Band Structure of the Jahn-Teller Polaron from Quantum Monte Carlo

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A path-integral representation is constructed for the Jahn-Teller polaron (JTP). It leads to a perturbation series that can be summed exactly by the diagrammatic Quantum Monte Carlo technique. The ground-state energy, effective mass, spectrum and density of states of the three-dimensional JTP are calculated exactly on an infinite lattice in the most difficult three-dimensional case. We found that the properties of JTP are very similar to that of the Holstein polaron (HP). JTP is as heavy as HP. It also displays some anomalous properties, again similar to HP. In particular, in the case of dispersionless phonons and low phonon frequency, JTP has a flat spectrum at large momenta and a very distorted density of states.

The simplest JTP is an electron that hops between doubly degenerate $e$ levels and interacts locally with a dispersionless phonon. The model Hamiltonian reads

$$H = H_e + H_{ph} + H_{e-ph},$$

$$H_e = -t \sum_{\langle nn' \rangle} (c_{n1}^\dagger c_{n'1} + c_{n2}^\dagger c_{n'2}),$$

$$H_{ph} = \sum_n \left[ \frac{1}{2M} (\vec{p}_{xn}^2 + \vec{p}_{yn}^2) + \frac{M \omega^2}{2} (x_n^2 + y_n^2) \right],$$

$$H_{e-ph} = -\kappa \sum_n \left[ (c_{n1}^\dagger c_{n2} + c_{n2}^\dagger c_{n1}) x_n + (c_{n1}^\dagger c_{n2}^\dagger - c_{n2}^\dagger c_{n1}) y_n \right].$$

Here $c_{n}^\dagger$ creates an electron on site $n$ on orbital $a$ ($a = 1$ or 2 is the orbital index), $t$ is the intersite hopping matrix element, $(\mathbf{m} \mathbf{u})$ denotes pairs of nearest neighbors; $x_n$ and $y_n$ are the two phonon displacements on the $n$th site, $\vec{p}_{xn}, \vec{p}_{yn} = -i\hbar \partial x_n, \partial y_n$; $M$ is the ionic mass; and $\kappa$ is the interaction parameter with dimensionality of force. The energy of the atomic level is set to zero. The model is parameterized by the phonon frequency $\omega$ and by the dimensionless coupling constant $\lambda = \kappa^2/(2M \omega^2 z t)$ where $z$ is the number of nearest neighbors. For the simple cubic lattice, considered in this work, $z = 6$. Two simplifications are introduced in the model (0)-6. First, the electron hopping is isotropic, and is diagonal in the orbital index. The latter leads to any change of orbital index taking place only when an $x$-phonon is emitted or
coordinates are twisted, always holds. The boundary conditions on the phonon amplitudes with any odd total number of emission and absorption acts. As a result, the off-diagonal in orbital index elements of the polaron density matrix are identically zero. One can show that such matrix elements determine the splitting between the two polaron bands. The conclusion is that in the model (1)-(4), the two polaron bands are degenerate in the whole Brillouin zone, and this is done as follows. Upon the self-multiplication of the electron action. Here $\bar{\tau}$ is the phonon action. Here $\bar{\tau}$ is the phonon action. The invariance implies the invariance of the $x$ and $y$ modes in the sense that the elastic and interaction energies associated with the two modes must be equal. The number of excited phonons are equal too. These general results serve as independent checks of numerical data.

Central in the proposed method is the path-integral representation for the density matrix $\rho$ of the model (1)-(4). For a small imaginary-time interval $\Delta \tau = \beta/\hbar$, where $\beta = (k_B T)^{-1}$ is the inverse temperature and $L \gg 1$, one obtains, up to the first order in $\Delta \tau$:

$$\rho(\Delta \tau) = \{\{r', a'; \{x_n', \{y_n\}\}\}, \{y_n\}\} e^{-\Delta \tau H} \{\{r, a; \{x_n\}, \{y_n\}\}\},$$

$$= [\delta_{rr'} \delta_{aa'} + \Delta \tau \delta_{rr'} \delta_{aa'} x_r + \Delta \tau t \delta_{aa'} \sum_{n'n'} \delta_{rr'} x_{n+n'} - \Delta \tau] e^{A_{ph}^{\Delta \tau}}, (5)$$

$$A_{ph}^{\Delta \tau} = \kappa \Delta \tau y_{\uparrow} (\delta_{a1} - \delta_{a2})$$

$$- \sum_n \left\{ \frac{M}{2\hbar^2 (\Delta \tau)} [(x_n - x'_n)^2 + (y_n - y'_n)^2] + (\Delta \tau) \frac{M \omega^2}{2} (x_n^2 + y_n^2) \right\}, (6)$$

$A_{ph}^{\Delta \tau}$ being the phonon action. Here $\hat{a} = 1, (2)$ when $a = 2, (1)$, i.e. $\hat{a}$ is ‘not’ $a$. The full density matrix is obtained by multiplying $\rho(\Delta \tau)$ by itself $L$ times, introducing integration over the internal coordinates, and taking the $L \to \infty$ limit. In doing so, we do not impose the periodic boundary conditions in imaginary time but rather leave initial $r(0), a(0)$ and final $r(\beta), a(\beta)$ coordinates of the electron arbitrary. [Except that $a(\beta) = a(0)$ always holds.] The boundary conditions on the phonon coordinates are twisted, $x_n(\beta) = x_n - r(\beta) + r(0)(0)$, and the same for $y$, as described in (2). The next step is to integrate over $x_n(\tau)$ and $y_n(\tau)$. This is a Gaussian integration and it can be done analytically. Here one faces an important difference between the two phonon modes. Displacements $y_n(\tau)$ interact with the electron density and do not change the electron coordinates. Therefore, for the oscillators $y_n$, the electron is simply a source of external force, the value and sign of which depend on the position and orbital index of the electron, cf. the second term in Eq. (4). The problem reduces to uncoupled oscillators in a time-dependent external field. The integration over $y_n(\tau)$ can be done by Feynman’s methods (13) to yield the factor $e^{A_y}$ in the density matrix, where

$$A_y[r(\tau), a(\tau)]$$

$$= \kappa^2 \int_0^\beta \int_0^\beta d\tau' d\tau' G(\tau - \tau') [\delta_{a(\tau), a(\tau')} - \delta_{a(\tau), \tilde{a}(\tau')}], (7)$$

$$G(\tau - \tau') = \frac{\hbar}{2M \omega} \left\{ e^{-\hbar \omega |\bar{\tau} - \tau'|} \delta_{r(\tau), r(\tau')} + e^{-\hbar \omega (|\tau| - |\tau'|)} \delta_{r(\tau), r(\tau') + \text{sign}(\tau' - \tau') \Delta \tau} \right\}, (8)$$

is the retarded action induced by the $y$ mode. The second term in the function $G(\tau - \tau')$ involves the net shift of the electron path $\Delta r = r(\beta) - r(0)$ and the sign of the time difference $\text{sign}(\tau' - \tau') = \pm 1$. The simple form (8) of $G$ is valid in the limit $e^{\beta \hbar \omega} \gg 1$ that is assumed henceforth. It is important that $A_y$ is an explicit functional of the electron path and can be calculated straightforwardly once the functions $r(\tau)$ and $a(\tau)$ are specified. Note, that the $y$-mode ‘favors’ the same orbital index throughout the whole electron path and ‘dislikes’ orbital changes.

Unlike the $y$-mode, the $x$-mode changes the orbital index of the electron. It therefore acts like the kinetic energy, but in the ‘orbital space’, compare the last two terms in brackets in Eq. (5). The only complication is that the rate of orbital change is not constant but depends on the local displacement $x_n(\tau)$. Nonetheless, the $x$-mode and kinetic energy can be treated in the same manner, and this is done as follows. Upon the self-multiplication of $\rho(\Delta \tau)$, a variety of terms with different powers of $(\Delta \tau)$ appear. A term with $n$ site changes (‘kinks’) and $m$ orbital changes has the weight

$$(\Delta \tau)^n (\kappa \Delta \tau)^m x_{\tau(\tau_1)}(\tau_1) x_{\tau(\tau_2)}(\tau_2) \cdots x_{\tau(\tau_m)}(\tau_m) \times \exp \left\{- \sum_n \int_0^\beta \left\{ \frac{M \omega^2}{2\hbar^2} + \frac{M \omega^2}{2\hbar^2} x_{\tau(n)}^2(\tau) \right\} d\tau \right\}. (9)$$

Here $\tau_n$ is the time of the $n$th orbital change ($s = 1, \ldots, m$), $r(\tau_n)$ is the electron position at this time, and $x_{\tau(\tau_n)}$ is the $x$-displacement at this site at this time. Integration over $x_n(\tau)$ in (2) can now be performed by introducing fictitious sources, calculating the generating functional and differentiating it $m$ times. For any odd $m$ the result is zero, since the $x$ action is even under the
global sign change \( x_n(\tau) \rightarrow -x_n(\tau) \). (This is the above-
mentioned averaging that leads to the complete degener-
cacy of the two polaron bands.) For even \( m \), the time
moments \( \tau_k \) should be combined in pairs, and each pair
contributes the factor \( \kappa^2 G(\tau_k - \tau_k') \) with \( G \) from Eq. (8).
Because \( G \) is always positive, the \( x \)-mode ‘favors’ a large
number of \( G \)-lines on the electron path, i.e., a large num-
ber of orbital changes. Such a tendency is opposite to
that of the \( y \)-mode. The competition between the two
modes leads to a dynamical balance and to some average
number of orbital changes per unit imaginary time. Note
also that the same function (8) determines both \( x \) and \( y \) contributions to the density matrix, which reflects the
equivalence of the two modes.

Now recall that each term (8) must be still integrated
over all the electron positions and orbital indices, i.e.,
over the time instances of its kinks and orbital changes.
Such an integration is denoted below as \( (dr)^n \) and \( (dr)^m \).
In the \( L \rightarrow \infty \), \( \Delta \tau \rightarrow 0 \) limit this leads to the path-
integral representation of \( \rho \) for JTP:

\[
\rho(\beta) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \int_0^\beta \cdots \int_0^\beta \rho_{nm} W_{nm} d\tau. \tag{10}
\]

One cannot proceed analytically any further. However,
all the integrands are positive-definite, which suggests
simulation of \( \rho \) by Monte Carlo (MC) methods. The
obvious difficulty is that an \textit{infinite series} of integrals
of ever-increasing dimensionality, rather than just one
integral, have to be evaluated. Nonetheless the recently
developed Diagrammatic MC method (13) is capable of
doing such an integration. The method works as follows.
Each \((n, m)\) term in the sum is represented by a diagram
(path) with \( n \) kinks and \( m/2 \) \( G \)-lines, see Fig. 1. The MC
process browses the configuration space by means of the
two elementary subprocesses: (i) inserting and removing
kinks, which changes the dimensionality of integration
by 1 \((n \rightarrow n + 1)\); (ii) attaching and removing \( G \)-lines,
which changes the dimensionality by 2 \((m \rightarrow m + 2)\).
The central idea of the method is the balance equation for the
two subprocesses (13). Let \( N_k \) be the number of kinks of a
given sort, \( N_k \leq n \). Next, let \( R(\tau') \) be the normalized
probability density with which one chooses the position
for the new kink. For example, one may decide that
all the times in the \([0, \beta]\) interval are equivalent, hence
\( R(\tau') = \beta \) is equal to \( \beta \). In the reciprocal removing process,
one may decide that any of the \( N_k + 1 \) existing kinks are
removed with equal probability \((N_k + 1)^{-1}\). The resulting
balance equation reads:

\[
\frac{1}{\beta} W_{nm} P[(n, m) \rightarrow (n + 1, m)] =
\frac{1}{N_k + 1} W_{n+1, m} P[(n + 1, m) \rightarrow (n, m)], \tag{12}
\]

from where the acceptance probabilities \( P \) follow in the
usual manner (14). The main feature to note is that the elements of the phase space associated with the two
sides of the equation have the same measure: \( W_{nm} \) brings
\((dr)^{n+m}\), and \( R(\tau') = 1/\beta \) adds one more \((dr)\) because \( R \)
is a probability density. The measure of the right-hand-side is also \((dr)^{n+m+1}\). That makes both transition probabilities be of the same order, and renders the whole process meaningful. In the case of \( G \)-lines, let \( S(\tau', \tau'') \) be the two-dimensional probability density to attach a new \( G \)-line at times \( \tau' \) and \( \tau'' \). While removing, each of
\( N_G + 1 \) \( G \)-lines may again be chosen with equal probability.
The balance equation reads

\[
S(\tau', \tau'') W_{nm} P[(n, m) \rightarrow (n, m + 2)] =
\frac{1}{N_G + 1} W_{n, m+2} P[(n + 2, m) \rightarrow (n, m)]. \tag{13}
\]

Again, the measures of the phase space elements are the
same because now \( S \) adds \((dr)^2\). A possible choice for \( S \)
is 

\[ S(r', r'') = \left(h\omega/\beta\right) \exp\left(-h\omega|\tau' - \tau''|\right). \]

The MC process that follows the rules (12)-(13) generates a Markov chain of paths distributed in accordance with Eq. (11). On such an ensemble various polaron properties can be measured with the standard Metropolis rules [14].

One physical quantity that can be calculated with this method is the ground state energy of the polaron \( E_0 = \langle -W_{nm}(\partial W_{nm}/\partial \beta) \rangle \) [11,12]. Here we present MC data for two other properties: the effective mass and density of states (DOS). The mass is calculated as the diffusion coefficient of the polaron path, \( m^0_1 = (\beta h^2)^{-1} (\Delta r_x^2) \) [12]. The inverse mass of the three-dimensional JTP is shown in Fig. 2. After the initial weak-coupling growth \( m/m_0 = 1 + \text{const} \cdot \lambda \), a transition to the small polaron state takes place at \( \lambda \lesssim 1.1 - 1.3 \), and after that the mass increases exponentially with coupling. The comparison with the Holstein polaron (HP) shows that both masses behave similarly. The polaron spectrum is calculated with the formula \( E_P - E_0 = -\beta^{-1} \ln(\cos P \Delta r) \) [12], and DOS is obtained by integrating \( E_P \) over the Brillouin zone. The resulting DOS appears to be strongly distorted in the adiabatic regime, \( h\omega = 1.0t \), see Fig. 3. The polaron spectrum is flat in the outer part of the Brillouin zone due to hybridization with dispersionless phonon modes [14], which results in a massive peak in DOS at the top of the band. The van Hove singularities are invisible because they are absorbed by the peak. All these features are very similar to that of the Holstein polaron [12]. The similarity suggests that such peculiar features of the band structure are common to polaron models with local interaction and dispersionless phonons in the adiabatic regime.

In conclusion, we have developed a path-integral representation for the Jahn-Teller polaron and used the Diagrammatic Monte Carlo method to simulate the series expansion for its density matrix. The ground state energy, effective mass, spectrum, and density of states have been calculated with no systematic errors. JTP has been found to be very similar to the Holstein polaron and, therefore, to possess some anomalous properties, in particular a strong distortion of the density of states in the adiabatic regime, \( h\omega \lesssim t \). Such a distortion may be a consequence of the short-range electron-phonon interaction and dispersionless phonon modes.

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[1] A.J. Millis, P.B. Littlewood, and B.I. Shraiman, Phys. Rev. Lett. 74, 5144 (1995).
[2] Guo-meng Zhao et al., Nature 381, 676 (1996).
[3] A.S. Alexandrov and A.M. Bratkovsky, Phys. Rev. Lett. 82, 141 (1999).
[4] P.B. Allen and V. Perebeinos, Phys. Rev. B 60, 10747 (1999).
[5] L. Vasiliiu-Doloc et al., Phys. Rev. Lett. 83 (1999) (to be...
[6] J. Kanamori, J. Appl. Phys. (Suppl.) 31, S14 (1960).
[7] A. Abragam and B. Bleaney, Electron paramagnetic resonance of transition ions (Clarendon Press, 1970).
[8] K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk 136, 621 (1982) [Sov. Phys. Usp. 25, 231 (1982)].
[9] I. G. Lang and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. 43, 1843 (1962); [Sov. Phys. JETP 16, 1301 (1963)]; A. A. Gogolin, Phys. Stat. Sol. B 109, 95 (1982). A. S. Alexandrov, Phys. Rev. B 46, 2838 (1992).
[10] S. Yunoki, A. Moreo, and E. Dagotto, Phys. Rev. Lett. 81, 5612 (1998); S. Yunoki, T. Hotta, and E. Dagotto, cond-mat/9909254; Y. Motome and M. Imada, J. Phys. Soc. Japan 68, 16 (1999).
[11] H. De Raedt and A. Lagendijk, Phys. Rev. Lett. 49, 1522 (1982); Phys. Rev. B 27, 6097 (1983).
[12] P. E. Kornilovitch, Phys. Rev. Lett. 81, 5182 (1998); Phys. Rev. B 60, 3237 (1999).
[13] N. V. Prokof’ev and B. V. Svistunov, Phys. Rev. Lett. 81, 2514 (1998); N. V. Prokof’ev, B. V. Svistunov, and I. S. Tupitsin, Zh. Eksp. Teor. Fiz. 114, 570 (1998) [Sov. Phys. JETP 87, 310 (1998)]; A. S. Mishchenko et al., cond-mat/9910023.
[14] R. P. Feynman, Phys. Rev. 97, 660 (1955); Statistical Mechanics (Benjamin, Reading, 1972).
[15] T. Holstein, Ann. Phys. 8, 325 (1959); ibid p. 343.
[16] N. Metropolis et al., J. Chem. Phys. 21, 1087 (1953).
[17] Y. B. Levinson and E. I. Rashba, Rep. Prog. Phys. 36, 1499 (1973); G. Wellein, H. Röder, and H. Fehske, Phys. Rev. B 53, 9666 (1996); W. Stephan, Phys. Rev. B 54, 8981 (1996).