Theory of super-para-electric large polaron for gigantic photo-enhancements of dielectric constant and electronic conductivity in SrTiO$_3$

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Abstract. In connection with the recent experimental discoveries on gigantic photo-enhancements of the electronic conductivity and the quasi-static dielectric susceptibility in SrTiO$_3$, we theoretically study a photo-generation mechanism of a charged ferroelectric domain in this quantum dielectric. The photo-generated electron, being quite itinerant in the 3d band of Ti $^{4+}$, is assumed to couple weakly but quadratically with soft-anharmonic T$_{1u}$ phonons in this quantum dielectric. The photo-generated electron is also assumed to couple strongly but linearly with the breathing type high energy phonons. Using a tight binding model for electron, we will show that these two types of electron-phonon couplings result in two types of polarons, a “super-para-electric (SPE) large polaron” with a quasi-global parity violation, and an “off-centre type self-trapped polaron” with only a local parity violation. We will also show that this SPE large polaron is nothing else but a singly charged (e$^-$) and conductive ferroelectric (or SPE) domain with a quasi macroscopic size. This polaron or domain is also shown to have a high mobility and a large quasi-static dielectric susceptibility.

1. Introduction

The perovskite type compound SrTiO$_3$ is already well-known to have very large static dielectric constants, as compared with other ordinary dielectrics[1]. This characteristic is usually attributed to the presence of the T$_{1u}$ (or TO) type soft phonon mode in this material[2-6]. Since Ti ion has a small radius, it is only loosely boxed up in the octahedral oxygen cage of the perovskite structure, and results in the aforementioned soft mode. The dielectric response of this odd and soft phonon mode becomes very large, being the typical characteristic of this material. It has been already shown that a simple anharmonic (or harmonic) phonon picture for this soft mode is quite inadequate to explain such the quantum para-electricity [7,8]. On the other hand, a sextic anharmonicity has been claimed experimentally to be a better depiction for this odd and soft phonon mode[8].

All these stories are only for the electronic ground state of SrTiO$_3$, while, if we proceed to its photo-excited states, we also encounter another quite new characteristic. Very recently, gigantic photo-enhancements of the electronic conductivity and the quasi-static dielectric constant have been observed experimentally in this SrTiO$_3$[9-11]. It was also pointed out that, this enhancement remains...
only under the ultraviolet (UV) light illumination, and disappears as this illumination is turned off. Thus, we can say, that this is a kind of photo-induced phase transition \[12-14\], and is expected to come from the coupling between the photo-excited electrons and the aforementioned soft-anharmonic phonons of this material \[15\]. However, the microscopic origin of these photo-induced phenomena has not been clarified theoretically.

An ultraviolet light shone to SrTiO$_3$ excites a valence band electron to the conduction band of this material. This excited electron interacts with phonons and constructs a polaron. Since this conduction band is mainly composed of 3d orbital of Ti, the excited electron will strongly couple to the breathing (A$_{1g}$ or E$_g$) mode of O$^{2-}$’s around the Ti ion. This excited electron will also couple to the aforementioned soft-anharmonic mode. However, this mode with the T$_{1u}$ symmetry is nothing else but the translational motion of the Ti ion itself. Hence, it does not couple to the 3d electron linearly, but couples only quadratically. While the aforementioned A$_{1g}$ mode of O$^{2-}$ around the Ti ion, can couple to the 3d electron through the ordinary linear electron-phonon (e-ph) interaction.

In this work, using a tight binding model for electrons, taking the aforementioned two types of e-ph interactions into account, we calculate the adiabatic energy surface of this system. We will clarify the microscopic origin of the dielectric enhancement. Also, by studying the translational motion of the polaron, we will clarify the mechanism of its metallic conduction.

2. Model Hamiltonian

We take a model Hamiltonian (\( \equiv H \)) to describe the electrons, in the 3d conduction band of SrTiO$_3$, coupling strongly and linearly with the A$_{1g}$ mode, and weakly but quadratically with the T$_{1u}$ mode,

\[
H = -T \sum_{l,i,\sigma} (a_{l,i,\sigma}^\dagger a_{l,i,\sigma} + h.c.) - S_b \omega_b \sum_i n_i B_i + \frac{\omega_b}{2} \sum_i \left( -\frac{\partial^2}{\partial B_i^2} + B_i^2 \right) - \frac{S_d \omega_d}{2} \sum_i n_i D_{i,1}^2 \\
+ \frac{\omega_d}{2} \sum_{l,i} \left( -\frac{\partial^2}{\partial B_i^2} + \frac{D_{l,1}^6}{3} \right) + U \sum_{l} n_{l,\alpha} n_{l,\beta}, \quad (n_{l,\alpha} = a_{l,\sigma}^\dagger a_{l,\sigma}, n_l = \sum_{\sigma} n_{l,\sigma}).
\]

Here \( a_{l,\sigma} (a_{l,\sigma}^\dagger) \) is the creation (annihilation) operator of an electron at the \( l \)th lattice site with spin \( \sigma (\equiv \alpha, \beta) \) in a simple cubic crystal, and \( T \) is the transfer energy between two neighbouring lattice sites \( l \) and \( l' \). \( S_b \) is the dimensionless constant of linear coupling between this electron and the site localized breathing mode, whose energy is \( \omega_b \) and dimensionless coordinate is \( B_i \). On the other hand, \( S_d \) is the dimensionless constant of quadratic coupling between the electron and the site localized T$_{1u}$ mode, whose energy is \( \omega_d \) and dimensionless coordinate in the direction \( l = x, y, z \) is \( D_{l,1} \). \( \beta \) is a mass parameter. According to ref.\[8\], we have used a quite specific, but simple model for the aforementioned soft-anharmonic phonon, that is, the sextic model, being enough to describe the quantum para-electricity. \( U \) denotes the intra-site Coulomb repulsion.

Within the adiabatic approximation, we rewrite \( H \) in the form (\( \equiv h_{ad} \)):

\[
h_{ad} = -T \sum_{l,i,\sigma} (a_{l,i,\sigma}^\dagger a_{l,i,\sigma} + h.c.) - S_b \omega_b \sum_i n_i B_i + \frac{\omega_b}{2} \sum_i B_i^2 \\
- \frac{S_d \omega_d}{2} \sum_i n_i D_{i,1}^2 + \frac{\omega_d}{2} \sum_{l,i} \frac{D_{l,1}^6}{3} + U \sum_{l} n_{l,\alpha} n_{l,\beta}.
\]

For a trial wave function of a polaron state (\( \equiv \psi \)), we take as
\[ |p\rangle = \sum_l \varphi(l) a_{l,\alpha}^* |0\rangle, \quad \sum_l |\varphi(l)|^2 = 1. \]  

(3)

Here \( |0\rangle \) is the true electron vacuum, and this \( \varphi(l) \) is assumed to be a Gaussian as

\[ \varphi(l) \sim \exp[-\frac{\Delta^2 (l \cdot l)}{2}], \quad l = (l_x, l_y, l_z), \]  

(4)

and \( \Delta \) is the reciprocal localization length, while \( l_x, l_y, l_z \) are the Cartesian components of \( l \). Using this \( |p\rangle \), we take the expectation value \( \langle p | h_{ad} | p \rangle \), but by the Helmann-Feynman’s theorem

\[ \frac{\partial \langle h_{ad} \rangle}{\partial B_i} = 0, \quad \frac{\partial \langle h_{ad} \rangle}{\partial D_{i,j}} = 0, \]

we can eliminate \( B_i \) and \( D_{i,j} \) from this \( \langle p | h_{ad} | p \rangle \). Thus, we obtain a simple form as

\[ \langle h_{ad} \rangle = -T \sum_{i,l,\sigma} \left\langle a_{i,\sigma}^* a_{i,\sigma} + h.c. \right\rangle - \frac{\omega_b S_b^2}{2} \sum_l \left\langle n_{l,\sigma} \right\rangle^2 - \frac{\omega_d S_d^{3/2}}{3} \sum_{i,j} \left\langle n_{l,\sigma} \right\rangle^{3/2}. \]  

(5)

It is already known that the conduction bandwidth \( 12T \) of \( \text{SrTiO}_3 \) is \( 2 \text{eV}[16] \). The energy of the breathing mode \( \omega_b \) is about \( 20 \text{meV}[17] \), and the energy of the \( T_{1u} \) mode \( \omega_d \) is about \( 1 \text{meV}[18] \). \( \beta \) is a mass parameter, which is taken to be \( 1.294 \), so that the lowest transition energy between the ground state and the first excited one of the original sextic oscillator, fits to the Raman data [18]. \( U \) is taken to be \( 4 \text{eV} \). The parameters \( S_b \) and \( S_d \) are determined so that they, as a set, reproduce the observed Stokes-shift (0.2 eV) of luminescence [17]. In eq.(5), the energy of the Franck-Condon state is \( -6T \). Hence, this condition becomes, \( -6T - \text{Min}(\langle h_{ad} \rangle) = 0.2 \text{eV} \). The quadratic coupling, being always subsidiary to the linear one, is assumed to be of the order of 10% of this Stokes-shift.

3. Results of calculations

The equation (5) can be easily calculated, and the result is shown in figure 1. It has two minima at

Figure 1. The adiabatic energy as a function of \( \Delta \).
Δ = 0.11 and at Δ = 2.2. The first one is a large polaron extended over about 10³ lattice sites with a \( T_{1u} \) type small lattice distortion at each site. Since the direction of this lattice distortion in the space of \( D_{ij} \) (i=x,y,z) is quite random with no inter-site order, it can be called super-para-electric(SPE) large polaron, and is equal to a charged ferroelectric (or SPE) domain. While the second one is the off-centre type self-trapped polaron strongly localized only in a single lattice site. The main energy gain of this strongly localized state is the \( A_{2g} \) type lattice distortion, and the energy gain due to the \( T_{1u} \) type lattice distortion is about 30% of it. Incidentally, the dashed line in the inset of figure 1 denotes the singlet SPE large bipolaron, \( n_{te} = n_{f} = 1 \).

4. Dielectric enhancement

Next, let us proceed to the dielectric enhancement due to the SPE large polaron. We focus only on a single \( T_{1u} \) mode at a typical lattice site, for example, the x direction of the central site of the SPE large polaron, and keep all coordinates of other modes at their equilibrium positions given by the previous adiabatic calculation. So we can get an effective Hamiltonian (≡ \( H'_{1u} \)) only for this \( T_{1u} \) mode as

\[
H'_{1u} = -S_{d} \omega_{d} \left| \phi(0) \right|^{2} D^{2} + \frac{\omega_{d}}{2} \left( -\frac{\hbar^{2} D^{2}}{\beta^{2} D^{2}} + \frac{D^{5}}{3} \right),
\]

where, the indices of D are dropped. If \( S_{d} \) is once given, the eigenstates (≡ \( | m(S_{d}) \rangle \)) and the eigenvalues (≡ \( E_{m}(S_{d}) \)), numbered from the lowest one to upper ones as, \( m = 0,1,2,.., \) of this effective Hamiltonian can be easily obtained numerically. Thus we can calculate the dielectric constant (≡ \( \varepsilon_{1}(S_{d}) \)) and its relative value (≡ \( \Delta \varepsilon \)) of this site. They are formally given as

\[
\varepsilon_{1}(S_{d}) \propto \sum_{m} \left| \frac{\langle m | p_{d} | 0 \rangle}{E_{m} - E_{0}} \right|^{2}, \quad \Delta \varepsilon \equiv \frac{\varepsilon_{1}(S_{d})}{\varepsilon_{1}(0)},
\]

where \( p_{d} \) is the dipole operator. The result of calculation is shown by black diamond marks in figure 2, wherein \( S_{d} \) is changed under the aforementioned condition shown in section 2. We can see that \( \Delta \varepsilon \) is enhanced, and this enhancement is mainly due to the further softening \((E_{1}(S_{d}) - E_{0}(S_{d})) < (E_{1}(0) - E_{0}(0)) \), or the decrease of the denominator, coming from the e-ph coupling in the first term of eq.(6). While the matrix element \( \langle m | p_{d} | 0 \rangle \) in the numerator of eq.(7) does not change so much. We should also note that this enhancement occurs at all the sites within the SPE large polaron, which is extended over \( 10^{3} \) lattice sites. Thus, the total enhancement

![Figure 2](image-url)
becomes very large. It should be noted that, as seen from figure 1, this SPE large polaron is energetically very close to the Franck-Condon state, which is the plane-wave state \((\Delta = 0)\) of an electron, created just after the photo-excitation. It is also well separated from the self-trapped polaron state by a high energy-barrier. Hence, we can expect that, after the photo-excitation, the system soon relaxes to this SPE large polaron state, and remains there long, resulting in the aforementioned enhancement.

5. Translational motion of polaron

In the absence of scattering of phonons, the conduction electron moves freely under an external electric field. However, with an account of the e-ph interaction, the conduction band electron will distort its nearby ions. On the contrary, the electron might get heavier, because wherever it moves, there will be an induced lattice distortion around it, as if its dress. This is just the mass enhancement of the polaron. In order to clarify this mass enhancement effect, we next study a translational motion of the polaron only by one site, as shown in figure 3.

The most simple way to estimate this mass enhancement is to calculate the expectation value of the electron transfer operator \(\sum a^*_i,\sigma a_{i+1,\sigma}\) between two polaron states, centred and localized at neighbouring two lattice sites, as schematically shown by the big dashed and big solid circles in figure 3. We can define a ratio \((=R)\) between the hypothetical bare electron transfer and the real polaron transfer as

\[
R = \frac{\langle \psi | \sum a^*_i,\sigma a_{i+1,\sigma} | \psi \rangle}{\langle \psi'_{\text{ele}} | \sum a^*_i,\sigma a_{i+1,\sigma} | \psi'_{\text{ele}} \rangle}, \quad (8)
\]

where, \(|\psi'_{\text{ele}}\rangle\) and \(|\psi_{\text{ele}}\rangle\) are the two electronic parts of a polaron centred at neighbouring two lattice sites, before and after the one-site translation, as shown in figure 3. These two states are already determined in section 2 within the adiabatic approximation. While \(|\psi'\rangle\) and \(|\psi\rangle\) correspond two polaron states, encompassing both electronic and phonon parts, before and after the one-site translation. Under the Hartree-Fork approximation, this polaron state can be approximated by the direct product of the electronic state \(|\psi'_{\text{ele}}\rangle\) and the corresponding phonon one \(\equiv |\psi_{\text{ph}}\rangle\) as

\[
|\psi\rangle = |\psi'_{\text{ele}}\rangle \cdot |\psi_{\text{ph}}\rangle.
\]

**Figure 3.** One-site transfer. \(r\) is the polaron radius.

**Figure 4.** \(R\) as a function of \(S_d\).
This approximation also holds for the neighbouring state $|\psi'\rangle$ as, $|\psi'\rangle = |\psi^{ele}_{e}\rangle \cdot |\psi^{ph}_{p}\rangle$. Thus, $R$ is reduced to the inner product of two phonon parts as $R = \langle \psi^{ele}_{e} | \psi^{ph}_{p} \rangle$. This inner product can also be decomposed into the partial inner products between the two lowest phonon states at each lattice site. While, these two lowest states at each site, can be calculated from the similar Hamiltonian as shown in eq.(6). It depends on the distance from the center of the corresponding polaron. As symbolically shown in figure 3, in the case of SPE large polaron, the two phonon parts before and after the one-site displacement, are almost common at the distant sites from the center, and also at the inner sites around the center. The difference occurs only at the sites around the so-called polaron radius ($\equiv r \approx \Delta^{-1}$), as shown in figure 3. Thus, we can easily calculate $R$ to be almost 1, as shown by black squares in figure 4. While, in the case of the self-trapped polaron, $R \approx 0$, as denoted by black triangles in figure 4. We can see that the SPE large polaron is highly mobile, while the self-trapped one is immobile.

6. Conclusion
We have thus employed a discrete lattice model to investigate a dual e-ph interacting system in SrTiO$_3$. The photo-generated electron is assumed not only linearly coupled with $A_{1g}$ phonons but also quadratically coupled with $T_{1u}$ phonons, and results in two kinds of polarons, the SPE large polaron and the off-center type self-trapped polaron. The photo-excited electron reaches this SPE large polaron state first, since it is energetically close to the Franck-Condon state. In this SPE large polaron, the quadratic e-p coupling results in phonon softening of $T_{1u}$ mode. This phonon softening causes gigantic static dielectric enhancement. The calculations of the ratio $R$ show, that SPE large polarons can contribute to the metallic conduction, while the self-trapped polarons are immobile.

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