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Electron-phonon interaction in Ba-K-Bi-O superconductor by quantum path integral molecular dynamics (QPIMD)

Lee, Chong Yong, Ph.D.
The University of Arizona, 1990
ELECTRON-PHONON INTERACTION IN BA-K-BI-O 
SUPERCONDUCTOR BY QUANTUM PATH INTEGRAL 
MOLECULAR DYNAMICS (QPIMD)

by

Chong-Yong Lee

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1990
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Chong Yong Lee entitled ELECTRON-PHONON INTERACTION IN BA-K-BI-O SUPERCONDUCTOR BY QUANTUM PATH INTEGRAL MOLECULAR DYNAMICS (QPIMD) and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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ABSTRACT

We have introduced two different techniques in this paper to investigate the high Tc superconductor $\text{BaK}B\text{i}O_3$. The first one is the rigid-ion molecular dynamics model to calculate classical properties of the crystal. This method provides the ionic anisotropic vibrational spectra. It is found that the oxygen modes dominate the vibrational spectrum from $150 \text{ cm}^{-1}$ up to $820 \text{ cm}^{-1}$. An increase in the number of substituted K around an oxygen favors high frequency vibrational modes. We have also determined by experiment IR spectrum. The absorption peaks are between $380$ to $880 \text{ cm}^{-1}$. Our experimental and computational data are in good agreement in the high frequency region. The second technique used to investigate this high Tc superconductor is based on a quantum path integral molecular dynamics. It has been applied for the first time to the determination of electron-phonon interaction energy. We estimate the electron phonon coupling constant at about 1.34. This value represents a weak to moderate electron-phonon coupling in $\text{Ba}_{1-x}\text{K}_x\text{Bi}O_3$ in agreement with current views of this pairing mechanism in this material.
Molecular Dynamics (MD) Simulation is a very useful and powerful tool for the study of the classical physics properties of the High Tc superconductors [1, 2]. Nevertheless, it is clear that quantum mechanical effects are an essential element in the superconductivity. In this dissertation we use MD and quantum path integral Molecular Dynamics (QPIMD) which includes both the dynamics of the lattice and quantum effects to study the superconducting oxides.

Since Müller and Bednorz [3] discovered copper-oxide high Tc material in 1986, the experimental and theoretical understanding in the high Tc superconductors have attracted the attention of many physicists. Most high Tc materials discovered so far are copper-oxide superconductors with d-band electrons. However, the bismate superconductor $Ba_{1-x}K_xBiO_3$ discovered by Mattheiss et al. [4] is of particular interest in the study of superconductivity in ceramic oxides. Recent measurements of the energy gap of the high Tc bismate superconductor $Ba_{6}K_{4}BiO_3$ are consistent with BCS type superconductivity [5]. Clearly, this superconductor with Bi(6s6p)-O(2p) does not include the d-band which the copper-oxide has and possesses different physical behaviors from copper-oxides, even though both material structures are similar to the original perovskite structure. There are two main differences between these two types of materials. One is the phase transition of the crystal structure. The crystal structure of $BaBiO_3$ and $La_2CuO_4$ as insulators is a perovskite structure [6, 7]. The bismate material becomes cubic in shape (see Fig 1) when doped with potassium $K^+$ and turns into a conductor [8]. In contrast, copper-oxide superconductor doped with $Ba^{++}$ becomes tetragonal or orthorhombic [9]. In the former the electron-phonon interaction behavior is
believed to be important for superconductivity.

The clear isotope effect of oxygen replacement with $\alpha \simeq 0.4$ for the bismate superconductor was measured by Hinks et al[10], in contrast to $\alpha \simeq 0.0$ in copper-oxide materials[11]. The source of this dominant contributions to quantum behavior can be anticipated. The electron-phonon coupling constant of 30 K Tc bismate superconductor[12] is about 1.0, which is consistent with weak coupling. The coupling constant of copper-oxide would have to be about 3.0 or bigger[13], which would be very strong coupling to explain a Tc $\simeq 90K$. The peaks of the infrared and Raman scattering below the transition temperatures related to electron-phonon coupling in bismate superconductor show a softening between 400 $cm^{-1}$ and 480 $cm^{-1}$ reported by Loong et al[14], and McCarty et al[15]. The significant evidence that the high Tc in the bismate superconductor is related to electron-phonon coupling with this background on the problems to be tackled, motivate our investigation of some elements of the atomistic behavior of the bismates in order to better understand the relationship between their structures and their vibrational properties. Atomistic methods have already been successfully applied to the study of phonon behavior of superconductivity. The originality of this work is that we used a discretized quantum path integral representation of the statistic mechanics, evaluated the normal state equilibrium thermal distributions, and calculated properties of an electron in bismate oxide such as the electron-phonon interaction. This method has been used intensively for the study of chemical systems[16, 17, 18]. To our knowledge this work constitutes the first application of this method to shed light on the mechanism for high Tc superconductivity.

We outline in Chapters 2 and 3 the theoretical background for this work and present a review of the pertinent literature. We also explain in these chapters the degree to which the electron-phonon interactions in superconductor is understood theoretically. Chapter 4 presents representative modeling and calculating methods of physical properties, among which we include time average values and vibrational properties. Chapter 5 includes the simulation results obtained from classical MD calculations and some experimental data such as powder X-ray diffraction and IR spectrums at room temperature
for $Ba_{1-x}K_xBiO_3$ which we have measured for the purpose of comparison with the simulation data because of a lack of data in current literature. We outline in Chapter 6 the theoretical background of the quantum path integral and its applications to $Ba_{1-x}K_xBiO_3$. In addition, Chapter 6 contains the simulation results and discussions including the electron-phonon interaction energy and the calculated coupling constant, plus some other physical parameters. The conclusion of this dissertation and future work are presented in the final chapter.
In 1986, Müller and Bednorz[3] found high temperature superconduction in $La_{2-x}Ba_xCuO_4$. That discovery has lead to a great deal of research in an effort to understand the physical origins of high Tc. Many new materials have been fabricated and tested. Of these copper-free oxide superconductors such as potassium doped $BaBiO_3$ are particularly interesting both because of their high Tc and because data suggest a BCS type mechanism. This a oxide has two important properties similar to the copper-oxide based superconductor. One is the perovskite structure and the other is the doped metallic conductivity. The electronic structure of this material is simple with conduction bands having Bi(6s6p)-O(2p) hybridized orbitals in contrast to the d-band character of the copper oxide material. Another difference resides in the fact that these new materials are not magnetic which the copper oxide based superconductor are magnetic with a strong electron correlation due to 3d electrons resulting in an antiferromagnetic ground state[19, 20].

Mattheiss et al[4]. found a value of Tc = 22 K in potassium-doped $BaBiO_3$; and later work by Hinks et al[21]. improved this to Tc = 30 K. This bismate is similar to superconducting Pb doped on the bismuth site by Sleight et al[22]. Since a half filled band of semiconducting $BaBiO_3$ by theoretical prediction is unstable, the system changes phase to the charge ordered insulating state.

The phase transition of the $BaBiO_3$ structure from an insulator to a superconductor occurs at different potassium doping concentrations. A 4 % concentration of
potassium ions replacing Ba leads to an orthorhombic phase from the monoclinic structure transformation with $\gamma = 90.2^\circ$ \(\text{BaBiO}_3\) with \((\text{Bi}^{4+}\) charge). The system of \(\text{BaBiO}_3\) has a lattice distortion with \(\text{BiO}_6\) octahedral as reported by Cox et al[6]. 13% and 25% to 50% of the potassium concentration result into the cubic symmetry from the tetragonal symmetry as well as a superconducting from nonsuperconducting character. Each of these two structures are described by Schneemeyer et al[23] as having a symmetric breathing mode distortion. This distortion is also characterized as a charge density wave. Above 50% doping, the material goes to the semiconducting state from the metallic state; this transition is not currently understood. The copper-oxide based system has also been observed by Jorgensen[9] to undergo a structural phase transition from orthorhombic to tetragonal when \(\text{La}_2\text{CuO}_4\) is doped using Ba to replace the La atoms. \(\text{Ba}_{1-x}\text{K}_x\text{BiO}_3\) has little bit of the anisotropic properties about the c-axis because of disordered \(\text{K}^+\) doping. It appears to have a granular structure the same as the copper oxide superconductors and electron pairs, However, this material is not similar to the characteristics of the low temperature, pure metallic superconductors.

One of the interesting properties that can be used to characterize superconductivity is the coherence length, $\xi$, described by Landau-Ginzberg[24]. In BCS superconductors, $\xi$ for most pure metals depends on the temperature below the transition temperature. This length has an especially important role in determining the properties of a type II superconductor[24]. The coherence length $\xi_0$ of a pure metallic superconductors is on the order of $10^{-4}$ cm. The coherence length of an impure metallic superconductor is given as \((\xi_0 l_e)^{1/2}\) where $l_e$ is the electron's mean free path. Kwok et al[12] reported $\xi = 36.8\text{Å}$ with 35% potassium doped \(\text{BaBiO}_3\) from high critical magnetic field. U. Welp et al[25] observed the variation in coherence length with different potassium doping concentrations by using various magnetic fields. This data showed that the smallest value is $40\text{Å}$ with 37% potassium doping and this length is much larger than the unit cell dimension ($a = b = c = 4.293\text{Å}$) unlike the yttrium barium copper oxide (YBCO) superconductor. A value of coherence length in \(\text{YBa}_2\text{Cu}_3\text{O}_x\) is about $10\text{Å}$ (average over crystal axes) which is of the order of the unit cell dimension[8]. This results in an extremely high
value for the upper critical field, $H_{c2} \sim 25$ Oe. The Ginzberger-Landau (GL) parameter, $\kappa$, is important to determine whether a superconductor is type I or type II[24]. At 20K, Kwok[12] also reported that the lower critical field for $Ba_{0.6}K_{0.4}BiO_3$ is 35 G and found a Ginzberger-Landau (GL) parameter $\kappa = 59$. In contrast, a GL parameter of $\kappa = 45$ was noted by Batlogg et al[26]. The field $= 750$ Oe and the penetration depth was calculated from the relationship $\lambda_{GL} = \kappa \xi$ and yielded a value of $\lambda_{GL} = 2200\AA$ at $T=0$.

Another of the important properties that characterize its superconductor is the specific heat from near $T_c$ to Room temperature. For $Ba_{0.6}K_{0.4}BiO_3$, there are two main different sets of data reported by Illinois[27] and the AT&T group[28]. The value of the electronic specific heat coefficient $\gamma$ is reported as 1.5 mJ/mol K by the AT&T group in contrast to the 0.299 mJ/mol K reported by the Illinois group. The difference in the specific heat between the normal and the superconductor state was found to be 0.86 mJ/mol K$^2$ by the AT&T group; in contrast the Illinois group found 3.39 mJ/mol K$^2$. The Debye temperature was estimated in their papers. The Illinois group predicted $\theta_D \sim 346$ K and the AT&T group predicted $\theta_D \sim 150$ to 200 K. Hundley et al[29] also reported measurement for the specific heat. They claimed that the value of slope $\gamma$ is almost zero such as $\gamma = 0.0 \pm 0.2$, $\theta_D \sim 200K$. For this material, the charge carrier density was reported by Batlogg et al[26], and Kondoh et al[30]. The former estimated about $4.5 \times 10^{21}/cm^3$ from their specific heat data and the latter estimated about $3.0 \times 10^{21}$ from their Hall effect measurement. Their data shows that the Hall coefficient is negative implying N type charge carriers and the temperature dependence of Hall coefficient was also reported by them. This data is quite different from that of Hall charge carriers in high $T_c$ copper-oxides materials.

Also of interest is the temperature dependence of the electrical resistivity of Ba-K-Bi-O. The resistivity increases from 300 K to 150 K and then slowly decreases until transition temperature as reported by Kondoh et al[31] and Jin et al[32]. These another claim that this behavior is related to the "pseudometallic behavior", although the charge carrier concentration is relatively large. Dabrowski et al[33] observed a
phonon-assisted variable range hopping between 160 and 300 K and concluded that it is an effect of grain boundaries or that sample inhomogeneities existed.

An important result of BCS theory reveals that

$$T_c = \langle w \rangle e^{\frac{1}{\lambda - \mu}}$$

where $\lambda$ is the electron phonon (e-ph) coupling constant, and $\mu$ is the $e^- - e^-$ coulomb repulsion of pseudopotential representation which is the electron repulsion on the Fermi surface due to the Coulomb interaction. A weighted average over the energy of the electron mediating field, $\langle w \rangle$, is represented as

$$\langle w \rangle = \frac{2}{\lambda} \int dw \alpha^2(w) F(w).$$

The $F(w)$ is expressed in terms of the frequency distribution in the phonon spectrum, and $\alpha^2(w)$ is the electron-phonon interaction matrix element. For BCS theory[34] the energy gap $\frac{\Delta}{k_B}$ is 3.53. Schlesinger et al[5] used optical measurements of infrared reflectance to determine an energy gap of a 40% doped potassium superconductor; their measurement a $3.5 \pm 0.5$ corresponds to moderate to weak e-ph coupling. This conventional gap ratio is different from YBCO for which a value of 8.0 was reported implying very strong coupling in the ab plane[35].

The isotope effect can demonstrate the dependence of $T_c$ on the phonon spectrum if different mass isotope of the same element produce a change in high $T_c$. For these new superconductivity materials, the oxygen isotope effect is interesting. From the BCS theory prediction, the dependence of $T_c$ on the isotope effect in measured by a coefficient $\alpha$. The value of $\alpha = 0.5$ corresponds to no anharmonicity for phonon modes. However, Coulomb interactions reduce $\alpha$, and the isotope effect may apply only to structure changes instead of effects on $\alpha$. From the various measurements of $T_c$, the following investigators found $\alpha$ to be: $0.41 \pm 0.03$ [Hinks et al[36]], $0.21 \pm 0.03$ [Batlogg et al[26]], and $0.35 \pm 0.05$ [Kondoh et al[30]]. These results indicate a conventional phonon mediated BCS mechanism of bismate superconductivity. The principal reason for the $\alpha$ differing from the BCS value according to Masafumi Shirai et al[37] is that the vibration of
positive atoms other than oxides contribute to the superconductivity in the case where a substantial phonon frequency renormalization is caused by the electron-phonon interaction. In the copper oxide superconductors, the observed values of $\alpha$ are almost zero or zero which may indicate absence of phonon mediated electron pairs and a non-BCS origin for superconductivity.

There are also data of electron-phonon coupling constants $\lambda$ based on the critical field slopes. The coupling constant $\lambda$ in $Ba_{1-x}K_xBiO_3$ was estimated by Batlogg et al[26], to have values of 0.6 to 0.8 near $T_c$ and 1.5 to 2.0 near the Debye temperatures of (150 to 200 K). Kwok et al[12]. using the same method estimated the value of $\lambda$ to be 1.0 near $T_c$, they also found $<w> \sim 40$ meV. The high quality tunneling measurement of Zasadzinski et al[38]. reported that the coupling constant $\lambda$ by using $\frac{dF}{dT}$ is about 1.0 near $28$ K, $\mu = 0.13$ for the coulomb pseudopotential, and $<w> = 40$ meV.

The phonon density of this state for our material was calculated with Molecular Dynamics simulation and determined by neutron scattering measurements [14] and by Raman scattering[15]. There is a softening of the phonon spectra in the K doped material at phonon energies of about 43 meV reported by Loong et al[14]. The correlation between the phonon of density of states determined by Loongs et al[14]. and the Raman spectra[15] suggested that there is a strong coupling of electrons to optical phonons.

In the work that follows we use Molecular Dynamics to obtain theoretical results for the vibrational properties of $Ba_{1-x}K_xBiO_3[1]$ and also to study the phonon behavior and defect properties in high $T_c$ superconducting states. Previous studies so far have been with YBaCuO[39, 2], LaCuO[40], BaKBiO[14]. For those cases, good agreement between the calculated properties and available experimental data was achieved using this classical model. While, we will study many properties with classical MD, we can also study more about quantum effects of the high $T_c$ superconductivity by using path integral method with MD (QPIMD). As described below we investigate physical properties related to quantum effects by using QPIMD.
CHAPTER 3

THEORY OF ELECTRON PHONON INTERACTION

3.1 Electron Phonon Interaction

In a problem involving electrons moving in a crystal, it is of great interest to explore the electron interaction with the lattice vibrations. In past years, many physicists have worked on this problem because of its relation to superconductivity. Polarons, in ionic compounds, have been explained on the basis of electron-phonon interactions. In this work, we are also interested in the electron-phonon interaction in relation to the formation of polarons, in order to study the Ba-K-Bi-O material which has been recently identified as a high Tc superconductor. This superconducting material displays metallic behavior at room temperature. The resistivity measurement by S. Jin et al[32] and S. Kondoh et al[30] demonstrated that above 100 K, the thermoelectric power of this material is nearly as linear with temperature as in a metallic case. The photoelectric measurements by H. Sato et al[41] showed that a metal-insulator transition occurred at a dopant concentration of 35% potassium. $Ba_{0.6}K_{0.4}BiO_3$ is considered to be a metallic superconductor, because density of charge carriers in this material is calculated to be $3.0 \times 10^{21}/cm^3$ from Hall effect measurements. Since this material is a metallic superconductor, we are interested in understanding the electron-phonon interactions (EPHI).

Some understanding of EPHI can be gained by considering the polaron theory. This theory treats the ion deformations caused by the electrons coming into the lattice. A simple way of studying electron-phonon interactions in this material is to assume that a conduction electron in the crystal is inelastically diffracted by the lattice vibrations or phonons. We derive some of the equations and basic concepts here. Following J.
Bardeen[42] and Frölich[43], most of derivation of this theory is carried out in momentum space in order to simplify the formalism. Two initial assumptions were made in order to simplify the calculations. The first assumption, consistent with Bloch theory, is that the matrix elements of the electron-phonon interaction depend only on the difference in wave vectors of initial and final states. The second is that the electrons interact only with the longitudinal wave of the crystal. We will explain the reason why the interaction is coupled to the longitudinal wave component later. With this second assumption, we can neglect the anisotropic effects which makes the equation rather complicated.

We start with the model in which all electrons are independent and do not interact with one-another in which the ions are well localized in position. Assume that the electron moves among the periodic and static ions in space. The Hamiltonian for the electron is written as $H_{el} = \frac{p^2}{2m} + V_0(\vec{x})$ where $V_0(\vec{x})$ has the periodicity of the crystal. In fact, the atoms in the lattice undergo small vibrations about their equilibrium positions. These vibrations will be distorted by the presence of the electron. The total Hamiltonian can be written as $H_T = H_{el} + H_{ph} + H_{e-ph}$. The electron Hamiltonian perturbing the perfect periodicity of the crystal in the second quantized notation of the electron is given by

$$H = \int d^3x \psi(\vec{x})^+ \left( \frac{p^2}{2m} + V(\vec{x}) \right) \psi(\vec{x})$$

(3.1)

where $\psi(\vec{x})$ and $\psi(\vec{x})^+$ are electron’s destruction and construction operators and $V(\vec{x})$ is the perturbed crystal potential. Let us assume that there is one atom per a unit cell and that the $l^{th}$ ion in the bravais lattice undergoes a displacement $u(l)$ due to the incoming electron:

$$V(\vec{x}) = \sum_r u(\vec{x} - R(\vec{l}))$$

where $R(\vec{l})$ is the actual position of a vibrating atom, and the equilibrium position $R_0(\vec{l})$, that is $R(\vec{l}) = R_0(\vec{l}) + u(\vec{l})$.

The local ionic potential can be thought to be rigidly shifted by ionic motion. This model is called the rigid ionic model. We know that $u(\vec{l})$ is small compare to $R_0$,
so we can use the Taylor expansion:

\[ v(\vec{x} - R(\vec{l})) = v(\vec{x} - R_0(\vec{l})) + \vec{u}(\vec{l}) \cdot \nabla_{R(\vec{l})} v(\vec{x} - R(\vec{l})) |_{R = R_0} \]

\[ = v(\vec{x} - R_0(\vec{l})) - \vec{u}(\vec{l}) \cdot \nabla_x v(\vec{x} - R_0(\vec{l})) + \ldots \]

so that

\[ V(\vec{x}) = \sum_{\vec{l}} v(\vec{x} - R_0(\vec{l})) - \sum_{\vec{l}} \vec{u}(\vec{l}) \cdot \nabla_x v(\vec{x} - R_0(\vec{l})) + \ldots \]

Here the first term on the right side is the periodic part of the crystal potential called \( V_0(\vec{x}) \) and the second term represents the perturbation. The Hamiltonian becomes \( H_T = H_0 + H_{e-ph} \) where \( H_0 \) is unperturbed electron and phonon Hamiltonian and \( H_{e-ph} \) is the interaction Hamiltonian. Hence we can rewrite the detailed phonon energy.

\[ H_0 = \int d^3x \psi(\vec{x})^\dagger \left[ \frac{p^2}{2m} + V_0(\vec{x}) \right] \psi(\vec{x}) + \sum_{\vec{q}} h\omega(\vec{q})(a^{+}_{\vec{q}}a_{\vec{q}} + \frac{1}{2}) \]

where \( \vec{j} \) is the site index, and \( a, a^+ \) are phonon operators

\[ H_{e-ph} = -\sum_{\vec{l}} \vec{u}(\vec{l}) \cdot \int d^3x \psi(\vec{x})^\dagger \nabla_x v(\vec{x} - R_0(\vec{l})) \psi(\vec{x}) \]

The e-ph Hamiltonian can be rewritten in the form.

\[ H_{e-ph} = \frac{2}{5} iE_f \sum_{\vec{k}\vec{q}} \sum_{\vec{q}} \left( \frac{\hbar}{2NMw(\vec{q})} \right)^\frac{1}{2} \hat{e}(\vec{q}) \cdot (\vec{k} - \vec{k}') K(|\vec{k} - \vec{k}'|) C^+_{\vec{k}+\vec{q}+\vec{q}'} C_{\vec{k}'}[a_{\vec{q}} + a^{+}_{-\vec{q}}] \]

where \( a_{\vec{q}} \) and \( C_{\vec{k}} \) are a phonon and an electron operator. Here we define the \( \hat{e} \) as the polarization vector, \( K(|\vec{k} - \vec{k}'|) \) as \( \int d^3x e^{i\vec{q} \cdot \vec{x}} \), and \( M \) as atomic mass. Detailed calculation can be found in Appendix A. Let's consider Debye phonons \( w(\vec{q}) = c_q \), and the normal(N) process. At the start we claimed that the electron is coupled only to longitudinal phonons, because the polarization vector \( \hat{e}(\vec{q}) \) is only parallel to the longitudinal mode. Then the matrix elements \( K \) become unity. Let's rewrite the above equation.

\[ H_{e-ph} = \frac{2}{5} iE_f \sum_{\vec{k}\vec{q}} \left( \frac{\hbar}{2NMc_q} \right)^\frac{1}{2} |\vec{q}|^{1/2} C^+_{\vec{k}+\vec{q}} C_{\vec{k}'}[a_{\vec{q}} + a^{+}_{-\vec{q}}] \]
where \( n \) is the number of unit cell of unit volume, \( N = nV \), \( \rho = nM \), and \( M \): mass. Then we can define a coupling constant as

\[
\alpha = \frac{2}{5} E_f \left( \frac{\hbar}{2 \rho c} \right)^{1/2}.
\]

With this definition, the previous equation becomes

\[
H_{e-ph} = i \alpha \sum_{kq} \sqrt{\frac{q}{V}} C^+_k C_k(a_q + a_{-q}^+.)
\]

(3.8)

### 3.2 Energy Shift

Let’s now determine the energy shifts due to the electron-phonon interaction. Here we study the coupling effect from the electron-phonon scattering of a quasiparticle. Most of this section is based on the work of Bardeen[42] and Harrison[89]. The general expression of the perturbation theory is

\[
E = E_0 + \langle 0 | H_{e-ph} | 0 \rangle + \sum_N \frac{\langle 0 | H_{e-ph} | N \rangle^2}{E_0 - E_N} + \ldots
\]

(3.9)

Where \( |0\rangle \) is correspond to the ground state of the system and \( |N\rangle \) is the exited states with energy \( E_N \). Since \( H_{e-ph} \) acting on a state changes the number of phonons, we have \( \langle 0 | H_{e-ph} | 0 \rangle = 0 \) and the second order perturbation term is dominant as reported by Frölich[43]. In order to calculate the second term as an energy shift, we use the Hamiltonian from the last section. Now let’s consider a state where both the electron and phonon states are characterized by well defined occupation numbers. The change in energy of the state is then

\[
\Delta E_0 = \sum_N \frac{\langle 0 | H_{e-ph} | N \rangle^2}{E_0 - E_N}
\]

(3.10)

where \( |0\rangle \) has electron and phonon states. To calculate this term, we insert (3.8) into equation (3.10).

\[
\Delta E_0 = \frac{\alpha^2}{V} \sum_N \langle 0 | \sum_{kq} q^{1/2} C^+_k C_k(a_q + a_{-q}^+) | N \rangle \frac{\langle N | \sum_{kq} q^{1/2} C^+_k C_k(a_q + a_{-q}^+) | 0 \rangle}{(E_0 - E_N)}
\]

(3.11)
\begin{equation}
+ \sum_N \langle 0 | \sum_{\mathbf{k}^i} q^{1/2} C_{\mathbf{k}+q}^+ C_{\mathbf{k}'} (a_{\mathbf{q}}^+ + a_{-\mathbf{q}}^-) | N \rangle < N | \sum_{\mathbf{k}^i} q^{1/2} C_{\mathbf{k}+q}^+ (a_{\mathbf{q}}^+ + a_{-\mathbf{q}}^-) | 0 \rangle \rangle (E_0 - E_N) \rangle \end{equation}

Since the state $|0\rangle$ corresponds to no phonons in any mode, the $a_{\mathbf{q}}^+$ enters the first and the $a_{-\mathbf{q}}^-$ enters the second matrix element. Each term in the summation corresponds to a different intermediate state $|N\rangle$. There are two matrix elements of final states with one less or one more electron and the differences are

\begin{equation}
\Delta E_0 = \sum_{\mathbf{k}^i} q^{1/2} \langle 0 | \sum_{\mathbf{k}^i} q^{1/2} C_{\mathbf{k}+q}^+ C_{\mathbf{k}'} a_{\mathbf{q}}^+ a_{\mathbf{q}}^- C_{\mathbf{k}+q}^+ | 0 \rangle (E_0 + q - E_{\mathbf{k}+q})
+ \sum_{\mathbf{k}^i} q^{1/2} \langle 0 | \sum_{\mathbf{k}^i} q^{1/2} C_{\mathbf{k}+q}^+ C_{\mathbf{k}'} a_{\mathbf{q}}^+ C_{\mathbf{k}+q}^+ a_{-\mathbf{q}}^- | 0 \rangle (E_0 - q - E_{\mathbf{k}+q})
\end{equation}

We introduce the second quantization language. Also the $|0\rangle$ state includes two independent states which are the electron state and the phonon state. The operators require that

\[ [a_{\mathbf{q}}, a_{\mathbf{q}}^-] = 0, [a_{\mathbf{q}}, a_{-\mathbf{q}}^+] = \delta_{-\mathbf{q}, \mathbf{q}} \{ C_{\mathbf{k}^i}, C_{\mathbf{k}^j}^+ \} = \delta_{\mathbf{k}^i, \mathbf{k}^j}, a_{-\mathbf{q}}^+ a_{\mathbf{q}}^- = n_{\mathbf{q}}, C_{\mathbf{k}+q}^+ C_{\mathbf{k}} = f_{\mathbf{k}} \]

where $n_{\mathbf{q}}$ is the occupation phonon number for the corresponding states and $f_{\mathbf{k}}$ is the occupation number of the electronic states. We use this operator to calculate the energy shift. The energy shift, $\Delta E_0$, becomes:

\begin{equation}
\Delta E_0 = \frac{\alpha^2}{V} \sum_{\mathbf{k}^i} q^{1/2} f_{\mathbf{k}} (1 - f_{\mathbf{k}+q}) \left[ \frac{n_{\mathbf{q}}}{E_0 + q - E_{\mathbf{k}+q}} + \frac{1 + n_{\mathbf{q}}}{E_0 - q - E_{\mathbf{k}+q}} \right]
\end{equation}

The energy of entire system due to the e-ph interaction is

\[ E_{\text{Tot}} = \sum_k E_k f_{\mathbf{k}} \]

\[ + \sum_q n_{\mathbf{q}} w_q + \frac{\alpha^2}{V} \sum_q \frac{1}{2} f_{\mathbf{k}+q} \left[ \frac{n_{\mathbf{q}}}{E_0 + q - E_{\mathbf{k}+q}} + \frac{1 + n_{\mathbf{q}}}{E_0 - q - E_{\mathbf{k}+q}} \right] \]

The first two terms are the unperturbed electron and phonon energy. The third term is related only to the interaction. We can also produce the electron-electron(e-e) interaction due to the electron-phonon(e-ph) coupling for the superconductivity by using the electron energy renormalization with occupation number changed. This e-e interaction is small compared the e-ph attractive interaction. So we can derive the effective mass and the resistivity by using the e-ph interaction only. In this work we investigate this
e-ph interaction by using Feynman path integrals with molecular dynamics. The total electron energy with the second order term includes the unperturbed total energy and the interacting energy. The second order term in equation (3.9) is determined by the ion displacement in real space due to the insertion of one electron into an ionic crystal model.
CHAPTER 4

CLASSICAL COMPUTATIONAL METHOD

4.1 Classical Molecular Dynamics

There are three approaches that can be adopted to try to understand nature: these are respectively, a theoretical, experimental, and numerical approaches. We have adopted a computational numerical method in order to determine the physical properties of high Tc superconductors. Here we study the crystal structures and their relation to the pair interatomic potentials with the method of Molecular Dynamics (MD). The best way to study time dependent fluctuations away from the equilibrium positions and momentums in the crystal is to employ MD. MD in our model is used to solve the Newtonian equation of motion of a classical many body system. Since the computer capacity is limited, we model only a finite number of interacting particles in the simulation cell (about 100 to 1000 particles), and apply periodic boundary conditions to reduce surface effects and mimic a bulk system. Thus, energy fluctuations and many other physical properties in dynamics due to the time variations in real crystals are computed by the MD technique. Historically, the MD technique was developed in 1957 by Alder and Wainwright[46] to study of the motion with time of an n particle system. MD was recently modified by Parrinello and Raman[48] to achieve isothermal and isobaric conditions in order to simulate systems of variable changing shape and size. To begin, let us give some background on the MD method.

A simulation cell is defined in three dimension by three variable vectors \( \vec{a}, \vec{b}, \vec{c} \) referred within a fixed cartesian coordinate system. The cell volume is then \( \Omega = \vec{a} \cdot (\vec{b} \times \vec{c}) \). And the system consists of N particles in a simulation cell that is periodically repeated.
to fill all space. A position \( \bar{r} \) is given by \( \bar{r} = h \cdot \bar{s} \), where \( h \) is a matrix formed with the coordination of \([\bar{a}, \bar{b}, \bar{c}]\). The \( i^{th} \) particle and column vector \( s_i \) is represented by components \( \xi_i, \eta_i, \) and \( \zeta_i \) as
\[
\bar{r}_i = h \cdot \bar{s}_i = \xi_i \bar{a} + \eta_i \bar{b} + \zeta_i \bar{c}
\] (4.17)

where \( 0 \leq \xi_i, \eta_i, \) and \( \zeta_i \leq 1 \). Since the Newtonian equations in classical statistical mechanics of well defined system is
\[
m_i \ddot{r}_i = -\sum_{j \neq i} \frac{1}{r_{ij}} \frac{d\phi_{ij}(\bar{r}_{ij})}{dr_{ij}} r_{ij}
\] (4.18)

where the potential energy of the system is often approximated as a sum of pair interaction terms, \( \phi_{ij}(\bar{r}_{ij}) \), as:
\[
V_N = \frac{1}{2} \sum_i \sum_j \phi_{ij}(\bar{r}_{ij})
\]

In these equations \( r_{ij} = |\bar{r}_{ij}| = |\bar{r}_i - \bar{r}_j| \). The equations of motion are solved by numerical methods. Introducing a variable system of coordinates \((\bar{a}, \bar{b}, \bar{c})\), we write
\[
r_{ij}^2 = [h(s_i - s_j)]^T [h(s_i - s_j)] = (s_i - s_j)^T G (s_i - s_j)
\] (4.19)

where the metric tensor \( G = h^T h \) and \( h^T \) stands for the transpose of \( h \). We may write the Lagrangian of that system in the form:
\[
L = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{s}_i^T G \dot{s}_i - \sum_{i=1}^{N} \sum_{i<j}^N \phi(r_{ij}) + \frac{1}{2} W T \gamma \dot{h}^T \dot{h} - p\Omega
\] (4.20)

where \( p \) is an external applied pressure, and \( W \) has dimension of mass. This mass may represent the inertia of the borders of the simulation cell. This mass affects the dynamics of the cell volume and is related to the relaxation time for recovery from the imbalance between internal and external pressures. In the above equation, the first and third terms are the kinetic energy of the particles and borders of the cell, while, the second and fourth terms are related to the potential energy. The equations of motion are derived from the Lagrangian and given in the form:
\[
\ddot{\bar{s}}_i = -\sum_{i \neq j} \frac{1}{m_i} \frac{\phi'}{r_{ij}} (\bar{s}_i - \bar{s}_j) - G^{-1} \dot{G} \dot{s}_i
\] (4.21)
where the matrix tensor $\pi$ represents the internal stress:

$$\Omega \pi = \sum_i m_i \ddot{u}_i \ddot{v}_i - \sum_i \sum_{i<j} \frac{\phi'}{r_{ij}} r_{ij}^2$$

(4.23)

$\phi'$ is defined as $\frac{d\phi_i(r_{ij})}{dr_{ij}}$ and $\sigma = \Omega(h^T)^{-1}$

Note that when the MD simulation cell shape and size are independent of time ie constant, $\dot{G} = 0$.

The Hamiltonian for this system is

$$H = \sum_i \frac{1}{2} m \dot{u}_i^2 + \sum_i \sum_{i<j} \phi(r_{ij}) + \frac{1}{2} WTr\dot{h}^T h + p\Omega$$

where the internal energy is

$$E = \sum_i \frac{1}{2} m \dot{v}_i^2 + \sum_i \sum_{i<j} \phi(r_{ij})$$

Therefore to a small error of $\frac{1}{2} WTr\dot{h}^T h$, the enthalphy is $H = E + p\Omega$ and the simulation is conducted in the isobaric-isoenthalpic ensemble. The equations of motion are solved numerically with a finite difference scheme. The time integration step, $\Delta t$, for a molecular dynamics simulation is on the order of $10^{-15}$ second or approximately 0.01 of the period for an atomic vibration.

### 4.1.1 Pair Potential

Before discussing the detailed study of the interatomic potential, we explain how the calculation is initiated. The Lagrangian for the set of N particles with the interacting potential is roughly

$$L(\vec{r}, \vec{v}) = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{v}_i^2 - V(\vec{r}_1 \cdots \vec{r}_N)$$

(4.24)

where $\vec{r}$ is a position vector, $\vec{v}$ is velocity vector, and $V(\vec{r}_1 \cdots \vec{r}_N)$ is the interacting potential energy of N particles. This energy is considered to depend on position only.
Two assumptions are introduced in order to simplify the numerical calculations. One is that we assume a pair potential such that the interaction between two particles $i$ and $j$ is not affected by the fact that $i$ interacts with another particle $k \neq j$. This assumption limits the model to two body interactions, hence the total potential energy written as a sum over all pairs is

$$V(\vec{r}_1 \cdots \vec{r}_N) = \sum_{\text{pairs} ij} \Phi_{ij}(\vec{r}_i \vec{r}_j)$$

where $\sum_{\text{pairs} ij}$ is $\frac{1}{2} \sum_{i} \sum_{j}$ with $i \neq j$ or which may be replaced by $\sum_{j > i} \sum_{i=1}$. The other assumption is the spherical symmetry of the interactions between the particles, that is the pair interactions depend only the magnitude of the distance between particles. Hence the total potential energy becomes

$$V(\vec{r}_1 \cdots \vec{r}_N) = \sum_{j > i} \sum_{i=1} \Phi_{ij}(|\vec{r}_{ij}|).$$

For evaluating the interatomic potential, we can choose from the many different theoretical potential models. For example a hard sphere, Morse, and square well potentials are empirical potentials while Lennard-Jones, Buckingham, and Born-Huggins-Mayer potentials are semiempirical models. For our molecular dynamics simulation of ionic crystal, We employ an ionic potential model. In 1960, Fumi and Tosi[49] applied the Born-Huggins-Mayer interionic potential for simple alkali halides and we will use their data for testing our computer program later. In this model of ionic bonds each ion is represented by a point charge and the interaction between two ions is described by a long range Cololumb interaction $V(\vec{r}_{12}) = \frac{e_1 e_2}{r_{12}}$ where the point charges are $e_1, e_2$. The Born-Huggins-Mayer potential also describes the interaction between ions at short distances and an attractive Van der Waals term. Thus this potential contains 3 terms. First is the Coulombic interaction which we already mentioned. The second is a core-core repulsion which is a short range repulsion decaying exponentially with distance. The third term is a Van der Waals attraction formed as:

$$\frac{e_{ij}}{r_{ij}^6} - \frac{d_{ij}}{r_{ij}^8}$$
describing the dispersion forces. The second of the Van der Waals terms will be neglected because of its very small contributions to the total energy. The final total pair potential in the Born-Huggin-Mayer model is written in the form

\[ V = \frac{Z_i Z_j e^2}{4\pi \varepsilon_0 r_{ij}} + A_{ij} e^{-\frac{r_{ij}}{r_0}} - \frac{c_{ij}}{r_{ij}^6} \]  

(4.25)

which is the sum of a long range coulombic term, a short range core-core repulsion, and a short range Van der Waals attractive term. Here \( r_{ij} \) is the distance between ion i and j, \( Z_{ij} \) is the ionic charge, and \( c_{ij} \) is a Van der Waals coefficient. The exponentially decaying repulsive term is composed of two parameters, \( A_{ij} \) and \( \rho_{ij} \) which are characteristic of the size and hardness of the interacting ions. The detailed calculation for the alkali halide is given in the Fumi and Tosi paper[49]. We employ the Ewald method for the summation of the long range Coulombic forces. The basic idea of the Ewald method is to approximate the Coulomb interaction as a short range interaction. The main concept used is that if ions are spherically symmetric, the electrostatic potential at one ion 'i', due to all other ions in the system can be written as the sum of two terms:

\[ \varphi = \varphi_1 + \varphi_2 \]

where \( \varphi_1 \) is the potential resulting from Gaussian charge distributions at each ionic site except at the reference site \( i' \). \( \varphi_2 \) results from the point charges with superposed Gaussian distribution with opposite charge excluding the reference point. The first term can be efficiently calculated in reciprocal space while the second is readily calculated in real space. The potentials \( \varphi_1 \), and \( \varphi_2 \) depend on a parameter characterizing the width of the Gaussian distribution while their sum does not. The coulomb potential is rewritten as

\[ \varphi = \frac{1}{\varepsilon_0 \Omega_0} \sum_k e \frac{\omega^2}{k^2} \sum_j q_j e^{-ik(\mathbf{r}_i - \mathbf{r}_j)} \]

\[ - \frac{q_i \eta^2}{2\varepsilon_0 \pi^2} + \frac{1}{4\pi \varepsilon_0} \sum_{\text{all cells } i \neq j} \frac{q_j \text{erfc}(\eta r_{ij})}{r_{ij}} \]  

(4.26)

where \( \Omega_0 \) is the cell volume and \( V \) is the desired total potential of the reference ion i in the field of all the other ions in the crystal. The first term in the equation is a reciprocal
space term and the last two term are real space contributions. The value of the width parameter $\eta$ most often used for all our simulations is

$$\frac{5.6}{L_{\text{max}}}$$

where $L_{\text{max}}$ is the longest edge of the simulation cell. With that value for $\eta$ the contribution of the first term is within the noise level of the numerical calculation. A more detailed description of this method can be found in Kittel[50].

### 4.1.2 Periodic Boundary Conditions

Since the number of particles in the simulation cell volume $\Omega$ is in the range of 100 to 1000, the periodic boundary conditions (PBC) described by Teller[51] is needed to embed the system in an infinite, homogeneous medium with the same macroscopic properties (such as temperature and pressure). This method avoids surface effects inherent to small clusters. The PBC consists of conserving and restricting the $N$ particles in the cell volume and to repeat this volume periodically in all directions. Also the particles in a simulation cell interact with the particles in the image cells (periodic cells) and the total number of cells in 3 dimension is 27 cells. Thus the potential energy in the cell becomes

$$V = \sum_{a=-1}^{1} \sum_{b=-1}^{1} \sum_{c=-1}^{1} \sum_{j>i} \Phi([r_i - (x+aL_x, y+bL_y, z+cL_z)] - [r_j - (x+aL_x, y+bL_y, z+cL_z)])$$

where $a, b, c \pm 1, 0$. $L_x, L_y, and L_z$ are the length of the edges of the cell. Since it is possible for the reference particle to interact only with image particles in an adjacent image cell, the radial distance for the interaction is restricted by the length of the simulation cell. This suggests that the potential would be zero outside a cut-off range of about $\frac{1}{2}$ the minimum length of the cell. See Fig 2. Therefore the total potential with PBC and the cut-off range of interaction, $R_i$, is:

$$V_c = \sum_{\text{Totalpairs}} A_{ij}(r_{ij})\Phi_{ij}(r_{ij})$$

with
\[ A_{ij} = 1 \quad \text{if} \quad r_{ij} < R_i \]
\[ 0 \quad \text{if} \quad r_{ij} > R_i \]

The time consuming part of computing the MD method reside in the calculation of forces between interacting particles. We employ an update process to reduce running time. The 'update' is necessary to optimize the calculation of interacting forces. The reference particle interacts with a restricted list of neighboring particles within a cutoff range, \( R_c > R_i \). As time goes on, the particles are moving in the cells and some of interacting particles move outside the cutoff range from the reference particle, only those particles have to be traced.

If any particle moves more than some specified distance, \( \delta \), since the last update, the list of neighbors of all particles is updated. \( \delta \) is defined by
\[ \delta = \frac{R_c - R_i}{2} \]
where \( R_c \) is the cutoff range and \( R_i \) is the interacting range. An additional PBC constraint is that the total number of particles in the simulation cell is conserved.

The simulation is conducted at constant temperature. That is, we use the classical relation between the total kinetic energy and the temperature such as:
\[ k_e = \frac{1}{2} \sum_{i=1}^{N} m v_i^2 = \sum \frac{p_i^2}{2m} = \frac{3NkT}{2} \]
We artificially by couple the system with a heat bath adding or subtracting momentum for the particles. This method is identical to the momentum rescaling method of Woodcock[52].

4.2 Calculation of Properties

4.2.1 Average Properties

In order to calculate the average properties from the MD trajectories, \( \bar{r}(t), \bar{\rho}(t) \), we define the average over same microscopic function \( X(\bar{r}(t), \bar{\rho}(t)) \). If \( X(t) \) is the time evolution of
a property $X$ (which depends on the position and momenta of particles along their trajectory), then thermodynamic averages are calculated as time averages in the form

$$< X > = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau X(t) dt.$$  

For the computer calculation using a finite number discrete, $n$, of time steps, along the trajectory their integral is represented by the sum:

$$< X > = \frac{1}{n} \sum_{i=1}^n X_i$$

In all simulations, the early period is discarded for time averaging because it corresponds to a transient period. The time averages have been only calculated after equilibrium has been reached.

4.2.2 Dynamical Properties

In order to find the vibrational spectra, we follow the atomic motion during the simulation. The Wiener-Khintchine theorem[53] connects the correlation function and the spectral density; if the velocity, $v(t)$, is the variable, the normalized velocity autocorrelation function is

$$C(\tau) = \frac{\langle \sum_{i=1}^N v_i(\tau)v_i(0) \rangle}{\langle v_i^2(0) \rangle}$$  (4.29)

And the Fourier transform of $C(\tau)$ is

$$S(\omega) = \int d\tau \cos \omega \tau \quad C(\tau)$$  (4.30)

where $S(\omega)$ is called the spectral density or power spectrum of random process $v(t)$. The dynamical properties depends strongly on the mass of the constituent of the system.
CHAPTER 5

RESULTS

5.1 Computational Results

5.1.1 Ionic model for $Ba_{1-x}K_xBiO_3$

The molecular dynamics method is one of the best tools for obtaining macroscopic properties of classical particle dynamics using appropriate interatomic potentials. The use of realistic interatomic pair potentials is critical for the generation of satisfactory MD results. For computational convenience, we have used central, pairwise additive interionic potentials to describe the interactions between ions in the cubic bismate perovskites. The interaction between an ion 'i' and another ion 'j' is modeled with a pair potential of the Born-Mayer-Huggins type as we already mentioned.

For the simulation of the $Ba_{1-x}K_xBiO_3$ lattices, the cation-cation short range interaction: Ba-Ba, K-K, Bi-Bi, Ba-K, Ba-Bi, K-Bi have been neglected. The charges on the ions Ba, K and O are taken as +2, +1 and -2, respectively. The charge on the Bi is adjusted with the potassium composition to balance the net charge of the lattice. The three parameters for the oxygen-oxygen short range interaction have been taken from quantum mechanical calculations[54]. The Ba-O parameters we have used are variations of the parameters for the oxide BaO [55]. The Van der Waals coefficients for all cation-cation interactions are set to zero.

The remaining parameters for the Bi-O and K-O bonds have been determined empirically by fitting the lattice parameters and interionic distances of the models to
experimental values.

To avoid artificial fluctuations of the shape of the simulation cell resulting from its small size, the edges of the cell were constrained to stretching only. From the Hamiltonian in MD theory, the total energy is the sum of the kinetic and potential energies of the set of particles, the kinetic energy of the borders of the simulation cell to which is artificially assigned a mass W. We set the mass of borders as \(10 \, m_{ox}\) (oxygen mass) to be light enough to give fast equilibrium. All physical properties are calculated in a computationally convenient system of units as: oxygen mass = 1.0, unit time = \(\sqrt{\frac{m_{ox} L^2}{E}}\), unit length \(L = 1\) Å, and unit energy \(E = \frac{e^2}{4\pi\epsilon_0 10^{-19}} = 2.303 \times 10^{-18} J = 14.4\) eV. The summation of the long-range coulombic forces and potential energy is conducted efficiently by the Ewald method [50]. This method is incorporated into MD algorithm to accelerate the convergence as we mentioned in the theory (4.1.1). All simulations in this study have been performed with the following set of conditions for the Ewald summation: the value of \(\eta\) was set at \(\eta = \frac{5.8}{L_{max}}\), the real space summations and reciprocal summations have been truncated at \(r_c = \frac{1}{2} L_{min} + 0.5\) Å and \(k^2 = 25 \times 4\pi^2\) as reciprocal wave number, respectively. \(L_{max}\) and \(L_{min}\) are the longest and shortest edges of the simulation cell. With these parameters, the contribution of the part of the total potential energy and force calculated on reciprocal space is within one hundredth of the contribution of the real space.

Initially we started with a \(BaBiO_3\) system containing 240 particles in a tetragonal simulation cell and then the \(Ba_{0.75}K_{0.25}BiO_3\) and \(Ba_{0.6}K_{0.4}BiO_3\) systems consisting of 320 particles in a cubic simulation cell. The greater the number of particles, the more realistic is the model, but we were limited to those numbers due to the computational time and space available. The compositions \(x=0.25\) and \(x=0.40\) are modelled by substitution of 16 and 26 Ba ions by K ions. In both cases the K ion are distributed randomly but uniformly on the Ba sites. The equations of motion of the ions and boundaries of the simulation cell were numerically integrated with a finite difference scheme. We used a time integration step of \(2.68 \times 10^{-15}\) sec which is based on the lightest atom in the simulation (oxygen mass). We used interatomic potentials and simulation environment
different from the work of Loong et al[14]. They have used effective interparticle interactions which include core repulsions between atoms, coulomb interaction due to charge transfer and charge dipole interactions to describe the polarization effect as well as bond angle dependent interactions. In contrast to the work of Loong et al. we have not used steric constraint in our model and the best sets of parameters are listed in Table 5.1.
5.1.2 Computational Results and Discussion

Structural properties

Before the computer simulation is started, the system must be set up with some initial configuration in the simulation cell. We used the experimental lattice parameter to determine the initial positions of the particles. The simulation of the $BaBiO_3$ tetragonal system was stabilized in about 20,000 time steps ($5.4 \times 10^{-11}$ sec). Since as shown in Table 5.2 the electron negativity differences between Bi and O are not very large, the system may be affected by covalent behavior. The simulations indicated that there were unstable atomic sites in the cell. We tried many different empirical ionic potential parameters, but we could not stabilize the $O_1$ ion in the xy plane or the $O_2$ along the z-axis at their equilibrium atomic sites in $BaBiO_3$. We believe that this may be covalent due to the each of covalent bonding in our crystal since bonding can not be simulated with a purely ionic model. By contrast the $BaBiO_3$ crystal has been successfully simulated by Loong et al. within an ionic model plus directionally restricted forces to mimick the covalent bonding.

The stability of $Ba_{1-x}K_xBiO_3$ with $X=0.25$, and $X=0.40$ cubic bismuth compounds at room temperature within a purely ionic model was verified in simulations lasting the same amount of steps as $BaBiO_3$. The cubic lattices were found to be stable and only vibrational processes about well defined lattice sites were observed. The lattice parameter of the two model compositions $a(x = 0.25) = 4.3030 \pm 0.0021$ Å and $a(x = 0.40) = 4.294 \pm 0.0021$ Å were fitted to the experimental values of '4.3030' [8] and '4.2932' [56]. Bond lengths between Bi-O, K-O, and Ba-O in Table 5.3 were also fitted with experimental results [23]. We calculated bond lengths from the atomic positions in a cell and we chose the experimental values of $Ba_{6.8}K_4BiO_3$ from the lattice parameter. There were some differences due to some distortion in the simulated structure. $Ba_{6.8}K_4BiO_3$ was also simulated at a temperature of 100 K for 20,000 steps. The lattices parameter at this low temperature is $a(x=0.40$ at $T = 100$ K) $= 4.287 \pm 0.002$ Å by our
Table [A]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Zi</th>
<th>$A_{io^2}$-(eV)</th>
<th>$\rho_{io^2}$-(Å)</th>
<th>$C_{io^2}$-(eVÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>+2</td>
<td>1,252.8</td>
<td>0.350</td>
<td>0.00</td>
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<tr>
<td>K</td>
<td>+1</td>
<td>1,195.2</td>
<td>0.310</td>
<td>0.00</td>
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<td>+4.25</td>
<td>2,016.0</td>
<td>0.353</td>
<td>0.00</td>
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<tr>
<td>O</td>
<td>-2</td>
<td>22,764.3</td>
<td>0.149</td>
<td>20.37</td>
</tr>
</tbody>
</table>

Table [B]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Zi</th>
<th>$A_{io^2}$-(eV)</th>
<th>$\rho_{io^2}$-(Å)</th>
<th>$C_{io^2}$-(eVÅ)</th>
</tr>
</thead>
<tbody>
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<td>1,252.8</td>
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<td>0.00</td>
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<td>-2</td>
<td>22,764.3</td>
<td>0.149</td>
<td>20.37</td>
</tr>
</tbody>
</table>

Table 5.1: Parameters used in the rigid-ion model of $Ba_{1-x}K_xBiO_3$. A and B stand for the composition $X = 0.25$ and $X = 0.40$, respectively.
calculation. From our calculation, the temperature dependence of the lattice parameter is given in a linear form as $a(A) = 3.5 \times 10^{-5}T(K) + 4.284$. The calculated linear expansion coefficient agrees very well with experimental values [57]. Even though there is some covalent contribution to the Bi and O interaction, these results demonstrate that contrary to previous models [14], high Tc bismates can be stabilized within a purely ionic model and do not require necessarily bond-bending restrictions.
Table 5.2: Relative electronegativities of each element in $Ba_{1-x}K_xBiO_3$.

Vibrational properties

We have used these models to calculate anisotropic vibrational spectra of individual atoms. The vibrational spectrum of a selected ion is calculated by Fast Fourier transformation of the ion's normalized velocity autocorrelation function [58] which was referred to the theory section. The velocities of Ba, K, Bi and O ions have been followed during long simulations (10,000 integration steps) at room temperature for different K environment. The vibrational density spectra were calculated from ions located near the center of the simulation cell to avoid any artifact that may be induced by periodic boundary conditions. The projection of the normalized spectra along the cubic directions of the simulation cell are shown in Figs. 3 and 4 for the potassium compositions, $x = 0.25$ and $x = 0.40$. The spectra for the composition $x = 0.25$ presents no significant difference with the composition $x = 0.40$. The lower energy vibrational modes of the bismate models (below 120 cm$^{-1}$) are dominated by contributions from the Ba and K ions, as well as some contribution from Bi. In this case, we have the same behavior as reported for $BaPbBiO_3$ by Winfried Reichardt et al[59]. $BaPbBiO_3$ is produced by doping $BaBiO_3$.
### Table [A]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Calculated (Å)</th>
<th>Observed (Å)</th>
<th>Difference (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-O</td>
<td>3.046</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K-O</td>
<td>3.090</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bi-O</td>
<td>2.208</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

### Table [B]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Calculated (Å)</th>
<th>Observed (Å)</th>
<th>Difference (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-O</td>
<td>3.026</td>
<td>3.022</td>
<td>+0.004</td>
</tr>
<tr>
<td>K-O</td>
<td>3.085</td>
<td>3.022</td>
<td>+0.063</td>
</tr>
<tr>
<td>Bi-O</td>
<td>2.200</td>
<td>2.137</td>
<td>+0.063</td>
</tr>
</tbody>
</table>

Table 5.3: Cation-anion distances in $X = 0.25$ (A) and $X = 0.4$ (B), $Ba_{1-x}K_xBiO_3$. 

with Pb on the Bi sites instead of Ba in $BaKBiO_3$. Both $BaPbBiO_3$ and $BaKBiO_3$ have many similar physical properties. The low frequency peaks at 100 and 150 $cm^{-1}$ measured by Reichardt are similar to low frequency cation vibrations of our simulation. Moreover our results agree with Loong et al[14], except the Bi mode. The Bi mode from Loong’s data showed that the peaks are lower than 20 meV($160 cm^{-1}$) in contrast to vibration of up to 200 $cm^{-1}$ from our simulations. Note that their results ignore the anisotropic effect in contrast to ours considering anisotropic contributions to the vibrational spectra. The high density of very low frequency vibrational modes of the Ba ion near 80 $cm^{-1}$ is in very good agreement with the acoustic modes dispersion curves for BaO[60]. All peaks below 140 $cm^{-1}$ in $BaPbBiO_3$ reported by W. Reichardt et al., are claimed to arise from acoustic phonons. From their claim, the peaks below 140 $cm^{-1}$ in our model of BKBO may possibly be acoustic mode, as well.

The very high energy modes are essentially associated with oxygen vibration. The anisotropy of the oxygen vibration is noteworthy. The oxygen ion exhibits vibrational modes at about 610 and about 800 $cm^{-1}$ parallel to the Bi-O bond while modes of vibration perpendicular to the Bi-O bond cover a wide interval of frequencies from 150 to 600 $cm^{-1}$. The density of vibrational modes of the oxygen ion depends on the potassium environment. The oxygen density of state with frequency 800 $cm^{-1}$ may decrease from 60 % to 25 % relative to the density at 610 $cm^{-1}$ depending upon the potassium environment. The proximity of potassium ions to the oxygen favor the high frequency modes. The larger the number of K neighbors, the higher the density of states at 800 $cm^{-1}$. This feature may be arising from a tighter BiO bond resulting from the substitution of the $Ba^{2+} - O^{2-}$ bonds by the weaker $K^{+} - O^{2-}$ Coulombic attraction. We clearly know that the doping potassium ion softens and broadens the peak from BaBiO3. Loong et al[14]. observed about 5 meV ($40 cm^{-1}$) softening and broadening of this oxygen mode. The phonon density of states of the oxides in $BaPbBiO_3$ has been measured by Masaki et al[61] by using inelastic neutron scattering. Their data also show that the phonons above 300 $cm^{-1}$ in the superconductor of $BaPb_{75}Bi_{25}O_3$ softened and broadened in comparison with $BaPbO_3$ or $BaBiO_3$. 
Assuming that the internal vibrational modes of the BiO$_6$ octahedron may be separated from the internal modes of the perovskite[62], the high frequency oxygen vibrational mode can be ascribed to a stretching mode of the BiO$_6$ octahedron and the lower frequency oxygen vibrational modes to a bending mode of the octahedron. This observation is in accord with the infrared absorption spectra of BaBiO$_3$ which exhibit bands at 265 and 440 cm$^{-1}$ associated with the bending and stretching of BiO$_6$ octahedron, respectively [63]. And according to infrared experiments from P. Ganguly et al[64], the related perovskite, La$_2$CuO$_4$, has optical phonons of the stretching modes of O atoms at higher frequency. It is, however, necessary to keep in mind that rigid-ion models like ours, because they neglect ionic polarizability, give rise to longitudinal optical (LO) modes which are a little high and longitudinal optical mode - transverse optical mode splittings which are large [65]. One, therefore, expects that the frequency of the BiO bond-stretching may be overestimated in comparison with our experimental results to be presented in the next chapter.

The effect of temperature on the vibrational properties of the $Ba_{0.6}K_{0.4}BiO_3$ compound was also investigated. We calculated the vibrational spectra of the selected ions at 100 K. The results are shown in Fig 5. These density of state exhibit sharper well defined peaks as the effect of anharmonicity decreases with temperature. The frequencies of the oxygen vibrations along the BiO bond are 600, 700 and 820 cm$^{-1}$. The modes perpendicular to the BiO bond modes have frequencies of 100, 170, 240, 330, 390, 500 and 610 cm$^{-1}$. We calculated the total phonon density of state for $Ba_{0.6}K_{0.4}BiO_3$ by compounding the individual ion vibrational spectra. (See Fig 4). At 300 K, there are three dominant features: a high density peak at 150 cm$^{-1}$, a broad band extending from 210 to 370 cm$^{-1}$ and a peak about 610 cm$^{-1}$. Other peaks with lower density of states are present at 475, 700 and 800 cm$^{-1}$. The experimental phonon density of state by Neutron scattering [14] and Raman scattering [15] show a shoulder at approximately 130 cm$^{-1}$. Two broad peaks at 240 and 485 cm$^{-1}$ are shown by Loong et al[14]. and two broad peaks at 375 and 573 cm$^{-1}$ are shown by McCarty et al[15]. In tunneling measurements[38], the expected spectrums are observed between 40 meV and 65 meV.
Also, from our IR data reported in the next section, we observe vibrational activities between 380 and 750 cm\(^{-1}\). Allowing for a little over estimates of the high frequency density of states in our ionic model, qualitative agreement with experimental data seems to have been achieved in the MD model.

Decreasing the temperature from 300 K to 100 K lowers the density of states at low energies and increase the density of states of the high energy modes by approximately 25 % and do not show any unusual temperature dependence like YBaCuO material. This behavior is the same as BaPb\(_{75}\)BiO\(_3\). The spectral shape was not changed over the temperature range (60 to 300 K) except for a tendency to move toward lower values reported as Lyons et al [66].

We also studied isotope effects. The isotope atoms which we used are oxygen \(O^{16}\) replaced by \(O^{18}\). We replaced O 16 by O 18 for all 192 oxygen atoms in our simulation cell. The mass ratio for oxygen in our material is smaller than for any other atomic isotope ratio. Thus the oxygen contribution to the shifted spectrum should be more effective because of the suspected phonon mediate behavior due to oxygen bismuth (BiO\(_6\)) vibrational mode. The results of the isotope effect on vibrational spectra are shown in Fig 6. The energy spectrum shows that vibrational modes of Ba, K are not much changed, however, vibrational modes of Bi and Ox are softened and the density of states of Ox is changed between 400 cm\(^{-1}\) and 600 cm\(^{-1}\). The isotope effect in a bismate high Tc superconductor is related with the optical modes of the oxygen phonon according to Loong et al[14].

5.2 Experimental Results

We prepared two set samples, BaBiO\(_3\) and Ba\(_{6.6}\)K\(_4\)BiO\(_3\) by using two different techniques. The low density sample of BaBiO\(_3\) was made by a sintering technique[67]. While the high density sample of Ba\(_{6.6}\)K\(_4\)BiO\(_3\) was made by melting processing technique[68]. The color of BaBiO\(_3\) is dark brown, while the color of Ba\(_{6.6}\)K\(_4\)BiO\(_3\) becomes dark bluish.
The crystal structure of $Ba_{1-x}K_xBiO_3$ was determined by powder X-ray diffraction. We used the Bragg-Brentano X-ray diffraction method with CuKα radiation. By using this standard $\theta - 2\theta$ diffractometer, we can measure the sample by fixing the angle $\theta$ of the sample and scanning through $2\theta$ of scattering beam. The measurement was made with an X-ray wide film Debye-Scherrer camera as explained in the book by Cullity[69]. A resolution function with a full width at half maximum (FWHM) of the peak is observed and calculated for a distribution of crystal orientations. The diffractions are shown in Figs 18, and 19. In Fig 18 we scanned angles from 28 to 42 degrees of $BaBiO_3$ because the spectrum in this region is of the highest intensity with 1st order and 2nd order peaks. We also determined the lattice parameter and structure by comparing our data with the card number 35-1020 of the "international centre for diffraction data "[70]. In $Ba_{0.6}K_{0.4}BiO_3$, we measured angles from 20 to 80 degrees and compared our results (Fig 19) with the data of Hinks et al[21]. and Fleming et al[57]. From their analysis, we calculated the lattice parameter. The lattice parameter in our calculation is $4.279 \pm 0.0005 \text{Å}$. This parameter agrees fairly well with Hinks et al[21]. We then studied the infrared properties. IR is good for direct measurement of the phonon vibration spectrum. The experimental measurements are shown in Fig 21. In order to measure the IR spectrum, we prepared the sample pellets by the following method:
(1) we grounded the dark brown sample of $BaBiO_3$ to a granular size of about 500μm and mixed it with Polyethylene powder. The composition of sample is about 5% $BaBiO_3$ and the rest is Polyethylene powder. Then we compressed the sample by about 8 kbar to make the pellet. The size of the pellet is 13 mm in diameter. This sample displays non-conducting behavior so we used the transmission IR measurement technique.
(2) we put the dark bluish sample in the jar and put KBr on top of the sample and then pressed with 8 kbar. The pellet has two separate layers: one is the sample layer and the other is the KBr layer. This material reacts easily with organic material, so we handled this material very carefully. Since the KBr powder might be on the face of the sample, we cleaned the surface with sand paper. We measured the IR spectrum soon afterwards because of our concern regarding reaction with KBr. We controlled the thickness of the sample layer to about 0.5 mm in order to prevent any transmission of
light through the sample. Since there are no peaks for KBr in the range 250 to 1000 cm$^{-1}$, KBr has no effect on the sample spectrum. We used a Perkin Elmer FTIR 1800 spectrometer to measure the IR spectrum. Fig 20 shows the trasmission IR spectrum of $BaBiO_3$. The peaks are at 465, 269, and 152 cm$^{-1}$. This is in agreement with Hair et al[63]. The peak at 465 cm$^{-1}$ is related with the Bi-O stretching mode while 269 cm$^{-1}$ is related with the Bi-O bending mode according to Hair et al. The peak at 152 cm$^{-1}$ is related to the rotational mode of BiO$_6$ octahedra as is reported by Sugai[71]. However our frequencies deviated slightly from their measurement, because we used a different spectroscopic method. We also changed the temperature to 100 K and checked the spectrums. There were no significant differences. Since the potassium doped super­
conductor has a strong conductiviy, we measured the IR spectrum with the reflectivity method. The experimental setup used for the measurement of infrared reflectivity of $Ba_{0.6}K_{0.4}BiO_3$ is shown in Fig 17.

Since the sample is conductive, the light is strongly observed. In order to collect the more light, We use the 2 mirror method(see Fig 17) for the infrared reflectivity measurement. Fig(21.b) shows the IR spectrum of $Ba_{0.6}K_{0.4}BiO_3$ determined by the measurement after the subtraction of the Al mirror background. The mirror position may have slightly changed between measurements of the sample and background,because the mirrors were not fixed. Fig(21.b) shows a magnified portion of the absorption spectrum in Fig(21.a). Because of the conductivity, index of reflection, n, is large near peaks. The dispersion of n is large leading to inflection of curve. We chose the peaks positioned at the inflection due to the conductivity behavior of the sample. The peaks are at 380, 530, 720, 800, and 880 cm$^{-1}$. However the peak at 800 cm$^{-1}$ is very narrow which is unusual. We believe that this peak is due to conduction electron’s thermal effects. The peak at 380 cm$^{-1}$ corresponds to a large transition in absorbed spectrum. This peak is related to the Bi vibration and some portion of oxygen vibrations according to our MD simulation. However this peak differs from McCarty et al[15]. and Loong et al[14]. McCarty reported a broad peak centered about 325 cm$^{-1}$ in the Raman spectrum data, and Loong reported that the peaks are at 240 and 480 cm$^{-1}$ each with neutron scattering
data. Sugai measured IR spectra and reported that peak of $BaPb_{1-x}Bi_xO_3$, which has similar physical behavior as our sample, is at about $325 \text{ cm}^{-1}$. We believed that this peak is related to the stretching mode of Bi-O and is similar to McCarty and Sugai's data. The peak at $530 \text{ cm}^{-1}$ is in agreement with McCarty and is similar to the BaPbBiO material. We believed that the peaks at 720 and $880 \text{ cm}^{-1}$ depend on the anisotropic structure and disorder of the materials. These peaks are not shown in previous papers such as Neutron scattering and Raman measurement. The reason is that these peaks have very small intensity. MD simulation of the anisotropic vibrational spectra matched these peaks. The oxygen vibrations are related to these peaks. We believe that these peaks depend on the oxygen and potassium environments. According to Rosenberg et al[72], the peaks at $900 \text{ cm}^{-1}$ of 1:2:3 type and $630 \text{ cm}^{-1}$ of 2:1:4 type of copper oxides are expected to be the frequency dependent anisotropy. However this peak is not seen in BaPbBiO in Sugai's work[71]. Our experimental results and the vibrational data of MD simulation are in fairly good agreement.
CHAPTER 6

QUANTUM PATH INTEGRAL

6.1 Theoretical Background

Ever since the Dutch physicist, Kamerling Onnes[73], found zero resistivity in Mercury in 1911, the study of superconductivity has been an active topic for research although the BCS theory[34] was not worked out until 40 years after its discovery. Before that time, the study of the electron-phonon interaction has been explored by Landau and many others in 1930's.

Before the BCS theory, many physicists suspected that the interaction between electrons and phonons was related to superconductivity. Frölich[43] in 1950 tried to explain the relation between the electron-phonon interaction and superconductivity. The basic idea of Frölich was that two electrons were coupled in such a way that they behaved as if there was a direct interaction between them. In this model, one electron emits a phonon which is then immediately absorbed by another. In certain circumstance, this emission and subsequent absorption of phonon could give rise to a weak attraction between electrons. He thought of the interaction between electrons as being a mediated by phonons. Bardeen[42] also published research on the e-ph interaction in a metal. His paper claimed that the long range electron-ion correlations give rise to plasma and to coupled electron-ion waves which correspond to longitudinal sound waves and, at long wavelength, that the e-ph interaction is identical with the e-ph matrix element by using a self-consistent field method. Several years after Bardeen's paper, BCS theory established that the interactions which occur in the superconducting state between any two electrons leads to the formation of a pair of electrons (Cooper pair), which have equal and opposite
momenta outside the Fermi surface. The effect of the presence of all the other electrons on any one pair is to limit, those states into which the interacting pair may be scattered. In contrast to BCS, Eliashberg[74] studied the electron-phonon interaction by using the Green-function method and calculated an electron-phonon coupling constant as

\[ \lambda = 2 \int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega} \]

and

\[ \alpha^2(\omega)F(\omega) = \frac{1}{N} \sum_{q\delta} \left| \frac{\langle 0| \hat{\epsilon}_j(q) \cdot \nabla U | N \rangle^2}{E_0 - E_N} \delta(\omega - \omega_j(q)) \right| \]

where \( U \) is the ionic potential, and \( \hat{\epsilon}_j(q) \) and \( \omega_j(q) \) are the frequency and the polarization vectors of the phonon branch with wave vector \( \vec{q} = \vec{k} - \vec{F} \). This coupling constant is important for the superconductivity and is also an important parameter needed to find the effective mass of polarons in ionic materials and semiconductors. Some groups[76] approached the e-ph interaction by using the path integral introduced by Feynman[77].

In particular, Schultz[79] explained the polaron formation using a path integral with a single electron Lagrangian based on the Frölich polaron theory. A few years ago, Parrinello and Rahman(P&R)[16] developed a program of path integration in MD. They studied an F center in molten KCL using a path integral for the quantum electron. This approach takes advantage of an isomorphism between classical particle representation of the electron and the quantum behavior of that electron. Since the classical trajectories have no meaning in the real dynamics of a quantum system, P&R included equilibrium statistical mechanics with the partition function and the time correlation function in a canonical ensemble of a many body system for one electron in KCL. The electron was substituted for one chlorine and electron localization at high temperature was studied. Since then, many papers have been published which have used path integral techniques; for example such calculation have studied one electron in water molecules[80], in helium atoms[81], and in molecular structure[82] using MD or Monte Carlo methods(MC).
Present quantum path integral (QPI) is another alternate approach to the treatment of the many body problem. One purpose for using the path integral formulation of quantum mechanics, is to relate the equilibrium quantum-many-body theory to classical statistical mechanics. The path integral technique originated with Feynman's paper[77]. Feynman mostly used nonrelativistic quantum mechanics with space-time relations. The density matrix, \( \rho(x, x'; u) \), in the coordination representation is

\[
\rho(x, x'; u) = \int \int \Phi(x(u)) \delta x(u)
\]

where

\[
\Phi(x(u)) = \lim_{n \to \infty} \rho(x, x_{n-1}; \epsilon) \cdots \rho(x, x'; \epsilon)
\]

and

\[
\delta x(u) = \lim_{n \to \infty} dx_1 dx_2 \cdots dx_{n-1}.
\]

A parameter, \( u \), is defined by \( \beta \hbar \) in time units and \( n \epsilon \) is equal to \( u \). Our procedure is based on an isomorphism between quantum path integrals and classical statistical mechanics. This notation employed here is the same as that used by Parrinello and Raman[16]. Now, we use a single quantum electron in an external potential \( \phi(r) \) The canonical partition function is \( Z = \int \rho(x, x') dx = Tr[\rho(x, x')] \)

where the density matrix \( \rho(x, x') \) is given by

\[
\rho(x, x') = \sum_i \phi_i(x') \phi_i^*(x) e^{\beta E_i}
\]

with complete sets \( \phi_i(x') \phi_i^*(x) \), or

\[
Z = Tr[e^{-\beta H}]
\]

where

\[
H = \frac{-\hbar^2 \nabla^2}{2m} + \phi(r)
\]

This path can also be described using only \( p \) configurational states; for this case the quantum partition function goes to the classical partition function. Since the partition function is a trace of the thermal density matrix, a path should begin and end at almost the same point in configuration space. To evaluate this trace, we divide the Boltzmann
factor $e^{-\beta H}$ into $p$ parts and insert $p$ complete sets of states with the partition function.

We also assume that the temperature factor $\beta$ is very small. Using the relation as

$$(e^{-\frac{\beta}{p} H})^p = e^{-\frac{\beta}{p} H} e^{-\frac{\beta}{p} H} \ldots$$

$$Z = \int dr_1 < r_1 | e^{-\frac{\beta}{p} H} e^{-\frac{\beta}{p} H} \ldots | r_1 >$$

In order to calculate this partition function, we assume that the potential depends only on the mean value positions. Then the partition function\textsuperscript{[16]} is

$$Z = \int dr_1 dr_2 dr_3 \ldots dr_p < r_1 | e^{-\frac{\beta}{p} H} | r_2 > < r_2 | e^{-\frac{\beta}{p} H} | r_3 > \cdots < r_p | e^{-\frac{\beta}{p} H} | r_1 >$$

Let's look at one of the sets and use the relation known as the Trotter product formula (or we assume that this is a very short time and $\beta$ has a very small value as the high temperature approximation)

$$< r_1 | e^{-\frac{\beta}{p} H} | r_2 > = < r_1 | e^{-\frac{\beta}{p} V} + \frac{\beta}{2} \frac{\partial V}{\partial r_2} | r_2 >$$

where $T$ is kinetic energy and $V$ is potential energy.

$$= < r_1 | e^{-\frac{\beta}{p} V} | r_k > < r_k | e^{-\frac{\beta}{p} T} | r_1 > < r_1 | e^{-\frac{\beta}{p} V} | r_2 >$$

$$= e^{-\frac{\beta}{p} V(1)} e^{-\frac{\beta}{p} V(2)} < r_1 | e^{-\frac{\beta}{p} T} | r_2 >$$

$$= \int dP_1 dP_2 < r_1 | P_1 > < P_1 | e^{-\frac{\partial^2}{2mp^2}} | P_2 > < P_2 | r_2 >$$

Where we use the momentum space operator, and momentum states $| P >$ : the detailed derivation is carried out in Baym\textsuperscript{[83]}. Eventually we get the results

$$< r_1 | e^{-\frac{\beta}{p} H} | r_2 > = \left( \frac{pm}{2\pi \hbar^2 \beta} \right)^\frac{3}{2} e^{\left( -\frac{pm(r_1 - r_2)^2}{2\hbar^2 \beta} \right)}$$

Inserting eq (6.36) to eq (6.34) the approximated expression for the partition function is

$$Z = \left( \frac{pm}{2\pi \hbar^2 \beta^2} \right)^\frac{3p}{2} \int dr_1 dr_2 dr_3 \ldots dr_p e^{-\beta V_{ff}(r_1 \cdots r_p)}$$

with

$$V_{ff}(r_1 \cdots r_p) = \sum_{i=1}^{p} \left[ \left( \frac{pm}{2\hbar^2 \beta^2} \right)(r_i - r_{i+1})^2 + \frac{1}{p} \phi(r_i) \right]$$
This is similar to a classical partition function. Here we should know that the classical isomorphism contains ring shaped compounds. That is, the quantum particle may be represented by a necklace such that a point on the necklace interacts with its first neighbors in the chain through a harmonic potential of spring constant \( \frac{pm}{kT\beta^2} \). Using Molecular Dynamics (MD) simulations for the complicated calculation of the quantum mechanical energy or force is generally impossible. However we can use the path integral in MD in order to simplify the phase space of the quantum particle. Note that the closer \( p \) is to infinity, the more accurate is the isomorphism. But the computer capacity is limited, we must use a finite number, \( p \), for the simulation and approximate \( Z \approx Z_p \). Now we can find the kinetic energy and the effective potential energy after we established the isomorphism. Energies are representatived by operators in quantum theory and need to be expressed by the classical expression in the isomorphism. Considering all contributions and \( p \) intermediate states, the total potential energy for a single electron in a crystal is given by

\[
V_{eff} = \sum_{i=1}^{p} \frac{pm}{2\hbar^2\beta^2}(r_i - r_{i+1})^2 + \frac{1}{p} \sum_{i=1}^{p} \sum_{J=1}^{N} \phi_{eJ}(r_i - R_J) + \frac{1}{2} \sum_{I=1}^{N} \sum_{J=1}^{N} \phi_{IJ}(R_I - R_J)
\]

where \( p \) is the number of intermediate states, the \( R_{I,J} \) are the ionic coordinates, \( r_i \) is the electron coordinate, and \( \phi_{eJ} \) and \( \phi_{IJ} \) are the electron-ion and ion-ion interaction potentials. The mean energy for the \( p \) discrete points by using the partition function \( Z_p \) is written as

\[
\langle E \rangle = -\frac{\partial \ln Z_p}{\partial \beta} = \frac{3p}{2\beta} - \frac{pm}{2\hbar^2\beta^2} \langle \sum_{i=1}^{p}(r_i - r_{i+1})^2 \rangle
\]

and the mean square fluctuation in the energy is

\[
\langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = kT^2 C_v(p)
\]

where the electron heat capacity is \( C_v = (\frac{\partial E}{\partial T})_v \). Thus we now have the kinetic energy and potential energy of the electron.

\[
K.E = \frac{3p}{2\beta} - \frac{pm}{2\hbar^2\beta^2} \langle \sum_{i=1}^{p}(r_i - r_{i+1})^2 \rangle
\]
However the numerical disadvantages of a finite number \( p \) for the calculation of mean square fluctuations in the above kinetic energy expression is that it could significantly depend on \( p \). We can rewrite this term for the mean square fluctuation using Hermann\[84\]'s paper. The final kinetic energy becomes

\[
P.E. = \sum_{i=1}^{p} \frac{1}{p} < \phi(r_i) > = < \sum_{i=1}^{p} \sum_{j=1}^{N} \frac{1}{p} \phi_{e,j}(r_i - R_j) >
\]

(6.40)

where the first term is called the free particle kinetic energy and the second term is called the interaction kinetic energy. The latter term is independent of the finite number \( p \) for the calculation of mean square fluctuations. In order to find the kinetic energy, the equation is

\[
\sum_{i,j} \frac{\partial \phi}{\partial r_{ij}} r_{ip}
\]

where \( j \) is an ion and \( i \) is an electron

\[
\frac{\partial \phi}{\partial \mathbf{r}} = \sum \frac{\partial V_{ij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \mathbf{r}}
\]

where

\[
r_{ij} = \sqrt{(x_i - X_j)^2 + (y_i - Y_j)^2 + (z_i - Z_j)^2}.
\]

Therefore the interactive kinetic energy is given by:

\[
\frac{1}{2p} < \sum_{ij} \frac{\partial V(r_{ij})}{\partial r_{ij}} \frac{1}{r_{ij}} r_{ij} > .
\]

This method has been demonstrated by Parrinello and Rahman to possess a better stability.

6.2 Model and Methods

The use of quantum path integrals in Molecular dynamics (QPIMD) is a new technique to study the electron-phonon interaction. QPIMD links the classical problem to quantum dynamics. We have used quantum statistical mechanics with partition functions
detailed in the theory given in the last section. Before we studied the electron-phonon interaction in the high Tc crystals, we first studied an F center in molten KCl as Parrinello and Raman (P&R) did in 1984 [16]. These calculations were performed to check the computer code which we had developed against already published data. We used P classical electrons to represent one quantum electron. The larger the value of P the more accurate the simulation; we used 100 particles which appears to be large enough to fit high temperature approximation and corresponds to optimized computer time and space.

In our model, the potassium and chlorine ions are treated as classical ions at a temperature of 1000 K. The interaction between the ions are modelled through a Born-Mayer-Huggins type potential. The ion potential parameters which we used were given by Sangster et al [85] and are listed in Table B.7. A core radius for the pseudopotential form of the attractive potential between the electron and potassium was taken from Parrinello and Raman [16]. Since this core radius is an important parameter for the pseudopotential following the P&R work we checked the effect of different core radii. We did not employ any core radius for the chlorine-electron interaction at short distance because the core contribution of chlorine is very small with respect to Coulombic repulsion. The interaction between any potassium positive ion and an electron is coulombic with core corrections. The pseudopotential is constructed as

\[ \phi_{e-K^+}(r) = \begin{cases} \frac{-e^2}{r} & r \leq R \\ \frac{-e^2}{R} & r \geq R \end{cases} \]

where R is the core radius. We considered the set of core radii: 1.5, 1.96, 2.5\AA. These variations of the core radius affected the physical behavior of the electron since the interaction in the core has very drastic effects on the total attractive potential. This potential will be slowly varying with r, which favors rapid convergence of the classical isomorphism. We start with a delocalized electron in the cell at the initial configurations set in Fig 7.

We used Periodic-Boundary Conditions (PBC) for all the simulations, subject to
a constant pressure constraint. The Hamiltonian is this model is

\[ H = \sum_{i=1}^{P} \frac{1}{2} m^* \dot{r}_i^2 + \sum_{j=1}^{N} \frac{1}{2} M_f \dot{R}_j^2 + \frac{1}{2} Wf \dot{r}^2 \hat{\mathbf{h}} + p\Omega \]

where \( W, h, p \) and \( \Omega \) were described in the previous theory section and the \( m^* \) is an arbitrary electron mass to be related to the time trajectories and is considered to be merely a computational device to define temperature for the classical electron. \( m^* \) has no physical meaning in our simulation. \( M_f \) is the ion mass, and \( r_i \) and \( R_j \) are the coordinates of electrons and ions respectively. For this calculation we used the chlorine mass as \( M_{cl} = 1.0 \) for the standard mass and set the electron mass to arbitrarily be \( m^* = 0.5M_{cl} \). Initially, we used 215 ions in the molten KCL with 108 \( K^+ \), 107\( Cl^- \), and established charge neutrality by considering one electron \( 'e^-'. \) For the calculation we used 100 \( e^- \) as \( P \) number of classical electrons at 1000 K. We ran the simulation at constant volume. The time step was \( 4.1 \times 10^{-15} \) sec. The initial ion configuration for the simulation was randomized as a liquid state. The cell volume was fixed. Here, the statistical mechanics with this effective potential is performed in microcanonical ensembles. The equilibrium state was reached after several thousand steps and the localization of electron was checked for an additional 2000 time steps.

We used the Ewald method [50] to evaluate the total effective long-range potential between e-K, K-Cl, and e-Cl both within the simulation cell and the image cells. Since the reciprocal space part of the Ewald potential calculation contributer little to the potential we neglected that portion for this calculation.

Most of our study for F-center was based on determining the \( K^+ - e^- \) correlation function, localization of necklace electrons, and the kinetic and potential energy of an electron with fixed \( P \) number. The correlation function which is related to the relaxation of the mean thermal positions away from the positive ions is calculated as:

\[ g_{e-K}(r) = \langle n_e \rangle > [4\pi r^2 \Delta r \frac{N^+}{\Omega}]^{-1} \]
where the \( \frac{N^+}{N} \) is the number density of potassium ion in the system, and \( < n_e > \) is the normalized average number of \( K^+ \) in a shell of radius and thickness \( \Delta r = 0.05\,\text{Å} \) around a point 'i' of interest on the electron necklace. We also found the correlation fluctuation as a function the distance between an electron and a lattice site. The results which represent by are given in Table B.7 and the Appendix B, show that the algorithm Fig 22 works well.

6.3 Electron-phonon in \( BaKBiO_3 \)

After testing our program for the quantum path integral in Molecular Dynamics for the case of an F center in molten KCl, we employed the same algorithm to investigate the electron-phonon interaction in a \( BaKBiO_3 \) crystal. We used the ionic model for \( Ba_{6.8}K_{4.4}BiO_3 \) developed in a previous section, and we insert a closed chain containing P electrons in the system at Room temperature. Given the charge carrier density in this material to be \( 3 \times 10^{21}/\text{cm}^3 \) as measured by Kondoh[30], or \( 4.5 \times 10^{21}/\text{cm}^3 \) by the AT&T group[26], we should set the number of conduction electrons in the MD cell to be about 15 quantum electrons in our volume of \( 5065\,\text{Å}^3 \), but computer space and time limitation imposed restrictions. So we inserted only one electron near the Bi ion centered in the simulation cell and we studied the electron-phonon interaction in the system within a one electron approximation. This one electron approximation is similar to Fröhlich's method[43].

A fundamental difference between this system and the F center studied for molten KCl is that the electrons now are located within a periodic crystal. In order to begin the computer simulation, the ions of the cubic \( Ba_{6.8}K_{4.4}BiO_3 \) were assigned to the same configuration as in previous section and 5000 time steps with integration steps of \( 2.68 \times 10^{-15} \,\text{sec} \) were run to reach equilibrium for the ionic crystal. After that period, a 400 particle necklace electron was inserted within a prescribed bismuth ion in contrast to spreading necklace electrons in molten KCl. When we inserted the one quantum electron, we also subtracted equivalent charges from each of the 64 individual Bi
ions to ensure charge neutrality in the whole system. The charges were subtracted from the bismuth, because the electron will end up concentrated at bismuth ions due to their approximate +4.4 valence charge. We also set the arbitrary electron mass \( m_e = 0.5m_0 \) since this electron mass affected only the classical temperature of the electron. The heavier artificial electron mass yields a slow convergence to the equilibrium state but more accurate trajectories.

The cation-electron interactions are modelled with a pseudopotential. The core radius of K was taken at 1.96 Å in reference to P&R[16], the core radius of Ba was arbitrarily taken at 1.96 Å. The core radius for the Bi was varied between 1.5 and 1.95 Å, because the variation of core radius in Bi may play an important role in the mobility of the electrons. 1.5 Å makes a deep well potential and over 1.75 Å one has overlapping cores between cation neighbors. Although the oxygen core radius exists in nature, we neglected the core corrections for oxygen because of the long-range repulsive interaction between \( e^- \) and \( O^{2-} \).

For the high temperature approximation, we used 400 necklace electrons instead of 100 as in molten KCl, because the temperature is lower and the total energy is bigger than in the case of KCl. The numerical simulations were performed for an electron interacting with ions at room temperature. Parrinello and Rahman[16] claimed that the calculation with over 100 particles in KCl at 1000 K was a reliable number for approximating the partition function \( Z \approx Z_p \) and U. Landman et al[17] used 399 classical electrons at room temperature in their study of solid KCl. Their data show that 400 electrons appears to be a reliable number at room temperature. They claimed that about 200 classical electrons in KCl are a minimum number to achieve relatively stable results from the simulation. A criterion for reliability of a high temperature approximation is \( k_BT \cdot P > \) Coulomb energy. From this, we use an average cation charge '+3' and an average electron-ion distance of 2 Å and find \( P > 833 \) electrons. This number should be taken as an order of magnitude, only. We tested 200, 400, and 500 classical electrons in a cell. We had a little higher potential energy with 200 classical electrons, but we had almost consistent results from 400 and 500 classical electrons in our simulation suggesting
convergence of the isomorphism. Thus, in order to save computer time, we chose 400 necklace electrons for our simulation.

We used the same expression as before for the calculation of the electron kinetic and potential energy. We calculated the standard deviation $\sigma^2$ for the energies as they were calculated for each integration time step. The Hamiltonian in QPIMD is $H = H_{ph} + H_{el} + H_{e-ph}$. In order to find the interaction energy between $e^-$ and phonons, we used a switch mode which controlled the forces of interaction between particles. The type1 was assigned in such a way that the total energy includes the electron-phonon interaction. Conversely, the type0 excludes all effects of forces of the electrons on the ions but includes effects of the ions on the electron. This latter mode will not allow the ions to displace to accommodate the electron, thus leading to no electron-phonon coupling. Thermal effects resulting from the phonon interaction with the electron are however still accounted for. These two types of simulations are referred as with (called type1) and without (called type0) electron-phonon interactions. The energy of interaction is calculated as the difference between the equilibrium value of the electron energy in both types of simulation (See Table 6.4, 6.5, 6.6).

Computer simulations for the study of electron-phonon interactions were performed with the same initial ionic configuration in the simulation cell as was set for the classical molecular dynamics simulation. The numerical simulations were performed for an electron interacting with ions at room temperature. The initial electron configuration was localized in the Bi ion potential well in the middle of the simulation cell because the attractive potential of Bi is the deepest (see Fig 9). The central Bi ion was chosen to reduce effects that may arise from PBC. The simulation was conducted for 8000 $\Delta t$.

During this time, the ions inside cell freely vibrated with an electron. During the time, the crystal inside the cell volume drifted because of the effects of the heavy arbitrary mass of electron which was $0.5 m_{ox}$. However this global drifting does not affect the energy of the system. It is equivalent to measuring different physical properties in different coordinate systems. The reason of the ion collection drifted is that the initial
average velocity of system in the canonical ensemble was not zero. In order to solve this drifting problem, we could rescale the total momentum of the system to zero by using a momentum correction. The relaxation of the ions mean thermal positions away from the ideal lattice sites due to the electron environment is an interesting problem for future.

Study for the rescaling of the electron momentum was done in the same way as the ions because the desired temperature of electrons should be equal to the actual temperature during a simulation. Without rescaling the electron momentum, the actual temperature of the electron did not reach the desired temperature in a long simulation (20000 steps), even though the ions temperature reached this desired temperature. This suggested that the rescaling of the electron momentum is a way of achieving faster equilibrium in the system. We also checked whether the energies obtained with 8000 time steps would be different in the long simulation. In the 20000 time steps simulation, the value of the electron energies calculated agree with those obtained with 8000 steps to within our targeted computational variation. We conclude that 8000 time step provides a good approach to the equilibrium state.

6.4 Results of electron-phonon interaction

6.4.1 Calculation of electron-phonon energies and Correlation function.

In order to find the electron-phonon energy of interaction, we calculated the electron energies. Regular QPIMD is self consistent. It means that the electron affects the lattice which in turn affects the electron until the new equilibrium state is reached. We have run two types of simulations. The first type includes the electron-phonon interaction and the second type excludes this interaction. We report the results in Tables 6.4, 6.5, 6.6. In Tables 6.4, 6.5, 6.6, we present the variation in electron potential, kinetic, and total energies as a function of the various Bi core radii. The values of the kinetic energy exclude the constant free electron kinetic energy, $\frac{3}{27}$ because this value, 0.0027, (E, unit) at room temperature is considerably smaller than our interacting kinetic energies. We
also used Eq (14) from P&R in order to determine the interacting kinetic energy and have a variance independent of the number of necklace electrons. We calculated the energy uncertainties, $\sigma$, in Tables 6.4, 6.5, 6.6, as follows. We ran a simulation of about 6000 time steps and then took the time average energies for each 100 time steps for next 2000 steps. The final average energy for the equilibrium states was taken as the average of the 20 average values of the individual 100 time steps. The uncertainty on energy was measured by the standard deviation of those 20 values.

In Tables 6.4, 6.5, 6.6, the core radius of Bi, $R = 1.95 \text{ Å}$, corresponds to overlapping Bi cores which is different physical condition than $R_c < 1.75$; we will discuss these energies later. We expect that for a deep well, $R = 1.5 \text{ Å}$, the electron is more confined than in the case of a shallower well such for $R = 1.65 \text{ Å}$, and $1.75 \text{ Å}$. A deeper well should lead to a higher interacting kinetic energy and potential. In the deeper well, the interaction between the ion and the electron is expected to be strong because the electrons are confined and forced to interact with the surrounding ions. Therefore the potential energy difference between the energies calculated with and without electron-phonon interaction (type1 and type0, respectively) should be big. However in the shallower well such as $R = 1.75$, the interaction between the ion and the electron is relatively weak due to the weak binding of the electron. Thus we anticipate a transition from rigidly localized to more delocalized electrons with various core radii of Bi. For cores bigger than a core radius of 1.65 Å for Bi, the electron clearly delocalizes, otherwise the electrons are localized. This can be understood on the basis of the electron binding to the Bi cations.

In Table 6.5, the contribution of the interaction to the K.E. in type1 is larger than for type0. The reason is that the potential in type0 is a rigid ionic potential. We know that the kinetic energy in a rigid ionic system depends mostly upon the temperature in the ion system. Thus, the interacting kinetic energies are smaller than for a type1 system and relatively consistent with various core radii. When the displacement of the ion potential is allowed, the electrons become less bounded because the potential well is shifted and distorted by the electron's motion. This distorted potential gives the electron more chances of interacting with the system. The displacement of the ion potential is
dependent on the core radius. Upon increasing the Bi core radius, this displacement become smaller. Thus there is a bigger difference of kinetic energy between type1 and type0 for a small core radius than for a larger core radius. The upper limit cation core radius, without overlap is supposed to be about 1.75 Å. We believe that this core R=1.75 Å, corresponds to a maximum anion / electron interaction and a minimum cation / electron interaction. In contrast, the electrons at R=1.5 Å strongly interacts with cations.

We show the electron energies with uncertainties in Figs 9, 10, and 11. The electron energies for cores bigger than R = 1.65 Å are representative of electron coupling with the oxygen phonons. We calculated the interaction potential energy at R = 1.75 Å to be about 0.15 eV. The correlation function between electrons and ions in Fig 13 shows clearly that at the core radius below 1.55 Å, the electrons are well localized within the Bi core, and the positive ions and electrons are strongly interacting. This represents a high concentration of electrons within the Bi core at R =1.5 Å in contrast with the 1.75 Å core. Above 1.65 Å, the electrons in the type1 are more delocalized and less bounded to the Bi ion because the potential well gets shallower. The location of the correlation peaks in type1 and type0 are the same. However, the superposition of electron-cation correlation shows that the cations do not displace significantly in response to the incoming electron. Part of the reason may be that the electron density is centered spherically symmetric on the Bi ion thus not perturbing its position very much. The electron cation correlation, as well as the difference in correlation between type1 and type0 simulation, is drastically reduced from R= 1.5 Å to R = 1.75 Å. At this latter value the electron-cation interaction is very weak to almost nonexistent.

We also present the electron-oxygen correlations for various Bi core radii. Fig 15 shows that the correlations calculated in type1 and type0 simulation differ due to electron-oxygen interactions. For small core radius R =1.5 Å, the electron is well localized inside the Bi core. This localization is also apparent in the sharpness of the electron oxygen correlation peak. In contrast as the Bi core increases to core R = 1.75 Å, broader peaks in the electron oxygen correlation appear, a sign of electron delocalization.
Furthermore, at $R = 1.5 \, \text{Å}$, a significant difference in location of the 1st peak in the electron oxygen correlation can be noted. This difference of approximately $\frac{1}{3} \, \text{Å}$ represents the oxygen relaxation due to the presence of the electron. For larger cores, such as $R = 1.75 \, \text{Å}$, smaller ($\frac{1}{3} \, \text{Å}$) differences in the 1st electron-oxygen correlation peak can be detected indicating a slightly weaker interaction between the electron and the oxygen ions. Note that the resolution limit on the calculation of the correlation function is 0.05 Å. Therefore at $R = 1.75 \, \text{Å}$, the electron-cation interaction are minimized while the electron-oxygen interaction is still significantly active.

We also changed the temperature from 300 K to 200 K, there was no anomalously different results. The electron at low temperature is more bounded in the potential well and this bounded electron causes more electron-phonon interactions to occur. There are some difference in the electron-cation and electron-anion correlation functions between 300 K and 200 K. (See Figs 14, 16) The electron-cation is more localized near the cation core radius at 200 K than at 300 K.
Table [A] (P.E.)

<table>
<thead>
<tr>
<th>R (Å)</th>
<th>(a) P.E. ($\sigma \times 10^{-3}$)</th>
<th>(b) P.E. ($\sigma \times 10^{-3}$)</th>
<th>$\Delta E_{PE}$ ($\sigma \times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>-1.1435 (2.4)</td>
<td>-0.5741 (2.0)</td>
<td>-0.5694 (4.4)</td>
</tr>
<tr>
<td>1.55</td>
<td>-0.8442 (1.0)</td>
<td>-0.5072 (3.5)</td>
<td>-0.3370 (4.4)</td>
</tr>
<tr>
<td>1.60</td>
<td>-0.5801 (1.5)</td>
<td>-0.4444 (1.0)</td>
<td>-0.1357 (2.4)</td>
</tr>
<tr>
<td>1.65</td>
<td>-0.3395 (7.0)</td>
<td>-0.3786 (1.0)</td>
<td>-0.0209 (7.6)</td>
</tr>
<tr>
<td>1.75</td>
<td>-0.3311 (1.0)</td>
<td>-0.3206 (1.7)</td>
<td>-0.0105 (2.3)</td>
</tr>
<tr>
<td>1.95</td>
<td>-0.5299 (3.9)</td>
<td>-0.2973 (4.4)</td>
<td>-0.2326 (8.3)</td>
</tr>
<tr>
<td>1.65(200K)</td>
<td>-0.5202 (1.6)</td>
<td>-0.3898 (1.4)</td>
<td>-0.1304 (3.0)</td>
</tr>
</tbody>
</table>

Table 6.4: Electron potential energy, P.E., (a) with $e^-\cdot\text{ph}$ interaction (b) without $e^-\cdot\text{ph}$ interaction; and $e^-\cdot\text{ph}$ interaction, $\Delta E_{PE}$, contribution to the potential energy, vs. Bi core radius, R. The $\sigma$ are the uncertainties on the calculated energies. 6 lines from the top are at 300 K and the last line is at 200 K.

6.4.2 Phonon softening

In Fig 15, the oxygen and electron correlation for core R = 1.5 Å which correspond to a localized pseudopotential well, shows that the oxygen displacement for type1 is a little longer Bi- O bond than type0. This clearly shows that the oxygen vibrational spectra should be softened. However, we can not clearly see the difference between type1 and type0 at R = 1.75 Å, since the electron is somewhat delocalized. The Bi vibration with the electron cloud is affected by the electrons because if the bismuth moved to one side of electrons cloud, the Bi would feel a restoring force due to those electrons. This electron
<table>
<thead>
<tr>
<th>R (Å)</th>
<th>(a) K.E.(σ × 10^{-3})</th>
<th>(b) K.E.(σ × 10^{-3})</th>
<th>ΔE_{KE}(σ × 10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>0.2211 (2.4)</td>
<td>0.0687 (2.6)</td>
<td>0.1524 (5.0)</td>
</tr>
<tr>
<td>1.55</td>
<td>0.1706 (1.0)</td>
<td>0.0310 (4.0)</td>
<td>0.1396 (4.9)</td>
</tr>
<tr>
<td>1.60</td>
<td>0.1552 (2.8)</td>
<td>0.0341 (1.0)</td>
<td>0.1211 (3.9)</td>
</tr>
<tr>
<td>1.65</td>
<td>0.0970 (4.5)</td>
<td>0.0245 (1.3)</td>
<td>0.0725 (5.8)</td>
</tr>
<tr>
<td>1.75</td>
<td>0.0868 (5.0)</td>
<td>0.0398 (1.7)</td>
<td>0.0470 (6.6)</td>
</tr>
<tr>
<td>1.95</td>
<td>0.1525 (4.0)</td>
<td>0.0390 (7.0)</td>
<td>0.1135 (11.0)</td>
</tr>
<tr>
<td>1.65(200K)</td>
<td>0.1234 (1.2)</td>
<td>0.0267 (1.6)</td>
<td>0.0967 (2.9)</td>
</tr>
</tbody>
</table>

Table 6.5: Electron kinetic energy, K.E., (a) with e⁻-ph interaction (b) without e⁻-ph interaction; and e⁻-ph interaction, ΔE_{KE}, contribution to the kinetic energy, vs. Bi core radius, R. The σ are the uncertainties on the calculated energies. 6 lines from the top are at 300 K and the last line is at 200 K.
<table>
<thead>
<tr>
<th>R (Å)</th>
<th>(a) T.E. ($\sigma \times 10^{-3}$)</th>
<th>(b) T.E ($\sigma \times 10^{-3}$)</th>
<th>$\Delta E_{TE} ($ $\sigma \times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>- 0.9224 (2.4)</td>
<td>- 0.5054 (2.5)</td>
<td>- 0.4170 (5.0)</td>
</tr>
<tr>
<td>1.55</td>
<td>- 0.6736 (1.0)</td>
<td>- 0.4762 (4.0)</td>
<td>- 0.1974 (5.0)</td>
</tr>
<tr>
<td>1.60</td>
<td>- 0.4250 (2.8)</td>
<td>- 0.4103 (1.0)</td>
<td>- 0.0147 (3.7)</td>
</tr>
<tr>
<td>1.65</td>
<td>- 0.3025 (4.3)</td>
<td>- 0.3463 (1.3)</td>
<td>+ 0.0438 (5.6)</td>
</tr>
<tr>
<td>1.75</td>
<td>- 0.2443 (4.7)</td>
<td>- 0.2808 (1.6)</td>
<td>+ 0.0365 (6.3)</td>
</tr>
<tr>
<td>1.95</td>
<td>- 0.3774 (3.9)</td>
<td>- 0.2583 (7.0)</td>
<td>-0.1191 (10.9)</td>
</tr>
<tr>
<td>1.65(200K)</td>
<td>- 0.3967 (1.1)</td>
<td>- 0.3631 (1.5)</td>
<td>- 0.0336 (2.7)</td>
</tr>
</tbody>
</table>

Table 6.6: Total electron energy, T.E., (a) with $e^-\text{-ph}$ interaction (b) without $e^-\text{-ph}$ interaction; and $e^-\text{-ph}$ interaction, $\Delta E_{TE}$, contribution to the total energy, vs. Bi core radius, R. The $\sigma$ are the uncertainties on the calculated energies. 6 lines from the top are at 300 K and the last line is at 200 K.
movement has more energy than the Bi ion. The result is that the Bi gains energy from the electron. This increase in energy for Bi is highly dependent upon the artificial mass $m^*$, of the electrons; since $m^* = 0.5m_{ox}$, the 400 electrons move very slowly and we are not in an adiabatic approximation. However, the oxygen vibration may be less sensitive to the dynamics of the electrons. The vibrational spectra of the ions cannot be calculated accurately because they will depend upon the artificial mass of the electron and we can not interpret any phonon change in terms of the electron-phonon interaction.

6.4.3 Estimation of Coupling constant

Loong et al\cite{14} claimed that the electron-phonon interaction in $Ba_{0.6}K_{4.4}BiO_3$ is dominated by the coupling of electrons to oxygen phonons at 30 and 60 meV (i.e. about 250 to 500 cm$^{-1}$). Also Hinks et al\cite{8} measured the oxygen isotope effect and explained it on the basis of coupling with oxygen. In Figs 13 and 15, for $R = 1.5 \AA$ we observe that the electron affects both cation and anions while for $R = 1.75 \AA$, the cation-electron interaction appears to be minimal. Thus, we take the simulation $R = 1.75 \AA$ as being representative of an electron-oxygen sublattice interaction in $Ba_{0.6}K_{4.4}BiO_3$. In this section, we estimated the electron-phonon coupling constant from the MD data. The coupling constant, $\alpha$ given by the strong-coupling expression in the book by Vonsovsky et al\cite{75}, is $\alpha \sim \frac{\Delta E}{\omega}$. where $\Delta E$ is the energy shift due to the electron-phonon interaction and $\omega$ is the longitudinal phonon frequency. Since we adopted a quantum path integral in real space, our coupling constant can be calculated following Frölich's theory\cite{43} which is applicable to ionic materials. In his theory, the coupling constant was obtained with the optical longitudinal phonon frequency. Here we use the potential energy difference, $\Delta E$, at $R = 1.75 \AA$. This core radius seems to be a good value for the characterization of the pseudopotential. For a lower limit for the coupling constant, we chose the oxygen frequency to be 800 cm$^{-1}$ from our MD simulation. This frequency corresponds to the highest frequency for the Bi-O stretching mode. The corresponding value of the coupling constant is about 1.18. For an upper bound for the coupling constant, we chose the oxygen frequency at about 600 cm$^{-1}$ which corresponds to the lowest frequency for the Bi-O
stretching mode. The corresponding value for the maximum coupling constant is 1.57. The appropriate value for the coupling is seemed to be about 1.34. It is believed that the coupling of the electrons to oxygen phonons is responsible for superconductivity in $Ba_{0.6}K_{4}BiO_3$. We also calculated the coupling constant at core $R=1.5$ to be about 100. This result showed that the deep well potential would have very strong electron-phonon interaction. There are no such materials known.
CHAPTER 7

CONCLUSIONS AND FUTURE

7.1 Conclusion

We have used two techniques for calculating the classical and quantum mechanical behavior of many body systems. One consists of a classical molecular dynamics ionic model which can represent the bismate high Tc superconductors. The other is a quantum path integral in molecular dynamics simulation. This later method allows the simulation of quantum systems. With the former technique, the static structural properties of $Ba_{1-x}K_xBiO_3$ (lattice parameter, interionic distance at room temperature, and temperature dependence of the lattice parameter) are in good agreement with experimental data. Furthermore, we determine the anisotropic vibrational spectra of individual ions. The vibrational spectra show that the peaks at high frequency are related to oxygen vibration which is in good agreement with Loong et al[14]. The change in oxygen mass from $O^{16}$ to $O^{18}$ (isotope effect) on vibrational spectra show that the peaks between 400 and 600 cm$^{-1}$ are altered. This region in $Ba_{0.6}K_{0.4}BiO_3$ is suspected to be related to the characteristics of superconductivity according to the experimental data. By adding the quantum path integral method to molecular dynamics, we can expand to study new physical parameters such as the electron-phonon interaction. We calculated the electron-phonon interaction for the first time in this work. We separated the forces between the ions and the electron, then obtain the electron energies for various Bi core radii. From our calculation, we estimated the electron-phonon coupling energy which is not directly available from experimental data. We also calculated the coupling constant, $\alpha$, by using the optical frequency in classical MD at room temperature. The coupling constant
depended upon the Bi core radius. At a Bi core radius \( R = 1.75 \text{Å} \) which was found to represent optimum oxygen-electron coupling, we determine a coupling constant of 1.34. At \( R_{Bi} = 1.75 \text{Å} \), the electron-phonon coupling displaces the oxygen ions by \( \frac{1}{8} \text{Å} \). This represents a weakening of the Bi-O bond. Finally, we employed a 2 mirror method for the measurement of the IR spectra of \( Ba_{0.6}K_{0.4}BiO_3 \) superconductor. With this method, we measured the optical infrared spectrum even though the peaks were very small in intensity. We measured IR absorption peaks at 380, 530, 720, and 880 \( \text{cm}^{-1} \) by this reflectivity IR method. These frequencies are in good accord with the vibrational modes calculated in this work using the MD technique.

7.2 Future

We have demonstrated the potential of QPIMD for the study of many body systems. In this work, we have investigated the electron-phonon interaction in high Tc superconductors. Clearly, this method could be used to study the very important problem of electron-electron interaction in a classical ionic crystal. Such a study however, would necessitate the introduction of exchange phenomena in the MD algorithm. Exchange in QPI has been described by Chandler and Wolynes[86] and used to study the He\(^4 \) '\( \lambda \) transition'[87]. We therefore believe that QPIMD may make a significant contribution to our understanding of a pairing mechanism in high Tc oxide superconductors. Furthermore, this technique could be advantageously employed to study the electron energy bands and transport properties in these ceramics. These advances will necessitate significant improvements of the QPIMD algorithm for optimizations of computational time and space.
APPENDIX A

ELECTRON PHONON INTERACTION

The theory presented here follows closely the development presented in Quantum Theory of Solids by C. Kittel[88] and in Solid State Theory by W.A. Harrison[89]. We start from equation (3.5) in Ch 3. If we use the Bloch state function in second quantization, a \( \psi(\vec{x}) \) is represented by a linear superposition of Bloch state \( \psi_{n\vec{k}}(\vec{x}) \):

\[
\psi(\vec{x}) = \sum_{n\vec{k}} C_{n\vec{k}} \psi_{n\vec{k}}(\vec{x}),
\]

\[
\psi_{n\vec{k}}(\vec{x}) = \exp^{i\vec{k} \cdot \vec{x}} u_{n\vec{k}}(\vec{x})
\]

where \( n \) is the band index and \( \vec{k} \) is the wave vector. The unperturbed total electron Hamiltonian becomes

\[
H_{el} = \sum_{n\vec{k}} E_{n\vec{k}} C_{n\vec{k}}^+ C_{n\vec{k}}
\]

where the Bloch functions, \( \psi_{n\vec{k}}(\vec{x}) \) have energy \( E_{n\vec{k}} \).

\( H_{e-ph} \) becomes

\[
H_{e-ph} = - \sum_{n\vec{k}, n'\vec{k}} \sum_{\vec{I}} \vec{u}(\vec{I}) \cdot \int d^3x \psi_{n'\vec{k}}^+(\vec{x}) \nabla_\vec{z} \psi(\vec{x} - R_0(\vec{I})) \psi_{n\vec{k}}(\vec{x}) C_{n\vec{k}}^+ C_{n\vec{k}}
\]

(A.42)

Consider the integral

\[
I(n'\vec{k}; n\vec{k}) = \int d^3x \psi_{n'\vec{k}}^+(\vec{x}) \nabla_\vec{z} \psi(\vec{x} - R_0(\vec{I})) \psi_{n\vec{k}}(\vec{x})
\]

(A.43)

Let \( \vec{r} = \vec{x} - R_0(\vec{I}) \) then

\[
\psi_{n\vec{k}}(\vec{x}) = \psi_{n\vec{k}}(\vec{r} + R_0(\vec{I})) = e^{ik.\vec{r}} u_{n\vec{k}}(\vec{r} + R_0(\vec{I})) \equiv e^{ik.\vec{r}} u_{n\vec{k}}(\vec{r})
\]

(A.44)
since $u_{nk}(\vec{r})$ is periodic, with periodicity of the underlying integral. The relation between

$\psi_{nk}(\vec{x})$ and $\psi_{nk}(\vec{r})$ is:

$$\psi_{nk}(\vec{x}) = e^{i\vec{k} \cdot \vec{R}_0(\vec{l})} \psi_{nk}(\vec{r})$$

Hence we can rewrite the e-ph Hamiltonian as

$$H_{e-ph} = -\sum_{nk} \sum_{n'k'} \left( \int d^3x \psi_{nk}(\vec{x}) \nabla_x \psi_{nk}(\vec{x}) \right) \cdot \sum_{\vec{l}} u(\vec{l}) e^{i(k-\vec{k}) \cdot \vec{R}_0(\vec{l})}$$

(A.45)

However, we need to integrate over all space. We make the assumption that the gradient of the potential is associated with one ion in a unit cell at the origin in order to simplify the calculation; little error is introduced by this assumption. Using phonon theory[44] and the canonical variables $a$ and $a^+$, the coordinate $u(\vec{l})$ is

$$u(\vec{l}) = \sum_{q} \left( \frac{h}{2NM w(\vec{q}^2)} \right)^{1/2} \hat{e}(\vec{q}^2)(a^+_{-\vec{q}} + a_{\vec{q}}) e^{i\vec{q} \cdot \vec{R}_0(\vec{l})}$$

(A.46)

where $\hat{e}(\vec{q}^2)$ is the polarization vector associated with the phonons, $\vec{j}$ is the site index and:

$w(\vec{k}) = w(-\vec{k})$, $\epsilon(\vec{k}) = \epsilon(-\vec{k})$.

Now we obtain the e-ph Hamiltonian;

$$H_{e-ph} =$$

$$-\sum_{nk} \sum_{n'k'} \sum_{\vec{l}} \sum_{\vec{q}} e^{i\vec{R}_0(\vec{l}) \cdot (\vec{k} + \vec{q} - \vec{k})} \left( \frac{h}{2NM w(\vec{q}^2)} \right)^{1/2} \hat{e}(\vec{q}^2)(a^+_{-\vec{q}} + a_{\vec{q}}) C_{nk}^+ C_{n'k'}$$

(A.47)

(A.48)

$$\int d^3x \psi_{nk}(\vec{x}) \nabla_x \psi_{nk}(\vec{x})$$

Let's look at the exponential factor with the sum over $\vec{l}$,

$$\sum_{\vec{l}} e^{i\vec{R}_0(\vec{l}) \cdot (\vec{k} + \vec{q} - \vec{k})} = N \sum_{\vec{G}} \delta_{\vec{R}_0(\vec{l}) \cdot \vec{G}}$$

(A.49)

which is nonzero only when $\vec{R}_0(\vec{l}) = \vec{k} + \vec{q} + \vec{G}$ and $\vec{G}$ is a reciprocal lattice vector. We can use the Bloch state function in a slightly different form for normalization purpose

$$\psi_{nk}(\vec{x}) = \frac{1}{\sqrt{N}} u_{nk}(\vec{x}) e^{i\vec{k} \cdot \vec{x}}.$$
Thus \( u_{n_k}(\vec{x}) \) can be normalized to \( \int d^3x |u_{n_k}(\vec{x})|^2 = 1 \) integrated over one cell only. Then the matrix element for the integral becomes

\[
M(n'_k; n_k) = \int d^3x u^+_n(\vec{x}) \nabla_x v(\vec{x}) u_{n_k}(\vec{x}) e^{i(\vec{k}' - \vec{k}) \cdot \vec{x}}.
\]  \hspace{1cm} (A.50)

These matrix elements belong to a given band of conduction electrons in the metal. The e-ph Hamiltonian can be written as

\[
H_{\text{e-ph}} = \sum_{\vec{k}, \vec{k} + \vec{q} + \vec{G}} \sum_{\vec{q}_j} \frac{\hbar}{2NM w(\vec{q}_j)} \frac{1}{2} \delta(\vec{q}_j) [a^+_{\vec{q}_j} + a_{-\vec{q}_j}] M(\vec{k}'; \vec{k}) C^+_k C_k.
\]  \hspace{1cm} (A.51)

Now the conduction electron is scattered by a phonon from the \( \vec{k} \) state to \( \vec{k} + \vec{q} + \vec{G} \) state. We only consider the longitudinal phonon contribution and \( \vec{G} = 0 \), (which is called the nomal or N process), in order to mathematically simplify the matrix elements because the U process (\( \vec{G} \neq 0 \)) has little effect on the calculations. As we mentioned before, we are making two assumptions for the metal case. One is that the unit cell is approximated by a spherical shape and so in the outer cell the gradient of the potential is approximately zero. The other is that since \( u_{n_k}(\vec{x}) \) is insensitive to \( \vec{k} \), because the potential is in the atomic core and very strong, we can write

\[
u_{\vec{k}}(\vec{x}) \simeq u_0(\vec{x}) \simeq u_0(|\vec{x}|).
\]  \hspace{1cm} (A.52)

The Schrödinger equation for the electron with wavevector \( \vec{k} = 0 \) is:

\[
\left[ \frac{\hbar^2}{2m} + v(\vec{x}) \right] u_0(\vec{x}) = E_0 u_0(\vec{x})
\]  \hspace{1cm} (A.53)

where \( E_0 \) is the minimum energy of the conduction band. Next consider the Schrödinger equation for a state \( \vec{k} \neq 0 \) and solve this equation for a unit cell located at the origin.

\[
- \frac{\hbar^2}{2m} \psi_{\vec{k}}(\vec{x}) + v(\vec{x}) \psi_{\vec{k}}(\vec{x}) = E_{\vec{k}} \psi_{\vec{k}}(\vec{x})
\]  \hspace{1cm} (A.54)

This can be rewritten as:

\[
\nabla^2 \psi_{\vec{k}}(\vec{x}) + (E_{\vec{k}} - v(\vec{x})) \psi_{\vec{k}}(\vec{x}) = 0
\]  \hspace{1cm} (A.55)

where \( \hbar = 1 \).

Taking the gradient \( \nabla \) of this Schrödinger equation and using the relation:

\[
\nabla \psi_{\vec{k}}(\vec{x}) = \nabla (e^{i\vec{k} \cdot \vec{z}} u_{\vec{k}}(\vec{x})) = i\vec{k} \psi_{\vec{k}}(\vec{x}) + e^{i\vec{k} \cdot \vec{z}} \nabla \cdot u_{\vec{k}}(\vec{x}).
\]  \hspace{1cm} (A.56)
We obtain:
\[
\psi_{k'}(x) \nabla_x v \psi_k(x) =
\]
\[
\psi_{k'}(x) i \hbar [E_k - v_x + \frac{\nabla^2}{2m}] \psi_k(x) + (E_k - v) e^{i \vec{k} \cdot \vec{x}} \psi_{k'}(x) \nabla u_k(x)
\]
\[
+ \psi_{k'}(x) \frac{\nabla^2}{2m} e^{i \vec{k} \cdot \vec{x}} \nabla u_k(x)
\]
(\text{A.57})

We are interested in the case \(E_k \simeq E_k'\) for all states connected by the electron-phonon interaction. Therefore the first term has vanished. If we use Green’s theorem in one cell;
\[
\int d^3x \psi_{k'}^+(x) \nabla_x v \psi_k(x)
\]
\[
= 1/2m \int_s d\vec{s} \cdot [\psi_{k'}^+(x) \nabla (e^{i \vec{k} \cdot \vec{x}} u_k(x)) - \nabla \psi_{k'}^+(x) \cdot e^{i \vec{k} \cdot \vec{x}} u_k(x)]
\]
\[
= 1/2m \int_s d\vec{s} \cdot [\psi_{k'}^+(x) e^{i \vec{k} \cdot \vec{x}} \nabla^2 u_k(x) +
\]
\[
i \vec{k} \psi_{k'}^+(x) e^{i \vec{k} \cdot \vec{x}} \cdot \nabla u_k(x) - \nabla \psi_{k'}^+(x) e^{i \vec{k} \cdot \vec{x}} \nabla u_k(x)]
\]
(\text{A.58})

By using the approximation \(u_k(x) \simeq u_0(x)\), we suppose that \(u_0\) has zero gradient on the boundary of the unit cell calculated by Wigner and Sitz[44]. Using a spherical cell of radius \(r_0\), we then have
\[
\int d^3x \psi_{k'}^+(x) \nabla_x v \psi_k(x) = 1/2m \int_s d\vec{s} e^{i (\vec{k} - \vec{q}) \cdot \vec{x}} u_0(x) \nabla^2 u_0(x)
\]
(\text{A.59})

where
\[
\nabla^2 u_0(x) = 2m[v(x) - E_0] u_0(x)
\]

The steps follow Mott and Jones [45].
\[
\int d^3x \psi_{k'}^+(x) \nabla_x v \psi_k(x) =
\]
\[
[v_x - E_0] \int_s d\vec{s} e^{i (\vec{k} - \vec{q}) \cdot \vec{x}} u_0^2(x) \equiv [v_x - E_0] \int_s d\vec{s} \psi_{k'}^+(x) \psi_k(x)
\]
\[
= [v_x - E_0] \int_s d\vec{s} \nabla (\psi_{k'}^+(x) \psi_k(x)).
\]
(\text{A.60})
Since $u_0$ is nearly unity everywhere in the unit cell, $\nabla (\psi_k^+ (\vec{x}) \psi_k (\vec{x})) = i(\vec{k} - \vec{k}') \psi_k^+ (\vec{x}) \psi_k (\vec{x})$.

Therefore the integral is

$$\int d^3 x \psi_k^+ (\vec{x}) \nabla_x v(\vec{x}) \psi_k (\vec{x}) = [v_s - E_0] i(\vec{k} - \vec{k}')(u_0^2 \int d^3 x e^{-i(\vec{k} - \vec{k}') \cdot \vec{x}}). \tag{A.61}$$

Now if we further set $u_0^2 = 1$, then

$$= iK(|\vec{k} - \vec{k}'|)(v_s - E_0)(\vec{k} - \vec{k}')$\tag{A.62}$$

where $K(\vec{q}) = \int d^3 x e^{i\vec{q} \cdot \vec{x}}$ and $\vec{q} = \vec{k} - \vec{k}'$. From the Mott and Jones's results, $v_s - E_0 \approx \frac{2}{5} E_f$

where $E_f$ is Fermi energy. So the integral becomes

$$\int d^3 x \psi_k^+ (\vec{x}) \nabla_x v(\vec{x}) \psi_k (\vec{x}) = i(\vec{k} - \vec{k}') \frac{2}{5} E_f K(|\vec{k} - \vec{k}'|). \tag{A.62}$$

Finally we can get the equation (3.6) in Ch 3.

$$H_{c-\nu h} = \frac{2}{5} i E_f \sum_{\vec{k} \vec{q}} \sum_{\sigma} \left( \frac{\hbar}{2NMw(\vec{q}^\sigma)} \right)^{1/2} \delta(\vec{q}^\sigma) \cdot (\vec{k} - \vec{k}') K(|\vec{k} - \vec{k}'|) \gamma_{\vec{k}+\vec{q}+\sigma}^+ \gamma_{\vec{k}} C_{\vec{k}} [a_{\vec{q} } + a_{\vec{q} }^+] \tag{A.63}$$
APPENDIX B

RESULTS FOR MOLTEN KCL

The necklace electrons of isomorphism were connected with pure harmonic forces. We assumed that there are no interactive forces between the classical electrons and that the electron necklace has a closed ring shape for its initial configuration. Since PBC were used for all of the molecular dynamics simulation, with the necklace electrons connected to only nearest neighbors by harmonic forces, the motion of the necklace electron with time occasionally caused it to drift through the cell boundary into an adjacent cell. Although all of the necklace electrons are remapped back to the other side of the initial cell as they drift and the near neighbor interactions are properly calculated within the cell, we had to take special care to account for those pair that were immediately adjacent to the cell wall since our program doesn't provide for electron coupling across a cell wall. We also modified the interaction kinetic energy term in the effective potential $V_{eff}$ which is the first term of equation (14) of Parrinello and Raman[16]. From Eq (14), we set the potential energy related to electron $\phi = \sum_{i,j} V_{ij}(\tau_{ij})$. In our model, the potential energy of the electron is used with the average value:

$$V_{int} = \langle \sum_{i=1}^{P} \sum_{I=1}^{N} P^{-1} \phi_{e-I}(\tau_{i} - R_{I}) \rangle$$

where $\phi_{eI}$ depends on the ions. Our main purpose for studying an F center in molten KCL was to verify the modifications made to the molecular dynamics code by insertion of the quantum path integral. The cell included 108$K^+$ and 107$Cl^-$ as randomly positioned ionic particles and 100 necklace electrons replacing one $Cl^-$ as an equivalent quantum electron. The typical value of $\Delta t$ for the simulation was about $4.2 \times 10^{-15}$ sec; this was based upon the vibrational period for the chlorine mass. We use the same Fumi-Tosi
potential form as in the Parrinello and Rahman paper[16], but we chose the potential parameters of Sangster et al[85]. For our simulation, in order to reach the equilibrium state, we ran several thousand time steps in an ionically neutral system without electrons. After which inserted the necklace electrons were inserted while removing one chlorine. The arbitrary classical electron mass was chosen at $\frac{1}{2}m_{cl}$. The simulation ran 4000 time steps with fixed cell volume at constant temperature (1000 K) in order to measure the physical properties. The initial cell volume was cubic in shape with cell size parameters $a = b = c = 20.49$ Å. This cell size with 215 $K^+$ and $Cl^-$ corresponds to the density of KCl at 1000 K. The kinetic energy and potential energy of the electron are calculated by numerical methods. The kinetic energy included two terms. One represented the purely free particle behavior and the other represented the interaction with the ionic medium. The potential energy between electron and ions is entirely coulombic. In Table B.7, we changed the core radius of potassium and $R=1.50, 1.96, \text{ and } 2.50$ Å with fixed electron number $P$ and constant temperature. The electron energies at core radius, $R=1.96$ Å in Table B.7 is in good agreement with Parrinello and Raman data. We studied the tendency toward localization for the electron necklace within a core radius $R=1.96$ Å. As an initial condition, we made the 100 electron necklace delocalized in the cell as in Fig 7 and ran for 4000 time steps. In Fig 7, the initially dispersed electron become well localized as the time progressed. During this period, ions are moving in the cell according to the equations in the molten state. In order to check this electron localization in molten KCl, the best way is to look at the electron distribution function near the $K^+$ shell; that is we calculated the pair correlation function between $K^+$ and $e^-$. Fig 8 shows that the electron is correlated to $K^+$ within 4 Å for a core radius $R=1.96$ Å. This result is identical with the findings of Parrinello and Rahman. We therefore believe that the computer code we have developed gives a realistic description of the behavior of quantum particles in ionic systems. We also change the core radius $R=1.50$ and 2.50 Å each. The smaller core radius pseudopotential produces a deeper well in potassium and most electrons moved within this core radius. The larger radius which corresponds to a shallower well gave rise to an opposite behavior. These observations are again in perfect accord with the results of Parrinello and Rahman.
Table B.7: Value(variance) of \( e^- \) potential and kinetic energy\((14.4 \text{ eV unit})\) in molten KCL. \( P \) is number of necklace electrons. The core radius is shown and compared with Parrinello and Rahman\([16]\) data.

<table>
<thead>
<tr>
<th>( P )</th>
<th>( R ) (Å)</th>
<th>P.E. ((\sigma \times 10^{-3}))</th>
<th>K.E. ((\sigma \times 10^{-3}))</th>
<th>T.E. ((\sigma \times 10^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.50</td>
<td>-0.5020 (3.5)</td>
<td>0.1260 (3.0)</td>
<td>-0.3760 (3.0)</td>
</tr>
<tr>
<td>( n )</td>
<td>1.96</td>
<td>-0.3899 (2.6)</td>
<td>0.0909 (2.0)</td>
<td>-0.2990 (2.0)</td>
</tr>
<tr>
<td>( n )</td>
<td>2.50</td>
<td>-0.2847 (2.2)</td>
<td>0.0723 (1.6)</td>
<td>-0.2124 (1.6)</td>
</tr>
<tr>
<td>100(P&amp;R)</td>
<td>1.96</td>
<td>-0.4158 (65.0)</td>
<td>0.1271 (30.0)</td>
<td>-0.2888 ( )</td>
</tr>
</tbody>
</table>
APPENDIX C

THE FIGURES
Figure 1: Perovskite Structure of $Ba_{1-x}K_xBiO_3$
Figure 2: Simulation cell and its 8 images in a two dimensional system with PBC. (A 3D system would have 26 image cells)
Figure 3: Room temperature anisotropic partial vibrational density of states of Ba$_{0.75}$K$_{0.25}$BiO$_3$. a, b, c, d, e refer to Ba, Bi, K, oxygen linked to Bi along Z direction with K rich environment and oxygen linked to Bi along X direction with K poor environment.
Figure 4: Room temperature anisotropic partial vibrational density of states of $Ba_{0.6}K_{0.4}BiO_3$. a, b, c, d, e refer to Ba, Bi, K, oxygen linked to Bi along Z direction with K poor environment and oxygen linked to Bi along X direction with K rich environment.
Figure 5: Low(100 K) temperature anisotropic partial vibrational density of states of $Ba_{0.6}K_{0.4}BiO_3$. a, b, c, d, e refer to Ba, Bi, K, oxygen linked to Bi along Z direction with K poor environment and oxygen linked to Bi along X direction with K rich environment.
Figure 6: Continue
Figure 6: Anisotropic vibrational spectra of two oxygen isotopes.
Figure 7: The xy projection of localizing electron in molten KCL.
Figure 8: Cation-electron pair correlation in molten KCL for three different values of K core radius.
Figure 9: Initial and equilibrium configuration for electron localization in $Ba_{0.6}K_{0.4}BiO_3$. 
Figure 10: Potential, Kinetic, Total Energy of electron with electron-phonon interaction in $Ba_{0.8}K_{0.4}BiO_3$. 
Figure 11: Potential, Kinetic, Total Energy of electron without electron-phonon interaction in $Ba_{0.6}K_{0.4}BiO_3$. 
Figure 12: Potential, Kinetic, Total Energy contributions to electron-phonon coupling.
Figure 13: Radial electron-cation pair correlation between electron-positive ions for various Bi core radii. The '—' and '—.-' stand for simulation type 1 and type 0 electron phonon coupling.
Figure 14: Electron - cation pair correlation at 300 K and 200 K for $R_{Bi} = 1.65$. The '—' and '—.' stand for simulation type1 and type0.
Figure 15: Electron-oxygen pair correlation for various Bi core radii. The '-' and '-' stand for simulation type1 and type0 electron phonon coupling.
Figure 16: Electron-anion pair correlation at 300 K and 200 K for $R_{Bi} = 1.65$. 
Figure 17: 2 mirror method for IR reflectivity measurement. Key: I, Interferometer; S, Sample; C, concave mirror; m, flat mirror; D, detector.
Figure 18: X-Ray diffraction spectrum for $BaBiO_3$. 

SPEED=.125
Ta=1
Tc=4
RATER=5X100
07-26-1990
Figure 19: X-Ray diffraction spectrum for $Ba_{0.6}K_{0.4}BiO_3$. 
Figure 20: Infrared Spectrum of $BaBiO_3$ by the transmission method.
Figure 21: Infrared Spectra of $Ba_8K_4BiO_3$ with the reflection method. (a) is reflectivity in all ranges and (b) is the expansion of intensity between 150 and 1000 $cm^{-1}$. 
Figure 21: Continue
$t = 0$

'initial condition' $\vec{r}_i(0), \vec{r}_i(\Delta t)$

Force on particles, $\vec{f}_i(0)$

$i=$ion or electron

Solve

$F_i = \frac{\partial^2 \vec{r}_i}{\partial \vec{r}_i}$

$\vec{r}_i(n\Delta t)$

Stop

$\vec{F}_i = \vec{F}_{i-\text{ion}} + \vec{F}_{i-\text{e}}$

switch on: $\vec{F}_{i-\text{e}} \neq 0$

switch off: $\vec{F}_{i-\text{e}} = 0$

Figure 22: QPIMD Algorithm
REFERENCES


