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Invited paper

Self-consistent polaron states in the presence of simultaneous local and nonlocal exciton-phonon coupling

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Abstract

A canonical transformation method originally proposed by Munn and Silbey is used to diagonalize partially a model Hamiltonian which incorporates both local and nonlocal exciton phonon coupling. At the heart of the method is a secular elimination principle which poses a difficult self-consistency problem. We take a numerical approach, solving the general self-consistency problem to desired accuracy. Among the differences between our findings and those of the original work are polaron binding energies much larger and Debye Waller factors much smaller than originally anticipated.

1. Introduction

In this paper we are concerned with that part of polaron theory focussed on the problem of "nonlocal" exciton-phonon (or electron-phonon) interactions. In order to distinguish clearly "local" from "nonlocal" coupling, we define local coupling as a nontrivial dependence of diagonal Hamiltonian matrix elements $< n|H|n >$ upon phonon states, and we similarly define nonlocal coupling as a nontrivial dependence of nondiagonal Hamiltonian matrix elements $< m|H|n >$ upon phonon states, where $|m >$ and $|n >$ are the rigid-lattice Wannier states of the exciton. The body of polaron theory identified with local coupling is quite large, including the "optical" polaron of Fröhlich [1, 2], small and large polaron of Holstein [3]. The body of polaron theory identified with nonlocal coupling is smaller, but includes the generic contribution of nonlocal coupling to

the phonon-assisted transport of excitons and charge carriers [4, 9] and applications more chemical in nature, such as the problem of excimer formation [10, 12].

In this paper we address ourselves to a method introduced by Munn and Silbey [9] which is essentially a perturbation method, but which contains an element of optimization. Munn and Silbey generalized the displaced oscillator transformation common in local-coupling polaron theory [13] to the case of combined local and nonlocal coupling. This involves a secular elimination principle which leads to a set of complicated self-consistency equations. Here we follow the approach of Munn and Silbey; however, we solve the problem numerically and examine the properties of the resulting solution. Related computations following different approaches have been performed by Song [14] and Umehara [15].

2. Local and nonlocal coupling

We begin with the general Hamiltonian describing the so-called linear local and nonlocal exciton-phonon coupling in a translationally invariant system.

$$H = \sum_n E a_n^+ a_n + \sum_{mn} J_{mn} a_m^+ a_n + \sum_n \left\{ \frac{P_n^2}{2M} + \tfrac{1}{2} M \omega^2 Q_n^2 \right\} + \sum_{lmn} \gamma_{mn}^l Q_l a_m^+ a_n, \tag{1}$$

where a_m^+ creates an exciton in the rigid-lattice Wannier state m, and Q_n and P_n are the coordinate and momentum describing the Einstein oscillator at the site m. For definiteness, we choose

$$J_{mn} = J(\delta_{m\,n+1} + \delta_{m\,n-1}), \tag{2}$$

$$\gamma_{mn}^l = \gamma_0 \delta_{ml} \delta_{nl} + \tfrac{1}{2}\gamma_1 [\delta_{ml}(\delta_{n\,l-1} - \delta_{n\,l+1}) + \delta_{nl}(\delta_{m\,l-1} - \delta_{m\,l+1})]. \tag{3}$$

It is advantageous to implement our analysis in k-space, for which we adopt the transformation conventions

$$Q_l = \sqrt{\frac{\hbar}{2NM\omega}} \sum_q e^{-iql} (b_{-q}^+ + b_q),$$

$$a_n = \frac{1}{\sqrt{N}} \sum_k e^{-ikn} a_k. \tag{4}$$

In order to define a momentum space form for the triadic γ^{l}_{mn}, we use translational invariance to define relative coordinates. We follow Munn and Silbey in defining coordinates relative to the site associated with the exciton creation operator (cf. (1)); thus, with $\mu = n - m$ and $v = l - m$

$$\gamma^{q}_{k} = \sum_{\mu\nu} \mathrm{e}^{\ \mathrm{i}q\nu}\mathrm{e}^{\mathrm{i}k\mu}\gamma^{\nu}_{0\mu}\ . \qquad (5)$$

This implies that the triple Fourier transform involved in going from (1) to (8) below yields

$$\sum_{lmn} \mathrm{e}^{-\mathrm{i}ql}\,\mathrm{e}^{\mathrm{i}k'm}\,\mathrm{e}^{-\mathrm{i}kn}\gamma^{l}_{mn} \equiv N\delta_{k'k+q}\gamma^{q}_{-k}. \qquad (6)$$

For the coupling geometry considered in this paper,

$$\gamma^{q}_{k} = \gamma_0 - \mathrm{i}\gamma_1\,[\sin k - \sin(k-q)]. \qquad (7)$$

We further define dimensionless coupling constants f^{q}_{k}, etc., such that any f is related to the corresponding γ through the relation $f = (2M\hbar\omega^3)^{-1/2}\gamma$. With these conventions,

$$H = \sum_{k}(\varepsilon + J_k)a^{+}_{k}a_k + \sum_{q}\hbar\omega_q(b^{+}_{q}b_q + \tfrac{1}{2})$$

$$+ N^{-1/2}\sum_{kq} f^{q}_{-k}\hbar\omega_q(b_q + b^{+}_{-q})a^{+}_{k+q}\,a_k. \qquad (8)$$

Transformation of the Hamiltonian is carried out as $H \rightarrow \tilde{H} = e^{L}\,He^{-L}$, with

$$L = N^{-1/2}\sum_{kq} A^{q}_{-k}(b^{+}_{-q} - b_q)\,a^{+}_{k+q}\,a_k, \qquad (9)$$

where the coefficients A^{q}_{k} have the symmetry property $A^{q}_{k} = \left(A^{-q}_{k-q}\right)^{*}$. This transformation yields polaron and dressed phonon operators

$$\tilde{a}_n \equiv \mathrm{e}^{L}a_n\mathrm{e}^{-L} = \sum_{m}\theta_{nm}a_m,$$

$$\tilde{b_q} \equiv \mathrm{e}^{L}b_q\mathrm{e}^{-L} = b_q - N^{-1/2}\sum_{mn} A^{-q}_{mn}a^{+}_{m}a_n. \qquad (10)$$

In the presence of nonlocal coupling, the polaron created by $\tilde{a}^{+}_{n}$ represents a superposition of bare exciton states which, although centered on the site *n,* is at least somewhat delocalized. This delocalization is manifested in the nondiagonality of θ_{nm}, and is in large measure responsible for the greater complexity of nonlocal coupling theory relative to comparable

analyses employing local coupling only.

The transformed Hamiltonian can be separated into a band Hamiltonian and a scattering interaction $\tilde{H} = \tilde{H}_0 + \Delta\tilde{H}$ where

$$\tilde{H}_0 = \sum_k (\varepsilon + \tilde{J}_k - N^{-1/2} \sum_q |A_k^q|^2 \hbar\omega_q) a_k^+ a_k + \sum_q \hbar\omega_q (b_q^+ b_q + \tfrac{1}{2}), \tag{11}$$

$$\begin{aligned}\Delta\tilde{H} = \sum_{kk'} \Big\{ & \sum_p J_p T_{pk;pk'} \\ & - 2N^{-1} \sum_{pq} \hbar\omega_q f_{-p}^q A_{-k'}^q T_{p-q,k;p,k'+q} \\ & + N^{-1/2} \sum_{pq} \hbar\omega_q f_{-p}^q [T_{p+q,k;p,k'} (b_q + b_{-q}^+) \\ & - \langle T_{p+q,k;p,k'} (b_q + b_{-q}^+) \rangle] \Big\} a_k^+ a_{k'} \\ & + N^{-1/2} \sum_{kq} \hbar\omega_q [A_{-k}^q - \sum_{k'} f_{-k'}^q \\ & \times \langle \theta_{k'+q,k+q}^+ \theta_{k'k} \rangle] (b_q + b_{-q}^+) a_{k+q}^+ a_k ,\end{aligned} \tag{12}$$

where

$$\tilde{J}_k = \sum_{k'} J_{k'} \langle \theta_{k'k}^+ \theta_{k'k} \rangle , \tag{13}$$

$$\theta_{kk'} = [\exp(-S)]_{kk'} , \quad \theta_{kk'}^+ = [\exp(S)]_{k'k} , \tag{14}$$

$$S_{kk'} = N^{-1/2} A_{k-k'}^{k-k'} (b_{k'-k}^+ - b_{k-k'}) . \tag{15}$$

$$T_{kk',pp'} = \theta_{kk'}^+ \theta_{pp'} - \langle \theta_{kk'}^+ \theta_{pp'} \rangle , \tag{16}$$

where <···> denotes the thermal average in the free-phonon basis at the temperature T.

This separation has the appeal that the thermal average of the perturbation $\Delta\tilde{H}$ vanishes, and every term of $\Delta\tilde{H}$ containing a $\boldsymbol{T}$ operator remains bounded in a mean-square sense. The one fly in the ointment is the last term of $\Delta\tilde{H}$ which contains phonon

displacement operators uncompensated by a ***T*** operator. This last term has the potential to grow with increasing temperature, motivating Munn and Silbey's choice of A_k^q to eliminate this potential secular growth

$$A^q_{-k} = \sum_{k'} f^q_{-k'} \langle \theta^\dagger_{k'+q,\,k+q} \theta_{k'k} \rangle . \qquad (17)$$

The problem of optimizing the zeroth-order Hamiltonian is now reduced to determining the transformation coefficients A_k^q for given exciton-phonon coupling parameters f_k^q. Using Eqs. (14) - (17), one may show that the transformation coefficients must satisfy the self-consistency equations

$$E^q_{kk'} = N^{-1}(2n_{k-k'} + 1)(A^{k-k'}_{k-q})^* A^{k-k'}_k , \qquad (18)$$

$$\langle \theta_k \rangle = \exp\Big[-\tfrac{1}{2} \sum_{k'} E^0_{kk'} \Big] , \qquad (19)$$

$$A^q_k = \langle \theta_{k-q} \rangle \langle \theta_k \rangle \sum_{k'} f^q_{k'} [\exp(E^q)]_{kk'} . \qquad (20)$$

in which n_q is the Bose distribution (since we compute only for the Einstein phonon model, $2n_q + 1 = \coth\frac{1}{2}\beta\hbar\omega$) and the triadic $E^q_{kk'}$ is an auxiliary intermediate quantity introduced for convenience. We emphasize that these self-consistency equations are the exact consequence of the Munn-Silbey secular elimination scheme. We note that the temperature enters explicitly only in (18), the exciton-phonon coupling constants enter explicitly only in (20), and the tunneling matrix element does not enter at all.

3. Numerical solutions

Our aim is to solve (18)-(20) numerically, avoiding any restriction on the form of the transformation coefficients. As a practical matter, however, computation is facilitated by representing A_k^q in the form

$$A^q_k = f_0 \xi^q_k - i f_1 \eta^q_k [\sin k - \sin(k-q)] . \qquad (21)$$

The reader may observe that this form is not completely general since the explicit sin functions force the imaginary part to vanish along the lines $q = 0$, $2k \pm \pi$. The $q = 0$ line constitutes no restriction, however, since symmetry relations force A_k^0 to be real. Similarly, although it is not clear from the known symmetries that the $q = 2k \pm \pi$ lines do not constitute a restriction, sample calculations using completely general $A_k^{q\prime}s$ consistently show that A_k^q is real along these lines. In our calculations we treat the $q = 0$

and $q = 2k \pm \pi$ lines as lines of removable singularities and choose the values of η_k^q along these lines to be continuous with neighboring values.

Computation proceeds by iteration, through which some initial guess for ξ and η is made and the output is fed back into the self-consistency equations in a controlled way to generate successive ξ and η. Computation ends when the output set is within precision requirements of the last input set.

Significant wave vector dependence emerges in ξ_k^q and η_k^q when both local and nonlocal coupling are order unity or greater (cf. Fig. 1), and wave vector dependence is strong when nonlocal coupling is significantly greater than local coupling (cf. Fig. 2). Regardless of coupling strength, the wave vector dependence of ξ_k^q and η_k^q has a characteristic "manta ray" shape. The detail of this shape can be understood through an examination of the real-space structure of the exciton-phonon coupling, which is addressed below.

Polaron bands are computed using $\tilde{H}_0$ only (cf. Eq. (11)):

$$\varepsilon_k = \varepsilon + J_k e^{-\sigma_k} - E_k^b, \tag{22}$$

in which we have written $\tilde{J}_k$ as $J_k e^{-\sigma k}$ so as to make the Debye-Waller factor explicit. In addition to the usual wave vector dependence due to the rigid lattice energy band J_k, this energy band derives its structure from the wave vector dependence of the Debye-Waller factor and the binding energy

$$e^{-\sigma_k} = \langle \theta_k \rangle^2 \sum_{k'} [\exp(E^0)]_{kk'} J_{k'}/J_k, \tag{23}$$

$$E_k^b = N^{-1} \sum_q |A_k^q|^2 \hbar\omega_q. \tag{24}$$

In the Munn-Silbey approximate results,

$$e^{-\sigma_k} = \exp(-(2n+1)(f_0^2 + \tfrac{1}{2}\eta^2 f_1^2(1 + 2\sin^2 k)), \tag{25}$$

$$E_k^b = \hbar\omega(f_0^2 + \tfrac{1}{2}\eta^2 f_1^2 (1 + 2\sin^2 k)). \tag{26}$$

Correspondence between our numerical results and this approximate analytical form is limited. While we always find a bimodal variation of σ_k and E_k^b symmetric about $k = 0, \pi$, and $\pm \pi/2$, the amplitude of this wave vector variation is strongly suppressed relative to (25) and (26); the average binding energy is significantly larger and the average Debye-Waller factor significantly smaller than predicted by (25) and (26). Of the two energy bands in Fig. 3 that we computed by our methods, the result for stronger nonlocal coupling ($f_1 = f_0 = 1.0$) actually *does* contain a coupling-induced minimum; however, the

modulation is too small to be resolved in the figure.

Using translational invariance and defining $A^l_{mn} = A^v_{0\mu}$, we may invert the double Fourier transformation of A^q_k as in (5) to examine the real-space structure of the transformation coefficients. Fig. 4 displays the result for the strong coupling case f_o = 0.03, f_l = 1.0. Apart from a renormalization of their magnitudes, the four dominant positive/negative peaks correspond to the nonlocal coupling components of the exciton-phonon interaction and the positive central positive peak corresponds to the local coupling component. The balance of the structure visible in this figure out to fifth neighbors must be attributed to an extended exciton structure supported by nonlocal exciton-phonon coupling. The width of this broad component is controlled by the ratio of nonlocal to local coupling.

It is the spreading of exciton-phonon correlations in space which is responsible for the characteristic "manta ray" shape of the momentum-space structure noted earlier. If $A^v_{0\mu}$ is truncated to include only the $\mu = 0, \pm 1$ components, the resulting ξ^q_k, and η^q_k are independent of wave vector. If this truncation is expanded to include $\mu = 0, \pm 1, \pm 2, \pm 3$, the dominant bimodal structure seen in Fig. 1 is recovered. Including higher space components of $A^v_{0\mu}$ does not alter the fundamental modulation frequency, but refines the shape of the fundamental. When nonlocal coupling is weak or moderate relative to local coupling (as in Fig. 1), $A^v_{0\mu}$ is fairly compact so that including components up to $\mu = \pm 3$ is sufficient to recover the basic shape of ξ^q_k and η^q_k. The modulation in this regime is smooth and nearly sinusoidal. When nonlocal coupling is large relative to local coupling (as in Figs. 2 and 4), $A^v_{0\mu}$ is more broad so that components well beyond $\mu = \pm 3$ make significant contributions. The modulation of ξ^q_k and η^q_k in this regime is quite anharmonic.

4. Conclusion

We have followed the approach of Munn and Silbey for determining appropriate zeroth-order polaron states in the presence of simultaneous local and nonlocal exciton-phonon coupling. This approach leads to a highly nonlinear system of self-consistency equations which we have solved numerically. The transformation coefficients which define the structure of polaron states and energy band structure in this approach respond to increasing nonlocal exciton-phonon coupling by developing dramatic momentum-space modulations. These distortions can be related to a spreading of exciton-phonon correlations in real space, suggesting a polaron state based on an extended exciton structure supported by phonon-assisted exciton transfers. The width of this extended structure is in rough empirical proportion to the ratio of the non-local to local exciton-phonon coupling constants (f_l/f_o); as a trend in the ratio of a tunneling parameter to a local coupling parameter, this resembles behavior found in the nonlinear theory of large polarons where the width of the self-consistent localized state is related to similar ratios [3, 16-19]. Debye-Waller factors and polaron binding energies familiar from local-coupling polaron theory acquire weak

wave vector dependences which display a characteristic modulation centered around$|k| = \pi/2$. These modulations have the potential to distort the polaron energy band, and for resonance integrals J small enough, introduce new extrema in the energy band, and new peaks into the density of states. The main consequences of nonlocal coupling, however, are found to be a strong enhancement of band narrowing and the binding energy.

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References

[1] H. Fröhlich, H. Pelzer and S. Zienau, Phil. Mag. Ser. 7 41 (1950) 221; H. Fröhlich, Proc. R. Soc. London Ser. A 215 (1952) 291; Adv. Phys. 3 (1954) 325.

[2] T.D. Lee, F.E. Low and D. Pines, Phys. Rev. 90 (1953) 297.

[3] T. Holstein, Ann. Phys. (NY) 8 (1959) 325, 343.

[4] G.L. Sewell, in: Polarons and Excitons, eds. C. Kuper and G. Whitfield (Plenum Press, New York, 1963).

[5] P. Gosar and I. Vilfan, Mol. Phys. 18 (1970) 49.

[6] A. Madhukar and W. Post, Phys. Rev. Lett. 39 (1977) 1424.

[7] V. Capek and R.W. Munn, Phys. Stat. Sol. (b) 109 (1982) 245.

[8] V.M. Kenkre and P. Reineker, in: Exciton Dynamics in Molecular Crystals and Aggregates, Vol. 94, Springer Tracts in Modern Physics, eds. G. Höhler (Springer, Berlin, 1982).

[9] R.W. Munn and R. Silbey, J. Chem. Phys. 83 (1985) 1843; (1985) 1854.

[10] L.A. Dissado and S.H. Walmsley, Chem. Phys. Lett. 87 (1982) 74; Chem. Phys. 86, (1984) 375.

[11] H. Sumi, Chem. Phys. 130 (1989) 433.

[12] T.M. Wu, D.W. Brown and K. Lindenberg, J. Lumin. 45 (1990) 245; in: Davydov's Soliton Revisited: Self-Trapping of Vibrational Energy in Protein, NATO ASI Series B: Physics, Vol. 243, eds. P. Christiansen and A.C. Scott (Plenum Press, New York, 1990) pp. 449-456; Phys. Rev. B 47 (1993) 10122.

[13] I.G. Lang and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. 43 (1962) 1843 [Sov. Phys. JETP 16 (1963) 1301].

[14] K.S. Song, J. Phys. Soc. Jap. 26 (1969) 1131.

[15] M. Umehara, J. Phys. Soc. Jap. 47 (1979) 852.

[16] E.I. Rashba, Opt. Spektrosk. 2 (1957) 75; (1957) 88 (in Russian).

[17] A.S. Davydov, Phys. Stat. Sol. 36 (1969) 211.

[18] G. Venzl and S.F. Fischer, J. Chem. Phys. 81 (1984) 6090.

[19] D.W. Brown and Z. Ivic, Phys. Rev. B 40 (1989) 9876.

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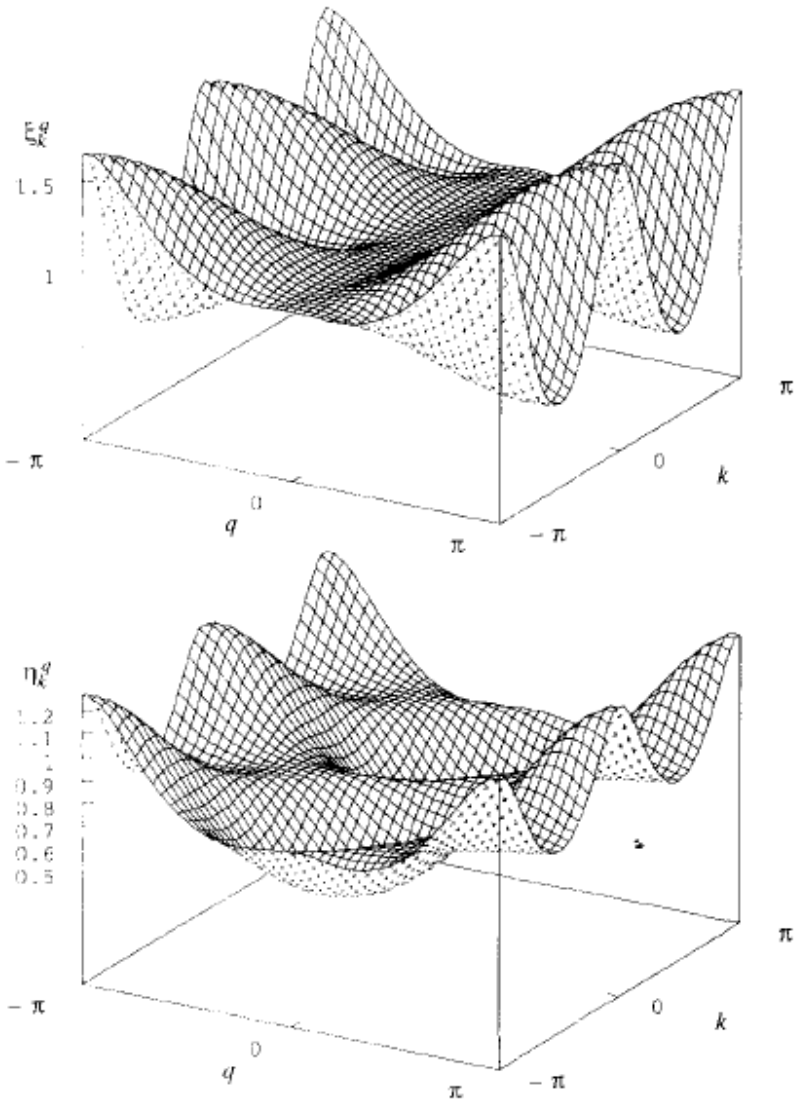
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Fig. 1.

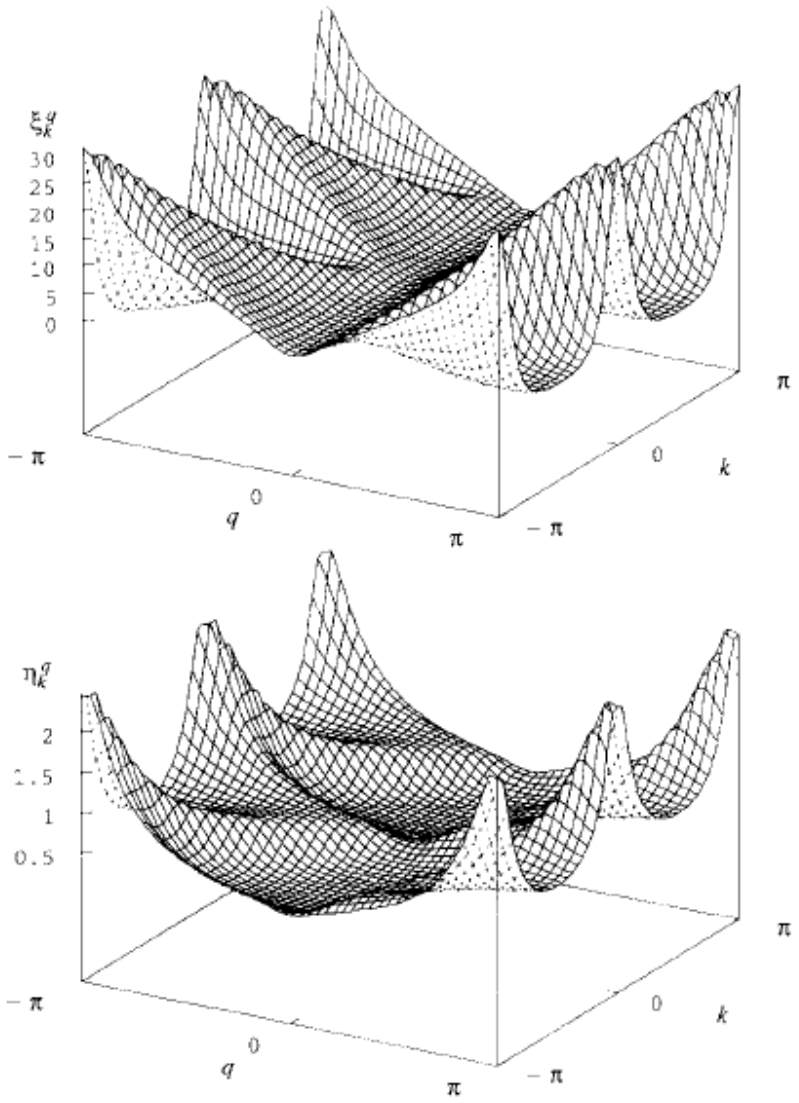
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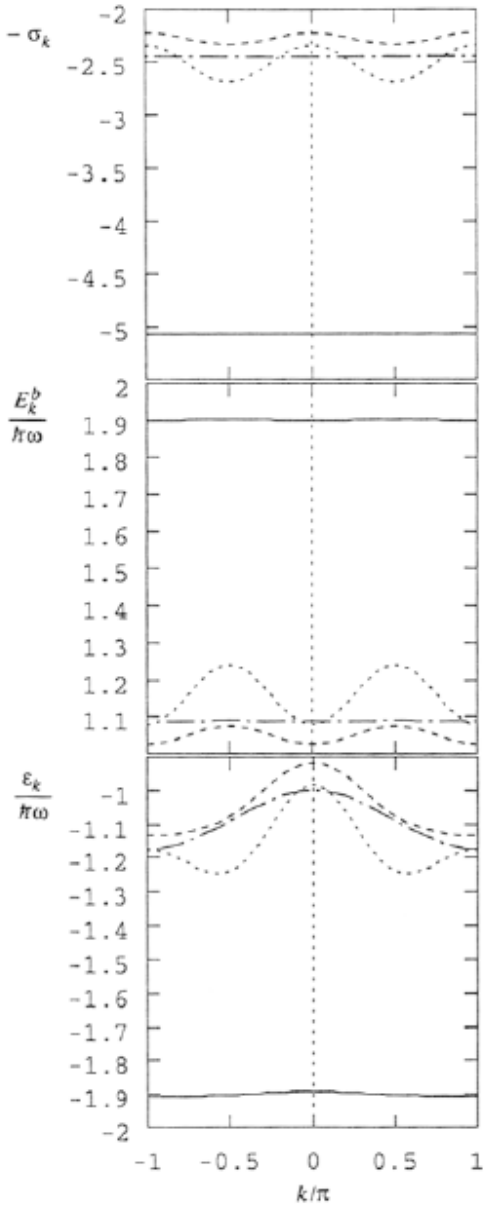
Fig. 2.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k/π

Fig. 3.

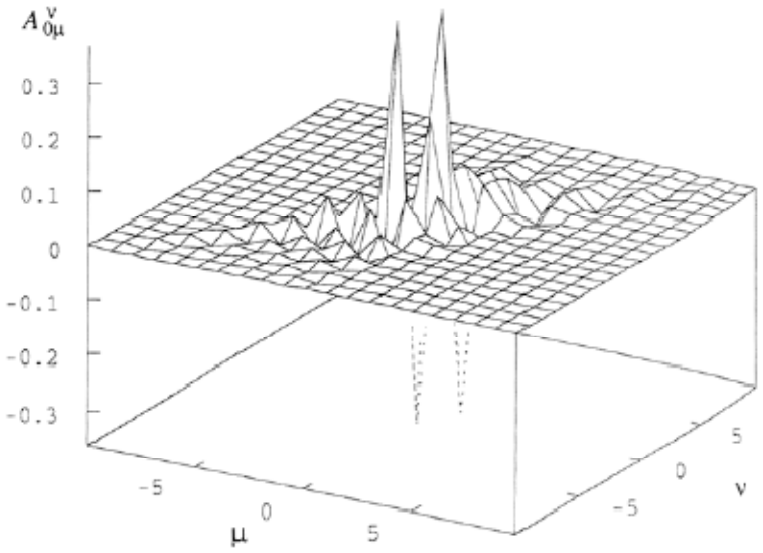

Fig. 4.