Exact numerical diagonalization of one-dimensional interacting electrons nonadiabatically coupled to phonons

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We study the role of non-adiabatic Holstein electron-phonon coupling on the neutral-ionic phase transition of charge transfer crystals which can be tuned from continuous to discontinuous, using exact numerical diagonalization. The variation of electronic properties through the transition is smoothed by nonadiabaticity. Lattice properties are strongly affected, and we observe both squeezing and antisqueezing, depending on details of the adiabatic potentials, and identify the quantum uncertainty of the phonons as the most sensitive measure of nonadiabaticity. The adiabatic limit is regular for a continuous transition but turns out completely inadequate near a discontinuous transition. The relevance of coherent state approaches is assessed critically.

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1Present Address
The adiabatic approximation is one of the most frequently used approximation schemes in many-particle physics, especially when applied to electron-phonon coupling. Following Born and Oppenheimer (BO), one solves the electronic Hamiltonian for fixed nuclear coordinates in all possible configurations $q$. The eigenvalues $E_n(q)$ generate the adiabatic potential which determines the phonon dynamics. The associated wave function is a product of the electronic and phonon functions. The anharmonicity of $E_n(q)$ makes this scheme rather cumbersome, and a more practical further approximation is obtained by expanding to second order about the equilibrium [Herzberg-Teller (HT) approximation or, in a more solid state language, mean-field theory augmented by Gaussian fluctuations].

The usual justification of the BO approximation is that due to the mass difference of electrons and ions, the bare energy scales, Fermi energy ($E_F$) and phonon frequency ($\omega$), are well separated, with $E_F \gg \omega$. However, important electron-electron interactions often produce renormalized low-energy excitations (charge-transfer, spin-exchange, etc.) whose frequencies may be comparable to $\omega$. Also, the polaronic mass enhancement may give the electrons a mass a sizable fraction of the ion mass. Moreover, structural phase transitions strongly mix electrons and phonons. These effects are particularly prominent in one dimension (1D) where the electron-phonon interaction drives the Peierls instability and electron-electron interactions are strong due to the narrow bands found in many materials. Is a description based on a product wavefunction, implying decoupling of the different degrees of freedom, still justified then?

That the adiabatic approximation could fail in 1D was suggested by renormalization group arguments where the antiadiabatic ($\omega \to \infty$) limit was identified as the attractive fixed point, and Quantum Monte Carlo provided some qualitative confirmation. At low $\omega$, however, the equations became uncontrollable and a reliable description could only be built on the adiabatic limit ($\omega \to 0$). Moreover, attention was directed only towards the stability of dimerized or other symmetry-broken ground states.
Another method uses variational one- and two-phonon coherent states to generate a lattice displacement and soften the phonon frequency, and thereby increase the quantum lattice fluctuations \[7\]. However, the product structure of the wave function is maintained. Moreover, the renormalized phonons remain harmonic and, in this sense, one has the antiadiabatic limit of the HT approximation. Despite its current popularity, the validity of this method has not been assessed critically. Quite detailed fully nonadiabatic (NA) studies were only possible on extremely small systems. Several groups could solve two-electron dimers \[8\], or a single polaron on a longer chain \[9\], or three spinless electrons on six sites \[10\]. To establish their relevance for a correlated many-particle system of finite size, a more general framework is required.

What is missing to date is an application of the powerful exact numerical diagonalization techniques which, despite their limitation to finite clusters, have provided so much insight into the physics of low-dimensional correlated fermions \[11\], to interacting electrons with nonadiabatic electron-phonon coupling (adiabatic coupling was frequently considered). Here we develop such a real-space NA diagonalization technique, attempting to provide the framework called for above, to identify situations and properties where the adiabatic approximation breaks down in 1D, and to critically evaluate the quality of the variational method there \[7\].

We have chosen as a toy problem a standard model \[12\] for the 1D Neutral-Ionic transition (NIT) observed in 1D mixed-stack donor–acceptor (DA) compounds such as TTF-Chloranil \[13\]. Our Hamiltonian is

\[
H_1 = -t \sum_{i,s} (c_{i,s}^{\dagger}c_{i+1,s} + H.c.) + U \sum_i n_{i,\uparrow}n_{i,\downarrow} - \frac{\Delta}{2} \sum_i (-1)^i n_i , \quad (1)
\]

\[
H_2 = \frac{1}{2} \sum_i \left( P_i^2 + \omega^2 Q_i^2 \right) \quad \rightarrow \quad \frac{1}{2} \left( P^2 + \omega^2 Q^2 \right) , \quad (2)
\]

\[
H_{12} = g \sqrt{\frac{\omega}{N}} \sum_i Q_i n_i \quad \rightarrow \quad g \sqrt{\frac{\omega}{N}} Q \sum_i (-1)^i n_i . \quad (3)
\]

c_{i,s}^{\dagger}$ creates an electron with spin $s$ at site $i$ which can hop with a matrix element $t$. $U$ is
the on-site repulsion and $\Delta$ models the energy difference between D and A sites, but more complex interactions are possible. $H_2$ describes local phonon modes with coordinates $Q_i$, momenta $P_i$, and frequency $\omega$. There is a local, Holstein-type coupling to the electrons with coupling constant $g$. The $N$-site lattice is half-filled. Neutral D and A sites are doubly occupied and empty, respectively. Double ionization of sites is forbidden in the $\Delta \to -\infty$, $U \to \infty$ limit; in this limit the only relevant parameter in (1) is $\Delta + U$, the charge transfer energy between adjacent sites [12].

For small ($\Delta + U$) the ground state is characterized by small charge transfer from D to A, i.e. by small ionicity $\rho = 1 + N^{-1} \sum_i (-1)^i n_i \sim 0$. By increasing ($\Delta + U$) the system is driven to an ionic phase with approximately uniform occupation of D and A sites ($\rho \sim 1$). No symmetry is broken at the crossover, and the NIT can be either continuous or discontinuous. Adiabatically [12], the NIT is governed by the strength of electron-phonon coupling, as measured by the small polaron binding energy $\varepsilon_{sp} = g^2/\omega$. For large $\varepsilon_{sp}$ the NIT is discontinuous; by decreasing $\varepsilon_{sp}$ it crosses a critical point and becomes continuous. When discontinuous, it is due to an electronic level crossing (two-well transition); when continuous, the level crossing is avoided, and there is a simple crossover (single-well transition).

We limit ourselves to the $q = 2k_F = \pi$-mode (in the extended zone representation) [12], and the corresponding forms of $H_2$ and $H_{12}$ are indicated in Eqs. (2) and (3). Other modes are not expected to contribute in any significant manner because (i) the Peierls divergence in this commensurate system singles out the $2k_F = \pi$-mode; (ii) it is further enhanced in half-filled bands due to Umklapp scattering; (iii) the external potential $\Delta$ generated by the donor-acceptor alternation with the same wavevector, quenches the phonons into this preselected mode. In other words, the NIT involves relaxation of just this mode - adiabatically the corresponding coordinate is proportional to the order parameter $\rho$- and a comparison of exact and adiabatic results obtained in this approximation gives important
information on NA effects near a structural phase transition. In general, however, this wavevector is selected dynamically; this may renormalize various properties and has to be critically examined.

The Hilbert space of a phonon is of infinite dimension. We truncate the basis by adopting a convergence criterion on the energies of the low-lying states. The number of phonons ($n_{\text{max}}$) required for convergence strongly depends on the phonon representation used. An initial attempt to use a Bargmann representation for the reference phonons was limited by the large $n_{\text{max}}$ needed to generate the adiabatic lattice displacement in the neutral phase (reference phonons are defined with respect to the $\rho = 1$ state) \cite{14}. In order to separate the adiabatic contribution we proposed a two step procedure \cite{15}. In the first step, we generate a set of adiabatic HT basis functions. We determine from an adiabatic diagonalization the equilibrium position $Q_0$, and softened frequency $\Omega = \omega \sqrt{1 - \chi_{\text{el}}(\pi)\varepsilon_{\text{sp}}}$ of the HT harmonic oscillator ($\chi_{\text{el}}$ is the electronic susceptibility at the mean-field $Q_0$). In a second step, the full Hamiltonian is represented in HT basis, forming a band diagonal symmetric matrix, and diagonalized. The choice of the optimal harmonic adiabatic basis reduces the number of phonon states required for convergence by a factor $\sim 6$ far from the NIT and $\sim 3$ close to the NIT where nonadiabaticity is important. This is an important achievement because the dimension of the NA basis increases as $n_{\text{max}}^m$ when $m$ phonon modes are included. The choice of the HT basis is critical in allowing calculations for larger systems and/or more than one phonon mode.

Calculations have been performed for rings of $N = 4 \ldots 12$ sites on a 32 Mbyte DEC 3000 AXP/400 workstation. We display results only for 10-site rings. In order to keep the curves in the same parameter range the results are given against $\gamma = (\Delta + U - \varepsilon_{\text{sp}})/2$; energies are measured in $\sqrt{2t}$ units. A systematic finite size analysis to the thermodynamic limit will be reported in a future publication. The HT results depend on the phonons only through $\varepsilon_{\text{sp}}$. We present results for two different values of $\varepsilon_{\text{sp}}$. For weak coupling,
$\varepsilon_{sp} = 1.28$, the NIT is continuous in the adiabatic limit, whereas for strong coupling ($\varepsilon_{sp} = 2.56$) it is discontinuous. This is gauged through the $\rho(\gamma)$-curves which in the first case exhibit a continuous increase from $\rho \ll 1$ at $\gamma \leq 0$ to $\rho \sim 1$ at $\gamma \geq 0.5$ while there is a finite jump at $\gamma_c$ in the second case ($\gamma_c \sim 0.2$ has a weak residual dependence on $\varepsilon_{sp}$). In both cases, due to phonon quantum fluctuations, the NA $\rho(\gamma)$ curves are smoother than the HT ones, in agreement with expectation. In particular, within the resolution of our data and for the parameter values used in the figures below, the adiabatically discontinuous transitions seem to become continuous.

A particularly pronounced influence of nonadiabaticity is found in the properties of the phonon subsystem. Figure 1 displays the phonon occupation number in the ground state. The HT ground state is the phonon vacuum. A finite occupation is generated in the vicinity of the NIT by mixing in higher states from the HT solution. This effect is an order of magnitude stronger for the two-well transition. However, in this case the deviations increase with decreasing phonon frequency which is counterintuitive. On the other hand, the adiabatic potentials at the BO level are clearly asymmetric. It is then necessary to discriminate between truly nonadiabatic and (adiabatic) anharmonic effects (the anharmonic oscillator has a $n > 0$ in the ground state). To this end, we have performed adiabatic BO calculations. For the single-well transition, the deviations from HT are very small: not larger than 0.02, and decreasing with $\omega$. For the two-well transition at large frequency the BO and NA curves are similar, but the BO deviations from HT decrease with decreasing $\omega$. Therefore, HT represents the low-frequency limit of adiabatic (BO) models for both single- and two-well transitions (i.e. adiabatic anharmonic effects vanish in the $\omega \to 0$ limit), but the adiabatic limit itself is well-defined only for single-well potential. For two-well transitions the $\omega \to 0$ limit of the true NA system does differ from the adiabatic limit. The point is that the BO approximation is an expansion about a well-defined equilibrium position and cannot be applied consistently to an adiabatic
potential with several degenerate minima. Of course, a Hamiltonian composed of such a potential and a kinetic term can be solved, but it is not guaranteed that it represents an adiabatic approximation to the original electron-phonon problem. In this case, the fully NA calculation is clearly preferrable.

In Fig. 2 we show the fluctuations of the phonon coordinate \( \delta Q^2 \). Since the HT phonon is softened with respect to the bare phonon, the fluctuations of the HT coordinate are larger than those of the reference phonon coordinate. This softening-induced “squeezing” of the phonon states is rather obvious and is included through two-phonon coherent states in Zheng’s approach [7]. From the curves shown in Fig. 2 it turns out however that NA fluctuations can either squeeze or antisqueeze phonon states with respect to HT phonons. Which effect occurs depends on details of the adiabatic potentials and cannot be decided a priori. For the single-well transition, the excited state potential is narrower than the ground state one, and the NA mixing therefore reduces \( \delta Q^2 \). For the two-well transition, the adiabatic potential has a more extreme minimum in the excited than in the ground state, allowing additional excursions of the phonon coordinate and thus increasing \( \delta Q^2 \) with respect to HT. We stress however that the squeezing or antisqueezing shown in Fig. 2 cannot be related to a softening or hardening of the phonons and therefore cannot be transformed away by canonical transformations. In fact \( \delta Q^2 \) is related to a frequency only for the harmonic oscillator, where the coordinate fluctuations are in inverse relation with the momentum fluctuations.

In Fig. 3 we show the behavior of \( \sqrt{\delta P^2 \delta Q^2} \). The ground state of a harmonic oscillator or any coherent phonon state has minimal uncertainty: \( \sqrt{\delta P^2 \delta Q^2} = 1/2 \). Of course, \( \delta P^2 \) peaks in the sense opposite to \( \delta Q^2 \) but importantly, the fully NA \( \sqrt{\delta P^2 \delta Q^2} \) is increased from the coherent state picture by about 10% near the single-well and about 90% near the two-well transition. Even more interesting is the comparison with \( \sqrt{\delta P^2 \delta Q^2} \) obtained in BO: its deviations from the minimum (1/2) value are completely negligible for the single-
well and (with all the *caveats* above) not larger than 10% for the two-well transition. The important implication is that (i) the anharmonicity of the BO potential cannot effectively account for the large incoherence generated by NA fluctuations, and (ii) $\sqrt{\delta P^2 \delta Q^2}$ is a sensitive probe of precisely the NA effects. Therefore, at least for the phonon subsystem, any picture based on coherent phonon states (like the two-phonon squeezed states) is inadequate near a (especially multi-well) phase transition.

Similar results are found when intersite electron-electron interactions are included. Unlike above, data not shown here seem to indicate that for large enough interactions the NA transition remains discontinuous up to some finite critical phonon frequency before turning continuous.

In summary, we have exactly solved a NA electron-phonon problem with real space numerical diagonalization. Important progress was made by using a renormalized adiabatic Herzberg-Teller basis which strongly reduces the number of phonon states required for convergence. In the future, this will allow the treatment of larger systems and/or inclusion of more phonon modes. (i) In agreement with expectation, we find that nonadiabatic electron-phonon coupling smoothes the variation of electronic properties through the Neutral-Ionic transition, and that sizable corrections to the lattice properties are generated there. (ii) We find that nonadiabaticity can either squeeze or antisqueeze phonon states, depending on details of the adiabatic potentials while current applications of coherent states to similar problems only allow for squeezing. (iii) By comparing with Born-Oppenheimer and coherent-state calculations, we identify $\sqrt{\delta P^2 \delta Q^2} - 1/2$ as a quantity particularly sensitive to nonadiabaticity and the concomitant loss of coherence of the phonons while it is insensitive to the anharmonic nature of the adiabatic potential. This loss of coherence is a universal feature of nonadiabaticity and must therefore be important near any structural phase transition, irrespective of its details. The coherent state picture is bound to miss the incoherence generated by the nonadiabatic mixing of electronic
and phonon degrees of freedom. It would be interesting to see if a variational description of such a situation could be achieved by introducing another parameter varying $\delta P^2$ and $\delta Q^2$ independently. (iv) Moreover, fully NA solutions are generally preferrable to an anharmonic Born-Oppenheimer calculation despite the bigger matrices involved. While for single-minimum potentials, they converge against BO as $\omega \to 0$, the NA calculation avoids the consistency problems of BO when several (nearly) degenerate minima emerge in the adiabatic potential.

Some (speculative) predictions can be made about the behaviour of systems which undergo symmetry-breaking structural transitions [2]. Here the lower adiabatic potential will change from single-minimum to a degenerate double minimum at the transition, while the first excited one in general has a narrower single-minimum shape. One will run into the same consistency problems of the BO approximation below that transition as in our two-well case. On the other hand, we expect that the NA coupling to the first electronic excited state will reduce the phonon coordinate fluctuations and therefore produce antisqueezing.

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Figure Captions

**Figure 1:** Phonon occupation number $n$ of the ground state as a function of $\gamma = (\Delta + U - \varepsilon_{sp})/2$. In the adiabatic Herzberg-Teller approximation $n \equiv 0$. Left panel: dash-dotted line: $\omega = 0.125$ dashed line: $\omega = 0.5$, full line: $\omega = 2.0$. Right panel: dashed line: $\omega = 0.5$, full line: $\omega = 1.0$.

**Figure 2:** Fluctuations $\delta Q^2$ of the phonon coordinate. Adiabatically $\delta Q^2 = 1$ in units of the renormalized frequency $\Omega$. Legend as in Fig. 1.

**Figure 3:** Uncertainty of phonon states. Adiabatically $\sqrt{\delta P^2\delta Q^2} = 1/2$. Legend as in Fig. 1.
