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Tuning ground states and excitations in complex electronic materials

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Abstract

Modern electronic materials are characterized by a great variety of broken-symmetry ground states and excitations. Their control requires understanding and tuning underlying driving forces of spin-charge-lattice coupling, critical to macroscopic properties and applications. We report representative model calculations which demonstrate some of the richness of the phenomena and the challenges for successful microscopic modeling.

Keywords: Broken symmetries; nonlinearity; spin-charge-lattice coupling, breathers, polarons

1. Introduction

The long ICSM journey through "complex electronic materials" has paralleled many discoveries in organic ((SN)_x, X-TCNQ, (CH)_x, etc.) and inorganic (transition metal perovskites, layered dicalchogenides, heavy fermions, etc.) materials. This exciting 2-decade era has revealed important paradigms for the interfaces between traditional fields of materials science, solid state physics, and chemistry which symbolize today's optimism for controlling and designing materials to meet present and future needs of technology.

Among the important lessons are: (i) Broken symmetries (charge-density-wave (CDW), spin-density-wave (SDW), spin-Peierls, ferroelectric, superconducting, etc.) are controlled by delicate competitions between often competing interactions (electron-electron (e-e), electron-phonon (e-ph), spin-phonon, disorder) and dimensionality effects. Likewise, the richness of nonlinear excitations (solitons, polarons, excitons, bags, etc.) depends on the reference broken symmetry and thus the same competitions. (ii) The holy grail in materials research and development is to understand and control relations between "synthesis (and processing), texture, and property." We may now translate this in complex electronic materials (as well as other materials and indeed many other disciplines) as the relations between "microscopic interactions, mesoscale patterns, and macroscopic functionality." This raises fundamental issues for a predictive control of materials: what are the microscopic driving forces linking micro to mesoscales; and what are the quantitative measures of complexity at the mesoscale relevant to physical macroscopic properties (e.g. electrooptic, transport)? (iii) Central to these questions is the level of appreciation and acceptance for the need to treat and manipulate *spin-charge-lattice* coupling. Arbitrarily slaving to a single degree-of-freedom is a luxury

not often available to the complex materials of ICSM interest. The science involved is typically and inescapably *nonlinear, nonequilibrium, nonadiabatic, nonlocal, . . .* The consequences are of dominating physical concern—metal-insulator and broken-symmetry transitions; intrinsic multiscale spatial structure (from atoms to domains); associated multiple timescales; the intimate correlation of electronic, optical, and magnetic properties, etc.

To answer these challenges of real materials requires new experimental techniques (local structure probes, time-resolved spectroscopy, high-magnetic fields, etc.) and a correspondingly multitechnique approach to theory and modeling. Much of this ICSM Meeting is devoted to those frontiers. Here we briefly report a few model calculations which serve to illustrate some of the richness (and challenge) of the phenomena, concepts and approaches.

2. CDW-AF crossover in a multiband Peierls-Hubbard chain

Including *both* electron-phonon and electron-electron interactions in *multiband* models appears [1, 2] to capture important aspects of competing broken-symmetry ground states and intrinsic charge-lattice-spin "textures." We summarize a 1-D, 2-band Peierls-Hubbard model [2] that mimics the 2-D structural distortion (oxygen sublattice) found to be anomalous in HTC cuprate planes, and that also faithfully described quasi-1-D halogen-bridged transition chain (*MX*) complexes—1-D paradigms of cuprate and bismuthate materials [2]. Even at stoichiometry, the competition (*e-e/e-ph*) drives qualitatively new ground states beyond period-4 charge-density-wave (CDW) or spin-density-wave (AF) phases—novel magnetic phases of frustrated, superlattice (long-period) or spin-Peierls type.

The 1-D Hamiltonian we consider is [2]

$$H = \sum_{l\sigma} \{ (-t_0 + \alpha\delta_l) (c_{l,\sigma}^\dagger c_{l+1,\sigma} + c_{l+1\sigma}^\dagger c_{l,\sigma}) + [\epsilon_l - \beta_l (\delta_l + \delta_{l-1})] c_{l,\sigma}^\dagger c_{l,\sigma} \} + \sum_l \left\{ U_l c_{l,\uparrow}^\dagger c_{l,\uparrow} c_{l,\downarrow}^\dagger c_{l,\downarrow} + \frac{1}{2} K (\delta_l - a_l)^2 + P \delta_l \right\}, \quad (1)$$

where $c_{l,\sigma}^\dagger$ creates an electron at site l with spin σ . $M(d_{z^2})$ and $X(p_z)$ Wannier orbitals are situated on even and odd sites, respectively. Each M_2X_2 unit cell has 6 electrons (i.e., 3/4 band filling). On-site energies are ϵ_l ($\epsilon_M = -\epsilon_X = \epsilon_0 \geq 0$). There is on-site (β_M, β_X) and inter-site (α) e -ph coupling, on-site e - e repulsion (U_M, U_X), and pressure P . a_l is the natural M - X spring length, and δ_l is the relative displacement of sites l and $l+1$. Both HF and exact diagonalization techniques are used.

Model (1) contains many phases [2]. We focus here on intermediate to large e - e correlations (large U_M). Consider first the zero-hopping limit, $t_0 = 0$. For U_M dominant, the lower, X -like band is full and nonmagnetic, while the upper, M -like band is 1/2 full with one electron per M site and uncorrelated spins. For $t_0 \neq 0$, as in the one-band case, there is an effective AF coupling between spins on neighboring metal sites, J_{MM} , driving AF order that competes with band splitting from the on-site e -ph coupling β . However, the lower band is not completely full and there are effective AF couplings between neighboring X sites, J_{XX} , and M and X sites, J_{MX} , not present in simple one-band models. When the splitting due to β is on the order of U and ϵ_0 , the AF state with neighboring M - X pairs singly occupied can become the ground state. Thus, the combination of e - e and e -ph coupling in the two-band model drives, in addition to nonmagnetic CDW and BOW (bond-order-wave) phases, three (competing) spin-Peierls phases: one on the X sublattice (XAF), one on the M sublattice (MAF), and one involving M - X pairs and large lattice distortion (MXP). Since J_{MM} , J_{XX} , and J_{MX} are all antiferromagnetic ($J > 0$), the system is frustrated. When only one of the J 's dominates, one can numerically check estimates of the size of the J from perturbation theory in t_0 by comparing the energies of the singlet and triplet ground states [2]. Note that the CDW phase has an entirely e -ph driven antiferromagnetic component: Even when the X (M)-sublattice distortion is large, some residual M (X)-sublattice magnetization remains.

Consider parameters where the lattice distortion is large and driven by the on-site e -ph coupling β , and/or the Hubbard U terms are large. Figure 1 presents exact diagonalization results. As U_M increases (lattice distortion decreases), there is a sharp transition from M - M charge coupling (CDW) to M - X spin coupling (MXP) to M - M spin coupling (MAF), agreeing with the $t_0 = 0$ results. For larger t_0 , the phases change more smoothly; and charge disproportionation, M - X spin coupling, and M - M spin

Fig. 1. Exact diagonalization, 16-site ring: (a) lattice distortion amplitude, (b) total energy E_T , and (c) NN and (d) NNN spin correlations as a function of U_M/ϵ_0 for MAF, CDW, and MXP phases at $t_0/\epsilon_0 = 0.5$. $\beta_X/\beta_M = 1$, $U_X/U_M = 1$, $\beta_M^2/K\epsilon_0 = 7 - 3U_M/4\epsilon_0$. For finite systems lattice distortion strongly pins competing phases.

coupling coexist, with the phase of the lattice distortion passing from CDW through MXP to BOW as the amplitude goes to zero. For large t_0 , even for $U_M = 0$, the CDW phase shows a strong tendency towards antiferromagnetic order driven by valence fluctuations.

The crossover between the period-4 CDW and MAF phases is accompanied by long-period superlattice phases when $|\beta_X/\beta_M| > 1$ or the intersite e -ph coupling α is large. Superlattices may be viewed as ordered arrays of discommensuration (bipolaron) defects with respect to nearby commensurate (period-4) order. Considering the effective J 's discussed above, it is natural to view such states in terms of ANNNI-like models. Hole doping into these soft crossover stoichiometric phases is especially intriguing, in view of doping dependencies found in spin-Peierls material (CuGeO_3) or frustrated spin-ladder AFs [3].

3. Spin-lattice polaronic defects in an antiferromagnetic background

The importance of lattice distortion, especially upon photo- or chemical doping, in materials exhibiting strong AF broken symmetries at stoichiometry has been appreciated recently both experimentally and theoretically. This is true, for example, in the HTC cuprates or manganites where the novelty of spin-charge-lattice polarons (bags) and their ordering at commensurate doping is increasingly realized [4,5,6]. Here, as a simple 1-D analog of HTC materials, we consider a model [7] of quasi-1-D NiX materials. Data are gradually being acquired for these AF/charge-transfer members of the MX class [8] which may have interpretations

along the directions below. However, our intent here is only to use a plausible 1-D model to illustrate that polarons may have strong local lattice distortion content even though the global stoichiometric symmetry is purely AF.

We again adopt model Hamiltonian (1) but with large on-site Coulomb energy U_M so that the AF ground state dominates CDW at 3/4 band-filling. We will use a representative parameter set for NiX materials, since data to fix parameters are currently incomplete: $t_0 = 0.95$ eV, $e_0 = 0.51$ eV, $\alpha = 1.59$ eV/Å, $\beta_M = 1.52$ eV/Å, $\beta_X = -0.76$ eV/Å, $U_M = 2.6$ eV, $U_X = 1.1$ eV, $K_{MX} = 7.9$ eV/Å², $K_{MM} = 2.0$ eV/Å². We use mean-field, HF and RPA to solve model (1). Vertex and quantum fluctuations may change the results quantitatively and deserve further study, but the basic feature we wish to emphasize is evident at the mean-field level. In addition to the uniform stoichiometric ground states, self-trapped excitations of interest include: polarons and bipolarons, solitons (kinks), and singlet or triplet excitons. These are studied systematically in Ref. [7]. All of the above defects are stable (with the given parameter set) except for the singlet exciton—this may be stabilized on, e.g., second neighbor Ni sites if a longer-range Coulomb term is included.

We emphasize that all of the above defects *locally* distort lattice dimerization patterns, in addition to local charge disproportionations, relative to the stoichiometric undistorted AF background. The phenomenon arises from lattice relaxation due to the electron-lattice coupling, present even in the strong electron-electron interaction background. Table II in Ref. [7] summarizes the distortion amplitudes Δ . The Δ values are one order of magnitude higher in the case of charged (chemical-doped) defects (P^- , P^+ , B^{2-} , B^{2+} , K^- , and K^+) than those of a neutral chain satisfying 3/4-filling (triplet exciton and K^0). Negatively doped defects have expansions, whereas positively doped ones show contractions. As an example, Fig. 2 shows the dimerization patterns and electron spin-up and -down distributions for an electron bipolaron developed in the AF background.

Because of the local lattice distortion, IR and Raman modes become active which are silent in the undimerized lattice—see Ref. [6] for details. These should be observed in NiX materials, as they are in doped HTC compounds [9]. Likewise, 2-magnon Raman should be a valuable tool in NiX, again as in HTC materials [10].

4. Quantum lattice dynamics: polaron tunneling in a small cluster

Many generic features of polarons—self-trapping and particle-like band motion due to quantum tunneling—are captured by small-cluster models envisaged to describe electronic correlation effects or electron-lattice interactions, outside the scope of conventional approaches. Perhaps the simplest model is a two-site cluster that already exemplifies the polaron dynamics arising from the linear coupling of electronic and phonon degrees of freedom [11]. A very similar example is the local dynamics of an axial-oxygen [O(4)] and chain-copper

Fig. 2. An electron bipolaron formed in a NiX AF background: (a) dimerization patterns; (b) electron charge distributions for both spin up (solid line) and down (dashed line). This is a 48-site NiX chain with an extra spin-up electron located at Ni-site 25 and a spin down one at Ni-site 27, as indicated.

[Cu(1)] cluster in YBa₂Cu₃O₇, for which polaron tunneling has been proposed [12] to be an essential component of the local dynamics. In this approach, the novel features arise from a dynamic double-well structure, inferred from, e.g., XAFS data, and described as polaron tunneling, specifically realizing local, directional “polarizability.”

We study a Hamiltonian (c.f., model (1)) that is naturally divided into three parts [10]:

$$H = H_{el} + H_{ph} + H_{el-ph} . \quad (2)$$

We assume that the dynamics of the O(4)-Cu(1)-O(4) cluster can be effectively separated from the rest of the lattice, because the dynamic coupling to the planes is weak due to the long bond lengths, and because some aspects of the coupling along the chain direction can be taken into account as an effective Hamiltonian by integrating out the degrees of freedom associated with the chain oxygens O(1).

First, the electronic part is given by the extended Hubbard model on a three-site cluster:

$$H_{el} = \sum_a \epsilon_a n_a + \sum_{ab,\sigma} t_{ab} (c_{a\sigma}^\dagger c_{b\sigma} + h.c.) + U \sum_a n_{a\uparrow} n_{a\downarrow} . \quad (3)$$

Here, $c_{a\sigma}^\dagger$ creates a hole of spin σ at site a , $n_{a\sigma} = c_{a\sigma}^\dagger c_{a\sigma}$, and $n_a = \sum_\sigma n_{a\sigma}$. Indices $a = 1, 3$ denote the axial O(4) sites and $a = 2$ is the chain Cu(1) site. The hopping matrix element is $t_{ab} = t$ between the O(4) and Cu(1) sites and $t_{ab} = t'$ for the effective hopping matrix element between the

O(4) sites. In the absence of disorder, the site energies can be parameterized by a single parameter ϵ_0 : $\epsilon_{1,3} = \epsilon_0$ and $\epsilon_2 = 0$.

Second, the cluster has two phonon modes corresponding to displacements in the z -direction (the cluster axis) that do not change the center of mass. These bare modes are assumed to be harmonic. If the spring constants between both Cu(1)-O(4) bonds and the two O(4) masses are equal, parity is a good quantum number. Consequently, one mode is even and the other is odd under inversion, where the symmetric phonon mode is Raman active and the antisymmetric one is infrared active. These are described by boson operators a_R and a_{IR} with bare frequencies ω_R and ω_{IR} , respectively. In terms of these operators, the phonon part of the Hamiltonian is

$$H_{ph} = \hbar\omega_{IR}a_{IR}^\dagger a_{IR} + \hbar\omega_R a_R^\dagger a_R. \quad (4)$$

It is useful to express the site coordinates in terms of the above normal modes. Let the site coordinates, r_a , be measured relative to their average positions $r_a^{(0)}$: $r_a = r_a^{(0)} + z_a$. Then the normal modes, defined as $u_{IR} = \sqrt{\hbar/2M_1\omega_{IR}}(a_{IR} + a_{IR}^\dagger)$ and $u_R = \sqrt{\hbar/2M_1\omega_R}(a_R + a_R^\dagger)$, are given by $u_{IR} = (z_1 - 2z_2 + z_3)/\sqrt{3}$ and $u_R = (z_1 - z_3)/\sqrt{2}$, where we have taken the ratio of the effective copper to oxygen masses $M_2/M_1 = 4$.

Third, we consider linear molecular-crystal type interaction between electron and phonon degrees of freedom. In accordance with inversion symmetry, this can be written as

$$h_{el-ph} = \gamma_{IR}(a_{IR} + a_{IR}^\dagger)(n_3 - n_1) + \gamma_R(a_R + a_R^\dagger)(n_1 + n_3 - s_0), \quad (5)$$

where γ_{IR} and γ_R are the respective coupling constants. The parameters s_0 is chosen to avoid any artificial shrinkage of the cluster, thus allowing the use of reduced basis set.

The physics of the above model was determined in Ref. [13] by numerical exact diagonalization. It was found that sufficiently large values of γ_{IR} dynamically generate a new length scale, δl associated with a double-well structure in the infrared coordinate. In this regime, the motion of the lattice is strongly correlated with the hole motion, corresponding to polaron formation and new time scales describing polaron tunneling are generated. Furthermore, as the system's parameters change from the weak-coupling to the strong-coupling regime, the energy of the Raman active states show pronounced minima in the intermediate regime, whereas the energy of the infrared-active states decrease monotonically. The location of the minima is close to the value of λ_{IR} where the double-well structure in bond-length distribution begins to develop, and the dynamics of the system becomes highly nonlinear. One characteristic signature of the highly nonlinear dynamics is the appearance of a very small energy scale $\hbar\omega_T$ corresponding to the polaron

tunneling energy and defined as the energy difference between the ground state and the first excited state.

Several structural and spectroscopic consequences of this model, as well as effects of disorder, and differences between absorption and fluorescence, have been investigated [12,13]. Quite generally, the coupled lattice-excitation issues faced in the cluster model are very similar to those for molecular eximers of current interest in conjugated polymer photophysics [14]. Here we briefly focus on just one issue, namely energy-resolved structure factors [13].

Unlike optical probes, neutron scattering is in principle able to measure dynamic structure factors as a function of momentum transfer. It can be written in the form

$$S(q, \omega) = \sum_{ab} v_{ab} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \langle e^{-iqr_a(0)} e^{iqr_b(t)} \rangle, \quad (6)$$

where we have included cross-section coefficients v_{ab} , determined by the scattering lengths of individual nuclei. $S(q, \omega)$ for our cluster is a sum of delta functions in ω at the same frequencies as the infrared or Raman lines; the intensity of each lines varies with q (the momentum transfer along the cluster axis).

We consider the intermediate strengths of the electron-phonon coupling constants that form the most interesting region and that seems also to be a physically relevant one [12]. The above model is solved by exact diagonalization, and the dynamic structure factors and their Fourier transforms are computed exactly numerically. The parameters in H_{el} are taken as $\epsilon_0 = 0.614$ eV, $t = -0.634$ eV, $t' = t/10$, and $U = 4.44$ eV, which are representative values for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [12]. For bare phonon energies, we choose $\hbar\omega_{IR} = 59.3$ meV and $\hbar\omega_R = 71.5$ meV. We fix $s_0 = 1.17$, which is satisfactory for the electron-phonon coupling constants $\gamma_{IR} = 0.155$ eV and $\gamma_R = 0.260$ eV.

Let us now demonstrate the usefulness of energy-resolved correlation functions in probing the physics at the characteristic time scales of our system and detecting dynamic length scales [13]. In Fig. 3, we show three structure factors, $S(r, \omega = 0)$, $\int_0^{\omega_T} d\omega S(r, \omega)$, and $S(r, t = 0)$, as a function of distance r . It is evident from these examples that the usual elastic structure factor contains no clear signature of the polaronic bond-length splitting, that the instantaneous structure factor (pair-distribution function) is barely able to resolve the splitting, and that $\int_0^{\omega_T} d\omega S(r, \omega)$ shows a pronounced double-peak structure. The difference is resolving power between the pair-distribution function and the partial-frequency sums stems from the fact that the partial-frequency sum emphasizes only the fluctuations at ω_T , whereas $S(r, t = 0)$ includes large quantum fluctuations. This difference becomes crucial when the bond-length splitting is small. Note that the ratio of the copper to oxygen masses deviates from the optimal value in the sense that the relative resolving power of $\int_0^{\omega_T} d\omega S(r, \omega)$ is not the best as compared to $S(r, t = 0)$, although it is

Fig. 3. The dynamic structure factors, (a) $S(r, \omega = 0)$, (b) $\int_0^\omega d\omega S(r, \omega)$, and (c) $S(r, t = 0)$ (in units of $\text{\AA}^{-1}$) as a function of distance r . For the chosen parameters $\delta\ell = 0.2 \text{ \AA}$ and we have used $\ell_0 = 1.87 \text{ \AA}$ for the average copper-oxygen bond length.

always better. Advances in local structural analysis techniques (especially pair-distribution function neutron scattering) make these kind of nonlinear-nonadiabatic considerations increasingly relevant to meaningful interpretation of data. Some of the many timescales intrinsic to this dynamic polaron are discussed in Ref. [15] in terms of a memory function approximation.

5. Quantum Lattice Fluctuations: Breathers in a Nonlinear Lattice

As a final example of the importance of quantum fluctuations, we consider here recent progress in our understanding of "breather" excitations, i.e., bound states of linear, e.g., phonon-like, excitations. These spatially correlated, time-periodic nonlinear excitations are important for transport and thermodynamic properties in many (especially low-d) materials; their possible role in photodecay processes in conjugated polymers has been discussed [16] and is likely to become central in the developing era of ultrafast time-resolved spectroscopy. Multiscale, nonadiabatic, quantum lattice considerations are unavoidable here. Studies of breathers in full Holstein-Hubbard and Peierls-Hubbard chains are in progress and will be reported elsewhere [17]. Here we briefly summarize a simpler but already rich system, namely a quantum anharmonic chain, described by the Hamiltonian [18]

$$H = \hbar\Omega \sum_n \left[\frac{\hat{p}_n^2}{2} + \frac{\eta}{2} (\hat{\phi}_n - \hat{\phi}_{n+1})^2 + w\hat{\phi}_n^2 + v\hat{\phi}_n^4 \right], \quad (7)$$

with periodic boundary conditions, and $\hat{p}_n$ and $\hat{\phi}_n$ being dimensionless canonical lattice momentum and displacement

operators. $[\hat{\phi}_m, \hat{p}_n] = i\delta_{mn}$. The coefficient $\hbar\Omega$ sets the scale of energy, whereas η , w , and v are dimensionless parameters. The first two terms describe a standard harmonic Debye lattice, while the second two terms for $w, v \geq 0$ describe a single-well ϕ^4 nonlinearity, which corresponds to the Taylor expansion of either a local nonlinear interaction due to anharmonicity or an effective lattice interaction arising from, e.g., electron-lattice coupling. Other nonlinear Hamiltonians can be treated by the same methods described below and can be expected to contain varieties of breathers. However, the simple form (7) isolates the breather without, e.g., complications of multiple degenerated ground states. Most importantly, the model (7) provides a clear example of the interplay of "nonintegrability" and lattice "discreteness" which are central to our current understanding of stability conditions for "breathers" [18].

There are two limiting cases for which the physics of the model becomes transparent. First, in the absence of nonlinearity ($v = 0$), the model is trivially solvable. The linear coupling between nearest-neighbor oscillators in Eq. (7) results in spatially extended Bloch-wave states of phonons. The w term acts merely as an adjustable factor controlling the dispersion of phonon bands and will be kept small throughout this study. Second, for $v(\sim 1) \gg \eta$, the ϕ^4 term plays the dominant role. However, we can again qualitatively understand many features of the system, including the appearance of breathers. The nearest-neighbor interaction governed by η will cause the local "Einstein" modes to become hybridized creating narrow continua of phonon states at each local vibrational energy. The ϕ^4 term produces a local repulsive interaction between two or more quanta if they are located at the same site. This interaction therefore leads to bound multiphonon states, breathers, that are split upwards from each multiphonon continuum. These states are the simplest form of breathers we expect to find in molecular systems, i.e., whenever local nonlinear vibrations are weakly coupled to neighboring ones. Below, we consider systems with $\eta \sim v \sim 1$, which are more interesting because of their relevance to many strongly interacting solid-state systems, such as quasi-one-dimensional polymers. In this case, the nearest-neighbor Debye coupling will compete with the ϕ^4 nonlinearity (v) to determine the spatial extension of eigenstates in the system. The main physical effects of the ϕ^4 term are: (i) opening finite gaps in the many-body excitation spectrum, which offers the possibility of bound states within the gaps; and (ii) suppression of the effective linear coupling facilitating the dynamic localization of certain eigenstates.

We study this problem [18] by numerical exact diagonalization using the Einstein phonon basis, where the only physical approximation is the truncation of the infinite Hilbert space. This restricts our numerical simulations to a parameter region where the nonlinearity is not too large. We adopt a modified Davidson method to perform the exact diagonalization for the large sparse matrix of the system Hamiltonian, and then a projective Lanczos method to calculate various correlation functions [18].

The low-lying eigenspectra for 4- and 8-site nonlinear chains with representative parameter sets are shown in Fig. 4. Several characteristic features can be noted: First, as anticipated above, there are finite gaps opened due to the effect of the nonlinearity v . Second, states which originally belong to the same band in the linear Debye or Einstein lattice now split into several bands. While the nonlinearity does not allow the ordering of these bands in terms of bare phonons of the linear system, one can still roughly distinguish different bands by the bare phonon number distribution function [18]. In contrast to the Debye lattice, the ground state is isolated with a finite gap to the excited eigenstates. The first band above the ground state is mainly formed from one phonon states. There are several different kinds of higher excited bands of states, including ones with small but finite bandwidths. The emergence of these isolated bands can be readily interpreted as the existence of particle-like states, where the bandwidth is a measure of the inverse particle mass. They can also be viewed as bound phonon states. We now argue that these narrow, isolated bands of states are quantum breathers.

Fig. 4. Eigenspectrum of the nonlinear system: (a) 4-site chain with the phonon basis truncated at 17 phonons per site (i.e., $\mathcal{M}_{ph} = 18$; 65,536 states), $\eta = 0.5$, $w = 0.2$, $v = 2.0$; (b) 8-site chain with $\mathcal{M}_{ph} = 6$ (1,679,616 states), $\eta = 5$, $w = 0.2$, $v = 0.56$. q_α labels the irreducible representation in the translation group. The dispersion is symmetric in q_α and only eigenstates with $q_\alpha \geq 0$ are shown. The solid circles denote breather states. Other states are plotted as open diamonds.

To identify breathers in the quantum excitation spectrum, we establish their main characteristics by examining key correlation functions. These functions are not only important for diagnostic purposes, but are also relevant to many measurable quantities. One characteristic of the classical breather is spatial localization of the envelope. To measure the corresponding spatial correlation of the displacements at sites separated by n lattice spacings in the translationally invariant quantum case, we examine the correlation function

$$f_\alpha(n - n', t - t') = \langle \alpha | \hat{\phi}_{n'}(t') \hat{\phi}_n(t) | \alpha \rangle, \quad (8)$$

where $|\alpha\rangle$ is an eigenstate of the system with crystal momentum q_α and energy ϵ_α . For the linear system, these correlation functions are readily computed and they in general have multiple spatial and temporal Fourier components reflecting the system's phonon modes propagating with various phase velocities. However, in a nonlinear system, multiphonon bound states can appear. The instantaneous spatial correlation function $f_\alpha(n, 0)$ of a typical state in the isolated bands is [18] localized at $n = 0$ and exhibits the particle-like nature of these states, a key feature of a breather. In this strongly nonlinear regime, the breathers have a small coherence length ξ (on the order of a lattice constant). The other states form a "continuum" of extended multiphonon states which have significant weight even at large n .

Because of the translational symmetry (i.e., breather band formation) through quantum tunneling, time-dependent correlation functions do *not* readily distinguish breathers from anharmonic phonons—both show complex multifrequency characteristics [18]. However, quantum breathers do exhibit distinctive experimentally observable signatures. One example is the density-density correlation function $S(r, t) = (1/N) \int dr' \langle \hat{\rho}(r', 0) \hat{\rho}(r' + r, t) \rangle$, where $\hat{\rho}(r, t) = \sum_n \delta(r - na_0 - \ell \hat{\phi}_n(t))$ is the density operator, a_0 is the lattice constant, N is the number of lattice sites, and $\ell = (\hbar/M\Omega)^{1/2}$. The qualitative behavior of $S(r, t)$ is sensitive to the ratio r/ξ . In principle, these correlations can be probed by neutron scattering, which directly measures the dynamic structure factor $S(q, \omega)$ (the spatial and temporal Fourier transform of $S(r, t)$), given at zero temperature by

$$S(q, \omega) = \sum_\alpha \delta(\hbar\omega - \epsilon_\alpha + \epsilon_0) \int dr e^{-iqr} \int dr' \frac{1}{N} \langle 0 | \hat{\rho}(r', 0) | \alpha \rangle \langle \alpha | \hat{\rho}(r' + r, 0) | 0 \rangle, \quad (9)$$

where $|0\rangle$ is the ground state. In the linear case, one would see a response in $S(q, \omega)$ which traces each multiphonon band dispersion, falling off exponentially in q (i.e., the quantum Debye-Waller factor) and decreasing algebraically with ω , with regular spacing in ω . The result for the nonlinear 4-site system of Fig. 4(a) is illustrated in Fig. 5. The elastic response of the ground state at $\omega = 0$ has now gained an exponentially decaying q -dependence which is different from the harmonic Debye-Waller factor. We also note that in this zero temperature calculation, there is no zero-frequency contribution from the breathers. In addition to the expected large low-energy contributions from the ground state and the first phonon band, breather excitations are the dominant contribution, whereas those contributions from the extended multiphonon "continua" are almost negligible. The sum rule, $\int d\omega \omega S(q, \omega) = \Omega q^2 \ell^2 / 2$, implies that the quenching of the extended-state contribution is consistent with breathers forming as bound states of nearby phonons and is similar to the transfer mechanism of the optical oscillator strength to local modes in the presence of electronic bound states [19]. The center of the response is shifted to higher q for

Fig. 5. The dynamic structure factor $S(q, \omega)$ of the system in Fig. 4(a) at zero temperature and $\ell = a_0/10$. Note that the equal-height δ -peaks of $S(q, \omega)$ at $q = 0$ are not shown. The delta function peaks along the ω -axis are broadened by a narrow Lorentzian.

higher breather bands, consistent with the fact that higher lying breathers (binding more phonons) are narrower in the classical limit [16]. Another clear feature of this nonlinear system revealed by $S(q, \omega)$ is that the breather bands are irregularly spaced.

5. Summary

The examples above, although simple model systems, demonstrate the complexity of coupled spin-charge-lattice effects which we must learn to understand and control in complex electronic materials. This is true of inorganic materials with complex unit cells, as in perovskite oxides studied for, e.g., ferroelectricity, high-temperature superconductivity, or colossal magnetoresistance. It is equally true of the organic materials now pursued for communication, display, storage, sensing, etc., technologies—the coupled degrees-of-freedom are critical science issues for exciting areas such as inorganic-organic interfaces and molecularly engineered materials.

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