_\mu^+ B_\nu + \sum_{\mu,\nu} (\mathcal{V}_\mu B_\mu^+ + \text{HC}) + \tfrac{1}{2} \sum_{\mu\nu\rho\sigma} \boldsymbol{Q}_{\mu,\nu} \cdot \boldsymbol{Q}_{\rho,\sigma} B_\mu^+ B_\rho^+ B_\nu B_\sigma. \tag{6}$$

The new quantities are defined as follows:

$$\Omega(k) = \omega(k) + \tfrac{1}{2}\boldsymbol{k}^2 \tag{7}$$

(where $\Omega(k)$ is the renormalized phonon frequency)

$$\Omega_{\mu,\nu} = \sum_{\boldsymbol{k}} u_\mu^*(\boldsymbol{k}) \Omega(k) u_\nu(\boldsymbol{k}) = \{\mu | \Omega(k) | \nu\} \tag{8a}$$

$$\mathcal{V}_\mu = \{\mu | V\} \qquad \boldsymbol{Q}_{\mu,\nu} = \{\mu | \boldsymbol{k} | \nu\}. \tag{8b}$$

In the last two expressions we have used the auxiliary bra and ket vectors $\{\,|, |\,\}$ to abbreviate the notation for the sums over $\boldsymbol{k}$. These should be distinguished from the bra and ket vectors $\langle\,|$ and $|\,\rangle$ which are reserved for denoting physical states.

The Hamiltonian (6) has the same eigenvalues as the starting Hamiltonian (3). Our basic idea is based on the variational approach with the specific form of the trial wavefunction $|\Phi\rangle$. Let us define the irrelevant phonon modes by the condition

$$B_\mu |\Phi\rangle = 0 \qquad \text{for } \mu \text{ irrelevant.} \tag{9}$$

For the relevant modes, $B_\mu |\Phi\rangle \neq 0$.

Then the expectation value of (6) in the state (9) is

$$\langle\Phi|H|\Phi\rangle = \langle\Phi|H_{\text{rel}}|\Phi\rangle. \tag{10}$$

The relevant part $H_{\text{rel}}$ of the Hamiltonian includes only the relevant modes:

$$H_{\text{rel}} = \sum_{\mu,\nu}^{\text{rel}} \Omega_{\mu,\nu} B_\mu^+ B_\nu + \sum_{\mu,\nu}^{\text{rel}} (\mathcal{V}_\mu B_\mu^+ + \text{HC}) + \tfrac{1}{2} \sum_{\mu\nu\rho\sigma}^{\text{rel}} \boldsymbol{Q}_{\mu,\nu} \cdot \boldsymbol{Q}_{\rho,\sigma} B_\mu^+ B_\rho^+ B_\nu B_\sigma. \tag{11}$$

The symbol $\Sigma^{\text{rel}}$ means the reduced summation over the relevant modes only. The

'relevant Hamiltonian' has, in contrast with (6), only a limited number of degrees of freedom, but its ground-state energy gives the upper bound to the exact ground-state energy.

In what follows we shall deal only with the relevant modes with the main quantum number $n = 0$. The corresponding functions $u_\mu(\boldsymbol{k})$ can be factorized in the form

$$u_{l,m}(\boldsymbol{k}) = A_{lm}(\boldsymbol{k}/k) f_l(k) \qquad k = |\boldsymbol{k}|. \tag{12}$$

The radial functions $f_l(k)$ are normalized to unity:

$$\{f_l | f_l\} = \sum_k f_l^*(k) f_l(k) = 1. \tag{13}$$

Owing to the Wigner–Eckart theorem we find that the matrix elements (8*a*) and (8*b*) depend only on the radial functions $f_l(k)$ by means of the reduced matrix elements defined by the relations

$$\begin{aligned} &\Omega_l \equiv \{f_l | \Omega(k) | f_l\} \\ &\mathcal{V}_0 \equiv \{f_0 | V\} \\ &\kappa_{l,l'} \equiv \{f_l | k | f_{l'}\} \qquad |l - l'| = 1. \end{aligned} \tag{14}$$

The coupling function $V(k)$ is assumed to be spherically symmetric.

The ground-state energy of the relevant Hamiltonian depends only on the radial functions $f_l(k)$ through the parameters (14). It is shown in the appendix how to find the optimal functions $f_l(k)$.

As an example we present the simple case of only one spherically symmetric phonon mode

$$u_0(\boldsymbol{k}) = f_0(k) \qquad \{f_0 | f_0\} = 1. \tag{15}$$

The one-mode relevant Hamiltonian

$$H^{(1)} = \Omega_0 B_0^+ B_0 + (\mathcal{V}_0^+ B_0 + \text{HC}) \tag{16}$$

represents the displaced oscillator. The ground-state energy is simply

$$E^{(1)} = -|\mathcal{V}_0|^2 / \Omega_0. \tag{17}$$

This energy is minimized by the function

$$f_0(k) \sim V(k)/\Omega(k).$$

The corresponding energy

$$E^{(1)} = -\sum_k \frac{|V(k)|^2}{\Omega(k)} \tag{18}$$

is exactly the intermediate-coupling result of the Lee–Low–Pines theory.

## 3. Four relevant phonon modes

The non-trivial results are obtained including one s mode (orbital momentum $l = 0$)

$$u_0(\boldsymbol{k}) = f_0(k) \qquad \{f_0 | f_0\} = 1 \tag{19a}$$

and three $p$-modes ($l = 1, i = 1, 2, 3$)

$$u_i(\boldsymbol{k}) = (k_i/k) f_1(k)\sqrt{3} \qquad \{f_1 | f_1\} = 1. \tag{19b}$$

$k_i$ represents the $i$th component of the vector $\boldsymbol{k}$; $k = |\boldsymbol{k}|$.

After straightforward calculations we obtain the four-mode relevant Hamiltonian

$$H^{(4)} = \Omega_0 B_0^+ B_0 + \Omega_1 \sum_{i=1}^{3} B_i^+ B_i + \mathcal{V}_0 B_0^+ + \mathcal{V}_0^* B_0 + \tfrac{1}{2} t \sum_{i=1}^{3} (B_i^{+2} B_0^2 + B_0^{+2} B_i^2 + 2 B_i^+ B_i B_0^+ B_0). \tag{20}$$

The coefficients are defined by (14) and by

$$t = \kappa_{01}\kappa_{10}/3. \tag{21}$$

The two unknown functions $f_0(k)$ and $f_1(k)$ are the variational parameters. The ground-state energy of the relevant Hamiltonian (20) is only a function of the parameters $\Omega_0$, $\Omega_1$, $\mathcal{V}_0$, $\mathcal{V}_0^*$ and $t$. Using this fact the functions $f_0(k)$ and $f_1(k)$ can be exactly parametrized (see appendix) by

$$f_0(k) \sim -V(k)/\{\Omega(k) - \lambda_0 - s_1 k^2/[\Omega(k) - \lambda_1]\} \tag{22a}$$

and

$$f_1(k) \sim f_0(k)/[\Omega(k) - \lambda_1]. \tag{22b}$$

The total set of the variational parameters is reduced to three real constants $\lambda_0$, $\lambda_1$ and $s_1$.

In what follows we shall calculate the ground-state energy of the relevant Hamiltonian $H^{(4)}$ (20). We follow Barentzen (1975) and apply the displacement operator

$$D = \exp(zB_0^+ - z^* B_0) \tag{23}$$

on (20):

$$\mathcal{H} = D^+ H^{(4)} D = \sum_{i=0}^{4} H_i \tag{24}$$

$$H_0 = \Omega_0 |z|^2 + \mathcal{V}_0 z^* + \mathcal{V}_0^* z \tag{24a}$$

$$H_1 = (\Omega_0 z^* + \mathcal{V}_0^*) B_0 + \text{HC} \tag{24b}$$

$$H_2 = \Omega_0 B_0^+ B_0 + \Omega_1 \sum_{i=1}^{3} B_i^+ B_i + \tfrac{1}{2} t \sum_{i=1}^{3} (B_i^{+2} z + B_i^2 z^* + 2 B_i^+ B_i |z|^2) \tag{24c}$$

$$H_3 = t \sum_{i=1}^{3} [B_i^{+2} B_0 z + B_0^+ B_i^2 z^* + B_i^+ B_i (B_0^+ z + B_0 z^*)] \tag{24d}$$

$$H_4 = \tfrac{1}{2} t \sum_{i=1}^{3} (B_i^{+2} B_0^2 + B_0^{+2} B_i^2 + 2 B_i^+ B_i B_0^+ B_0). \tag{24e}$$

The most simple approximate solution of (24) is the squeezed-phonon vacuum (Loudon and Knight 1987)

$$|\tilde{0}\rangle = \exp\left(\tfrac{1}{2}\varphi \sum_{i=1}^{3} (B_i^{+2} - B_i^2)\right)|0\rangle \tag{25}$$

which diagonalizes $H_2$ (24*c*). (The unsqueezed vacuum state $|0\rangle$ is defined by the standard relations $B_\mu|0\rangle = 0$ for all $\mu$.) The squeezing angle is

$$\varphi = \tfrac{1}{4}\log(1 + 2t|z|^2/\Omega_1). \tag{26}$$

The expectation value of the energy

$$E(z) = \langle\tilde{0}|\mathcal{H}|\tilde{0}\rangle = H_0 - \tfrac{3}{4}\Omega_1[(1 + 2t|z|^2/\Omega_1)^{1/2} - 1]^2 \tag{27}$$

has to be minimized with respect to $z$. The result (27) reproduces both the intermediate- and the strong-coupling theory of the polaron. For $\alpha \ll 1$ we obtain evidently the intermediate result. For $\alpha \gg 1$ we obtain $z = -\mathcal{V}_0/(\Omega_0 - \frac{3}{2}t)$ and the energy functional

$$E^{(4)} = -|\mathcal{V}_0|^2/(\Omega_0 - \tfrac{3}{2}t) \tag{28}$$

has the minimum value

$$E^{(4)} = -\sum_k \frac{|V(k)|^2}{\omega(k)} + O(\alpha^0) \qquad \text{for } \alpha \gg 1. \tag{29}$$

The leading term which is proportional to $\alpha$ is the same as in the strong-coupling theory.

Let us now proceed to the more precise handling of the Hamiltonian (20). Owing to small number of the phonon modes the Hamiltonian (20) can be diagonalized to any order of accuracy. One of the possibilities is to look for the solution in the form of the more general squeezed state

$$|\tilde{0}\rangle = \exp\left(\tfrac{1}{2}\psi(B_0^{+2} - B_0^2) + \tfrac{1}{2}\varphi \sum_{i=1}^{3} (B_i^{+2} - B_i^2)\right)|0\rangle \tag{30}$$

with two squeezing angles as variational parameters. The expectation value of the energy is

$$\begin{aligned} E^{(4)} = {} & \Omega_0|z|^2 + \mathcal{V}_0 z^* + \mathcal{V}_0^* z + \tfrac{3}{2}\Omega_1[\cosh(2\varphi) - 1] \\ & + \tfrac{3}{2}t|z|^2[\exp(2\varphi) - 1] + \tfrac{1}{2}\{\Omega_0 + \tfrac{3}{4}t[\cosh(2\varphi) - 1]\} \\ & \times [\cosh(2\psi) - 1] + \tfrac{3}{4}t\sinh(2\varphi)\sinh(2\psi). \end{aligned} \tag{31}$$

The extreme values of $z$ and $\psi$ can be found analytically; the remaining extremalization with respect to the angle $\varphi$ and the parameters $\lambda_0$, $\lambda_1$ and $s_1$ can be done numerically.

## 4. Numerical example and discussion

Let us deal with the acoustic polaron in three dimensions. The phonon dispersion law is

$$\omega(k) = k \tag{32}$$

and the coupling

$$V(k) = (4\pi\alpha/V)^{1/2}k^{1/2}. \tag{33}$$

$\alpha$ is the dimensionless coupling constant and $V$ is the volume of the sample. We express

**Table 1.** Values of the ground-state energy for the different methods (see text).

| $\alpha$ | $E_{\text{Feyn}}$ | $E_{\text{rel}}$ | $E_{\text{interm}}$ |
|---|---|---|---|
| 0.05 | −2.4030 | −2.4065 | −2.3661 |
| 0.10 | −4.8906 | −4.8972 | −4.7322 |
| 0.15 | −7.4849 | −7.4773 | −7.0984 |
| 0.20 | −9.8079 | −10.1521 | −9.4645 |
| 0.25 | −13.162 | −12.926 | −11.830 |
| 0.30 | −16.531 | −15.805 | −14.831 |
| 0.35 | −20.530 | −18.791 | −16.563 |
| 0.40 | −25.137 | −21.889 | −18.929 |
| 0.45 | −30.197 | −25.100 | −21.295 |
| 0.50 | −35.608 | −29.716 | −23.661 |

the energies in units of $ms^2$, the lengths in units of $\hbar/ms$ and the circular frequencies in units of $ms^2/\hbar$ with $s$ being the velocity of sound (Peeters and Devreese 1985). The sum over the phonon wavevectors $\boldsymbol{k}$ is replaced by the integral according to

$$\sum_{k} 1_k \to \frac{V}{(2\pi)^3} \int_{k<k_0} \mathrm{d}^3 k. \tag{34}$$

In table 1 we present the ground-state energies $E_{\text{rel}}$ for different values of the coupling constant $\alpha$ compared with the results obtained by the Feynman method and with the intermediate-coupling theory. The cut-off wavevector is $k_0 = 10$.

As a reference we take the Feynman approximation (Peeters and Devreese 1985). Our results improve the intermediate-coupling theory considerably. For $\alpha < 0.3$ they are even better than the reference results (the reference value of $E_{\text{Feyn}}$ for $\alpha = 0.2$ is probably erroneous). For $\alpha \gg 1$ we again come very close to the strong-coupling limit. In the region $0.3 < \alpha < 1$ which corresponds to the transition between the intermediate- and strong-coupling regime our results fail to improve the reference results. All this indicates that the structure of the phonon cloud in the transition region is very complex. To penetrate into this region of coupling constant with an appropriate approximation we have two possibilities.

(i) The number of the relevant phonon modes can be increased, e.g. including phonon modes with higher orbital momentum. In the appendix it is shown how to parametrize the radial function for the d wave in the form of the continued fraction. In the relevant Hamiltonian, new terms arise which describe the interaction between the p and d waves.

(ii) The relevant Hamiltonian can be diagonalized numerically. It is inconvenient to use the multimode Fock states as a basis for the direct diagonalization of the Hamiltonian (20) because of large numbers of states needed. A more sophisticated method is to start from the transformed Hamiltonian (24) with the displacement $z = -\mathcal{V}/\Omega_0$ which eliminates the term linear in the operator $B_0$ (24*b*) and apply the Lanczos method.

**Acknowledgments**

The author gratefully acknowledges inspiring discussions with E Majerníková and F M Peeters for providing the numerical data.

**Appendix**

The expectation value of the energy including only the relevant phonon modes (12) is a function of the parameters (14):

$$E = E(\Omega_l, \mathcal{V}_0, \kappa_{l,l'}). \tag{A1}$$

We determine the optimal functions $f_l(k)$ from the equations

$$\delta E/\delta\{f_l| = 0 \qquad \text{with constraints } \{f_l|f_l\} = 0. \tag{A2}$$

Let us denote the derivatives of the energy (A1) as follows:

$$a_l = \partial E/\partial\Omega_l \qquad a_v = \partial E/\partial\mathcal{V}_0 \qquad a_{l,l'} = \partial E/\partial\kappa_{l,l'}. \tag{A3}$$

Using the definitions (14) and (A3) we obtain from the extreme condition (A2) the set of equations

$$ka_{l,l-1}|f_{l-1}\} + a_l[\Omega(k) - \lambda_l]|f_l\} + ka_{l,l+1}|f_{l+1}\} = -\delta_{0,l}a_v|V\}. \tag{A4}$$

$\lambda_l$ are the Lagrange multipliers. For the finite set of function $f_l(k)$ with

$$l = 0, 1, \ldots, L \tag{A5}$$

the solution of (A4) can be found in the form

$$|f_0\} = -F_0(k)(a_v/a_0)|V\} \tag{A6a}$$

and

$$|f_l\} = -F_l(k)(a_{l,l-1}/a_l)k|f_{l-1}\} \qquad l = 1, 2, \ldots, L. \tag{A6b}$$

The quantities $F_l(k)$ obey the recurrence equations

$$F_l(k) = 1/[\Omega(k) - \lambda_l - k^2 s_{l+1}F_{l+1}(k)]. \tag{A7}$$

The parameter $s_l$ is

$$s_{l+1} = |a_{l,l+1}|^2/a_l a_{l+1}. \tag{A8}$$

For the maximal value of $l = L$ we define

$$F_L(k) = 1/[\Omega(k) - \lambda_L]. \tag{A9}$$

The solution of the recurrence equation is a continued fraction

$$F_l(k) = \frac{1}{[[\Omega(k) - \lambda_l - k^2 s_{l+1}/\{\Omega(k) - \lambda_{l+1} - k^2 s_{l+2}/\ldots[\Omega(k) - \lambda_{L-1} - k^2 s_L/(\Omega(k) - \lambda_L)]\}]]}. \tag{A10}$$

For $L = 1$ we can easily find the formulae (22*a*) and (22*b*).

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