FERROELECTRIC PHASE TRANSITIONS IN A LATTICE PSEUDO-JAHN-TELLER MODEL

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Abstract A lattice generalization of the $(b_{1u} \oplus b_{2g}) \otimes b_{3u}$ pseudo-Jahn-Teller model is analyzed within mean-field theory. Ferroelectric or antiferroelectric ground states are found for sufficiently large pseudo-Jahn-Teller coupling.

Introduction

Inspired by the family of fullerene-based polymeric structures synthesized [1, 2], a model describing vibronic effects in a linear chain of molecules is introduced and analyzed within mean-field theory. The zero-temperature phase diagrams at carrier concentrations $n = 1$ and 2 are presented for this model. Only a local $(b_{1u} \oplus b_{2g}) \otimes b_{3u}$ pseudo-Jahn-Teller interaction is considered here; spin and charge fluctuation effects are ignored.

The local symmetry of the molecule is taken to be $D_{2h}$ for simplicity; the set of $b$-representations transform as components of a vector. The electronic structure of the molecule is taken to have a $b_{1u}$ level as the HOMO and a $b_{2g}$ level as the LUMO. A distortion of $b_{3u}$ symmetry will vibronically couple these levels. For a molecule with some ionic bonding character, such a $b_{3u}$ distortion produces an electric dipole moment in proportion to the displacement [3]. It is the ordering of these local dipole moments that is the concern of this work.
1. THE HAMILTONIAN

The Hamiltonian is given by

\[ H = H_0 + H_{PJT} + H_{elast} \] (1.1)

where

\[ H_0 = -t \sum_n (c_{1,n}^\dagger c_{1,n+1} + c_{2,n}^\dagger c_{2,n+1} + \text{h.c.}) + \sum_n \Delta c_{2,n}^\dagger c_{2,n} \] (1.2)

where \( n \) runs over molecule sites, \( c_{1,n}^\dagger \) (\( c_{1,n} \)) creates (annihilates) an electron in orbital \( b_{1u} \) at site \( n \), \( c_{2,n}^\dagger \) (\( c_{2,n} \)) creates (annihilates) an electron in orbital \( b_{2g} \) at site \( n \), and \( \Delta \) is the energy spacing between the \( b_{1u} \) and \( b_{2g} \) orbitals. The hopping matrix is taken to be diagonal in orbital type and spin, and the spin indices are suppressed for clarity.

The pseudo-Jahn-Teller Hamiltonian on the \( n \)th molecular site is

\[ H_{PJT} = -g \sum_n (c_{1,n}^\dagger c_{2,n} Q_n + \text{h.c.}) \] (1.3)

where \( g \) is the pseudo-Jahn-Teller coupling strength, and \( Q_n \) is a displacement of \( b_{3u} \) symmetry on the \( n \)th molecule. The magnitude of the induced local electric dipole is proportional to \( Q_n \). Hence, a ferrodis- torrhetic state is equated with a ferroelectric one.

\( H_{elast} \) is the elastic energy for the molecular displacements.

\[ H_{elast} = \frac{\kappa}{2} \sum_n Q_n^2 \] (1.4)

The Hamiltonian can be written in \( k \)-space as

\[ H = \sum_{\alpha,k} \epsilon_{\alpha}(k) c_{\alpha,k}^\dagger c_{\alpha,k} - \frac{g \Delta}{\sqrt{N}} \sum_{k,q} (c_{1,k+q}^\dagger c_{2,k} Q_q + \text{h.c.}) + \frac{\kappa}{2} \sum_q |Q_q|^2 \] (1.5)

where \( \epsilon_g(k) = \Delta - 2t \cos k \) and \( \epsilon_u(k) = -2t \cos k \).

2. MEAN FIELD THEORY

With a single mode of distortion given by a non-vanishing \( Q_q \), \( H \) can be diagonalized with a canonical transformation so that

\[ H = \sum_k (E_{k+} n_{k+} + E_{k-} n_{k-}) + \frac{\kappa}{2} |Q_q|^2 \] (1.6)

where

\[ E_{k\pm} = \frac{1}{2} (\epsilon_u(k) + \epsilon_g(k + q)) \pm \frac{1}{2} \sqrt{\left[ (\epsilon_g(k + q) - \epsilon_u(k))^2 + \frac{4g^2}{N} |Q_q|^2 \right]} \] (1.7)
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and $n_{k\pm}$ are the usual occupation number operators of the vibronic quasi-particles.

The ground state energy of a chain with $n$ carriers ($0 \leq n \leq 2$) per molecule on average is obtained by fractionally filling the lowest energy vibronic band. In the continuum limit,

$$E(Q_q) = \frac{N}{\pi} \int_{-\pi n/2}^{\pi n/2} dk \, E_{k-} + \frac{\kappa}{2} |Q_q|^2$$  \hspace{1cm} (1.8)

Minimizing $E(Q_q)$ with respect to the distortion gives the mean-field equation to determine the magnitude of $Q_q$.

$$\frac{\pi \kappa}{2 g^2} = \int_{-\pi n/2}^{\pi n/2} dk \, \frac{1}{\sqrt{4Q_q^2 + (\Delta + 4t \sin q/2 \sin(k + q/2))^2}}$$  \hspace{1cm} (1.9)

For sufficiently small coupling, this equation can not be satisfied. There is a $q$-dependent critical coupling strength $g_c$ given by

$$g_c^2(q) = \frac{\frac{\pi \kappa \Delta}{2}}{\int_{-\pi n/2}^{\pi n/2} dk \, \frac{1}{1 + u \sin q/2 \sin(k + q/2)}}$$  \hspace{1cm} (1.10)

where $u = \frac{4t}{\Delta}$. For values of $g$ above $g_c(q)$, a mean-field distortion of wavenumber $q$ sets in; for values of $g$ below $g_c(q)$, there is no such distortion.

3. THE PHASE DIAGRAM

For the case of an average occupancy of one carrier per molecule, the ground state is found to have a $q = 0$ distortion for $g > g_0 (= \sqrt{\frac{\pi \Delta}{2}})$, consequently breaking inversion symmetry of the chain. The phase diagram is pictured in Fig. 1.

For the case of two carriers per molecule, the ground state has a $q = \pi$ distortion when

$$g^2 > \frac{g_0^2}{2} \sqrt{1 - u^2}$$  \hspace{1cm} (1.11)

The results are summarized in Fig. 2.

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Figure 1  Zero-temperature phase diagram for $n = 1$.

Figure 2  Zero-temperature phase diagram for $n = 2$.

References

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