Polarons with a twist

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We consider a polaron model where molecular rotations are important. Here, the usual hopping between neighboring sites is affected directly by the electron-phonon interaction via a twist-dependent hopping amplitude. This model may be of relevance for electronic transport in complex molecules and polymers with torsional degrees of freedom, such as DNA, as well as in molecular electronics experiments where molecular twist motion is significant. We use a tight-binding representation and find that very different polaronic properties are already exhibited by a two-site model – these are due to the nonlinearity of the restoring force of the twist excitations, and of the electron-phonon interaction in the model. In the adiabatic regime, where electrons move in a low-frequency field of twisting-phonons, the effective splitting of the energy levels increases with coupling strength. The bandwidth in a long chain shows a power-law suppression with coupling, unlike the typical exponential dependence due to linear phonons.

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There has been considerable interest in the study of electronic transport in organic materials. They provide technologically relevant alternatives for new electronic and optical materials, and offer an opportunity to gain deeper understanding of quantum transport processes. Moreover, transport in molecules also constitutes the basis for important biological phenomena, such as photosynthesis and other charge transfer events. Recent developments in the fabrication of high electron mobility systems using organic semiconductors, have further emphasized the need to understand mobile polaronic behavior in complex molecular crystals. In addition, a series of beautiful experiments in the area of molecular electronics have underscored the importance of atomic vibrations in the measured current-voltage characteristics of these systems.

In typical inorganic materials the atomic degrees of freedom (DOF) associated with translation are the most important in electronic transport. In contrast, the twisting DOF (or “librons”) of molecular complexes may also play important roles in organic and molecular solids. In a wide variety of organic linear-chain crystals of stacked molecules, the librons may in fact be essential. For instance, it was found that libron scattering was important in the understanding of conductivity mechanisms in the TTF-TCNQ system, as well as in phthalocyanine-based “molecular metals”. More recently, the conductivity of DNA and constituent base crystals has been studied experimentally and theoretically. Since DNA can be viewed as a “molecular wire”, a one-dimensional twisted chain of stacked base pairs with a somewhat flexible structure, it is likely that parallel rotation of adjacent base pairs will be important in electronic transfer mechanisms. Notice that these modes would have a stronger impact on the electronic overlaps along the chain than other flexural modes. In fact, a variable range hopping theory where the twist angle fluctuations between base pairs are taken into account was used recently to explain the temperature dependence of electrical conductivity along the DNA double helix. Bruinsma et al. have also studied charge migration along DNA based on a model in which large structure fluctuations, including relative rotation between adjacent bases, are considered.

There exist a few models of electron-libron interactions in the literature. Many of them have considered the situation of small rotation angles in a harmonic or nearly harmonic approximation. Although other authors have considered large angle rotations, the molecular kinetic energy term was neglected, and thus the inertial backreaction effects in molecules were not taken into account. Our model considers the possibility of large rotation effects, which are not negligible in systems such as (TTF)$_2$I$_3$, and others with similarly flexible structure. We also include the full kinetics of the molecule in order to include backreaction effects. Our description is fully quantum mechanical and includes strong anharmonic interactions, shown to be essential for polaron self-trapping. From the full solution of a two-site model, we find that in the adiabatic regime, where electrons move in a low frequency field of twisting-phonons, the splitting of the energy levels (and therefore the effective intersite hopping) increases with phonon coupling strength. In the opposite, non-adiabatic regime, the effective hopping constant increases with phonon frequency, but saturates at high values. For a long chain model with local-twists, we find a power-law suppression of the bandwidth, unlike the exponential result for translational polarons. These results arise from the different coupling scheme and the nonlinear twist-polaron restoring force, as we now describe.

The twist polaron model. The on-site interaction of the electron with phonon modes tends to localize the elec-
tron. On the other hand, the molecular transfer (hopping) integral in a given atomic or molecular configuration results in electron delocalization. In an extended system, the hopping integral competes with the phonon interaction, and depending on the relative strengths of the different terms, one obtains a mobile polaron (with a heavier effective mass), or a self-localized polaron. Our model allows for such physical behavior as well. Most importantly, however, the phonon enters here modifying also the hopping integral and is then substantially different to typical models for translation-phonon polarons.

For simplicity, let us first consider a two-site model. The dynamics of the system is described by the Hamiltonian

\begin{equation}
H = -(c_1^+ c_1 + c_2^+ c_2)\varepsilon^* \cos \theta - (t_0 + t_1 \cos \theta)(c_1^+ c_2 + c_2^+ c_1) - \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2} - K \cos \theta ,
\end{equation}

where the first term represents the possible on-site energy modulation due to the molecular rotations with angular DOF \( \theta \), and the \( c_i^+ \) operators describe the two electronic wave functions (“sites”). The second term is the rotation-dependent hopping term. Notice that the molecular rotation would either enhance or suppress electron hopping in this model, depending on whether \( t_1 \) and \( t_0 \) have the same or opposite sign. A microscopic calculation of stacked molecules, such as the base pairs in DNA, or the phthalocyanine stacks, allows one to estimate the effect of molecular twists on the electron hopping or overlap. Recent results for guanosine crystals [19] for example, show clearly that eclipsing of molecules in successive “layers” is essential for substantial electron hopping between them. This twist dependence is introduced in our model via the hopping amplitude \( t_1 \), and then plays the role of a coupling constant. The last two terms in (1) are the relative kinetic energy for the molecules and the interaction potential characterized by the librion restoring ‘force constant’ \( K \). Here, \( \theta = \theta_1 - \theta_2 \), where \( \theta_i \) is the rotation angle of each molecule, and \( I \) is the reduced moment of inertia for the relative rotation of the two adjacent molecules (see inset Fig. 1). An overall rotation of the pair is gapless and neglected. Notice also that the first term in (1) leads to a constant shift of \( K \), which is then implicit in the following discussion. Notice that this model considers nonlinear coupling to the electrons via \( t_1 \), as well as a non-linear restoring force for the relative rotation of this two-molecule stack. On the other hand, the model does not consider the possible mixing of rotation DOF with translation displacements, although this coupling is for the most part small [18]. We believe that our model contains the main physics of polaronic excitations corresponding to the rotation DOF.

In the following, we use the energy unit \( \hbar^2/2I \) for convenience, so that all energy quantities are dimensionless from now on. In order to solve the eigenvalue problem \( H\psi = E\psi \), we use

\begin{equation}
|\psi\rangle = \delta(\theta)c_1^+|0\rangle + \beta(\theta)c_2^+|0\rangle ,
\end{equation}

which yields, from \((H - \varepsilon)|\psi\rangle = 0\), a set of secular equations for \( \delta \) and \( \beta \). Defining \( A = \delta + \beta \), and \( B = \delta - \beta \), we have

\begin{equation}
\begin{aligned}
\left( \frac{\partial^2}{\partial \theta^2} + \varepsilon + t_0 + p \cos \theta \right) A = 0, \\
\left( \frac{\partial^2}{\partial \theta^2} + \varepsilon - t_0 + q \cos \theta \right) B = 0 ,
\end{aligned}
\end{equation}

with \( q = K - t_1 \), and \( p = K + t_1 \). The solutions are periodic Mathieu functions [17] with properties which depend on the values of the coefficients \( p \) and \( q \).

As we will see below, the rotation DOF in the model produce modifications of the electronic hopping. In order to reveal the physics more clearly, we analyze the two-site problem in more detail in the adiabatic and non-adiabatic regimes.

**Non-adiabatic regime.** In the non-adiabatic regime \( K \gg t_0, t_1 \), the electrons move in a field of high frequency twist-phonons. We first neglect fully the hopping terms. We find two degenerate states

\begin{equation}
\psi_1 = \left( \begin{array}{c} \phi_0 \\ 0 \end{array} \right) , \quad \psi_2 = \left( \begin{array}{c} 0 \\ \phi_0 \end{array} \right) ,
\end{equation}

where \( \phi_0 \) is the normalized ground state (with eigenvalue \( \varepsilon_0 \)), solution of the equation

\begin{equation}
\frac{d^2 \phi}{d\theta^2} + (\varepsilon + K \cos \theta) \phi(\theta) = 0 .
\end{equation}

To calculate the first order correction, we take the wave function \( \psi = \alpha\psi_1 + \beta\psi_2 \), so that the secular equation becomes

\begin{equation}
\begin{pmatrix}
\varepsilon_0 - \varepsilon & -(t_0 + t_1') \\
-(t_0 + t_1') & \varepsilon_0 - \varepsilon
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} = 0 ,
\end{equation}

where the renormalized twist-dependent hopping constant is

\begin{equation}
t_1' = t_1 \int \phi_0^* \cos \theta \phi_0 d\theta .
\end{equation}

The eigenvalues are simply \( \varepsilon_{1,2} = \varepsilon_0 \pm |t_0 + t_1'| \), so that the splitting of the two originally degenerate eigenvalues is \( \Delta \varepsilon = 2|t_0 + t_1'| \). It is easy to see from Eq. (4) that \( t_1' \leq t_1 \). Therefore, \( \Delta \varepsilon \leq T \), where \( T = 2t_0 + 2t_1 \) is the hopping constant “without rotation”, i.e. \( \theta = 0 \).

In the regime of large \( K \) (\( K \gg 1 \)), the local twist potential is effectively harmonic and one can write the solution as a superposition of local harmonic oscillators about \( 2m\pi \),

\begin{equation}
\phi_0 = \sum_m \frac{\alpha^{1/2}}{\pi^{1/4}} e^{-\alpha^2(\theta - 2m\pi)^2/2} ,
\end{equation}

where \( m \) is an integer. The secular equations now become

\begin{equation}
\begin{aligned}
\left( \frac{\partial^2}{\partial \theta^2} + \varepsilon + t_0 + p\cos \theta \right) A = 0, \\
\left( \frac{\partial^2}{\partial \theta^2} + \varepsilon - t_0 + q\cos \theta \right) B = 0 ,
\end{aligned}
\end{equation}

with \( q = K - t_1 \), and \( p = K + t_1 \). The solutions are periodic Mathieu functions [17] with properties which depend on the values of the coefficients \( p \) and \( q \).
where \( \alpha^4 = K/2 \), and the eigenvalue is \( \varepsilon_0 = -K + \alpha^2 \).

Correspondingly,
\[
t_1' = t_1 e^{-1/4\alpha^2} \simeq t_1 \left(1 - \frac{1}{4\alpha^2}\right),
\]
and \( \Delta \varepsilon = 2t_0 + 2t_1(1 - 1/4\alpha^2) \lesssim T \), with \( \Delta \varepsilon \) approaching \( T \) in the large \( K \) limit. In this case, the molecule is weakly oscillating about \( \theta = 0 \) (mod \( 2\pi \)), with a relatively minor impact on the electron hopping. Notice that the resulting “bandwidth narrowing” is similar in form to the result of a two-site vibrational polaron. There, the effective bandwidth in the non-adiabatic regime is \( J = J e^{-\gamma^2/2} \), where \( J \) is the original bandwidth and \( \gamma \) is the electron-phonon coupling constant. Notice however the different role that \( K \) plays here, and that the bandwidth is only weakly suppressed in this case.

When \( K \) is small \( (1 \gg K \gg t_0, t_1) \), the ground state function can be written as
\[
\phi_0(\theta) \simeq \frac{1}{\sqrt{2\pi(1 + K^2/2)}}(1 + K \cos \theta),
\]
and the eigenvalue is \( \varepsilon_0 = -\frac{1}{2}K^2 \). We find that \( t_1' = t_1 \frac{K}{1 + K^2/2} \simeq Kt_1 \), and \( \Delta \varepsilon = 2t_0 + 2Kt_1 \ll T \). Notice that in this limit of soft restoring force, the molecules are nearly uniformly rotating at all angles, and strongly suppress the electron intersite hopping.

We see that with increasing \( K \), the renormalized twist-dependent hopping constant \( t_1' \) increases and saturates to \( t_1 \), as shown schematically in Fig. 1. We should emphasize that one can view the resulting \( \Delta \varepsilon \) as akin to a bandwidth in the long chain limit. These results then indicate that the twisting DOF strongly prevent the electron from propagating along the chain. The “stiffer” the rotation mode or libron, the easier for the electrons to move from site to site.

**Adiabatic regime.** In this limit, \( K \ll t_0, t_1 \), the electron moves ‘rapidly’ in a field of low frequency ‘slow’ phonons. We assume a wave function of the form
\[
\left( \begin{array}{c} \alpha(\theta) \\ \beta(\theta) \end{array} \right) = S(\theta) \left( \begin{array}{c} s_1(\theta) \\ s_2(\theta) \end{array} \right),
\]
and first consider the electron moving in a frozen background,
\[
\left( \begin{array}{cc} -E_0(\theta) & -(t_0 + t_1 \cos \theta) \\ -(t_0 + t_1 \cos \theta) & -E_0(\theta) \end{array} \right) \left( \begin{array}{c} s_1(\theta) \\ s_2(\theta) \end{array} \right) = 0.
\]
The corresponding eigenvalues \( E_0^\pm = \pm |t_0 + t_1 \cos \theta| \) play the role of a potential energy term in the equations for \( S(\theta) \),
\[
\left\{ \frac{\partial^2}{\partial \theta^2} + K \cos \theta - E_0^\pm(\theta) + \varepsilon \right\} S(\theta) = 0.
\]
These equations can also be solved in terms of Mathieu functions. It is easy to find that when \( K \ll t_0, t_1 \), and \( t_1 \gg 1 \), the eigenvalues of the problem are given by
\[
\varepsilon_1 = \varepsilon_{op} - t_0 - K + \frac{K}{\sqrt{8t_1}},
\]
\[
\varepsilon_2 = \varepsilon_{op} + t_0 + K - \frac{K}{\sqrt{8t_1}},
\]
where \( \varepsilon_{op} = -t_1 + \sqrt{t_1^2/2} \) is the polaronic energy shift due to the electron-libron off-site interaction. In this case, \( \Delta \varepsilon = 2t_0 + 2K - K/\sqrt{8t_1} \). Unlike the non-adiabatic case, \( \Delta \varepsilon \) saturates to \( 2t_0 + 2K \) for increasing \( t_1 \), and it therefore shows a strong bandwidth narrowing. Notice, however, that the two-site adiabatic problem for the small Holstein polaron yields an even stronger suppression of tunneling. In that case, one finds an exponential narrowing with coupling, \( \sim e^{-\gamma^2/2} \), similar to the non-adiabatic case mentioned above, but with large \( \gamma \) values.

**Long chain rotational polaron.** The long-chain generalization of the two-site model is an interesting physical problem with additional mathematical complexity which will be reported elsewhere. Here, we focus on a simpler local-twist model involving local angular coordinates. The local-twist Hamiltonian is given by
\[
H = \sum_i \left\{ -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta_i^2} - K \cos \theta_i - \varepsilon_1 c_i^\dagger c_i \cos \theta_i - t_0 (c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i) \right\},
\]
which includes anharmonic restoring force and local nonlinear electron-phonon coupling via \( \varepsilon_1 \) (the more general \( t_1 \)-dependence is also discussed in Ref. [30].

In the non-adiabatic regime, \( K \gg 1 \), one can generalize the two-site approach and identify two limiting cases. For strong restoring force, \( K \gg \varepsilon_1 \), it is possible to show that the polaron energy shift is \(-\varepsilon_1 \), while the bandwidth is slightly reduced to \( \Delta = 2t_0(1 - \varepsilon_1/K) \). In the case of softer twist frequency, \( \varepsilon_1 \gg K \gg 1 \), the bandwidth is given by \( 2t_0(K/\varepsilon_1)^{1/8} \). This power
law suppression of hopping is much weaker than the usual Holstein ‘translational’ polaron in long chains. The different dependence arises mostly from the local anharmonic coupling in this case, and would result in the polaron state having a higher mobility along the chain, despite the strong coupling constant.

**Conclusion.** We have introduced the idea of librions interacting with electrons in a complex molecular system. The strong coupling of rotational DOF yields a unique class of **twisting** polarons. Inclusion of anharmonic coupling to the electron via hopping and a nonlinear restoring potential, were shown to result in rather different polaronic behavior. We find electronic bandwidth suppression thanks to the excitation of twisting phonons, just as in the case of the usual vibrational DOF, but with a comparatively weaker effect in our case. This difference is due to both of the nonlinear characteristics mentioned, and provides a possible route for differentiation in experiments. We anticipate that the twist polaronic features could be tested by performing experiments in a variety of different molecules, where the restoring force is changed systematically, for example. We expect that our model will provide some insights on the low-temperature transport properties of interesting systems, such as recent molecular electronics experiments, and helical polymer “soft” crystals. Notice however that a detailed comparison with experiments will require one to consider the coupling of these polarons to charge or current leads. Such effects in vibrational polarons have only recently been studied and one would anticipate qualitative differences, which will be discussed elsewhere.

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**FIG. 1:** Effective tunneling between sites, $t'_1$, as a function of twist mode restoring force, $K$. $t'_1$ is given by Eq. (9) for large $K$ values, and is linear for small $K$, all in the non-adiabatic regime. Inset: diagram of parallel twist deformation of stack of molecular units with rotational degree of freedom along the stack.

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