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Chaotic Polaronic and Bipolaronic States in the Adiabatic Holstein Model

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A rigorous proof for the existence of bipolaronic states is given for the adiabatic Holstein model for any lattice at any dimension, periodic or not, and for an arbitrary band filling, provided that the electron–phonon coupling (in dimensionless units) is large enough. The existence of mixed polaronic–bipolaronic states is also proven, but for larger electron–phonon coupling. These states consist of arbitrary distributions of bipolarons (or of bipolarons and polarons) localized in real space which can be simply labeled by pseudospin configurations as for a lattice gas model. The theory not only applies to periodic crystals, but also to quasicrystals, amorphous structures, polymer network, etc.

When these bipolaronic and mixed polaronic–bipolaronic states exist, it is proven that: (1) These bipolaronic (and mixed polaronic–bipolaronic) states exhibit a nonzero phonon gap with a nonvanishing lower bound and an electronic gap at the Fermi energy. (2) These structures are insulating. The perturbation generated by any local change in the bipolaronic or polaronic distribution or by any charged impurity or defect decays exponentially at long distance. (3) These bipolaronic (and mixed polaronic–bipolaronic) states persist for any uniform magnetic field. (4) For large enough electron–phonon coupling, the ground state of the extended adiabatic Holstein model is a bipolaronic state when there is no uniform magnetic field or when it is small enough. It becomes a mixed polaronic–bipolaronic state for large enough magnetic field (note that the mixed polaronic–bipolaronic states are magnetic).

In one-dimensional models, the ground state is an incommensurate (or commensurate) charge density wave (CDW) as predicted by Peierls (this result is not rigorous, but has been confirmed numerically). It is proven that the ground state becomes a "bipolaronic charge density wave" (BCDW) at large enough electron–phonon coupling. The existence of a transition by breaking of analyticity (TBA), which was numerically observed as a function of the electron–phonon coupling, is then confirmed. In that case, the shape of the effective bipolaron can be numerically calculated. It is observed that its size diverges at the TBA. The physical properties of BCDWs are rather different from those

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predicted by standard charge density wave theory. Bipolaronic charge density waves can also exist in models which are not only low-dimensional, but purely two- or three-dimensional.

The technique for proving these theorems is an application of the concept of anti-integrability initially developed for Hamiltonian dynamical systems. It consists in proving that the eigenstates of the (trivial) Hamiltonian (called anti-integrable) obtained by canceling all electronic and lattice kinetic terms survive as a uniformly continuous function of the electronic kinetic energy terms in the Hamiltonian up to a certain threshold.

KEY WORDS: Chaos; anti-integrability; bipolaron; polaron; charge density wave; breaking of analyticity.

1. INTRODUCTION

This paper follows the work of refs. 1 and 2, where the concept of anti-integrability and some of its applications were first described on the Frenkel–Kontorowa (FK) model and the associated standard map as an example. Technically, the present work consists in the application of this concept of anti-integrability to a coupled electron–phonon model. We choose as a first example the Holstein model. Physically, it brings new information concerning the effect of the electron–phonon coupling which leads to potentially important consequences for understanding real materials.

The reader who is only interested in the physical consequences of this work could focus mostly on this introduction and on the end of the conclusion, Section 5. He or she could also refer to ref. 6, where much of the physical ideas about bipolaronic structures were presented empirically. The reader who is interested in the mathematical techniques should refer first to refs. 1 and 2, where the basic ideas used here were applied to the FK model.

1.1. Bipolaron, Polarons, and Anti-Integrability

This paper is mainly devoted to the study of the "anti-integrable" limit of the adiabatic Holstein mode, which can be treated exactly in perturbations. The proof for the existence of chaotic bipolaronic states is obtained in a nonvanishing region of the parameter space. Within this approach, the effective bipolarons play a role similar to the effective discommensurations in the FK models.[2] Polarons are also involved, but have no analog in the FK model. As also noted in refs. 3–6, there are strong similarities between the properties of the ground state of 1D Peierls chains and of those of the 1D FK model. Although in the FK model the existence of chaotic metastable states at large coupling is intuitive for physicists, the mathe-

matical formulation of a rigorous proof was still missing in the literature. We proposed a proof[2] in this simple case with a strategy based on the fixed-point theorem of Banach (1921).[2] The same strategy can be used here for the adiabatic Holstein model, although its implementation becomes more complex and the physical intuition much looser. Although the same method can be extended to many other adiabatic electron–phonon models or to mean-field models with electron–electron interactions, it is preferable in a first step to focus on the Holstein model, which is one of the simplest for electron–phonon coupled systems.

The concept of the polaron was first introduced by Landau.[14] It is now well known that because of the electron–phonon coupling, a single electron in a lattice creates a lattice distortion and may localize in the self-consistent associated with this lattice distortion. This localization occurs in one-dimensional models at any nonvanishing electron–phonon coupling, but in two dimensions and more, this must exceed a certain critical value. The combination of an electron with its associated lattice distortion is called a polaron. When the electron–electron interaction is small enough, the localization of a pair of electrons with opposite spins in the same electronic state is energetically more favorable, and then the system forms a bipolaron (for a standard review of problems of polarons and bipolarons see refs. 15 and 16). However, up to now, these polarons have been investigated only at low density.

Here, our approach is somewhat different. It has been numerically observed[3–6] that for large enough electron–phonon coupling, one-dimensional Peierls systems could exhibit chaotic metastable states beyond the "transition by breaking of analyticity" (TBA). These states were interpreted empirically as Fermi glasses due to the localization of the electrons into potential wells which are randomly distributed. These potential wells are generated self-consistently by the lattice deformation created by the electron density (self-trapping). The numerical observation of these Fermi glasses suggests that they are in fact glasses of bipolarons and thus that the concept of bipolaron (or of polaron) could remain valid for many-electron systems, provided that the electron–phonon coupling is large enough.

Indeed, when there are many electrons in the system, the polarons (or the bipolarons) strongly overlap, so that it is not clear whether the concept of polaron or bipolaron remains well-defined. This paper answers the question for the adiabatic Holstein model (at any dimension) and with or without magnetic field, by proving that these chaotic many-bipolaron structures are generated by continuity from a limit ("anti-integrable") where their existence is trivial. In thus provides precise definitions for the

[2] For the Banach fixed-point theorem see, e.g., ref. 8.

many-bipolaron states and, on the same footing, for the mixed polaron–bipolaron states. For the adiabatic Holstein model with an electron–phonon coupling larger than a given bound, it is proven that there is a one-to-one map between the whole set $\mathscr{S}$ of pseudospin configurations on the lattice $\{\sigma_i = 0 \text{ or } 1\}$ and a set of metastable configurations $\mathscr{S}'$ of the adiabatic Holstein model which are the bipolaronic states. The pseudospin configurations $\{\sigma_i\}$ determine the location of the maxima of the electronic density of the bipolaron arrangement on the lattice. When $\sigma_i = 0$ at site i, the electronic density is smaller than 1/2 and we say that no bipolaron is present around this site i. When $\sigma_i = 1$, the electronic density becomes larger than 1/2 and we say that a bipolaron is present at this site. The lattice distortion due to each bipolaron is not strictly localized on a single site, but extends over some distance around the occupied site. The important result coming from our theorem is that the bipolaronic configurations can be simply described by pseudospin configurations which represent symbolically their spatial distribution.

Similarly, the mixed polaronic–bipolaronic configurations are described by pseudospin configurations $\{\sigma_i\}$, where σ_i now takes three possible values, 0, 1/2, and 1 instead of 0 and 1. When $\sigma_i = 1$ at site i, there is a bipolaron at site i. When $\sigma_i = 0$, there is no bipolaron and no polaron at site i. When $\sigma_i = 1/2$, a polaron is present at site i. This polaron also extends over some distance around its site and exhibits a *physical* spin which is that of a single electron. However, since we consider here a model with no direct electron–electron interaction, the global energy of this state does not depend on this physical spin and then these mixed polaronic–bipolaronic states are spin degenerate with a nonzero entropy. This spin degeneracy should be raised by an external magnetic field or by a direct electron–electron interaction, allowing the occurrence of magnetic structures.

Our exact results imply for the adiabatic Holstein model at large enough electron–phonon coupling that *the bipolarons or the polarons can be treated as individual particles localized in real space* which can be added or subtracted locally and one by one to the whole structure. Let us warn the reader that this property does not mean that the wavefunctions of the electrons in the self-consistent lattice potential are *localized.* In fact, in our case, this property is meaningless because excitations in the electronic systems modify this self-consistent potential and therefore the electronic eigenstates. Let us consider, for example, a case where the pseudospin configuration $\{\sigma_i\}$ is periodic; the resulting lattice distortion and the self-consistent lattice potential of the associated bipolaronic structure is also periodic and the electronic states are extended Bloch states. When the pseudospin configuration $\{\sigma_i\}$ is random, the electronic states might be

localized. But in any case, the physical properties of the system *remain the same*: the bipolarons behave as localized particles. These bipolaronic states are always insulating at zero degrees kelvin with a finite gap for the electronic eigenenergies at the Fermi level (and also for the phonon excitations). We now make some remarks about the definition of an insulating state.

1.2. Charge Defectibility and Insulating States

According to very old and well-known experimental facts, an insulator can be defined by considering only *electrostatic* properties instead of transport properties as usual. The characteristic property which determines whether the system is insulating or conducting (or semiconducting) is the *charge defectibility*. An electric charge which is injected into an insulator at some point does not extend over the whole system, but remains *localized in real space* in the vicinity of the point where it has been injected: the system preserves inhomogeneous electrostatic charge distributions. In principle due to thermal agitation, this inhomogeneous distribution should relax after a finite time (relaxation time) which becomes strictly infinite only at 0 K. However, in practice, this lifetime can be so long that it can be already considered as infinite for "good insulators" at room temperature. By contrast, for conductors and semiconductors, a locally injected charge extends over the whole sample within a very short time even at 0 K. It is this property which allows the transport of electrons through the system (electric current). We can say in equivalent words that when a system is charge-defectible, the mobility of the localized charge carriers is either zero or is physically negligible (the charges are pinned to the lattice), while when it is charge-undefectible, the mobility of the charge carriers becomes high or is at least nonnegligible, which prevents them from remaining localized. This mobility could be found to be infinite in the simplest models.

It clearly appears that the standard electronic band model for a periodic crystal always yields an undefectible system since the electronic excitations of the system, which correspond to extra electrons in the conduction band, are Bloch wave states and thus extend over the whole crystal. In fact, this band scheme allows one to discriminate only between conductors and semiconductors. For a semiconductor, the Fermi energy lies between two bands. At 0 K, applying a small electric field does not allow one to generate any electronic excitations, because of the nonvanishing electronic gap. Then, the conductivity of this semiconductor is strictly zero essentially because of the absence of any charge carriers. When electronic excitations which are mobile are created, for example, by thermal

activation, by photoexcitation, or by doping, such systems become conducting, unlike true insulators, where charged defects are not mobile.

By contrast, for a conductor (metal), the Fermi energy lies inside an electronic band. At 0 K, a small electric field generates mobile electronic excitations because of the absence of an electronic gap at the Fermi energy, so that the system is a conductor at 0 K. However, in this ideal band model, the conductivity is infinite. For obtaining a finite conductivity, it is necessary to involve *additional effects* which could be due either to the static potential of random impurities or lattice defects, to a direct electron–electron interaction, or an electron–phonon coupling. It is well known that two of these effects could also lead to true insulating states (which are charge-defectible) by an Anderson localization of the electrons due to random impurities (or defects) or to a Mott insulator transition due to the electron–electron interaction. It is thus interesting to complete this picture by proving (which will be done here) that a true insulating states (which is "charge-defectible") can be also generated when the electron–phonon interaction is sufficiently strong.

It appears that the concept of charge defectibility which we propose for defining an insulator is analogous to the concept of phase defectibility for incommensurate structures introduced some years ago.[7] It is more general than but extends the concept of localization, which requires independent particles. The bipolaronic states which we found in the model studied here are by construction charge-defectible and thus explicitly fulfill this definition for an insulating state. At low temperature, the relevant excitations of the whole electron–phonon system are defects in the bipolaronic structure which cannot be described as single electronic excitations in the "conduction band." At larger temperature or with a magnetic field, the mixed polaronic–bipolaronic excited states may become relevant (if they exist, that is, for an electron–phonon coupling large enough). The transition between a charge-undefectible system and a charge-defectible system can be considered in some respect as a transition wave–corpuscle since in the first case, the electrons have to be considered as delocalized particles (waves) and in the second case as exponentially localized particles (corpuscles).

Turning back to the properties of the bipolaronic states, it is proven that the ground state of the adiabatic Holstein model without magnetic field or with a small enough magnetic field is one of these metastable bipolaronic states, which of course corresponds to a particular nonchaotic ordering of the bipolarons. When the magnetic field is sufficiently large, the ground state becomes a mixed polaronic–bipolaronic state. In one dimension, numerical calculations have shown that it corresponds to a periodic or a quasiperiodic sequence $\{\sigma_i\}$ with wave vector $2k_F$ (which depends on

the band filling).[3–6] This commensurate or incommensurate array of bipolarons just forms the charge density wave (CDW) expected from the theory of Peierls instabilities. The obtained structure does not exhibit any phonon mode with zero frequency (called the phason mode), but the low-lying excited states correspond to metastable configurations associated with pseudospin sequences $\{\sigma_i\}$. They can be equivalently interpreted as localized defects or discommensurations. At the present stage we are unable to predict the ordering of the bipolaronic or mixed polaronic–bipolaronic configuration for the ground state at arbitrary band filling. Nevertheless, we can expect (mostly in models with several dimensions), a very righ variety of possible structures (commensurate, incommensurate, weakly periodic? etc.) with first- or second-order phase transitions and devil's staircases, which need to be explored.

1.3. Outline

This paper is organized in five sections.

Following this present introductory section, Section 2 is devoted to definitions and notations. In Section 2.1, we define the Holstein model on a d-dimensional square lattice. In Section 2.2, the anti-integrable and adiabatic limits are defined. At the adiabatic limit, finding the eigenstates of the Holstein model is equivalent to extremalizing a variational form. In Section 2.3, we describe the extension of the Holstein model to arbitrary lattices, since the mathematical treatment of the next section can be applied identically to a periodic one.

Section 3 describes the two main theorems of the paper and the essential parts of their proofs. The parts which become too technical or tedious are given in Appendices A–C. Section 3.1 describes the bipolaronic and mixed polaronic states at the anti-integrable limit. The long Section 3.2 describes the theory of perturbation for the bipolaronic states at the anti-integrable limit. It starts with the description of our strategy of proof. We define an operator $\mathbf{S}$, the fixed points of which are the bipolaronic states and apply our strategy by proving Lemma 1 and Proposition 1. The proof of Proposition 2 comes out from the results of Appendices A (polynomial approximations) and B. Then Theorem 1 for the persistence of the bipolaronic states close to the anti-integrable limit is given and proven. Section 3.3, extends this theory to situations where the electrons are in excited states. Theorem 2 then predicts the existence of mixed polaronic–bipolaronic states. Its proof is essentially based on the same ideas as that to Theorem 1. It is described in parallel to the initial proof of this Theorem 1 in Appendix C, where only the differences are pointed out. Theorem 3 states that the limits of these bipolaronic and polaronic states

are well defined when the size of the system diverges. However, the proof of this theorem is given later at the end of Section 4.3, after the properties of these states which are needed for establishing this theorem have been described and proved.

Section 4 is devoted to the physical properties of the bipolaronic states and mixed polaronic–bipolaronic states the existence of which is predicted by Theorems 1 and 2. In Section 4.1 we prove the existence of an electronic gap, and in Section 4.2 the existence of a phonon gap for all these states. Section 4.3 proves that the linear response of these states to local perturbations decays exponentially as a function of the distance, which allows one to define a coherence length. In addition, we prove that the finite perturbation due to any local change in the polaronic and bipolaronic distribution also decays exponentially at large distance (note that this result is not a differential property, but is valid for nonvanishing perturbations). This result confirms that polarons and bipolarons can be treated physically as individual particles since their arrangement can be chosen arbitrarily. In Section 4.4 we show that a small amount of disorder on the electronic transfer integrals does not affect the existence Theorems 1 and 2, nor does a magnetic field, uniform or not, when only the orbital effects are taken into account. In addition, it is shown that the bounds for the existence of bipolaronic and mixed polaronic bipolaronic states can be improved by the presence of a magnetic field. Theorems 1 and 2 still hold, but only for a uniform magnetic field, when the magnetic spin effects are taken into account. Finally, in Section 4.5 it is proven that for large enough electron–photon coupling, the ground states of the adiabatic Holstein model are either bipolaronic (without or with a small enough uniform magnetic field) or mixed polaronic–bipolaronic (for a large enough uniform magnetic field).

Section 5 gathers comments and remarks about the previous results and their consequences and sets new questions to be studied in more detail in further works. In Section 5.1, assuming a perfect similitude between the FK model (where rigorous results are available) and the one-dimensional adiabatic Holstein model, the analysis of early numerical data yields the exact shape of a bipolaron. In Section 5.2 we discuss the conditions which are required for other models for extending the mathematical method used for the Holstein model. Next, it is noted in Section 5.3 that the perturbation theory is often only applicable to a subset of the "anti-integrable states" (pruning condition). An example is given. We show in Section 5.4 with an example that there exist many other metastable states which are not obtained by perturbation of those obtained at the anti-integrable limit. We mention in Section 5.5, that there exist models without any well-defined anti-integrable limit and thus to which our theory does not apply in the

present form. Some of these models are "integrable" and have no anti-integrable limit. For others the question is open. In Section 5.6 we briefly mention, by introducing a Hubbard term as an example, that our theory can include a direct electron–electron interaction but within a mean-field description. In Section 5.7, we briefly recall some recent results partially published elsewhere concerning the validity of the adiabatic approximation. Corrections to this approximation are generally totally negligible for well-defined bipolaronic and polaronic structures. On contrary, the role of the anti-adiabatic terms becomes predominant when the size of the bipolarons (or polarons) diverges. Finally, we conclude with some discussions about the applications of this work to real compounds. Although the standard interpretation of CDW by the Peierls–Fröhlich theory is found to be acceptable in the literature, we suggest that our approach could provide an alternative basis of a new interpretation not only for the main experimental facts, but also for many others which up to now have not received a consistent interpretation.

2. THE *d*-DIMENSIONAL HOLSTEIN MODEL AND ITS EXTENSIONS

2.1. Definitions and Notations

The standard Holstein model[17] consists of a system of electrons described within the tight-binding representation coupled to phonons on a d-dimensional square lattice. As for the Frenkel–Kontorowa model, this model naturally involves the period of the underlying lattice and thus the tight-binding representation which makes the space variable discrete appears to play a role similar to the Poincaré representation of surfaces of section for continuous-time dynamical systems which makes the time variable discrete. Instead of describing immediately the adiabatic Holstein Hamiltonian which we will study here, it is useful to describe first the fully quantum Holstein model in order to make clear the physical approximations and to identify the anti-integrable limit. It is the sum of three terms,

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

(i) H_k is the Hamiltonian of a single band of noninteracting electrons in a tight-binding representation,

$$H_k = -T \sum_{\langle i,j\rangle,\sigma} c^+_{i,\sigma} c_{j,\sigma} \tag{2a}$$

where T is the transfer integral between neighboring sites $\langle i, j\rangle$ on a

d-dimensional square lattice $\mathbb{Z}^d$ and σ is the electron spin $\pm 1/2$ along the z direction denoted $\uparrow$ or $\downarrow$. Here $c^+_{i,\sigma}$ and $c_{i,\sigma}$ are the standard anticommuting creation and annihilation fermions operators of an electron at site $i \in \mathbb{Z}^d$ with spin σ, respectively, for which we recall that the anticommutators fulfill

$$\{c^+_{i,\sigma}, c_{j,\sigma'}\} = c^+_{i,\sigma} c_{j,\sigma'} + c_{j,\sigma'} c^+_{i,\sigma} = \delta_{\sigma,\sigma'} \delta_{i,j} \tag{2b}$$

where $\delta_{i,j} = 0$ for $i \neq j$ and $\delta_{i,j} = 1$ for $i = j$, and $\{c_{i,\sigma}, c_{j,\sigma'}) = \{c^+_{i,\sigma}, c^+_{j,\sigma'}\} = 0$. This Hamiltonian is often written in its diagonal form in the reciprocal space representation as

$$H_k = \sum_{q,\sigma} E(q)\, c^+_\sigma(q)\, c_\sigma(q) \tag{3a}$$

with

$$E(q) = -2T \sum_{\alpha=1}^{d} \cos q_\alpha \tag{3b}$$

For a d-cubic finite system $\mathbb{C} \subset \mathbb{Z}^d$ with N^d sites and standard periodic boundary conditions, $q = \{q_\alpha = 2\pi p_\alpha / N\}$, $\alpha = 1, 2, ..., d$, where p_α are integers fulfilling $-N/2 < p_\alpha \leqslant N/2$. The sum in (3a) then becomes finite, with new fermion in (3a), which are

$$c_\sigma(q) = N^{-d/2} \sum_{n \in \mathbb{C}} c_{n,\sigma} e^{iqn} \tag{4a}$$

$$c^+_\sigma(q) = [c_\sigma(q)]^* = N^{-d/2} \sum_{n \in \mathbb{C}} c^+_{n,\sigma} e^{-iqn} \tag{4b}$$

The ground state $|G\rangle$ of this free-electron Hamiltonian H_k is given by the Fermi rule. The fermion states q, σ are occupied, provided that $E(q)$ is smaller than E_F, the Fermi energy. This is chosen in order that the number of occupied states, which is the number of electrons, is fixed to a given number $0 < P < 2N^d$. In other words,

$$|G\rangle = \prod_{E_q \leqslant E_F} c^+_{q\uparrow} c^+_{q\downarrow} |0\rangle \tag{4c}$$

where $|O\rangle$ is the vacuum.

(ii) H_p is the Hamiltonian of quantum phonons corresponding to a dispersionless optical branch (constant-frequency Einstein oscillators)

$$H_p = \sum_i \hbar\omega_0 (a_i^+ a_i + \tfrac{1}{2}) \tag{5a}$$

where a_i^+ and a_i are the standard commuting creation and annihilation boson operators of phonons at site i, respectively. We recall the standard boson commutation rule

$$[a_i, a_j^+] = a_i a_j^+ - a_j^+ a_i = \delta_{i,j} \tag{5b}$$

This Hamiltonian has a trivial ground state, which is the vacuum (no boson or phonon).

(iii) These two Hamiltonians H_k and H_p are coupled by the on-site electron–phonon interaction H_{ep} with constant g, described by the Hamiltonian

$$H_{ep} = g \sum_i \mathbf{n}_i (a_i^+ + a_i) \tag{6a}$$

where the electronic density operator at site i is

$$\mathbf{n}_i = c_{i\uparrow}^+ c_{i\uparrow} + c_{i\downarrow}^+ c_{i\downarrow} \tag{6b}$$

Of course, H_{ep} does not commute with H_k and H_p. In previous papers,[6,9–12] we introduced two dimensionless independent parameters

$$\gamma = \frac{\hbar\omega_0}{T} \tag{7a}$$

measuring the "quantum character" of the phonons, and

$$k = \frac{2g}{(\hbar\omega_0 T)^{1/2}} \tag{7b}$$

which is the reduced electron–phonon coupling constant in the classical phonon limit. (Thus, unlike the constant γ, this constant k has to be insensitive to the phonon energy quanta $\hbar\omega_0$, which implies that k does not depend on any isotopic substitution.)

In this paper, it turns out to be more convenient to introduce different notations. We set

$$\mathbf{u}_n = \frac{\hbar\omega_0}{4g}(a_n^+ + a_n) = \frac{\sqrt{\gamma}}{2k}(a_n^+ + a_n) \tag{8a}$$

as the atomic position operator (in appropriate units) and its conjugate momentum

$$\mathbf{p}_n = \frac{2g}{\hbar\omega_0} i(a_n^+ - a_n) = \frac{ik}{\sqrt{\gamma}}(a_n^+ - a_n) \tag{8b}$$

with commutator

$$[\mathbf{u}_n, \mathbf{p}_m] = i\delta_{m,n} \tag{8c}$$

Then, the initial Hamiltonian **H** can be represented in units of energy

$$E_0 = \frac{8g^2}{\hbar\omega_0} \tag{9a}$$

and becomes the sum of three terms,

$$\hat{H} = \frac{H}{E_0} = H_{AI} + tH_K + \beta H_Q \tag{9b}$$

where

$$H_{AI} = \sum_i \frac{1}{2}(\mathbf{u}_i^2 + \mathbf{n}_i \mathbf{u}_i) \tag{9c}$$

$$H_K = -\frac{1}{2} \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^+ c_{j,\sigma} \tag{9d}$$

$$H_Q = \frac{1}{2} \sum_i \mathbf{p}_i^2 \tag{9e}$$

The amplitudes of the perturbations, which are the electronic and lattice kinetic energy terms, are given respectively by

$$t = \frac{T\hbar\omega_0}{4g^2} = \frac{1}{k^2} > 0 \tag{10a}$$

and

$$\beta = \frac{1}{4}\left(\frac{\hbar\omega_0}{2g}\right)^4 = \frac{1}{4}\left(\frac{\gamma}{k^2}\right)^2 \tag{10b}$$

2.2. The Anti-Integrable and the Adiabatic Limit

In the limit where t and β are both zero, this Hamiltonian becomes essentially the potential energy of the initial Hamiltonian where all *lattice and electronic quantum* terms have been dropped. More generally, we propose the following definition.

Anti-Integrability. A tight-binding electron–phonon Hamiltonian without kinetic terms (concerning both the electrons and the lattice) is called anti-integrable.

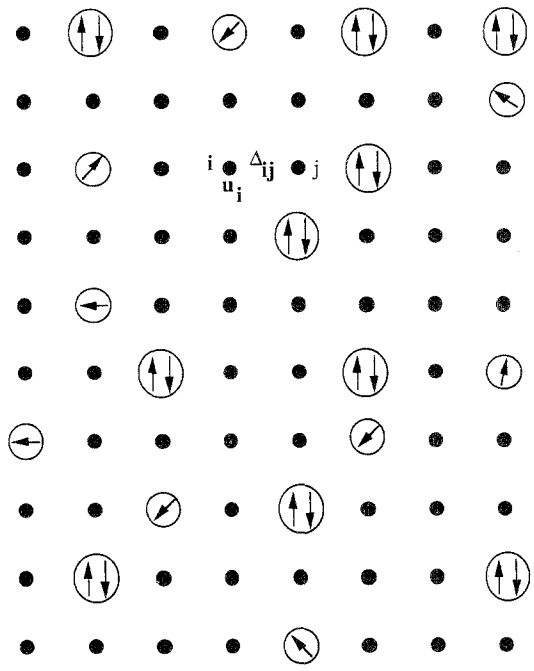

Fig. 1. A random electronic configuration on a two-dimensional square lattice at the anti-integrable limit. The black dots represent empty sites i, $n_{i\uparrow} = n_{i\downarrow} = 0$, the open circles with two opposite arrows represent the doubly occupied sites $n_{i\uparrow} = n_{i\downarrow} = 1$ (bipolarons), and the smaller open circles with a single arrow represent the singly occupied sites $n_{i\uparrow} + n_{i\downarrow} = 1$ (polarons) (in the absence of a magnetic field, the single electrons have a arbitrary spin).

The eigenstates of such a Hamiltonian, built only with the commuting operators n_i and u_i, are trivial and correspond to any arbitrary distribution of electrons where $n_{i\uparrow} = \langle \mathbf{n}_{i\uparrow} \rangle = 0$ or 1 and $n_{i\downarrow} = \langle \mathbf{n}_{i\downarrow} \rangle = 0$ or 1 (see Fig. 1). We have

$$u_i = -\frac{n_{i\uparrow} - n_{i\downarrow}}{2} = 0, -\frac{1}{2}, \text{ or } -1 \tag{11a}$$

The wave function of these states is

$$|G\rangle = \prod_i \delta\left(u_i + \frac{n_i}{2}\right) \times \prod_i (1 - n_{i\uparrow} + n_{i\uparrow} c_{o\uparrow}^+) \prod_i (1 - n_{i\downarrow} + n_{i\downarrow} c_{i\downarrow}^+) |O\rangle \tag{11b}$$

where $|O\rangle$ is the vacuum. $\delta(x)$ is the Dirac function. Thus, the whole set

of eigenstates of the system is labeled by random configurations of electrons. This situation is formally similar to those of structural models and dynamical systems at their anti-integrable limit.[1]

Let us emphasize that nevertheless the anti-integrable Hamiltonian does not describe the "dynamics of some associated classical system." In fact, this limit is highly singular and physically pathological. This situation was also true for dynamical systems, where the hyperbolicity of the anti-integrable trajectories is infinite, or equivalently for anti-integrable structures, the coherence length is strictly zero.

In spite of this, a perturbation theory can be built from this limit and yields physical results. Thus, for dynamical systems, *nonsingular* chaotic trajectories or structures are obtained as smooth, continuous functions of the amplitude of the perturbation. In the present model, we are able to perform this perturbation theory only with respect to the kinetic energy of the electron ($t \neq 0$) and *without any quantum lattice fluctuations* ($\beta = 0$) which then define the adiabatic Holstein model. Note that because of definition (10a), a small kinetic energy for the electrons (t small) is equivalent to a large electron–phonon coupling (k large).

Adiabadicity. A tight-binding electron–phonon Hamiltonian without lattice kinetic energy terms ($\beta = 0$) is called adiabatic.

In that limit, the operator $\mathbf{u}_i$ commutes with the Hamiltonian and thus can be considered as a scalar variable $u_i = \langle \mathbf{u}_i \rangle$. The adiabatic approximation is widely used for physical models because the mass of the atoms is much larger by several orders of magnitude than the mass of the electrons. It is often (but not always) a good approximation. Its validity is rarely checked, but it should be. In further publications, it will be shown that the condition for the validity of the adiabatic approximation requires the existence of a finite gap for the phonon spectrum, which indeed is a condition fulfilled by the bipolaronic and mixed polaronic–bipolaronic states predicted to exist in this paper.

In this paper, we only consider the adiabatic Holstein Hamiltonian ($\beta = 0$), on which we can obtain rigorous results

$$\hat{H}_{ad} = \sum_i \frac{1}{2}(u_i^2 + \mathbf{n}_i u_i) - \frac{t}{2} \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^+ c_{j,\sigma} \tag{12a}$$

For any finite piece of lattice in $\mathbb{Z}^d$, the electronic part of the Hamiltonian can be formally diagonalized

$$\hat{H}_{ad} = \sum_i \frac{1}{2} u_i^2 + \frac{1}{2} \sum_{\nu,\sigma} E_\nu(\{u_i\}) c_{\nu,\delta}^+ c_{\nu,\sigma} \tag{12b}$$

with

$$c_{\nu,\sigma} = \sum_n \Psi_n^\nu c_{n,\sigma} \tag{13a}$$

and

$$c_{\nu,\sigma}^+ = (c_{\nu,\sigma})^* \tag{13b}$$

where $\{\Psi_n^\nu\}$ are normalized

$$\sum_n |\Psi_n^\nu|^2 = 1 \tag{13c}$$

and fulfill the eigenequations

$$-t(\bar{\bar{\Delta}}\Psi^\nu)_n + u_n \Psi_n^\nu = E_\nu(\{u_i\})\Psi_n^\nu \tag{14a}$$

with eigenenergies $E_\nu(\{u_i\})$. This equation can be written formally as

$$\bar{\bar{A}}(\{u_i\}) \cdot \bar{\Psi}^\nu = E_\nu(\{u_i\})\bar{\Psi}^\nu \tag{14b}$$

with the electronic Hamiltonian defined as

$$\bar{\bar{A}}(\{u_i\}) = \bar{\bar{D}}(\{u_i\}) - t\bar{\bar{\Delta}} \tag{14c}$$

The diagonal part $\bar{\bar{D}}(\{u_i\})$ of $\bar{\bar{A}}(\{u_i\})$ describes the interaction of the electrons with the lattice distortion $\{u_n\}$,

$$D_{n,m} = u_n \delta_{n,m} \tag{14d}$$

and the operator $\bar{\bar{\Delta}} = \{\Delta_{n,m}\}$,

$$(\bar{\bar{\Delta}}\Psi^\nu)_n = \sum_{m \curlyvee n} \Psi_m^\nu = \sum_m \Delta_{n,m} \Psi_m^\nu \tag{14e}$$

corresponds to the kinetic electronic energy. We denote by $m \curlyvee n$ the nearest neighboring site m to site n. Thus, the sum (14e) is done over m on the d-dimensional square lattice. In other words, we have $\Delta_{n,m} = 1$ if $m \curlyvee n$ and $\Delta_{n,m} = 0$ otherwise. The diagonal terms of $\bar{\bar{\Delta}}$ are zero.

The eigenstates of the adiabatic Holstein Hamiltonian are obtained as extrema of the variational form

$$\Phi(\{u_i\}; \{\sigma_\nu\}) = \Phi_{\text{elast}}(\{u_i\}) + \Phi_{\text{electr}}(\{u_i\}; \{\sigma_\nu\}) \tag{15a}$$

which is then sum of the elastic energy of the lattice and of the electronic energy:

$$\Phi_{\text{elast}}(\{u_i\}) = \sum_i \frac{1}{2} u_i^2 \tag{15b}$$

$$\Phi_{\text{electr}}(\{u_i\}; \{\sigma_\nu\}) = \sum_\nu \sigma_\nu E_\nu(\{u_i\}) \tag{15c}$$

The electronic energy depends on the population factor $\{\sigma_\nu\}$ of the electronic eigenstates ν, which can be chosen in various ways.

2.3. Extensions of the Adiabatic Holstein Model to Arbitrary Lattices

Instead of working with this special operator (14e), it will hardly cost more work in the following to consider more generally an arbitrary self-adjoint operator $\bar{\bar{A}}$ defined for an arbitrary nonexponential lattice. Let us define precisely what is a nonexponential lattice.

Definition 1. We call a lattice $\mathbb{L} = \{\mathbb{A}, \mathbb{B} \subset \mathbb{A} \times \mathbb{A}\}$ the association of a countable set $\mathbb{A}$ of points i called sites and of a set $\mathbb{B} = \{(i, j)\}$ of connected sites (called bonds) fulfilling the conditions $(i, i) \notin \mathbb{B}$ for all i and $(i, j) \in \mathbb{B} \Rightarrow (j, i) \in \mathbb{B}$. Connected sites are called nearest neighbors. A connected path $\{q_\iota\}$ with length p between two given sites n and m on the lattice $\mathbb{L}$ is a sequence of $p+1$ sites q_ι ($\iota = 0, 1, \ldots, p$) such that $q_0 = m$ and $q_p = n$ and such that $[q_\iota, q_{\iota+1}]$ are nearest neighbors.

We assume in the following that there exists a connected path with a finite length between any pair of sites $(m, n) \in \mathbb{A} \times \mathbb{A}$ (percolation condition for the lattice $\mathbb{L}$). The distance on the lattice between n and m then can be defined for all pairs of sites.

Definition 2. The minimum length $p = \mathcal{d}(m, n)$ of the connected paths which connect two given sites n and m of the lattice $\mathbb{L}$ is the distance between m and n. For $m = n$, $\mathcal{d}(n, n) = 0$.

It is straightforward to check that $\mathcal{d}(m, n)$ satisfies the properties of a distance. For example, for a d-dimensional square lattice $\mathbb{Z}^d$, we have $\mathcal{d}(m, n) = |m - n| = \sum_{\alpha=1}^{d} |m_\alpha - n_\alpha|$, where $\{m_\alpha\}$ (or $\{n_\alpha\}$) are the d integer coordinates of m (or n).

We define $N_{\mathbb{L}}(r; n)$ as the number of sites m at distance r to a given site n and $N_{\mathbb{L}}(r) = \text{Sup}_n N_{\mathbb{L}}(r; n)$. Then we make the following statement.

Definition 3. A lattice $\mathbb{L}$ is called nonexponential when for any strictly positive number λ, we have $\sum_r N_{\mathbb{L}}(r) \exp(-\lambda r) = \varphi(\lambda) < +\infty$.

Since this series is absolutely convergent, $\varphi(\lambda)$ is a smooth, differentiable function of λ for $\lambda > 0$. Most lattices $\mathbb{L}$ of physical interest, such as standard periodic lattices and also fractal lattices, fulfill Definition 3 and thus are nonexponential. In most cases, the maximum number $N_{\mathbb{L}}(r)$ of sites m at distance r from a fixed site n is finite and grows algebraically as r^{D-1}, where D is some "dimension" which is called by various names in the physics literature depending on the context, for example, spreading, chemical, connectivity, or topological (...?) dimension.

By contrast, for a Bethe lattice (also called a Cayley tree in mathematics) with coordination number $n_{\mathbb{L}}$, the number of sites m at distance r of a site n of the lattice $\mathbb{L}$ is $n_{\mathbb{L}}^r$ for all n. For λ going to zero, the sum in Definition 3 becomes divergent. Thus, such a lattice is exponential. Although to some extent we could apply our theory but with some extra care to these exponential lattices, we ignore here the study of these lattices, with are not physically realistic.

We now consider the self-adjoint linear operator $\bar{\bar{A}}$ defined on such a lattice. It maps $\mathbb{C}^{\mathbb{A}} = \{\Psi_n \in \mathbb{C},\ n \in \mathbb{L}\}$ onto itself, where $\mathbb{C}$ is the set of complex numbers and $\mathbb{A}$ is the set of sites.

In the following, we assume: (i) the lattice $\mathbb{L}$ is nonexponential; (ii) $A_{i,j} = 0$ for sites i, j which are not nearest neighbors on the lattice $\mathbb{L}$ $[(i, j) \notin \mathbb{B}]$; in particular, $A_{i,i} = 0$ for all i, and (iii) the supremum norm $\|\bar{\bar{A}}\|_\infty = \mathrm{Sup}_i \sum_j |A_{i,j}|$ is finite.

Such an operator $\bar{\bar{A}}$ can be defined, for example, for all kinds of periodic lattices (triangular, honeycomb, etc.) and also for periodic lattices with electronic transfer integrals between next-nearest-neighboring sites and farther, provided that the transfer integral $A_{i,j}$ vanishes beyond some finite distance $D\,|i-j| > D$. It can be also extended to periodic lattices with randomly distributed missing bonds (percolation), to fractal lattices, to certain random lattices, etc. For a given lattice $\mathbb{L}$, electronic transfer integrals $A_{i,j}$ can be also chosen random, complex, or both, which will allow one to also consider the effect of magnetic fields.

The following lemma and propositions are proven for any lattice $\mathbb{L}$ and operator $\bar{\bar{A}}$ which fulfills the above conditions. The nonvanishing bounds t_3 to t_3' on t which appear in Thedorems 1 and 2 depend on several parameters involving the properties of the lattice $\mathbb{L}$ and the operator $\bar{\bar{A}}$. The method for having explicit bounds is given, but the explicit calculation for each specific model is left to the reader. In order to fix the ideas, we only calculate explicitly t_3 and t_3' for the standard d-dimensional square lattice $\mathbb{A} = \mathbb{Z}^d$, $\mathbb{B} = \{(i, j) \in \mathbb{Z}^d \times \mathbb{Z}^d,\ |i-j| = 1\}$.

Our proofs are performed for arbitrary large finite subsets $\mathbb{S}$ with arbitrary topology of the considered lattice $\mathbb{L}$. Then, the operators $\bar{\bar{A}}$, $\bar{\bar{\Delta}}$, and $\bar{\bar{D}}$ are restricted to $\mathbb{S} \subset \mathbb{L}$ (which means that we set $A_{n,m}=0$ and $\Delta_{n,m}=0$ if $n \notin \mathbb{S}$ or $m \notin \mathbb{S}$). We take advantage of the fact that $\bar{\bar{A}}_{\mathbb{S}}$ involves a finite number of eigenvalues and eigenvectors which can be used in finite sums without any convergence problems. The final bounds turn out to be independent of the finite subset $\mathbb{S} \subset \mathbb{L}$. To be complete, we prove that the limits of the bipolaronic and mixed polaronic–bipolaronic configurations for the infinite system are well defined.

3. CHAOTIC POLARONIC AND BIPOLARONIC STATES: EXISTENCE THEOREMS

At the anti-integrable limit ($t=0$), the electronic eigenstates are trivially localized at the lattice sites of $\mathbb{L}$. According to the Pauli principle, each of these eigenstates is either empty, occupied by a single electron with arbitrary spin, or doubly occupied by two electrons with opposite spins. Thus, the many-bipolaronic and the mixed polaronic–bipolaronic states are obviously well defined at this limit.

3.1. Bipolaronic and Mixed Polaronic–Bipolaronic States at the Anti-Integrable Limit ($t=0$)

We first examine the simplest case corresponding to the bipolaronic states, where, by definition, the electronic eigenstates are either doubly occupied by a pair of electrons or are empty. Then, the electronic eigenstate of the whole system can be characterized by a pseudospin configuration $\{\sigma_i\}$ defined as

$$\sigma_i = \frac{n_{i\uparrow} + n_{i\downarrow}}{2} = 0 \text{ or } 1 \tag{16a}$$

(*Warning:* These pseudospins σ_i which take two values 0 or 1 must not be confused with the physical spins of the electrons.)

The extremalization of the adiabatic energy (15) yields that the lattice distortion at the sites i which are doubly occupied ($\sigma_i=1$) is $u_i=-1$, which is also the corresponding electron eigenenergy E_v at this site. For sites i which are empty ($\sigma_i=0$), the lattice distortion is $u_i=0$ and there is a zero electron eigenenergy E_v. Since a pair of electrons localized on a single site and associated with a lattice distortion is called a bipolaron, these structures are by construction bipolaronic structures. The pseudospin

configuration $\{\sigma_i\}$ explicitly describes the spatial distribution of these bipolarons.

Since the doubly occupied states are degenerate at the eigenenergies -1 and the empty states at the eigenenergies 0, the electronic part of the system is in its ground state with a Fermi energy E_F which can be chosen arbitrarily in the electronic gap $]-1, 0[$. For example, $E_F = -1/2$ is a convenient choice. For these bipolaronic states at the anti-integrable limit, the electronic population factors $\{\sigma_v\}$ in (15c) can be given by a simple characteristic function

$$\sigma_v = \chi(E_v) \tag{16b}$$

Then,

$$\chi(x) = 1 \qquad \text{for} \quad x < E_F = -\tfrac{1}{2} \tag{16c}$$

$$\chi(x) = 0 \qquad \text{for} \quad x > E_F = -\tfrac{1}{2} \tag{16d}$$

When switching on the electronic kinetic energy terms $t \neq 0$, it is essential to keep this electronic population factor invariant in order to preserve the continuity of the investigated state when varying the perturbation.

More generally, at the anti-integrable limit, the electrons can be taken in excited states. The electronic eigenstates may be empty, singly occupied, or doubly occupied. Since there is no electron–electron interaction in the model, the energy of the whole system (15a) does not depend on the *physical spins* $\uparrow$ or $\downarrow$ of the single electrons and the total energy (15) only depends on the pseudospin configuration $\{\sigma_i\}$,

$$\sigma_i = \frac{n_{i\uparrow} + n_{i\downarrow}}{2} = 0, \frac{1}{2}, \text{ or } 1 \tag{17a}$$

where σ_i now can take three different values. At sites i where $\sigma_i = 1/2$, there is a localized single electron associated with a lattice distortion which is called a polaron, while at sites where $\sigma_i = 1$, there is a bipolaron. Thus, these structures are called mixed polaronic–bipolaronic states. Since the eigenenergy of the localized electronic state and the lattice distortion at site i are both equal to $-\sigma_i$, the population factor in (15c)

$$\sigma_v = \chi(E_v) \tag{17b}$$

can be defined by a function $\chi(x) = 0$, 1/2, or 1 which takes three values

instead of two as in the purely bipolaronic case. We can choose, for example,

$$\chi(x) = 1 \quad \text{for} \quad x < E_{F1} = -\tfrac{3}{4} \tag{17c}$$

$$\chi(x) = \tfrac{1}{2} \quad \text{for} \quad E_{F1} < x < E_{F2} = -\tfrac{1}{4} \tag{17d}$$

$$\chi(x) = 0 \quad \text{for} \quad E_{F2} < x \tag{17e}$$

E_{F1} and E_{F2} belong to their corresponding gaps of the electronic eigenenergies. As for the pure bipolaronic case, this electronic population factor will be kept invariant when switching on the electronic kinetic energy term.

Since the electronic population factor $\sigma_v = \chi(E_v)$ is well-defined by (16) or (17), the variational form (15) is also well-defined and the problem which consists in its extremalization takes a form similar to those which we studied for Hamiltonian dynamical systems.

We are going to prove that each of these eigenstates at the anti-integrable limit (characterized by an arbitrary pseudospin configuration $\{\sigma_i\}$) persists and depends uniformly on small enough perturbations due to a nonvanishing electronic kinetic energy term in the Hamiltonian, that is, for small enough t or equivalently for large enough electron–phonon coupling k defined by (7b). Since it will be also proven that their physical properties (electronic gaps, defectibility, etc.) at the anti-integrable limit are also preserved, *physical continuity* makes it reasonable to keep the terms bipolaronic states or mixed polaronic–bipolaronic states for these persisting states.

3.2. Perturbations of the Bipolaronic States

We study first the perturbations at the anti-integrable limit of the bipolaronic structures characterized by pseudospins σ_i which take two values 0 or 1. We consider a finite part $\mathbb{S}$ of the infinite lattice $\mathbb{L}$ with arbitrary shape with N sites and P electron pairs with $0 < P < N$. The bound t_3 on t which will be found for the existence of bipolaronic states is independent of P, of N, and of the shape and the size of the finite system $\mathbb{S}$. It thus remains valid for arbitrarily large and thus infinite systems in the physical sense.

Our strategy for performing an exact perturbation theory for these bipolaronic states at the anti-integrable limit is based on the following scheme:

1. Define an operator $\mathbf{S}$, which maps $\mathbb{R}^{\mathbb{S}}$ onto itself and such that its fixed points are extrema of the variational form (15a) for the population factor defined by (16).

2. For each given pseudospin configuration $\{\sigma_n\}$, defined a compact domain $\mathscr{E}(\{\sigma_n\};\tau)\subset\mathbb{R}^{\mathbb{S}}$ which is a closed ball with radius τ, the center of which is (approximately) configuration $\{\sigma_n\}$.

3. For a given τ and t, find τ' such that $\mathbf{S}_t$ maps $\mathscr{E}(\{\sigma_n\};\tau)$ into $\mathscr{E}(\{\sigma_n\};\tau')$.

4. Find an upper bound for $\|\partial\mathbf{S}_t\|_\infty$ restricted to the domain $\mathscr{E}(\{\sigma_n\};\tau)$.

5. Show that τ can be chosen in order that there exists t_1 such that for $t<t_1$, $\mathscr{E}(\{\sigma_n\};\tau)$ is stable by $\mathbf{S}_t$ (which is obtained for $\tau'<\tau$), and t_2 such that for $t<t_2$, we have $\|\partial\mathbf{S}_t\|_\infty<K_0$ in the domain $\mathscr{E}(\{\sigma_n\};\tau)$, where K_0 is a constant strictly smaller than 1.

When $t<t_3=\mathrm{Min}(t_1,t_2)$, according to the Banach fixed-point theorem, there exists a unique fixed point for $\mathbf{S}_t$ in $\mathscr{E}(\{\sigma_n\};\tau)$ which will prove Theorem 1.

Remark 1. The ball $\mathscr{E}(\{\sigma_n\};\tau)$ with radius τ is defined with the Banach metric $d(\{u_n\},\{v_n\})=\mathrm{Sup}_{n\in\mathbb{S}}|u_n-v_n|$. Since we wish to apply the Banach fixed-point theorem[8] in this *finite closed* ball, the condition $\|\partial\mathbf{S}_t\|_\infty<K_0<1$ has to be fulfilled for *the supremum norm* $\|\partial\mathbf{S}\|_\infty$ of $\mathbf{S}_t$ in order that this condition implies $d(\mathbf{S}_t(\{u_n\}),\mathbf{S}_t(\{v_n\})<K_0 d(\{u_n\},\{v_n\})$ and that $\mathbf{S}_t$ be contracting in $\mathscr{E}(\{\sigma_n\};\tau)$.

It is essential for a clear understanding of the following proofs to recall some standard definitions for operator norms. The norm of an operator $\bar{\bar{B}}$ depends on the norm which is used for the space of vectors $\bar{X}$ on which this operator is defined. We essentially use the following.

1. The supremum norm

$$\|\bar{\bar{B}}\|_\infty=\mathrm{Sup}_{\bar{X}\neq 0}\frac{\|\bar{\bar{B}}\bar{X}\|_\infty}{\|\bar{X}\|_\infty}$$

of a given operator $\bar{\bar{B}}$ is defined when the norm which is used for $\bar{X}=\{X_i\}$ is the supremum norm $\|\bar{X}\|_\infty=\mathrm{Sup}_i|X_i|$. Then, we have $\|\bar{\bar{B}}\|_\infty=\mathrm{Sup}_i\sum_j|B_{i,j}|$, where $B_{i,j}$ are the matrix elements of $\bar{\bar{B}}$.

2. The spectral norm

$$\|\bar{\bar{B}}\|_2=\mathrm{Sup}_{\bar{X}\neq 0}\frac{\|\bar{\bar{B}}\bar{X}\|_2}{\|\bar{X}\|_2}$$

of the operator $\bar{\bar{B}}$ is defined when the Hilbert norm $\|\bar{X}\|_2=(\sum_i X_i X_i^*)^{1/2}$ is used for $\bar{X}$. For a self-adjoint operator, $\|\bar{\bar{B}}\|_2$ is also the supremum of

the modulus of the spectrum of $\bar{\bar{B}}$ (for a finite operator, it is the largest eigenvalue modulus).

The standard inequality $\|\bar{\bar{B}}\|_2 \leqslant \|\bar{\bar{B}}\|_\infty$ holds between these two norms. In general, these two norms are not equivalent: note, for example, that for some operators $\bar{\bar{B}}$, $\|\bar{\bar{B}}\|_2$ may be finite while $\|\bar{\bar{B}}\|_\infty$ is infinite.

The unpublished proofs of the theorem (essentially Theorem 1 in the following) which we described in early papers[10–13] were wrong because we confused norms $\|\cdot\|_2$ and $\|\cdot\|_\infty$. More precisely, we proved the existence of a constant $K_0 < 1$ under appropriate conditions such that $\|\partial \mathbf{S}_t\|_2 < K_0$. This condition did not imply that $\|\partial \mathbf{S}_t\|_\infty < 1$ and thus did not warrant the conditions of applicability of the Banach fixed-point theorem. The new proof presented here of Theorem 1, which follows much of the ideas of the initial one, is now correct, but we paid for this correction by more technical and tedious calculations. Finally, the theorem given in early references was confirmed, but for bounds on t smaller than initially.

Definition of Operator S_t. For $\{u_i\} \in \mathbb{R}^{\mathbb{S}}$, the extrema of $\Phi(\{u_i\}; \{\sigma_\nu\})$ satisfy the equation

$$0 = \frac{\partial \Phi(\{u_i\}; \{\sigma_\nu\})}{\partial u_n} = u_n + \sum_\nu \sigma_\nu \frac{\partial E_\nu}{\partial u_n} = u_n + \sum_\nu \sigma_\nu |\Psi_n^\nu(\{u_i\})|^2 \quad (18a)$$

obtained by using the standard perturbation theory of Schrödinger operators. The $\{\Psi_n^\nu\}$ are the eigensolutions of eigenequation (14b). We define the operator $\mathbf{S}_t$ applied to an arbitrary configuration $\{u_n\}$ as

$$\{v_n\} = \mathbf{S}_t(\{u_n\}) \quad (18b)$$

where

$$v_n = -\sum_\nu \sigma_\nu |\Psi_n^\nu(\{u_i\})|^2 \quad (18c)$$

This operator has been defined in order that its fixed points $\{u_n\}$, which fulfill $\{u_n\} = \mathbf{S}_t(\{u_n\})$, are the solutions of Eq. (18a) and thus extrema of the variational form (15a). By the definition of (18c), $-v_n$ is the density of electron pairs at site n for the lattice potential $\{u_n\}$, which is obviously between 0 and 1 since $\sum_\nu |\Psi_n^\nu|^2 = 1$. Consequently, we have for all n

$$-1 \leqslant v_n \leqslant 0 \quad (18d)$$

We now study the operator $\mathbf{S}_t$ in a restricted compact domain $\mathscr{E}(\{\sigma_n\}; \tau) \subset \mathbb{R}^{\mathbb{S}}$ determined by the pseudospin configuration $\{\sigma_i\}$ given

arbitrarily and a given positive number $\tau < 1/2$. This domain $\mathscr{E}(\{\sigma_n\}; \tau) \subset \mathbb{R}^{\mathbb{S}}$ is defined as the set of configurations $\{u_n\} \in \mathscr{E}(\{\sigma_n\}; \tau)$ fulfilling for all $n \in \mathbb{S}$ the inequalities $-1 \leqslant u_n \leqslant 0$ and $|u_n + \sigma_n| \leqslant \tau$, or equivalently

$$\left| u_n + \sigma_n(1-\tau) + \frac{\tau}{2} \right| \leqslant \frac{\tau}{2} \tag{19a}$$

For any $\{u_n\} \in \mathscr{E}(\{\sigma_n\}; \tau)$, it is convenient to write

$$u_n = -(1-\tau)(\sigma_n + \varepsilon_n) + \frac{\tau}{2} \tag{19b}$$

where

$$|\varepsilon_n| \leqslant \frac{\tau}{2(1-\tau)} \tag{19c}$$

We first prove a lemma which asserts that for an appropriate domain of parameters, there always exists a nonvanishing gap in the electronic spectrum given by (14b) which separates the occupied electronic states at lower energy from the empty states at larger energy. Thus, in a domain close to the anti-integrable limit, we avoid degeneracy problems due to the possible crossing of occupied eigenenergies with an empty eigenenergy.

This lemma involves essentially the spectral norm $\|\bar{\bar{A}}\|_2$ of the operator $\bar{\bar{A}}$ [defined by (14e)] which is twice the dimension d for a square lattice.

Lemma 1. For $0 < \tau < 1/2$ and any configuration $\{u_n\}$ in $\mathscr{E}(\{\sigma_n\}, \tau)$, let us consider the eigenequation (14b) with operator $\bar{\bar{A}}_{\mathbb{S}}$ restricted to a finite lattice subset $\mathbb{S} \subset \mathbb{L}$ with N sites. Let us set $P = \sum_{i \in \mathbb{S}} \sigma_i$.

Then, for

$$t \leqslant \frac{1-2\tau}{2\|\bar{\bar{A}}\|_2} = t_0 \tag{20a}$$

$\bar{\bar{A}}_{\mathbb{S}}$ has P eigenvalues in the closed interval $[-1 - \|\bar{\bar{A}}\|_2 \cdot t, -1 + \|\bar{\bar{A}}\|_2 \cdot t + \tau]$ and the $N-P$ other eigenvalues in the closed interval $[-\|\bar{\bar{A}}\|_2 \cdot t - \tau, \|\bar{\bar{A}}\|_2 \cdot t]$.

In other words, the eigenenergies E_v can be written as

$$E_v = -(1-\tau)(\sigma_v + \varepsilon_v) - \frac{\tau}{2} \tag{20b}$$

where σ_ν is the electronic population factor

$$|\varepsilon_\nu| \leqslant \frac{2\|\bar{\bar{A}}\|_2 \cdot t + \tau}{2(1-\tau)} \tag{20c}$$

For a periodic d-dimensional square lattice $\mathbb{L} = \mathbb{Z}^d$ with operator (14e), take $\|\bar{\bar{A}}\|_2 = 2d$ in (20a) and (20c).

Proof. The intervals $[-1-t\|\bar{\bar{A}}\|_2, -1+t\|\bar{\bar{A}}\|_2+\tau]$ and $[-t\|\bar{\bar{A}}\|_2-\tau, t\|\bar{\bar{A}}\|_2]$ do not overlap when condition (20a) is fulfilled. For $t=0$, the P eigenvalues of the diagonal operator $\bar{\bar{A}}$ are $\{u_n\}$. Because of (19b) and since $\sum_{n\in\mathbb{S}} \sigma_n = P$, there are P eigenvalues in the interval $[-1, -1+\tau]$ and $N-P$ eigenvalues in the interval $[-\tau, 0]$ and Lemma 1 is proven.

Let us now consider $t \neq 0$. When z does not belong to the extended intervals $[-1-t\|\bar{\bar{A}}\|_2, -1+t\|\bar{\bar{A}}\|_2+\tau]$ or $[-t\|\bar{\bar{A}}\|_2-\tau, t\|\bar{\bar{A}}\|_2]$, the shortest distance of z to the spectrum of $\bar{\bar{D}}$ is strictly larger than $t\|\bar{\bar{A}}\|_2$; then we have

$$\|(z\bar{\bar{1}} - \bar{\bar{D}})^{-1}\|_2 < \frac{1}{t\|\bar{\bar{A}}\|_2} \tag{21a}$$

and

$$\|t\bar{\bar{A}}(z\bar{\bar{1}} - \bar{\bar{D}})^{-1}\|_2 < 1 \tag{21b}$$

The inverse of the operator $(z\bar{\bar{1}} - \bar{\bar{A}})$ with $\bar{\bar{A}} = \bar{\bar{D}} - t\bar{\bar{A}}$ can be written as a convergent series,

$$(z\bar{\bar{1}} - \bar{\bar{A}})^{-1} = (z\bar{\bar{1}} - \bar{\bar{D}})^{-1} \sum_{n=0}^{\infty} (-t)^n (\bar{\bar{A}}(z\bar{\bar{1}} - \bar{\bar{D}})^{-1})^n \tag{21c}$$

with a bounded spectral norm and thus is invertible. Consequently, the whole set of eigenvalues of Eq. (14b) is included in the union I of intervals

$$I = [-1-t\|\bar{\bar{A}}\|_2, -1+t\|\bar{\bar{A}}\|_2+\tau] \cup [-t\|\bar{\bar{A}}\|_2-\tau, t\|\bar{\bar{A}}\|_2] \tag{21d}$$

Since for a fixed set $\{u_n\}$ the eigenvalues E_ν are continuous function of t, and for $t=0$ the number of eigenvalues in each interval remains constant, Lemma 1 is proven. QED

Now we can use this lemma for proving a property which allows one to determine domains $\mathscr{E}(\{\sigma_n\}, \tau)$ stable under the operator $\mathbf{S}_t$ when $\tau' < \tau$.

Proposition 1. For any pseudospin configuration $\{\sigma_n\}$ restricted to an arbitrary finite subset $\mathbb{S} \subset \mathbb{L}$ and $t \leqslant t_0$ [defined in (20a)], the operator $\mathbf{S}_t$ maps $\mathscr{E}(\{\sigma_n\}, \tau)$ into $\mathscr{E}(\{\sigma_n\}, \tau')$, where

$$\tau' = \frac{4t^2 S_{\Delta} + \tau^2}{4(1-\tau)(1-2\tau-2t\|\bar{\bar{\Delta}}\|_2)} \tag{22a}$$

with

$$S_{\Delta} = \operatorname*{Sup}_n \sum_m |\Delta_{n,m}|^2 \leqslant \|\bar{\bar{\Delta}}\|_2^2 \tag{22b}$$

For a periodic d-dimensional square lattice $\mathbb{L} = \mathbb{Z}^d$ with operator (14e), let us take $\|\bar{\bar{\Delta}}\|_2 = S_{\Delta} = 2d$ in (22a).

Proof. For a finite lattice $\mathbb{S}$ with N sites, the matrix of the operator $\bar{\bar{A}}_{\mathbb{S}} = \bar{\bar{D}} - t\bar{\bar{\Delta}}$ which corresponds to the first member of Eq. (14b) is an $N \times N$ symmetric matrix with a complete base of N orthogonal and normalized eigenvectors $\{\Psi_n^{\nu}\}$ which thus fulfill

$$\sum_{\nu} \Psi_n^{\nu} \Psi_m^{\nu *} = \delta_{m,n} \tag{23a}$$

Multiplying both members of (14b) by $\Psi_n^{\nu *}$ and summing over the index ν, this property yields

$$u_n = \sum_{\nu} E_{\nu}(\{u_i\}) |\Psi_n^{\nu}|^2 \tag{23b}$$

The eigenequation $\bar{\bar{A}} \bar{\Psi}^{\nu} = E_{\nu}(\{u_i\}) \bar{\Psi}^{\nu}$ implies

$$\bar{\bar{A}}^2 \bar{\Psi}^{\nu} = (\bar{\bar{D}}^2 - t\bar{\bar{\Delta}}\bar{\bar{D}} - t\bar{\bar{D}}\bar{\bar{\Delta}} + t^2\bar{\bar{\Delta}}^2)\bar{\Psi}^{\nu} = E_{\nu}^2(\{u_i\})\bar{\Psi}^{\nu} \tag{24a}$$

or

$$u_n^2 \Psi_n^{\nu} - t u_n \bar{\bar{\Delta}} \Psi_n^{\nu} - t\bar{\bar{\Delta}}(u_n \Psi_n^{\nu}) + t^2 \bar{\bar{\Delta}}^2 \Psi_n^{\nu} = E_{\nu}^2(\{u_i\}) \Psi_n^{\nu} \tag{24b}$$

After multiplication of both members of (24b) by $\Psi_n^{\nu *}$ and summation over ν, we find after using (23a) that

$$u_n^2 + t^2 \sum_m |\Delta_{n,m}|^2 = \sum_{\nu} E_{\nu}^2(\{u_i\}) |\Psi_n^{\nu}|^2 \tag{24c}$$

For $\{u_n\} \in \mathscr{E}(\{\sigma_n\}, \tau)$ we now calculate the expression

$$I = \sum_{\nu} \left[E_{\nu} + \frac{\tau}{2} + (1-\tau)\sigma_n \right]^2 |\Psi_n^{\nu}|^2 \tag{25a}$$

By using the equalities (23b) and (24c),

$$I = t^2 \sum_m |\Delta_{n,m}|^2 + \left[u_n + \frac{\tau}{2} + (1-\tau)\sigma_n \right]^2 = t^2 \sum_m |\Delta_{n,m}|^2 + (1-\tau)^2 \varepsilon_n^2 \qquad (25b)$$

where we have used the definition (19b). Using (19c), we have

$$I \leqslant t^2 \sum_m |\Delta_{n,m}|^2 + \frac{\tau^2}{4} \leqslant t^2 S_\Delta + \frac{\tau^2}{4} \qquad (25c)$$

with S_Δ defined by (22b). This expression can be calculated differently by using the definition (20b),

$$I = (1-\tau)^2 \sum_v (\sigma_n - \sigma_v \times \varepsilon_v)^2 \, |\Psi_n^v|^2$$

$$\geqslant (1-\tau)^2 \left(\sum_v (\sigma_n - \sigma_v)^2 \, |\Psi_n^v|^2 - 2 \sum_v |\sigma_n - \sigma_v| \, |\varepsilon_v| \, |\Psi_n^v|^2 \right) \qquad (26a)$$

Using (20c) and the identity $(\sigma_n - \sigma_v)^2 = |\sigma_n - \sigma_v| = 0$ or 1, we find

$$I \geqslant (1-\tau)^2 \sum_v |\sigma_n - \sigma_v| \, (1 - 2|\varepsilon_v|) \, |\Psi_n^v|^2$$

$$\geqslant (1-\tau)^2 \left(1 - \frac{2\|\bar{\bar{\Delta}}\|_2 t + \tau}{1-\tau} \right) \sum_v |\sigma_n - \sigma_v| \, |\Psi_n^v|^2$$

$$= (1-\tau)(1 - 2\tau - 2t\|\bar{\bar{\Delta}}\|_2) \sum_v |\sigma_n - \sigma_v| \, |\Psi_n^v|^2 \qquad (26b)$$

By using the definition (18b) of $\{v_n\} = \mathbf{S}_t(\{u_n\})$, this inequality yields

$$I \geqslant (1-\tau)(1 - 2\tau - 2t\|\bar{\bar{\Delta}}\|_2) \, |\sigma_n + v_n| \qquad (26c)$$

Combination of inequalities (25c) and (26c) yields

$$|\sigma_n + v_n| \leqslant \frac{4t^2 S_\Delta + \tau^2}{4(1-\tau)(1 - 2\tau - 2t\|\bar{\bar{\Delta}}\|_2)} \qquad (27)$$

which readily implies Proposition 1, since $-1 \leqslant v_n \leqslant 0$. QED

Calculation of $\partial \mathbf{S}_t$. For continuing our proof, we have now to prove that the operator $\mathbf{S}_t$ becomes contracting for small enough t. For that purpose we consider the Jacobi matrix $\bar{\bar{J}}(\{u_n\})$ at a configuration $\{u_n\}$ of the operator $\mathbf{S}_t$,

$$\bar{\bar{J}} = \{J_{m,n}\} \qquad (28a)$$

with

$$J_{m,n} = \frac{\partial v_m}{\partial u_n} = -\sum_{\nu} \sigma_\nu \Psi_m^{\nu *} \frac{\partial \Psi_m^{\nu}}{\partial u_n} - \text{CC} \tag{28b}$$

CC means the complex conjugate of the previous term. In order to fix the ideas, we assume first that there is no degenerate eigenenergies. Then, standard perturbation theory for the eigensolutions of Eq. (14b) yields

$$\frac{\partial \Psi_m^{\nu}}{\partial u_n} = -\sum_{\nu' \neq \nu} \Psi_m^{\nu'} \frac{\Psi_n^{\nu' *} \Psi_n^{\nu}}{E_{\nu'} - E_\nu} \tag{29a}$$

and

$$\begin{aligned} J_{m,n} &= \sum_{\nu, \nu' \neq \nu} \sigma_\nu \Psi_m^{\nu *} \Psi_m^{\nu'} \frac{\Psi_n^{\nu' *} \Psi_n^{\nu}}{E_{\nu'} - E_\nu} + \text{CC} \\ &= \sum_{\nu, \nu' \neq \nu} \sigma_\nu (1 - \sigma_{\nu'} + \sigma_{\nu'}) \frac{\Psi_m^{\nu *} \Psi_m^{\nu'} \Psi_n^{\nu' *} \Psi_n^{\nu}}{E_{\nu'} - E_\nu} + \text{CC} \end{aligned} \tag{29b}$$

The expression $\sigma_\nu \sigma_{\nu'} \Psi_m^{\nu *} \Psi_m^{\nu'} \Psi_n^{\nu' *} \Psi_n^{\nu} / (E_{\nu'} - E_\nu) + \text{CC}$ is antisymmetric with respect to the indices ν and ν'. Thus, the sum of these terms in (29b) over ν and $\nu' \neq \nu'$ is zero and

$$J_{m,n} = \sum_{\nu, \nu'} \sigma_\nu (1 - \sigma_{\nu'}) \frac{\Psi_m^{\nu *} \Psi_m^{\nu'} \Psi_n^{\nu' *} \Psi_n^{\nu}}{E_{\nu'} - E_\nu} + \text{CC} \tag{29c}$$

We now note that in the conditions where Lemma 1 holds, the possible degeneracy between the eigenenergies E_ν never causes a problem in formula (29c) because $E_\nu = E_{\nu'}$ implies $\sigma_\nu = \sigma_{\nu'}$. Then, the prefactor $\sigma_\nu (1 - \sigma_{\nu'})$ in (29c) necessarily vanishes, which presents any divergence of $J_{m,n}$ due to the zero denominator in (29c). Consequently, when there is a nonzero gap between the occupied electronic states ($\sigma_\nu = 1$) and the empty electronic states ($\sigma_\nu = 0$), the matrix of derivatives $\bar{\bar{J}}$ remains well-defined even in the case of degenerate eigenenergies.

We have to find an upper bound for the supremum norm $\|\bar{\bar{J}}\|_\infty$ of operator $\bar{\bar{J}}$,

$$\|\bar{\bar{J}}\|_\infty = \operatorname{Sup}_{\bar{X}} \frac{\|\bar{\bar{J}} \cdot \bar{X}\|_\infty}{\|\bar{X}\|_\infty}, \qquad \text{where} \quad \|\bar{X}\|_\infty = \operatorname{Sup}_{i \in \mathbb{S}} |X_i| \tag{30a}$$

The supremum norm (30a) is equivalently defined as

$$\|\bar{\bar{J}}\|_\infty = \operatorname{Sup}_m \sum_n |J_{m,n}| \tag{30b}$$

For the estimation of $\|\bar{\bar{J}}\|_\infty$, we propose to bound the matrix elements $|J_{m,n}|$ as a function of the distance $\mathcal{d}(m,n)$ between the two sites $m \in \mathbb{Z}^d$ and $n \in \mathbb{Z}^d$. For proving that the operator $\mathbf{S}_t$ could be contracting, we prove the following result.

Proposition 2. Let us consider $\mathbb{L}$ an arbitrary lattice as defined in Section 2.3 and an arbitrary finite set $\mathbb{S} \subset \mathbb{L}$ on which the operator $\mathbf{S}_t$ is restricted. Let us assume

$$t < \frac{1}{6\|\bar{\bar{A}}\|_2} [e^{-\gamma_0} - \tau(3 + e^{-\gamma_0})] \tag{31a}$$

with $\gamma_0 = e^{-3/2}/2 \cong 0.11156508$.

Then there exist two constants γ and C

$$\gamma = \gamma_0 \left(\frac{1 - 2\|\bar{\bar{A}}\|_2 t - 2\tau}{1 + 2\|\bar{\bar{A}}\|_2 t} \right)^2 \leqslant \gamma_0 \tag{31b}$$

$$C = (15t\|\bar{\bar{A}}\|_\infty)^2 \tag{31c}$$

such that for all m and n in $\mathbb{S}$, we have

$$|J_{m,n}| \leqslant C \exp[-\gamma \mathcal{d}(m,n)] \tag{32a}$$

Thus, for a nonexponential lattice $\mathbb{L}$, we have

$$\|\bar{\bar{J}}\|_\infty \leqslant C \operatorname*{Sup}_n \left(\sum_m \exp[-\gamma \mathcal{d}(m,n)] \right) = C\varphi(\gamma) < \infty \tag{32b}$$

and for a periodic d-dimensional square lattice $\mathbb{L} = \mathbb{Z}^d$ with operator (14e),

$$\|\bar{\bar{J}}\|_\infty \leqslant C \left(\frac{e^\gamma + 1}{e^\gamma - 1} \right)^d \tag{32c}$$

[then take $\|\bar{\bar{A}}\|_2 = \|\bar{\bar{A}}\|_\infty = 2d$ in (31b) and (31c)].

Proof. Step 1. Using the eigenequation (14b), we first rewrite the form $J_{m,n}$ in order that the parameter t appears as a coefficient. Thus, for t going to zero, it becomes easier to prove that $J_{m,n}$ goes to zero as well as the supremum norm $\|\bar{\bar{J}}\|_\infty$. This will prove the existence of a domain in t and τ such that $\|\bar{\bar{J}}\|_\infty < 1$ and where the operator $\mathbf{S}$ is contracting.

By elimination of u_n between the two eigenequations

$$-t\,\Delta\Psi_n^\nu + u_n \Psi_n^\nu = E_\nu \Psi_n^\nu \tag{33a}$$

$$-t\,\Delta\Psi_n^{\nu'*} + u_n \Psi_n^{\nu'*} = E_{\nu'} \Psi_n^{\nu'*} \tag{33b}$$

we obtain the identity

$$t(\Psi_n^{\nu'*} \Delta\Psi_n^{\nu} - \Psi_n^{\nu} \Delta\Psi_n^{\nu'*}) = (E_{\nu'} - E_{\nu})\, \Psi_n^{\nu} \Psi_n^{\nu'*} \tag{33c}$$

By substitution in (29c), we obtain

$$J_{m,n} = t^2 \sum_{\nu,\nu'} \frac{\sigma_\nu(1-\sigma_{\nu'})}{(E_{\nu'} - E_\nu)^3} \times [(\Psi_m^{\nu'} \Delta\Psi_m^{\nu*} - \Psi_m^{\nu*} \Delta\Psi_m^{\nu'})(\Psi_n^{\nu'*} \Delta\Psi_n^{\nu} - \Psi_n^{\nu} \Delta\Psi_n^{\nu'*}) + \text{CC}] \tag{34a}$$

Since the terms in the sum can be easily bounded, this form makes it explicit that for $t \to 0$, $J_{m,n}$ goes to zero. Expanding the product in (29c), we obtain four kinds of terms:

$$J_{m,n} = t^2 \sum_{p,q} \Delta_{m,q} \Delta_{n,p} (T_{m,n,p,q} + T_{p,q,m,n} - T_{p,n,m,q} - T_{m,q,p,n}) + \text{CC} \tag{34b}$$

with

$$T_{m,n,p,q} = \sum_{\nu,\nu'} \frac{\sigma_\nu(1-\sigma_{\nu'})}{(E_{\nu'} - E_\nu)^3} \Psi_m^{\nu'} \Psi_n^{\nu'*} \Psi_p^{\nu*} \Psi_q^{\nu} \tag{34c}$$

which is easily bounded by

$$|J_{m,n}| \leqslant 8t^2 \left(\sum_q |\Delta_{m,q}| \right) \left(\sum_p |\Delta_{m,p}| \right) \boldsymbol{T}_{m,n} \leqslant 8t^2 \|\bar{\bar{\Delta}}\|_\infty^2 \boldsymbol{T}_{m,n} \tag{34d}$$

where $\boldsymbol{T}_{m,n}$ is an upper bound for all terms (34c) which appear in (34b).

Step 2. We now calculate this upper bound $\boldsymbol{T}_{m,n}$. The first condition (31) implies

$$\tau < \frac{1}{3e^{\gamma_0} + 1} = \tau_0 \cong 0.22966 \tag{35a}$$

$$t < \frac{e^{-\gamma_0}}{6\|\bar{\bar{\Delta}}\|_2} < t_0 \tag{35b}$$

which allows one to apply Lemma 1. Let us consider, for example, the first term of (34c), $T_{m,n;p,q}$, in (34b). With σ_ν as defined by (16), it can be written as

$$T_{m,n,p,q} = \sum_{\nu,\nu'} F(E_\nu, E_{\nu'})\, \Psi_m^{\nu'} \Psi_p^{\nu*} \Psi_n^{\nu'*} \Psi_q^{\nu} \tag{36a}$$

where $F(x, y)$ is a two-variable function defined as

$$F(x, y) = 2\frac{[1 - Y(x+1/2)]\, Y(y+1/2)}{(y-x)^3} \tag{36b}$$

where $Y(x)$ is the Heaviside function defined as $Y(x) = 1$ for $x \geqslant 0$ and $Y(x) = 0$ for $x < 0$.

Our method consists in finding an approximation of $F(x, y)$ by a polynomial $P_r(x, y)$ with degree $r = \mathrm{Min}(\mathscr{d}(p, q), \mathscr{d}(m, n)) - 1$,

$$F(x, y) = P_r(x, y) + R_r(x, y) \tag{37a}$$

with an error

$$|R(x, y)| < \varepsilon_r = Ce^{-\kappa r} \tag{37b}$$

which decays exponentially as a function of r. Each term $x^i y^j$ of this polynomial yields a contribution to the sum (36a) of the form

$$\sum_{\nu,\nu'} E_\nu^i E_{\nu'}^j \Psi_m^{\nu'} \Psi_p^{\nu *} \Psi_n^{\nu' *} \Psi_q^\nu = \left(\sum_\nu E_\nu^i \Psi_p^{\nu *} \Psi_q^\nu\right) \times \left(\sum_{\nu'} E_{\nu'}^j \Psi_m^{\nu'} \Psi_n^{\nu' *}\right) = \bar{\bar{A}}_{p,q}^i \bar{\bar{A}}_{n,m}^j \tag{37c}$$

and can be expressed as matrix elements of powers i and j of the operator (14c), $\bar{\bar{\mathbf{A}}} = \bar{\bar{D}} - t\bar{\bar{A}}$. Since by definition the matrix elements p, q of the operator $\bar{\bar{A}}$ (or $\bar{\bar{A}}$) are zero for sites p, q at a distance $\mathscr{d}(p, q) > 1$, it readily turns out that the matrix elements p, q of $\bar{\bar{A}}^i$ are zero when $\mathscr{d}(p, q) > i$. Since the degree r of the polynomial $P(x, y)$ with respect to x is smaller than or equal to $\mathscr{d}(p, q) - 1$, the contribution to $T_{m,n;p,q}$ of this polynomial is zero, and the term which is left is bounded, by using (37b), as

$$|T_{m,n;p,q}| = \left|\sum_{\nu,\nu'} R(E_\nu, E_{\nu'})\, \Psi_m^{\nu'} \Psi_p^{\nu *} \Psi_n^{\nu' *} \Psi_q^\nu\right| < \varepsilon_r \sum_{\nu'} |\Psi_m^{\nu'}| \cdot |\Psi_n^{\nu' *}| \times \sum_\nu |\Psi_p^{\nu *}| \cdot |\Psi_q^\nu| < \varepsilon_r \tag{38a}$$

A rather tedious explicit calculation of the polynomial approximations is done in Appendices A and B (however, we did not find the optimum approximation). We obtain

$$|T_{m,n;p,q}| \leqslant 25 \exp\{-\kappa[\mathscr{d}(p, q) + \mathscr{d}(m, n)]\} \tag{38b}$$

where $\kappa = \gamma/2$ is given by (B4c). Similar inequalities for the other terms in (34b), such as $T_{p,n,m,q}$, involve $\mathcal{d}(p,n)+\mathcal{d}(m,q)$. In the sum (34b), m and q are nearest neighbors $[\mathcal{d}(m,q)=1]$, as are n and p $[\mathcal{d}(n,p)=1]$. Thus, these distances fulfill the well-known triangular inequalities $\mathcal{d}(p,n) \geqslant \mathcal{d}(m,n)-1$, $\mathcal{d}(m,q) \geqslant \mathcal{d}(m,n)-1$ and $\mathcal{d}(p,q) \geqslant \mathcal{d}(m,n)-2$, which implies $2[\mathcal{d}(m,n)-1]$ and $\mathcal{d}(p,n)+\mathcal{d}(m,q) \geqslant 2[\mathcal{d}(m,n)-1]$. Then, we can choose in (34d), with $\gamma = 2\kappa \leqslant \gamma_0$,

$$\boldsymbol{T}_{m,n} = 25 \exp(\gamma_0) \exp[-\gamma \mathcal{d}(m,n)] \tag{38c}$$

Definition (31b) implies $2e^{\gamma_0} < (3/2)^2$. Then, (34d) yields

$$\begin{aligned} |J_{m,n}| &\leqslant 8t^2 \|\bar{\bar{A}}\|_\infty^2 \cdot 25 \exp(\gamma_0) \exp[-\gamma \mathcal{d}(m,n)] \\ &< (15t \|\bar{\bar{A}}\|_\infty)^2 \exp[-\gamma \mathcal{d}(m,n)] \end{aligned} \tag{39a}$$

which proves inequality (32a). If $n=m$, we have the same bound for $|J_{m,n}|$ with m and n nearest neighbors and for $|J_{n,n}|$, and (32a) is fulfilled *a fortiori*.

The supremum norm of $\bar{\bar{J}}$ defined by (30b) is obviously bounded, because of the assumption that $\mathbb{L}$ is a nonexponential lattice.

For a square lattice $\mathbb{Z}^d$, $D=d$ is the true dimension of the lattice and it is readily found that

$$\|\bar{\bar{J}}\|_\infty = \operatorname*{Sup}_m \sum_n |J_{m,n}| \leqslant C \sum_{n \in \mathbb{Z}^d} e^{-\gamma |n|} = C \left(\sum_{i=-\infty}^{+\infty} e^{-\gamma |i|} \right)^d \tag{39b}$$

which yields (32c). QED

Using the above results, it is now easy to prove the first existence theorem of this paper.

Theorem 1 (Bipolaronic States). Let $\mathbb{L}$ be a given infinite nonexponential lattice fulfilling the conditions of Section 2.3 and $\bar{\bar{A}}$ an operator defined on $\mathbb{L}$. Let us consider an arbitrary finite subset $\mathbb{S} \subset \mathbb{L}$ with N sites.

Let $\{\sigma_n\}$ be an arbitrary configuration of pseudospin ($\sigma_n = 0$ or 1) with $n \in \mathbb{L}$.

Then there exists a strictly positive constant $t_3 > 0$ *independent* of $\mathbb{S}$, such that for

$$t < t_3 \tag{40a}$$

there is a unique local minimum $\{u_n(t)\}$ of the adiabatic energy (15)

restricted to $\mathbb{S}$ with a population factor for the electrons given by (16d) which is a uniformly continuous function of t and such that for $t=0$

$$u_n(0) = -\sigma_n \tag{40b}$$

For example, for $\mathbb{L}=\mathbb{Z}^d$ and $\bar{\bar{A}}$ defined by (14e), we have the bound

$$t_3 = \frac{1}{30d}\left(\frac{e^{\gamma_0}+1}{\gamma_0}\right)^{-d/2}\left(\frac{3e^{\gamma_0}-1}{3e^{\gamma_0}+1}\right)^{d} \cong \frac{1}{30d}(0.124086)^d \tag{40c}$$

This solution $\{u_n(t)\}$ is the unique fixed point of $\mathbf{S}_t$ in $\mathscr{E}(\{\sigma_n\}, \tau)$ with, for example, $\tau = 1/5$.

Proof. Propositions 1 and 2 allow one to find t and τ in order that the operator $\mathbf{S}_t$ maps $\mathscr{E}(\{\sigma_n\}, \tau)$ into itself with a Jacobian matrix $\bar{\bar{J}}$ with a supremum norm $\|\bar{\bar{J}}\|_\infty$ strictly smaller than 1.

1. Proposition 1 shows that τ' goes to $\tau^2/4(1-\tau)(1-2\tau)$ when t goes to zero. It is sufficient that τ fulfills (35a) for having this limit strictly smaller than τ. Consequently, there exists $t_1(\tau)$ such that for $t < t_1$, the domain $\mathscr{E}(\{\sigma_n\}, \tau)$ is stable under $\mathbf{S}_t$.

2. For τ fulfilling (35a), Proposition 2 shows that when t goes to zero γ goes to $\gamma_0(1-2\tau)^2 > 0$ and $\|\bar{\bar{J}}\|_\infty$ goes to zero as $C = C_{\mathbb{L}}(15t\|\bar{\bar{A}}\|_\infty)^2$. Therefore, there exists $t_2(\tau)$ such that for $t < t_2$, we have $\|\bar{\bar{J}}\|_\infty < K_0 < 1$ and $\mathbf{S}_t$ becomes contracting.

As a result, by choosing a value for τ which fulfills (35a), there exists $0 < t_3 = \mathrm{Min}(t_1(\tau), t_2(\tau))$ such that for $t < t_3$, the conditions for the application of the Banach fixed-point theorem[8] to the operator $\mathbf{S}_t$ in the domain $\mathscr{E}(\{\sigma_n\}, \tau)$ are fulfilled. This unique fixed point is the configuration $\{u_n(t)\}$ solution of Eq. (18a).

For proving that $\{u_n(t)\}$ is a uniformly continuous function of t, it suffices to prove that the operator $\mathbf{S}_t$ defined by (18b) is a uniform function of t. Indeed, we consider the derivative $\partial \mathbf{S}_t/\partial t$ with respect to the parameter t of this operator:

$$\begin{aligned}\left(\frac{\partial \mathbf{S}_t(\{u_i\})}{\partial t}\right)_n &= \frac{\partial v_n}{\partial t} = \sum_{\nu,\nu'} \frac{\sigma_\nu(1-\sigma_{\nu'})}{E_{\nu'}-E_\nu} \Psi_n^{\nu *}\Psi_n^{\nu'} \sum_m \Psi_m^{\nu' *}\, \Delta\Psi_m^{\nu} + \mathrm{CC} \\ &= \sum_{m,p} \Delta_{p,m} \sum_{\nu,\nu'} \frac{\sigma_\nu(1-\sigma_{\nu'})}{E_{\nu'}-E_\nu} \Psi_n^{\nu *}\Psi_n^{\nu'}\Psi_m^{\nu' *}\Psi_p^{\nu} + \mathrm{CC}\end{aligned} \tag{41a}$$

A uniform bound can be found for $|\partial v_n/\partial t|$ by using exactly the same scheme as that of Appendix B but where the series (B3a) is replaced by the simpler expansion

$$\frac{1}{E_{v'}-E_v}=\frac{1}{1-\tau}\sum_{i=0}^{\infty}\left(\frac{(1-\tau)-(E_{v'}-E_v)}{1-\tau}\right)^i \tag{41b}$$

Keeping the same definitions for κ, λ, and $r=\mathrm{Min}(\mathcal{d}(m,n),\ \mathcal{d}(p,q))$, we obtain by inspection of inequality (B8b) for $T_{m,n;p,q}$

$$\begin{aligned}|S_{m,n;p,q}| &< \frac{1}{1-\tau}\sum_{i=0}^{r-1}\exp\{-\kappa[\mathcal{d}(q,p)+\mathcal{d}(m,n)-2-2i]\}\lambda^i+\frac{1}{1-\tau}\sum_{i=r}^{\infty}\lambda^i \\ &= \exp\{-\kappa[\mathcal{d}(q,p)+\mathcal{d}(m,n)]\}\frac{\exp(2\kappa)}{(1-\tau)[1-\lambda\exp(2\kappa)]} \\ &\quad +\frac{\lambda^r}{(1-\tau)[1-\lambda\exp(2\kappa)]}\end{aligned} \tag{42a}$$

where

$$S_{m,n;p,q}=\sum_{v,v'}\frac{\sigma_v(1-\sigma_{v'})}{E_{v'}-E_v}\Psi_m^{v'}\Psi_n^{v'*}\Psi_p^{v*}\Psi_q^{v}=S^*_{n,m;q,p} \tag{42b}$$

Thus $S_{n,p;n,m}$ decays exponentially as a function of the distance $\mathcal{d}(m,n)$ since $\mathcal{d}(p,n)\geqslant\mathcal{d}(m,n)-\mathcal{d}(p,m)=\mathcal{d}(m,n)-1$ and $\mathcal{d}(m,n)+\mathcal{d}(p,n)\geqslant r\geqslant 2\mathcal{d}(m,n)-2$. Since with (B12a), $\lambda<e^{-2\kappa}=e^{-\gamma}$, there exists a constant K_1 such that

$$|S_{m,n;n,p}|\leqslant K_1\exp[-\gamma\mathcal{d}(m,n)] \qquad \text{for } p \text{ and } m \text{ nearest neighbors} \tag{42c}$$

This result is enough for showing that for n fixed, the sum (41a), which can be written as

$$\frac{\partial v_n}{\partial t}=\sum_{m,p}\Delta_{m,p}S_{m,n;n,p}+\mathrm{CC} \tag{43}$$

is absolutely convergent and uniformly bounded. In addition, this upper bound $\mathrm{Sup}_n\,|\partial v_n/\partial t|<\infty$ does not depend on $\{u_n\}$. Consequently, since the operator $\mathbf{S}_t$ is differentiable with respect to the variable t with a uniformly bounded norm for its derivative operator $\partial\mathbf{S}_t/\partial t$, $\mathbf{S}_t$ is a uniform function of t. The configuration $\{u_n(t)\}$, which is a fixed point of $\mathbf{S}_t$, is also a uniformly continuous function of t in the domain $t<t_3$.

We also have to prove that the fixed point $\{u_i\}$ of this operator $\mathbf{S}_t$ are always local minima of the variation energy (15). This is a straightforward consequence of the contracting property of $\mathbf{S}_t$. The matrix $\bar{\bar{M}}(\{u_i\}) = \{M_{m,n}\}$ of second-order derivatives of this energy

$$M_{m,n} = \frac{\partial^2 \Phi(\{u_i\}, \{\sigma_\nu\})}{\partial u_m \, \partial u_n} = \delta_{n,m} + \sum_\nu \sigma_\nu \frac{\partial^2 E_\nu}{\partial u_n \, \partial u_m}$$

$$= \delta_{n,m} + \sum_\nu \sigma_\nu \frac{\partial |\Psi_m^\nu|^2}{\partial u_n} \tag{44a}$$

(which corresponds to the QEAM introduced for dynamical systems[1]) can be expressed as a function of the matrix $\bar{\bar{J}}(\{u_i\}) = \partial \mathbf{S}_t(\{u_i\})$ defined in (28) as

$$\bar{\bar{M}}(\{u_i\}) = \bar{\bar{1}} - \bar{\bar{J}}(\{u_i\}) \tag{44b}$$

The supremum norm $\|\bar{\bar{J}}(\{u_i\})\|_\infty$ is strictly smaller than 1, since $\mathbf{S}_t$ is contracting at $\{u_i\}$. Using the property that the spectral norm $\|\bar{\bar{J}}(\{u_i\})\|_2$ of an operator is always smaller than or equal to its supremum norm $\|\bar{\bar{J}}(\{u_i\})\|_\infty$, we have $\|\bar{\bar{J}}(\{u_i\})\|_2 < 1$. As a consequence, with the quadratic form $\langle \bar{X} | \bar{Y} \rangle$ denoting the Hermitian product of $\bar{X}$ and $\bar{Y}$, we have that

$$\langle \bar{X} | \bar{\bar{M}} | \bar{X} \rangle = \langle \bar{X} | \bar{\bar{1}} | \bar{X} \rangle - \langle \bar{X} | \bar{\bar{J}} | \bar{X} \rangle \geqslant \langle \bar{X} | \bar{X} \rangle [1 - |\bar{\bar{J}}(\{u_i\})\|_2] > 0 \tag{44c}$$

is strictly positive and the configuration $\{u_n\}$ is a local minimum of the variational form (15).

Particular Case. In the case of a d-dimensional square lattice, with operator (14e), we calculate an explicit value for the bound t_3. Using (31a), (32a), and (32b), we have

$$\|\bar{\bar{J}}\|_\infty \leqslant C \left(\frac{e^\gamma + 1}{e^\gamma - 1} \right)^d \leqslant (30td)^2 \frac{(e^{\gamma_0} + 1)^d}{\gamma^d}$$

$$= (30td)^2 \left(\frac{e^{\gamma_0} + 1}{\gamma_0} \right)^d \left(\frac{1 + 4dt}{1 - 4dt - 2\tau} \right)^{2d}$$

$$\leqslant (30td)^2 \left(\frac{e^{\gamma_0} + 1}{\gamma_0} \right)^d \left(\frac{3 + e^{-\gamma_0} - \tau(3 + e^{-\gamma_0})}{3 - 6\tau - e^{-\gamma_0} + \tau(3 + e^{-\gamma_0})} \right)^{2d}$$

$$= (30td)^2 \left(\frac{e^{\gamma_0} + 1}{\gamma_0} \right)^d \left(\frac{3e^{\gamma_0} + 1}{3e^{\gamma_0} - 1} \right)^{2d} \tag{45a}$$

which yields $\|\bar{\bar{J}}\|_\infty < 1$ when

$$t < \frac{1}{30d}\left(\frac{e^{\gamma_0}+1}{\gamma_0}\right)^{-d/2}\left(\frac{3e^{\gamma_0}-1}{3e^{\gamma_0}+1}\right)^{d} = t_2 < t_0 \tag{45b}$$

Finally, we check that when $t < t_2$, τ can be chosen in order that Lemma 1 and Propositions 1 and 2, which were used for finding this bound (45b), are indeed applicable. We have to satisfy inequality (20a), condition $\tau' < \tau$ with τ' given by (22a), and inequality (31a), which yields, with $\|\bar{\bar{A}}\|_2 = 2d$, the following conditions:

$$\tau < \frac{1-4dt_2}{2} \tag{46a}$$

$$\frac{4dt_2^2+\tau^2}{4(1-\tau)(1-2\tau-4dt_2)} < \tau \tag{46b}$$

$$\tau < \frac{1-12tde^{\gamma_0}}{3e^{\gamma_0}+1} \tag{46c}$$

One can check, for example, that the value

$$\tau = 1/5 \tag{46d}$$

is a convenient choice at any dimension d. Consequently, for t and τ fulfilling (45b) and (46d), the operator $\mathbf{S}_t$ maps $\mathscr{E}(\{\sigma_n\}, \tau)$ onto itself and is contracting for the supremum norm. Thus, we have explicitly a domain $\mathscr{E}(\{\sigma_n\}, 1/5)$, where the Banach fixed-point theorem applies for $t < t_2 = t_3$. QED

To be more explicit, the bound (40a) yields

$$t \leqslant 0.004136 \quad (\text{or } k > 15.5489) \quad \text{for} \quad d = 1 \tag{47a}$$

$$t \leqslant 0.000256 \quad (\text{or } k > 62.4242) \quad \text{for} \quad d = 2 \tag{47b}$$

$$t \leqslant 0.0000212 \quad (\text{or } k > 217.039) \quad \text{for} \quad d = 3... \tag{47c}$$

We recall that k is defined by (10b).

We pay by rather loose bounds for the crude estimations which were done in order to reduce the tedious calculations. In fact, the numerical calculations[3] (mostly done in one-dimensional models, but recently also in

[3] Dor $d = 1$, see refs. 3–6; for $d = 2$, numerical calculations by R. L. Raimbault and P. Quemerais are in progress.

two dimensions) yield much larger bounds for t_3 (or much smaller k) for the existence of bipolaronic states. On the basis of the numerical observations, we can estimate roughly the best bound to be $t_3 \approx 1/(4d)$ for a d-dimensional square lattice, which is much larger than the values (47)! Let us note that for t larger than $1/(4d)$, Lemma 1 suggests that the interval of occupied eigenenergies starts to overlap the interval of eigenenergies of the empty states, so that degeneracy problems emerge. As for the Frenkel–Kontorowa model, they are likely related to bifurcations.

In fact, although we exhibit here a common bound t_3 valid for the existence of the bipolaronic states for any configuration $\{\sigma_n\}$, the domain of existence *for many particular bipolaronic configurations* $\{\sigma_n\}$ *can be wider (especially for well-ordered configurations).* As for the FK model, where the domain of existence of the anti-integrable trajectories sharply depends on their coding sequence,[1] the domain of existence of the bipolaronic configurations also depends on their pseudospin configuration $\{\sigma_n\}$.

It is obviously possible to improve analytically this bound t_3, for example, by refining the polynomial approximation in Appendix A and by "stressing" the inequalities given in Appendix B, but we believe that in any case these more precise estimations should remain far below the numerical accuracy and thus should have a minor practical interest. The interest of Theorem 1 is essentially conceptual, since it proves the existence of a *non-vanishing* domain in t where the *bipolaronic states do exist.* For comparison, recall that the KAM theorems predict the existence of invariant tori for dynamical systems in domains of parameters which also have a negligible physical extension, while the numerical investigations reveal a much larger physical domain. But in both situations, having exact results gives a solid support for the interpretation of numerical observations.

3.3. Perturbations of the Mixed Polaronic–Bipolaronic States

The method used for proving Theorem 1 can be extended with few changes for studying the case where the electrons are not in their ground state with regard to the lattice distortion. Then the electrons are in excited states with the population factor (17). We obtain the following theorem (see Fig. 2).

Theorem 2 (Mixed Polaronic–Bipolaronic States). Let $\mathbb{L}$ be a given infinite nonexponential lattice fulfilling the conditions of Section 2.3 and $\bar{\bar{A}}$ an operator defined on $\mathbb{L}$. Let us consider an arbitrary finite subset $\mathbb{S} \subset \mathbb{L}$ with N sites.

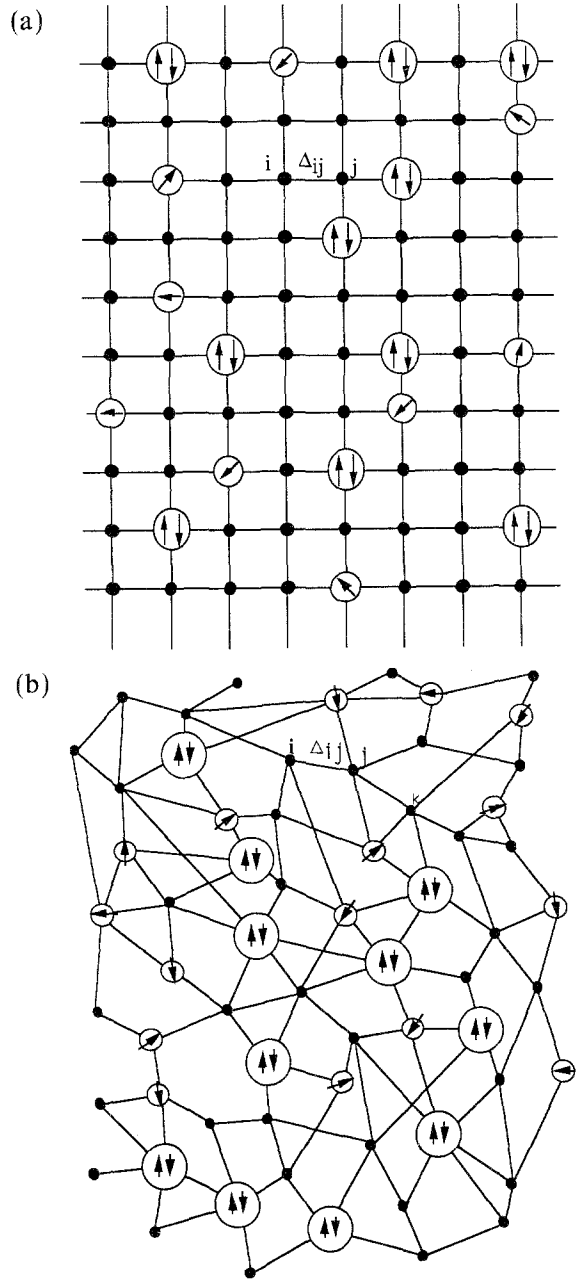

Fig. 2. Illustration of Theorem 2: (a) The electronic transfer integral Δ_{ij} is nonzero along the lines which connect the sites on the square lattice. When this perturbation is not too large ($t < t_3'$), there exists an eigenstate of the adiabatic Holstein model which is uniformly close to an eigenstate at the anti-integrable limit (shown in Fig. 1). (b) The same results hold for an arbitrary nonsquare lattice at any dimension, random or not. Theorem 1 could be illustrated by similar figures containing only black dots (empty sites) and circles with two opposite arrows (bipolarons).

Let $\{\sigma_n\}$ be an arbitrary configuration of pseudospin ($\sigma_n = 0, 1/2, 1$), where $n \in \mathbb{L}$.

Then there exists a constant $t_3' > 0$ *independent* of $\mathbb{S}$ such that for

$$t < t_3' \tag{48a}$$

there is a unique local minimum of the adiabatic energy $\{u_n(t)\}$ of the adiabatic energy (15) restricted to $\mathbb{S}$, with the population factor for the electrons is given by (17b), which is a uniformly continuous of t and such that for $t = 0$

$$u_n(0) = -\sigma_n \tag{48b}$$

For example, for $\mathbb{L} = \mathbb{Z}^d$ and $\bar{\bar{A}}$ defined by (14e), we have the bound

$$t_3' = \frac{1}{63d}\left(\frac{e^{\gamma_0}+1}{\gamma_0}\right)^{-d/2}\left(\frac{(2-e^{-\gamma_0})(5-3e^{-\gamma_0})}{14-e^{-\gamma_0}-3e^{-2\gamma_0}}\right)^{d} \cong \frac{1}{63d}(0.054909)^d \tag{48c}$$

This solution $\{u_n(t)\}$ is the unique fixed point of $\mathbf{S}_t$ in $\mathscr{E}(\{\sigma_n\}, \tau)$ with, for example, $\tau = 1/8$.

Proof (see Appendix C). The ideas for the proof of this theorem are the same as those used for Theorem 1. However, there are some technical differences which make the bound t_3' smaller than t_3. It is not necessary to reproduce the complete proof. Appendix C essentially focus on the changes from the proof of Theorem 1 which need to be done for obtaining Theorem 2.

The same remarks as for Theorem 1 apply. The best common bound t_3' which could be numerically observed is much larger than the one which is given by this theorem. In addition, it also depends on each configuration $\{\sigma_n\}$.

These mixed polaronic–bipolaronic states have the property that the electronic eigenenergies can be grouped into three packets separated by two energy gaps. The low-energy packet corresponds to double occupied eigenstates, the medium-energy packet above to singly occupied eigenstates, and the last one at the top to empty states. Compared to the bipolaronic states, where there are only two packets of eigenstates, the medium-energy packet appears in the middle of the electronic gap.

Consequently, we can say that the mixed polaronic–bipolaronic states correspond to bipolaronic states where many *midgap states* are excited. Midgap states were already known to exists in some models. For example, the "soliton" in the SSH model[18] corresponds to a single midgap excitation. Thus, this theorem generalizes the concept by proving the existence of states with many-midgap excitations localized in real space. However, it is

important to note that the metastability of these many-midgap states requires smaller values for the amplitude t of the transfer integrals.

A simple argument proving that t_3' has to be smaller than t_3 is obtained by noting that when only the polaronic states (with $\sigma_i = 0$ or $1/2$) are considered (all the electronic states are singly occupied and $\sigma_\nu = 1/2$ or 0), the variational form (15) can be written

$$\sum_i \frac{1}{2} u_i^2 + \frac{1}{2} \sum_\nu \sigma_\nu' E_\nu(\{u_i\}) \tag{49a}$$

where

$$\sigma_\nu' = 2\sigma_\nu = 0 \text{ or } 1 \tag{49b}$$

With the change of variables $u_i = u_i'/2$ and $t' = 2t$, the lattice distortion associated with this polaronic structure $\{u_i\}$ corresponds to those of the bipolaronic state $\{u_i'\}$ characterized by $\sigma_i' = 2\sigma_i$. Consequently, the bound for the existence of mixed polaronic–bipolaronic states is necessarily at least twice as small as the bound for the existence of bipolaronic states: $t_3' \leqslant t_3/2$. Numerical observations suggest for the common bounds that $t_3' \cong t_3/2$.

Finally, before ending this section, let us give a theorem which asserts that we have well-defined limits in the limit of an infinite system.

By definition, a sequence of finite subset $\mathbb{S}_n \subset \mathbb{L}$ converges to $\mathbb{L}$, $\lim_{n \to \infty} \mathbb{S}_n = \mathbb{L}$, when for any site $i \in \mathbb{L}$ there exists an integer N_i such that for $n \geqslant N_i$ we have $i \in \mathbb{S}_n$.

Then, we have the following result.

Theorem 3. For $t < t_3$ (or $t < t_3'$) and a given pseudospin configuration $\{\sigma_i\}$ ($i \in \mathbb{L}$), bipolaronic structures (or mixed polaronic–bipolaronic structures) $\{u_i\}$ depend on the subset $\mathbb{S}_n$ of the infinite lattice $\mathbb{L}$. Then, for all i, $\lim_{n \to \infty} u_i(\mathbb{S}_n)$ is defined and does not depend on the sequence of subsets $\mathbb{S}_n \subset \mathbb{L}$ which converges to $\mathbb{L}$.

Proof. The proof of this theorem makes use of the "secateur method" described in Section 4.3 for proving Property 4. Since we need preliminarily the proof of Property 3, the proof of Theorem 3 will be given in the subsection following this result.

4. PROPERTIES OF THE MIXED POLARONIC–BIPOLARONIC AND BIPOLARONIC STATES

We now analyze the physical properties of these bipolaronic and mixed polaronic–bipolaronic states predicted by Theorems 1 and 2. These

properties concern (1) the electronic spectrum, (2) the phonon spectrum, (3) the coherence length and the effective localization length of the polarons or bipolarons, (4) the effect of a magnetic field, uniform or not, and (5) the ground state of the variational form (15) without or with a uniform magnetic field.

4.1. Electronic Gap

The electronic spectrum of the electrons in the potential which is created self-consistently by the lattice deformation has simple properties which are direct consequences of Lemma 1 for the bipolaronic states and

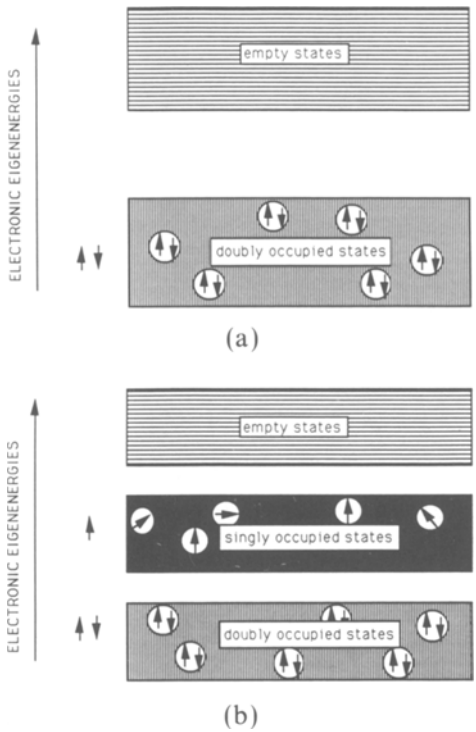

Fig. 3. (a) Scheme of the distribution of the electronic eigenenergies for a bipolaronic structure. The occupied electronic states belong to the lower band and the empty states to the upper band. (Note that the spectrum does not necessarily fill completely the two intervals and might be very singular.) (b) Scheme of the distribution of the electronic eigenenergies for a mixed polaronic–bipolaronic structure. There are three bands instead of two. The middle band corresponds to midgap states.

Lemma C for the mixed polaronic–bipolaromic states. There exists one or two gaps in the electronic density of states. We just summarize the consequences of these lemma (see the scheme of Fig. 3).

Property 1. For the purely bipolaronic states, there is an open interval $]E_g^-, E_g^+[$ in energy such that:

a1. The electronic Hamiltonian $\bar{\bar{A}} = \bar{\bar{D}} - t\bar{\bar{A}}$ defined by Eq. (14b) has no eigenenergy in this interval.

a2. The electronic eigenstates with eigenenergy E_v fulfilling $E_v \leqslant E_g^-$ are occupied by a pair of electrons with opposite spins.

a3. The electronic eigenstates with eigenenergy E_v fulfilling $E_g^+ \leqslant E_v$ are empty.

For the mixed polaronic–bipolaronic states, there exists two disjoint intervals $]E_{g1}^-, E_{g1}^+[$ and $]E_{g2}^-, E_{g2}^+[$ such that:

b1. The matrix $\bar{\bar{D}} - t\bar{\bar{A}}$ defined by Eq. (14b) has no eigenenergy in both intervals.

b2. The electronic eigenstates with eigenenergy E_v fulfilling $E_v \leqslant E_{g1}^-$ are occupied by a pair of electrons with opposite spins.

b3. The electronic eigenstates with eigenvalues E_v fulfilling $E_{g1}^+ \leqslant E_v \leqslant E_{g2}^-$ are occupied by a single electron with arbitrary spin.

b4. The electronic eigenstates with eigenenergy E_v fulfilling $E_g^+ \leqslant E_v$ are empty.

4.2. Gap Parameter, Phonon Spectrum

We already know by Theorems 1 and 2 that the bipolaronic and mixed polaronic–bipolaronic states are local minima of the variational energy, that is, the quadratic form associated with the matrix of second-order derivatives of the adiabatic energy (15) is strictly positive.

It is a straightforward consequence to prove that their phonon spectrum exhibits a nonvanishing gap. The phonon spectrum is obtained within the adiabatic approximation from the classical dynamical equation for the atomic lattice,

$$m\ddot{u}_i = -\frac{\partial^2 \Phi(\{u_n\})}{\partial u_i \, \partial u_j} \tag{50a}$$

By an appropriate choice of the time unit, the mass m of the atoms can be chosen equal to 1. The electrons are supposed to remain in

adiabatic equilibrium with the lattice. A time Fourier transform yields the eigenvalue equation for $\bar{u} = \{u_i(\omega)\} = \{\int u_i(t) e^{i\omega t}\, dt\}$,

$$\omega^2 \bar{u}(\omega) = \bar{\bar{M}} \bar{u} \tag{50b}$$

As for Hamiltonian systems, we have the following statement.

Definition 4. The square frequencies ω^2 of the phonons are the eigenvalues of the matrix $\bar{\bar{M}}(\{u_n\}) = \bar{\bar{1}} - \bar{\bar{J}}(\{u_n\})$. The gap parameter of a bipolaronic or mixed polaronic–bipolaronic structure is defined as

$$\Delta = \frac{1}{\|\bar{\bar{M}}(\{u_n\})\|_2 \cdot \|\bar{\bar{M}}^{-1}(\{u_n\})\|_2} \tag{51}$$

Since the bipolaronic or mixed polaronic–bipolaronic structures are attractive fixed points of the operator $\mathbf{S}_t$ for the supremum norm, we have $\|\partial \mathbf{S}_t\|_\infty = \|\bar{\bar{J}}(\{u_n\})\|_\infty < 1$, which implies $\|\bar{\bar{J}}(\{u_n\})\|_2 < 1$ for the spectral norm and that all the eigenvalues of $\bar{\bar{J}}(\{u_n\})$ have a modulus strictly smaller than 1.

Otherwise, let us prove that $\bar{J}(\{u_n\})$ determines a positive quadratic form. For a mixed polaronic–bipolaronic state, we use the decomposition (C7) of $\bar{\bar{J}}(\{u_n\})$ described in Appendix C. Then, for any vector $\bar{X}$, the expression

$$\begin{aligned}
\bar{X}\bar{\bar{J}}\bar{X} &= \sum_{n,m} X_n^* (J^{(1)}_{m,n} + J^{(2)}_{m,n}) X_m \\
&= \sum_{n,m,\nu,\nu'} \chi_1(E_\nu)[1 - \chi_1(E_{\nu'})] \frac{X_n^* \Psi_n^{\nu *} \Psi_n^{\nu'} \Psi_m^{\nu' *} \Psi_m^{\nu} X_m}{E_{\nu'} \times E_\nu} + \text{CC} \\
&\quad + \sum_{n,m,\nu,\nu'} \chi_2(E_\nu)[1 - \chi_2(E_{\nu'})] \frac{X_n^* \Psi_n^{\nu *} \Psi_n^{\nu'} \Psi_m^{\nu' *} \Psi_m^{\nu} X_m}{E_{\nu'} - E_\nu} + \text{CC} \\
&= 2 \sum_{\nu,\nu'} \{\chi_1(E_\nu)[1 - \chi_1(E_{\nu'})] + \chi_2(E_\nu)[1 - \chi_2(E_{\nu'})]\} \frac{|\sum_m \Psi_m^{\nu' *} \Psi_m^{\nu} X_m|^2}{E_{\nu'} - E_\nu}
\end{aligned} \tag{52a}$$

is the sum of positive terms, and thus is always positive. When

$$X_m = 1 \qquad \text{for all } m \tag{52b}$$

we have

$$\bar{X}\bar{\bar{J}}\bar{X} = 0 \tag{52c}$$

since we have $\nu \neq \nu'$ and the orthogonality property $\sum_m \Psi_m^{\nu' *} \Psi_m^{\nu} = \delta_{\nu,\nu'}$.

Consequently, $\bar{\bar{J}}(\{u_n\})$ determines a positive form, but zero belongs to its spectrum.

For purely bipolaronic states, the method for proving that $\bar{\bar{J}}(\{u_n\})$ also has this property is the same but simpler, since $\bar{\bar{J}}(\{u_n\})$ does not need to be decomposed into the sum of two matrices as in (52a).

The eigenvectors $|\iota\rangle$ of matrix $\bar{\bar{J}}$ and matrix $\bar{\bar{M}} = \bar{\bar{1}} - \bar{\bar{J}}$ are identical and the eigenvalues ω_ι^2 of $\bar{\bar{M}}$ can be written as $1 - \lambda_\iota$, where $0 \leqslant \lambda_\iota \leqslant \|\bar{\bar{J}}\|_2 < 1$ are eigenvalues of $\bar{\bar{J}}$. Consequently, we have

$$\|\bar{\bar{M}}\|_2 = 1 \tag{53a}$$

and

$$\|\bar{\bar{M}}^{-1}\|_2 = \frac{1}{1 - \|\bar{\bar{J}}\|_2} \tag{53b}$$

which yields that the gap parameter Δ of the mixed polaronic–bipolaronic configuration is

$$\Delta = 1 - \|\bar{\bar{J}}\|_2 > 0 \tag{54}$$

and we have the following result.

Property 2. The gap parameter Δ of the bipolaronic and mixed polaronic–bipolaronic structures is strictly nonzero. Moreover, the spectrum of the QEAM (which determines the phonon spectrum) lies in the interval $]0,1[$ and contains 1.

If the absence of electron–phonon coupling, the QEAM is the identity and the degenerate spectrum reduces to 1. Thus, this property proves that the electron–phonon coupling necessarily decreases all the eigenvalues of the QEAM except one. This phenomenon is called physically phonon softening.

4.3. Coherence Length

In structural models such as the FK model (e.g., see ref. 4), the coherence length of a stationary structure characterizes the spatial extension of the perturbation due to a linear local perturbation. It is the inverse Lyapunov coefficient of the trajectory associated with this structure.

The coherence length of a bipolaronic or mixed polaronic–bipolaronic state $\{u_j\}$ in the adiabatic Holstein model is defined similarly. The local minima $\{v_i(h)\}$ of the adiabatic variational form (15) with a local field

h at site m is the extremum of $\Phi(\{v_i\}, \{\sigma_v\}) - hv_m$, which fulfills $\{v_i(0)\} = \{u_i\}$ and depends continuously on h in some neighborhood of 0. Thus, we have

$$\frac{\partial \Phi(\{v_i(h)\}, \{\sigma_v\})}{\partial v_n} = h\delta_{n,m} \tag{55a}$$

By derivation with respect to h, we obtain

$$\sum_p \frac{\partial^2 \Phi(\{v_i(h)\})}{\partial v_n \, \partial v_p} \frac{\partial v_p}{\partial h} = \delta_{n,m} \tag{55b}$$

By definition, the linear susceptibility to the local field h at site m is

$$\chi_{pm} = \frac{\partial v_p}{\partial h} \tag{55c}$$

and we have the following result.

Property 3. For the Holstein model on an arbitrary lattice $\mathbb{L}$ restricted to an arbitrary finite subset $\mathbb{S}$ under conditions where Theorem 1 holds, the linear susceptibility $\chi_{n,m}$ (for n and m both in $\mathbb{S}$) to a local field h at site m decays exponentially as a function of the distance $\mathscr{d}(n, m)$. In other words, there exist two constants C_2 and $\gamma_2 < \gamma$ which do not depend on $\mathbb{S}$, such that

$$|\chi_{n,m}| = [\bar{\bar{M}}^{-1}]_{n,m} < C_2 e^{-\gamma_2 \mathscr{d}(n,m)} \tag{56}$$

Inequality (56) also holds for the mixed polaronic–bipolaronic structures, but with different constants C_2' and $\gamma_2' < \gamma'$ instead of constants C_2 and γ_2, respectively.

The coherence length $\xi = 1/\gamma$ is the characteristic length associated with the exponential decay $\exp[-\gamma \mathscr{d}(n, m)]$ of $\chi_{n,m}$ for sites m and n far from each other.

Proof. In order to fix the idea, let us consider the case of bipolaronic states. With definition (44a), we can write (55b)

$$\bar{\bar{M}}\bar{\chi} = \bar{\delta}_m \tag{57a}$$

where $\bar{\delta}_m$ is the vector with components $\{\delta_{n,m}\}$. The solution to this equation $\{\chi_i\} = \bar{\chi} = \bar{\bar{M}}^{-1}\bar{\delta}_m$ is the column m of the inverse matrix $\bar{\bar{M}}^{-1}$,

$$\chi_{n,m} = \sum_{p \in \mathbb{S}} [\bar{\bar{M}}^{-1}]_{n,p} \delta_{p,m} = [\bar{\bar{M}}^{-1}]_{n,m} \tag{57b}$$

Our proof is performed when the modulus of the coefficients of $\bar{\bar{J}}$ fulfill inequality (32a) when Theorem 1 is applicable,

$$|J_{i,j}| \leqslant C \exp[-\gamma d(i,j)] \tag{58a}$$

We have, under the conditions of Theorem 1 or 2,

$$\|\bar{\bar{J}}\|_\infty \leqslant C\varphi(\gamma) < 1 \tag{58b}$$

where because the lattice $\mathbb{L}$ is nonexponential (Definition 3), $\varphi(\gamma)$ is a smooth function of γ for $\gamma > 0$. When (58b) is fulfilled, the series

$$\bar{\bar{M}}^{-1} = \sum_{m=0}^{\infty} \bar{\bar{J}}^m \tag{58c}$$

is absolutely convergent since $\|\bar{\bar{J}}\|_2 \leqslant \|\bar{\bar{J}}\|_\infty < 1$. By setting $J_{i,j}(1) = J_{i,j}$, $J_{i,j}(0) = \delta_{i,j}$, and $J_{i,j}(p)$, the coefficient (i,j) of $\bar{\bar{J}}^p$ which is thus defined for $p \geqslant 2$,

$$J_{i,j}(p) = \sum_{k \in \mathbb{S}} J_{i,k}(p-1) J_{k,j} \tag{59a}$$

we obtain from (57b)

$$\chi_{i,j} = \sum_{p \in \mathbb{S}} J_{i,j}(p) \tag{59b}$$

For proving Property 3, we first prove recursively the existence of three positive numbers K_2, θ, and ω such that

$$|J_{i,j}(p)| \leqslant K_2 \exp(-\theta p) \exp[-\omega d(i,j)] \qquad \text{for all} \quad p \geqslant 0 \text{ and } (i,j) \tag{60a}$$

This inequality is fulfilled for $p = 1$ and $p = 0$ by choosing $0 < \theta$, $0 < \omega \leqslant \gamma$, and $K_2 \exp(-\theta) \geqslant C$. Next, let us assume that (60a) is fulfilled for $n = 1, 2, \ldots, p-1$ and let us prove it for $n = p$. We have from (59a) and (60a)

$$\begin{aligned} |J_{i,j}(p)| &\leqslant \sum_{k \in \mathbb{S}} |J_{i,k}(p-1)| \cdot |J_{k,j}| \\ &\leqslant K_2 C \sum_{k \in \mathbb{L}} \exp[-\theta(p-1)] \exp[-\omega d(i,k)] \exp[-\gamma d(k,j)] \end{aligned} \tag{60b}$$

The metric property

$$\mathcal{d}(i,k) \geqslant \mathcal{d}(i,j) - \mathcal{d}(j,k) \tag{61a}$$

implies

$$|J_{i,j}(p)| \leqslant K_2 \exp[-\omega \mathcal{d}(i,j)] \exp(-\theta p) C \exp(\theta) \sum_{k \in \mathbb{L}} \exp[-(\gamma-\omega)\, \mathcal{d}(k,j)]$$

$$\leqslant K_2 \exp[-\omega \mathcal{d}(i,j)] \exp(-\theta p) C \exp(\theta)\, \varphi(\gamma-\omega) \tag{61b}$$

It suffices to choose θ and ω such that

$$K_2 \exp[-\omega \mathcal{d}(i,j)] \exp(-\theta p) C \exp(\theta)\, \varphi(\gamma-\omega)$$

$$\leqslant K_2 \exp(-\theta p) \exp[-\omega \mathcal{d}(i,j)] \tag{62a}$$

or

$$C \exp(\theta)\, \varphi(\gamma-\omega) \leqslant 1 \tag{62b}$$

For $\theta = 0$ and $\omega = 0$, the first member of (62b) is strictly smaller than 1. Since $e^{\theta}\, \varphi(\gamma-\omega)$ is a continuous function of θ and ω, we can choose $\theta > 0$ and $\omega > 0$ such that (62b) is fulfilled. Consequently, (60a) is fulfilled with $K_2 = Ce^{\theta}$. Inequality (56) holds with

$$\gamma_2 = \omega < \gamma \tag{63a}$$

and

$$C_2 = Ce^{\theta} \frac{1}{1-e^{-\theta}} \tag{63b}$$

A similar proof can be done for the mixed polaronic–bipolaronic states when Theorem 2 holds, but of course with different constants. QED

This result gives information about the effect of small perturbations on the bipolaronic and mixed polaronic–bipolaronic states. It can be used for obtaining a nondifferential property about finite perturbations concerning changes in the bipolaronic or polaronic distribution.

Property 4. For the Holstein model on an arbitrary lattice $\mathbb{L}$ under conditions where Theorem 1 holds for arbitrary finite subset $\mathbb{S}$, let us consider two bipolaronic structures $\{u_n\}$ and $\{u'_n\}$ characterized by two pseudospin configurations $\{\sigma_n\}$ and $\{\sigma'_n\}$, respectively, which differ by the presence or the absence of a unique bipolaron at site m, that is, we have $\sigma_n = \sigma'_n$ for all $n \neq m$ and $\sigma_m \neq \sigma_{m'}$.

Then, there exist two constants C_3 and γ_2 (defined in Proposition 3) which do not depend on $\mathbb{S}$, such that

$$|u_n - u'_n| < C_3 \exp[-\gamma_2 \mathcal{d}(n,m)] \tag{64}$$

The same inequality holds for the mixed polaronic–bipolaronic states with constants C_3' and γ_2', but then we have $\sigma_n = \sigma_n'$ for all $n \neq m$ and $|\sigma_m - \sigma_m'| = 1/2$ or 1.

In other words, this result points out the corpuscular character of the bipolarons (or of the polarons), since adding or subtracting such particles (either a pair of electrons or a single electron) at an arbitrary site only modifies the close environment of this site (over a finite coherence length shorter than $1/\gamma_2$). Thus; the bipolaronic and the mixed bipolaronic–polaronic structures have the characteristic property of insulators mentioned in the Introduction.

Proof. Our method of proof is called the *secateur method* (see the scheme of Fig. 4). This method consists in replacing the operator $\bar{\bar{\Delta}}$ defined in Section 3.3 by an operator which continuously depends on the parameter ξ in the close vicinity of the given site m. We set

$$\Gamma_{m,j}(\xi, m) = \Gamma^*_{j,m}(\xi, m) = \xi \Delta_{m,j} \tag{65a}$$

$$\Gamma_{i,j}(\xi, m) = \Delta_{i,j} \tag{65b}$$

for $i \neq m$ and $j \neq m$.

With this operator and for $0 \leqslant \xi \leqslant 1$, all the bounds found in the lemma and propositions are unchanged, so that Theorems 1 and 2 hold identically. We prove Property 4 in the following way.

1. We continuously vary ξ from 1 to 0. The bipolaronic (or mixed polaronic–bipolaronic) configurations $\{u_i(\xi)\}$ depend continuously on ξ.

2. For $\xi = 0$, site m is totally isolated from the remainder of the lattice. We switch the pseudospin at site m, which has no effect on the atomic coordinates u_i for $i \neq m$.

3. We restore continuously ξ from 0 to 1 in order to get back to the initial model. The bipolaronic or mixed polaronic–bipolaronic configurations $\{u_i'\}$ again depend continuously on ξ. An upper bound to the length of the path which has been run by the atom i, $|u_i - u_i'| < |u_i(1) - u_i(0)| + |u_i'(1) - u_i'(0)|$, can be obtained using Property 3.

For a given set $\{\sigma_i\}$ and each ξ, the bipolaronic structure $\{u_i(\xi)\}$ is a solution of

$$\frac{\partial \Phi(\{u_n\}; \{\sigma_\nu\}; \xi)}{\partial u_i} = u_i(\xi) + \sum_\nu \sigma_\nu |\Psi_i^\nu(\{u_n\}, \xi)|^2 = 0 \tag{66a}$$

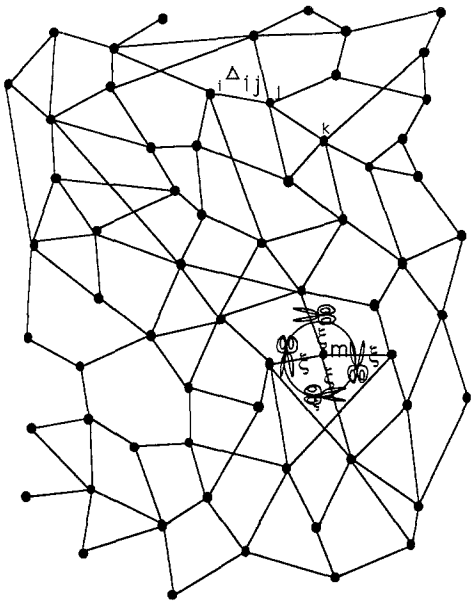

Fig. 4. Illustration of the "secateur method": A parameter ξ is introduced in the kinetic energy operator $\bar{\bar{\Gamma}}(\xi, m)$ of the electrons. For $\xi = 1$, $\bar{\bar{\Gamma}}(1, m)$ is the initial operator $\bar{\bar{\Delta}}$, and for $\xi = 0$, this operator is such that a certain region becomes disconnected from the remainder of the lattice. In the example shown in this figure, the single site m becomes disconnected from the remainder of the lattice.

Since $\bar{\bar{\Gamma}}(\xi, m)$ is uniformly continuous and differentiable with respect to ξ, $\{\partial u_i(\xi)/\partial\xi\}$ is defined and is a solution of the equation

$$\sum_j \frac{\partial^2 \Phi(\{u_n\}; \{\sigma_\nu\}; \xi)}{\partial u_i \, \partial u_j} \frac{\partial u_j(\xi)}{\partial \xi} + \sum_\nu \sigma_\nu \frac{\partial |\Psi_i^\nu(\{u_n\}, \xi)|^2}{\partial \xi} = 0 \qquad (66b)$$

or

$$\sum_j M_{i,j}(\{u_n\}, \{\sigma_\nu\}) \frac{\partial u_j}{\partial \xi}$$

$$+ \sum_{j,\nu,\nu'} \sigma_\nu (1 - \sigma_{\nu'}) \frac{\Psi_i^{\nu *} \Psi_i^{\nu'}}{E_{\nu'} - E_\nu} (\Psi_j^{\nu' *} \Delta_{j,m} \Psi_m^\nu + \Psi_m^{\nu' *} \Delta_{m,j} \Psi_j^\nu) + \mathrm{CC} = 0 \qquad (67a)$$

or

$$\sum_j M_{i,j} \frac{\partial u_j}{\partial \xi} = -\sum_j \Delta_{j,m}(S_{i,j;i,m} + S_{m,i;j,i})$$

$$-\sum_j \Delta_{m,j}(S_{i,m;i,j} + S_{j,i;m,i}) = Y_i \qquad (67b)$$

with definition (42b). With inequality (42c), it turns out that

$$|Y_i| < K_2 e^{-\gamma \mathcal{A}(i,m)} \tag{68a}$$

where K_2 is some positive constant which fulfills

$$K_2 \leqslant 4 \|\bar{\bar{A}}\|_\infty K_1 \tag{68b}$$

For the bipolaronic structures, the constant γ in (68a) is given by Theorem 1. For mixed polaronic–bipolaronic structures, we find with similar arguments that the constant γ has to be replaced by the constant γ' given by Theorem 2, and K_1 by K_1'. Consequently, using inequality (56), we have

$$\frac{\partial u_j}{\partial \xi} = \sum_k (\bar{\bar{M}}^{-1})_{j,k} Y_k \tag{69a}$$

and

$$\begin{aligned} \left|\frac{\partial u_j}{\partial \xi}\right| &\leqslant K_2 C_2 \sum_{k \in \mathbb{S}} e^{-\gamma_2 \mathcal{A}(j,k)} e^{-\gamma \mathcal{A}(k,m)} \\ &\leqslant K_2 C_2 e^{-\gamma_2 \mathcal{A}(j,m)} \sum_{k \in \mathbb{L}} e^{-(\gamma - \gamma_2)\mathcal{A}(k,m)} \end{aligned} \tag{69b}$$

Since $\gamma > \gamma_2$, there exists

$$C_3 = K_2 C_2 \sum_{k \in \mathbb{L}} e^{-(\gamma - \gamma_2)\mathcal{A}(k,m)}$$

such that

$$\left|\frac{\partial u_j}{\partial \xi}\right| \leqslant \frac{C_3}{2} e^{-\gamma_2 \mathcal{A}(j,m)} \tag{70a}$$

The proof of Property 4 is now readily obtained. By varying ξ from 1 to 0, we have

$$|u_j(1) - u_j(0)| \leqslant \frac{C_3}{2} e^{-\gamma_2 \mathcal{A}(j,m)} \tag{70b}$$

Since for $\xi = 0$, site m is disconnected from the remainder of the lattice, we can switch σ_m to another value without changing u_j for $j \neq m$. From this

new bipolaronic configuration, we continuously restore the value of ξ to unity and find identically

$$\left|\frac{\partial u_j'}{\partial \xi}\right| \leqslant \frac{C_3}{2} e^{-\gamma_2 \mathcal{d}(j,m)} \tag{71a}$$

We find globally

$$|u_j - u_j'| \leqslant |u_j(1) - u_j(0)| + |u_j'(1) - u_j'(0)| \leqslant C_3 e^{-\gamma_2 \mathcal{d}(j,m)} \tag{71b}$$

which proves (64). A similar proof holds in the case of mixed polaronic–bipolaronic structures. QED

Using the same secateur method, it is now possible to provide a proof for Theorem 3.

Proof of Theorem 3. We prove that for any positive ε and any given site i, there exists a ball $\mathbb{B}_i(\rho_\varepsilon)$ with radius the integer ρ_ε and center i such that for any finite subsets $\mathbb{S}$ and $\mathbb{S}^*$ which contain $\mathbb{B}_i(\rho_\varepsilon)$ [that is, $\mathbb{B}_i(\rho_\varepsilon) \subseteq \mathbb{S}$ and $\mathbb{B}_i(\rho_\varepsilon) \subseteq \mathbb{S}^*$] we have

$$|u_i(\mathbb{S}) - u_i(\mathbb{S}^*)| \leqslant \varepsilon \tag{72}$$

[A ball $\mathbb{B}_i(\rho)$ is defined as the subset of sites $j \in \mathbb{L}$ such that $\mathcal{d}(i, j) \leqslant \rho$.] Since the condition $\lim_{n \to \infty} \mathbb{S}_n = \mathbb{L}$ implies that for any site $i \in \mathbb{L}$ there exists an integer N_i such that for $n \geqslant N_i$, we have $i \in \mathbb{S}_n$; by choosing

$$n \geqslant N_{i,\rho} = \operatorname*{Sup}_{j \in \mathbb{B}_i(\rho)} N_j$$

we have $\mathbb{B}_i(\rho) \subseteq \mathbb{S}_n$. Therefore, for n and $n' \geqslant N_{i,\rho_\varepsilon}$ the Cauchy condition $|u_i(\mathbb{S}_n) - u_i(\mathbb{S}_{n'})| \leqslant \varepsilon$ is fulfilled, which implies that $\lim_{n \to \infty} u_i(\mathbb{S}_n)$ is uniquely defined.

For that purpose, we use the secateur differently than for Proposition 4. For a given integer ρ, we consider the set $\mathbb{C}_i(\rho)$ of bonds (m, p) cut by the surface of the ball $\mathbb{B}_i(\rho)$, that is, the set of neighboring sites m, p such that $\mathcal{d}(i, m) = \rho$ and $\mathcal{d}(i, p) = \rho + 1$. Sites m and p are nearest neighbors with m in the ball $\mathbb{B}_i(\rho)$ and p outside the ball. There exist at most $n_{\mathbb{L}} \times N_{\mathbb{L}}(\rho)$ bonds in $\mathbb{C}_i(\rho)$. The "secateur" operator is defined as

$$\Gamma_{m,p}(\xi, i, \rho) = \Gamma^*_{p,m}(\xi, i, \rho) = \xi \Delta_{m,p} \qquad \text{for} \quad (m, p) \in \mathbb{C}_i(r) \tag{73a}$$

$$\Gamma_{m,p}(\xi, i, \rho) = \Delta_{m,p} \qquad \text{otherwise} \tag{73b}$$

We consider the bipolaronic configuration $\{v_j(\xi)\}$ restricted to the

arbitrary subset $\mathbb{S} \supseteq \mathbb{B}_i(\rho)$ which is a continuous function of ξ and such that for $\xi = 1$,

$$\{v_j(1)\} = \{u_j(\mathbb{S})\} \qquad \text{for} \quad j \in \mathbb{S} \tag{74a}$$

By varying ξ from 1 to 0 we disconnected the inside of the ball $\mathbb{B}_i(\rho)$ from the outside and thus we have

$$\{v_j(0)\} = \{u_j(\mathbb{B}_i(\rho))\} \qquad \text{for} \quad j \in \mathbb{B}_i(\rho) \tag{74b}$$

The derivatives $\{dv_j(\xi)/d\xi\}$ are obtained as in (66) and (67) and fulfill

$$\begin{aligned} &\sum_j M_{k,j}(\{v_n\}, \{\sigma_\nu\}) \frac{\partial v_j}{\partial \xi} \\ &\quad = - \sum_{(m,p) \in \mathbb{C}_i(\rho), \nu, \nu'} \sigma_\nu (1 - \sigma_{\nu'}) \frac{\Psi_k^{\nu *} \Psi_k^{\nu'}}{E_{\nu\nu'} - E_\nu} \\ &\qquad \times (\Psi_m^{\nu' *} \Delta_{m,p} \Psi_p^\nu + \Psi_p^{\nu' *} \Delta_{p,m} \Psi_m^\nu) + \text{CC} \end{aligned} \tag{75a}$$

which yields with definition (68a)

$$\begin{aligned} &\sum_j M_{k,j}(\{v_n\}, \{\sigma_\nu\}) \frac{\partial v_j}{\partial \xi} \\ &\quad = - \sum_{(m,p) \in \mathbb{C}_i(\rho)} (\Delta_{m,p} S_{k,m;p} + \Delta_{p,m} S_{k,p;m}) - \text{CC} = Z_k \end{aligned} \tag{75b}$$

Inequality (42a) implies with (B12a) the existence of a constant K_4 such that for $(m, p) \in \mathbb{C}_i(\rho)$

$$|S_{k,m;k,p}| \leqslant K_4 \exp[-\gamma \mathcal{d}(k, m)] \tag{76a}$$

and

$$\begin{aligned} |Z_k| &\leqslant 4K_4 \operatorname*{Sup}_{m,p} |\Delta_{m,p}| \sum_{(p,m) \in \mathbb{C}} \exp[-\gamma \mathcal{d}(k, m)] \\ &\leqslant 4K_4 n_{\mathbb{L}} \operatorname*{Sup} |\Delta_{m,p}| \sum_{m, \mathcal{d}(i,m) = \rho} \exp[-\gamma \mathcal{d}(k, m)] \end{aligned} \tag{76b}$$

or using the metric inequality $|\mathcal{d}(k, i) - \mathcal{d}(m, i)| \leqslant \mathcal{d}(k, m)$,

$$|Z_k| \leqslant 4K_4 \|\bar{\bar{\Delta}}\|_\infty N_{\mathbb{L}}(\rho) \exp[-\gamma\, |\mathcal{d}(k, i) - \rho|\,] \tag{76c}$$

From (75b) and using (56),

$$\left|\frac{\partial u_i}{\partial \xi}\right| \leqslant \sum_{k \in \mathbb{S}_n} |(\bar{\bar{M}}^{-1})_{i,k}| \cdot |Z_k|$$

$$\leqslant 4K_4 |\bar{\bar{A}}|_\infty C_2 N_{\mathbb{L}}(\rho) \sum_{k \in \mathbb{L}} \exp[-\gamma_2 \measuredangle(k, i)] \exp[-\gamma |\measuredangle(k, i) - \rho|]$$

$$\leqslant K_5 N_{\mathbb{L}}(\rho) \sum_{r=0}^{\infty} N_{\mathbb{L}}(r) \exp(-\gamma_2 r) \exp(-\gamma |r - \rho|) = F_\rho \tag{77}$$

For proving that the last member of (77) goes to zero as ρ goes to infinity, we split it as $F_\rho = S_1 + S_2$, where S_1 can be bounded using Definition 3 of nonexponential lattices, as

$$S_1 = \sum_{r < \rho/2} N_{\mathbb{L}}(r) \exp(-\gamma_2 r) \exp(-\gamma |r - \rho|)$$

$$\leqslant \exp\left(-\gamma \frac{\rho}{2}\right) \sum_{r < \rho/2} N_{\mathbb{L}}(r) \exp(-\gamma_2 r)$$

$$< \exp\left(-\gamma \frac{\rho}{2}\right) \varphi(\gamma_2) \tag{78a}$$

We have for S_2

$$S_2 = \sum_{r \geqslant \rho/2}^{\infty} N_{\mathbb{L}}(r) \exp(-\gamma_2 r) \exp(-\gamma |r - \rho|)$$

$$\leqslant \exp\left(-\gamma_2 \frac{\rho}{2}\right) \sum_{r \geqslant \rho/2}^{\infty} N_{\mathbf{L}}(r) \exp\left(-\frac{\gamma_2}{2} r\right) \exp(-\gamma |r - \rho|)$$

$$\leqslant \exp\left(-\gamma_2 \frac{\rho}{2}\right) \varphi\left(\frac{\gamma_2}{2}\right) \tag{78b}$$

which yields

$$\left|\frac{\partial v_i}{\partial \xi}\right| \leqslant K_5 N_{\mathbb{L}}(\rho) \left[\exp\left(-\gamma \frac{\rho}{2}\right) \varphi(\gamma_2) + \exp\left(-\gamma_2 \frac{\rho}{2}\right) \varphi\left(\frac{\gamma_2}{2}\right)\right] = G_\rho \tag{79a}$$

Since the series $\varphi(\gamma/2) = \sum_\rho N_{\mathbb{L}}(\rho) \exp(-\frac{1}{2}\gamma\rho)$ is convergent for any positive γ, $N_{\mathbb{L}}(\rho) \exp(-\frac{1}{2}\gamma\rho)$ goes to zero as ρ goes to infinity. Consequently, both terms in (79a) goes to zero and $\lim_{\rho \to \infty} G_\rho = 0$. In addition, for any $0 < \gamma_3 < \gamma_2/2 < \gamma/2$, there exists a finite constant K_6 such that

$$0 < G_\rho < K_6 \exp(-\gamma_3 \rho) \tag{79b}$$

The inequality

$$\left|\frac{\partial v_i}{\partial \xi}\right| \leqslant G_\rho \tag{80a}$$

implies with (74)

$$|v_i(1)-v_i(0)| = |u_i(\mathbb{S})-u_i(\mathbb{B}_i(\rho))| \leqslant G_\rho < K_6 \exp(-\gamma_3 \rho) \tag{80b}$$

Thus, there exists ρ_ε such that for $\rho \geqslant \rho_\varepsilon$, we have $0 < G_\rho < \varepsilon/2$. For any $\mathbb{S} \supseteq \mathbb{B}_i(\rho_\varepsilon)$ and $\mathbb{S}^* \supseteq \mathbb{B}_i(\rho_\varepsilon)$, we have

$$|u_i(\mathbb{S})-u_i(\mathbb{S}^*)| \leqslant |u_i(\mathbb{S})-u_i(\mathbb{B}_i(\rho))| + |u_i(\mathbb{S}^*)-u_i(\mathbb{B}_i(0))| < \varepsilon \tag{80c}$$

which proves (72) and consequently Theorem 3. QED

This result proves that the infinite-size limit of finite systems is well defined and that the properties which are proven for arbitrary large system remains valid for the infinite system. For the sake of simplicity, the proof of the following properties are done for arbitrary finite systems.

4.4. Bipolaronic and Mixed Polaronic–Bipolaronic Structure with a Uniform Magnetic Field

We now analyze the effect of a magnetic field on the obtained structures. It is straightforward to prove that the domain of existence of bipolaronic and mixed polaronic–bipolaronic structures is at least preserved in the presence of a magnetic field, but our proof strongly suggests that this domain of existence should be extended.

Electrons interact with a magnetic field within two terms in the Hamiltonian. The first one describes the orbital effect, which corresponds classically to the force on a moving electric charge due to the magnetic field. The second term describes the direct interaction of the spin of the electron with the magnetic field.

4.4.1. Magnetic Orbital Effects. We first consider the orbital effects of the magnetic field.[19,22],[4] The transformation of the Hamiltonian under a magnetic field appears through gauge transformations of the electronic wave functions with the form $\Psi \to e^{i\alpha}\Psi$ [group $U(1)$] with a space-

[4] For the effect of a magnetic field within a tight-bindinig model see, e.g., ref. 20.

dependent phase α_i. For a tight-binding model with a magnetic field, $\Delta_{i,j}$ is replaced by the transfer integral $\Gamma_{i,j}$, which is a complex number,

$$\Gamma_{i,j} = \Delta_{i,j} \exp(i\varphi_{i,j}) \tag{81a}$$

In the absence of a magnetic field, $\varphi_{i,j}$ has the form $\varphi_{i,j} = \alpha_i - \alpha_j$ or equivalently the number of quantum flux $\phi_{\mathbf{C}}$ through any arbitrary closed loop $\mathbf{C} = \{i_1, i_2, i_3, ..., i_n = i_0\}$ on the lattice $\mathbb{L}$ ($\mathcal{A}(i_{p-1}, i_p) = 1$ for $p = 1$ to n), defined as

$$\phi_{\mathbf{C}} = \frac{1}{2\pi} \sum_{p=1}^{n} \varphi_{i_{p-1}, i_p} \tag{81b}$$

is zero. Introducing a magnetic field is equivalent to relaxing the condition that $\phi_{\mathbf{C}}$ is identically zero. Physically, $\phi_{\mathbf{C}}$ is precisely the number of quantum flux of the magnetic field through this closed loop $\mathbf{C} = \{i_1, i_2, i_2, ..., i_n = i_0\}$ in units hc/e, where h is the Planck constant, c the light speed, and e the electronic charge.

If we assume that all nonzero $\Delta_{i,j}$ are real, positive numbers, (72a) implies

$$\|\bar{\bar{\Gamma}}\|_2 \leqslant \|\bar{\bar{\Delta}}\|_2 \tag{81c}$$

By contrast, the supremum norms $\|\bar{\bar{\Delta}}\|_\infty = \|\bar{\bar{\Gamma}}\|_\infty$ and $S_\Delta = S_\Gamma$ [defined by (22b)] do not depend on the phases $\varphi_{i,j}$ and thus on the magnetic field. The theorems described above are unchanged when the electronic transfer integrals $\Delta_{i,j}$ are replaced by complex $\Gamma_{i,j}$ (which also can be random or both) since for a given lattice $\mathbb{L}$, the bounds t_3 and t_3' only depend on the upper bounds for the norms $\|\bar{\bar{\Delta}}\|_2$, $\|\bar{\bar{\Delta}}\|_\infty$, and S_Δ [defined by (22b)], which are equal or smaller when a magnetic field is present. In summary, we have the following statement.

Property 5a. Assume that the transfer integral couplings $\Delta_{i,j}$ on the lattice $\mathbb{L}$ are real, positive numbers.

Consider only the orbital effects of an arbitrary magnetic field, uniform or not.

Then Theorems 1 and 2 hold with bounds t_3 and t_3' which are the same as without a magnetic field (Theorem 3 also holds).

Remark 2. The bipolaronic structures and the mixed polaronic–bipolaronic structures do depend on the magnetic field but not necessarily in a smooth way. Indeed, the operator $\mathbf{S}_t$ is not a uniformly continuous function of a uniform magnetic field. Let us consider, for example, a two-

dimensional square alattice with sites $n=(n_1, n_2)$ with a uniform magnetic field. The gauge can be chosen in order that

$$\Gamma_{(n_1,n_2),(n_1+1,n_2)}=1 \tag{82a}$$

$$\Gamma_{(n_1,n_2),(n_1,n_2+1)}=e^{2i\pi n_1\phi} \tag{82b}$$

where ϕ is the number of flux quanta per plaquette, which is proportional to the uniform magnetic field. The supremum norm of the derivative $d\bar{\bar{\Gamma}}/d\phi$ of $\bar{\bar{\Gamma}}$ with respect to ϕ, with elements

$$d\Gamma_{(n_1,n_2),(n_1+1,n_2)}/d\phi=0 \tag{82c}$$

and

$$d\Gamma_{(n_1,n_2),(n_1,n_2+1)}/d\phi=2i\pi n_1 e^{2i\pi n_1\phi} \tag{82d}$$

is obviously infinite. Therefore, the eigenenergies of Eq. (14a) are not expected to be smooth functions of the magnetic field as well as the operator $\mathbf{S}_t$. The spectrum of the operator $\bar{\bar{\Gamma}}(\phi)$ has been numerically studied as a function of the magnetic field by Hofstadter,[22] who indeed found a nonsmooth behavior. He found a well-known Cantor set known as the Hofstadter butterfly. Therefore, we cannot conclude rigorously about the smoothness of the self-consistent bipolaronic or mixed polaronic–bipolaronic states $\{u_i(\phi)\}$ as a function of the magnetic field ϕ. We conjecture that at each site i, $u_i(\phi)$ should depend continuously on ϕ but should not be a differentiable function of ϕ at rational values of ϕ.

Remark 3. One can check by this example with a periodic square lattice and a constant magnetic field that inequality (81c) is strict except when $\Phi_{\mathbf{C}}=0 \bmod(1)$ for all closed loops $\mathbf{C}$. Consequently, in that cases the constrants γ and γ' defined by (321b) and (C8b) increase, while the upper bounds for $\|\bar{\bar{J}}\|_\infty$ given by (32c) and (10d) decrease. Otherwise, (22a) or (C3) yields smaller values for τ' or τ'' for a given τ, which thus extends the domain in t and τ where τ' (or τ'') $\leqslant \tau$. As a result, the bounds t_3 and t_3' proposed for the existence of bipolaronic or of mixed polaronic–bipolaronic structures get necessarily larger. But in fact, our theorems give only upper bounds, which are not the best ones, and thus this remark does not prove rigorously that the domain of existence of bipolaronic or mixed polaronic–bipolaronic structures is extended.

Nevertheless, this remark suggests an interesting point (which we plan to check numerically), which is that *bipolaronic and mixed polaronic–bipolaronic structures seem to be favored by the existence of a magnetic field.* Physically, *the orbital effects of the magnetic field on the electrons* favor the formation of both bipolaronic and mixed polaronic–bipolaronic structures.

This conjecture might be connected with the fact that some experiments on the quantum Hall effect under a large magnetic field also seems to favor the localization of the electrons (see, e.g., ref. 21).

4.4.2. Magnetic Spin Effects. Let us now consider the standard contribution to the initial Holstein Hamiltonian (1) which comes from the action of the magnetic field on the electronic spins[19,20]

$$H_M = -g_L \mu_B \sum_i \mathbf{H}_i \mathbf{s}_i \tag{83a}$$

We recall that $\mu_B$is a universal constant (the Bohr magneton) easily found in textbooks, $\mathbf{H}_i$ is the magnetic field at site i, and $\mathbf{s}_i$ is the physical spin at size i. As a function of the fermion operators, the components of the electronic spin operator at site i are

$$s_i^x = \frac{1}{2}(c_{i\downarrow}^+ c_{i\uparrow} + c_{i\uparrow}^+ c_{i\downarrow}) \tag{83b}$$

$$s_i^y = \frac{i}{2}(c_{i\downarrow}^+ c_{i\uparrow} - c_{i\uparrow}^+ c_{i\downarrow}) \tag{83c}$$

$$s_i^z = \frac{1}{2}(c_{i\uparrow}^+ c_{i\uparrow} - c_{i\downarrow}^+ c_{i\downarrow}) \tag{83d}$$

(the eigenvalues of s_i^x, s_i^y, and s_i^z are $\pm 1/2$ or 0). For electrons with spin 1/2, the Landé factor g_L is very close to 2. In order that Theorems 1 and 2 hold with the same bounds, it is necessary to assume that the magnetic field is uniform, $\mathbf{H}_i = \mathbf{H} = \text{const}$. (Note, however, that these theorems could be extended, but with different bounds. The modified proofs will bot be done here.) Suppose that the direction of the uniform magnetic field is along the z direction [used for describing the spin orientation σ in our definition (2a) for the electronic operators]; then the spin contribution to the electronic Hamiltonian (2a) due to the magnetic field is

$$\begin{aligned} H_M &= -\frac{1}{2} g \mu_B H \sum_i (c_{i\uparrow}^+ c_{i\uparrow} - c_{i\downarrow}^+ c_{i\downarrow}) \\ &= -\frac{1}{2} g \mu_B H \sum_v (c_{v\uparrow}^+ c_{v\uparrow} - c_{v\downarrow}^+ c_{v\downarrow}) \end{aligned} \tag{83e}$$

Using the energy units (9a), $E_0 = 8g^2/\hbar\omega_0$, the spin correction to the Hamiltonian $\hat{H}$ of (9b) is

$$\hat{H}_M = -h \sum_i (c_{i\uparrow}^+ c_{i\uparrow} - c_{i\downarrow}^+ c_{i\downarrow}) = -h \sum_v (c_{v\uparrow}^+ c_{v\uparrow} - c_{v\downarrow}^+ c_{v\downarrow}) \tag{84a}$$

with

$$h = \frac{1}{2} g_L \mu_B \frac{\hbar\omega_0}{8g^2} H \tag{84b}$$

Since the magnetic field is uniform, $\hat{H}_M$ commutes with $\hat{H}$ and also with the adiabatic Hamiltonian $\hat{H}_{ad}$, (12a), and there is a common base of eigenstates for $\hat{H}_{ad}$ and $\hat{H}_M$. However, the spin orientation degeneracy of the eigenstates of the adiabatic Hamiltonian $\hat{H}_{ad}$ is raised by H_M and the spin of the eigenstates has to be aligned in the direction z of the magnetic field.

Property 5b. Property 5a holds identically when considering the electronic spin interactions but with a uniform magnetic field.

But then, the (real) spin degeneracy in energy of the mixed polaronic–bipolaronic state is raised.

The total energy $\Phi_H(\{u_i\})$ of a given atomic configuration $\{u_i\}$ of the variational form (15) corresponding to the Hamiltonian $\hat{H}_{ad} + \hat{H}_M$ does not depend only on the electronic population factor $\{\sigma_v\}$ in (15c), but on the detailed electronic population according to both their eigenstate v and their spins. Two sets of pseudospins $\{\sigma_{v\uparrow}\}$ and $\{\sigma_{v\downarrow}\}$ with $\sigma_{v\uparrow}$ and $\sigma_{v\downarrow} = 0$ or 1 are required instead of a single set $\{\sigma_v\}$ with $\sigma_v = \frac{1}{2}(\sigma_{v\uparrow} + \sigma_{v\downarrow})$. Then, we have

$$\Phi_H(\{u_i\}; \{\sigma_{v\uparrow}\}, \{\sigma_{v\downarrow}\}) = \Phi(\{u_i\}, \{\sigma_v\}) - h \sum_v (\sigma_{\sigma\uparrow} - \sigma_{v\uparrow}) \tag{85}$$

At the anti-integrable limit ($t = 0$), the eigenstates of the Hamiltonian $\hat{H}_{ad} + \hat{H}_M$ are characterized by two pseudospin configurations $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$ with $\sigma_{i\uparrow} = 0$ or 1 and $\sigma_{i\downarrow} = 0$ or 1 and the spatial distribution of the spin configuration is $\{s_i^z\} = \{\frac{1}{2}(\sigma_{i\uparrow} - \sigma_{i\downarrow})\}$ ($s_i^z = \pm 1/2$ or 0). It could correspond to a spin density wave (SDW) in the case of ordering of $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$. According to Theorems 1 and 2, theses eigenstates persist for t small enough in the presence of the magnetic orbital orbital terms and yield bipolaronic and mixed polaronic–bipolaronic states.

4.5. Ground States without and with a Uniform Magnetic Field

For completing this set of exact results, we prove that for t small enough (or k large enough), the ground state of the adiabatic Holstein model is one of these bipolaronic or mixed polaronic–bipolaronic states. However, at the present stage, we cannot give the precise configuration

$\{\sigma_i\}$ or $\{\sigma_{i\uparrow}\}$ and $\{\sigma_{i\downarrow}\}$ which describes the bipolaronic or polaronic ordering of these ground states, which are generally not chaotic.

Finding the ground state of the adiabatic Holstein model requires finding both the atomic configuration $\{u_i\}$ and the electronic population factor $\sigma_{\nu\uparrow}$ and $\sigma_{\nu\downarrow}$ which yields the absolute minimum of the variational form (84a). This ground state is well defined for any finite system. It may be not unique. For example, an incommensurate ground state is degenerate with respect to its phase.

We now prove the following theorem.

Property 6. In the absence of or for a small enough uniform magnetic field and for t small enough, the ground state(s) of the adiabatic Holstein model restricted to any finite subset $\mathbb{S} \subset \mathbb{L}$ is a bipolaronic structure as predicted by Theorem 1 (i.e., it is characterized by the pseudospin configuration which describes the distribution of the bipolarons).

In the presence of a large enough magnetic field and for t small enough, the ground state(s) is a mixed polaronic–bipolaronic structure as predicted by Theorem 2.

Proof. In the case with a uniform magnetic field, the ground state is characterized by the electronic populations factors $\{\sigma_{\nu\uparrow}\}$ and $\{\sigma_{\nu\downarrow}\}$ and the atomic configuration $\{u_n\}$. In order to minimize the electronic energy with fixed $\{u_n\}$, it is convenient to define two Fermi levels $E_{F\uparrow}$ and $E_{F\downarrow}$ instead of one, fulfilling

$$E_{F\uparrow} - E_{F\downarrow} = 2h \tag{86}$$

[with h given by (83b)]. For the electronic eigenstates with energy $E_\nu \leqslant E_{F\uparrow}$ [E_ν is the eigenenergy of Eq. (14a) which contains the orbital terms due to the magnetic field], we have $\sigma_{\nu\uparrow} = 1$, and $\sigma_{\nu\uparrow} = 0$ otherwise. For those fulfilling $E_\nu \leqslant E_{F\downarrow}$, we have $\sigma_{\nu\downarrow} = 1$ and $\sigma_{\nu\downarrow} = 0$. Since we work with a fixed number of electrons, the global Fermi energy $E_F = \frac{1}{2}(E_{F\uparrow} + E_{F\downarrow})$ has to be fixed in order to obtain the chosen number of electrons in the system.

Let us assume that $\{u_n\}$ is the ground-state atomic configuration. By definition, any change in this configuration should increase the total energy. We use again the "secateur" method" which has been explained above. For a given site m, the operator $\bar{\bar{\Gamma}}(\xi, m)$ is defined by (65).

1. We vary ξ from 1 to 0. Unlike for the proof of Property 4, we do not let the configuration $\{u_n\}$ relax as ξ varies, but we fix $\{u_n\}$ to its set of initial values. Thus, the elastic energy (15b) is constant and only the electronic energy (15c) varies, since the eigenenergies given by (14) depend on ξ.

2. When $\xi = 0$, site m is isolated. Then, we put the atom m in its "local ground state" at u'_m and calculate the energy gain.

3. We vary ξ back from 0 to 1 while keeping the atomic position fixed. We then return to the initial Hamiltonian and we bound again the variation of the electronic energy.

At the end, we bound from above the energy difference between the final configuration $\{u'_n\}$ and the initial configuration $\{u_n\}$, which are identical except for the position u_m of the atom m. This quantity has to be positive since $\{u_n\}$ is assumed to be a ground state.

Step 1. The set of N (real) eigenenergies is the set of N zeros of a polynomial of degree N, the coefficients of which are smooth, continuous functions of ξ. Thus, when varying ξ from 1 to 0, each eigenenergy $E_\nu(\xi)$ varies continuously. It may become degenerate for some values of ξ. Then, in order to follow unambiguously each eigenenergy $E_\nu(\xi)$ as a function of ξ, these eigenenergies $E_\nu(\xi)$ are put in increasing order and this order is preserved when ξ varies while the population factor σ_ν for each eigenstate ν is kept constant. The electronic energy (15c) is thus a continuous function of ξ. When the eigenenergy $E_\nu(\xi)$ is nondegenerate, it is differentiable with respect to ξ and we have

$$\frac{dE_\nu(\xi)}{d\xi} = \langle \bar{\Psi}^\nu | \frac{d\bar{\bar{\Gamma}}(\xi, m)}{d\xi} | \bar{\Psi}^\nu \rangle$$

$$= t \sum_n \Psi_n^{\nu *} \Delta_{nm} \Psi_m^\nu + t \sum_n \Psi_m^{\nu *} \Delta_{mn} \Psi_n^\nu \tag{87a}$$

which implies

$$\left| \frac{dE_\nu(\xi)}{d\xi} \right| \leqslant 2t \sum_n |\Psi_n^{\nu *}| \cdot |\Delta_{nm}| \cdot |\Psi_m^\nu| \tag{87b}$$

When $E_\nu(\xi)$ is degenerate, we can choose the eigenstates $\bar{\Psi}^\nu$ in the degenerate subspace in order that this formula holds for the right or the left derivative. Consequently, the electronic energy (15c) is left and right differentiable and both derivatives are bounded as

$$\left| \frac{\partial \Phi_{\text{electr}}}{\partial \xi} \right| \leqslant \left| \sum_\nu \sigma_\nu \frac{dE_\nu(\xi)}{d\xi} \right|$$

$$\leqslant 2t \sum_n |\Delta_{nm}| \sum_\nu \sigma_\nu |\Psi_n^{\nu *}| \cdot |\Psi_m^\nu|$$

$$\leqslant 2t \sum_n |\Delta_{nm}| \leqslant 2t \|\bar{\bar{\Delta}}\|_\infty \tag{88}$$

Since $\Phi_{\text{electr}}(\{u_i\}; \{\sigma_v\})$ depends continuously on ξ, the total variation $V[\Phi_{\text{electr}}; \xi: 1 \to 0; \{u_n\}]$ of the electronic energy for ξ varying from 1 to 0 is bounded as

$$V[\Phi_{\text{electr}}(\{u_n\})]_{\xi=1}^{\xi=0} \leqslant 2t \|\bar{\bar{A}}\|_\infty \tag{89a}$$

Step 2. For $\xi = 0$, u_m is an electronic eigenenergy. Therefore there exists $v = v_m$ such that $E_{v_m}(0) = u_m$ with the population factor σ_{v_m}. The ground state of this isolated site m is obtained for $u_m = -\sigma_{v_m}$. We consider the new configuration $\{u'_n\}$, where $u'_n = u_n$ for $n \neq m$ and $u'_m = -\sigma_{v_m}$. The electron population factors σ_v and σ_{v_m} are kept constant. This atomic displacement yields a variation $V[\Phi;\ \xi = 0;\ \{u_n\} \to \{u'_n\}]$ of the total energy which is the sum of the variation of the electronic energy $E_{v_m}(0)$ and of the elastic energy at the isolated site m,

$$\begin{aligned} &V[\Phi; \{u_m\}: u_m \to u'_m]_{\xi=0} \\ &\quad = (\tfrac{1}{2}u'^2_m + \sigma_{v_m} u'_m) - (\tfrac{1}{2}u_m^2 + \sigma_{v_m} u_m) \\ &\quad = \tfrac{1}{2}\sigma^2_{v_m} - \sigma^2_{v_m} - \tfrac{1}{2}u_m^2 - \sigma_{v_m} u_m = -\tfrac{1}{2}(u_m + \sigma_{v_m})^2 \end{aligned} \tag{89b}$$

Step 3. We now restore ξ to its initial value 1. When ξ varies from 0 to 1, the eigenenergies vary continuously while preserving their new order determined at $\xi = 0$ at step 2. The electronic population factor σ_v is kept constant. The bound for the variation of the electronic energy is the same as in (89a),

$$V[\Phi_{\text{electr}}(\{u'_n\})]_{\xi=0}^{\xi=1} \leqslant 2t \|\bar{\bar{A}}\|_\infty \tag{89c}$$

At the end of this sequence of transformations, only atom m has been moved. The corresponding eigenenergies have been changed, but no physical spin has been flipped, so that the spin energy (83e) in the magnetic field is unchanged. The variation $V[\Phi; \{u_n\} \to \{u'_n\}]_{\xi=1}$ of the total energy (15a) obtained by changing u_m into u'_m is bounded by the sum of the three upper bounds in (89), which yields

$$\begin{aligned} &V[\Phi; \xi = 1; u_m \to u'_m] \\ &\quad = \Phi(\{u'_n\}) - \Phi(\{u_n\}) \leqslant 4t \|\bar{\bar{A}}\|_\infty - \tfrac{1}{2}(u_m + \sigma_{v_m})^2 \end{aligned} \tag{90a}$$

Since we assume that $\{\{u_n\}, \{\sigma_v\}\}$ is the ground state, the right member of (90a) has to be positive, which yields

$$|u_m + \sigma_{v_m}| \leqslant (8t \|\bar{\bar{A}}\|_\infty)^{1/2} = \tau(t) \tag{90b}$$

for all m.

From now on, we distinguish two cases, $\sigma_{\nu_m}=0$ or 1 for all m, and $\sigma_{\nu_m}=0$, 1/2, or 1.

Case without magnetic field. The first case is obtained in the absence of magnetic field h, which implies $E_{F\uparrow}=E_{F\downarrow}$ in (86) and $\sigma_\nu=\frac{1}{2}(\sigma_{\nu\uparrow}+\sigma_{\nu\downarrow})=\sigma_{\nu\uparrow}=\sigma_{\nu\downarrow}=0$ or 1 for all ν. When

$$\tau(t)+t\|\bar{\bar{A}}\|_2=(8t\|\bar{\bar{A}}\|_\infty)^{1/2}+t\|\bar{\bar{A}}\|_2<\tfrac{1}{2} \tag{91a}$$

then condition (90b) implies that there exists a unique pseudospin configuration $\{\sigma_n\}=\{\sigma_{\nu_n}\}$ such that $\{u_n\}\in\mathscr{E}(\{\sigma_n\};\tau(t))$, and Lemma 1 applies. There exists a new set of pseudospins $\{\sigma'_\nu\}$ with $\sigma'_\nu=0$ or 1 such that

$$E_\nu=-[1-\tau(t)](\sigma'_\nu+\varepsilon_\nu)-\frac{\tau(t)}{2} \tag{91b}$$

with

$$|\varepsilon_\nu|\leqslant\frac{2\|\bar{\bar{A}}\|_2 t+\tau(t)}{2[1-\tau(t)]} \tag{91c}$$

However, for proving that $\{u_n\}\in\mathscr{E}(\{\sigma_n\};\tau(t))$ can be obtained as a fixed point of the operator $\mathbf{S}_t$ defined above, we need to prove that the electronic population factor $\{\sigma_\nu\}$ fulfills the definition (16) of Section 3.1. This is equivalent to proving that $\sigma'_\nu=\sigma_\nu$ for all ν. Let us prove this identity for t small enough.

Step 4. Let us assume that we do not have $\sigma'_\nu=_\nu$ for all ν, and then choose ν such that $\sigma'_\nu\neq\sigma_\nu$. Then we have $|\sigma'_\nu-\sigma_\nu|=1$. As a consequence of Lemma 1, there exist sites m such that $\sigma_m=\sigma'_\nu$. Let us choose such a site m and perform again the secateur method in the form described just above. We perform again the transformation of the ground state described in step 1, but at step 2 we insert a permutation in the electronic population factor to relax m. The occupation number of the electronic eigenstate ν is changed from σ_ν to $\sigma'_\nu=\sigma_m$, while the occupation number of the state located at u_m is changed from σ'_ν to σ_ν. Then, we move atom m from u_m to $u''_m=-\sigma_\nu$ and set $u''_n=u_n$ for $n\neq m$. The energy variation (89b) is replaced by

$$\begin{aligned}
&V[\Phi;\{u_n\}:u_m\to-\sigma_\nu;\sigma'_\nu\leftrightarrow\sigma_\nu]_{\xi=0}\\
&\quad=(\tfrac{1}{2}u''^2_m+\sigma_\nu u''_m)-(\tfrac{1}{2}u_m^2+\sigma'_\nu u_m)+(\sigma'_\nu-\sigma_\nu)E_\nu\\
&\quad=\tfrac{1}{2}\sigma_\nu^2-\sigma_\nu^2-\tfrac{1}{2}(u_m+\sigma'_\nu)^2+\tfrac{1}{2}\sigma'^2_\nu+(\sigma'_\nu-\sigma_\nu)E_\nu\\
&\quad=-\tfrac{1}{2}(\sigma'_\nu-\sigma_\nu)^2-(\sigma'_\nu-\sigma_\nu)\varepsilon_\nu-\tfrac{1}{2}\varepsilon_m^2
\end{aligned} \tag{92a}$$

We now perform again step 3, which restores ξ to its initial value 1 while the atomic position u_i'' and the electronic population factors remains constant and the eigenenergies have same ordering. The total energy variation between the two states is now bounded as

$$\begin{aligned} 0 &< V[\Phi; u_m \to u_m''; \sigma_\nu' \leftrightarrow \sigma_\nu]_{\xi=1} \\ &= \Phi(\{u_n''\}) - \Phi(\{u_n\}) \\ &\leqslant 4t \|\bar{\bar{A}}\|_\infty - \tfrac{1}{2}(\sigma_\nu' - \sigma_\nu)^2 - (\sigma_\nu' - \sigma_\nu)\varepsilon_\nu - \tfrac{1}{2}\varepsilon_m^2 \end{aligned} \tag{92b}$$

This condition implies, with (91c),

$$0 \leqslant 4t \|\bar{\bar{A}}\|_\infty + \frac{2\|\bar{\bar{A}}\|_2 t + \tau(t)}{2[1-\tau(t)]} - \frac{1}{2} \tag{92c}$$

When t goes to zero, the right member of (92c) goes to the negative value $-1/2$ and for small enough t, this inequality (92c) cannot be fulfilled. Consequently, there exists t_4 such that for $t < t_4$ we necessarily have $\sigma_\nu' = \sigma_\nu$ for all ν. Using the fact that $\|\bar{\bar{A}}\|_2 \leqslant \|\bar{\bar{A}}\|_\infty$, we can check, for example, that

$$t_4 = \frac{1}{200} \frac{1}{\|\bar{\bar{A}}\|_\infty} \tag{93a}$$

fulfills this condition. Since we have $\tau(t) < 1/5$ for $t < t_4$, the ground state without magnetic field $\{u_n\}$ belongs to a certain set $\mathscr{E}(\{\sigma_n\}; 1/5)$. When

$$t < \mathrm{Min}(t_3, t_4) = t_5 \tag{93b}$$

the operator $\mathbf{S}_t$ has a unique fixed point $\{u_n\}$, according to Theorem 1, in $\mathscr{E}(\{\sigma_n\}; 1/5)$, which then is a bipolaronic state.

Case with magnetic field. In the case with a magnetic field, we may have $\sigma_\nu = 0$, $1/2$, or 1. Then, Lemma C holds for configuration $\{u_n\}$ when instead of condition (91a) we have

$$\tau(t) + t\|\bar{\bar{A}}\|_2 = (8t\|\bar{\bar{A}}\|_\infty)^{1/2} + t\|\bar{\bar{A}}\|_2 < \tfrac{1}{4} \tag{94a}$$

which yields a new pseudospin configuration $\{\sigma_\nu''\}$ such that we have

$$E_\nu = -[1-\tau(t)](\sigma_\nu'' + \varepsilon_\nu) - \frac{\tau(t)}{2} \tag{94b}$$

with

$$|\varepsilon_\nu| \leqslant \frac{\|\bar{\bar{A}}\|_2 t + \tau(t)}{1-\tau(t)} \tag{94c}$$

We prove $\sigma_\nu'' = \sigma_\nu$ for all ν, with the same method as in step 4. If $\sigma_\nu'' \neq \sigma_\nu$, $|\sigma_\nu'' - \sigma_\nu| \geqslant 1/2$, inequality (92b) holds and implies, with (94c),

$$0 \leqslant 4t \|\bar{\bar{A}}\|_\infty + \frac{\|\bar{\bar{A}}\|_2 t + \tau(t)}{2[1-\tau(t)]} - \frac{1}{8} \tag{95a}$$

When

$$t < t_4' = (1/512)(1/\|\bar{\bar{A}}\|_\infty) \tag{95b}$$

inequality (95a) cannot be fulfilled, which implies $\sigma_\nu'' = \sigma_\nu$ for all ν. Then the ground-state configuration $\{u_n\}$ belongs to a certain set $\mathscr{E}(\{\sigma_n\}; 1/8)$ with $\sigma_n = 0$, 1/2, or 1. According to Theoreml 2, it is the unique fixed point of $\mathbf{S}_t$ in $\mathscr{E}(\{\sigma_n\}; 1/8)$, i.e., a mixed polaronic–bipolaronic configuration, when

$$t < \mathrm{Min}(t_3', t_4') = t_5' \tag{95c}$$

In order that the ground state $\{u_n\}$ be a mixed polaronic–bipolaronic configuration, the magnetic field has to be sufficiently large. We can bound this field by using again the secateur method.

Estimation of the critical magnetic field for a transition between a bipolaronic ground state and a mixed polaronic–bipolaronic ground state. This problem is studied in the regime $t < t_5' < t_5$, where both bipolaronic and mixed polaronic–bipolaronic states are proven to exist.

First, we analyze the energy for breaking a bipolaron. We assume that the ground state contains both bipolarons and empty sites. Let us consider a site n occupied by a bipolaron, where $\sigma_n = 1$, and an empty site m, where $\sigma_m = 0$.

We use a "secateur" operator similar to (65) which disconnects both sites m and n from the remainder of the lattice. Thus, after step 1, the obtained bound for the energy variation is twice the energy variation calculated in (89a),

$$|V[\Phi_{\mathrm{electr}}(\{u_n\})]_{\xi=1}^{\xi=0}| \leqslant 4t \|\bar{\bar{A}}\|_\infty \tag{96a}$$

We transfer a single electron from the disconnected site n to the disconnected site m. For the new pseudospin condiguration $\{\sigma_i'\}$ we have $\sigma_m' = \sigma_n' = 1/2$ and align the two real spins along the magnetic field. The variation of the configuration energy is the variation of the elastic and electronic energy plus the gain in the magnetic spin energy (84),

$$\begin{aligned} V[\Phi; \{u_n\}: u_n \to -\tfrac{1}{2}; \sigma_n \to \tfrac{1}{2}; u_m \to -\tfrac{1}{2}; \sigma_m \to \tfrac{1}{2}]_{\xi=0} \\ = [-\tfrac{1}{2}\sigma_n'^2 - \tfrac{1}{2}(u_n + \sigma_n)^2 + \tfrac{1}{2}\sigma_n^2] + [-\tfrac{1}{2}\sigma_m'^2 - \tfrac{1}{2}(u_m + \sigma_m)^2 + \tfrac{1}{2}\sigma_m^2] - 2h \\ \leqslant \tfrac{1}{4} - 2h \end{aligned} \tag{96b}$$

We restore the conection of sites m and n with the remainder of the lattice, which costs an energy variation again bounded as in (96a). Thus, the energy variation for breaking a bipolaron is bounded as

$$V[\Phi; \{u_n\}: \sigma_n \to \tfrac{1}{2}; \sigma_m \to \tfrac{1}{2}]_{\xi=1} \leqslant \tfrac{1}{4} - 2h + 8t \|\bar{\bar{A}}\|_\infty \tag{97a}$$

It must be strictly positive, since the initial state was supposed to be the ground state. Consequently, when

$$h \geqslant \tfrac{1}{8} + 4t \|\bar{\bar{A}}\|_\infty = h_M \tag{97b}$$

and when the electron density per site is smaller than 1, the ground state contains only polarons and empty sites ($\sigma_n = 1/2$ or 0). When the electron density per site is larger than 1, the ground state contains only bipolarons and polarons and no empty sites ($\sigma_n = 1/2$ or 1). In both cases, the number of polarons in the ground state is maximum. We call these states saturated mixed polaronic–bipolaronic structures.

Second, we now analyze the energy for combining two polarons into a bipolaron. We assume that the ground state contains at least two polarons at site n and site m (where $\sigma_m = \sigma_n = 1/2$) and do the same secateur method as just above for disconnecting sites m and n from the remainder of the lattice. Then, we transfer an electron from site m to n, for example, and restore the connection of sites m and n with the remainder of the lattice. The final energy variation is bounded as

$$V[\Phi; \{u_n\}: \sigma_n \to 1; \sigma_m \to 0]_{\xi=1} \leqslant -\tfrac{1}{4} + 2h + 8t \|\bar{\bar{A}}\|_\infty \tag{98a}$$

which must be positive. Thus, when

$$h \leqslant \tfrac{1}{8} - 4t \|\bar{\bar{A}}\|_\infty = h_m \tag{98b}$$

the ground state only contains bipolarons and empty sites (except possibly a single polaron if the number of electrons is odd). QED

In the regime where both the pipolaronic and the mixed polaronic bipolaronic states exist, finding the ground-state configuration $\{u_n\}$ is then equivalent to the problem of finding a pseudospin configuration $\{\sigma_n\}$. Exact results in the general case seem to be very difficult to obtain. However, we think that it might be possible to prove rigorously by using variations about the secateur method that in the 1D periodic adiabatic Holstein model the ground state is indeed a quasiperiodic structure of bipolarons, in agreement with numerical observations. Understanding the transformations of the bipolaronic ground states under a magnetic field is also a very interesting question in the interval $h_m < h < h_M$ where we can

expect a complex phase diagram as a function of the magnetic field with nonsaturated mixed polaronic–bipolaronic ground states.

5. COMMENTS AND CONCLUDING REMARKS

This last section is devoted to numerical analysis which illustrate the above results, and to comments, possible extensions, and physical applications. We also set new problems to be studied in further work. We first report a numerical analysis done in one dimension only, which suggests that for a periodic lattice, the bipolarons in their ground state could have a well-defined shape.

5.1. Transition by Breaking of Analyticity (TBA): Effective Shape of a Bipolaron (Numerical Analysis)

The values given for the physical quantities and for the bounds on the parameters *must not* be considered as *realistic physical estimations.* These quantities can be calculated accurately by numerical means. We report now the interpretation in terms of bipolaronic structures of early numerical calculations[3–6] confirmed and completed by those of refs. 25 and 26. The ground state $\{u_i\}$ of the one-dimensional periodic adiabatic Hostein model was calculated. It has been observed that, as predicted by the standard Peierls–Fröhlich theory, this ground state is indeed a CDW. For an irrational density ξ of electronic pair per site, it can be described with a 2π-periodic hull function $g(x)$ as

$$u_i = g(2k_F i + \alpha) \tag{99a}$$

where $k_F = \pi\zeta$ is the Fermi wave vector and α is an arbitrary phase. In addition, a transition by breaking of analyticity was found as in the FK model with the same critical behavior (within numerical accuracy). For $\zeta = (3-\sqrt{5})/2$, it was found that for $k = 1/\sqrt{t} < k_c(\zeta) \cong 1.58 \pm 0.01$, the hull function $g(x)$ appears as a smooth function, while for $k > k_c(\zeta)$, it exhibits many discontinuities. This observation suggests that, as for the FK model, the set of values taken by the full function $g(x)$ could be a Cantor set. By analogy with similar observations in the FK model (which are supported there by rigorous results), it was suggested that $g(x)$ could be analytic for $k < k_c(\zeta)$ and purely discrete for $k > k_c(\zeta)$. Critical quantities which could be measured in the Peierls chain at this transition were found with the same critical exponents as those corresponding to the FK model and for the same incommersurability ratio.

In addition, it was observed that the ground states (up to an arbitrary

phase shift) were the only minima of the variational form. By contrast, for $k > k_c(\zeta)$, there are a large number of metastable states which are bipolaronic structures, as predicted by the present theory. In addition, when varying k, these metastable states exhibit complex cascades of bifurcations[26] similar to those of the FK model.

It was proven in the extended FK model[8] that the ground state can be described as a linear superposition of effective discommensurations. This exact result does not hold for arbitrary metastable configurations, but only for a set of a few special configurations to which the ground state belongs. Although we do not have any extension of this rigorous theory concerning the ground state of the presently studied model, it is interesting to check from our numerical data whether a similar property holds for the ground state of the adiabatic Holstein model.

By analogy with the exact decomposition described by formulas (36) in ref. 2, we should expect that the ground-state configuration $\{u_i\}$ can be put into the form

$$u_n = \sum_i \sigma_i b_{i+n} \tag{99b}$$

where $\{\sigma_i\}$ is a pseudospin configuration with $\sigma_i = 0$ or 1 (the bipolaronic configuration), which is described by a period-1 characteristic function

$$\sigma_i = \chi(i\zeta + \alpha) \tag{100a}$$

with

$$\chi(x) = 1 \qquad \text{for} \quad 0 \leqslant x < \zeta \tag{100b}$$

$$\chi(x) = 0 \qquad \text{for} \quad \zeta \leqslant x < 1 \tag{100c}$$

and $\{b_i\}$, which represents the effective shape of a bipolaron.

Using the deconvolution of formula (98b) for our numerical data $\{u_i\}$ with the pseudospin configuration (99), these effective bipolarons $\{b_i\}$ are found to be well defined and localized, and, as expected, in the regime $k > k_c(\zeta)$ only.

Figure 5 represents the density $\rho_i = -b_i$ of electron pairs corresponding to this "effective bipolaron" for several values of k. It is straightforward to prove that because of Eq. (18a) we have $\sum_i \rho_i = 1$. The value of b_i goes exponentially to zero as $\exp(-|i|/\xi)$, where ξ is the coherence length of the bipolaronic structure.

It is remarkable to note that for the ground state, although the size of these bipolarons could become much larger than their distance one from each other, a well-defined shape can be defined. Since the effective shape of

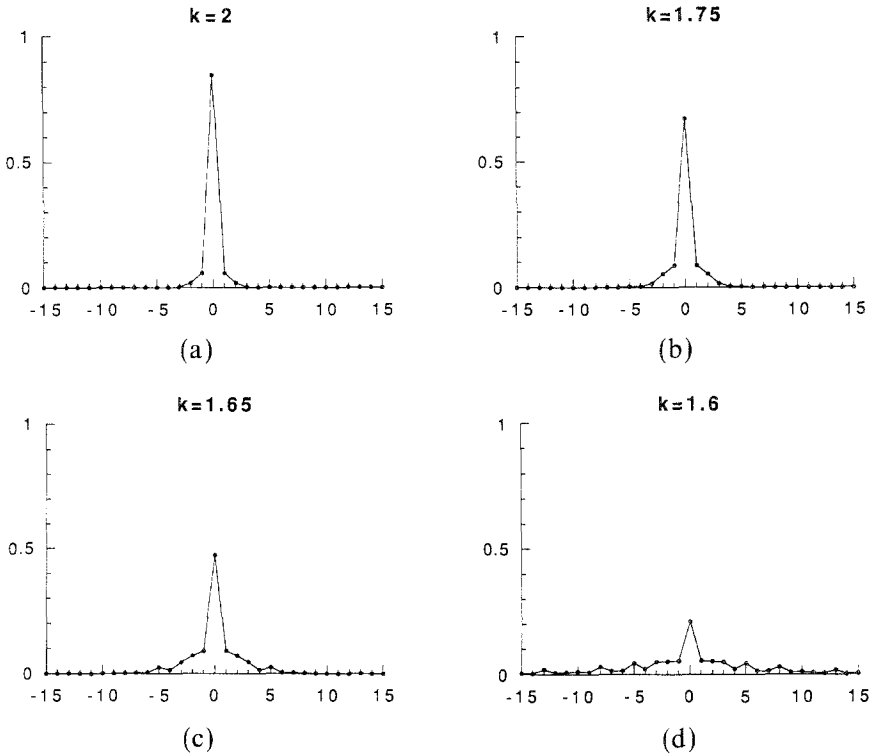

Fig. 5. Effective electron density $\{\rho_i\}$ versus i in the one-dimensional adiabatic Holstein model for $\zeta = (\sqrt{5}-1)/2$ for $1/\sqrt{t} = k = 2$, 1.75, 1.65, and 1.6 [$k_c(\zeta) \cong 1.58$]. This bipolaron is well localized far above the TBA and spreads out when approaching $k_c(\zeta)$ from above. It is undefined for $k < k_c(\zeta)$ (for an infinite system).

these bipolarons takes into account their relative environment, it depends not only on the electron–phonon coupling, but on the electron pair density (band filling).

When k goes to $k_c(\zeta)$ from above, the size ξ of these bipolarons diverges (with a critical exponent which is, for example, $\nu \cong 0.9874$ when ζ is a noble number, see ref. 6). For $k \leqslant k_c(\zeta)$, in principle formula (99) could yield the effective shape of an effective bipolaron $\{\rho_i\}$, but this is highly sensitive to the size of the system which is analyzed. In fact, the electronic density ρ_i is rather uniformly distributed over the whole system, so that for a large system, ρ_i goes to zero since $\sum_i \rho_i = 1$. Within our definition, the bipolarons which are not localized in the real space do not exist.

As mentioned in ref. 2 for the FK model, when $k > k_c(\zeta)$, these effective bipolarons can be used analogously to the effective discommensurations for describing the weak disorder around the ground state. These

choatic bipolaronic configurations are described with an "exponentially" good accuracy by formula (99b) where the sequence of pseudospins $\{\sigma_i\}$ are slightly random (see the end of ref. 2 and refer to refs. 27–29 for a precise definition of "slightly random" for an incommensurate structure). Thus, the knownledge of the characteristic parameters of the effective bipolaron turns out to be physically meaningful for describing the low-temperature behavior of this incommensurate CDW.

It seems clear that this property does not hold for random lattices, but an interesting question remains: Could the concept of effective bipolaronic shape be extended to periodic d-dimensional lattices? Or is it restricted to periodic one-dimensional lattices?

5.2. Possible Extensions of the Mathematical Method

This Holstein model has been chosen in this paper for the sake of (relative) simplicity. We now discuss how the technique used here for proving the existence of bipolaronic and polaronic states could be extended for larger classes of models, thus anticipating on future work. The required conditions on the considered models should be the analogue of the conditions[36] for uniform hyperbolicity in symplectic dynamical systems. Indeed, it is well known by specialists in this field that uniform hyperbolic sets are robust under "perturbation." On this basis, we expect the stability of polaronic and bipolaronic structures in coupled electron–phonon systems when there exist both a nonvanishing gap in the phonon spectrum and a nonvanishing gap in the electronic spectrum between the occupied and the empty states.

In wide generality, we expect that Theorem 1 for the existence of bipolaronic states extends to adiabatic electron–phonon models with several phonon branches β with dispersion and several electronic bands α. These models are tight binding on an arbitrary nonexponential lattice and can be written as the sum of three terms as in (1), which have the following properties.

1. There exists a well-defined anti-integrable limit with a set of stable eigenstates $\mathscr{C}$ ($H_k = 0$) described by pseudospin configurations $\{\sigma_i\}$.

2. There is a subset $\mathscr{C}' \subseteq \mathscr{C}$ of eigenstates with a nonvanishing gap between the occupied electronic states and the empty electronic states.

3. The QEAM (which determines the bare phonon spectrum) must be invertible. Note that in principle our method also works when this form is not positive. However, the positivity condition should be required for ensuring the physical stability of the bipolaronic and polaronic structures.

4. The electron–phonon coupling term H_{ep} must be a form which *depends linearly* on the electron densities $n_{i\alpha\uparrow}$ and $n_{i\alpha\downarrow}$,

$$H_{ep} = \sum_{i,\alpha,\sigma} g_{i\alpha\sigma}(\{u_n^\beta\}) n_{i\alpha\sigma} \tag{101a}$$

Then, we claim that our theory can be extended without any essential changes provided that the electron kinetic part H_k is a self-adjoint *form of degree 2* which only depends on fermion operators. Several coupled electronic bands α can be considered. The kinetic electron Hamiltonian H_k has the general form

$$H_k = -t \sum_{\langle i,j\rangle,\sigma,\sigma'} \Delta(i,\alpha,\sigma;j,\alpha',\sigma') c^+_{i,\alpha,\sigma} c_{j,\alpha',\sigma'} \tag{101b}$$

where $\Delta(i,\alpha,\sigma;j,\alpha',\sigma')$ is the transfer integral between nearest neighboring sites i and j on the nonexponential lattice and between bands α and α' [we assume $|\Delta(i,\alpha,\sigma;j,\alpha',\sigma')| < 1$]. As in the adiabatic Holstein model, the orbital effect of a magnetic field can be included by an appropriate choice of the phase of the complex transfer integrals $\Delta(i,\alpha,\sigma;j,\alpha',\sigma')$.

In the absence of spin–orbit coupling, that is, when $\Delta(i,\alpha,\sigma;j,\alpha',\sigma') = 0$ for $\sigma \neq \sigma'$, proof for the existence of mixed polaronic–bipolaronic states can also be obtained for pseudospin configurations in $\mathscr{C}'$, but then the existence of two nonvanishing electronic gaps in the energy at the anti-integrable limit instead of one is required. The first gap lies between the doubly occupied states and the singly occupied states, and the second one between the singly occupied states and the empty states.

Spin–orbit coupling can be also included in (101b) by considering transfer integrals $\Delta(i,\alpha,\sigma;j,\alpha',\sigma') \neq 0$ for $\sigma \neq \sigma'$. Then we must require extra conditions for time reversal invariance. When spin–orbit coupling is present, the degeneracy between spin $\uparrow$ and $\downarrow$ is raised without a magnetic field. The electronic eigenstates mix $\uparrow$ and $\downarrow$ spin states, so that we cannot define separately an electronic population factor for the spins $\uparrow$ and $\downarrow$. Our techniques allows us to prove that only the bipolaronic states are robust under perturbations by H_k. The behavior of the mixed polaronic–bipolaronic states is questionable when a spin–orbit coupling is present.

For the proof of this conjecture, we propose to study the fixed points of an operator defined similarly as $\mathbf{S}_t$ in (18). Giving a set of atomic positions $\{u_i^\beta\}$ and an electronic population factor with a cutoff in the electronic gap, the electronic eigenequations determine a set of electronic densities $\{\rho_i^{\beta,\sigma}\}$. Then the extremalization equation of the variational form which relates implicitly the atomic positions to the electronic densities is used for determining atomic coordinates $\{v_i^\beta\}$ from $\{\rho_i^{\beta,\sigma}\}$. The extended

operator $\mathbf{S}_t$ is defined by $\{v_i^\beta\} = \mathbf{S}_t(\{u_i^\beta\})$ and its fixed points are extrema of the variational form of the mode. However, only a subset $\mathscr{C}' \subseteq \mathscr{C}$ of the anti-integrable states may fulfill the conditions 2 and 3 which we just proposed for extending our method.

5.3. Pruning Condition

Only the configurations belonging to this subset $\mathscr{C}' \subseteq \mathscr{C}$ should be stable under perturbation by the electronic kinetic operator. This restriction is called "pruning the set of pseudospin configurations." We have seen above that for the adiabatic Holstein model no pruning condition was necessary.

It is of pedagogical interest to analyze an example where thus pruning condition become effective. We consider a variation of the one-dimensional Holstein model obtained by replacing only the elastic energy (15b) by

$$\Phi_{\text{elast}}(\{u_i\}) = \sum_i \frac{1}{2} u_i^2 + \frac{C}{2}(u_{i+1} - u_i)^2 \tag{102a}$$

For a given distribution of pseudospin $\{\sigma_i\}$ with $\sigma_i = 0$ or 1 at the anti-integrable limit, we have to minimize with respect to $\{u_i\}$ the variational form

$$\Phi_{\text{elast}}(\{u_i\}) + \sum_i \sigma_i u_i = \sum_i \frac{1}{2}(u_i + \sigma_i)^2 + \frac{C}{2}(u_{i+1} - u_i)^2 - \frac{1}{2}\sigma_i^2 \tag{102b}$$

For $C > 0$, the form (102b) always yields a nonvanishing gap for the phonon spectrum, since this quadratic form is strictly positive. Note that at the anti-integrable limit, due to the dispersion of the bare phonon branch, the interactions between the bipolarons and the polarons do not vanish, unlike for the initial Holstein model. The ground-state model of this model is not degenerate at the anti-integrable limit. At this limit and close to it, its structure essentially depends on the phonon properties and very little on the shape of the Fermi surface.

The pruning condition requires that at the anti-integrable limit, there also exists a nonvanishing gap c for the electronic spectrum. Therefore, for any pair of sites i and j such that $\sigma_i = 0$ and $\sigma_j = 1$, we have $u_i > u_j + c$, since the set of eigen values $\{E_\nu\}$ is also the set of $\{-u_i\}$. The extremalization of (102b) yields

$$u_i + \sigma_i + C(2u_i - u_{i+1} - u_{i-1}) = 0 \tag{103a}$$

and

$$u_i = -K \sum_n \lambda^{|n|} \sigma_{i+n} \tag{103b}$$

with

$$\lambda = \tfrac{1}{2}[2 + C - (C^2 + 4C)^{1/2}] \tag{104a}$$

and

$$K = \frac{1-\lambda}{1+\lambda} \tag{104b}$$

The pruning condition becomes

$$1 - \sum_{n \neq 0} \lambda^{|n|}(\sigma_{i+n} - \sigma_{j+n}) > \frac{c}{K} \tag{105a}$$

For $\lambda > 1/3$, there exist pseudospin configurations which do not fulfill this condition. It can be fulfilled by requiring that the sequence of pseudospins $\{\sigma_n\}$ be made of blocks of equal spins with minimum length N, where N will be chosen in an appropriate way. Since each pseudospin equal to 1 belongs to a block of consecutive pseudospins equal to 1 with minimum length N and since each pseudospin equal to 0 belongs to a block of consecutive pseudospins equal to 0 with minimum length N, we find the following inequality when $\sigma_i = 0$ and $\sigma_j = 1$:

$$\begin{aligned} 1 - \sum_{n \neq 0} \lambda^{|n|}\sigma_{i+n} + \sum_{n \neq 0} \lambda^{|n|}\sigma_{j+n} \\ \geqslant 1 - \left(\frac{2\lambda}{1-\lambda} - \lambda\frac{1-\lambda^{N-1}}{1-\lambda}\right) + \lambda\frac{1-\lambda^{N-1}}{1-\lambda} = 1 - 2\frac{\lambda^N}{1-\lambda} \end{aligned} \tag{105b}$$

For N large, the right member of (105b) goes to 1. Thus for $c < K$, N can be chosen in order that the pruning condition (105a) is be fulfilled.

Consequently, we prove for this example that given this block size condition, there exist infinitely many pseudospin configurations which fulfill this pruning condition. The entropy of this subset is finite. When $\lambda < 1/3$ there exists $c > 0$ such that the pruning condition is fulfilled for $N = 1$. Then the pruning condition is fulfilled by all pseudospin configurations and can be discarded. In fact, the pruning condition depends sharply on the model.

Physically, when there are local arrangements of bipolarons which are already unstable at the anti-integrable limit (depending on the interactions between the bipolarons), this pruning condition allows one to discard these nonphysical configurations. The remaining set of pseudospins determines the "robust" bipolaronic configurations under the quantum electronic perturbations. After pruning, the stability domain depends on the

pseudospin configuration. When t is growing, the instability of each bipolaronic configuration often occurs by the merging of the local minima with other extrema. As for the FK model, we have complex cascades of inverse bifurcations which prune out progressively the set of bipolaronic configurations (as observed numerically in ref. 26). At these bifurcations, the phonon matrix (QEAM) becomes gapless.

5.4. More Metastable States: Breaking of a Single Bipolaron (or of a Polaron) into a Finite Number of Pieces

Since we only found local minima for the variational form, these cascades of bifurcations necessarily involve extrema which do not exist at the anti-integrable limit. Clearly, as for the FK model, this anti-integrable limit is highly singular, although it is possible to use it for perturbation expansions. The adiabatic Holstein model exhibits in fact many metastable states other than those generated at the anti-integrable limit. This problem appears to be very complex in general. We only briefly describe a simple example proving the existence of these extra metastable states.

Let us consider a single bipolaron in the one-dimensional Holstein model (see ref. 5). In that case, there is only one occupied electronic eigenstate $\{\Psi_n\}$ in the whole system. Equation (18a) yields

$$u_n = -|\Psi_n|^2 \tag{106a}$$

with

$$-t\Psi_{n+1} - t\Psi_{n-1} + u_n \Psi_n = E\Psi_n \tag{106b}$$

which implies

$$-t\Psi_{n+1} - t\Psi_{n-1} - |\Psi_n|^2 \Psi_n = E\Psi_n \tag{106c}$$

This equation can be solved recursively for real Ψ_n by using the two-dimensional area-preserving map

$$\Psi_{n+1} = -\frac{E}{t}\Psi_n - \frac{1}{t}\Psi_n^3 - \Psi_{n-1} \tag{107a}$$

$$\Psi_n = \Psi_n \tag{107b}$$

which is obtained from the generating form

$$\sum_n \left[\frac{t}{2}(\Psi_{n+1} - \Psi_n)^2 - \frac{1}{2}(E+2t)\Psi_n^2 - \frac{1}{4}\Psi_n^4\right] \tag{107c}$$

Since we must have

$$\sum_n |\Psi_n|^2 = 1 \tag{108a}$$

the trajectory associated with the solution of (107c) and generated by the map (108a) has to be a homoclinic trajectory to the fixed point $(\Psi_n, \Psi_{n-1}) = (0, 0) = F$.

Indeed, for $E < -2t$, this fixed point bifurcates and becomes hyperbolic without reflection. In that case, such a map (which is similar the well-known Hénon map) is a typical example exhibiting a "horseshoe" with infinitely many homoclinic trajectories. Since this map (107) has an anti-integrable limit for $t = 0$, it is convenient to note that this result can be easily proven for $E < 0$ and a small perturbation $t \neq 0$ with the same technique as in ref. 1. Then, the chaotic trajectories of the horseshoe can be obtained by perturbations of the anti-integrable trajectories. For $t = 0$, they are given by $\{\Psi_n\} = \{\sigma_n \sqrt{-E}\}$, where $\{\sigma_n\}$ is an arbitrary coding sequence with $\sigma_n = 0, -1$, or 1. The coding sequences $\{\sigma_n\}$ with bounded support (that is, such that $\sigma_n \neq 0$ for only a finite number of values of n) yield after perturbation for $t \neq 0$ the homoclinic trajectories of the fixed point $F = (0, 0)$ since the corresponding trajectories converge to F both for n going to $+\infty$ and $-\infty$. If one requires that the pair of electrons be in its ground state with respect to the lattice distortion, the sequence $\{\Psi_n\}$ has no node, which requires that $\sigma_n = 0$ or 1 for all n (or equivalently by symmetry $\sigma_n = 0$ of -1 for all n).

Since there exist homoclinic trajectories associated with any sequence $\{\sigma_n\}$ with bounded support for t small enough, let us consider $\{\phi_n\}$ one of these homoclinic trajectories. The series

$$\sum_n \phi_n^2 = S \tag{108b}$$

is convergent but not necessarily 1. Giving such a solution $\{\phi_n\}$, the solution $\{\Psi_n\} = \{\phi_n / \sqrt{S}\}$ fulfills

$$-\frac{t}{S}\Psi_{n+1} - \frac{t}{S}\Psi_{n-1} - |\Psi_n|^2 \Psi_n = \frac{E}{S}\Psi_n \tag{109}$$

It determines a bipolaronic configuration for $t' = t/S$ and $E' = E/S$. This bipolaronic configuration can be stable or unstable. The ground-state bipolaronic configuration is obtained for a coding sequence such that $\sigma_n = 0$ for all n except for a single value n_0 of n where $\sigma_{n_0} = 1$. When there are several values of σ_n which are not zero, the corresponding bipolaronic

configurations have a larger energy and spread over several sites in the lattice. It can break into several pieces, which could be far apart, depending on the number of blocks where $\sigma_n \neq 0$ in the coding sequence $\{\sigma_n\}$. Such structures were found numerically.[5]

The existence of such bipolaronic configurations, which is physically rather surprising, is essentially due to the discreteness of the lattice. This fact is responsible for the existence of infinitely many homoclinic points for the associated map, which means physically that the bipolaron can break into several pieces pinned to the lattice and which could be in a metastable equilibrium.

If we make an estimation of the minimum energy required for breaking a single bipolaron (those obtained at the anti-integrable limit) into two pieces which are far away, the energy involved is smaller than but comparable to the energy required for annihilating this bipolaron (that is, for making the system without atomic distortion and an extended constant electronic wave function). This phenomenon could play an important role in some physical processes because it yields many extra excited states close to the gap edge. Physically, these states seem to have some similarities with impurity states. However, the density of these states has not been studied. However, it seems reasonable for the application of this theory at low temperature that these excited states be neglected in a first approach and that we restrict the phase space to only bipolaronic states obtained by expansion at the anti-integrable limit.

5.5. Models without (Trivial) Anti-integrable Limit

It is also worthwhile to describe situations where at the present stage of our studies the methods used for proving the existence of chaotic bipolaromic and mixed polaronic–bipolaronic states cannot be extended in the present form.

The first case occurs when the anti-integrable limit is not obviously defined. For example, in the adiabatic one-dimensional SSH model[18]

$$H_{\mathrm{SSH}} = -\sum_{i,\sigma} [1 - \lambda(u_{i+1} - u_i)]\, c^{+}_{i+1,\sigma} c_{i,\sigma} + \mathrm{CC} + \sum_i \tfrac{1}{2}(u_{i+1} - u_i)^2 \qquad (110)$$

the coupling with constant λ between the phonons and the electrons occurs via the transfer integral. For small λ, the Peierls electronic instability then produces a CDW which is called a bond order wave (BOW). The limit $\lambda \to \infty$, which is not an anti-integrable limit, cannot be used for starting expansions in $1/\lambda$. Nevertheless, although our mathematical method does not work, numerical calculations[3–6] suggest the existence of chaotic

metastable states which are random distributions of "bond bipolarons" for λ in some interval. In that case the bipolarons are nothing else than chemical bonds. This problem is technically more difficult than the case of the Holstein model, but on the basis of numerical observations, we believe that the existence of bipolaronic and mixed polaronic–bipolaronic states should be provable and that the physical behavior is very similar to that of the adiabatic Holstein model.

Another case where the anti-integrable limit is not defined concerns continuous models. Indeed, the above theory holds because of the existence of an underlying discrete atomic lattice. This is not an approximation because in any real solid (crystal, incommensurate structure, quasicrystal, amophous structure) the field of atomic displacements u_i in indeed a discrete function of i, since i represents the labeling of the atoms. The assumption, which considers the field of atomic displacement $u(\mathbf{r})$ as depending continuously on the space $\mathbf{r}$ instead of the discrete variable i, is thus an approximation. This is often introduced when working with the Fourier transform of the atomic and electronic operators and linearizing the electronic energies close to the Fermi surface.

The practical advantage of the continuum approximation is to gain a certain amount of "integrability" and to work out explicit formulas and quantitative results. It is well known that to be integrable, a model requires special conditions which are convenient for calculations but are physically exceptional. A convenient consequence of such an approximation (which turns out to become a severe flaw) is that the "anti-integrable" limit no longer exists in the model. This approximation washes out the model of all possible metastable chaotic bipolaronic and polaronic states, which, however, should be essential for understanding the physical behavior of the model. Such models have specific properties which either do not represent real physical behavior or must be interpreted carefully.

Let us also mention the existence of a tight-binding model which has been especially constructed for being integrable. This model is related to a Toda lattice problem with solitons. It exhibits only commensurate or incommensurate structures with gapless phonons (phasons) and no chaotic states. It is clear that this peculiar model does not exhibit any anti-integrable limit.[38]

5.6. Electron–Electron Interections + Electron–Phonon Interactions within a Mean-Field Model Magnetism

The introduction of a direct electron–electron interaction breaks down our exact theory because up to now, it has not been possible to treat exactly the many-body electronic Hamiltonian. However, it turns out to be

possible to take this interaction into account within a standard mean-field approximation.

Let us consider, for example, the adiabatic Holstein model with an extra Hubbard term with constant U in the energy units of (9a), $E_0 = 8g^2/\hbar\omega_0$ (note that U is not measured in units of the electronic bandwidth as usual, but in units related to the electron–phonon coupling). Then the Hamiltonian (12a) becomes

$$\hat{H}_{ad,h} = \sum_i \frac{1}{2}\left[u_i^2 + (n_{i\uparrow} + n_{i\downarrow})u_i\right] + U\sum_i n_{i\uparrow}n_{i\downarrow} - \frac{t}{2}\sum_{\langle i,j\rangle,\sigma} c_{i,\sigma}^{+}c_{j,\sigma} \tag{111a}$$

Although the anti-integrable limit is well defined, the term $\sum_i n_{i\uparrow}n_{i\downarrow}$ does not allow us to use the nice properties of one-particle Schrödinger operators as $\bar{\bar{A}}$ defined by (14). This term can be treated within a standard mean-field approximation. We introduce a Hamiltonian with two parametric fields $\{v_{i,\uparrow}\}$ and $\{v_{i,\downarrow}\}$

$$\hat{H}_{\mathrm{mf}} = \frac{1}{2}\sum_{i,\sigma} v_{i,\sigma}n_{i,\sigma} - \frac{t}{2}\sum_{\langle i,j\rangle,\sigma} c_{i,\sigma}^{+}c_{j,\sigma} \tag{111b}$$

and minimize with respect to $\{u_i\}$, $\{v_{i,\uparrow}\}$, and $\{v_{i,\downarrow}\}$ the mean-field variational form

$$\begin{aligned}\Phi(\{u_i\},\{v_{i\uparrow}\},\{v_{i\downarrow}\}) &= \sum_i \frac{1}{2}u_i^2 + U\sum_i \langle n_{i\uparrow}\rangle\langle n_{i\downarrow}\rangle \\ &\quad + \frac{1}{2}\sum_i \left[(u_i - v_{i\uparrow})\langle n_{i\uparrow}\rangle + (u_i - v_{i\downarrow})\langle n_{i\downarrow}\rangle\right) \\ &\quad + \frac{1}{2}\sum_{\nu,\sigma} \sigma_{\nu,\sigma}E_{\nu,\sigma}(\{v_{i,\sigma}\})\end{aligned} \tag{112a}$$

where $E_{\nu,\sigma}(\{v_{i,\sigma}\})$ are the eigenenergies of the Schrödinger equation

$$-t\,\Delta\Phi_n^{\nu,\sigma} + v_{n,\sigma}\Psi_n^{\nu,\sigma} = E_{\nu,\sigma}(\{v_{i,\sigma}\})\Psi_n^{\nu,\sigma} \tag{112b}$$

and the electronic densities are given by

$$\langle n_{i,\sigma}\rangle = \sum_\nu \sigma_{\nu,\sigma}|\Psi_n^{\nu,\sigma}|^2 \tag{112c}$$

$\sigma_{\nu,\sigma} = \sigma_{\nu,\uparrow}$ or $\sigma_{\nu,\downarrow}$ are the population factors for the electrons with spins $\uparrow$

or $\downarrow$, respectively. We can minimize this form with respect to $\{u_i\}$, which yields

$$u_i = -\tfrac{1}{2}(\langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle) \tag{113}$$

and allows one to eliminate this phonon field $\{u_i\}$. The variational form (112a) becomes

$$\Phi(\{v_{i\uparrow}\}, \{v_{i\downarrow}\}) = -\frac{1}{8}\sum_i (\langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle)^2 + U\sum_i \langle n_{i\uparrow}\rangle\langle n_{i\downarrow}\rangle$$
$$-\frac{1}{2}\sum_i (v_{i\uparrow}\langle n_{i\uparrow}\rangle + v_{i\downarrow}\langle n_{i\downarrow}\rangle) + \frac{1}{2}\sum_{\nu,\sigma} \sigma_{\nu,\sigma} E_{\nu,\sigma}(\{v_{i,\sigma}\}) \tag{114a}$$

Minimizing over $\{v_{i\uparrow}\}$ and $\{v_{i\downarrow}\}$ yields

$$v_{i\uparrow} = 2U\langle n_{i\downarrow}\rangle - \tfrac{1}{2}(\langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle) \tag{114b}$$

$$v_{i\downarrow} = 2U\langle n_{i\uparrow}\rangle - \tfrac{1}{2}(\langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle) \tag{114c}$$

and

$$\langle n_{i,\uparrow}\rangle = \frac{1}{4U(1-2U)}[-v_{i,\uparrow} + (4U-1)v_{i,\downarrow}] \tag{115a}$$

$$\langle n_{i,\uparrow}\rangle = \frac{1}{4U(1-2U)}[(4U-1)v_{i,\uparrow} - v_{i,\downarrow}] \tag{115b}$$

We now change the relation (112c) between $\langle n_{i,\sigma}\rangle$ and $\{v_{i,\sigma}\}$ and substitute (115) in the variational form (113a). Thus, we obtain a new variational form,

$$\Phi_{\mathrm{mf}}(\{v_{i\downarrow}\}, \{v_{i\downarrow}\})$$
$$= \frac{1}{16U(1-2U)}\sum_i [v_{i\uparrow}^2 + v_{i\downarrow}^2 + 2(4U-1)v_{i\uparrow}v_{i\downarrow}] + \frac{1}{2}\sum_{\nu,\sigma} \sigma_{\nu,\sigma} E_{\nu,\sigma}(\{v_{i,\sigma}\}) \tag{116}$$

which is not identical to the variational form (114a), but which has the same extrema. However, in this transformation the nature of the extrema may be changed. For example, a minimum may be replaced by a maximum.

For a given pseudospin configuration describing the electronic population $\{\sigma_{i,\sigma}\}$ with $\sigma_{i,\sigma} = 0$ or 1, at the anti-integrable limit ($t = 0$), $\{v_{i,\sigma}\}$ is given by (114b) and (114c), where $\sigma_{i,\sigma} = \langle n_{i,\sigma}\rangle = 0$ or 1. The conditions for

developing a theory similar to the one described here are fulfilled when $U \neq 0$, $U \neq 1/2$, and $U \neq \pm\infty$, since at the anti-integrable limit:

1. The quadratic form corresponding to the phonon fields is non-degenerate (i.e., the QEAM is invertible).

2. There exist nonvanishing gaps between the electronic states which are occupied and empty. More precisely, the electronic eigenenergies given by (112b) can take four values:

$$\begin{aligned} &0 \text{ and } 2U - \tfrac{1}{2} && \text{for the empty states} \\ &-\tfrac{1}{2} \text{ and } 2U - 1 && \text{for the occupied states} \end{aligned}$$

Thus, we can define as in (16) or (17) the electronic population factor $\sigma_v = \chi(E_v)$ by a simple characteristic function $\chi(x)$. When $0 < U < 1/2$, $\chi(x)$ is defined as

$$\chi(x) = 1 \quad \text{for} \quad x < -\tfrac{1}{2} + U \qquad \text{and} \qquad \chi(x) = 0 \quad \text{for} \quad -\tfrac{1}{2} + U < x \tag{117a}$$

When $1/2 < U$, $\chi(x)$ is defined as

$$\begin{aligned} &\chi(x) = 1 \quad \text{for} \quad x < -\tfrac{1}{4} \quad \text{and} \quad U - \tfrac{1}{2} < x < 2U - \tfrac{3}{4} \\ &\chi(x) = 0 \quad \text{for} \quad -\tfrac{1}{4} < x < U - \tfrac{1}{2} \quad \text{and} \quad 2U - \tfrac{3}{4} < x \end{aligned} \tag{117b}$$

When $U < 0$,

$$\begin{aligned} &\chi(x) = 1 \quad \text{for} \quad x < 2U - \tfrac{3}{4} \quad \text{and} \quad U - \tfrac{1}{2} < x < -\tfrac{1}{4} \\ &\chi(x) = 0 \quad \text{for} \quad 2U - \tfrac{3}{4} < x < U - \tfrac{1}{2} \quad \text{and} \quad -\tfrac{1}{4} < x \end{aligned} \tag{117c}$$

A theory similar to the above allows one to prove that there exists $t(U)$ such that for $t < t(U)$, there exists a mixed polaronic–bipolaronic structure $\{v_{i,\sigma}(t)\}$ which depends uniform continuously on t and such that $\{v_{i,\sigma}(0)\}$ fulfills (114c), where $\sigma_{i,\sigma} = \langle n_{i,\sigma} \rangle = 0$ or 1. Although the stability analysis of these states [with respect to the variational form ((114a)] has not been performed, we do believe that the bipolaronic and polaronic states are stable for t small enough.

The cases $U = 0$ and $U = 1/2$ require a particular treatment. For $U = 0$, the two phonon fields $\{v_{i\uparrow}\}$ and $\{v_{i\downarrow}\}$ reduce in fact to a single phonon field, since (114b) and (114c) yields $v_{i\uparrow} = v_{i\downarrow}$ for all i. Then, the quadratic form in (116) just becomes $\sum_i \frac{1}{2} v_{i\uparrow}^2$ and we get back to the problem solved above.

For $U = 1/2$, we get $v_{i\uparrow} = -v_{i\downarrow}$ for all i. We also get a single phonon field, but the signs of its coupling constants with the electrons with spin $\uparrow$ and $\downarrow$ are opposite. $U = 1/2$ is just the value at which the energy of a bipolaron is equal to the energy of two polarons at the anti-integrable limit. For $U > 1/2$ the ground state is obviously magnetic at the anti-integrable limit and remains magnetic close enough to this limit within this mean-field theory.

For $U = \pm\infty$, the first term in the variational form (116a) disappears and $\lim_{U \to \infty} t(U) = 0$. Our theory is not applicable to the mean-field Hubbard model (without electron–phonon coupling).

As a result, this calculation suggests that the role of the electron–phonon coupling is essential for the stabilization of magnetic structures which are due to direct electron–electron interactions. These magnetic structures do exist for $U > 1/2$. Further work is necessary to understand better the consequences of this approach.

Mean-field approximations are widely used under various forms for solving electronic models. A method which belongs to this class consists in introducing n flavors for the electrons i, σ ($\sigma = 1, 2, \ldots, n$) with n large. The physical situation corresponds to $n = 2$ since the spin of the electron is 1/2. For n large, the model becomes exactly soluble by a mean-field calculation. Then $1/n$ expansions are often performed in order to get some insight into the physical case $n = 2$. The theory presented here suggests that this limit of n large might be much more complex than expected due to the existence of these bipolatonic and polatonic states and that a $1/n$ expansion may become wrong at least for discrete lattices.

5.7. Quantum Lattice Fluctuations

An important question which would be probably asked by the reader concerns the validity of the adiabatic approximation. In other words, could the quantum lattice fluctuation destroy the polaronic and bipolaronic structures (at 0 K)?

We believe that they do destroy *in principle* most of these structures. This fluctuation problem should involve not only the polaron or bipolaron ordering, but also the dimensionality of the model. However, this physical question must bed asked differently in more physical terms: What is the lifetime (at 0 K) of a bipolaron or a polaron at a given site? In standard physical situations, due to the fact that the atoms are rather heavy particles compared to the electrons, estimation of this lifetime[9–12] yields values which could easily become much longer than the age of the universe! Then for such real systems, the quantum lattice fluctuations are irrelevant, that is, absolutely negligible compared to other sources of fluctuations and

especially the thermal fluctuations. This situation is typically found when the size of the bipolarons and polarons (the inverse coherence length defined in Section 5.3) is comparable to or smaller than the lattice spacing.

When the size of the bipolarons or of the polarons diverges, the validity of the adiabatic as well as the Born–Oppenheimer approximation is no longer granted. We found for the adiabatic Holstein model the following criterion given by formula (12) in ref. 12 concerning the phonon softening $\lambda < 1$, which is the smallest eigenvalue of the phonon matrix defined in (50). When this criterion is not fulfilled, the Born–Oppenheimer approximation is not valid, because of the existence of nonnegligible "anti-adiabatic" terms in the Hamiltonian. The role of the dimensionality d of the model which appeared in the initial formula was due to the fact that we made exact bounds. Physically, we expect that it can be dropped in the formula. Thus, this criterion becomes in our units

$$2\sqrt{\beta} \ll \frac{\lambda}{1-\lambda^2} \tag{118}$$

where β is given by (10b). Physically, the phonon softening is the ratio of the smallest phonon frequency to the bare phonon frequency. For small t, the phonon softening λ is close to 1. It goes to zero at the bifurcations of the bipolaronic or mixed polaronic–bipolaronic configuration or at the TBA for a bipolaronic CDW. When the phonon softening goes to zero we suggest that the system becomes unstable against quantum lattice fluctuations. We speculate that this instability occurs by the appearance of (tunneling) Cooper pairs. Therefore, the gound state of the system could be superconducting. However, with physical parameters t and β, it can be checked that the phonon softening which is acceptable with criterion (118) can be very small, typically 10^{-2} or smaller. This fact is compatible with the few experiments in real materials which did exhibit phonon softening, since these experiments also show the existence a small (strictly) nonzero residual gap compatible with criterion (118). These points will be studied in more detail in further publications. We conjecture as follows:

Taking into account quantum lattice fluctuations (even very small) at 0 K, the TBA becomes a transition between a superconducting ground state and a bipolaronic ground state.

Let us emphasize that the physical consequences of this exact theory contradict some common assumptions concerning the effect of large electron–phonon coupling. The phenomenology of the bipolaronic and mixed polaronic–bipolaronic configurations described here, which can be

chaotic and have physically very long lifetime, proves that, for small t and β, *the electron–photon coupling cannot be reduced to an effective attractive electron–electron interaction.* However, this approximation is often used in the literature. It is generally believed that the ground state is superconducting (e.g., see ref. 37), with possibly bipolaronic fluctuations, which contradicts the fact that it is a quasistatic structure of bipolarons or polarons, as we proved.

Alexandrov *et al.*[23,24] discuss the possible existence of bipolaronic superconducting states. Their theory is based on an exact expansion, but at the lowest order only, with respect to t of a large class of models, including the fully quantum Holstein model. Then they map these models onto quantum spin models (the spins of their model correspond in fact to our pseudospin described here). The quantum lattice fluctuation generates a small spin quantum term corresponding to transverse coupling between the spins. However, the truncation of their expansion at first order in t corresponds to a truncation of their spin Hamiltonian to nearest neighbors. This approximation is drastic, since a degeneracy is introduced for the ground states (except for the half-filled case) which in fact does not exist for $t \neq 0$. In particular, because of that, their approximation cannot yield the well-known incommensurate CDW structures. Consequently, the role of the quantum terms in raising the degeneracy is overestimated and supposed to produce a superconducting state but in any case with a very low critical temperature. They essentially neglected the spatial extension of the bipolarons, which are not on-site, as we saw in Section 5.1. We totally disagree with their physical conclusion of the possible existence of bipolaronic superconductivity. Our studies prove in fact the physical existence of insulating bipolaronic states at 0 K when the criterion (118) is fulfilled. This is just the domain of parameters where their theory is supposed to apply.

5.8. A Glance at Physical Applications. The Chemist's Approach—Bipolaronic Charge Density Waves

Physicists are used to understanding the electrons in solids by starting from a band model. Chemists describe many real materials by well-localized chemical (covalent) bonds. In fact, a chemical bond turns out to be somewhat similar to the physical picture of a bipolaron. It is indeed a pair of electrons with opposite spins in the same eigenstate which bonds two atoms or, more generally, a cluster of atoms. The distribution of the atomic distance (geometry of the molecule) is a function of the spatial distribution of chemical bonds (electron–phonon coupling). Although the

chemist's approach seems to oppose to the physiscist's description which is based on band theory, it is well known that the chemist's approach is often efficient for predicting the structure not only of finite-size molecules but also of solids of some insulating materials.

The concepts of bipolaron and polaron are in fact extensions of the concept of chemical bond. Our theory proves that in the large electron–phonon coupling regime and for the Holstein model, the chemist's description is prevalent over the physicist's description in term of the standard band theory. It also shows that for smaller electron–phonon coupling, the bipolarons do not remain localized in real space on a few sites at a single chemical bond, but extend and diverge at the TBA. Then the system is better described by a band theory and we return to the physicist's description.

Incidentally, even for systems as small as molecules with a few atoms, the existence of isomeric chemical compounds with a practically infinite lifetime (at room temperature) proves that quantum tunneling (quantum lattice fluctuations) is not sufficient for transforming a molecule into one of its isomers. Quantum tunneling does not transform a non-mirror-symmetric molecule into its mirror image (enanthiomers) with strictly the same energy. Nature thus confirms the prediction of the previous subsection, that quantum lattice fluctuations can be neglected for many systems (except possibly for systems with very light atoms such as hydrogen).

Although this paper is not the appropriate place for discussing in detail the applications of this work to real experiments, it is important to emphasize that the ideas developed here could provide a novel basis for understanding some phenomena existing in nature. The physical ideas developed here are not restricted to the adiabatic Holstein model (chosen for convenience), but are universal and could be extended to many other models. Let us also recall that the concepts of polaron and bipolaron presented here are different from the usual picture described in the literature (polaronic band). On the basis of approximate theories, it is generally considered that the polarons are quantum particles (fermions) and form a band. They can be viewed just as heavier electrons with an effective renormalized mass due the narrowing of the bare electronic bandwidth. The bipolarons are bound states of such polarons and are bosons. By contrast, our new versions for the concepts of *bipolaron* and *polaron* are intrinsically related to the concept of *chaos*. For a strong enough electron–phonon coupling, these particles behave as *classical particles* because the quantum lattice fluctuations are negligible. This new picture should be useful *in practice* for the interpretation of *real experiments*. The application we have in mind mostly concerns charge

density wave systems[5] for the bipolaronic structures, but we guess that it also has potential applications to spin density waves and magnetic structures (with mixed polaronic bipolaronic structures), although we have not yet explored this point.

It appears that the bipolaronic description yields on many points physical predictions which are sharply different from those of the standard CDW theories and which are in better qualitative agreement with the observations. Although still unpublished, some of the ideas presented here were developed in ref. 25.

5.9. Predictions for Bipolaronic CDWs: A Qualitative Scenario

For this last section, we refer the reader to the abundant experimental literature on this topic and especially to review papers. There is wide variety of unusual phenomena in these systems which by far have not been globally interpreted. Some of the experimental observations are supposed to be due to the action of impurities (which indeed always exist in a real sample) on a standard sliding Peierls–Fröhlich CDW, but there are many other observed features with no consistent interpretation. Considering the real CDWs as bipolaronic structures could open the way of both reinterpreting known experiments and interpreting unexplained experiments with the same unified interpretation. Let us sketch some of the qualitative characteristic properties of a bipolaronic CDW which result from our theory.

a. Zero-Degree State. When the electron–phonon coupling is large enough, the ground state in the absence of a magnetic field of a coupled electron–phonon system (here the adiabatic Holstein model) corresponds to a specific ordering of bipolarons which *a priori* is not known. It could be a simple commensurate structure, an incommensurate structure, or possibly something more complex, closer to a glass of bipolarons (that is, a weakly periodic structure[30]). The structure at 0 K could be also a metastable structure out of equilibrium, that is, a glass of bipolarons, which should be obtained by fast quenching of the system at low temperature. The disorder of the obtained structure should depend on the kinetics of the bipolarons and the quenching velocity.

b. A Lattice Gas Model at Low Temperature. When the thermal energy $k_B T$ is much lower than the phonon gap and the electronic gap energy, the system remains in a bipolaronic state. In that temperature regime, the roles of the phonons and of the purely electronic excitations in the thermodynamics are not essential and can be dropped. This system

[5] For review of CDWs see refs. 31–35.

essentially evolves by thermal hopping of the bipolarons. The relevant excitations at low temperature correspond to defects (vacancies and interstitials) in the bipolaronic ground state. The gap in energy for these defects may vanish for incommensurate structures or may be finite for commensurate structures. A similar analysis has already been done for the one-dimensional FK model at low temperature.

Consequently, the only relevant degrees of freedom of the system are the pseudospin configurations $\{\sigma_i\}$ which characterize the bipolaron distribution. The total energy (15) of the corresponding bipolaronic configurations allows one to reduce formally the initial Hamiltonian to *a pseudospin Hamiltonian* (in other words, a lattice gas model). For example, for the Holstein model at the anti-integrable limit ($k=\infty$ or $t=0$), this pseudospin Hamiltonian is trivial and corresponds to noninteracting pseudospins, since then the ground state is degenerate. For $t\neq 0$, it can be calculated explicitly at the lowest orders on a square lattice.[6] The expansion involves not only pair interactions between the pseudospins which decrease exponentially as a function of the distance, but also three-spin, four-spin, etc., interactions, which makes the Hamiltonian rather complex. In fact, these extra terms become important when the size of the bipolarons starts to diverge (approaching the TBA). Even when this Hamiltonian is truncated to pair interactions between the pseudospins, its ground state is not trivial except for the model in one dimension, which yields an incommensurate or commensurate structure with the expected Peierls wave vector at $2k_F$.

c. Low-Temperature Behavior: Bipolaronic Glasses? The fact that a bipolaronic structure can be described by a pseudospin model (thus with *discrete* variables) has experimentally observable consequences for the behavior of the CDW structures at low temperature, which for some effects can be unambiguously distinguished from those of the standard theory for CDWs. These consequences concern, for example, the glassy behavior of the CDW structure and the thermal variation of the wave vector of the CDW and the intensity of harmonics of the diffraction peaks.

Specific heat measurements at low temperature in CDW compounds reveal anomalies at low temperature which recall similar behavior observed in glasses.[48] Time-dependent heat diffusion experiments also reveal anomalies, with stretched exponentials as in many glasses. Conductivity experiments also exhibit hysteresis and memory effects. These experiments could be interpreted by the fact that the bipolaronic diffusion becomes negligible at low temperature and thus that the structure remains in metastable states. This metastability is intrinsic and not due to impurities.

d. Wave-Vector Variation. A significant variation of the wave vector as a function of temperature has been observed in all known CDWs. A recent interpretation[40] based on the standard mean-field approximation has been recently proposed. This theory considers the effect of the band energy curvature (effective electronic mass). In this way some of the lattice effects are introduced in disguise. It is found that the variation of the wave vectors can be nonnegligible only in the case of a strong enough electron–phonon coupling, that is, in the case of a bipolaronic structure. Otherwise, a mean-field treatment of incommensurate lattice gas models (for a fixed band filling) yields a variation of the wave vector of the modulation. This variation (which is a devil's staircase) is small for extended bipolarons and becomes very large for small bipolarons.[41]

e. Harmonics Saturation at Low Temperature. However, the most suggestive feature showing that real CDWs are bipolaronic is given by accurate measurements of the diffraction peaks. This measurement has been recently done (up to order 4) in the real CDW system $NbSe_3$ at low temperature.[39] (Note that $NbSe_3$ exhibits two CDWs with different modulation wave vectors. This observation concerns the first CDW which has the highest critical temperature.) It is essentially observed that the intensity of the harmonics of the CDW modulation saturates at *temperatures* which are inversely proportional to the order of the harmonics. These observed results sharply disagree with the prediction of the standard theory of CDWs. The bipolaronic interpretation is very simple, and is based on the fact that at low temperature the thermal fluctuations disappear. Then the occupation probability $\langle \sigma_i \rangle$ of any given site i necessarily saturates either to zero or to one, which is the pseudospin value at site i in the ground state (or in the metastable state). This phenomenon for the harmonic saturation is primarily a consequence of the existence of pseudospins and thus of a bipolaronic structure.

In addition, we have some hope that a careful analysis of the complete data of the scattering experiments could yield the shape of the bipolarons associated with the first CDW in $NbSe_3$, as shown Fig. 5. However, it is already clear by inspection of the existing data that the bipolarons of $NbSe_3$ are not localized at single sites, but extend over several unit cells. This physical situation should be rather close to the TBA at which the size of the bipolaron becomes infinite. It is not unreasonable to consider that the superconducting transition which occurs in $NbSe_3$ under pressure[42,43] is due to the crossing of the TBA, which eliminates the CDW lattice modulation by the quantum lattice fluctuations as suggested in the preceding subsection. Then, each CDW disappears and the system becomes a superconductor beyond a second-order transition under pressure. This

phenomenon occurs successively for both CDWs, but at different critical pressure.

f. Violation of the BCS Relation between Electronic Gap and the Melting Temperature. While the temperature increases, any bipolaronic structure should melt at some critical temperature T_c.

For the adiabatic Holstein model close to the anti-integrable limit, the interaction between nearest-neighbor pseudospins[6] is $4T/k^2 = 4Tt$ [with the initial energy units of model (1)]. The characteristic energy $k_B T_c$ calculated within the standard mean-field approximation is at most around $4T/k^2$ (while the half electronic gap is $\Delta = Tk^2$). For quasi-one-dimensional CDWs and k large, we have $\frac{1}{4}k^4(k_B T_c) \cong \Delta$, which obviously violates the standard BCS relation $3.52 k_B T_c \cong \Delta$. This result should not be surprising, since this BCS relation was established for weak electron–phonon coupling.

For models with dispersion in the phonon branch, the ground state is no longer degenerate at the anti-integrable limit. Since the interaction between the pseudospins only depends on the phonon dispersion, for large electron–phonon coupling the critical temperature T_c tends to be independent of any electronic properties and thus of the electronic gap, which proves again that the BCS relation cannot be fulfilled at the anti-initegrable limit. The fact that in real CDWs the electronic gap is found two or three times larger[49] than the expected BCS value is a clear indication that these systems are not in the weak coupling regime but could be in the bipolaronic regime.

g. Order–Disorder and Displacive Bipolaronic Structures. Above the critical temperature, the states of the system are disordered bipolaronic structures which survive up to the (crossover) temperature T_{co} where these bipolarons break up. Note that this region between T_c and T_{co} corresponds to the region where experimentalists observe a "pseudogap" due the fact that the fluctuations corresponding to the CDW are still present since the bipolarons still exist for a reasonably long lifetime. There are two extreme regimes with of course a continuum of intermediate regimes.

The first regime, which we call order–disorder, is obtained when the binding energy of a bipolaron is large (that is, close to the anti-integrable limit). T_{co} is very large. The bipolaronic structure survives at all the temperatures which are physically accessible. The mobility of the bipolarons, which are thermally activated, increases with the temperature as well as the conductivity of the material. This system behaves as an insulator at all temperatures. There is almost no phonon softening due to the electron–phonon coupling.

The opposite regime, which we call displacive, is the situation where T_{co} is close above T_c. This situation is obtained close to the TBA, when the spatial extension of the bipolarons is rather large. The conductivity increases as a function of temperature up to T_{co}. Above T_{co}, the bipolarons break up into free electrons and the system returns to a metallic regime with a rather strong electron–phonon interaction. Then the conductivity decreases with temperature. That regime is also characterized by a sharp phonon softening above T_c. However, we noted above that the stability of the structure against quantum lattice fluctuations requires that this softening not be total. A nonvanishing phonon gap should persist in the ordered CDW at lower temperature.

h. Non-Ohmic Conductivity Experiments. For small electric field, the electronic transport properties of such systems are determined by the thermal diffusion of the bipolaron through the CDW, since the whole structure is pinned by the lattice and cannot move collectively. Except for $NbSe_3$, which remains conducting at low temperature, because one subset of chains out of three remains metallic and does not develop a CDW at any temperature, all known CDWs are insulators at zero degrees. As for all phase transitions in nature, the ordered phase of a CDW has to be polydomain. These structure are indeed metastable, because of the lattice pinning. In each domain, the phase of the incommensurate CDW is constant. The phase defects are walls which separate these domains. Because of charge neutrality requirements, these walls have to be parallel to the wave-vector modulation, yielding a cylindrical geometry of domains. This is the same factor which forces the domain wall of a ferroelectric to be parallel to the electric polarization.

As for a ferroelectric, when a certain coercive field is reached, the phase domain walls can move and in addition, new domains can nucleate. In that situation, it is well known that the pinning of the walls and the existence of nucleation centers are highly sensitive to the quality of the sample and more precisely to mesoscopic defects (but not of microscopic defects as suggested in many CDW interpretations). Unlike a ferroelectric, where the depolarizing current is transitory and ceases when the sample becomes monodomain, this electric current persists in a CDW because of the nucleation of new phase domain walls. This depolarizing current is the extra non-Ohmic current which is observed beyond a certain electric field threshold. As, for example, for the Barkhausen effect, which is the noise generated by wall propagations in a ferromagnet, this extra current exhibits a time dependence which could be more or less oscillatory or be a white noise, depending on the electric field, the sample quality, the geometry of the sample, etc.

Actual experiments[31–35] are in fact as compatible with this model as with the standard model of CDW pinning by microscopic impurities. In addition, and in agreement with experiments, this model expects that the mobility of the phase domain wall, which at a microscopic scale is due the thermally activated hopping of the bipolarons, is sharply temperature dependent. Thus, at low temperature the electric threshold should diverge. However, this variation could become more complicated (due to the thermal variation of the wave vector and commensurability effects).

Unexpectedly, two pinning frequencies were observed experimentally in CDWs. In the standard model, such an interpretation is meaningless. Within our interpretation, this fact is obviously expected. One of the pinning frequencies is the frequency of the bipolarons pinned to the lattice. In order words, it is the nonvanishing gap of the phonon spectrum. This frequency is for example, at 100 GHz in blue bronze and at 30 GHz in TaS_3. Neutron scattering experiments for blue bronze suggest that this high pinning frequency is indeed the gap of the phason branch. It is too high to correspond to the electric threshold, which is rather low (note larger than 1 V/cm). The second pinning frequency, which is measured in MHz, corresponds to the pinning frequencies of the phase domain walls, that is, to the real pinning of the CDW.

The observation of a non-Ohmic extra current requires that the bipolaronic structure be sufficiently plastic, that is, relatively mobile bipolarons for having a mobile phase domain wall, or rather extended bipolarons. Thus, the observation of the non-Ohmic conductivity seems to be restricted to sufficiently displacive bipolaronic structures with soft modes and "quasiphasons," that is, with a small gap. In TTF-TCNQ, where the phonon softening is rather moderate, we probably are in an intermediate regime between the displacive and order–disorder regimes. Indeed, the observation of a non-Ohmic conductivity in that compound can be done only beyond a very large electric threshold.

More details about this interpretation can be found in ref. 25.

i. Behavior of CDWs under a Magnetic field. Field-Induced Transitions. First let us note the possible existence of magnetic susceptibility anomalies above T_c. When $T > T_{co}$ and when the electron–phonon coupling is large enough, the bipolarons of the CDW break up into polarons, giving an enhancement of the magnetic susceptibility. For the Holstein model at the anti-integrable limit $t = 0$, which reduces to a collection of independent one-site systems, this magnetic susceptibility can be easily exactly calculated. Indeed, this calculation confirms the existence of a sharp peak in the magnetic susceptibility corresponding to the cross-over temperature $T_{co} \gg T_c$. For smaller values of the electron–phonon

coupling the bipolarons persist and there are arguments showing that the susceptibility peak at T_{co} smooths down. For larger temperatures, corresponding to the binding energy of the electron to a single polaron, the system returns to the standard behavior of a metal. Then one recovers the standard Pauli magnetic susceptibility of a metallic system. For intermediate values of k the system returns directly to the metallic regime above T_{co}. Otherwise, it is reasonable to expect sharper anomalies if the real system involves direct electron–electgron interaction. By contrast, in the standard theory of CDWs the magnetic susceptibility should be very small for $T < T_c$ and should directly become the Pauli susceptibility for $T > T_c$. But in fact many CDW systems show pronounced magnetic susceptibility anomalies above T_c which have not been explained.

Another intriguing phenomenon is the sharp dependence of the electric threshold field as a function of the magnetic field.[42] Magnetic-field induced phase transitions can be also be expected naturally within a bipolaronic description since we proved above that the ground state of an electron–phonon coupled system in a magnetic field could become a mixed polaronic bipolaronic structure. The critical magnetic field required for this transition, which exists in principle in the absence of direct electron–electron interaction, can be very much lowered when this interaction is present. Indeed, magnetoresistance experiments[44] foir $NbSe_3$ suggested the existence of mixed charge and spin density waves, which could be very well interpreted as the mixed polaronic–bipolaronic states predicted here.

In summary, we have established many rigorous results concerning the existence and the properties of chaotic bipolaronic structures, and also proved the existence of bipolaronic CDWs. The properties of these CDWs disagree on many points with those predicted by the standard scheme proposed in the literature. It is noted that a wide collection of experimental features which concern real CDWs can be better described with the basic assumption that real CDWs are bipolaronic structures. It is hoped that this novel approach will attract the interest of other theoreticians, since, as pointed by Monceau[35] in the conclusion of his recent review paper about CDWs and their standard interpretation, "The general properties of these states are more or less analyzed.... However, in spite of all these efforts, most of the fundamental questions remain unsolved"!

APPENDIX A. POLYNOMIAL APPROXIMATION OF A STEP FUNCTION

In this Appendix, we calculate a polynomial approximation restricted to given intervals for two particular functions. Although there exists an abundant literature on the general theory of polynomial approximations of

functions, apart from existence theorems we have not found any constructive theorem which could help for finding polynomial approximations with precisely our two specific functions which is suitable for the proof of Proposition 2 in Appendix B.

Let us consider the Heaviside function defined as

$$Y(x)=0 \qquad \text{for} \quad x<0 \tag{A1a}$$

$$Y(x)=1 \qquad \text{for} \quad x\geqslant 0 \tag{A1b}$$

For two given a and b fulfilling $0<a<b$, we wish to find a sequence of polynomials $P_n(x)$ of degree n such that the error on the two intervals $[-b, -a]$ and $[a, b]$ is as small as possible and converge exponentially to zero as a function of n. We prove the following.

Proposition A. There exists a sequence of polynomials $P_n(x)$ with degree n such that

$$t_n = \operatorname*{Sup}_{1\leqslant |x|\leqslant b} |P_n(x)-Y(x)| < C' e^{-\kappa n} \tag{A2a}$$

with

$$C'=1 \tag{A2b}$$

$$\kappa = \frac{1}{4} e^{-3/2} \frac{a^2}{b^2} \tag{A2c}$$

Proof. For solving this problem, we propose (1) to search for an analytic function with an infinite radius of convergence which provides a good approximation of the Heaviside function for $a\leqslant |x|\leqslant b$, (2) to approximate this analytic function by its series truncated at order n, and (3) to bound the errors and then to optimize the parameters of the analytic function.

1. A good analytic function for approximating $Y(x)$ is the error function

$$I(\gamma x)=\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\gamma x} \exp(-t^2)\, dt \tag{A3a}$$

For $x\geqslant 0$

$$Y(x)-I(\gamma x)=\frac{1}{\sqrt{\pi}} \int_{\gamma x}^{+\infty} \exp(-t^2)\, dt \tag{A3b}$$

We have for all x

$$[Y(x)-I(\gamma x)]^2=\frac{1}{\pi}\int_{\gamma|x|}^{\infty}\int_{\gamma|x|}^{\infty}\exp[-(u^2+v^2)]\,du\,dv$$
$$<\frac{1}{\pi}\int_0^{\pi/2}d\theta\int_{\gamma|x|}^{\infty}r\exp(-r^2)\,dr=\frac{\exp(-\gamma^2x^2)}{4} \quad \text{(A3c)}$$

which yields an upper bound of the error

$$|Y(x)-I(\gamma x)|\leqslant\frac{\exp(-\frac{1}{2}\gamma^2a^2)}{2} \qquad \text{for} \quad |x|\geqslant a \quad \text{(A4)}$$

2. $I(\gamma x)$ can be expanded as a series with an infinite radius of convergence,

$$I(\gamma x)=\frac{1}{2}+\sum_{n=0}^{\infty}(-1)^n\gamma^{2n+1}\frac{x^{2n+1}}{\sqrt{\pi}\,(2n+1)\cdot n!} \quad \text{(A5a)}$$

We define the polynomial with degree $2p-1$

$$Q_p(\gamma x)=\frac{1}{2}+\sum_{n=0}^{p-1}(-1)^n\frac{x^{2n+1}}{\sqrt{\pi}\,(2n+1)\cdot n!} \quad \text{(A5b)}$$

For $|x|<b$, we have

$$|I(\gamma x)-Q_p(\gamma x)|\leqslant\sum_{n=p}^{\infty}\frac{|\gamma b|^{2n+1}}{\sqrt{\pi}\,(2n+1)\cdot n!}$$
$$\leqslant\frac{|\gamma b|^{2p+1}}{\sqrt{\pi}\,(2p+1)\cdot p!}\sum_{n=p}^{\infty}\frac{|\gamma b|^{2(n-p)}}{(n-p)!}$$
$$<\frac{|\gamma b|^{2p+1}}{\sqrt{\pi}\,(2p+1)\cdot p!}\exp(\gamma^2b^2) \quad \text{(A5c)}$$

Using the inequality

$$p!\geqslant\exp\left(\int_0^p\ln t\,dt\right)=\exp\left(p\ln\frac{p}{e}\right)=\left(\frac{p}{e}\right)^p$$

we have

$$|I(\gamma x)-Q_p(\gamma x)|\leqslant\frac{1}{2p+1}\frac{\gamma b}{\sqrt{\pi}}\left(\frac{e\gamma^2b^2}{p}\right)^p\exp(\gamma^2b^2) \quad \text{(A6)}$$

3. By combination of (A5c) and (A4), we have for $a \leqslant |x| \leqslant b$

$$|Y(x) - Q_p(\gamma x)| \leqslant \frac{\exp(-\frac{1}{2}\gamma^2 a^2)}{2} + \frac{1}{2p+1}\frac{\gamma b}{\sqrt{\pi}}\left(\frac{e\gamma^2 b^2}{p}\right)^p \exp(\gamma^2 b^2) \tag{A6a}$$

For each p, it is convenient to choose $\gamma = \gamma_p = (\alpha p)^{1/2}/b$, where α is some constant, which yields

$$|Y(x) - Q_p(\gamma_p x)| \leqslant \frac{1}{2}\exp\left(-\alpha p \frac{a^2}{2b^2}\right) + \frac{1}{2p+1}\left(\frac{\alpha p}{\pi}\right)^{1/2} \exp[(\alpha + 1 + \ln \alpha)\, p] \tag{A6b}$$

If we choose α in order that $\alpha + 1 + \ln \alpha$ be negative, the right member of (A6b) will converge exponentially to zero when p goes to infinity. Since we do not need an optimized choice, we choose, for example,

$$\alpha = e^{-3/2} \tag{A7a}$$

which yields

$$|Y(x) - Q_p(\gamma_p x)| \leqslant \frac{1}{2}\exp\left(-pe^{-3/2}\frac{a^2}{2b^2}\right) + \frac{1}{2p+1}\left(\frac{\alpha p}{\pi}\right)^{1/2} \exp\left[-p\left(\frac{1}{2} - e^{-3/2}\right)\right] \tag{A7b}$$

Since we have $0 < a < b$, then it is straightforward to prove

$$\frac{e^{-3/2}}{2}\frac{a^2}{b^2} < \frac{e^{-3/2}}{2} < \frac{1}{2} - e^{-3/2} \tag{A7c}$$

Using this inequality and $\alpha < 1$, we obtain from (A7b)

$$|Y(x) - Q_p(\gamma_p x)| \leqslant \exp(-2\kappa p) \tag{A8a}$$

with

$$\kappa = \frac{1}{2}e^{-3/2}\frac{a^2}{b^2} \tag{A8b}$$

Then, choosing the polynomials $P_n(x)$ as $P_{2p-1}(x) = P_{2p}(x) = Q_p(\gamma_p x)$, we obtain a sequence of polynomials $P_n(x)$ of maximum degree n such that we have for r_n defined by (A2a)

$$r_n < \exp(-\kappa n) \tag{A8b}$$

Note that $\delta = 0$ yields $\kappa = 0$. Since the error at the discontinuity of the approximation of a step function by any continuous function is necessarily larger than or equal to the amplitude of this discontinuity, r_n cannot converge to zero when $\delta = 0$.

APPENDIX B

We calculate an upper bound for

$$T_{m,n;p,q} = \sum_{v,v'} \chi(E_v)[1-\chi(E_{v'})] \frac{\Psi_m^{v'} \Psi_n^{v'*} \Psi_p^{v*} \Psi_q^{v}}{(E_{v'} - E_v)^3} \tag{B1}$$

with the condition (31) in Proposition 2. $\chi(x)$ is defined by (16).

Step 1. According to Lemma 1, for $\chi(E_v) = 1$ in (B1), the eigenvalue E_v given by Eq. (14b) belongs to the interval $[-1 - \|\bar{\bar{A}}\|_2 t, -1 + \|\bar{\bar{A}}\|_2 t + \tau]$, while for $1 - \chi(E_{v'}) = 1$, $E_{v'}$ belongs to the interval $[-\|\bar{\bar{A}}\|_2 t - \tau, \|\bar{\bar{A}}\|_2 t]$. Thus, for the values in (B1), we have

$$1 - 2\tau - 2\|\bar{\bar{A}}\|_2 t \leqslant E_{v'} - E_v \leqslant 1 + 2\|\bar{\bar{A}}\|_2 t \tag{B2a}$$

which is equivalent to

$$\left| \frac{(1-\tau) - (E_{v'} - E_v)}{1-\tau} \right| < \frac{\tau + 2\|\bar{\bar{A}}\|_2 t}{1-\tau} = \lambda < 1 \tag{B2b}$$

Thus, for $t \leqslant t_0 = (1-2\tau)/(2\|\bar{\bar{A}}\|_2)$, the series

$$\begin{aligned} \frac{1}{(E_{v'} - E_v)^3} &= \frac{1}{(1-\tau)^3} \left(\frac{1}{[E_{v'} - E_v - (1-\tau)]/(1-\tau) + 1} \right)^3 \\ &= \frac{1}{(1-\tau)^3} \sum_{i=0}^{\infty} (i+1)(i+2) \left(\frac{(1-\tau) - (E_{v'} - E_v)}{1-\tau} \right)^i \end{aligned} \tag{B3}$$

is absolutely convergent, since $\lambda < 1$. As shown in Appendix A, on the intervals

$$a = \tfrac{1}{2} - \|\bar{\bar{A}}\|_2 t - \tau \leqslant |E_v + \tfrac{1}{2}| \leqslant \tfrac{1}{2} + \|\bar{\bar{A}}\|_2 t = b \tag{B4a}$$

We can approximate $1 - \sigma_v = \chi(E_v) = Y(E_v + 1/2)$ by a polynomial $P_\rho(E_v)$ with degree ρ with an error $R_\rho(E_v)$ bounded as

$$|R_\rho(E_v)| = |\chi(E_v - P_\rho(E_v)| \leqslant \exp(-\kappa\rho) \tag{B4b}$$

with

$$\kappa = \frac{1}{4} e^{-3/2} \frac{a^2}{b^2} = \frac{1}{4} e^{-3/2} \left(\frac{1 - 2 \| \bar{\bar{A}} \|_2 t - 2\tau}{1 + 2 \| \bar{\bar{A}} \|_2 t} \right)^2 = \frac{\gamma}{2} \tag{B4c}$$

We have

$$0 < \kappa \leqslant \kappa_0 = \frac{1}{4} e^{-3/2} = \frac{\gamma_0}{2} \tag{B4d}$$

Step 2. We use these expansions (B3a) and (B4b) to split $T_{m,n;\,p,\,q}$ into two parts as

$$\begin{aligned} T_{m,n;\,p,q} = & \frac{1}{(1-\tau)^3} \sum_{i=0}^{r-1} (i+1)(i+2) \\ & \times \sum_{\nu,\nu'} [1 - P_{\mathscr{d}(p,q)-1-i}(E_\nu) - R_{\mathscr{d}(p,q)-1-i}(E_\nu)] \\ & \times [P_{\mathscr{d}(m,n)-1-i}(E_{\nu'}) + R_{\mathscr{d}(m,n)-1-i}(E_{\nu'})] \\ & \times \Psi_m^{\nu'} \Psi_p^{\nu *} \Psi_n^{\nu'} \Psi_q^{\nu} \left(\frac{(1-\tau) - (E_{\nu'} - E_\nu)}{1-\tau} \right)^i \\ & + \frac{1}{(1-\tau)^3} \sum_{i=r}^{\infty} (i+1)(i+2)\, \Psi_m^{\nu'} \Psi_n^{\nu' *} \Psi_p^{\nu *} \Psi_q^{\nu} \\ & \times \sum_{\nu,\nu'} \sigma_\nu (1 - \sigma_{\nu'}) \left(\frac{(1-\tau) - (E_{\nu'} - E_\nu)}{1-\tau} \right)^i \end{aligned} \tag{B5a}$$

with

$$r = \mathrm{Min}(\mathscr{d}(m, n), \mathscr{d}(p, q)) \tag{B5b}$$

The terms in the sums (B5a) either depend on the variable E_ν as a polynomial factor of degree smaller than or equal to $\mathscr{d}(p, q) - 1$, or depend on the variable $E_{\nu'}$ as a polynomial factor of degree smaller than or equal to $\mathscr{d}(m, n) - 1$, or depend on both variables in the same way, and involve, for example, the matrix elements

$$(\bar{\bar{A}}^s)_{p,q} = \sum_\nu E^s{}_\nu \Psi_p^{\nu *} \Psi_q^{\nu} = 0 \tag{B6a}$$

of the electronic operator $\bar{\bar{A}}$ at some some power $s < \mathscr{d}(p, q)$. Since on the lattice $\mathbb{L}$, $\bar{\bar{A}}$ only involves a nearest-neighbor transfer integral,

$$A_{p,q} = 0 \qquad \text{for} \quad \mathscr{d}(p, q) > 1 \tag{B6b}$$

implies

$$(\bar{\bar{A}}^s)_{p,q}=0 \qquad \text{for} \quad \mathscr{d}(p,q)>s \tag{B6c}$$

Thus, the nonvanishing terms which are left in (B5a) are

$$\begin{aligned} T_{m,n;p,q}=&\frac{1}{(1-\tau)^3}\sum_{i=0}^{r-1}(i+1)(i+2)\sum_{v,v'}R_{\mathscr{d}(p,q)-1-i}(E_v)\,R_{\mathscr{d}(m,n)-1-i}(E_{v'})\\ &\times\Psi_m^{v'}\Psi_p^{v*}\Psi_n^{v'*}\Psi_q^{v}\left(\frac{(1-\tau)-(E_{v'}-E_v)}{1-\tau}\right)^i\\ &+\frac{1}{(1-\tau)^3}\sum_{i=r}^{\infty}(i+1)(i+2)\\ &\times\sum_{v,v'}\sigma_v(1-\sigma_{v'})\,\Psi_m^{v'}\Psi_p^{v*}\Psi_n^{v'*}\Psi_q^{v}\left(\frac{(1-\tau)-(E_{v'}-E_v)}{1-\tau}\right)^i \end{aligned} \tag{B7}$$

Step 3. This sum can be easily bound by using (B3b), (B4b), and the fact that Ψ_p^v are normalized vectors, which implies

$$\sum_v|\Psi_p^v|\cdot|\Psi_q^v|\leqslant 1 \tag{B8a}$$

We obtain

$$\begin{aligned} |T_{m,n;p,q}|\leqslant&\frac{1}{(1-\tau)^3}\sum_{i=0}^{r-1}(i+1)(i+2)\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)-2-2i]\}\lambda^i\\ &+\frac{1}{(1-\tau)^3}\sum_{i=r}^{\infty}(i+1)(i+2)\lambda^i\\ =&\frac{\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}}{(1-\tau)^3}e^{2\kappa}\sum_{i=0}^{r-1}(i+1)(i+2)[\lambda\exp(2\kappa)]^i\\ &+\frac{1}{(1-\tau)^3}\sum_{i=r}^{\infty}(i+1)(i+2)\lambda^i \end{aligned} \tag{B8b}$$

Although we lose on the quality of the bound, it is convenient for the sake of simplicity to reduce this complex form to a simpler one. With two derivatives with respect to x, the identity valid for $0<x<1$

$$\frac{1-x^{n+2}}{1-x}=\sum_{i=0}^{n+1}x^i \tag{B9a}$$

yields

$$\sum_{i=0}^{n-1}(i+1)(i+2)x^i$$
$$=\frac{1-(n+1)(n+2)x^n+2n(n+2)x^{n+1}-n(n+1)x^{n+2}}{(1-x)^3}\leqslant\frac{1}{(1-x)^3} \quad \text{(B9b)}$$

and

$$\sum_{i=n}^{\infty}(i+1)(i+2)x^i=\frac{x^n}{(1-x)^3}[(n+1)(n+2)-2n(n+2)x+n(n+1)x^2]$$
$$\leqslant(n+1)(n+2)\frac{x^n}{(1-x)^3} \quad \text{(B9c)}$$

which combined with (B8b) implies

$$|T_{m,n;p,q}|\leqslant\frac{\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}}{(1-\tau)^3}\frac{\exp(2\kappa)}{[1-\lambda\exp(2\kappa)]^3}$$
$$+\frac{(r+1)(r+2)}{(1-\tau)^3}\frac{\lambda^r}{(1-\lambda)^3} \quad \text{(B10)}$$

Step 4. The relation between the indices m, n, p, q of $T_{m,n;p,q}$ defined by (34b) implies

$$|(\mathscr{d}(p,q)-\mathscr{d}(m,n)|\leqslant 2 \quad \text{(B11a)}$$

and thus with definition (B5b), we have

$$\mathscr{d}(p,q)+\mathscr{d}(m,n)\leqslant r+2 \quad \text{(B11b)}$$

which implies

$$(r+1)(r+2)\lambda^r\exp\{\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}$$
$$\leqslant(r+1)(r+2)(\lambda e^{2\kappa})^r e^{2\kappa} \quad \text{(B11c)}$$

We now use the hypothesis (31a), which is equivalent to

$$\lambda e^{2\kappa}<\lambda e^{2\kappa_0}=\lambda e^{\gamma_0}<\tfrac{1}{3} \quad \text{(B12a)}$$

Then, the sequence $(r+1)(r+2)(\lambda e^{2\kappa})^r$ is monotone decreasing. Its maximum value, which is obtained for $r=0$, is 2. Thus, (B11c) implies, for all $r\geqslant 0$,

$$(r+1)(r+2)\lambda^r\exp\{\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}<2e^{2\kappa} \quad \text{(B12b)}$$

Step 5. Inequality (B12b) combined with (B10) implies

$$|T_{m,n;p,q}| \leqslant \frac{\exp(2\kappa)}{(1-\tau)^3}\left(\frac{1}{[1-\lambda\exp(2\kappa)]^3}+\frac{2}{(1-\lambda)^3}\right) \times \exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}$$
$$\leqslant \frac{\exp(2\kappa)}{(1-\tau)^3}\frac{3}{[1-\lambda\exp(2\kappa)]^3}\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}$$
$$\leqslant \frac{\exp(\gamma_0)}{(1-\tau)^3}\frac{3}{[1-\lambda\exp(\gamma_0)]^3}\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\} \tag{B13a}$$

Using (B12a), (35a), and (31b), we find

$$|T_{m,n;p,q}| \leqslant \frac{\exp(\gamma_0)}{(1-\tau)^3}\frac{3}{[1-\lambda\exp(\gamma_0)]^3}\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\}$$
$$\leqslant 25\exp\{-\kappa[\mathscr{d}(p,q)+\mathscr{d}(m,n)]\} \quad \text{QED} \tag{B13b}$$

APPENDIX C. PROOF OF THEOREM 2 (MIXED POLARONIC–BIPOLARONIC STATES)

It is not necessary to reproduce here the whole detailed proof of Theorem 2 since it is almost identical to that of Theorem 1. Instead, we follow that proof from the beginning to the end and only point out the variations which have to be made at some specific points for obtaining Theorem 2 with different bounds.

For the proof of Theorem 2, we also search for a fixed point for the same operator $\mathbf{S}_t(\{u_n\})=\{v_n\}$ defined in (18b), but it is now restricted to different domains $E(\{\sigma_n\},\tau)$ defined as in (19) but with pseudospin configurations $\sigma_n=0$, 1/2, or 1. We now assume

$$0<\tau<\tfrac{1}{4} \tag{C1a}$$

so that for $\{u_n\}\in E(\{\sigma_n\},\tau)$ we can write

$$u_n=-(1-\tau)(\sigma_n+\varepsilon_n)-\frac{\tau}{2} \tag{C1b}$$

with

$$|\varepsilon_n|\leqslant\frac{\tau}{1-\tau} \tag{C1c}$$

With almost the same proof, Lemma 1 is readily extended to a three-band case. We have the following result.

Lemma C. For $\{u_n\} \in E(\{\sigma_n\}, \tau)$ with $\{\sigma_n\} \in \{0, 1/2, 1\}^{\perp}$, and for

$$t < t_0' = \frac{1-4\tau}{4\|\bar{\bar{\Delta}}\|_2} \tag{C2a}$$

the eigenenergies can be written as

$$E_\nu = -(1-\tau)(\sigma_\nu + \varepsilon_\nu) - \frac{\tau}{2} \tag{C2b}$$

with

$$|\varepsilon_\nu| \leqslant \frac{\tau + t\|\bar{\bar{\Delta}}\|_2}{1-\tau} \tag{C2c}$$

and $\sigma_\nu = 1$ for the doubly occupied electronic states, $\sigma_\nu = 1/2$ for the singly occupied states, and $\sigma_\nu = 0$ for the empty states.

Since the bound in the lemma has been modified, Proposition 1, which makes use of it, also needs to be modified. We have, with the same notations, the following statement.

Proposition C1. For any pseudospin configuration $\{\sigma_n\}$ (with $\sum_n \sigma_n = P$) and $t \leqslant t_0'$, the operator $\mathbf{S}_t$ maps $\mathscr{E}(\{\sigma_n\}, \tau)$ into $\mathscr{E}(\{\sigma_n\}, \tau'')$, where

$$\tau'' = \frac{2(\tau^2 + t^2 S_\Delta)}{(1-5\tau-4t\|\bar{\bar{\Delta}}\|_2)(1-\tau)} \tag{C3}$$

Proof. The beginning of this proof is identical to that of Proposition 1 up to formulas (24). The evaluation of I in (25a) is slightly different, since ε_n is bounded as in (C1c). Thus, (25c) becomes

$$I \leqslant \tau^2 + t^2 S_\Delta \tag{C4a}$$

Inequality (26a) is unchanged and since for $\sigma_n = 0$, 1/2, or 1 and $\sigma_\nu = 0$, 1/2, or 1 we have the inequality

$$(\sigma_n - \sigma_\nu)^2 \geqslant \tfrac{1}{2}|\sigma_n - \sigma_\nu| \tag{C4b}$$

it imples, by using (C2c),

$$I \geqslant (1-\tau)^2 \sum_{\nu} |\sigma_n - \sigma_\nu| \left(\frac{1}{2} - 2|\varepsilon_\nu|\right) |\Psi_n^\nu|^2$$

$$\geqslant (1-\tau)^2 \left(\frac{1}{2} - 2\frac{\tau + t\|\bar{\bar{A}}\|_2}{1-\tau}\right) \sum_{\nu} |\sigma_n - \sigma_\nu| \, |\Psi_n^\nu|^2 \tag{C4c}$$

This inequality implies both

$$I \geqslant \tfrac{1}{2}(1-\tau)(1-5\tau-4t\|\bar{\bar{A}}\|_2) \sum_{\nu} (\sigma_n - \sigma_\nu) |\Psi_n^\nu|^2$$

$$= \tfrac{1}{2}(1-\tau)(1-5\tau-4t\|\bar{\bar{A}}\|_2)(\sigma_n + \nu_n) \tag{C5a}$$

and

$$I \geqslant \tfrac{1}{2}(1-\tau)(1-5\tau-4t\|\bar{\bar{A}}\|_2) \sum_{\nu} -(\sigma_n - \sigma_\nu) |\Psi_n^\nu|^2$$

$$= -\tfrac{1}{2}(1-\tau)(1-5\tau-4t\|\bar{\bar{A}}\|_2)(\sigma_n + \nu_n) \tag{C5b}$$

and consequently

$$I \geqslant \tfrac{1}{2}(1-\tau)(1-5\tau-4t\|\bar{\bar{A}}\|_2) |\sigma_n + \nu_n| \tag{C5c}$$

Then (C4a) combined with (C5c) yields $\{\nu_n\} \in \mathscr{E}(\{\sigma_n\}, \tau'')$ with τ'' given by (C3). QED

For continuing the proof in parallel with that of Theorem 1, we write the population factor $\chi(x)$ given by (17) as the average of two characteristic functions,

$$\chi(x) = \tfrac{1}{2}[\chi_1(x) + \chi_2(x)] \tag{C6a}$$

where

$$\begin{aligned} &\chi_1(x) = 1 \qquad \text{for} \quad x < -\tfrac{3}{4} \\ &\chi_1(x) = 0 \qquad \text{for} \quad x > -\tfrac{3}{4} \end{aligned} \tag{C6b}$$

and

$$\begin{aligned} &\chi_2(x) = 1 \qquad \text{for} \quad x < -\tfrac{1}{4} \\ &\chi_2(x) = 0 \qquad \text{for} \quad x > -\tfrac{1}{4} \end{aligned} \tag{C6c}$$

Then the Jacobi matrix $\bar{\bar{J}}$ of the operator $\mathbf{S}_t$ can be split into the sum of two matrices,

$$J_{m,n} = \frac{\partial \nu_m}{\partial u_n} = -\sum_{\nu} \chi(E_\nu) \Psi_m^{\nu *} \frac{\partial \Psi_m^\nu}{\partial u_n} - \text{CC}$$

$$= J_{m,n}^{(1)} + J_{m,n}^{(2)} \tag{C7a}$$

with

$$J^{(1)}_{m,n} = -\sum_{\nu} \chi_1(E_\nu)\, \Psi^{\nu *}_m \frac{\partial \Psi^{\nu}_m}{\partial u_n} - \mathrm{CC}$$

$$= \sum_{\nu,\nu'} \chi_1(E_\nu)[1-\chi_1(E_{\nu'})]\, \frac{\Psi^{\nu *}_m \Psi^{\nu'}_m \Psi^{\nu' *}_n \Psi^{\nu}_n}{E_{\nu'} - E_\nu} + \mathrm{CC} \tag{C7b}$$

$$J^{(2)}_{m,n} = -\sum_{\nu} \chi_2(E_\nu)\, \Psi^{\nu *}_m \frac{\partial \Psi^{\nu}_m}{\partial u_n} - \mathrm{CC}$$

$$= \sum_{\nu,\nu'} \chi_2(E_\nu)[1-\chi_2(E_{\nu'})]\, \frac{\Psi^{\nu *}_m \Psi^{\nu'}_m \Psi^{\nu * }_n \Psi^{\nu}_n}{E_{\nu'} - E_\nu} + \mathrm{CC} \tag{C7c}$$

instead of the terms (34c). When the conditions of application of lemma C hold, the arguments used for showing that (29c) remains well defined even in the case of the degeneracy of eigenenergies hold for proving that the coefficients of $\bar{\bar{J}}^{(1)}$ and $\bar{\bar{J}}^{(2)}$ are well defined.

Then, similarly to Proposition 2, we can bound the coefficients of $\bar{\bar{J}}^{(1)}$ and $\bar{\bar{J}}^{(2)}$.

Proposition C2. Let us assume

$$16t \|\bar{\bar{A}}\|_2 < (3e^{-\gamma_0} - 2) - 4(2 + e^{-\gamma_0})\tau \tag{C8a}$$

with $\gamma_0 = e^{-3/2}/2 \cong 0.111565080$, given by (31b), and set

$$\gamma' = \gamma_0 \left(\frac{1 - 4\tau - 4t\|\bar{\bar{A}}\|_2}{3 + 4t\,\|\bar{\bar{A}}\|_2} \right)^2 \leqslant \gamma_0 \tag{C8b}$$

$$C' = \left(\frac{63}{2}\, t \|\bar{\bar{A}}\|_\infty \right)^2 \tag{C9c}$$

We have for all m and n in $\mathbb{S}$

$$|J^{(1)}_{m,n}| \leqslant C' \exp[-\gamma' d(m,n)] \tag{C10a}$$

$$|J^{(2)}_{m,n}| \leqslant C' \exp[-\gamma' d(m,n)] \tag{C10b}$$

$$|J_{m,n}| \leqslant C' \exp[-\gamma' d(m,n)] \tag{C10c}$$

For a nonexponential lattice $\mathbb{L}$ we have

$$\|\bar{\bar{J}}\|_\infty \leqslant C' \left[\sum_{r=0}^{\infty} N_{\mathbb{L}}(r) \exp(-\gamma' r) \right] = C' \varphi(\gamma') < \infty \tag{C10d}$$

Proof. This proof is also based on polynomial approximations, as for Proposition 2. In order to fix the ideas, the proof of Proposition 2 is performed for the matrix $\bar{\bar{J}}^{(1)}$, but it can be performed identically for the matrix $\bar{\bar{J}}^{(2)}$.

Step 1. As in the first step of the proof of Proposition 2, we transform the coefficients of $J^{(1)}_{m,n}$ as in formulas (34). We obtain

$$J^{(1)}_{m,n} = t^2 \sum_{p,q} \Delta_{m,q} \Delta_{n,p} (T^{(1)}_{m,n,p,q} + T^{(1)}_{p,q,m,n} - T^{(1)}_{p,n,m,q} - T^{(1)}_{m,q,p,n}) + \text{CC} \quad \text{(C11a)}$$

with

$$T^{(1)}_{m,n;p,q} \sum_{\nu,\nu'} \chi_1(E_\nu)[1-\chi_1(E_{\nu'})] \frac{\Psi^{\nu'}_m \Psi^{\nu *}_p \Psi^{\nu' *}_n \Psi^{\nu}_q}{(E_{\nu'} - E_\nu)^3} \quad \text{(C11b)}$$

$$|J^{(1)}_{m,n}| \leqslant 8t^2 \|\bar{\bar{\Delta}}\|^2_\infty \boldsymbol{T}^{(1)}_{m,n} \quad \text{(C11c)}$$

Now we follow Appendix B for finding an upper bound $\boldsymbol{T}^{(1)}_{m,n}$ to the term $|T^{(1)}_{m,n;p,q}|$ in (C11a).

Step 2. As a consequence of Lemma C, when $\chi_1(E_\nu) = 1$, the eigenvalues E_ν which appear in (C7b) belong to the interval $[-1 - t\|\bar{\bar{\Delta}}\|_2, -1 + t\|\bar{\bar{\Delta}}\|_2 + \tau]$. When $1 - \chi_1(E_{\nu'}) = 1$, the eigenvalues $E_{\nu'}$ belong to the interval $[-\frac{1}{2} - t\|\bar{\bar{\Delta}}\|_2 - \tau, t\|\bar{\bar{\Delta}}\|_2]$. Consequently, we have in (C8)

$$0 < \tfrac{1}{2} - 2\tau - 2t\|\bar{\bar{\Delta}}\|_2 < E_{\nu'} - E_\nu < 1 + 2t\|\bar{\bar{\Delta}}\|_2 \quad \text{(C12a)}$$

which is equivalent to

$$\frac{|E_{\nu'} - E_\nu - \frac{3}{4} + \tau|}{\frac{3}{4} - \tau} < \frac{\frac{1}{4} + \tau + 2t\|\bar{\bar{\Delta}}\|_2}{\frac{3}{4} - \tau} = \frac{1 + 4\tau + 8t\|\bar{\bar{\Delta}}\|_2}{3 - 4\tau} = \lambda' < 1 \quad \text{(C12b)}$$

which replaces the inequalities (B2). Then, as in (B3), the denominator in (C11b) is replaced by the convergent expansion

$$\frac{1}{(E_{\nu'} - E_\nu)^3} = \frac{1}{[(E_{\nu'} - E_\nu - \frac{3}{4} + \tau) + (\frac{3}{4} - \tau)]^3}$$
$$= \frac{1}{(\frac{3}{4} - \tau)^3} \sum_{i=0}^{\infty} (i+1)(i+2) \left(\frac{\frac{3}{4} - \tau - (E_{\nu'} - E_\nu)}{\frac{3}{4} - \tau} \right)^i \quad \text{(C13)}$$

Step 3. As in (B4b), we approximate $\chi_1(E_\nu) = Y(E_\nu + \frac{3}{4})$ defined by (C6b) by a polynomial $P_r(E_\nu)$ the degree r of which is given by (B5b) and with an error $R_r(E_\nu)$ bounded as $\exp(-\kappa' r)$. Lemma C implies

$$a' = \tfrac{1}{4} - t\|\bar{\bar{\Delta}}\|_2 - \tau \leqslant |E_\nu + \tfrac{3}{4}| \leqslant t\|\bar{\bar{\Delta}}\|_2 + \tfrac{3}{4} = b' \quad \text{(C14a)}$$

which yields, by Proposition A in Appendix A,

$$|\chi_1(E_v) - P'_r(E_v)| \leqslant \exp(-\kappa' r) \tag{C14b}$$

with

$$\kappa' = \frac{\gamma_0}{2}\frac{a'^2}{b'^2} = \frac{\gamma_0}{2}\left(\frac{1-4\tau-4t\|\bar{\bar{A}}\|_2}{3+4t\|\bar{\bar{A}}\|_2}\right)^2 = \frac{\gamma'}{2} \tag{C14c}$$

Step 4. Then a bound for $|T^{(1)}_{m,n;p,q}|$ can be obtained identically as for $|T_{m,n;p,q}|$ in (B8b),

$$|T^{(1)}_{m,n;p,q}| \leqslant \frac{1}{(\frac{3}{4}-\tau)^3}\sum_{i=0}^{r-1}(i+1)(i+2)\exp\{-\kappa'[\mathcal{d}(p,q)+\mathcal{d}(m,n)-2-2i]\}\gamma'^i + \frac{1}{(\frac{3}{4}-\tau)^3}\sum_{i=r}^{\infty}(i+1)(i+2)\lambda'^i \tag{C15a}$$

which implies by using the inequalities (B9)

$$|T^{(1)}_{m,n;p,q}| \leqslant \frac{1}{(\frac{3}{4}-\tau)^3}\left(\frac{\exp(2\kappa')\exp\{-\kappa'[\mathcal{d}(p,q)+\mathcal{d}(m,n)]\}}{[1-\lambda'\exp(2\kappa')]^3}(r+1)(r+2)\frac{\lambda'^r}{(1-\lambda')^3}\right) \tag{C15b}$$

Step 5. For sake of simplicity, we look for a looser bound with a simpler exponential form. The method which we used is similar to that used in step 4 of Appendix B, but has to be slightly modified, since the condition $\lambda' e^{2\kappa'} < 1/3$, which would correspond to (B12a), cannot be fulfilled. In fact, λ' defined in (C12b) and also $\lambda' e^{2\kappa'}$ are always larger than 1/3. Instead of this condition, we assume the condition

$$\lambda' e^{2\kappa'} < \lambda' e^{\gamma_0} < \tfrac{1}{2} \tag{C16a}$$

[which is equivalent to (C8a)], so that the largest term in the sequence $(r+1)(r+2)(\lambda' e^{2\kappa'})^r$ is obtained for $r=1$ instead of $r=0$ as in (B12b). Thus, we have for all r

$$(r+1)(r+2)(\lambda' e^{2\kappa'})^r \leqslant 6\lambda' e^{2\kappa'} < 3 \tag{C16b}$$

or

$$(r+1)(r+2)\lambda'^r \exp\{\kappa'[\mathcal{d}(m,n)+\mathcal{d}(p,q)]\} < 3e^{2\kappa'} \tag{C16c}$$

By substitution of this inequality in (C15b), we obtain

$$|T^{(1)}_{m,n;p,q}| \leqslant \frac{1}{(\frac{3}{4}-\tau)^3}\frac{4e^{\gamma_0}}{(1-\lambda' e^{\gamma_0})^3}\exp\{-\kappa'[\mathcal{d}(m,n)+\mathcal{d}(p,q)]\} \tag{C17a}$$

instead of (B13b). Condition (C8a) [or (C16a)] implies

$$\tau < \frac{3e^{-\gamma_0} - 2}{4(2 + e^{-\gamma_0})} \tag{C17b}$$

which yields, when combined with (C17a),

$$\begin{aligned} |T^{(1)}_{m,n;p,q}| &\leqslant 4[2 + \exp(-\gamma_0)]^3 \exp(\gamma_0) \exp\{-\kappa'[\mathcal{d}(m,n) + \mathcal{d}(p,q)]\} \\ &\leqslant 109 \exp\{-\kappa'[\mathcal{d}(m,n) + \mathcal{d}(p,q)]\} \end{aligned} \tag{C17c}$$

Using inequality (B11a), we obtain that

$$T^{(1)}_{m,n} = 109 \exp(\gamma_0) \exp[-\gamma' \mathcal{d}(m,n)] \tag{C17d}$$

is an upper bound for the terms $|T^{(1)}_{m,n;p,q}|$ in (C11a). Using this bound valid for $T^{(1)}_{m,n;p,q}$ and $T^{(2)}_{m,n;p,q}$, we obtain that (C11c) yields (C10a). The same bound holds for $|J^{(2)}_{m,n}|$ and $J_{m,n}$ in (C7a), which proves Proposition C2. QED

The proof of Theorem 2 follows the same steps as those of Theorem 1. The arguments for the first part of the proof apply identically in both theorems, although the bound t_2' for Theorem 2 is different from t_2. We check that the operator $\mathbf{S}_t$ is still a uniform function of t when the pseudospins σ_n can take three values (0, 1/2, or 1) instead of two (0 or 1), by splitting the derivative $\partial v_n/\partial t$ into the sum of two terms as in (C7). Each of these terms has the form (41), where the pseudospins are given by $\sigma_v = \chi_1(E_v)$ and $\sigma_v = \chi_2(E_v)$, respectively. It is proven as for Theorem 1 that each of these terms in a uniform function of t as well as their sum $\partial v_n/\partial t$.

The calculation of an explicit value for t_2' is qualitatively identical to that of Theorem 1 but quantitatively different. Proposition 2 yields, if (C8a) is fulfilled,

$$\begin{aligned} \|\bar{\bar{J}}\|_\infty &\leqslant C' \left(\frac{e^{\gamma'} + 1}{e^{\gamma'} - 1}\right)^d \leqslant (63td)^2 \frac{(e^{\gamma_0} + 1)^d}{\gamma'^d} \\ &= (63td)^2 \left(\frac{e^{\gamma_0} + 1}{\gamma_0}\right)^d \left(\frac{3 + 8dt}{1 - 4\tau - 8dt}\right)^2 \end{aligned} \tag{C18}$$

By using (C8a) and (C17b), we obtain

$$\begin{aligned} \frac{3 + 8dt}{1 - 4\tau - 8dt} &\leqslant \frac{12 + (3e^{-\gamma_0} - 2) - 4(2 + e^{-\gamma_0})\tau}{4 - 16\tau - (3e^{-\gamma_0} - 2) + 4(2 + e^{-\gamma_0})\tau} \\ &< \frac{2 + e^{-\gamma_0}}{2 - e^{-\gamma_0}} + \frac{4}{(3 - 4\tau)(2 - e^{-\gamma_0})} \\ &< \frac{14 - e^{-\gamma_0} - 3e^{-2\gamma_0}}{(2 - e^{-\gamma_0})(5 - 3e^{-\gamma_0})} \end{aligned} \tag{C19a}$$

Consequently, we have $\|\bar{\bar{J}}\|_\infty < 1$ when

$$t < t_2' = \frac{1}{63d}\left(\frac{e^{\gamma_0}+1}{\gamma_0}\right)^{-d/2}\left(\frac{(2-e^{-\gamma_0})(5-3e^{-\gamma_0})}{14-e^{-\gamma_0}-3e^{-2\gamma_0}}\right)^{d} \tag{C19b}$$

Finally, in step 5, we prove that there exists an appropriate choice of τ fulfilling

$$\tau < \frac{1-8t_2'\cdot d}{4} \tag{C20a}$$

$$\frac{2(\tau^2+2t_2'^2\cdot d)}{(1-5\tau-8t_2'\cdot d)(1-\tau)} < \tau \tag{C20b}$$

$$\tau < \frac{3e^{-\gamma_0}-2-32t_2'\cdot d}{4(2+e^{-\gamma_0})} \tag{C20c}$$

such that for $t < t_2'$, Lemma C and Proposition C1 and C2 hold. It is easy to check that, for example, $\tau = 1/8$ is a convenient choice. QED

NOTE ADDED IN PROOF

R. MacKay and C. Baesens[50] recently improved the proof of Theorem 1. The existence proof of a fixed point for operator S_t defined by (18) was obtained elegantly by using a resolvant operator integrated on a contour in the complex plane instead of complicated polynomial approximants. The rigorous bound obtained for the existence of bipolaronic states is $t < 0.089939$ which is more than 20 times better than our bound given by (47a).

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