CHAOTIC POLARONIC and BIPOLARONIC STATES IN COUPLED ELECTRON-PHONON SYSTEMS

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For large electron-phonon coupling, many models describing the electron-phonon coupling have a limit called anti-integrable with trivially chaotic states. For example, let us consider the Holstein Hamiltonian which is the sum of three terms which are

$$\mathbf{H} = H_k + H_{ep} + H_p \tag{1-a}$$

1- H_k is an electronic Hamiltonian

$$H_k = -T \sum_{<i,j>,\,\sigma} c^+_{i,\sigma}\, c_{j,\sigma} \tag{1-b}$$

which corresponds to a band of electrons (described with standard Fermion operators $c^+_{i,\sigma}$ and $c_{i,\sigma}$) propagating on an arbitrary lattice $\mathbb{L}$ periodic or not ($<i,j>$ denotes neighboring sites and σ the spin of the electron which can be $\uparrow$ or $\downarrow$)

2- H_p is the phonon Hamiltonian

$$H_p = \sum_i \hbar\omega_0 \left(a^+_i\, a_i + \frac{1}{2} \right) \tag{1-c}$$

which corresponds to Einstein oscillators with frequency ω_0 at the sites i of the lattice $\mathbb{L}$ (a^+_i and a_i are standard Boson operators) and

3- H_{ep} is the electron-phonon coupling Hamiltonian

$$H_{ep} = g \sum_i \mathbf{n}_i \left(a^+_i + a_i \right) \tag{1-d}$$

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where

(1-e) $$\mathbf{n}_i = c_{i\uparrow}^{+} c_{i\uparrow} + c_{i\downarrow}^{+} c_{i\downarrow}$$

It couples the electronic density operator $\mathbf{n}_i$ at site i with the oscillator position Choosing for this operator (in appropriate units) as

(2-a) $$\mathbf{u}_n = \frac{\hbar \omega_0}{4g} (a_n^{+} + a_n)$$

and its conjugate momentum

(2-b) $$\mathbf{p}_n = \frac{2g}{\hbar \omega_0} \; i \; (a_n^{+} - a_n)$$

and choosing

(2-c) $$E_0 = \frac{8 g^2}{\hbar \omega_0}$$

as the unit of energy, this Hamiltonian $\mathbf{H}$ becomes the sum of three terms

(3-a) $$\hat{\mathbf{H}} = \frac{\mathbf{H}}{E_0} = H_{AI} + t H_K + \beta H_Q$$

where

(3-b) $$H_{AI} = \sum_i \frac{1}{2} \left(\mathbf{u}_i^2 + \mathbf{n}_i \mathbf{u}_i \right)$$

(3-c) $$H_K = - \frac{1}{2} \sum_{<i,j>, \sigma} c_{i,\sigma}^{+} c_{j,\sigma}$$

(3-d) $$H_Q = \frac{1}{2} \sum_i \mathbf{p}_i^2$$

This Hamiltonian contains two dimensionless parameters which are

(4-a) $$t = \frac{T\,\hbar\omega_0}{4\,g^2} > 0$$

and

(4-b) $$\beta = \frac{1}{4}\left(\frac{\hbar\,\omega_0}{2g}\right)^4$$ respectively.

This new formulation of the initial Hamiltonian is specially interesting for making appearent two important physical limits which are the (standard) adiabatic limit and the anti-integrable limit. Up to now, the importance of this second limit for understanding the physical behavior of the model, was not recognized in the litterature although it has been already considered implicitly but unperfectly in few articles.

Adiabatic Limit: The standard adiabatic limit is obtained when β is zero. This approximation is valid when

(5-a) $$g >> \hbar\omega_0$$

that is for large enough electron coupling g. In that case, the effect of the quantum lattice fluctuations is negligible. At the adiabatic limit, the problem becomes variational since operator $\mathbf{u}_i$ commutes with the Hamiltonian and can be considered as a scalar $u_i = \langle \mathbf{u}_i \rangle$. Note that the adiabatic Hamiltonian obtained for $\beta=0$, is equivalent to the standard meanfield Hamiltonian which is the selfconsistent Hamiltonian obtained by replacing operator $\mathbf{u}_i\mathbf{n}_i$ by $\mathbf{u}_i\langle \mathbf{n}_i \rangle + \langle \mathbf{u}_i \rangle \mathbf{n}_i - \langle \mathbf{u}_i \rangle\langle \mathbf{n}_i \rangle = \mathbf{u}_i\, n_i + u_i\, \mathbf{n}_i - u_i\, n_i$ in (3-b). This approximation neglects the fluctuation $(\mathbf{u}_i - u_i)(\mathbf{n}_i - n_i)$ which becomes zero only when $\beta=0$.

For the adiabatic Hamiltonian, the eigenstates are characterized by the atomic configurations $\{u_i\}$ which are obtained as local minima of the variational form

(5-b) $$\Phi(\{u_n\}) = \sum_\nu \sigma_\nu\, E_\nu(\{u_n\}) + \sum_i \frac{1}{2} u_i^2$$

where $E_\nu(\{u_n\}))$ are the eigenenergies of the tight-binding Schroedinger equation

(6-a) $$-t\,(\bar{\bar{\Delta}}\Psi^\nu)_n + u_n\,\Psi^\nu_n = E_\nu(\{u_i\})\,\Psi^\nu_n$$

($(\bar{\bar{\Delta}}\Psi)_n = \sum_{m\mathcal{V}h} \Psi_m$ is the sum over the neighboring sites m to n on the lattice denoted m$\mathcal{V}$h).This eigenequation also determines the electronic eigenstates $\{\Psi_n^\nu\}$ for the atomic configuration $\{u_n\}$. σ_ν is the population number of state ν. We have

(6-b) $$\sigma_\nu = < c_{\nu,\uparrow}^{+} c_{\nu,\uparrow} > + < c_{\nu,\downarrow}^{+} c_{\nu,\downarrow} > = 0 \text{ , } 1 \text{ or } \frac{1}{2}$$

It can be chosen according to the standard Fermi rule

(7-a) $$\sigma_\nu = 1 \qquad \text{for} \qquad E_\nu(\{u_n\}) \leq E_F$$

and

(7-b) $$\sigma_\nu = 0 \qquad \text{for} \qquad E_\nu(\{u_n\}) > E_F$$

when the electrons are in the ground-state determined by the lattice potential. We also consider situations where the electrons are in excited states as in polaronic or mixed polaronic-bipolaronic states.

Anti-Integrable Limit: When considering large electron-phonon coupling g, the relevant limit is obtained for t=0 (and β=0). This condition is fulfilled when

(8-a) $$g >> \sqrt{T\ \hbar\omega_0}$$

the model becomes trivially soluble since the Hamiltonian **H** (or $\hat{H}$) commutes with the electronic density operators $c_{i\uparrow}^{+} c_{i\uparrow}$ and $c_{i\downarrow}^{+} c_{i\downarrow}$ for spins $\uparrow$ and $\downarrow$. For any arbitrary pseudo-spin configurations $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$ with

(8-b) $$\sigma_{i\uparrow} = 0 \text{ or } 1 \quad \text{and} \quad \sigma_{i\downarrow} = 0 \text{ or } 1$$

there exists an eigenstate of the "anti-integrable" Hamiltonian such that

(8-c) $$<c_{i\uparrow}^{+} c_{i\uparrow}> = \sigma_{i\uparrow} \qquad \text{and} \qquad <c_{i\downarrow}^{+} c_{i\downarrow}> = \sigma_{i\downarrow}$$

These eigenstates are periodic, quasi-periodic, chaotic or else as the pseudo-spin configurations $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$ which label it. By analogy with dynamical systems where the anti-integrable limit is a limit where the chaotic behavior is perfect, we called this limit anti-integrable[1,2].

For t=0, when a single electron is present at site i, there exists a lattice distortion at this site. The electron associated with the lattice distortion is called a *polaron.* This object is magnetic because of the free spin of the electron. When two electrons with opposite spins are present at site i, this pair of electrons associated with the corresponding lattice distortion is called a *bipolaron*. This object is non magnetic.

Thus, the eigenstates determined by pseudospin configurations fulfilling $\{\sigma_{i\uparrow}\}=\{\sigma_{i\downarrow}\}$ are bipolaronic configurations. Those where $\sigma_{i\uparrow} \times \sigma_{i\downarrow} = 0$ for all i, are polaronic configurations. In the general case, the eigenstates determined by $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$ are mixed polaronic-bipolaronic configurations.

We have proven through tedious mathematics[3], that these chaotic polaronic and bipolaronic states obtained trivially for t=0, survives to perturbations in t, that is for large enough electron-phonon coupling. This proof holds very generally for most arbitrary lattices which could be random or not (except for exponential lattices such as Bethe lattices), also in the presence of an arbirary uniform magnetic field (not represented in the model described here).

More precisely, for each eigenstate $\Psi(\{\sigma_{i\uparrow}\},\{\sigma_{i\downarrow}\})$ at the anti-integrable limit, there exists a positive non zero number t_c (independant of the system size) such that for $|t| < t_c$, there exists an eigenstates $\Psi(\{\sigma_{i\uparrow}\},\{\sigma_{i\downarrow}\}, t)$ of the adiabatic Holstein model (with $t\neq0$ and $\beta=0$) which depends uniformly continuously on the parameter t and such that for t=0, we have $\Psi(\{\sigma_{i\uparrow}\},\{\sigma_{i\downarrow}\},0) = \Psi(\{\sigma_{i\uparrow}\},\{\sigma_{i\downarrow}\})$.This exact result means that for large enough electron-phonon coupling, there exists infinitely many local minima of the adiabatic energy.

Since they originate by continuity from the anti-integrable limit, these states are also called bipolaronic, polaronic or mixed polaronic-bipolaronic structures. However, note that these polarons and bipolarons become interacting "particles" for $t\neq0$

For larger t, (that is for smaller electron-phonon coupling), these structures disappear through complex cascade of bifurcations qualitatively similar to those observed for dynamical systems.

The real bounds which can be observed numerically for t_c are much larger than the bounds obtained rigorously. Although these last bounds were found independent of the pseudo-spin configuration, the real bound in t of these configurations depends on the choice of the pseudo-spin configurations $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$. In fact the dimensionless parameter t_c ranges not very far from unity which proves for many systems the physical relevance of the domain of existence for these polaronic and bipolaronic states.

Many other exact results concerning the properties of these states are obtained. All these structures are proven to be insulating with both a non vanishing electronic gap and a non-vanishing phonon gap. These structures are "charge defectible" which means that non uniform distribution of the electronic charges are metastable as in true insulators unlike metals and semi-conductors. The local perturbations due for example to impurities or to extra-electrons decay exponentially at long distance.

For large enough t, the ground-state of the adiabatic Holstein model, is proven to correspond to an ordered bipolaronic structure which may be commensurate, incommensurate (or else?) and thus is a *bipolaronic charge density wave*. It is characterized by a periodic, quasi-periodic (or else) ordering of the pseudo-spin configuration $\{\sigma_{i\uparrow}\} = \{\sigma_{i\downarrow}\}$. Therefore, the other bipolaronic and mixed polaronic-bipolaronic structures correspond to low energy configurational excitations of this ordered ground-state. Again, this exact result holds at any dimension and for most lattices.

For small magnetic field, the ground-state remains a bipolaronic structure but for a large enough magnetic field, the ground-state is proven to become a mixed polaronic-bipolaronic state which is magnetic, through complex and unexplored cascades of transitions.

The role of the dimensionless parameter β describing the quantum lattice fluctuations which is not strictly zero but small, has been analysed[5]. It has been shown that their effect are negligible for the polaronic and bipolaronic structures providing that the phonon gap remains large enough. By contrast, it has been proven[5-d] that the existence of a gapless phonon mode (e.g. phason), breaks down the validity of the Born-Oppenheimer approximation on which the standard theory of Charge Density Waves (CDW) is based. In that case, superconductivity is conjectured. As a result, all CDW's should be viewed as Bipolaronic CDW's, that is an incommensurate ordering of bipolarons. The physical consequences of this description sharply differ on many points from those of the widely admitted standard Peierls-Frohlich theory of CDW[6] and could provide a new fruitful basis for understanding many experiments in CDW systems which up to now received inconsistent theoretical interpretations[7].

In summary, this work confirms and extends early numerical studies and conjectures on the Peierls instability in this model in one dimension model where a transition by "breaking of analyticity" toward a bipolaronic CDW was already observed[4]. This recently obtained exact result should break down some wrong ideas concerning the effects of large electron-phonon coupling which are widely spread in the litterature. It opens a new direction for understanding globally the properties of Charge Density Waves Systems and perhaps in further stages, other structural problems concerning for example magnetic structures.

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[7] see for example P.MONCEAU *Recent Developments in Charge Density Wave Systems* in *Application of Statistical and Field Theory Methods to Condensed Matter* p.357 Ed D.BAERISWYL et al Plenum NY (1990) and refs. therein.