Electron hopping integral renormalization due to anharmonic phonons

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Abstract. Interpretation of some experimental data of temperature-dependent transport properties of a solid material has led to a hypothesis that some renormalization has occurred to the electron hopping integral, making it decrease as temperature increases up to some limit. Such a renormalization may be attributed to the effect of coupling of electrons with anharmonic phonons. Namely, the presence of anharmonic vibration of two adjacent atoms yields an increase of their equilibrium distance as temperature increases, this in turn weakens the electron hopping integral connecting the two atomic sites. Despite that the above qualitative picture is pretty clear, little has been explored on the detail of how such an electron hopping integral evolves as a function of temperature. Motivated by this issue, here, we propose a tight-binding model incorporating the presence of anharmonic phonons and electron-phonon coupling, and solve it using Green function technique. We define the renormalized electron hopping integral from the band width of the interacting system, and perform self-consistent calculations to demonstrate the evolution of the electron hopping integral as a function of equilibrium distance between adjacent atoms and temperature.

1. Introduction
Previous experimental and theoretical studies [1, 2] have led us interpret that electron hopping integrals in the materials may evolve with temperature. This has motivated us to do a theoretical study to investigate how this phenomenon actually occurs. For this purpose, below we provide some theoretical background of what electron hopping integral is, how it is affected by temperature, and how we develop the algorithm to compute it.

In studying physical properties of a material theoretically, it has been common, whenever still adequate, that one approximates the relevant part of the band structure of the system through a tight-binding model [3]. This is usually aimed to avoid complexities in the calculations resulting from the presumably-irrelevant details of the system in connection to specific material properties being studied. A tight-binding model relies on an assumption that the electronic degrees of freedom in the system can be effectively reduced by considering only a few selected atomic orbitals such that the dynamics of the electrons occurs as a result of the movement, or popularly termed as hopping, of electrons from one orbital to another in the same atom or between nearby atoms. The parameters for the tight-binding model may simply be guessed based on some intuitive reasons, or may be derived by mapping the results of an ab initio calculation [4]. In the second-quantized formalism a tight-binding Hamiltonian can be expressed as

\[ H = \sum_{i,j} \sum_{\alpha,\beta} \sum_{\sigma} H_{ij}^{\alpha\beta} c_{i,\sigma}^{\alpha\dagger} c_{j,\sigma}^{\beta}, \]
where $i$ and $j$ denote the atomic sites, while $\alpha$ and $\beta$ are indices representing the atomic orbitals in the basis set, $\sigma$ is the spin index, and $c^\dagger_{i,\sigma}$ and $c_{j,\sigma}$ are the corresponding creation and annihilation operators, respectively. Here, $H^{\alpha,\beta}_{i,j,\sigma}$ are the tight-binding parameters formally derived from

$$
H^{\alpha,\beta}_{i,j,\sigma} = \int dr \, \phi^*_{\alpha}(r - R_i) \left\{-\frac{\hbar^2}{2m} \nabla^2 + \sum_n V(|r - R_n|)\right\} \phi_{\beta}(r - R_j). \tag{2}
$$

The simplest version of a tight-binding model assumes that the unit cell of the system contains only one atom and there is only one orbital per atom taken in the basis set. Further, if the hopping of electrons is assumed to be only between nearest-neighbor atoms, the Hamiltonian form reduces to

$$
H = \epsilon_0 \sum_{i,\sigma} c^\dagger_{i,\sigma} c_{i,\sigma} - t \sum_{<i,j>} \sum_{\sigma} c^\dagger_{i,\sigma} c_{j,\sigma}. \tag{3}
$$

In Eq. (3) $\epsilon_0 \equiv H_{i,i,\sigma}$ is referred to as the on-site energy which is assumed equal for all sites; while $t \equiv -H_{i,j,\sigma}$ with $i$ and $j$ being indices of nearest-neighbor sites, is referred to as the nearest-neighbor hopping integral; and $\sum_{<i,j>}$ denotes the summation over only nearest-neighbor pairs of $i, j$ sites. This Hamiltonian is easily solved by performing Fourier transformation to $k$-space, leading to

$$
H = \sum_{k,\sigma} \epsilon(k) c^\dagger_{k,\sigma} c_{k,\sigma}, \tag{4}
$$

where $\epsilon(k) = \epsilon_0 - t \sum_n e^{-i k \delta_n}$ is the energy dispersion of the model, with $\delta_n$ being a translation vector connecting a site with its $n^{th}$ nearest neighbor. If we assume the system to be a simple cubic lattice with lattice constant $a$, and set $\epsilon_0 = 0$, then we have

$$
\epsilon(k) = -2t (\cos k_x a + \cos k_y a + \cos k_z a). \tag{5}
$$

The energy dispersion of Eq. (20) spans from $-6t$ to $6t$, with the band width being $W = 12t$. From this simple relation, we get the idea that the band width of some energy dispersion is, to some extent, proportional to the value of the hopping integral of the system. Or, conversely, we may say that the hopping integral $t$ is proportional to the band width $W$ of the energy dispersion of the system.

Our focus of study is the hopping integral $t$, which according to Eq.(2) may change if the equilibrium distance between the nearest neighbor atoms changes. Here, we are interested in exploring how $t$ changes if we vary the temperature of the material. The most plausible way to manifest the effect of temperature on $t$ is through atomic vibrations, namely phonons. From elementary solid-state physics we know that equilibrium distance between atoms does not change with purely harmonic atomic vibrations, instead it requires some anharmonicity in addition to the harmonic part [5]. Hence, we hypothesize that the presence of anharmonic phonons would also affect the effective value of electron hopping integral $t$. In this study, we aim to confirm through explicit calculations how $t$ changes with temperature as a result of the presence of anharmonic phonons.

2. Model

Generically an electron-phonon system can be described by the following Hamiltonian terms

$$
H = H_{\text{el}} + H_{\text{ph}} + H_{\text{el-ph}}, \tag{6}
$$

where $H_{\text{el}}$ is the purely electronic part of the Hamiltonian that may be constructed from a tight-binding model, e.g. Eq. (3). Here, $H_{\text{ph}}$ is the purely phononic part that we define in the
simplest way to include anharmonic effects such that
\[
H_{\text{ph}} = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} M \Omega^2 x_i^2 - \lambda_3 x_i^3 - \lambda_4 x_i^4,
\]
(7)
where \( P_i \) is the momentum operator of the \( i \)th atom; \( M \) is the mass of each atom which is assumed the same for all atoms; \( \Omega \) is the frequency of lattice vibration, which for simplicity is assumed to be non-dispersive, i.e. only a single value like in the Einstein model. \( x_i \) is the displacement of the \( i \)th atom from its equilibrium position along any direction in three-dimensional space; and \( \lambda_3 \) and \( \lambda_4 \) are positive coefficients measuring the strength of the third- and fourth-order anharmonic terms, respectively. Lastly, \( H_{\text{el-ph}} \) represents the electron-phonon coupling that we construct within Holstein model [6, 7] as
\[
H_{\text{el-ph}} = g \sum_i c_i^\dagger \sigma c_i \sigma x_i,
\]
(8)
with \( g \) being the electron-phonon coupling strength.

3. Method

Our technical goal is to compute the equilibrium change of interatomic distance, \( \langle x \rangle \), and the renormalized electron hopping integral, \( \tilde{t} \), as functions of temperature. In the subsequent discussion below, we present how we formulate the method and algorithm to eventually compute \( \langle x \rangle \) and \( \tilde{t} \).

We start by constructing the electron Green function in \( k \) space, \( G(k, z) \), through the Dyson equation
\[
G_\sigma(k, z) = \frac{1}{z - \epsilon(k) - \Sigma_\sigma(k, z)},
\]
(9)
where \( \sigma \) is the spin index and \( z \) is complex frequency variable. Note that in our formulation, frequency and energy are set in the same unit, i.e. eV. We shall work in both Matsubara and real-frequency domains, where in the Matsubara formalism, \( z \) is to be substituted with \( z = i\omega_n + \mu \), with \( \omega_n = (2n + 1)\pi k_B T \) being the fermionic Matsubara frequency, \( k_B \) the Boltzmann constant, \( T \) temperature, \( \mu \) the chemical potential of the system, and \( n \) integer numbers ranging from \(-\infty \) to \( \infty \); while in the real-frequency domain, \( z = \omega + i0^+ \). Here, \( \Sigma_\sigma(k, z) \) is the self energy formally manifesting all interactions occurring in the system experienced by the electrons. In the computation process, we initialize the self energy value with an initial guess, then we recompute it later on through some approximate procedure until the guessed and the calculated values come into convergence. We detail the self-consistency algorithm below.

To tackle this problem, we choose to treat the phonon field semi-classically, and implement the dynamical mean-field theory (DMFT) algorithm [8] suitable for this choice [9, 10]. Within DMFT spatial correlations are suppressed yielding the self-energy become \( k \) independent, namely \( \Sigma_\sigma(k, z) \rightarrow \Sigma_\sigma(z) \). Further, since we do not consider any spin-dependent interactions, we can keep \( \Sigma_\uparrow(z) = \Sigma_\downarrow(z) \), such that \( G_\uparrow(k, z) = G_\downarrow(k, z) \) as well, accordingly. Upon this choice of treatment, the next step is to coarse-grain the Green function over the Brillouin zone to make it \( k \) independent,
\[
\overline{G_\sigma(z)} = \frac{1}{N} \sum_k \frac{1}{z - \epsilon(k) - \Sigma_\sigma(z)},
\]
(10)
and then extract the mean-field Green function through
\[
G_\sigma(z)_{\text{MF}} = \left( \overline{G_\sigma(z)}^{-1} + \Sigma_\sigma(z) \right)^{-1}.
\]
(11)
From here, we compute the local interacting Green function by adding the electron-phonon interaction to the mean-field Green function as

\[ G_{\sigma}(z,x)_{\text{loc}} = \left( G_{\sigma}(z)_{\text{MF}}^{-1} - gx \right)^{-1}. \]  

\( G_{\sigma}(z,x)_{\text{loc}} \) has a physical meaning as the interacting Green function defined at a particular site of atom undergoing a displacement of \( x \) from its equilibrium position. Since atoms at other sites are undergoing displacements of different values of \( x \), then we must average \( G_{\sigma}(z,x)_{\text{loc}} \) over \( x \) to obtain the \( x \)-independent interacting Green function representing the whole system. To do this, we first need to define the statistical weighting factor \( P(x,T) \) that depends on temperature \( T \) and the \( x \) value. That is,

\[ P(x,T) = e^{-S_{\text{eff}}(x,T)}, \]  

\[ S_{\text{eff}}(x,T) = -\sum_n \sum_{\sigma} \ln \det \left\{ G_{\sigma}(z)_{\text{MF}} G_{\sigma}(i\omega_n + \mu, x)_{\text{loc}}^{-1} \right\} e^{i\omega_n \xi^+} + \frac{\frac{1}{2} M \Omega^2 x^2 - \lambda_3 x^3 - \lambda_4 x^4}{k_B T}. \]

Once we have obtained \( P(x,T) \) we can do the averaging process over \( x \) variable for all the relevant quantities, such as the Green function itself

\[ G_{\sigma}(z)_{\text{ave}} = \int_{-\infty}^{\infty} dx \, P(x,T) G_{\sigma}(z,x)_{\text{loc}}, \]

and the equilibrium change of interatomic distance

\[ x_{\text{ave}} = \int_{-\infty}^{\infty} dx \, P(x,T) x. \]

Along the self-consistent process we need to update the chemical potential \( \mu \). We may do so by first obtaining the density of states (DOS), that is

\[ \text{DOS}(\omega) = -\frac{1}{\pi} \text{Im} \sum_{\sigma} G_{\sigma}(\omega + i0^+)_{\text{ave}}, \]

and then apply the constraint of the fixed electron filling \( \langle n \rangle \) such that

\[ \int d\omega \, \text{DOS}(\omega) f(\omega,T,\mu) = \langle n \rangle, \]

where \( f(\omega,T,\mu) \) is the Fermi-Dirac distribution function.

The most essential part of the self-consistency process is to recompute the self energy. We do this by applying the Dyson equation again, that is

\[ \Sigma_{\sigma}(z) = G_{\sigma}(z)_{\text{MF}}^{-1} - G_{\sigma}(z)_{\text{ave}}^{-1}. \]

The computed self energy will then be compared with the initial guessed value. If the difference is bigger than some tolerance value, the new guessed value may be defined by taking the computed result mixed with previous guessed value. The self-consistency process repeats with a new guessed self energy and the updated chemical potential until the convergence condition is achieved.

As we aim to compute the renormalized electron hopping integral \( \tilde{t} \), we may use the computed DOS profile to extract the information of the interacting band width \( \tilde{W} \). But note that this procedure is good only as long as the profile of the interacting energy dispersion, assuming simple cubic lattice, is roughly still of the form

\[ \tilde{\epsilon}(k) \approx -2\tilde{t} (\cos k_x a + \cos k_y a + \cos k_z a). \]

With this condition, we can then take \( \tilde{t} \approx \tilde{W}/12. \)
4. Discussion
Now that we have set up the algorithm we need to explore the model by fixing or varying the necessary parameters. For making the calculation easier, we choose the system to be half filled by taking one electron per site, i.e. $\langle n \rangle = 1$. We may choose the lattice constant value $a$ to be of a typical value of a few angstroms. The the value of product of $M\Omega^2$ may be set somewhat arbitrarily, but it is desirable to make the $(1/2)M\Omega^2 x^2$ value falls in the range comparable to the band width $W$. The $g$ parameter in the electron-phonon coupling is desired to set such that it delivers the effect of the presence of phonons to the electron DOS, but not strong enough to form a pseudo gap or gap in the DOS when the anharmonic terms are switched-off. Next, we need to turn on and carefully vary the anharmonic parameters $\lambda_3$ and $\lambda_4$, such that we can observe the evolution of the DOS profile due to the anharmonic effects. Once we have obtained the best combination of parameters that can give us meaningful changes in the DOS as compared to states with no phonons or no anharmonic effects, we may fix that combination of parameters and then vary the temperature to see how $\tilde{t}$ and $x_{ave}$ evolve as functions of temperature.

5. Summary
We have introduced the real physical problems from some previous experimental studies, giving us motivation to theoretically study the temperature dependence of the electron hopping integral in the system. We hypothesize that the change in the electron hopping integral is due to anharmonic effects. We formulate our Hamiltonian of the electron-phonon system within Holstein model with additional anharmonic terms. We then develop the dynamical mean-field theory algorithm to compute the renormalized electron hopping integral $\tilde{t}$ and the equilibrium change in the interatomic distance $x_{ave}$ as functions of temperature. Finally, we discuss how to explore our model with the so-constructed algorithm. The computational step of this project is being in progress.

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