# CHARGE DENSITY WAVES AND SUPERCONDUCTIVITY IN THE HOLSTEIN MODEL

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The electron-phonon coupling in conducting materials may produce at low temperature either a charge density wave (CDW) or standard superconductivity (SC).The aim of this talk is to shed a new light on the competition between CDW and SC through an approach based on previous works on incommensurate and chaotic structures in PEIERLS models which are currently under development. For this purpose, we focus on the HOLSTEIN Hamiltonian written as :

$$(1) \qquad H = -\frac{1}{2} \sum_{<i,j>,\sigma} c^{+}_{i,\sigma} c_{j,\sigma} + \frac{k}{2} \sum_{i} n_i u_i + \frac{1}{2} \sum_{n} (u_n^2 + \frac{\gamma^2}{4} p_n^2)$$

This model consists into a band of electrons with on-site coupling with dispersionless optical phonons. The energy unit is chosen such that the exchange constant between neighboring sites <i,j> on a d-dimensional square lattice be $-\frac{1}{2}$.The band width is thus 2d. $\sigma$ is the electron spin $\pm\frac{1}{2}$ noted $\uparrow$ or $\downarrow$. $c^{+}_{i,\sigma}$ and $c_{i,\sigma}$ are the creation and annihilation Fermions operators of an electron at site i with spin $\sigma$ respectively. The electron density operator is

$$(2\text{-a}) \qquad n_i = n_{i,\uparrow} + n_{i,\downarrow} = c^{+}_{i\uparrow} c_{i,\uparrow} + c^{+}_{i,\downarrow} c_{i,\downarrow}$$

The unit for the atomic position operator $u_n$ is such that the elastic constant be 1. $p_n$ is the conjugate operator to $u_n$ defined such that $[u_n, p_n] = i$. Creation and annihilation boson operator $a_n^{+}$ and $a_n$ are defined as

$$(2\text{-b}) \qquad u_n = \frac{\sqrt{\gamma}}{2} (a_n^{+} + a_n) \quad \text{and} \quad (2\text{-b}) \quad p_n = \frac{i}{\sqrt{\gamma}} (a_n^{+} - a_n) = -i \frac{\partial .}{\partial u_n}$$

Thus, the phonon term in the Hamiltonian (1) becomes $\frac{1}{2} (u_n^2 + \frac{\gamma^2}{4} p_n^2) = \gamma (a_n^{+} a_n + \frac{1}{2})$.The physical units are chosen in order that this model depends on two dimensionless parameters which are k the "classical" electron-phonon coupling obtained within the assumption that the atoms are classical particles and $\gamma$ the quantum parameter which is the phonon energy in energy band units.

## THE ADIABATIC LIMIT. BIPOLARONIC STATES

The adiabatic approximation ($\gamma$=0 : slow atoms-fast electrons), is equivalent to the mean field Hamiltonian $H_{MF}$ which decouples electrons and phonons.

$$(3) \quad H_{MF} = -\frac{1}{2} \sum_{<i,j>,\sigma} c^{+}_{i,\sigma} c_{j,\sigma} + \frac{k}{2} \sum_{i} n_i <u_i> +$$

$$+ \frac{k}{2} \sum_{i} <n_i> u_i + \frac{1}{2} \sum_{n} (u_n^2 + \frac{\gamma^2}{4} p_n^2) - \frac{k}{2} \sum_{i} <n_i> <u_i>$$

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Its parameters are selfconsistently determined as the mean values $\langle n_i \rangle = \langle \Psi | n_i | \Psi \rangle$ and $\langle u_i \rangle = \langle \Psi | u_i | \Psi \rangle$. The fluctuation terms $(n_i - \langle n_i \rangle)(u_i - \langle u_i \rangle)$ are neglected. Since it comes out $\langle u_i \rangle = -\frac{k}{2} \langle n_i \rangle$, Hamiltonian (1) is recovered for $\gamma=0$ and $\langle u_i \rangle = u_i$.

For model (1) with arbitrary dimension d and $\gamma=0$, a recently proven theorem[3] confirms the existence of the "transition by breaking of analyticity" found in early one dimensional numerical simulations. This result is an explicit consequence of the discreteness of the lattice and cannot be found within standard continuum approximations.

We briefly explain here its physical meaning. In the limit $k = \infty$, the electronic kinetic energy can be dropped and the ground-state of Hamiltonian (1) is trivially degenerate.The lattice sites i are either doubly occupied by a pair of electrons with opposite spins or not occupied at all. Thus, the groundstates can be described by an arbitrary pseudospin configuration $\{\sigma_i\}$ where $\sigma_i = \frac{\langle n_i \rangle}{2} = 0$ or 1. When $\sigma_i = 1$, there is a lattice distortion at site i and we say that this site is occupied by a bipolaron. For periodic (or quasiperiodic) configuration $\{\sigma_i\}$, the ground-state is either commensurate (or incommensurate) CDW.

For finite k, the ground-state degeneracy is raised. Our theorem asserts that for k large enough, these bipolaronic states survive despite the kinetic energy of the electrons is no more zero. More precisely, for any arbitrary bipolaronic distribution $\{\sigma_i\}$, there exists an eigenstate $|\Psi\rangle$ of the adiabatic Holstein model, with the density of electron pairs $\{\rho_i(k)\}$ defined as $\rho_i = \frac{1}{2} \langle n_i \rangle$, which continuously depends on k and with $\{\rho_i(\infty)\} = \{\sigma_i\}$. Most these bipolaronic states are chaotic but they may also form commensurate and incommensurate superlattices (which are CDWs). The ground-state is a particular bipolaronic superlattice (which is generally unknown in models in 2 and more dimensions!). The electronic eigenstates may be extended or localized but in any case, the bipolaronic states are proven to be insulating with a finite gap at the Fermi energy and a finite gap in their phonon spectrum (no gapless phasons!):

*The bipolaronic structures are always insulating and pinned to the lattice.*

The analytic rigorous bound $k > 2\sqrt{5}d$ for the existence of bipolaronic states in d dimensions, is in fact found to be much smaller by numerical analysis. When k decreases, there is cascades of bifurcations at which chaotic bipolaronic states becomes unstable. Thus, decreasing k, they gradually disappear and beyond the transition by "breaking of analyticity" (TBA) which is reached at some critical value $k_c(\zeta)$, there is no more chaotic states. $k_c(\zeta)$ depends on the electron concentration $\zeta$ per site (for example in 1d and for $\zeta = \frac{3-\sqrt{5}}{2}$, $k_c(\zeta) \cong 1.58$). The density of electron pairs $\{r_i(k)\}$ (or the atomic distortion $\{b_i\}$ with $b_i = -k\, r_i(k)$ ) of the "single" bipolarons belonging to a given bipolaronic configuration $\{\sigma_i\}$ can be defined as

$$\rho_i(k) = \sum_n \sigma_n \, r_{i+n}(k) \qquad (4)$$

For $k=\infty$, $\{b_i\}$ is peaked on a single site at the origin. For finite k, the next talk, shows examples of well localized bipolarons $\{b_i(k)\}$ calculated in one dimensional models. At the TBA, the size of these bipolarons diverges and below $k_c(\zeta)$, the ground-state becomes "undefectible". Bipolarons do not exist as localized objects in real space.

When $k > k_c(\zeta)$ and at temperature low enough, the energy of model (1) essentially depends on the bipolaronic configurations. Its thermodynamical and transport properties should be well described on the basis of a pseudospin Hamiltonian (lattice gas model).

## QUANTUM LATTICE FLUCTUATIONS CLOSE TO THE ADIABATIC REGIME

The eigenstates of the mean field Hamiltonian (3) have the form

$$(5)\ |\Psi> = \exp\left( \sum_i \frac{<u_i>}{\sqrt{\gamma}} ( a_i^+ - a_i ) \right) \prod_{\nu\ occ,\sigma} c^+_{\nu,\sigma}(\{<u_i>\})\ |vacuum>$$

where $<u_i>$ is the average distortion and $c^+_{\nu,\sigma}(\{<u_i>\})$, the Fermion operators of the occupied states which diagonalize the electronic part in (3). The overlaps $<\Psi_2|\Psi_1>$ and $<\Psi_2|$ H $|\Psi_1>$ between two adiabatic eigenstates $|\Psi_1>$ and $|\Psi_2>$ can be calculated exactly and explicitly with the initial Hamiltonian. Then, it is found analytically (and confirmed numerically) that for small $\gamma$ and k far above $k_c(\zeta)$, these overlaps are small which confirms that the adiabatic (or mean field) approximation is valid for $k>k_c(\zeta)$.

When, k aproaches $k_c(\zeta)$ from above, the overlaps between certain states become close to unity which proves that the mean-field eigenstates cannot remain good approximations. The calculation of these overlaps can be used for calculating the tunnelling energy of a discommensuration. It is found that when its pinning energy barrier goes to zero, the tunnelling energy gain of an advanced as well as a retarded discommensuration becomes larger than the positive potential energy of this discommensuration. Since the total discommensuration energy becomes negative, the commensurate CDW structure becomes unstable under quantum lattice fluctuations even very close to the adiabatic limit for small but non zero $\gamma$ (see the next talk ref4)

When approaching the TBA, the size of a bipolaron diverges. Beyond a certain critical size, it cannot remain localized in the local potential created by the lattice and the neighboring bipolarons and delocalizes through the lattice.The CDW order in real space disappears. (A rough interpretation of this transition is a Bose condensation of bipolarons). New studies in d dimensional systems which are currently developped, show that the "anti adiabatic" terms of the Hamiltonian necessarily becomes essential for determining the new structure (the bipolaron becomes antiadiabatic when it tunnels"). They confirm that any CDW becomes unstable against superconductivity when the phason gap is too small, independantly of the dimensionality of the model.

Whatever will be the conclusion of these new calculations, it is proven unambiguously that the standard adiabatic approximation cannot describe properly CDWs when their phason gap become too small (in the unprobable event, it could survive to quantum lattice fluctuations).

## THE ANTI-ADIABATIC LIMIT

Although this limit is not very physical, it is instructive to discuss briefly the antiadiabatic limit obtained for $\gamma = \infty$. Then, the atoms follows adiabatically the electrons (fast atoms-slow electrons). The Lang-Firsov unitary transformation of Hamiltonian (1):

$$(6\text{-a})\ \hat{H} = \exp(iS_{LF})\, H \exp(-i\, S_{LF}) \quad \text{with } i\, S_{LF} = \frac{k}{2\sqrt{\gamma}} \sum_i \left(\sum_\sigma c^+_{i,\sigma} c_{i,\sigma}\right)( a_i^+ - a_i )$$

yields:

$$(6\text{-b})\ \hat{H} = -\frac{1}{2} \sum_{<i,j>,\sigma} \hat{t}_{i,j}\, c^+_{i,\sigma}\, c_{j,\sigma} - \frac{k^2}{8} \sum_i \left(\sum_\sigma c^+_{i,\sigma} c_{i,\sigma}\right)^2 + \gamma \sum_i \left(a_i^+ a_i + \frac{1}{2}\right)$$

$$(6\text{-c})\ \hat{t}_{i,j} = \exp\left( \frac{k}{2\sqrt{\gamma}} \left( ( a_i^+ - a_i ) - ( a_j^+ - a_j ) \right) \right)$$

When $k^2 << \gamma$, the electrons and phonon decouple since $\hat{t}_{i,j} \approx 1$. In that limit, the electronic part of this model is a negative U Hubbard model with the electron-electron attraction $-\frac{k^2}{4} n_{i,\uparrow} n_{i,\downarrow}$. It is well admitted that the ground-state of this model is superconducting (see Nozières and Schmitt-Rink quoted in ref.3). Since U only depends on k and is independant of the quantum parameter of the lattice $\gamma$, this superconductivity has to be insensitive to any isotopic effects.

## A NEW BASIS FOR THE INTERPRETATION OF CDWs

The global agreement between the most common theories describing CDWs and the experiments on real compounds is presently very poor even on the qualitative point of view. In addition, there is a large number of experimental observations (reported for example in this conference) which have either no qualitative explanations, or explanations which are inconsistent with other observations. The impurities and defects (which certainly exist) which are supposed to play the crucial role for the pinning interpretation of CDW, have still never been identified! We suggest that a new CDW's theory can be built on the basis of the following remarks:

All CDWs should be bipolaronic structures intrinsically pinned to the lattice. The physical cases with non linear conductivity, are very close to superconducting states (where the bipolaronic structure becomes "superfluid"). (Otherwise, these systems would be insulating at all temperatures) and the bipolarons are rather extended (few unit cells) . Therefore, these bipolaronic structures are quite plastic and easy to flow. The small but non zero phason gap is renormalized by thermal fluctuations but soften incompletely at $T_{CDW}$. It is however quite sufficient to pin the CDW under any applicable macroscopic electric field. (For example, close to $T_{CDW}$, neutron measurements show in Blue Bronze a phason gap $\cong 0.5\ 10^{-4}$ eV incompatible by several order of magnitudes with the depinning field observed by transport measurements!). The CDW transition corresponds to the disordering of the incommensurate bipolaronic structure. Bipolaronic fluctuations survives in some critical region above $T_{CDW}$.(Because of the existence of a central peak, non linearity in the conductivity may persist above $T_{CDW}$).

Above and below $T_{CDW}$, the bipolarons have a diffusive behavior by thermal hopping which vanishes at 0K and yields linear conductivity. For larger electric field, there is an extra CDW motion due to the generation and to the motion of neutral "phase walls".(To be neutral, these phase walls have to be parallel to the highest conductivity axis as the domain walls of a ferroelectrics.). $2\pi$-relaxation in the phase walls configurations generate the current noise. The current noise is essentially and necessarily the consequence of the current gradients which always exist in any sample 1-at the contacts, 2-at the surface of the sample, 3- by special current geometry ...4) and also because of "large scale defects" such as dislocations and grain boundaries. All these non linear effects are strongly temperature dependant because the phase wall motions and relaxations originate from the microscopic bipolaronic diffusion(the effect of few microscopic impurities on this diffusion, is neglegible). Non linear conductivity in CDW is analogous to the depolarizing current of a ferroelectric in an electric field but in a stationary regime.

For more details see the following references and the references quoted therein.

[1] S. AUBRY and P. QUEMERAIS "Breaking of Analyticity in Charge Density Waves Systems. Physical Interpretation and Consequences" p. 295-405 in " Low Dimensional Electronic Properties of Molybdenum Bronzes and Oxides" Editor Claire SCHLENKER Kluwer Academic Publishers Group (1989)

[2] S.AUBRY S. and P. QUEMERAIS "Lattice Pinning of a CDW and Quantum Fluctuations" in " Singular Behaviour & Nonlinear Dynamics" Ed. St. Pnevmatikos, T. Bountis & Sp. Pnevmatikos, Riedel (1989)

[3] S. AUBRY, G. ABRAMOVICI, D. FEINBERG, P. QUEMERAIS and J.L. RAIMBAULT "Charge Density Wave and Superconductivity: Localized Bipolarons versus Cooper Pairs?" in "Non-Linear Coherent Structures in Physics, Mechanics and Biological Systems" submitted to Lectures Notes in Physics, Springer (1989)

[4] P. QUEMERAIS, J.L. RAIMBAULT and S. AUBRY, this proceeding