Theoretical studies of structural and electronic properties in transition metal oxides

Tsezar F. Seman
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ABSTRACT

THEORETICAL STUDIES OF STRUCTURAL AND ELECTRONIC PROPERTIES IN TRANSITION METAL OXIDES

by
Tsezár F. Seman

The following studies are presented: theory of K-edge resonant inelastic x-ray scattering and its application for La$_{0.5}$Sr$_{1.5}$MnO$_4$, effects of rare earth ion size on the stability of the coherent Jahn-Teller distortions in undoped perovskite manganites, and symmetry-mode-based classical and quantum mechanical formalism of lattice dynamics.

The formula based on tight-binding approach for the calculation of K-edge resonant inelastic x-ray scattering (RIXS) spectrum for transition metal oxides is presented first, by extending the previous existing result to include explicit momentum dependence and a basis with multiple core-hole sites. This formula is applied to layered charge, orbital and spin ordered manganites, La$_{0.5}$Sr$_{1.5}$MnO$_4$, and good agreement with experimental data was obtained, in particular, with regard to the large variation of the intensity with momentum. As a consequence, it is established that the electron screening in La$_{0.5}$Sr$_{1.5}$MnO$_4$ is highly localized around the core hole site and demonstrates the potential of K-edge RIXS, as a probe for the screening dynamics in materials.

Theoretical study is then introduced on the relation between the size of the rare earth ions, often known as chemical pressure, and the stability of the coherent Jahn-Teller distortions in undoped perovskite manganites. Using a Keating model expressed in terms of atomic scale symmetry modes, it is shown that there exists a coupling between the uniform shear distortion and the staggered buckling distortion within the Jahn-Teller energy term. It is found that this coupling provides a mechanism by which the coherent Jahn-Teller distortion is more stabilized by smaller rare
earth ions. Further analysis shows the appearance of the uniform shear distortion below the Jahn-Teller ordering temperature; the Jahn-Teller ordering temperature is estimated and its variation between NdMnO$_3$ and LaMnO$_3$, and the relations between distortions are obtained. A good agreement is found between theoretical results and the experimental data.

Finally, the classical and quantum mechanical descriptions of lattice dynamics are presented, from the atomic to the continuum scale, using atomic scale symmetry modes and their constraint equations. This approach is demonstrated for a one-dimensional chain and a two-dimensional square lattice on a monatomic basis. For the classical description, it is found that rigid modes, in addition to the distortional modes found before, are necessary to describe the kinetic energy. The long wavelength limit of the kinetic energy terms expressed in terms of atomic scale modes is shown to be consistent with the continuum theory, and leading order corrections are obtained. For the quantum mechanical description, conjugate momenta for the atomic scale symmetry modes are presented. In direct space, graphical rules for their commutation relations are obtained. Commutation relations in the reciprocal space are also calculated. As an example, phonon modes are analyzed in terms of symmetry modes. The approach presented here based on atomic scale symmetry modes could be useful for the study of complex emerging materials, in which competing structural phases and non-linearity of the lattice energy play an important role.
THEORETICAL STUDIES OF STRUCTURAL AND ELECTRONIC PROPERTIES IN TRANSITION METAL OXIDES

by

Tsezár F. Seman

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For planting the seed of love
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4.2 The lattice modes for the one-dimensional chain in Figure 4.1.

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For the lower branch, they correspond to \( (a)|r|^2, \ (b)|e_3|^2, \ (c)|e_2|^2, \ (d)|e_1|^2, \ (e)|t_y|^2, \ (f)|t_x|^2, \ (g)|s_y|^2, \ (h)|s_x|^2, \ (i)|t_-|^2, \ (j)|t_+|^2, \ (k)|s_-|^2, \ (l)|s_+|^2. \]

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# LIST OF TERMS

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<th>Abbreviation</th>
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<tbody>
<tr>
<td>AK</td>
<td>Alkali metal element</td>
</tr>
<tr>
<td>bk</td>
<td>Buckling term</td>
</tr>
<tr>
<td>br</td>
<td>“breathing” term</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
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<tr>
<td>Coul</td>
<td>Coulomb term</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock approximation</td>
</tr>
<tr>
<td>Hund</td>
<td>Hund’s term</td>
</tr>
<tr>
<td>JT</td>
<td>Jahn-Teller term</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic Energy term</td>
</tr>
<tr>
<td>LDA</td>
<td>Local-Density Approximation from density functional theory</td>
</tr>
<tr>
<td>RE</td>
<td>Rare Earth element</td>
</tr>
<tr>
<td>RXS</td>
<td>Resonant X-ray Scattering</td>
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<tr>
<td>RIXS</td>
<td>Resonant Inelastic X-ray Scattering</td>
</tr>
<tr>
<td>r.l.u.</td>
<td>Reciprocal Lattice Unit</td>
</tr>
<tr>
<td>WFC</td>
<td>Wannier Function Center</td>
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<tr>
<td>1s</td>
<td>Term related to 1s electron configuration</td>
</tr>
<tr>
<td>3d</td>
<td>Term related to 3d electron configuration</td>
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CHAPTER 1
INTRODUCTION

In recent years, there have been a great interest in the K-edge resonant inelastic x-ray scattering (RIXS) (Ament et al. 2011), because of its unique advantages over other probes. K-edge RIXS provides information on momentum dependence of excitations, sensitive to the bulk properties, and can be directly compared with the electronic band structures because final states do not have the core hole. It is suggested that the K-edge RIXS intensity for transition metal oxides essentially represents the dynamics of electrons near the Fermi energy which screens the 1s core hole created by the x-ray (Ahn et al. 2009; Semba et al. 2008).

\[ \text{EF} \quad 4p \quad 3d \quad 1s \]

Figure 1.1 Indirect or K-edge RIXS process best described by three stages: (a) in the initial stage, from incoming photon an electron is excited from deep 1s core level into 4p valence band, (b) in the intermediate stage, excitations are created in the 3d band through Coulomb interaction between the core hole and the valence electron, and (c) in the final stage, electron decays leaving the excitation in the valence band and a photon is emitted. Courtesy of Ahn et al. (2009).

The result in Ahn et al. (2009) allows an approximation of replacing the sum over the intermediate states to a single lowest energy intermediate state. The study further showed that expanding RIXS intensity according to the number of final electron-hole pairs is a fast converging expansion with one-electron hole pair states dominant, particularly for insulators. From this consideration, the calculation showed that the electron excitation is from the whole unoccupied band, reflecting the
localized nature of screening of core hole by electron in direct space, whereas the hole excitation is mostly from occupied states close to the gap to minimize the kinetic energy, particularly when the gap energy is smaller than the band width. In Ahn et al. (2009), however, the focus was on energy dependence of the electron-hole excitations, and momentum dependence of RIXS spectrum was not considered explicitly. Further presented is a formula that includes the full momentum dependence, as well as multiple core hole sites within unit cell in the tight binding approach. In this approach, the formula is expressed in terms of the intermediate state basis with a completely localized 1s core hole, so that the RIXS spectrum in reciprocal space can be readily compared with the screening pattern in direct space.

Figure 1.2 (Color) In-plane structural layout of Mn ions depicting $t_{2g}$ spin arrangement along zig-zag chain.

To explain the K-edge RIXS spectrum, applied formula is recently obtained for La$_{0.5}$Sr$_{1.5}$MnO$_4$, which shows a drastic variation of the RIXS intensity in reciprocal space in spite of almost no change in the peak energy (Liu et al. 2012). La$_{0.5}$Sr$_{1.5}$MnO$_4$ has a layered two-dimensional perovskite structure and the hopping
of the Mn 3d $e_g$ electrons between different MnO$_2$ layers is believed to be negligible. K-edge RIXS spectrum is measured on a single crystal of La$_{0.5}$Sr$_{1.5}$MnO$_4$ at 20 K (Liu et al. 2012), which has a magnetic, charge and orbital ordering known as CE-type ordering in the MnO$_2$ plane, schematically shown in Figure 1.2, where “Mn$^{3+}$” and “Mn$^{4+}$” are used to indicate the two sites not related by the symmetry. The strong Hund’s coupling between the $e_g$ electron spin and the $t_{2g}$ electron spin channels the $e_g$ electron hopping only along the zigzag chain, which influence the screening of the core hole in the RIXS intermediate state. This work is presented in depth in Chapter 2, as well as in Liu et al. (2012).

Since the discovery of the colossal magnetoresistance effect, a lot of attention has focused on a class of materials known as perovskite manganites (von Helmolt et al. 1993; Jin et al. 1994; Salamon and Jaime 2001). During the last two decades, substantial progress has been made in the theory for perovskite manganites. Importance of the electron-lattice coupling was identified shortly after the discovery of colossal magnetoresistance effect (Millis et al. 1995; Röder et al. 1996; Millis et al. 1996). First-order character of the metal-insulator phase transition has been found from Monte Carlo simulations (Vergés et al. 2002). Mechanism for inhomogeneity and its relation to metal-insulator transition have been studied (Moreo et al. 1999). Effects of disorder have been investigated for doped manganites (Kumar and Majumdar 2006; Pradhan et al. 2007). The competition between short range superexchange interaction and long range double exchange interaction has been analyzed for multiferroic undoped manganites (Salafranca and Brey 2006). Most recently, novel mechanisms for ferroelectricity, including electronic ferroelectricity, have been proposed for undoped manganites with E-type antiferromagnetic ordering (Sergienko et al. 2006; Yamauchi et al. 2008). These materials have the chemical formula in the form of $RE_{1-x}AK_xMnO_3$, where $RE$ and $AK$ represent the rare earth and alkali metal elements, and have a perovskite structure. One of the major research themes
for these materials is the relation between their physical properties and the average size of ions at the $RE/AK$ site, often known as the chemical pressure effect. The size of the $RE/AK$ ion is usually parameterized by a tolerance factor and one of the most important phase diagrams for these materials has been the one in the temperature versus tolerance factor plane for a fixed 30% ($x = 0.3$) doping ratio (Hwang et al. 1995). The $RE/AK$ ions with size smaller than the space created by the surrounding MnO$_6$ octahedra induce buckling of the Mn-O-Mn bonds, observed through various structural refinement analyses.

To understand the effect of the chemical pressure, semi-classical theories (Millis et al. 1995; Röder et al. 1996; Millis et al. 1996; Moreo et al. 1999; Sergienko et al. 2006; Pradhan et al. 2007; Vergés et al. 2002; Salafranca and Brey 2006; Kumar and Majumdar 2006; Yamauchi et al. 2008) with quantum mechanical electrons coupled with the classical lattice through the Jahn-Teller (JT) interaction often present the phase diagram with one axis representing the ratio between the electron hopping energy and the JT energy gain. This ratio parameterizes the competition between the kinetic and potential energy in perovskite manganites. Theoretical phase diagrams from these approaches agree well with experimental phase diagrams, when this ratio is related to the Mn-O-Mn buckling distortion due to smaller $RE/AK$ ions. However, whether this buckling distortion affects the electron hopping energy or the JT energy gain has been controversial. It is well known from experimental observations that there is a strong competition between the insulating phase with a coherent JT distortion and the metallic phase without such distortion (Salamon and Jaime 2001). So far, most of the attention has centered on the impact of the buckling on the metallic phase, in particular, the possible change in the effective Mn-O-Mn electron hopping parameter and the band width (Hwang et al. 1995). At the same time, there has been a debate whether the variation of the hopping parameter due to the Mn-O-Mn bond angle change of several degrees would be significant enough to
explain the observed metal-insulator transition (Dzero et al. 2000; Fernandez-Baca et al. 1998; Liu et al. 1999; Lynn et al. 1996; Radaelli et al. 1997). For instance, the spin wave stiffness, which depends sensitively on the electron hopping amplitude in double exchange model in ferromagnetic metallic phase, shows very little dependence on Mn-O-Mn bond angle (Lynn et al. 1996; Fernandez-Baca et al. 1998). A less studied effect of the Mn-O-Mn bond buckling, except for a few early efforts based on experimental data (Louca et al. 2001), is the possibility that the buckling distortion may significantly stabilize the insulating phase with a coherent JT distortion, by affecting the JT energy gain. The main goal of this topic is to examine such a possibility with a simplified model of the perovskite manganites. To be specific, the interplay between the JT ordering and chemical pressure is analyzed for undoped perovskite manganites. With one localized \( e_g \) electron per site, the electronic degrees of freedom can be integrated out in undoped manganites (except for electronically ferroelectric undoped manganites postulated at low temperatures for very small \( RE \) ions), which allows us to adopt a purely classical model with the energy expressed in terms of lattice distortions only. The study on undoped manganites is merited, because they are not only parent compounds of doped perovskite manganites (Millis 1996), but also because one of the first multiferroic materials discovered is an undoped manganite, TbMnO\(_3\), with a relatively small \( RE \) element (Kimura, Goto, Shintani, Ishizaka, Arima and Tokura 2003). Recently, electronic ferroelectricity has been also proposed for undoped perovskite manganites (Sergienko et al. 2006; Yamauchi et al. 2008). Therefore, the chemical pressure effect in undoped manganites reported in this thesis would also be relevant for future studies on how the multiferroic and electronically ferroelectric properties would appear in \( REMnO_3 \) with small \( RE \) ions, as well as how the chemical pressure affects the distorted insulating phase of doped manganites. This work is presented in Chapter 3, as well as in Seman, Ahn, Lookman, Saxena, Bishop and Littlewood (2012).
Further presented is classical and quantum mechanical multi-scale descriptions of lattice dynamics, from the atomic scale to the continuum scale, using symmetry modes and their constraint equations. This approach is demonstrated for a one-dimensional chain and a two-dimensional monatomic square lattice. For the classical description, it is found that rigid modes, in addition to the strain modes found before, are necessary to describe the kinetic energy, and obtain constraint equations among these modes. Lagrangian equations, modified with the Lagrange multiplier terms, are solved for phonon dispersion relations without using displacement variables explicitly. The long wavelength limit of the kinetic energy terms expressed in terms of atomic scale modes is shown to be consistent with the continuum theory, and the leading order corrections are obtained. The phonon in terms of symmetry modes is analyzed, and it is found how the contribution of different symmetry modes varies depending on the phonon branch and wavevector. For the quantum mechanical description, conjugate momenta derived for the atomic scale symmetry modes. In direct space, graphical rules for their commutation relations are obtained. Commutation relations in the reciprocal space are also calculated. It is emphasized that the approach based on atomic-scale symmetry-modes could be useful for description of multi-scale lattice dynamics, materials with electron-phonon coupling, and the dynamics of structural phase transition. Theoretical aspects of this topic are studied in Chapter 4, and also presented in Seman, Moon and Ahn (2012).

Summary and closing remarks are presented in Chapter 5. Several core algorithms used extensively in calculations can be found in Chapter 6.
CHAPTER 2
THEORY OF K-EDGE RESONANT INELASTIC X-RAY SCATTERING AND ITS APPLICATION FOR La_{0.5}Sr_{1.5}MnO_{4}

The work in this chapter was done in collaboration with Michel van Veenendaal from Advanced Photon Source at Argonne National Laboratory, John P. Hill, Xuerong Liu, and Diego Casa from Brookhaven National Laboratory, Andrew Boothroyd and Prabhakaran Dharmalingam from Department of Physics at University of Oxford, Hong Ding from Beijing National Laboratory for Condensed Matter Physics, as well as Keun H. Ahn from Department of Physics at New Jersey Institute of Technology.

2.1 Introduction

The dynamic screening of the Coulomb interaction plays a central role in determining the electronic properties of materials (Fetter and Walecka 2003). The response of valence electrons to a potential, in particular on time scales of the order of femtoseconds, is through excitation of electron-hole pairs which screen “bare” charges in the system. The screening is described theoretically by the density-density correlation function, or its Fourier transform, the dynamic structure factor (Pines and Nozières 1999). Spectroscopies that probe the valence band, such as photoemission, are sensitive to these screening dynamics. However, it is often not obvious how to separate the kinetics of a charged particle and the response of the rest of the system to its presence (Hüfner 2003). In contrast, core-level spectroscopies provide an alternative way of studying the screening dynamics. By removing a deep-lying core electron, a strong local potential is created that exists for a very short time, i.e., the core hole lifetime. Essentially, one creates a short-lived localized “test” particle, and measures the response of the electrons to this local transient potential. This type of
screening dynamics has intrigued scientists for decades (Nozières and de Dominicis 1969; van der Laan et al. 1981; van Veenendaal and Sawatzky 1993).

For transition metal compounds, $K$-edge resonant inelastic x-ray scattering (RIXS) (Ament et al. 2011) offers the intriguing possibility of projecting the excitations related to the core hole screening onto valence band excitations. Specifically, it has been shown that $K$-edge RIXS can be directly related to the dynamic structure factor in the limit of a strong or weak core hole potential, $U_{\text{core}}$, relative to the band width (van den Brink and van Veenendaal 2006). For the case where $U_{\text{core}}$ is comparable to the bandwidth, more typical for $3d$ transition metal compounds, the screening is more complicated because there is an asymmetry between the electron and hole excitations and the intermediate states cannot be integrated out (Ahn et al. 2009). In this case, the RIXS response is believed to be sensitive to the transient screening of the intermediate states to the core hole potential (Ahn et al. 2009).

Further presented are RIXS measurements of the momentum and energy dependence of the screening dynamics for a transient local potential in a CE-type charge, orbital, and spin ordered manganite, $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. Strong momentum dependence of the intensity of the across-gap excitation is found, with a dramatic increase on moving away from the two-dimensional (2D) zone center. It is shown that this behavior reflects the size and shape of the real-space screening cloud and demonstrate that in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, the screening distance is very short, with a screening cloud of about 0.4-0.5 interatomic distances in size.

### 2.2 Experiments

A single crystal of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ was grown by the traveling solvent floating zone method. It has a tetragonal structure at room temperature with $I4/mmm$ symmetry and undergoes a charge and orbital ordering transition around 230 K, accompanied by complex structural distortions (Herrero-Martín et al. 2011). For simplicity, the
$I_4/mmm$ notation is used here throughout. The wave vectors of the charge and orbital ordering are then of the form $\left(\frac{1}{2}, \frac{1}{2}, L\right)$ and $\left(\frac{1}{4}, \frac{1}{4}, L\right)$, respectively. In the low temperature ordered state, La$_{0.5}$Sr$_{1.5}$MnO$_4$ is an insulator with a large gap between the $e_g$ states (Bala and Horsch 2005; Lee, Onoda, Arima, Tokunaga, He, Kaneko, Nagaosa and Tokura 2006). The behavior of the excitation between these predominantly Mn 3$d$ states, labeled as a $d$-$d$ transition, is the focus of this study. The Mn K-edge RIXS experiments were performed at Advanced Photon Source on beamlines 30-ID and 9-ID with an instrumental energy resolution of about 270 meV (FWHM). The polarization dependence of the RIXS process is controlled by placing the [001] and [110] directions of the crystal in the scattering plane. The incident beam polarization is perpendicular to the scattering plane, i.e., parallel to the [1\bar{1}0] direction. Thus the incident polarization condition is fixed for all the $Q = (H, H, L)$ points surveyed. All the data presented were collected at $T = 20$ K, well below the Néel temperature (110K) (Sternlieb et al. 1996). Data are normalized by incident beam intensity and corrected for footprint variations.

In Figure 2.1(a), RIXS spectra is taken at three $Q$ points. In each case, there is a large elastic line centered at zero energy loss. The $d$-$d$ transition appears as a peak on the tails of the elastic scattering at around 2 eV, consistent with optics (Lee et al. 2007) and EELS (Kraus et al. 2011) observations. This across-gap transition has also been observed by K-edge RIXS on other manganites (Inami et al. 2003; Grenier et al. 2005; Weber et al. 2010). Remarkably, the RIXS spectra show a strong momentum dependence of the intensity of this feature. At $Q_0 = (-0.03, -0.03, 7.20)$ with very small in-plane momentum transfer, the 2 eV peak is almost unobservable. This momentum dependence is confirmed with RIXS spectra collected at a large number of $Q$ points, as shown in Figure 2.1(b) and 2.1(c). To control the systematics resulting from polarization factors, the data were taken either at fixed sample angle $\theta$, or fixed detector angle $2\theta$. These conditions result in data taken along three lines
in reciprocal space. In all cases, the incident polarization is parallel to the [1\bar{1}0] direction. With the detector position $2\theta$ fixed, polarization effects associated with the outgoing x-ray are eliminated. Figure 2.1(c) shows RIXS spectra with the elastic line subtracted\(^1\) for the $Q$ points with $2\theta = 68^\circ$. The integrated intensity, $I(Q)$, is taken over the 1-3 eV range as a measure of the strength of the 2 eV peak. The size of the symbols in Figure 2.1(b) is proportional to $I(Q)$. A clear systematic dependence on momentum transfer is observed.

![Graph](image)

**Figure 2.1** (a) RIXS spectra at three $Q$ points. (b) The $Q$ points surveyed in the $(H, H, L)$ plane. The radius of the dot is proportional to the integrated intensity of the 2 eV peaks. $\theta$ and $2\theta$ are the incident and detector angles. (c) RIXS spectra for the $Q$ points along the $2\theta = 68^\circ$ line, with the elastic intensity subtracted. The grey shaded region is the energy window used in calculating the integrated intensity of the feature.

\(^1\)The elastic line was subtracted by using a model function. The latter was determined by measuring the elastic scattering at an off-resonant energy (7 eV below the edge), where there are negligible inelastic contributions.
The integrated intensities of the d-d excitation are plotted as a function of the in-plane momentum transfer in Figure 2.2(b). In order to quantitatively compare the experimental data with the theoretical calculations (discussed below), the integrated intensities are plotted relative to the intensity at $Q_0 = (-0.03, -0.03, 7.20)^2$, i.e., $I(Q) - I(Q_0)$. This removes the uncertainty in determining the common background for all $Q$ points. The strength of the 2 eV d-d excitation exhibits a minimum at zero in-plane momentum transfer and a maximum at (0.5, 0.5, $L$). Interestingly, although there is a large variation in the $L$ values for the various $Q$ points [see Figure 2.1(b)], all the measurements collapse onto a single curve in Figure 2.2(b). This demonstrates that there is negligible $L$ dependence to this behavior, a result consistent with the 2D nature of this single layered manganite. Further, it implies that the polarization factors are indeed constant for the experimental geometry. From here on, the momentum transfer will be denoted simply as $Q_{2D} = (H, H)$ since the $L$ component is irrelevant.

The experimental data in Figures 2.1 and 2.2 show the main experimental observations. The across-gap d-d excitation in La$_{0.5}$Sr$_{1.5}$MnO$_4$, as observed in the RIXS process, exhibits a strong momentum dependence. While the position of the peak shows no appreciable dispersion, the intensity increases rapidly as the in-plane momentum transfer increases away from the 2D zone center. Near the zone center, the spectral weight of the 2 eV feature almost disappears. This is a surprising result. The disappearance of this RIXS spectral weight at the 2D zone center cannot be the result of the dynamic structure factor going to zero, since this feature is still observed in the optical response (Lee et al. 2007), which probes the zero momentum transfer response function. This demonstrates that K-edge RIXS in La$_{0.5}$Sr$_{1.5}$MnO$_4$ is indeed in the intermediate core-hole potential regime, discussed in the introduction. In the following, momentum-dependence is described in detail and it is shown that it arises

$^2$Q points such as (0, 0, L), which would have been preferable, are intentionally avoided due to specular reflection enhancement of the elastic line at such points.
from the intermediate state screening dynamics and in particular that it reflects the real-space extent of the screening cloud.

2.3 Results from Theory and Comparison With Experiments

To understand this strong in-plane momentum dependence, the RIXS response is calculated from La$_{0.5}$Sr$_{1.5}$MnO$_4$ for a two-dimensional 16 × 16 Mn cluster with periodic boundary conditions. The initial and final states of the unperturbed system, and the intermediate states in the presence of the 1s core hole on-site Coulomb potential, are solved numerically with a tight-binding approach. The Hamiltonian employed is similar to the one in Ahn and Millis (2000), which includes the nearest-neighbor electron hopping within the MnO$_2$ plane, the Jahn-Teller and isotropic electron-lattice coupling, the Hund’s coupling to the CE-type ordered $t_{2g}$ spins, and the Coulomb interaction between $e_g$ electrons within the Hartree-Fock approximation, as later introduced in depth in Section 2.5. The sizes of the distortions of the oxygen octahedra are taken from Herrero-Martín et al. (2011). The RIXS spectra are then calculated from the Kramers-Heisenberg formula (Ament et al. 2011; Ahn et al. 2009):

$$I \propto \sum_f \sum_n \frac{\langle f | \mathcal{D}^\dagger | n \rangle \langle n | \mathcal{D} | g \rangle}{E_g + \hbar \omega_k - E_n + i \Gamma_n} \left| \delta(E_f - E_g - \hbar \Delta \omega) \right|^2,$$

(2.1)

where $|f\rangle$, $|n\rangle$, and $|g\rangle$ represent the final, intermediate and initial states, and $E_f$, $E_n$ and $E_g$ their energies. $\Gamma_n$ is the inverse of the intermediate state lifetime, and $\mathcal{D}^\dagger$ and $\mathcal{D}$ are the RIXS dipole transition operators. $\hbar \omega_k$ and $\hbar \Delta \omega$ are the incident x-ray energy and the energy loss, respectively. The calculated RIXS intensity is averaged over configurations in which the zig-zag chains of orbital order are along either the [110] or the [1̅10] directions, to take into account twinning effects in real crystals. Details of the calculation will be published elsewhere.
The calculated RIXS spectra were found to be most sensitive to the $e_g$-$e_g$ hybridization and the coupling of the $e_g$ electrons to the distortions of oxygen octahedra. These two effects are parameterized as $t_0$ and $\lambda$ in the Hamiltonian, where $t_0$ is the hopping between $3x^2-r^2$ orbitals along the $x$ direction and $\lambda$ is proportional to the strength of the electron-phonon coupling. With reasonable parameter values, as introduced in Section 2.5, and the combination of $t_0 = 0.9$ eV and $\lambda = 7.41$ eV/Å, the calculated spectra shown in Figure 2.2(a) and the thick (blue) line in Figure 2.2(b)
closely resemble the experimental observations. The intensity of the calculated RIXS response peaks near 2 eV, and increases rapidly as \( \mathbf{Q}_{2D} \) increases away from (0, 0), towards (0.5, 0.5), as seen in the experiments. The calculated spectra in Figure 2.2(a) suggest a slight dispersion of about 130 meV of the 2 eV peak, which is much smaller than that reported for LaSr$_2$Mn$_2$O$_7$ (Weber et al. 2010). Such a small dispersion, roughly equal to the experimental step size taken in Figure 2.1(c), is below the detection limit of the experiment.

The sensitivity of the RIXS response to intersite hopping and the electron-phonon coupling is shown in Figure 2.2(b) by varying \( t_0 \) and \( \lambda \), see Section 2.5. For a given \( t_0 \), \( \lambda \) is constrained such that the \( d-d \) excitation in the RIXS response peaks near 2 eV. Henceforth, only \( t_0 \) is mentioned for simplicity. The details of the combinations of \( t_0 \) and \( \lambda \) can be found in Section 2.5. As was done for the experimental data, the calculated response is integrated over the same 1-3 eV window to generate the curves in Figure 2.2(b), and again the value at \( \mathbf{Q}_{2D} = (-0.03, -0.03) \) is subtracted. The calculated results show the best agreement with the experimental observations when \( t_0 = 0.9 \) eV. For larger \( t_0 \) values, the calculated RIXS response differs significantly from the experimental data. Thus, this study sets the upper limit of \( t_0 \). Note that the inability to precisely determine the parameter values is largely due to the difficulty in determining the contributions from other inelastic scattering processes that give rise to a smooth “background” in the low energy loss region.

### 2.4 Discussion

To further understand the implications of the observed momentum dependence of the RIXS spectrum for the screening dynamics, the real-space screening configurations are calculated from the lowest energy intermediate eigenstates. These are shown in the top panels of Figure 2.3. Figures 2.3(a) and 2.3(b) compare the charge redistributions for \( t_0 = 0.9 \) and 1.5 eV, respectively, with the core hole at either a Mn$^{3+}$
or a Mn\textsuperscript{4+} site. The volumes of the red and blue spheres scale with the screening electron and hole densities on individual sites. Figures 2.3(c) and 2.3(d) show the calculated RIXS intensities for the two \( t_0 \) values over half of a Brillouin zone.

**Figure 2.3** (Color) (a) and (b): Screening configuration in real space for \( t_0 = 0.9 \) and 1.5 eV, respectively. The top left half corresponds to the case with the core hole at a Mn\textsuperscript{3+} site, while the bottom right it is at a Mn\textsuperscript{4+} site. The volumes of the red and blue spheres are proportional to the electron and hole numbers. The big red spheres at Mn\textsuperscript{4+} core hole sites represent about 0.9 electrons. (c) and (d): Integrated RIXS intensity plotted in the \((H, K, 0)\) plane of reciprocal space for \( t_0 = 0.9 \) eV and \( t_0 = 1.5 \) eV, respectively. Red and blue represent the maximum and minimum intensities, respectively.

As expected, the excited hole distributions are more localized near the core hole sites for the smaller value of \( t_0 \). For \( t_0 = 0.9 \) eV, the screening hole is tightly bound to the excited electron with more than 90 % of the excited charge located on the three nearest neighbor sites along the zig-zag chain. The predominant wave vector for these electron and hole distributions is \((0.5, 0.5)\), coincident with the location of the RIXS peak intensity maximum in reciprocal space in Figure 2.3(c)
and in agreement with the experimental results. For the large hopping parameter, \( t_0 = 1.5 \, \text{eV} \), the screening pattern in real space changes drastically. The majority of the hole distribution in Figure 2.3(b) is now beyond the nearest neighbor sites, and is spread throughout the zig-zag chains. This difference in screening dynamics is directly reflected in the RIXS response, with the maximum of the RIXS response then shifted to around (0.25, 0.25), as shown in Figures 2.2(b) and 2.3(d). This pattern is completely at odds with that seen in the experiment results.

![Figure 2.4](Color) The excited hole number normalized by the excited electron number at the core hole site, plotted in semi-logarithmic scale with respect to the distance from the core hole site along the zig-zag chain.

The relationship between the hopping strength and the charge redistribution in the screening process apparent in the theoretical calculations is shown more clearly in Figure 2.4, where the relative hole number at a given site is plotted as a function of the distance from the core hole site, as measured along the zig-zag chain. The semi-logarithmic plot reveals an exponential decay of the hole density, confirming the presence of exciton-like screening clouds. The size of the screening cloud, which characterizes the screening dynamics and determines the RIXS response, depends strongly on the hopping strength \( t_0 \). Taking the \( t_0 = 0.9 \, \text{eV} \) case, which best describes the RIXS data, the excited hole distributions is fitted to an exponential function to
find that the size of the screening clouds are 0.4 and 0.5 atomic spacings for the Mn\(^{3+}\) and Mn\(^{4+}\) sites, respectively.

2.5 Details of Theory and Calculations

2.5.1 Tight Binding Hartree-Fock Hamiltonian and Core Hole Potential for La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\)

In this section, the tight binding Hamiltonian is introduced that was used to calculate the RIXS spectrum for La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\). In the experimental results for this material (Liu et al. 2012), shown in Figure 2.1 after subtracting the elastic peak, the RIXS peak at around 2 eV shows prominent changes with momentum, which is the focus of the current study. This peak is believed to be from the transitions between Mn 3\(d\) \(e_g\) levels, and, therefore, Mn \(e_g\) levels are considered only in the tight binding Hamiltonian. As mentioned above, the MnO\(_2\) planes in La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\) are separated from each other by the intervening, electronically inert, Sr, La, and O ions, which allows the use of the Hamiltonian for a single MnO\(_2\) layer for the RIXS calculation.

Term \(a_{\sigma \iota \xi}^\dagger\) is defined as the creation operator of the \(e_g\) electron with the spin state \(\sigma = \uparrow, \downarrow\) and orbital state \(\xi = 1 \equiv \xi_1\) for \((3z^2 - r^2)/\sqrt{6}\) and \(\xi = 2 \equiv \xi_2\) for \((x^2 - r^2)/\sqrt{2}\) \(e_g\) at a Mn site with an index vector \(\vec{i} = (i_x, i_y)\), where \(i_x\) and \(i_y\) are integers. The electron hopping term, that is, kinetic energy term, is

\[
\hat{H}_{KE} = -\frac{1}{2} \sum_{\sigma, \iota, \delta, \xi, \xi', \delta'} t_{\delta \xi \xi'}^{\iota \delta \iota} \left( a_{\sigma \iota \xi}^\dagger a_{\sigma, \iota + \delta, \xi'} + a_{\sigma, \iota + \delta, \xi'}^\dagger a_{\sigma \iota \xi} \right). \tag{2.2}
\]

The unit vector \(\vec{\delta} = \pm \hat{x}, \pm \hat{y}\) represent the directions of the nearest neighbor sites of a Mn ion. The form of the hopping matrices within the MnO\(_2\) plane are

\[
t_x = t_{-x} = t_o \begin{pmatrix} 1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 3/4 \end{pmatrix}, \tag{2.3}
\]

\[
t_y = t_{-y} = t_o \begin{pmatrix} 1/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 3/4 \end{pmatrix}. \tag{2.4}
\]
reflecting the symmetry of the $e_g$ orbitals. The parameter $t_0$ represents the effective hopping constant between two $(3x^2 - r^2)/\sqrt{6}$ orbitals along the $x$-direction.

Two kinds of electron-lattice couplings are included. The distortion of oxygen octahedron around a Mn ion at $\vec{i}$ is parameterized as follows. $u^\zeta_i (\zeta = x, y)$ represents the $\hat{\zeta}$ direction displacement of an oxygen ion located between Mn ions at $\vec{i}$ and $\vec{i} + \hat{\zeta}$ from the position for the ideal undistorted square MnO$_2$ lattice with the average in-plane Mn-O bond distance. The $u^{+z}_i$ and $u^{-z}_i$ represent the $z$ direction displacements of oxygen ions, right above and right below the Mn ion at $\vec{i}$, from the location of the average in-plane Mn-O bond distance. The parameters, $Q_1, \vec{i}$, $Q_2, \vec{i}$, and $Q_3, \vec{i}$, represent the distortion modes of the oxygen octahedron around a Mn ion at site $\vec{i}$ and are defined in the following way.

\[
Q_{1,\vec{i}} = \frac{(u^x_i - u^x_{i-\hat{x}} + u^y_i - u^y_{i-\hat{y}} + u^{+z}_i - u^{-z}_i)}{\sqrt{3}} \quad (2.5)
\]
\[
Q_{2,\vec{i}} = \frac{(u^x_i - u^x_{i-\hat{x}} - u^y_i + u^y_{i-\hat{y}})}{\sqrt{2}} \quad (2.6)
\]
\[
Q_{3,\vec{i}} = \frac{(2u^{+z}_i - 2u^{-z}_i - u^x_i + u^z_{i-\hat{x}} - u^y_i + u^y_{i-\hat{y}})}{\sqrt{6}} \quad (2.7)
\]

The Mn-O bond distances estimated from the structural refinement of high-resolution synchrotron x-ray powder diffraction for La$_{0.5}$Sr$_{1.5}$MnO$_4$ in Herrero-Martín et al. (2011) indicate $Q_1 = 0.0531$ Å, $Q_2 = 0.1089$ Å, and $Q_3 = 0.0955$ Å around “Mn$^{3+}$” site and $Q_1 = -0.0531$ Å, $Q_2 = 0$, and $Q_3 = 0.1192$ Å around “Mn$^{4+}$” site.

The $Q_2$ and $Q_3$ distortions break the cubic symmetry of oxygen octahedron around Mn and interact with the $e_g$ orbital state through the following Jahn-Teller Hamiltonian term,

\[
\hat{H}_{JT} = -\lambda_Q \sum_i \sigma \left( \begin{array}{c} a_{\sigma\uparrow i} \\ a_{\sigma\downarrow i} \end{array} \right)^T \left( \begin{array}{cc} Q_{3,\vec{i}} & -Q_{2,\vec{i}} \\ -Q_{2,\vec{i}} & Q_{3,\vec{i}} \end{array} \right) \left( \begin{array}{c} a_{\sigma\uparrow i} \\ a_{\sigma\downarrow i} \end{array} \right) \quad (2.8)
\]

where $\lambda_Q$ represents the strength of this coupling.\(^3\) The isotropic $Q_1$ distortion interacts with total $e_g$ electron charge through the following “breathing” electron-

\(^3\)Unlike the three-dimensional manganites, the degeneracy of the $e_g$ levels are broken even without the $Q_2$ or $Q_3$ distortions because of the layered crystal structure. Therefore,
lattice Hamiltonian term,
\[
\hat{H}_{\text{br}} = -\beta \lambda Q \sum_{\vec{i} \sigma} \left( \begin{array}{c} a_{\sigma \vec{i}1}^\dagger \\ a_{\sigma \vec{i}2}^\dagger \end{array} \right)^T \left( \begin{array}{cc} Q_{1,\vec{i}} & 0 \\ 0 & Q_{1,\vec{i}} \end{array} \right) \left( \begin{array}{c} a_{\sigma \vec{i}1} \\ a_{\sigma \vec{i}2} \end{array} \right),
\]
where \( \beta \) represents the ratio between the strengths of the breathing and the Jahn-Teller couplings, likely larger than 1.

In addition, the Hund’s coupling of the \( e_g \) electron spin state to the CE-type magnetic ordering of the \( t_{2g} \) spins is included,
\[
\hat{H}_{\text{Hund}} = -\sum_{\sigma',\sigma''} J_{\text{Hund}} S_{t_{2g},\vec{i}} \cdot \sigma' \sigma'' a_{\sigma' \vec{i}\xi}^\dagger \tau_{\sigma'' \sigma'} a_{\sigma'' \vec{i}\xi},
\]
where \( S_{t_{2g},\vec{i}} \) represents the \( t_{2g} \) spin and \( \tau \) the Pauli matrix.

As in Ahn and Millis (2000), the 3\textit{d}-3\textit{d} same-site Coulomb interaction with parameter \( U \) is also included,
\[
\hat{H}_{3d3d,\text{Coul}} = \sum_{\vec{i}} \sum_{\sigma,\eta=\pm} \sum_{\sigma',\eta'=-,+} U \hat{n}_{\sigma \eta \vec{i}} \hat{n}_{\sigma' \eta' \vec{i}},
\]
where \( \hat{n}_{\sigma \eta \vec{i}} = a_{\sigma \eta \vec{i}}^\dagger a_{\sigma \eta \vec{i}} \) is the number operator. \( \eta = - \) and \( + \) represent the local orbital eigenstates of \( \hat{H}_{\text{JT}} \) with lower and higher energies, respectively, chosen for the following Hartree-Fock approximation,
\[
\hat{H}_{3d3d,\text{Coul}}^{\text{HF}} = \sum_{\vec{i}} U_{\gamma+} a_{\gamma+ \vec{i}}^\dagger a_{\gamma+ \vec{i}} + U_{\gamma-} a_{\gamma- \vec{i}}^\dagger a_{\gamma- \vec{i}} + U_{\gamma+} a_{\gamma+ \vec{i}}^\dagger a_{\gamma- \vec{i}} + U_{\gamma-} a_{\gamma- \vec{i}}^\dagger a_{\gamma+ \vec{i}} - \text{ etc.,}
\]
where \( U_{\gamma} = U < \hat{n}_{\gamma \vec{i}}^+ > + U < \hat{n}_{\gamma \vec{i}}^- > + U < \hat{n}_{\gamma \vec{i}}^- > + \text{ etc.,} \)

The total Hamiltonian for the calculations of RIXS initial state and final states is the sum of the terms described so far.
\[
\hat{H}_{3d} = \hat{H}_{\text{KE}} + \hat{H}_{\text{JT}} + \hat{H}_{\text{br}} + \hat{H}_{\text{Hund}} + \hat{H}_{3d3d,\text{Coul}}^{\text{HF}}.
\]
\( E_{\text{JT}} \) should be considered as the effective Hamiltonian that includes not only the effect of the oxygen octahedron but also the crystal field of farther ions.
The CE type ordering of $t_{2g}$ spins and lattice distortions gives rise to the unit cell shown in dotted lines in Figure 1.2. With the distance between Mn-Mn in undistorted lattice represented as a unit distance and the $x$ and $y$ axes chosen along Mn-O bond directions, the primitive reciprocal lattice vectors are $(\pi/2, \pi/2)$ and $(\pi/2, -\pi/2)$, and the first Brillouin zone is $\Omega_{1BZ} = \{ k | -\pi/2 < k_x + k_y \leq \pi/2, -\pi/2 < k_x - k_y \leq \pi/2 \}$.

The $1s$-$3d$ on-site Coulomb interaction is generally expressed as

$$\hat{H}_{1s3d,Coul} = -U_c \sum_{\sigma, \xi} a^\dagger_{\sigma, \xi} a_{\sigma, \xi} s^\dagger_{\beta, \gamma} s_{\beta, \gamma}, \quad (2.14)$$

As shown in the next section, in the limit of completely localized $1s$ core hole, the RIXS intermediate energy eigenstates can be chosen as states with a single completely localized $1s$ core hole, which can be found from

$$\hat{H}_{total, \vec{i}_c} = \hat{H}_{3d} + \hat{H}_{1s3d,Coul, \vec{i}_c}, \quad (2.15)$$

where

$$\hat{H}_{1s3d,Coul, \vec{i}_c} = -U_c \sum_{\sigma, \xi} a^\dagger_{\sigma, \xi, \vec{i}_c} a_{\sigma, \xi, \vec{i}_c}, \quad (2.16)$$

and $\vec{i}_c$ represents the $1s$ core hole site.

The parameter values chosen for the best fit of the measured RIXS spectrum are: $t_0 = 0.9$ eV, $\lambda_Q = 7.4$ eV/Å, $\beta = 1.5$, $J_H|\vec{k}_{t_{2g}, \vec{i}}| = 2.2$ eV, $U = 3.5$ eV, and $U_c = 4.0$ eV. As a comparison, different values of $t_0$ and $\lambda_Q$ are considered, including $t_0 = 1.5$ eV and $\lambda_Q = 3.5$ eV/Å, to study the implication of the momentum dependent RIXS intensity for the screening dynamics.

Further, $\hat{H}_{3d}$ and $\hat{H}_{total, \vec{i}_c}$ are transformed into the reciprocal space as follows,

$$\hat{H}_{3d} = \sum_{\sigma, \xi, \kappa, \xi', \kappa'} H_{3d, \sigma, \xi, \kappa, \xi', \kappa'}, \quad (2.17)$$

and

$$\hat{H}_{total, \vec{i}_c} = \sum_{\sigma, \xi, \kappa, \xi', \kappa'} H_{total, \vec{i}_c, \sigma, \kappa, \xi, \kappa', \xi'}, \quad (2.18)$$
where \( \vec{k}, \vec{k}' \in \Omega_{1BZ} \), \( \vec{K}, \vec{K}' \in \{ \vec{K}_1, \vec{K}_2, \vec{K}_3, \vec{K}_4, \vec{K}_5, \vec{K}_6, \vec{K}_7, \vec{K}_8 \} \), and \( \vec{K}_n \) represents \((0,0), (\pi,0), (0,\pi), (-\pi/2,-\pi/2), (\pi/2,-\pi/2), (-\pi/2,\pi/2), (\pi/2,\pi/2)\), for \( n = 1, 2, 3 \ldots, 8 \), respectively. The details of these expressions are presented in the Appendix 2.A.

From the elements of the eigenvectors of the matrices \( \hat{H}^{3d}_{\sigma, \vec{k} + \vec{K}, \xi, \vec{k}' + \vec{K}', \xi'} \) and \( \hat{H}^{\text{total}, \vec{i}_c}_{\sigma, \vec{k} + \vec{K}, \xi, \vec{k}' + \vec{K}', \xi'} \), the coefficients \( \alpha \)'s and \( \gamma \)'s are defined in the following way:

\[
b_{\sigma l k}^\dagger = \sum_{\vec{K}, \xi} a_{\sigma, \vec{k} + \vec{K}, \xi}^\dagger \alpha_{\sigma, \vec{k} + \vec{K}, \xi} b_{\sigma l k}^\dagger, \quad (2.19)
\]

\[
c_{\sigma m}^\dagger = \sum_{\vec{K}, \xi} a_{\sigma, \vec{k} + \vec{K}, \xi}^\dagger \gamma_{\sigma, \vec{k} + \vec{K}, \xi} c_{\sigma m}^\dagger, \quad (2.20)
\]

where \( b_{\sigma l k}^\dagger \) and \( c_{\sigma m}^\dagger \) are the creation operators of the eigenstates of \( \hat{H}^{3d} \) with the wavevector \( \vec{k} \in \Omega_{1BZ} \) within the \( l \)-th lowest energy band and the \( m \)-th lowest energy eigenstates of \( \hat{H}^{\text{total}, \vec{i}_c} \), respectively. (Though it is suppressed in the notations for simplicity, \( c_{\sigma m}^\dagger \) and \( \gamma_{\sigma, \vec{k} + \vec{K}, \xi} \), defined above, and \( \beta_{\sigma l k m} \), defined below, depend on the core hole site \( \vec{i}_c \).)

The relation between \( a_{\sigma l k}^\dagger \) and \( b_{\sigma l k}^\dagger \) is inverted in the Equation (2.19) to further obtain \( \tilde{\alpha} \)'s defined from

\[
a_{\sigma, \vec{k} + \vec{K}, \xi}^\dagger = \sum_{\vec{k}} b_{\sigma l k}^\dagger \tilde{\alpha}_{\sigma \vec{k} l k} \tilde{\alpha}_{\sigma \vec{k} l k}^\dagger, \quad (2.21)
\]

where the matrix of \( \tilde{\alpha} \)'s corresponds to the inverse of the matrix of \( \alpha \)'s. From \( \tilde{\alpha} \)'s and \( \gamma \)'s, the coefficients \( \beta \)'s can be found, which represent the eigenstates in the presence of the core hole in terms of the eigenstates in the absence of the core hole according to

\[
c_{\sigma m}^\dagger = \sum_{l k} b_{\sigma l k}^\dagger \beta_{\sigma l k m} c_{\sigma m}^\dagger, \quad (2.22)
\]

where

\[
\beta_{\sigma l k m} = \sum_{\vec{K}, \xi} \tilde{\alpha}_{\sigma l k \vec{k} + \vec{K}, \xi} \gamma_{\sigma, \vec{k} + \vec{K}, \xi} \beta_{\sigma l k m}. \quad (2.23)
\]
2.5.2 K-edge RIXS Formula in the Limit of Completely Localized 1s Core Hole

The following Kramers-Heisenberg formula (Ament et al. 2011) is the starting point for the derivation of the RIXS formula:

\[ I \propto \sum_f \sum_n \langle f | D'^\dagger | n \rangle \langle n | D | g \rangle \left| \frac{\delta(E_f + \hbar \omega_{\vec{k}'} - E_g - \hbar \omega_{\vec{k}} - i\Gamma_n)}{E_g + \hbar \omega_{\vec{k}} - E_n + i\Gamma_n} \right|^2, \tag{2.24} \]

where \(|f\), \(|n\), and \(|g\) represent the final, intermediate and initial state, \(E_f, E_n\) and \(E_g\) their energies, \(\Gamma_n\) inverse of the intermediate state life time, \(\hbar \omega_{\vec{k}'}\) and \(\hbar \omega_{\vec{k}}\) the energy of outgoing and incoming x-ray with wavevector \(\vec{k}'\) and \(\vec{k}\), and \(D'^\dagger\) and \(D\) the RIXS transition operators.

In general, the 1s core hole component within the intermediate eigenstates \(|n\rangle\) can be chosen as a delocalized state with the momentum index (Semba et al. 2008). In the limit that the 1s electron hopping amplitude becomes zero, the intermediate state energy levels with different core hole momenta become degenerate, and the appropriate linear combinations can be made to form intermediate energy eigenstates with a 1s core hole completely localized at a site (Davis and Feldkamp 1979; Feldkamp and Davis 1980; Ahn et al. 2009). Therefore, the state \(|n\rangle\) can be written as \(|n_{\vec{R}+\vec{d}}\rangle\), which represents the intermediate energy eigenstate with the core hole at a site \(\vec{R}+\vec{d}\) within the unit cell at a lattice point \(\vec{R}\). Sum over intermediate state, \(\sum_n\) is written as three kinds of sums, \(\sum_{\vec{R}} \sum_{\vec{d}} \sum_{n_{\vec{R}+\vec{d}}}\).

Dipole approximation (Ament et al. 2011) is taken for the RIXS transition operator \(D'^\dagger\) and \(D\). By analyzing how the phases of intermediate and final eigenstates change with the translation by the lattice vector \(\vec{R}\), it is found that the sum over \(\vec{R}\) just contributes as a constant factor to the RIXS spectrum and the crystal momentum conservation. It should be noted that creation and annihilation of the intermediate 4p excited states do not introduce any phase factor. Polarization effect in the K-edge RIXS is a constant factor and the dipole operators can be replaced by
the core hole creation and annihilation operators, resulting in the following expression,

\[ I \propto \sum_{\vec{K}} \sum_{f} \left| \sum_{\vec{d}} \sum_{n_{\vec{d}}} e^{-i(\vec{k}' - \vec{k}) \cdot \vec{d}} \langle f | \sum_{\vec{d}} n_{\vec{d}} \rangle \langle n_{\vec{d}} | g \rangle \right|^2 \frac{E_g + \hbar \omega_{\vec{k}} - E_{n_{\vec{d}}} + i \Gamma_{n_{\vec{d}}}}{\delta(E_f + \hbar \omega_{\vec{k}} - E_g - \hbar \omega_{\vec{k}}) \delta(\vec{k}_f + \vec{k}' - \vec{k} + \vec{K})}. \]  

Further detail of the derivation of the above formula is presented in Appendix 2.B.

**Figure 2.5** (Color) (a) Density of states per site. Core hole at Mn\(^{3+}\) with \(t_0 = 0.9\) eV: (b) Final distribution compared to electron and hole RIXS intensity. (c) Intermediate distribution compared to density of states per site. Core hole at Mn\(^{4+}\) with \(t_0 = 0.9\) eV: (d) Final distribution compared to electron and hole RIXS intensity. (e) Intermediate distribution compared to density of states per site.

As discussed in the introduction, further approximation is made to replace the sum \(\sum_{n_{\vec{d}}}\) by a single term with \(n_{\vec{d}} = n_{\vec{d}}^{low}\), that is, the lowest energy eigenstate with the core hole at site \(\vec{d}\). Final states \(\langle \sigma l_{\vec{e}} \vec{k}_{\vec{e}} l_{\vec{h}} \vec{k}_{\vec{h}} | \) are considered with only one pair of
an electron with momentum $\vec{k}_e$ and band index $l_e$ and a hole with momentum $\vec{k}_h$ and band index $l_h$ both with spin $\sigma$, while neglecting possible differences in resonance energy $E_{n_{d_{\text{low}}}} - E_g$ and life time broadening $\Gamma_{n_{d_{\text{low}}}}$ for different core hole site $\vec{d}$ within the unit cell. These approximations lead to the following formula for the numerical calculation of the RIXS spectrum.

$$I \propto \sum_{R} \sum_{\sigma l_e l_h} \left| \sum_{\vec{d}'} e^{-i(\vec{k}' - \vec{k}) \cdot \vec{d}'} (\sigma l_e \vec{k}_e l_h \vec{k}_h | n_{d_{\text{low}}} \vec{d}^\dagger | g) \langle n_{d_{\text{low}}} | \vec{d}^\dagger | g \rangle \right|^2 \\
\delta(\varepsilon_{l_e \vec{k}_e} - \varepsilon_{l_h \vec{k}_h} + \hbar \omega_{\vec{k}'} - \hbar \omega_{\vec{k}}) \delta(\vec{k}_e - \vec{k}_h + \vec{k}' - \vec{k} + \vec{K}).$$  (2.26)

Further, consider comments on the general features of the above expression. If the solid has one core hole site per unit cell like high $T_c$ cuprate, $\vec{d} = 0$ can be chosen to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.6.png}
\caption{(Color) (a) Density of states per site. Core hole at Mn$^{3+}$ with $t_0 = 1.5$ eV: (a) Final distribution compared to electron and hole RIXS intensity. (b) Intermediate distribution compared to density of states per site. Core hole at Mn$^{4+}$ with $t_0 = 1.5$ eV: (a) Final distribution compared to electron and hole RIXS intensity. (b) Intermediate distribution compared to density of states per site.}
\end{figure}
simplify the above expression by omitting a constant factor as follows,

\[ I \propto \sum_{\vec{K}} \sum_{\sigma_{le}\ell_h,\ell_h} \left| \langle \sigma_{le}\vec{k}_e\ell_h\vec{k}_h | \Sigma_{\vec{d}=0} | n_{\text{low}} \rangle \right|^2 \delta(\varepsilon_{\vec{k}_e} - \varepsilon_{\ell_h\vec{k}_h} + \hbar\omega_{\vec{k}_e} - \hbar\omega_{\vec{k}_h}) \delta(\vec{k}_e - \vec{k}_h + \vec{k}' - \vec{k} + \vec{K}). \]  

If the outgoing x-ray momentum is changed by reciprocal lattice vector \( \vec{K}' \) to \( \vec{k}'' = \vec{k}' + \vec{K}' \) while the outgoing x-ray energy is unchanged \( \hbar\omega_{\vec{k}'} = \hbar\omega_{\vec{k}''} \), the RIXS intensity would be unchanged, consistent with the result in Kim et al. (2007) for cuprate. If the solid have multiple core hole sites per unit cell, such symmetry with respect to the shift by reciprocal lattice vectors does not exist in general. However, if the core hole sites within the unit cell can be approximated as a lattice, part of the symmetry can be approximately restored. For example, for La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\), the Mn ion core hole sites within MnO\(_2\) plane approximately form a square lattice with the average Mn-Mn distance as a lattice constant. Since the reciprocal lattice vector for the approximate square core hole site, \( \vec{K}_{\text{core}} \), is one of the reciprocal lattice vectors of the actual lattice, and since \( e^{i\vec{R}_{\text{core}} \cdot \vec{d}} \approx 1 \) in Equation (2.26), the RIXS spectrum has an approximate symmetry of \( I(\vec{k}' + \vec{K}_{\text{core}} - \vec{k}) \approx I(\vec{k}' - \vec{k}) \). Therefore, the approximate symmetry in reciprocal lattice is not with respect to the actual reciprocal lattice vectors, but with respect to the “core hole reciprocal lattice vectors” if the core hole sites approximately form a lattice.

Calculated \( \langle n_{\text{low}}^{\vec{d}} | s_{\vec{d}} \rangle \) represents the transition probability from the initial to the lowest energy intermediate state, according to the following formula, where \( N_e \) represents the total electron number.

\[
\langle n_{\text{low}}^{\vec{d}} | s_{\vec{d}} \rangle = \prod_{\sigma = \uparrow \downarrow} \begin{vmatrix}
\beta_{\sigma\vec{k}_{1,1}} & \beta_{\sigma\vec{k}_{1,2}} & \cdots & \beta_{\sigma\vec{k}_{1,N}} \\
\beta_{\sigma\vec{k}_{2,1}} & \beta_{\sigma\vec{k}_{2,2}} & \cdots & \beta_{\sigma\vec{k}_{2,N}} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{\sigma\vec{k}_{N,1}} & \beta_{\sigma\vec{k}_{N,2}} & \cdots & \beta_{\sigma\vec{k}_{N,N}} 
\end{vmatrix}.
\]
Further calculated is \( \langle \sigma_l \vec{k}_e l_h \vec{k}_h | \hat{S}^d | n_{\downarrow}^{\vec{k}_h} \rangle \), the transition probability from the intermediate to the final state, according to the following formula,

\[
\langle \sigma_l \vec{k}_e l_h \vec{k}_h | \hat{S}^d | n_{\downarrow}^{\vec{k}_h} \rangle = \begin{vmatrix}
\beta_{\sigma_1 \vec{k}_1 1} & \beta_{\sigma_1 \vec{k}_1 2} & \cdots & \beta_{\sigma_1 \vec{k}_1 \frac{N_e}{2}} \\
\beta_{\sigma_1 \vec{k}_2 1} & \beta_{\sigma_1 \vec{k}_2 2} & \cdots & \beta_{\sigma_1 \vec{k}_2 \frac{N_e}{2}} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{\sigma_1 \vec{k}_{N_k} 1} & \beta_{\sigma_1 \vec{k}_{N_k} 2} & \cdots & \beta_{\sigma_1 \vec{k}_{N_k} \frac{N_e}{2}} \\
\end{vmatrix} \times \begin{vmatrix}
\beta_{-\sigma \vec{k}_N 1} & \beta_{-\sigma \vec{k}_N 2} & \cdots & \beta_{-\sigma \vec{k}_N \frac{N_e}{2}} \\
\beta_{-\sigma \vec{k}_1 1} & \beta_{-\sigma \vec{k}_1 2} & \cdots & \beta_{-\sigma \vec{k}_1 \frac{N_e}{2}} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{-\sigma \vec{k}_{N_k} 1} & \beta_{-\sigma \vec{k}_{N_k} 2} & \cdots & \beta_{-\sigma \vec{k}_{N_k} \frac{N_e}{2}} \\
\end{vmatrix}
\]

In the above determinant, the set of band and momentum indices, \((l_h', \vec{k}_h')\) and \((l_h'', \vec{k}_h'')\), represent the occupied states right before and right after the hole state represented by \((l_h, \vec{k}_h)\) when the eigenstates of \(\hat{H}_{3d}\) are ordered according to the band index and momentum index.\(^4\)

### 2.5.3 Electronic Density of States in the Absence and in the Presence of the Core Hole

First, the results on energy eigenstates and eigenvalues of the Hamiltonians are presented, which are then used to calculate the RIXS spectrum. The electron density

\(^4\)In other words, from the \(N_e/2 \times N_e/2\) part of the matrix of \(\beta\)'s with \(m = 1, \cdots, N_e/2\) and \(\varepsilon_{\sigma lk} < \varepsilon_F\), the row corresponding to \(k = \vec{k}_h\) and \(l = l_h\) is replaced by the spin \(\sigma\) part of the row corresponding to \(k = \vec{k}_e\) and \(l = l_e\) in the matrix of \(\beta\)'s.
of states (DOS) $D_{3d,\uparrow}(\varepsilon)$ for spin $\uparrow$ in the absence of the core hole is found from $\hat{H}_{3d}$ for $16 \times 16$ cluster is shown in Figure 2.5(a) for $t_0 = 0.9$ eV and in Figure 2.6(a) for $t_0 = 1.5$ eV. The Lorentz broadening of $2\Gamma = 0.1$ eV is used to make the DOS curve smooth. Due to spin degeneracy in CE-type antiferromagnetic ordering, the electron DOS for spin $\downarrow$, $D_{3d,\downarrow}(\varepsilon)$, is identical to $D_{3d,\uparrow}(\varepsilon)$. In the absence of the electron hopping, the $e_g$ levels with spin parallel to the local $t_{2g}$ spin direction are shown schematically in Figure 1.2 for Mn$^{3+}$ and Mn$^{4+}$ sites in La$_{0.5}$Sr$_{1.5}$MnO$_4$. With one $e_g$ electron per two Mn ions, the $e_g$ electron would occupy the lower JT level at the Mn$^{3+}$ site with spin parallel to the $t_{2g}$ spin. With electron hopping between Mn sites, the lowest JT levels on Mn$^{3+}$ and Mn$^{4+}$ hybridize along the zigzag chain and form the occupied and unoccupied bands right around the gap, separated roughly by 2 eV, as shown in the electron DOS. The excitation across this gap is responsible for the 2 eV RIXS peak, which is the focus of the comparison with experiment data.

In the presence of the core hole at site $\vec{\imath}_c$, the Hamiltonian $\hat{H}_{\text{total},\vec{\imath}_c}$ is analyzed. The $t_{2g}$ spin direction at $\vec{\imath}_c$ breaks the spin degeneracy in DOS. The green lines in Figures 2.5(b) and 2.5(b) show the density of states for spin $\uparrow$, $D_{\text{total},\vec{\imath}_c,\uparrow}(\varepsilon)$, in the presence of the core hole at Mn$^{3+}$ site (0,0) and Mn$^{4+}$ site (1,0), respectively, with $\uparrow$ spin $t_{2g}$ electrons. The $e_g$ energy levels with the spin states opposite to the $t_{2g}$ spin direction at $\vec{\imath}_c$ play a minor role for the RIXS spectrum, typically less than 10 % of the total RIXS spectrum, because the $e_g$ electrons with the same spin direction as the $t_{2g}$ at $\vec{\imath}_c$ dominantly screen the core hole due to the large Hund’s splitting.

For $t_0 = 0.9$ eV, as discussed in Figures 5(c) and 5(d) in Ahn et al. (2009), the core hole potential pulls bound states from band continuum, identified as vertical lines in DOS in Figures 2.5(b) and 2.5(b). One of the bound state for the core hole at Mn$^{3+}$ is at around -4 eV, $U_c$ below the occupied band with states primarily at Mn$^{3+}$ site. Similarly, one of the bound states for the core hole at Mn$^{4+}$ is located at around -2 eV, $U_c$ below the unoccupied band with states primarily at Mn$^{4+}$ site.
The DOS for the band continuum is almost unchanged, except that the number of states within each band continuum below and above the gap is one less to make up for the created bound states, since total number of states is unchanged, similar to the result in Ahn et al. (2009). Occupying from the lowest energy levels by the same number of electrons in the intermediate states, the lowest energy intermediate state is then obtained, that is \( s|n_{\text{low}} \rangle \). Therefore, the bound state below the lowest band is occupied and the bound state within the gap is empty in the intermediate state, and these two bound states play important roles in the formation of electron-hole pairs in the final state as well as the RIXS spectrum, as further analyzed in the following subsections.

For \( t_0 = 1.5 \text{ eV} \), the DOS in the presence of the core hole at Mn\( ^{4+} \) is qualitatively similar to the one for \( t_0 = 0.9 \text{ eV} \) case. The bound state within the gap is closer to the edge of the lower band continuum compared to \( t_0 = 0.9 \text{ eV} \) case, so that the core distribution is more delocalized. Qualitatively different behavior occurs for the case with the core hole at Mn\( ^{3+} \) sites. In this case, the state that would be in the gap for smaller \( t_0 \) resides in the occupied band and become a “resonant” rather than “bound” state. With this resonant state and the bound state below the lower band occupied, the top of the lower band is empty in the lowest energy intermediate state, responsible for the delocalized hole excitation, which will be analyzed further in the next subsection.

### 2.5.4 Contributions of the Intermediate and Initial/Final Eigenstates to Electron and Hole Excitations

As done in Ahn et al. (2009), further analysis is made on how the intermediate eigenstates contribute to the electron-hole excitations with \( n_{\text{int}, \alpha}^h(\varepsilon) \) and \( n_{\text{int}, \alpha}^e(\varepsilon) \), and how the final/initial eigenstates contribute to the electron-hole excitations with
$n^e_{\text{fin,}\sigma}(\varepsilon)$ and $n^h_{\text{fin,}\sigma}(\varepsilon)$, defined by

$$n^e_{\text{int,}\sigma}(\varepsilon) = \sum_{\varepsilon_{\sigma k^e} > \varepsilon_F} \sum_{m \leq N_e/2} |\beta_{\sigma k^e m}|^2 \delta(\varepsilon - \varepsilon_{\sigma m}),$$

(2.30)

$$n^h_{\text{int,}\sigma}(\varepsilon) = \sum_{\varepsilon_{\sigma k^h} < \varepsilon_F} \sum_{m > N_e/2} |\beta_{\sigma k^h m}|^2 \delta(\varepsilon - \varepsilon_{\sigma m}),$$

(2.31)

$$n^h_{\text{fin,}\sigma}(\varepsilon) = \sum_{\varepsilon_{\sigma k^h} < \varepsilon_F} \sum_{m > N_e/2} |\beta_{\sigma k^h m}|^2 \delta(\varepsilon - \varepsilon_{\sigma k^h}),$$

(2.32)

$$n^e_{\text{fin,}\sigma}(\varepsilon) = \sum_{\varepsilon_{\sigma k^e} > \varepsilon_F} \sum_{m \leq N_e/2} |\beta_{\sigma k^e m}|^2 \delta(\varepsilon - \varepsilon_{\sigma k^e}),$$

(2.33)

for each chosen core hole site, similar to $n^e_m$, $n^h_m$, $n^h_{k^e}$, and $n^e_{k^h}$ defined in Ahn et al. (2009). These are plotted in Figures 2.5 and 2.6 for $\sigma = \uparrow$ for the core hole at Mn$^{3+}$ and Mn$^{4+}$ site with spin $\uparrow t_{2g}$ electrons. For example, $n^h_{\text{int,}\sigma}(\varepsilon)$ represents the sum of the squared coefficients connecting the eigenstates occupied in the intermediate state and eigenstates empty in the initial state, with the intermediate energy $\delta$-function multiplied, and, therefore, represents the contribution of intermediate state to the electron excitation. Electron and hole distributions for spin $\downarrow$ state are less than 10% of those for spin $\uparrow$ state. The plot of $n^h_{\text{int,}\uparrow}(\varepsilon)$ and $n^e_{\text{int,}\uparrow}(\varepsilon)$ show that the bound states in the intermediate state dominantly contribute to the electron-hole excitations, as identified in Figure 5(d) in Ahn et al. (2009), except the case with $t_0 = 1.5$ eV and core hole at Mn$^{3+}$ site in Figure 2.6, for which the resonance within the lower band and the state at the top of the occupied band dominantly contribute $n^e_{\text{int,}\uparrow}(\varepsilon)$ and $n^h_{\text{int,}\uparrow}(\varepsilon)$.

The plot of $n^h_{\text{fin,}\uparrow}(\varepsilon)$ and $n^e_{\text{fin,}\uparrow}(\varepsilon)$ also confirms the conclusion in Figure 5(c) in Ahn et al. (2009) that the hole [electron] distribution projected into the final/initial eigenstates near the gap becomes sharper as the intermediate hole [electron] bound state becomes closer to the top [bottom] of the initial occupied [empty] band, which gives rise to asymmetric electron and hole distributions, namely, the hole distribution sharper than the electron distribution, representing different screening dynamics between electrons and holes. The above analysis in this subsection shows that the
main conclusions of the study in Ahn et al. (2009), which mainly focuses on the
energy-dependence of the screening dynamics associated with the RIXS process,
holds for La$_{0.5}$Sr$_{1.5}$MnO$_4$, confirming the foundation of the current study. As pointed
out above, the case with $t_0 = 1.5$ eV and core hole at Mn$^{3+}$ site shows a different
behavior. With the resonance state occupied in the intermediate state, the reso-
nance state contribute to the electron excitation predominantly because the second
bound state is pulled from the initially unoccupied bands, whereas the first bound
state is mostly from the initially occupied band. The delocalized state at the top
of the occupied band predominantly contributes to the hole excitation, because it is
occupied in the initial state and empty in the intermediate state.

In Figures 2.5 and 2.6, also plotted are

$$ I_{\text{RIXS},\sigma}^h(\varepsilon) = \sum_{l_e, k_e} \sum_{l_h, k_h} |F_\sigma(l_e, k_e; l_h, k_h; \Delta \vec{K})|^2 \delta(\varepsilon_{l_h k_h} - \varepsilon) $$

(2.34)

$$ I_{\text{RIXS},\sigma}^e(\varepsilon) = \sum_{l_e, k_e} \sum_{l_h, k_h} |F_\sigma(l_e, k_e; l_h, k_h; \Delta \vec{K})|^2 \delta(\varepsilon_{l_h k_h} - \varepsilon). $$

(2.35)
Figure 2.8 (Color) Screening configuration in real space for $t_0 = 1.5$ eV case for core hole at (left) Mn$^{3+}$, and (right) Mn$^{4+}$.

For comparison, the results for $I_{\text{RIXS},\sigma}(\varepsilon)$ and $I_{\text{RIXS},\sigma}(\varepsilon)$ in Figures 2.5(b,d) and 2.6(b,d) indeed show good agreement with $n_{\text{fin},\sigma}(\varepsilon)$ and $n_{\text{fin},\sigma}(\varepsilon)$, confirming close connection between electron-hole excitation and RIXS spectrum.

2.5.5 Electron and Hole Excitations by the Core Hole Represented in Direct Space

In this subsection, the pattern of electrons and holes excited by the core hole examined in direct space is related to the pattern of the RIXS spectrum in reciprocal space after being integrated with respect to the energy. In the absence of the core hole, the electron number $\langle \hat{n}_{\sigma\eta} \rangle$ is calculated for each spin state $\sigma = \uparrow, \downarrow$ and orbital state $\eta = +, -$ at each site $\vec{i}$ from the initial ground state $|g\rangle$ of the Hamiltonian $\hat{H}_{3d}$. The total $e_g$ electron numbers calculated for the $16 \times 16$ cluster model in the absence of the core hole are 0.87 at the nominal Mn$^{3+}$ site and 0.13 at the nominal Mn$^{4+}$ site, indicating a difference of 0.74 in charge density. It must be noted that these numbers should not be directly compared with the LDA theory results or resonant
x-ray spectroscopy results, because the local basis states are not pure Mn orbital states but combinations of Mn and O orbitals, similar to the Zhang-Rice singlet for cuprates. Proper comparison is described in Appendix 2.A, which shows the electron numbers in the model are consistent with LDA or RXS results. It is found that most of these electrons occupy the lower Jahn-Teller level $\eta = -$ of spin parallel to $t_{2g}$ spin at each site, approximately $x^2 - z^2/y^2 - z^2$ orbital at Mn$^{3+}$ site and $3z^2 - r^2$ orbital at Mn$^{4+}$ site, consistent with the orbital ordering proposed in Zeng et al. (2008). In the intermediate state, these electron numbers change to screen the core hole. The change in the electron number is shown in Figures 2.7 and 2.8 for the core hole at a Mn$^{3+}$ site and a Mn$^{4+}$ site (the site with the largest red dot in each panel), respectively. The gray solid and dashed lines in the background represent the zigzag chain with $t_{2g}$ spin $\uparrow$ and $\downarrow$, respectively. The volume of the blue sphere is proportional to the decrease in the total electron number at each Mn site. Similarly, the volume of the red sphere represents the increase in the total electron number.

Figures 2.7(a) and 2.7(b) show that the electron excitations are mostly confined right at the core hole site, consistent with the relatively flat electron distribution, $n_{\text{fin}}\uparrow$, in Figure 2.5(a). Comparing the largest solid red circles in Figures 2.7(a) and 2.7(b) show that more screening electrons accumulate at the core hole site when the core hole is created at the Mn$^{4+}$ site (0.92 electron) than at the Mn$^{3+}$ (0.11 electron). This result can be understood from the orbital ordering pattern: Initially the Mn$^{4+}$ site has less $e_g$ electrons on the site itself but more electrons at nearest neighbor Mn sites along the zigzag chain with orbitals pointing towards the Mn$^{4+}$ site, compared to the Mn$^{3+}$ site. Hole distribution in Figures 2.7(a) and 2.7(b) show that these screening electrons are mostly from the nearest or next nearest neighbors along the zigzag chain. For the case of the core hole at the Mn$^{3+}$ and Mn$^{4+}$ site for $t_0 = 0.9$ eV, the holes at two nearest neighbor sites constitute 91.0% and 91.4%, respectively, of the total hole number. The results show that even though the hole excitation is not
as localized, as the electron excitation, residing over a few sites instead of just one site, consistent with different sharpness of $n_{\text{fin}}^{h}$ and $n_{\text{fin}}^{e}$ in Figure 2.5(b), the holes are still tightly bound to the core hole site with almost exciton-like electron and hole pair state. Such screening pattern in real space can be related to the variation of the RIXS intensity in reciprocal space, which is discussed in Section 2.4.

![Contour plot of RIXS intensity calculated for $t_0 = 0.9$ eV case along the chosen path.](image)

**Figure 2.9** (Color) Contour plot of RIXS intensity calculated for $t_0 = 0.9$ eV case along the chosen path.

The situation changes for cases with a core hole at Mn$^{3+}$ and with a large electron hopping, for example, $t_0 = 1.5$ eV. The hole distribution becomes delocalized, and only about 8.0% of the core is localized within the nearest neighbors, and the majority of the hole is delocalized along the zigzag chains with the same spin direction as the core hole site. The hole number does not decay with the distance from the core hole site, which indicates qualitatively different nature of the screening dynamics.

### 2.5.6 Calculated RIXS Spectrum and Comparison with Experimental Data

Once the Hamiltonians are solved in the absence and in the presence of the core hole, the RIXS intensity, $I_{\text{RIXS}}(\vec{q}, \omega)$ can be calculated according to the formula in Section 2.2. In this RIXS calculation, a small displacement is included of the Mn$^{4+}$
ions of 0.0265 Å along the diagonal direction from the ideal square lattice (Zeng et al. 2008). The results are shown in Figures 2.9 and 2.10 for $t_0 = 0.9$ eV and 1.5 eV, along a path in the extended zone $\Omega_{ExZ}$ in reciprocal space. As mentioned above, the electron-lattice coupling parameter $\lambda$ was adjusted to $\lambda = 3.509$ eV/Å for $t_0 = 1.5$ eV from $\lambda = 7.407$ eV/Å for $t_0 = 0.9$ eV, so that the lowest energy RIXS peak stays near 2 eV.

Comparison between the experimental data and the calculated result for $t_0 = 0.9$ eV is made. In addition to the momentum dependent RIXS peak at around 2 eV, the experimental RIXS spectrum shows momentum independent spectral weight, in particular above 3 eV as shown in Figure 2.1(a). The RIXS spectrum at $H = 0.03$ is indicative that the RIXS spectral weight above 3 eV may have the same origin as the 4-5 eV O2p-Mn3d transition observed in optical experiments in related manganites. Based on such assumption, the experimental RIXS spectrum is fitted with a momentum-independent O2p-Mn3d transition peak centered at 4.5 eV and half-width at half-maximum 1.5 eV, similar to the optical peak, and the calculated momentum-dependent 3d-3d peaks. The results are shown in Figure 2.11 and show

Figure 2.10 (Color) Contour plot of RIXS intensity calculated for $t_0 = 0.9$ eV case along the chosen path.
Figure 2.11 (Color) Theoretical RIXS intensity lines with Lorentzian broadening shown in brown color scheme, superimposed with experimental data represented in symbols connected with lines. Both, theoretical and experimental data have a distinctive peak at 2 eV. Experimental data measured along (a) $2\theta = 68^\circ$, (b) $2\theta = 78^\circ$, and (c) $\theta = 48^\circ$, refer to Figure 2.1(b) for surveyed $\vec{Q}$-points in the $(H, H, L)$ plane. Thin grey line at the bottom is added to the theoretical result, as a Lorentzian peak centered at 4.5 eV with $\gamma_{bk} = 1.5$ eV.

A reasonable agreement between theory and experiment. The O2p-Mn3d transition has a substantial spectral weight tail even in the range of 1–3 eV. Such momentum-independent RIXS spectral weights with substantial tails even in the low energy range have been also observed in bilayer manganites (Weber et al. 2010). To make more quantitative comparison, the O2p-Mn3d peak is subtracted from experimental data, and the spectrum is integrated from 1 eV to 3 eV and compared with corresponding integrated intensity from theory results. The comparison is shown in Figure 2.12, in which both theoretical results and experimental data are normalized with respect to the integrated intensity at $(\pi, \pi)$ point.
Figure 2.12 (Color) Integrated RIXS intensity variation for several $t_0$ cases normalized at $(|\pi|, |\pi|)$ for comparison. Symbols represent experimental data.

2.5.7 Periodicity of K-edge RIXS Spectrum in Reciprocal Space

In earlier studies of La$_2$CuO$_4$ by Kim et al. (2007), it was shown that the spectra did not depend on the choice of Brillouin zone being measured. This observation, depicted in Figure 2.13, led to the following conclusion: momentum dependence observed in K-edge RIXS obeys the periodicity of reduced wave vector $\vec{k}$, which defined as $\vec{q} = \vec{k} + \vec{G}$, where $\vec{q}$ is the total momentum change, and $\vec{G}$ is a reciprocal lattice vector (Ament et al. 2011, p.715). Hence, RIXS spectra depends purely on $\vec{k}$, and has a translational symmetry of the reciprocal lattice in reciprocal space.

The RIXS calculation and the experimental data for La$_{0.7}$Sr$_{1.3}$MnO$_4$ described in this chapter, clearly indicates that such periodicity is not present. Figure 2.14 shows integrated RIXS intensity in $k$-space, based on 16x16 Mn lattice. The diamond shape at the center enclosed by line running through the points $\vec{k} = (\pi/2, 0), (0, \pi/2), (-\pi/2, 0)$, and $(0, -\pi/2)$, is the first Brillouin zone, whereas the outer square domain $|k_x| \leq \pi$ and $|k_y| \leq \pi$, denotes the “extended Brillouin zone”,
Figure 2.13 Kim et al. (2007) presents the experimentally observed comparison of RIXS spectra on La$_2$CuO$_4$ taken at different total $q$ positions but with an equivalent reduced wave vector $\vec{k}$ for seven different $q$s corresponding to $\vec{k} = (0, 0), (\pi, 0), \text{and} (\pi, \pi)$, from top to bottom. The two-dimensional reciprocal space net is shown in the top panel.

or in some instances referred to as $|H| \leq 0.5$ (r.l.u.). To bring more clarity to the term “extended”, for example if a system does not have an orbital ordering, charge ordering, magnetic ordering, and Jahn-Teller distortion, then for a unit cell with one manganese atom, first Brillouin zone would be equivalent to the extended Brillouin zone. As it is further shown in Figure 2.14, the calculations were done over the neighboring extended Brillouin zones to cover wider domain within $|k_x| \leq 3\pi$ and $|k_y| \leq 3\pi$. It is evident that RIXS spectrum does not exhibit periodicity with respect to the first Brillouin zone, however the spectrum shows approximate periodicity with respect to the extended Brillouin zone.

Emphasis must be made, that even this periodicity is only approximate. In the extended Brillouin zone of Figure 2.14, global maximum of RIXS intensity occurs
at four \((\pm \pi, \pm \pi)\) points, whereas global minimum occurs at \((0, 0)\). In Figure 2.14, the spectrum looks almost periodic with respect to the extended Brillouin zone, but after careful examination one may observe slight differences between corresponding points with maximums at \((\pm \pi, \pm \pi)\) and \((\pm 3\pi, \pm 3\pi)\), as well as minimums at \((0, 0)\) and \((\pm 2\pi, \pm 2\pi)\). This “slight” non-periodicity of the extended Brillouin zone can be further attributed to the experimental bond length data describing lattice geometry, particularly through inclusion of small diagonal displacements at Mn\(^{4+}\) ions (Zeng et al. 2008). Removing those displacements from calculation makes extended Brillouin zone periodic. Analytically, it can be shown through Equation (2.25). Similar results for \(t_0 = 1.5\) eV is shown in Figure 2.15. In addition, this aperiodic behaviour can be seen more clearly in Figure 2.2(b), especially with the \(t_0 = 1.32\) eV line.

### 2.6 Conclusions

In summary, highly momentum-dependent K-edge resonant inelastic x-ray scattering intensity is observed in the orbital ordered, layered manganite \(\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4\).
Figure 2.15 (Color) Integrated RIXS intensity in extended reciprocal space for $t_0 = 1.5$ eV case. First Brillouin zone is at the center bounded by diamond shape marked by points ($\pi/2, 0$), ($0, \pi/2$), ($-\pi/2, 0$), and ($0, -\pi/2$), whereas the square domain bounded by $|k_x| \leq \pi$ and $|k_y| \leq \pi$ denotes the extended Brillouin zone.

This is interpreted through a comparison with calculations based on a tight-binding approach, and also showed that these observations imply a highly localized, nearest neighbor screening of the local charge perturbation. It is further found that the momentum dependence of the RIXS spectrum reflects the pattern and range of the screening in real space, and thus the size and shape of the screening cloud can be measured. It is determined that the screening cloud is localized to a few Mn sites in the Mn-O plane, emphasizing the short range nature of the Coulomb interactions in the manganites. These results also show the potential of K-edge RIXS, as a probe of the screening dynamics in strongly correlated materials.
APPENDIX

2.A Hamiltonians in Reciprocal Space Without and With 1s Core Hole

In the absence of the core hole, the Hamiltonian has the following form in reciprocal space,

\[ \hat{H}_{3d} = \sum_{\sigma, \vec{k} \in \text{BZ}} a_{\sigma \vec{k}}^\dagger \hat{H}_{3d, \sigma \vec{k}}^d a_{\sigma \vec{k}}, \tag{2.36} \]

where \[ \hat{H}_{3d, \sigma \vec{k}}^d = \hat{H}_{3d, \text{nonint}}^d + \hat{H}_{3d, \text{HF}}^d, \]

\[ a_{\sigma \vec{k}}^\dagger = \begin{pmatrix} a_{\sigma, \vec{k}+\vec{K}_1,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_1,2}^\dagger & a_{\sigma, \vec{k}+\vec{K}_2,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_2,2}^\dagger \\ a_{\sigma, \vec{k}+\vec{K}_3,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_3,2}^\dagger & a_{\sigma, \vec{k}+\vec{K}_4,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_4,2}^\dagger \\ a_{\sigma, \vec{k}+\vec{K}_5,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_5,2}^\dagger & a_{\sigma, \vec{k}+\vec{K}_6,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_6,2}^\dagger \\ a_{\sigma, \vec{k}+\vec{K}_7,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_7,2}^\dagger & a_{\sigma, \vec{k}+\vec{K}_8,1}^\dagger & a_{\sigma, \vec{k}+\vec{K}_8,2}^\dagger \end{pmatrix} \tag{2.37} \]

with \[ \vec{K}_1, \vec{K}_2, \vec{K}_3, \vec{K}_4, \vec{K}_5, \vec{K}_6, \vec{K}_7, \] and \[ \vec{K}_8 \] representing \((0,0), (\pi,0), (0,\pi), (\pi,\pi), (-\pi/2,-\pi/2), (\pi/2,-\pi/2), (-\pi/2,\pi/2), \) and \((\pi/2,\pi/2),\) respectively,

\[ H_{3d, \text{nonint}}^d = \begin{pmatrix} H_1 & H_2 \\ H_2 & H_3 \end{pmatrix}, \tag{2.38} \]

with matrix blocks defined as follows

\[ H_1 = \begin{pmatrix} M_1 + W_{3u} & -G_\sigma & G_\sigma & W_{1s} + W_{3s} \\ -G_\sigma & M_2 + W_{3u} & W_{1s} + W_{3s} & G_\sigma \\ G_\sigma & W_{1s} + W_{3s} & M_3 + W_{3u} & -G_\sigma \\ W_{1s} + W_{3s} & G_\sigma & -G_\sigma & M_4 + W_{3u} \end{pmatrix}, \tag{2.39} \]

\[ H_2 = \begin{pmatrix} W_{2s} & G_\sigma & G_\sigma & W_{2s} \\ G_\sigma & W_{2s} & W_{2s} & G_\sigma \\ G_\sigma & W_{2s} & W_{2s} & G_\sigma \\ W_{2s} & G_\sigma & G_\sigma & W_{2s} \end{pmatrix}, \tag{2.40} \]
\[ H_3 = \begin{pmatrix}
M_5 + W_{3u} & -G_\sigma & G_\sigma & W_{1s} + W_{3s} \\
-G_\sigma & M_6 + W_{3u} & W_{1s} + W_{3s} & G_\sigma \\
G_\sigma & W_{1s} + W_{3s} & M_7 + W_{3u} & -G_\sigma \\
W_{1s} + W_{3s} & G_\sigma & -G_\sigma & M_8 + W_{3u}
\end{pmatrix}, \quad (2.41) \]

where all the terms further defined as

\[ M_j = \begin{pmatrix}
-\frac{t_0}{2} \left[ \cos(k_x + K_{j,x}) + \cos(k_y + K_{j,y}) \right] & \frac{\sqrt{3} u}{2} \left[ \cos(k_x + K_{j,x}) - \cos(k_y + K_{j,y}) \right] \\
\frac{\sqrt{3} u}{2} \left[ \cos(k_x + K_{j,x}) - \cos(k_y + K_{j,y}) \right] & -\frac{3u}{2} \left[ \cos(k_x + K_{j,x}) + \cos(k_y + K_{j,y}) \right]
\end{pmatrix}, \quad (2.42) \]

\[ G_\uparrow = \begin{pmatrix}
-\frac{J_H S_z}{2} & 0 \\
0 & -\frac{J_H S_z}{2}
\end{pmatrix}, \quad (2.43) \]

\[ G_\downarrow = \begin{pmatrix}
\frac{J_H S_z}{2} & 0 \\
0 & \frac{J_H S_z}{2}
\end{pmatrix}, \quad (2.44) \]

\[ W_{1s} = \begin{pmatrix}
-\beta \lambda Q_{1s} & 0 \\
0 & -\beta \lambda Q_{1s}
\end{pmatrix}, \quad (2.45) \]

\[ W_{2s} = \begin{pmatrix}
0 & \lambda Q_{2s} \\
\lambda Q_{2s} & 0
\end{pmatrix}, \quad (2.46) \]

\[ W_{3u} = \begin{pmatrix}
-\lambda Q_{3u} & 0 \\
0 & \lambda Q_{3u}
\end{pmatrix}, \quad (2.47) \]

\[ W_{3s} = \begin{pmatrix}
-\lambda Q_{3s} & 0 \\
0 & \lambda Q_{3s}
\end{pmatrix}, \quad (2.48) \]
\( Q_{1s} = 0.053 \text{ Å}, \ Q_{2s} = 0.054 \text{ Å}, \ Q_{3u} = 0.107 \text{ Å}, \) and \( Q_{3s} = -0.012 \text{ Å} \) (Herrero-Martín et al. 2011). The element of 16 \( \times \) 16 matrix \( H^{3d,\text{HF}}_{\sigma\vec{k}} \) is independent of \( \vec{k} \),

\[
\left( H^{3d,\text{HF}}_{\sigma\vec{k}} \right)_{2(j-1)+\xi,2(j'-1)+\xi'} = \sum_{i_u,\eta} \frac{U_{\sigma\vec{i}_u\eta}}{8} e^{-i(\vec{K}_j-\vec{K}_{j'}) \cdot \vec{i}_u} \left( R_{\vec{i}_u\eta} \right)_{\xi'\xi} \tag{2.49}
\]

where \( \eta = +, - \), \( j, j' = 1, 2, ..., 8 \), \( \xi, \xi' = 1, 2 \), \( \vec{i}_u \) represents the position index vector of the Mn ions within the unit cell, that is, \( (0,0), (1,0), (2,0), (3,0), (1,-1), (2,-1), (1,1), \) and \( (2,1) \),

\[
R_{\vec{i}_u-} = \begin{pmatrix}
\cos^2 \theta_{\vec{i}_u} & \cos \theta_{\vec{i}_u} \sin \theta_{\vec{i}_u} \\
\cos \theta_{\vec{i}_u} \sin \theta_{\vec{i}_u} & \sin^2 \theta_{\vec{i}_u}
\end{pmatrix},
\]

\[
R_{\vec{i}_u+} = \begin{pmatrix}
\sin^2 \theta_{\vec{i}_u} & -\cos \theta_{\vec{i}_u} \sin \theta_{\vec{i}_u} \\
-\cos \theta_{\vec{i}_u} \sin \theta_{\vec{i}_u} & \cos^2 \theta_{\vec{i}_u}
\end{pmatrix},
\]

\( \theta_{\vec{i}} \) is defined from the local lower \((-\)) and upper \((+\)) Jahn-Teller eigenstate,

\[
a_{\vec{i}} \sigma^- = a \sigma^1 \cos \theta_{\vec{i}} + a \sigma^2 \sin \theta_{\vec{i}},
\]

\[
a_{\vec{i}} \sigma^+ = -a \sigma^1 \sin \theta_{\vec{i}} + a \sigma^2 \cos \theta_{\vec{i}}
\]

At Mn\(^{3+}\) sites in the \( x/y \) directional legs of the zigzag chain,

\[
\tan \theta_{\vec{i}} = \pm \frac{Q_{3u} + Q_{3s} - \sqrt{(Q_{3u} + Q_{3s})^2 + 4Q_{2s}^2}}{2Q_{2s}} \tag{2.54}
\]

At Mn\(^{4+}\) sites, \( \theta_{\vec{i}}=0 \). To evaluate \( U_{\sigma\vec{i}\eta} \), the matrix for the number operator in reciprocal space is necessary, the element of which is given below.

\[
\left( n_{\vec{i}\vec{k}} \sigma^\eta \right)_{2(j-1)+\xi,2(j'-1)+\xi'} = e^{-i(\vec{K}_j-\vec{K}_{j'}) \cdot \vec{i}_u} \left( R_{\vec{i}_u\eta} \right)_{\xi'\xi} \tag{2.55}
\]

The eigenstates and eigenenergies of 16 \( \times \) 16 matrix \( H^{3d}_{\sigma\vec{k}} \) are found through the Hartree-Fock iterative calculations at chosen set of \( k \) points, which gives the electronic DOS in Figure 2.5.
The Hamiltonian in the presence of the core hole at a site $\vec{r}_c$ for $N \times N$ clusters, with $N$ multiple of 4, is presented below. The $k$ points within the first Brillouin zone are $\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_{N_k}$, where $N_k = N^2/8$.

$$\hat{H}_{\text{total}} = \sum_\sigma a_\sigma^\dagger (H_{3d, \text{nonint}}^\sigma + H_{3d3d, \text{HF}}^\sigma + H_{1s3d, \vec{r}_c}^\sigma) a_\sigma$$ (2.56)

where

$$a_\sigma^\dagger = (a_{\sigma \vec{k}_1}^\dagger, a_{\sigma \vec{k}_2}^\dagger, \ldots, a_{\sigma \vec{k}_{N_k}}^\dagger)$$ (2.57)

$$H_{3d, \text{nonint}}^\sigma = \left( \begin{array}{cccc} H_{3d, \text{nonint}}^\sigma & 0 & \cdots & 0 \\
0 & H_{3d, \text{nonint}}^\sigma & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & H_{3d, \text{nonint}}^\sigma \
\end{array} \right)$$ (2.58)

$$H_{3d3d, \text{HF}}^\sigma = \left( \begin{array}{cccc} H_{3d3d, \text{HF}}^\sigma & H_{3d3d, \text{HF}}^\sigma & \cdots & H_{3d3d, \text{HF}}^\sigma \\
H_{3d3d, \text{HF}}^\sigma & H_{3d3d, \text{HF}}^\sigma & \cdots & H_{3d3d, \text{HF}}^\sigma \\
\vdots & \vdots & \ddots & \vdots \\
H_{3d3d, \text{HF}}^\sigma & H_{3d3d, \text{HF}}^\sigma & \cdots & H_{3d3d, \text{HF}}^\sigma \
\end{array} \right)$$ (2.59)

where

$$\left( H_{3d3d, \text{HF}}^\sigma \right)_{2(j-1)+\xi, 2(j'-1)+\xi'} = \sum_{i, \eta} \frac{U_{\sigma \vec{r}_c}}{N^2} e^{-i(\vec{k}_h - \vec{k}_{h'}) \cdot \vec{i}} e^{-i(\vec{K}_j - \vec{K}_{j'}) \cdot \vec{i}} (\hat{R}_{\vec{r}_c})_{\xi \xi'}$$ (2.60)

where $\eta = +, -, j, j' = 1, 2, \ldots, 8, \xi, \xi' = 1, 2, \vec{i}$ represents the site index vector for $N \times N$ Mn cluster. Again, for the evaluation of $U_{\sigma \vec{r}_c}$, the matrix for the number operator in reciprocal space is necessary, shown below.

$$n^{\sigma \vec{r}_c} = \left( \begin{array}{cccc} n_{\sigma \vec{k}_1 \vec{k}_1}^{\vec{r}_c} & n_{\sigma \vec{k}_1 \vec{k}_2}^{\vec{r}_c} & \cdots & n_{\sigma \vec{k}_1 \vec{k}_{N_k}}^{\vec{r}_c} \\
n_{\sigma \vec{k}_2 \vec{k}_1}^{\vec{r}_c} & n_{\sigma \vec{k}_2 \vec{k}_2}^{\vec{r}_c} & \cdots & n_{\sigma \vec{k}_2 \vec{k}_{N_k}}^{\vec{r}_c} \\
\vdots & \vdots & \ddots & \vdots \\
n_{\sigma \vec{k}_{N_k} \vec{k}_1}^{\vec{r}_c} & n_{\sigma \vec{k}_{N_k} \vec{k}_2}^{\vec{r}_c} & \cdots & n_{\sigma \vec{k}_{N_k} \vec{k}_{N_k}}^{\vec{r}_c} \
\end{array} \right)$$ (2.61)
with
\[
\left( n^{\sigma \vec{n}}_{k_h \vec{k}_{h'}} \right)_{2(j-1)+\epsilon,2(j'-1)+\epsilon'} = e^{-i(\vec{k}_h - \vec{k}_{h'}) \cdot \vec{R}} e^{-i(\vec{R}_j - \vec{R}_{j'}) \cdot \vec{l}} \left( R_{\vec{m}} \right)_{\xi \xi'}. \tag{2.62}
\]

Finally, the 1s-3d Coulomb interaction for the core hole present at \( \vec{i}_c \) is represented by the following Hamiltonian matrix.

\[
H^{1s3d,\vec{i}_c}_{\sigma} = \begin{pmatrix}
H^{1s3d,\vec{i}_c}_{\sigma k_1 k_1} & H^{1s3d,\vec{i}_c}_{\sigma k_1 k_2} & \cdots & H^{1s3d,\vec{i}_c}_{\sigma k_1 k_N} \\
H^{1s3d,\vec{i}_c}_{\sigma k_2 k_1} & H^{1s3d,\vec{i}_c}_{\sigma k_2 k_2} & \cdots & H^{1s3d,\vec{i}_c}_{\sigma k_2 k_N} \\
\vdots & \vdots & \ddots & \vdots \\
H^{1s3d,\vec{i}_c}_{\sigma k_N k_1} & H^{1s3d,\vec{i}_c}_{\sigma k_N k_2} & \cdots & H^{1s3d,\vec{i}_c}_{\sigma k_N k_N}
\end{pmatrix} \tag{2.63}
\]

where
\[
\left( H^{1s3d,\vec{i}_c}_{\sigma k_h \vec{k}_{h'}} \right)_{2(j-1)+\epsilon,2(j'-1)+\epsilon'} = U_{\vec{c}} e^{-i(\vec{k}_h - \vec{k}_{h'}) \cdot \vec{l}} e^{-i(\vec{R}_j - \vec{R}_{j'}) \cdot \vec{l}} \delta_{\xi \xi'}. \tag{2.64}
\]

where \( j, j' = 1, 2, \ldots, 8 \) and \( \xi, \xi' = 1, 2 \).

Eigenvectors and eigenvalues are found for the \( 2N^2 \times 2N^2 \) Hamiltonian matrix, \( H^{tot}_{\sigma} = H^{3d,nonint}_{\sigma} + H^{3d3d,\text{HF}}_{\sigma} + H^{1s3d,\vec{i}_c}_{\sigma} \) for each spin direction \( \sigma \) with the core hole potential, through Hartree-Fock iterative calculations. When necessary, Pullay mixing method is used to have a convergence. The eigenstates and energies in the absence of the core hole for the same cluster are found by setting \( U_{\vec{c}} = 0 \) and repeating Hartree-Fock iterative calculations. The two sets of eigenstates and eigenvalues give \( \epsilon_{\sigma \vec{l} \vec{k}}; \alpha_{\sigma \vec{k} + \vec{R}, \xi \vec{k}}; \epsilon_{\sigma \vec{m}}; \) and \( \gamma_{\sigma \vec{k} + \vec{R}, \xi \vec{m}} \), which are fed into the RIXS formula.
APPENDIX

2.B RIXS Formula Derivation

As explained in the text, the following formula is obtained from the Kramers-Heisenberg formula, Equation (2.24), in the limit of completely localized core hole,

\[ I \propto \sum_f \sum_{\vec{R}} \sum_{\vec{R}+\vec{d}} \sum_{n\vec{R}+\vec{d}} \left| \langle f|D^\dagger|n\vec{R}+\vec{d}\rangle \langle n\vec{R}+\vec{d}|D|g \rangle \right|^2 \delta(E_f + \hbar \omega_{k'} - E_g - \hbar \omega_k), \quad (2.65) \]

where \(|n\vec{R}+\vec{d}\rangle\) represents the intermediate energy eigenstate with the core hole at a site \(\vec{R}+\vec{d}\) within the unit cell at a lattice point \(\vec{R}\). Further applying dipole approximation to the RIXS transition operator, following expression is obtained,

\[ \langle f|D^\dagger|n\vec{R}+\vec{d}\rangle \langle n\vec{R}+\vec{d}|D|g \rangle = e^{-i(\vec{k'} - \vec{k} + \vec{k}_f) \cdot \vec{R}} \times \epsilon' \cdot \langle f|\vec{r} - (\vec{R} + \vec{d})|n\vec{R}+\vec{d}\rangle \epsilon \cdot \langle n\vec{R}+\vec{d}|\vec{r} - (\vec{R} + \vec{d})|g \rangle \quad (2.66) \]

Two many-body states \(|\Psi^0\rangle\) and \(|\Psi^{-\vec{R}}\rangle\) with total momentum \(\hbar \vec{k}\) with identical wave functions in two different coordinate systems, coordinate for \(|\Psi^{-\vec{R}}\rangle\) is shifted with respect to the coordinate for \(|\Psi^0\rangle\) by \(-\vec{R}\), are related to each other by a phase factor, \(|\Psi^{-\vec{R}}\rangle = e^{i\vec{k} \cdot \vec{R}} |\Psi^0\rangle\). Assuming that \(|g\rangle\) and \(|f\rangle\) have net momenta of zero and \(\hbar \vec{k}_f\), following relations are obtained,

\[ \langle f|\vec{r} - (\vec{R} + \vec{d})|n\vec{R}+\vec{d}\rangle = e^{-i\vec{k}_f \cdot (\vec{R} + \vec{d})} \langle f|\vec{r} - \vec{d}|n\vec{d}\rangle \]
\[ \langle n\vec{R}+\vec{d}|\vec{r} - (\vec{R} + \vec{d})|g \rangle = \langle n\vec{d}|\vec{r} - \vec{d}|g \rangle \quad (2.67) \]

Therefore, the sum over lattice point \(\vec{R}\) for \(e^{-i(\vec{k'} - \vec{k} + \vec{k}_f) \cdot \vec{R}}\) leads to the conservation of the crystal momentum \(\delta(\vec{k'} - \vec{k} + \vec{k}_f + \vec{K})\), where \(\vec{K}\) represents the reciprocal lattice vectors, and the following expression for the RIXS intensity,

\[ I \propto \sum_f \sum_{\vec{K}} \sum_{\vec{R}} \sum_{\vec{R}+\vec{d}} \sum_{n\vec{d}} \left| e^{-i(\vec{k'} - \vec{k} + \vec{k}_f) \cdot \vec{R}} \cdot \langle f|\vec{r} - \vec{d}|n\vec{d}\rangle \epsilon \cdot \langle n\vec{d}|\vec{r} - \vec{d}|g \rangle \right|^2 \delta(E_f + \hbar \omega_{k'} - E_g - \hbar \omega_k) \delta(\vec{k}_f + \vec{k}' - \vec{k} + \vec{K}). \quad (2.68) \]
By further neglecting a constant factor associated with the polarization vectors $\vec{\epsilon}'$ and $\vec{\epsilon}$ as well as the dipole moment between $4p$ and $1s$ wave functions, Equation (2.25) is obtained.
CHAPTER 3

EFFECTS OF RARE EARTH ION SIZE ON THE STABILITY OF THE COHERENT JAHN-TELLER DISTORTIONS IN UNDOPED PEROVSKITE MANGANITES

The work in this chapter was done in collaboration with Turab Lookman, Avadh Saxena, and Alan R. Bishop from Theoretical Division at Los Alamos National Laboratory, and Peter B. Littlewood from Physical Sciences and Engineering Division at Argonne National Laboratory, as well as Keun H. Ahn from Department of Physics at New Jersey Institute of Technology.

3.1 Introduction

Since the discovery of the colossal magnetoresistance effect, a lot of attention has focused on a class of materials known as perovskite manganites (von Helmolt et al. 1993; Jin et al. 1994; Salamon and Jaime 2001). During the last two decades, substantial progress has been made in the theory for perovskite manganites. Importance of the electron-lattice coupling was identified shortly after the discovery of colossal magnetoresistance effect (Millis et al. 1995; Röder et al. 1996; Millis et al. 1996). First-order character of the metal-insulator phase transition has been found from Monte Carlo simulations (Vergés et al. 2002). Mechanism for inhomogeneity and its relation to metal-insulator transition have been studied (Moreo et al. 1999). Effects of disorder have been investigated for doped manganites (Kumar and Majumdar 2006; Pradhan et al. 2007). The competition between short range super-exchange interaction and long range double exchange interaction has been analyzed for multiferroic undoped manganites (Salafranca and Brey 2006). Most recently, novel mechanisms for ferroelectricity, including electronic ferroelectricity, have been proposed for undoped manganites with E-type antiferromagnetic ordering (Sergienko et al.
These materials have the chemical formula in the form of $RE_{1-x}AK_xMnO_3$, where $RE$ and $AK$ represent the rare earth and alkali metal elements, and have a perovskite structure. One of the major research themes for these materials is the relation between their physical properties and the average size of ions at the $RE/AK$ site, often known as the chemical pressure effect. The size of the $RE/AK$ ion is usually parameterized by a tolerance factor and one of the most important phase diagrams for these materials has been the one in the temperature versus tolerance factor plane for a fixed 30% ($x = 0.3$) doping ratio (Hwang et al. 1995). The $RE/AK$ ions with size smaller than the space created by the surrounding MnO$_6$ octahedra induce buckling of the Mn-O-Mn bonds, observed through various structural refinement analyses.

To understand the effect of the chemical pressure, semi-classical theories (Millis et al. 1995; Röder et al. 1996; Millis et al. 1996; Moreo et al. 1999; Sergienko et al. 2006; Pradhan et al. 2007; Vergés et al. 2002; Salafranca and Brey 2006; Kumar and Majumdar 2006; Yamauchi et al. 2008) with quantum mechanical electrons coupled with the classical lattice through the Jahn-Teller (JT) interaction often present the phase diagram with one axis representing the ratio between the electron hopping energy and the JT energy gain. This ratio parameterizes the competition between the kinetic and potential energy in perovskite manganites. Theoretical phase diagrams from these approaches agree well with experimental phase diagrams, when this ratio is related to the Mn-O-Mn buckling distortion due to smaller $RE/AK$ ions. However, whether this buckling distortion affects the electron hopping energy or the JT energy gain has been controversial. It is well known from experimental observations that there is a strong competition between the insulating phase with a coherent JT distortion and the metallic phase without such distortion (Salamon and Jaime 2001). So far, most of the attention has centered on the impact of the buckling on the metallic phase, in particular, the possible change in the effective Mn-O-Mn
electron hopping parameter and the band width (Hwang et al. 1995). At the same time, there has been a debate whether the variation of the hopping parameter due to the Mn-O-Mn bond angle change of several degrees would be significant enough to explain the observed metal-insulator transition (Dzero et al. 2000; Fernandez-Baca et al. 1998; Liu et al. 1999; Lynn et al. 1996; Radaelli et al. 1997). For instance, the spin wave stiffness, which depends sensitively on the electron hopping amplitude in double exchange model in ferromagnetic metallic phase, shows very little dependence on Mn-O-Mn bond angle (Lynn et al. 1996; Fernandez-Baca et al. 1998). A less studied effect of the Mn-O-Mn bond buckling, except for a few early efforts based on experimental data (Louca et al. 2001), is the possibility that the buckling distortion may significantly stabilize the insulating phase with a coherent JT distortion, by affecting the JT energy gain. The main goal of this chapter is to examine such a possibility with a simplified model of the perovskite manganites. To be specific, the interplay between the JT ordering and chemical pressure is analyzed for undoped perovskite manganites. With one localized $e_g$ electron per site, the electronic degrees of freedom can be integrated out in undoped manganites (except for electronically ferroelectric undoped manganites postulated at low temperatures for very small RE ions), which allows us to adopt a purely classical model with the energy expressed in terms of lattice distortions only. The study on undoped manganites is merited, because they are not only parent compounds of doped perovskite manganites (Millis 1996), but also because one of the first multiferroic materials discovered is an undoped manganite, TbMnO$_3$, with a relatively small $RE$ element (Kimura, Goto, Shintani, Ishizaka, Arima and Tokura 2003). Recently, electronic ferroelectricity has been also proposed for undoped perovskite manganites (Sergienko et al. 2006; Yamauchi et al. 2008). Therefore, the chemical pressure effect in undoped manganites presented in this chapter would also be relevant for future studies on how the multiferroic and electronically ferroelectric properties would appear in $RE$MnO$_3$ with small $RE$ ions,
as well as how the chemical pressure affects the distorted insulating phase of doped manganites.

### 3.2 Model System and Energy Expression

A study of a two-dimensional (2D) model for the perovskite structure is presented, which incorporates both buckling and the JT distortions. A 2D perovskite structure shown in Figure 3.1 is then defined, which includes the following aspects of the three-dimensional (3D) perovskite structure for undoped manganites: (1) symmetry breaking distortion of O ions around Mn ion, (2) chemical pressure effect, which is the attraction of surrounding O ions toward the small \( RE \) ions, and (3) the rotation of O ions with alternating directions around Mn ions, which is, in effect, the buckling of Mn-O-Mn bonds. Although the 2D model inevitably misses some aspects of 3D lattice distortions, it is proposed that the correct order of magnitude estimation of energies associated with the chemical pressure and the JT effect can still be achieved. For example, the size of the 3D tetragonal JT distortion mode, commonly known as \( Q_3 \) mode (Ahn and Millis 2001) with Mn-O bond lengths changed in all directions, is typically about a third of the size of the planar JT distortion mode, commonly known as \( Q_2 \) mode with Mn-O bond lengths changed only in the plane. The \( Q_2 \) mode is kept in the 2D model, but the \( Q_3 \) mode is not. The error from omitting the \( Q_3 \) mode in the 2D model can be estimated by comparing actual 3D and the approximate 2D Jahn-Teller energy gain, proportional to \( \sqrt{Q_2^2 + Q_3^2} \) and \( \sqrt{Q_2^2} \), respectively, which are different by only about 10%. The \( Q_2 \) mode is expected to couple dominantly with the in-plane Mn-O-Mn bond buckling and the in-plane contraction of O ions surrounding a small \( RE \) ion. Therefore, it is expected that the 2D model would be sufficient for an order of magnitude estimation of the energy associated with the stabilization of the phase with the JT distortion by small \( RE \) ions.
Figure 3.1 Two-dimensional model for the perovskite structure considered in the text.

For the 2D model of perovskite structure, the recently developed atomic scale description of lattice distortions (Ahn et al. 2003, 2004) is applied to describe the elastic energy of the system. In this approach, atomic scale modes of lattice distortions and their constraints are used instead of displacement variables. The structural motifs can be chosen in any convenient way as long as they have the symmetry of the crystal structure. Two “structural motifs” shown in Figure 3.2 are chosen: one consists of one Mn ion and four surrounding O ions and the other comprises one \textit{RE} ion and four surrounding O ions. Further, ten symmetry modes for each motif are obtained, which are shown in Figure 3.3 for the MnO$_4$ motif.$^1$ Similar symmetry modes are defined for the REO$_4$ motif and are distinguished with primes on the symbols in this chapter. The modes defined for each plaquette on the lattice are constrained by each other because neighboring motifs share ions, which leads to constraint equations between the Fourier components of the modes. In terms of these twenty modes and constraint equations, any distortion of the 2D perovskite structure shown in Figure 3.1 can be described.

For the current study, since interest is in the ordered state, distortions with wavevectors $\vec{k} = (0, 0)$ and $(\pi, \pi)$ are considered only. For these wavevectors, the

\footnote{The normalization factor is chosen in such a way that, for example, $e_3 = 2d_O$ if each O ion around Mn ion is displaced by $d_O$ in the way shown in Figure 3.3.}
constraint equations are as follows, where subscripts 0 and s are used to represent $\vec{k} = (0,0)$ and $(\pi,\pi)$, respectively: $e_{10} = e'_{10}$, $e_{20} = e'_{20}$, $e_{30} = e'_{30}$, $s_{x0} = -s'_{x0}$, $s_{y0} = -s'_{y0}$, $e_{1s} = -e'_{2s}$, $e'_{1s} = -e_{2s}$, $s_{xs} = s_{ys} = s'_{xs} = s'_{ys} = 0$. Rest of the modes are unconstrained, particularly, $e_{3s}$ and $e'_{3s}$. The search for the interplay between the staggered deviatoric distortion mode $e_{3s}$ and the staggered rotation of O ions around Mn ion (or equivalently staggered Mn-O-Mn bond buckling mode) $e'_{3s}$ is undertaken, where the latter is due to the compression $e'_{10} = e_{10}$ by small RE ions. Therefore, only the modes $e_{10} = e'_{10}$, $e_{20} = e'_{20}$, $e_{3s}$, and $e'_{3s}$, are shown in Figure 3.4. The uniform shear mode $e_{20} = e'_{20}$ is included because it is coupled to $e'_{3s}$ through the JT term, as will be discussed later in this chapter.

Even though it is possible to analyze an energy expression including higher order symmetry-allowed anharmonic energy terms, such a method would generate many parameters and would make the model less predictive. Therefore, starting with a Keating model with a small number of parameters (Keating 1966; Littlewood 1986), the Keating model is mapped onto the approach based on the symmetry modes. In the Keating approach, the elastic energy is represented in terms of bond length and bond angle changes from equilibrium. For the 2D perovskite structure, the following set of Keating variables and harmonic moduli for each Mn ion are considered, as shown in Figure 3.5: $\delta l_n$ ($n = 1, 2, 3, 4$) and modulus $a_1$ for Mn-O bond length change, $\delta \theta_n$ ($n = 1, 2, 3, 4$) and $b_1/4$ for 90° O-Mn-O bond angle change, $\delta r_n$ ($n = 1, 2, 3, 4$) and $a_2$ for RE-O bond length change, and $\delta \phi_n$ ($n = 1, 2$) and $b_2/4$ for 180°
Figure 3.3 Distortion modes for the motif around the Mn ion in Figure 3.2. Similar distortion modes, $e'_1, e'_2, e'_3, s'_x, s'_y, t'_x, t'_y, w'_x, w'_y$, and $r'$ are defined for the motif around the RE ion.

Mn-O-Mn bond angle change. It should be noted that the MnO$_4$ motif is considered as relatively stiff compared to other components of the structure, so that $a_1 \gg a_2$ and $b_1 \gg b_2$.

Consider the following Keating elastic energy expression per Mn ion,

$$E_{\text{elastic}} = \frac{1}{2} a_1 \sum_{n=1,2,3,4} (\delta l_n)^2 + \frac{1}{2} b_1 \sum_{n=1,2,3,4} (\delta \theta_n/2)^2 + \frac{1}{2} a_2 \sum_{n=1,2,3,4} (\delta r_n)^2 + \frac{1}{2} b_2 \sum_{n=1,2} (\delta \varphi_n/2)^2. \quad (3.1)$$
Figure 3.4 Four distortion modes considered in the current study: (a) uniform dilatation mode $e_{10}$, (b) uniform shear mode $e_{20}$, (c) staggered deviatoric mode $e_{3s}$, and (d) staggered buckling mode $e_{3s}'$. All figures are drawn for the positive values of the modes with the Mn site at the bottom left corner chosen as the origin.

The Keating variables are then expressed in terms of $e_{10}$, $e_{20}$, $e_{3s}$ and $e_{3s}'$. For example, one obtains

$$
\delta l_1 = \frac{\sqrt{(1 + e_{10} + e_{3s})^2 + (e_{20} + e_{3s}')^2} - 1}{2}, \quad (3.2)
$$

$$
\delta \theta_1 = \tan^{-1} \left( \frac{e_{20} + e_{3s}'}{1 + e_{10} + e_{3s}} \right) + \tan^{-1} \left( \frac{e_{20} - e_{3s}'}{1 + e_{10} - e_{3s}} \right). \quad (3.3)
$$

The Taylor expansion of $E_{\text{elastic}}$ in terms of $e_{10}$, $e_{20}$, $e_{3s}$ and $e_{3s}'$ produces all the terms of any order. An approximation that $b_2$ is much smaller than other parameters is made, as mentioned above, and the terms with $b_2$ are dropped. All harmonic order terms are then kept and the cubic and quartic order terms that are responsible for the Mn-O-Mn bond buckling instability are selected, which are shown below as $E_{\text{har}}$, $E_{\text{cubic}}$, and $E_{\text{quartic}}$. 

Figure 3.5 The Keating variables considered for each Mn ion. $l_1$, $l_2$, $l_3$, and $l_4$ represent the Mn-O bond lengths. $\theta_1$, $\theta_2$, $\theta_3$, and $\theta_4$ represent the O-Mn-O bond angles. $r_1$, $r_2$, $r_3$, and $r_4$ represent RE-O bond lengths. $\varphi_1$ and $\varphi_2$ indicate Mn-O-Mn bond angles.

Further, the JT energy per Mn ion $E_{JT}$ is defined and the energy associated with the tolerance factor per Mn ion $E_{tol}$ is as follows:

$$E_{JT} = -\frac{\lambda}{2} |\delta l_1 + \delta l_3 - \delta l_2 - \delta l_4|,$$

$$E_{tol} = \frac{\tilde{p}}{2}(\delta r_1 + \delta r_2 + \delta r_3 + \delta r_4),$$

where “chemical pressure” is defined as

$$\tilde{p} = C_1'(1 - t).$$

The parameter $t$ is a two-dimensional analog of the tolerance factor for the 3D perovskite structure, and the coefficient $C_1'$ represents the coupling between the average RE-O bond length and the tolerance factor $t$. The chemical pressure $\tilde{p}$ induces the shortening of the average RE-O bond length due to small RE ions. In addition, the JT distortion mode is defined as

$$e_{JT} = (\delta l_1 + \delta l_3 - \delta l_2 - \delta l_4)/2,$$
which represents the anisotropic bond length change, similar to the JT distortion modes $Q_2$ and $Q_3$ for 3D perovskite manganites (Ahn and Millis 2001). As mentioned above, $e_{JT}$ in the 2D model corresponds to $Q_2$ mode only and thus omitting the $Q_3$ mode. The expression $E_{JT} = -\lambda|e_{JT}|$ is based on the 3D JT energy $E_{JT,3D} = -\lambda Q \sqrt{Q_2^2 + Q_3^2}$, which is obtained after minimizing JT electron-lattice coupling energy in manganites with respect to the $e_g$ orbital state (Ahn and Millis 2001). In undoped manganites, $Q_3/Q_2$ is about 0.3 – 0.4 (Rodríguez-Carvajal et al. 1998; Balagurov et al. 2004), which allows an approximation $E_{JT,3D} \approx -\lambda Q Q_2 |1 + (Q_3/Q_2)^2/2|$. Further neglecting the small $(Q_3/Q_2)^2/2$ term of about 0.1, the 2D analog of the JT energy $E_{JT}$ can be obtained with the 2D JT distortion $e_{JT}$ corresponding to 3D JT distortion $Q_2$ except for a normalization factor difference.

Expressions $E_{JT}$ and $E_{tol}$ are expanded in the form of a Taylor series in $e_{10}$, $e_{20}$, $e_{3s}$ and $e_{3s}'$. Only the leading order energy terms being kept, the total energy expression per Mn ion $E_{tot}$ is given below.

\[
E_{tot} = E_{har} + E_{JT} + E_{tol} + E_{cubic} + E_{quartic}, \tag{3.8}
\]

\[
E_{har} = \frac{1}{2}(a_1 + a_2)(e_{10})^2 + \frac{1}{2}(4b_1)(e_{20})^2 \\
+ \frac{1}{2}a_1 e_{3s}^2 + \frac{1}{2}a_2 (e_{3s}')^2, \tag{3.9}
\]

\[
E_{JT} = -\lambda|e_{3s} + e_{20}e_{3s}'|; \tag{3.10}
\]

\[
E_{tol} = \tilde{p}e_{10}; \tag{3.11}
\]

\[
E_{cubic} = \frac{1}{2}a_1 e_{10}(e_{3s}')^2; \tag{3.12}
\]

\[
E_{quartic} = \frac{1}{4}a_1 \left(\frac{1}{2}e_{3s}'\right)^4, \tag{3.13}
\]

where the relation

\[
e_{JT} \approx e_{3s} + e_{20}e_{3s}' \tag{3.14}
\]

is used for $E_{JT}$. The physical origin of the coupling between $e_{20}$ and $e_{3s}'$ is important for the current study and is explained in more detail in Section 3.5.1.
3.3 Estimation of Parameters

In this section, the estimation of the parameters is described. The Mn-Mn distance before the distortion is chosen, which is around $u = 4$ Å, as 1. Therefore, $e_{10}$, $e_{20}$, $e_{3s}$, and $e'_{3s}$ are unitless, and $a_1$, $b_1$, $a_2$, $b_2$, and $\lambda$ have the unit of energy. The parameter $a_1$ can be estimated from the Mn-O bond stretching phonon mode energy, which is about 70 meV from optical measurements (Ahn and Millis 2001). From $\hbar \sqrt{2a_1/m_O} = 70$ meV with $m_O$ the mass of the O ion, $a_1 \approx 150$ eV is obtained. From the elastic modulus $b_1$, $c_{44}$ are estimated. From Darling et al. (1998), $c_{44} \approx 55–60$ GPa. The uniform shear mode $e_{20}$ corresponds to the conventional $e_{xy}/2$ (Ashcroft and Mermin 1976). Using the identity 1 GPa Å$^3 = 6.3$ meV, it implies that $b_1 \approx 20–25$ eV. To estimate $b_2$, the results (Mirgorodsky and Smirnov 1993) for ReO$_3$ are used, which have no RE/AK ion and, therefore, $a_2 = 0$ and the buckling of Re-O-Re bond depends only on $b_2$. According to the analysis in Mirgorodsky and Smirnov (1993), the oxygen oscillation along Re-O-Re direction has the angular frequency $\omega_x^o = 905$ cm$^{-1}$, whereas the oscillation perpendicular to Re-O-Re direction has the angular frequency $\omega_y^o = 30$ cm$^{-1}$, from which $b_2/a_1 = (\omega_y^o/\omega_x^o)^2/2 \approx 0.5 \times 10^{-3}$ can be estimated. Similar order of magnitude for $b_2$ in manganites can be expected, order of $10^{-3}a_1$, for example 0.2 eV, which is negligible compared to other parameter values, while it justifies neglecting the terms with $b_2$ as mentioned above. Various probes, such as neutron or optical spectroscopy, indicate the buckling mode frequency in manganites of about 35–50 meV (Zhang et al. 2001). From the analysis of $(\pi, \pi)$ phonon mode for this model, the frequency of buckling mode $\omega_{bk} = \sqrt{(2a_2 + 4b_2)/m_O}$ is then obtained. Therefore, one arrives to $a_2 \approx 30–80$ eV. For the estimation of $\lambda$, the JT energy gain for the 2D model is matched with that for the 3D model to ensure that the 2D model represents the energy scale of the 3D materials correctly. For the 2D model $\Delta E_{JT} = -\lambda^2/(2a_1)$. For the 3D model in Ahn and Millis (2000, 2001), $\Delta E_{JT} \approx -0.39$ eV, and therefore, $\lambda \approx 10.8$ eV is obtained.
3.4 Interplay Between Mn-O-Mn Bond Buckling and the Jahn-Teller Distortions

3.4.1 Buckling Instability Without the Jahn-Teller Term

The condition for the buckling instability is found to be without the effect of the JT energy term $E_{JT}$. A perturbative approach is further applied, rather than an attempt to solve high order polynomial equations. By minimizing $E_{har} + E_{tol}$, one obtains

$$ (e_{10})_{\text{min,*}} = -\frac{\tilde{p}}{a_1 + a_2}, $$  

where the superscript * indicates that the JT term is not yet taken into consideration. This isotropic compression of the MnO$_4$ motif renormalizes the coefficient of the $(e'_{3s})^2$ term through the $E_{cubic}$ term. From this, the critical condition for the buckling instability is then obtained,

$$ \tilde{p}^c = \frac{a_2}{a_1} (a_1 + a_2), $$  

(3.16)

$$ (e_{10})_{c,\text{min,*}} = -\frac{a_2}{a_1}. $$  

(3.17)

If $\tilde{p} > \tilde{p}^c$, Mn-O-Mn bond buckling occurs and the quartic order term, $E_{quartic}$, should be considered for the equilibrium $e'_{3s}$,

$$ |(e'_{3s})_{\text{min,*}}| = \sqrt{\frac{2}{a_1 + a_2}} \sqrt{\tilde{p} - \tilde{p}^c} $$  

(3.18)

$$ = \sqrt{2} \sqrt{(e_{10})_{c,\text{min,*}} - (e_{10})_{\text{min,*}}}.$$  

(3.19)

The minimized $E_{tot}$ without the $E_{JT}$ term is given by

$$ E_{tot,\text{min,*}} = -\frac{\tilde{p}^2}{2(a_1 + a_2)} - \frac{a_1}{2} \left( \frac{\tilde{p}}{a_1 + a_2} - \frac{a_2}{a_1} \right)^2. $$  

(3.20)

3.4.2 Buckling Instability with the Jahn-Teller Term

It is now examined, on how the JT energy term $E_{JT}$ alters the buckling instability. From $E_{har} + E_{tot} + E_{JT}$, one obtains

$$ (e_{10})_{\text{min}} = -\frac{\tilde{p}}{a_1 + a_2}, $$  

(3.21)
\[(e_{3s})_{\text{min}} = \frac{\lambda}{a_1}, \quad (3.22)\]

where the \((e_{3s})_{\text{min}} > 0\) case is considered only. The buckling instability is found from the second order terms in \(e_{20}\) and \(e'_{3s}\) in \(E_{\text{tot}}\):

\[
\frac{1}{2}(4b_1)(e_{20})^2 + \frac{1}{2}[a_2 + a_1(e_{10})_{\text{min}}](e'_{3s})^2 - \lambda e_{20}e'_{3s}, \quad (3.23)
\]

where it is assumed \((e_{3s})_{\text{min}} + e_{20}e'_{3s} > 0\). From the condition \(4b_1[a_2 + a_1(e_{10})_{\text{min}}] < \lambda^2\), one obtains the critical condition

\[
\tilde{p}_c = \frac{a_2}{a_1}(a_1 + a_2) - \frac{\lambda^2}{4b_1a_1}(a_1 + a_2) \quad (3.24)
\]

and the buckling distortion occurs for \(\tilde{p} > \tilde{p}_c\). Comparing with \(\tilde{p}_c^*\) in Equation (3.16), it is easy to find that the JT energy makes buckling more likely. After this buckling instability, the \(E_{\text{quartic}}\) term should be included to find the equilibrium result. For this, \(E_{\text{tot}}\) is first minimized with respect to the shear distortion \(e_{20}\) to obtain

\[
(e_{20})_{\text{min}} = \frac{\lambda}{4b_1}e'_{3s}, \quad (3.25)
\]

Inserting this back, an energy expression for \(E_{\text{tot}}\) is then obtained in terms of \(e'_{3s}\) only, which gives the equilibrium buckling distortion and the minimum energy,

\[
(e'_{3s})_{\text{min}} = \sqrt{\frac{2}{a_1 + a_2} \sqrt{\tilde{p} - \tilde{p}_c}}, \quad (3.26)
\]

\[
E_{\text{tot}}^{\text{min}} = -\frac{\tilde{p}^2}{2(a_1 + a_2)} - \frac{\lambda^2}{2a_1} - \frac{a_1}{2} \left( \frac{\tilde{p}}{a_1 + a_2} - \frac{a_2}{a_1} + \frac{\lambda^2}{4b_1a_1} \right)^2. \quad (3.27)
\]

Therefore, the energy gain due to the JT energy term is given by

\[
\Delta E_{\text{JT}} = -\frac{\lambda^2}{2a_1} - \frac{(\tilde{p} - \tilde{p}_c^*)\lambda^2}{4(a_1 + a_2)b_1} \quad (3.28)
\]

up to order \(\lambda^2\). The second term corresponds to the part of \(\Delta E_{\text{JT}}\) which depends on the size of \(RE\) ion, or \(\tilde{p}\). This result shows that the small rare earth ion, or large chemical pressure, stabilizes the JT distortion.
3.5 Comparison with Experiments

Comparisons between the model and experimental results are further presented. In Section 3.5.1, the simultaneous appearance of the uniform shear distortion and the long range JT distortion observed in undoped manganites (Rodríguez-Carvajal et al. 1998) are explained. In Section 3.5.2, the changes in the JT ordering temperature $T_{JT}$ are estimated among LaMnO$_3$, PrMnO$_3$, and NdMnO$_3$, and then compared with the experiments. In Section 3.5.3, the ratios between different distortion modes are calculated and compared with the experimental data for LaMnO$_3$, PrMnO$_3$, NdMnO$_3$, and other undoped manganites with even smaller RE ions.

3.5.1 Appearance of Uniform Shear Distortion Below the Jahn-Teller Ordering Temperature

Experimental data in Rodríguez-Carvajal et al. (1998), Balagurov et al. (2004), and Sánchez et al. (2002) show that the difference between the lattice constants $a$ and $b$ along the diagonal directions in the plane appears simultaneously with the long range JT distortion below $T_{JT}$ for LaMnO$_3$, PrMnO$_3$, and NdMnO$_3$. This distortion corresponds to the uniform shear distortion in the model, related by $e_{20} = (b - a)/(2\sqrt{2}u)$ with $u = 4$ Å. The coupling between the JT distortion and the uniform shear distortion is then analyzed, which is important for the stabilization of JT ordered state by the chemical pressure. In this model, such coupling originates from the term $e_{20}e_{3s}'$ in $e_{JT}$ in Equation (3.14) or in $E_{JT}$ in Equation (3.10), which can be understood as follows. Applying a positive $e_{20}$ shear distortion to the lattice is initially considered, as shown in Figure 3.6 by the axis of elongation and compression along $45^\circ$ and $135^\circ$, respectively. Such uniform shear distortion makes the Mn-O bond lengths either longer or shorter depending on whether the direction of the bond is closer to the orientation of elongation ($45^\circ$) or compression ($135^\circ$), except for the bonds with directions right between the two directions. If the system does not have $(\pi, \pi)$ buckling, as shown by the thin solid lines in Figure 3.6, all Mn-O bonds...
make equal angles from the axis of elongation/compression, and therefore $e_{20}$ shear distortion keeps all Mn-O bond lengths equal. This implies that $e_{20}$ distortion alone does not contribute to the JT distortion or JT energy gain. In contrast, if the system has a buckling distortion $e'_{3s}$ with a wave vector $\vec{k} = (\pi, \pi)$, as shown by the thick solid lines in Figure 3.6, the $e_{20}$ shear distortion elongates Mn-O bonds marked with $l$ and shortens Mn-O bonds marked with $s$, depending on whether the bond direction is closer to the axis of elongation or the axis of compression, which results in the JT distortion $e_{JT}$ with a wave vector $\vec{k} = (\pi, \pi)$. If this extra JT distortion is in the same [opposite] phase as [to] the deviatoric $e_{3s}$ distortion, in other words, if $e_{20}e'_{3s}$ and $e_{3s}$ have the same [opposite] sign, this extra JT distortion increases [decreases] the net JT distortion, which explains the expression for $E_{JT}$ in Equation (3.10) or $e_{JT}$ in Equation (3.14). It is emphasized here that the extra JT energy gain occurs only when the $e_2$, $e_3$ and $e'_3$ distortions are in the right phase with respect to each other. Experiments (Rodríguez-Carvajal et al. 1998) show that the $(\pi, \pi)$ Mn-O-Mn bond buckling persists even above $T_{JT}$ without much change in size. However, above $T_{JT}$, the coherent $e_3$ distortion does not exist, and therefore the extra JT distortion due to the uniform $e_{20}$ distortion in the presence of staggered buckling distortion would increase the JT energy gain in some regions and decrease the JT energy gain in other regions, and does not change the net JT energy. In other words, the energy gain due to the cooperative effect between $e_3$, $e'_3$, and $e_2$ does not exist at $T > T_{JT}$. Therefore it is expected that the $e_{20}$ mode does not exist above $T_{JT}$ and appears simultaneously with the long range JT ordering, consistent with the experimental results.

3.5.2 Jahn-Teller Ordering Temperature and Its Variation Among LaMnO$_3$, PrMnO$_3$, and NdMnO$_3$

It is reported (Kimura, Ishihara, Shintani, Arima, Takahashi, Ishizaka and Tokura 2003; Sánchez et al. 2002) that $T_{JT}$ changes from 750 K for LaMnO$_3$ to 1050 K
Figure 3.6 Superposition of \((\pi, \pi)\) buckling \(e_{3s}'\) and uniform shear distortion \(e_{20}\) effectively generates the extra \((\pi, \pi)\) JT distortion of Mn-O bond lengths, as indicated by the \(s\) and \(l\) for the shortened and elongated bonds, which is responsible for the \(e_{20}e_{3s}'\) coupling within \(e_{JT}\) and the JT coupling \(E_{JT}\). In the \((\pi, \pi)\) JT ordered state, this adds up to the \(e_{3s}\) deviatoric mode if \(e_{3s}\) and \(e_{20}e_{3s}'\) have the same sign. This mechanism is responsible for the appearance of the uniform shear distortion below the JT ordering temperature, as explained in Section 3.5.1. The extra JT energy gain for the buckled lattice is responsible for the increase in \(T_{JT}\) in \(RE\text{MnO}_3\) with small \(RE\) ions, as explained in Section 3.5.2.

for PrMnO\(_3\), and further to 1100 K for NdMnO\(_3\), that is, by about \(\Delta T_{JT}(\text{Pr}) = 300\) K and \(\Delta T_{JT}(\text{Nd}) = 350\) K relative to LaMnO\(_3\) respectively, where \(\Delta T_{JT}(RE) = T_{JT}(RE\text{MnO}_3) - T_{JT}(\text{LaMnO}_3)\). The term \(\Delta T_{JT}(RE)\) is further estimated from the model to understand how such a drastic change of the JT ordering temperature can occur by the increase in chemical pressure.

The term \(E_{\text{tot}}^{\text{min}}\) in Equation (3.27) is rewritten for \(\tilde{p} > \tilde{p}_c\) as follows.

\[
E_{\text{tot}}^{\text{min}} = -\frac{\tilde{p}^2}{2(a_1 + a_2)} - \frac{\lambda^2}{2a_1} - \frac{a_1(\tilde{p} - \tilde{p}_c)^2}{2(a_1 + a_2)^2},
\]

(3.29)

where

\[
\tilde{p}_c = \tilde{p}_c^* - \delta\tilde{p}_c, \quad \delta\tilde{p}_c = \frac{\lambda^2}{4b_1a_1}(a_1 + a_2),
\]

(3.30)
and $\tilde{p}_c^*$ represents the critical chemical pressure without the JT energy term. Since $\delta \tilde{p}_c$, the change in the critical chemical pressure due to the $E_{JT}$ term, is small relative to $\tilde{p} - \tilde{p}_c^*$, with $\delta \tilde{p}_c/(\tilde{p} - \tilde{p}_c^*) \approx 0.3$ for parameter values in Section 3.3, the terms linear in $\delta \tilde{p}_c$ are kept only and then rewritten according to the origin of each term as follows.

$$E_{tot}^{min} \approx E_{comp}^{min} + E_{JT}^{min} + E_{bk}^{min} + E_{bk, JT, sh}^{min}, \quad (3.32)$$

$$E_{comp}^{min} = -\frac{1}{2} \frac{\tilde{p}^2}{a_1 + a_2}, \quad (3.33)$$

$$E_{JT}^{min} = -\frac{1}{2} \frac{\lambda^2}{a_1}, \quad (3.34)$$

$$E_{bk}^{min} = -\frac{1}{2} \frac{a_1}{(a_1 + a_2)^2} (\tilde{p} - \tilde{p}_c^*), \quad (3.35)$$

$$E_{bk, JT, sh}^{min} = -\frac{a_1}{(a_1 + a_2)^2} (\tilde{p} - \tilde{p}_c^*) \delta \tilde{p}_c, \quad (3.36)$$

The first three terms, $E_{comp}^{min}$, $E_{JT}^{min}$, and $E_{bk}^{min}$, represent the energy terms purely due to compression, JT distortion, and buckling, respectively. The fourth term is the energy due to the coherent buckling, JT and shear distortions, indicated by its dependence on $\tilde{p} - \tilde{p}_c^*$, $\lambda$ and $b_1$, which gives extra stability to the JT ordering due to the chemical pressure.

To estimate $T_{JT}$, a high temperature state with random JT distortions must be considered, for which the energy can be written in a similar way as Equation (3.32) except for the absence of the fourth term due to the lack of coherence among distortions as explained in Section 3.5.1,

$$E_{tot}^{ran} = E_{comp}^{ran} + E_{JT}^{ran} + E_{bk}^{ran}. \quad (3.37)$$

It is expected that $E_{comp}^{ran} \approx E_{comp}^{min}$ and $E_{bk}^{ran} \approx E_{bk}^{min}$, since the unit cell volume and buckling angle do not change very much as the temperature crosses $T_{JT}$ (Rodríguez-Carvajal et al. 1998). Therefore, the energy difference between JT ordered and JT disordered state is

$$E_{tot}^{ran} - E_{tot}^{min} \approx E_{JT}^{ran} - E_{JT}^{min} - E_{bk, JT, sh}^{min}. \quad (3.38)$$
It is important to verify that this model gives the correct order of magnitude of $T_{JT}$ itself. An order of magnitude estimate for $T_{JT}$ can be made from the energy difference between two different JT ordered states, one the most favored state and the other relatively unfavored state. The most favored state is that with the JT distortion of $\vec{k} = (\pi, \pi)$ considered so far in this chapter and has the JT energy of $E_{JT}^{\min} = -\lambda^2/(2a_1)$. A state with the same size of JT distortion $e_3$ is chosen but with a wave vector $\vec{k} = (0,0)$, as a relatively unfavored state, with energy $E_{JT}^{\text{unif}} = -\lambda^2/[2(a_1 + a_2)]$. Using the estimated parameter values, $a_1 = 150$ eV, $a_2 = 30–80$ eV, $\lambda = 10.8$ eV, $E_{JT}^{\text{unif}} - E_{JT}^{\min} \approx 600–1300$ K are then obtained, which have the same order of magnitude, as the experimentally observed $T_{JT}$ in the range of 750–1100 K.

For the change in $T_{JT}$ between LaMnO$_3$ and $RE$MnO$_3$ ($RE=Pr$, Nd), the only term in Equation (3.38) which changes with the $RE$ ion size is $-E_{bk, JT, \text{shear}}^{\min}$. Therefore, the JT ordering temperature variation between LaMnO$_3$ and $RE$MnO$_3$ can be related to $-E_{bk, JT, sh}^{\min}(RE\text{MnO}_3) + E_{bk, JT, sh}^{\min}(\text{LaMnO}_3)$ within a factor of the order of one. Further, $E_{bk, JT, sh}^{\min}$ is expressed in terms of $(e'_{3s})^{\min}$,

$$E_{bk, JT, sh}^{\min} = -\frac{\lambda^2}{2b_1}[(e'_{3s})^{\min}]^2. \quad (3.39)$$

According to the experimental data (Kimura, Ishihara, Shintani, Arima, Takahashi, Ishizaka and Tokura 2003; Rodríguez-Carvajal et al. 1998; Sánchez et al. 2002; Balagurov et al. 2004), the Mn-O-Mn bond angle is 155.1° for LaMnO$_3$, 150.5° for PrMnO$_3$, and 149.8° for NdMnO$_3$, which corresponds to $(e'_{3s})^{\min}$ of 0.217, 0.257, and 0.264, respectively. These distortions, along with parameter values $\lambda = 10.8$ eV and $b_1 = 20–25$ eV, result in $-E_{bk, JT, sh}^{\min}(RE\text{MnO}_3) + E_{bk, JT, sh}^{\min}(\text{LaMnO}_3)$ of 11–14 meV $\approx 130–160$ K for $RE=Pr$ and 12–16 meV $\approx 140–190$ K for $RE=Nd$. From a classical Monte Carlo simulation for the double-well potential model in Ahn et al. (2003), it has been found that the structural ordering temperature is
about twice the energy difference between the distorted ground state and undistorted high energy state.\textsuperscript{2} Although such a relation would depend on the details of the model, if a similar situation in the current model is assumed, the JT ordering temperature variation can be estimated as twice the energy difference, therefore,

\[ T_{JT}(\text{NdMnO}_3) - T_{JT}(\text{LaMnO}_3) \approx 2 \times [-E_{\text{bk},JT,sh}^{\text{min}}(\text{NdMnO}_3) + E_{\text{bk},JT,sh}^{\text{min}}(\text{LaMnO}_3)] = 300-375 \text{ K}, \]

which agrees well with the experimental change in \( T_{JT} \), 350 K. Similar analysis for \( \text{PrMnO}_3 \) leads to \( T_{JT}(\text{PrMnO}_3) - T_{JT}(\text{LaMnO}_3) \approx 255-320 \text{ K} \), which agrees well with the experimental value of 300 K.

This agreement shows that indeed the JT ordered state is more stabilized when the buckling increases for smaller \( RE \) ions for undoped compounds. The relatively large increase in the JT ordering temperature, both in theory and experimental data, shows that the interplay between the \( RE \) ion size and the JT distortion is significant, and should be taken into account to explain the well-known temperature-tolerance factor phase diagram of both undoped and doped perovskite manganites.

### 3.5.3 Relation Between Shear, Buckling, and Deviatoric Distortion and Comparison for Other Undoped Manganites

Equations (3.22) and (3.25) imply that the following quantities remain constant regardless of the variation in chemical pressure:

\[
\begin{align*}
(e_{3s})^{\text{min}} &= \frac{\lambda}{a_1}, \\
(e_{20})^{\text{min}} &= \frac{\lambda}{4b_1}, \\
(e_{3s})^{\text{min}}(e_{3s}')^{\text{min}} &= \frac{a_1}{4b_1}.
\end{align*}
\]

These quantities are calculated from the experimental data for \( \text{LaMnO}_3 \), \( \text{PrMnO}_3 \), and \( \text{NdMnO}_3 \), and in turn present the results shown in Table 3.1, in which the\textsuperscript{2}Classical Monte Carlo simulations is carried out with the same energy expression and parameter values used for the results in Figure 3 in Ahn et al. (2003). Further, the structural phase transition temperature is about 0.15, which is about twice the depth of the potential well 0.08.
relation between the distortion variables in the model and experimental parameters is also shown, while the estimate of $T_{JT}$ and $\Delta T_{JT}$ is obtained in Section 3.5.2. The results show that $(e_{3s})^{\text{min}}, (e_{20})^{\text{min}}/(e'_{3s})^{\text{min}},$ and $(e_{20})^{\text{min}}/[(e_{3s})^{\text{min}}(e'_{3s})^{\text{min}}]$ agree well with theoretical estimates obtained from the parameters in Section 3.3, and vary 7%, 29%, and 32%, respectively, smaller than up to 41% changes in $(e_{20})^{\text{min}}$ and $(e'_{3s})^{\text{min}}$. The results underscore the strong coupling between these distortions, in particular, the important role played by the uniform shear distortion in connecting the JT and buckling distortions, an aspect neglected in the literature so far.

The analysis to undoped perovskite manganites is further extended with even smaller $RE$ ions. The results are summarized in Figure 3.7, along with values from available experimental data. Figure 3.7(a) shows the JT ordering temperature variation with respect to $\text{LaMnO}_3$ from the theory along with measured $T_{JT}$ for $\text{LaMnO}_3$, $\text{PrMnO}_3$, and $\text{NdMnO}_3$, which indicates rapid increase of the JT energy gain as the $RE$ size becomes smaller. Figure 3.7(b) shows that the ratio $e_{20}/e'_{3s}$ from experimental data remains relatively close to the range of theoretical constant ratios of $\lambda/(4b_1)$. Explanation for the deviation from theoretically estimated constant for the whole range of $RE$ ions may require higher order expansions of the energy expression. Figure 3.7(c) shows $e_{JT}$ from experimental data and theory. For the experimental data, $e_{JT}$ is calculated from $(l - s)/u$, where $l$ and $s$ are in-plane long and short Mn-O bond lengths, as in Table I. Theoretical range of $e_{JT}$ versus $e'_{3s}$ is from $e_{JT} \approx e_{3s} + e_{20} e'_{3s}$ with $e_{3s} \approx \lambda/a_1$ and $e_{20} \approx e'_{3s} \lambda/(4b_1)$. Both theory and experiment consistently show an overall increase of $e_{JT}$ as Mn-O-Mn bond buckling increases.

3.6 Discussion on How to Extend the Model to Doped Manganites and Electronically Ferroelectric Undoped Manganites

Although primary focus in this chapter is the high temperature JT structural phase transition in undoped perovskite manganites, it is briefly commented on in this sec-
Table 3.1 Parameters from Experimental Data and Comparison with Theoretical Estimates

<table>
<thead>
<tr>
<th>Parameters</th>
<th>LaMnO$_3$</th>
<th>PrMnO$_3$</th>
<th>NdMnO$_3$</th>
<th>Theoretical estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant, $a$</td>
<td>5.54 Å</td>
<td>5.45 Å</td>
<td>5.41 Å</td>
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</tr>
<tr>
<td>Lattice constant, $b$</td>
<td>5.75 Å</td>
<td>5.81 Å</td>
<td>5.73 Å</td>
<td></td>
</tr>
<tr>
<td>Long Mn-O bond length within $ab$ plane, $l$</td>
<td>2.18 Å</td>
<td>2.21 Å</td>
<td>2.20 Å</td>
<td></td>
</tr>
<tr>
<td>Short Mn-O bond length within $ab$ plane, $s$</td>
<td>1.91 Å</td>
<td>1.91 Å</td>
<td>1.90 Å</td>
<td></td>
</tr>
<tr>
<td>Mn-O-Mn bond angle within $ab$ plane, $\varphi$</td>
<td>155.1°</td>
<td>150.5°</td>
<td>149.8°</td>
<td></td>
</tr>
<tr>
<td>Mn-Mn distance with $e_{10}$ only, $(a + b)/(2 \sqrt{2})$</td>
<td>3.99 Å</td>
<td>3.98 Å</td>
<td>3.94 Å</td>
<td>Compressed from $u \approx 4$ Å</td>
</tr>
<tr>
<td>$e_{20} = (b - a)/(2 \sqrt{2}u)$</td>
<td>0.0186</td>
<td>0.0322</td>
<td>0.0280</td>
<td></td>
</tr>
<tr>
<td>$e_{3s}' = (\pi - \varphi)/2$</td>
<td>0.217</td>
<td>0.257</td>
<td>0.264</td>
<td></td>
</tr>
<tr>
<td>$e_{20}/e_{3s}'$</td>
<td>0.086</td>
<td>0.125</td>
<td>0.106</td>
<td>$\lambda/(4b_1) = 0.108–0.135$</td>
</tr>
<tr>
<td>$e_{JT} = (l - s)/u$</td>
<td>0.0678</td>
<td>0.0753</td>
<td>0.0750</td>
<td>$\lambda/a_1 = 0.072$</td>
</tr>
<tr>
<td>$e_{3s} \approx e_{JT} - e_{20}e_{3s}'$</td>
<td>0.0637</td>
<td>0.0670</td>
<td>0.0676</td>
<td>$a_1/(4b_1) = 1.5–1.9$</td>
</tr>
<tr>
<td>$e_{20}/(e_{3s}e_{3s}')$</td>
<td>1.35</td>
<td>1.86</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>$T_{JT}$</td>
<td>750 K</td>
<td>1050 K</td>
<td>1100 K</td>
<td>$E_{JT}^{\text{unif}} - E_{JT}^{\text{min}} = 600–1300$ K</td>
</tr>
<tr>
<td>$\Delta T_{JT}(\text{Pr}) = T_{JT}(\text{PrMnO}<em>3) - T</em>{JT}(\text{LaMnO}_3)$</td>
<td></td>
<td></td>
<td></td>
<td>$-2\Delta E_{\text{bk,JT,sh}} = 255–320$ K</td>
</tr>
<tr>
<td>$\Delta T_{JT}(\text{Nd}) = T_{JT}(\text{NdMnO}<em>3) - T</em>{JT}(\text{LaMnO}_3)$</td>
<td></td>
<td></td>
<td></td>
<td>$-2\Delta E_{\text{bk,JT,sh}} = 300–375$ K</td>
</tr>
</tbody>
</table>

Experimental data for the lattice constants, bond lengths, and bond angles for LaMnO$_3$, PrMnO$_3$ and NdMnO$_3$ are from Rodríguez-Carvajal et al. (1998), Balagurov et al. (2004), Sánchez et al. (2002), and Liu et al. (1996), measured at room temperature.
Figure 3.7 Available experimental data and bounds estimated from theory, plotted against Mn-O-Mn bond angle and $e'_{3s}$, for (a) JT ordering temperature, (b) $e_{20}/e'_{3s}$ ratio, and (c) $e_{JT}$. Experimental data are from Sánchez et al. (2002), Liu et al. (1996), Alonso et al. (2000), Mochizuki and Furukawa (2009), and references therein.

Ation on how to extend the model to doped manganites and electronically ferroelectric undoped manganites. In the case of doped manganites, each Mn site has a fractional number of 3$d$ $e_g$ electrons, which would require quantum mechanical description of $e_g$ electrons, similar to the ones in Moreo et al. (1999); Pradhan et al. (2007); Vergés et al. (2002); Salafranca and Brey (2006); Kumar and Majumdar (2006). Furthermore, RE and AK ions with different sizes distribute randomly, effectively generating site-dependent chemical pressure. Experimentally, it is observed that the increased
variance of $RE$ and $AK$ ion sizes has a similar effect as the decreased average $RE$
and $AK$ ion size in doped manganites. If focus is set on the effects of chemical pres-
sure, the first necessary modification to the existing models in Moreo et al. (1999);
Pradhan et al. (2007); Vergés et al. (2002); Salafranca and Brey (2006); Kumar and
Majumdar (2006) would be a classical coupling between local chemical pressure and
local dilatation mode of surrounding O ions, similar to $\epsilon'_1$. The second necessary
modification would be anharmonic lattice energy terms obtained from the Keating
model, similar to the ones presented in this chapter. Because chemical pressure $\tilde{p}_i$
is dependent on site, one should consider all modes shown in Figure 3.3 at each site
and the constraints between Fourier transforms of these variables, instead of just the
four modes in Figure 3.4. With many variables involved, numerical approaches, such
as Monte Carlo methods, would be essential.

This model can be extended and serve as a phenomenological model for the
magnetism and electronic ferroelectricity in undoped manganites (Kimura, Ishihara,
Shintani, Arima, Takahashi, Ishizaka and Tokura 2003; Mochizuki and Furukawa
2009; Sergienko et al. 2006), complementing existing theories, such as the ones based
on local density approximation (Yamauchi et al. 2008). In undoped manganites, the
magnetic interaction also shows a prominent dependence on the size of $RE$ ions,
changing the ground state from A-type to E-type antiferromagnetic phase through
incommensurate phases as $RE$ ion becomes smaller. This behavior has been proposed
to originate from the reduced nearest neighbor ferromagnetism and the increased next
nearest neighbor antiferromagnetism (Kimura, Ishihara, Shintani, Arima, Takahashi,
Ishizaka and Tokura 2003), or alternatively, the reduced antiferromagnetism between
$t_{2g}$ spins and long range ferromagnetic double exchange interaction (Salafranca and
Brey 2006). It has been further proposed that electronically ferroelectric phase may
emerge in E-type antiferromagnetic phase, associated with the displacement of Wann-
ier function center (WFC) from the ionic location due to the magnetic inversion
symmetry breaking for E-type spin ordering (Yamauchi et al. 2008). Within this phenomenological approach, the dependence of the first nearest and the second nearest neighbor magnetic interaction $J_1$ and $J_2$ on the Mn-O-Mn bond buckling can be expressed as $J_1 = J_{10}(1 + \alpha_1 e'_3 s)$ and $J_2 = J_{20}(1 + \alpha_2 e'_3 s)$ for a small range of $e'_3 s$, in which the linear coefficients $\alpha_1$ and $\alpha_2$ can be decided from more fundamental theories. The $t_{2g} − t_{2g}$ super-exchange interaction can be expressed in a similar way.

As for the electronic ferroelectricity, although the explicit form of the Wannier function would require quantum mechanical analysis, the WFC itself can be treated as a classical variable and the lattice of the WFC can be considered in addition to the lattice of Mn ions. Therefore, symmetry-based analysis can be applied to both the WFC lattice and the ionic lattice. To demonstrate the idea, an example of three connected Mn-O motifs at sites (-1,0), (0,0), and (1,0) must be considered that is shown in Figure 3.8. The $x$ directional displacement of Mn ion at site $\vec{i}$, the $x$ directional displacement of WFC associated with Mn $3d_{\frac{3}{2}} \frac{3}{2} \frac{r}{2}$ state with spin parallel to the $t_{2g}$ core spin at site $\vec{i}$, and the $t_{2g}$ spin at site $\vec{i}$ with magnitude of $|S_{t_{2g}}|$ are represented by $d_\vec{i}$, $D_\vec{i}$, and $\vec{S}_\vec{i}$. In addition, the buckling distortion $e'_3 s$ is considered. If a situation without any other distortions persists, the energy associated with these limited degrees of freedom can be written in the following form based on the symmetry:

$$
E_{eFE} = \frac{K_d}{2} \left( d_{(-1,0)}^2 + d_{(0,0)}^2 + d_{(1,0)}^2 \right) + \frac{K_D}{2} \left[ \left( D_{(-1,0)} - d_{(-1,0)} \right)^2 + \left( D_{(0,0)} - d_{(0,0)} \right)^2 + \left( D_{(1,0)} - d_{(1,0)} \right)^2 \right] + J_{10} \vec{S}_{(-1,0)} \cdot \vec{S}_{(0,0)} \left[ 1 + \alpha_1 e'_3 s + \beta \left( D_{(0,0)} - D_{(-1,0)} \right) \right] + J_{10} \vec{S}_{(0,0)} \cdot \vec{S}_{(1,0)} \left[ 1 + \alpha_1 e'_3 s + \beta \left( D_{(1,0)} - D_{(0,0)} \right) \right],
$$

(3.43)

where the terms with $\beta$ represent how the magnetic interaction depends on the distance between the nearest neighbor WFC’s. In the case of $d_{(0,0)} = d_{(-1,0)} = d_{(1,0)} = 0$ due to other elastic energy terms that are not considered above and $\vec{S}_{(-1,0)} = \vec{S}_{(0,0)} = \vec{S}_{(1,0)} = 0$.
\( \vec{S}_{(0,0)} = -\vec{S}_{(1,0)} \) due to the E-type magnetic ordering, the minimization with respect to \( D_{(0,0)} \) leads to \( D_{(0,0)} = -2J_{10}|S_{t_{2g}}|^2/\beta/K_D \), shown schematically in Figure 3.8 with a thin arrow and an open square representing WFC, which demonstrates how this model can be expanded for modeling of ferroelectric moment of electronic origin. The symmetry-mode-based approach can be also used to model conventional ionic ferroelectricity in perovskite transition metal oxides by including energy terms with inversion symmetry breaking modes, such as \( t_x, t_y, t'_x, \) and \( t'_y \) in Figure 3.3.

![Figure 3.8](image-url)

Figure 3.8 Schematic drawing that demonstrates how this model can be extended to include electronic ferroelectricity in undoped manganites. Three connected MnO\(_4\) motifs are shown. Open and solid circles represent O and Mn ions. Open squares represent WFC’s associated with the Mn 3\(d_{3z^2-r^2}\) state with spin parallel to the \( t_{2g} \) core spin, which would coincide with Mn ions in the non-ferroelectric phase. Thick arrows at the bottom represent the \( t_{2g} \) spin directions for E-type antiferromagnetic phase of undoped manganites. Thin horizontal arrow represents the displacement of WFC from Mn ion location, resulting in the ferroelectric moment of electronic origin.

### 3.7 Conclusions

From the analysis of a Keating energy expression expanded in terms of the atomic-scale symmetry-modes, it is found that the effect of small \( RE \) ion size, known as chemical pressure effect, is significant in stabilizing the long range JT distortion in undoped perovskite manganites. A good agreement with the experimental data on the JT ordering temperature and the substantial increase of the JT ordering temperature from LaMnO\(_3\) to PrMnO\(_3\) and NdMnO\(_3\) have been obtained. It is proposed that similar effects need to be considered to understand the phase diagram for the
doped perovskite manganites. Further, the explanation is presented on the appearance of the uniform shear distortion below the JT ordering temperature in terms of the coupling between coherent shear, buckling, and deviatoric distortions within the JT energy. Moreover, the ratio between these distortions at low temperature is estimated, and a good agreement with experimental data for LaMnO$_3$, PrMnO$_3$, and NdMnO$_3$ is found, which confirms the coupling proposed in this model.
CHAPTER 4

SYMMETRY-BASED ATOMIC-SCALE DESCRIPTIONS OF LATTICE DYNAMICS

The work in this chapter was done in collaboration with Jichan Moon from Department of Physics, Konkuk University of Seoul, South Korea, as well as Keun H. Ahn from Department of Physics at New Jersey Institute of Technology.

4.1 Introduction

These days a lot of attention has been focused on physical properties in nanometer length scale. In particular, materials with competing ground states, such as high temperature superconducting cuprates (Lee, Nagaosa and Wen 2006) and colossal magnetoresistive manganites (Jin et al. 1994; Millis 1998; Salamon and Jaime 2001), often show nanometer scale features, either static or dynamic. Examples are stripes in cuprates (Tranquada et al. 1995; Kivelson et al. 2003) and anisotropic correlations in manganites (Kiryukhin 2004; Ahn et al. 2004). It is believed that understanding these nano-scale features is essential to explain macroscopic properties of these materials.

For the description of mesoscopic scale domain structures and phase transitions, phenomenological Ginzburg-Landau formalism has been very successful (Shenoy et al. 1999; Lookman et al. 2003). One of the keys for such success is the use of symmetry in the definition of variables, which makes the selection of free energy terms self-evident. Motivated by the success of symmetry-based continuum approach, symmetry-based atomic-scale description of lattice distortions has been recently proposed, and demonstrated for a two-dimensional square lattice (Ahn et al. 2003). In this approach, atomic-scale symmetry-modes are defined on a plaquette of atoms, and are used to express potential energy terms associated with lattice distortions. This method has been used to understand atomic scale structures of twin boundaries (Ahn
et al. 2003) and antiphase boundaries and associated electronic textures (Ahn et al. 2005), strain-induced metal insulator phase-coexistence in manganites (Ahn et al. 2004), superconducting order parameter textures around structural defects (Zhu et al. 2003), and the coupling between electronic nematic order parameter and structural domains in metamagnets near a quantum critical point (Doh et al. 2007).

So far, this approach has been used for frozen lattices or the relaxation of lattice distortions through the Euler method (Shenoy et al. 1999), which does not require kinetic energy terms. In the current chapter (Moon 2006), the study on how the approach based on atomic scale symmetry modes can be extended to include kinetic energy terms and describe lattice dynamics within the formalism of both classical and quantum mechanics is presented. The study within the formalism of classical mechanics is first presented in Section 4.2, where the comparison with the continuum results (Lookman et al. 2003) are presented, and the phonon spectrum in terms of symmetry modes is also analyzed. Quantum mechanical formalism is formulated in terms of atomic scale symmetry modes in Section 4.3, whereas the conclusions are given in Section 4.4. In addition, intermediate steps of the calculations and 2D phonon spectrum examples are presented in Appendix 4.A.

### 4.2 Classical Formalism

#### 4.2.1 One Dimensional Lattice with a Monatomic Basis

The underlying idea of mode-based lattice dynamics for one-dimensional lattice is first demonstrated, with a monatomic basis shown in Figure 4.1. The displacements of atoms are confined along the direction of the chain, and are represented by $u(i)$.

![Figure 4.1](image-url)

**Figure 4.1** The one-dimensional lattice.
where $i$ is the index for sites. $M$ is the mass of the atom. To be specific, it is assumed that the interaction between nearest neighbor atoms are described by a spring with a spring constant $k$ and other potential energy terms are negligible, which gives rise to the following Lagrangian.

$$L_{\text{chain}} = \sum_i \frac{1}{2}M \dot{u}(i)^2 - \frac{1}{2}k[u(i + 1) - u(i)]^2.$$  \hfill (4.1)

A two-atom unit is taken as a motif for this lattice (Ahn et al. 2003), and the symmetry modes are defined, $e(i)$ and $t(i)$, as follows, where a normalization factor is introduced according to the number of displacement variables in the definition.

$$e(i) \equiv \frac{1}{\sqrt{2}}[u(i + 1) - u(i)],$$ \hfill (4.2)

$$t(i) \equiv \frac{1}{\sqrt{2}}[u(i + 1) + u(i)].$$ \hfill (4.3)

![Figure 4.2](image.png)

**Figure 4.2** The lattice modes for the one-dimensional chain in Figure 4.1.

The two variables, $e$ and $t$, correspond to the distortion and rigid translation of the motif, respectively. Similarly to the findings in Ahn et al. (2003), since the two modes are defined at each site $i$ from one physically independent displacement variable, these modes are related through one constraint equation, shown below in the reciprocal space and direct space, respectively.

$$f_k \equiv (e^{ik} + 1)e(k) - (e^{ik} - 1)t(k) = 0,$$ \hfill (4.4)

$$e(i + 1) + e(i) - t(i + 1) + t(i) = 0$$ \hfill (4.5)

In terms of these modes, the Lagrangian in Equation (4.1) can be expressed in the following way.

$$L_{\text{chain}} = \sum_i \frac{1}{2} (\frac{M}{2}) \dot{e}(i)^2 + \frac{1}{2} (\frac{M}{2}) \dot{t}(i)^2 - \frac{1}{2} (2k) e(i)^2,$$ \hfill (4.6)
The result shows that the introduction of atomic scale rigid modes, such as \( t \), which are not considered in Ahn et al. (2003), allows the kinetic energy term expressed in a quadratic form in terms of modes. To obtain the equations of motion for constrained variables, the Lagrangian with Lagrange multiplier, \( \lambda_k \), and constraint equations, \( f_{-k} \) are modified, as shown below.

\[
\tilde{L} = \sum_k \frac{1}{2} \left( \frac{M}{2} \right) (\dot{e}_k \dot{e}_{-k} + \dot{t}_k \dot{t}_{-k}) - \frac{1}{2}(2k)e_k e_{-k} + \lambda_k \{(e^{-ik} + 1)e_{-k} - (e^{-ik} - 1)t_{-k}\}.
\]

(4.7)

Lagrangian formalism of dynamics leads to the two equations of motion,

\[
\frac{M}{2} \ddot{e}_k + 2ke_k - \lambda_k(e^{-ik} + 1) = 0,
\]

(4.8)

\[
\frac{M}{2} \ddot{t}_k + \lambda_k(e^{-ik} - 1) = 0,
\]

(4.9)

and a well-known dispersion relation for one-dimensional chain (Kittel 2005),

\[
\omega = \sqrt{\frac{k}{M}(1 - \cos k)}.
\]

(4.10)

This result shows that the lattice dynamics can be studied within the framework of atomic scale symmetry modes and their constraint equations, without using the displacement variables explicitly. The advantage of this approach lies in the convenience in expressing high order anharmonic potential energy terms in more concise ways, compared to the approach based on displacement variables. Such advantage will be more relevant for lattices in 2D or 3D, where anharmonic energy landscape with multiple local energy minima and consequent domain structures could occur naturally (Ahn et al. 2003). In the next subsection, it is demonstrated how this approach can be applied for lattices in higher dimensions, for example, a two-dimensional square lattice with a monatomic basis.

4.2.2 Two-Dimensional Square Lattice With a Monatomic Basis

Symmetry-based atomic scale modes for a two-dimensional square lattice with a monatomic basis, shown in Figure 4.3, have been studied in Ahn et al. (2003, 2004),
where strain modes, \( e_1, e_2, \) and \( e_3, \) and short wavelength modes, \( s_x \) and \( s_y, \) are defined, as shown in Figure 4.4. Specifically, in terms of displacement variables, \( u_x(i) \) and \( u_y(i), \) shown in Figure 4.3, where \( i_x \) and \( i_y \) represent site indices, these modes are expressed as follows along with proper normalization factors.

\[
e_1(i) = \frac{1}{2\sqrt{2}} [ -u_x^i - u_y^i + u_x^{i+10} - u_y^{i+10} \\
- u_x^{i+01} + u_y^{i+01} + u_x^{i+11} + u_y^{i+11} ] ,
\]

(4.11)

\[
e_2(i) = \frac{1}{2\sqrt{2}} [ -u_x^i - u_y^i - u_x^{i+10} + u_y^{i+10} \\
+ u_x^{i+01} - u_y^{i+01} + u_x^{i+11} + u_y^{i+11} ] ,
\]

(4.12)

\[
e_3(i) = \frac{1}{2\sqrt{2}} [ -u_x^i + u_y^i + u_x^{i+10} + u_y^{i+10} \\
- u_x^{i+01} - u_y^{i+01} + u_x^{i+11} - u_y^{i+11} ] ,
\]

(4.13)

\[
s_x(i) = \frac{1}{2} [ u_x^i - u_x^{i+10} - u_x^{i+01} + u_x^{i+11} ] ,
\]

(4.14)

\[
s_y(i) = \frac{1}{2} [ u_y^i - u_y^{i+10} - u_y^{i+01} + u_y^{i+11} ] .
\]

(4.15)

Instead of \( s_x \) and \( s_y \) modes, the following \( s_+ \) and \( s_- \) modes can be used.

\[
s_+(i) = \frac{1}{\sqrt{2}} [ s_x(i) + s_y(i) ]
\]

(4.16)
\[ s_-(\vec{i}) = \frac{1}{\sqrt{2}}[s_x(\vec{i}) - s_y(\vec{i})] \] (4.17)

These five modes have been used to describe various forms of potential energy terms for lattice distortions, in which harmonic and anharmonic interactions among atoms within the same plaquette have been considered (Ahn et al. 2003, 2004). However, these five modes are not sufficient to represent the kinetic energy term adequately. For example, to obtain the phonon spectrum shown in Figure 2 in Ahn et al. (2003), the expression has been converted back to the displacement variables.

In current work, it is shown that additional modes, associated with the rigid motion of the motif, similar to the mode \( t \) in the previous subsection, allow a formalism entirely based on symmetry modes without resorting to displacement variables. The three rigid modes for the two-dimensional square lattice are shown in Figure 4.5 and are defined as follows.

\[
t_x(\vec{i}) = \frac{1}{2}[u^x_i + u^x_{i+10} + u^x_{i+01} + u^x_{i+11}],
\]

\[
t_y(\vec{i}) = \frac{1}{2}[u^y_i + u^y_{i+10} + u^y_{i+01} + u^y_{i+11}],
\]

\[
r(\vec{i}) = \frac{1}{2\sqrt{2}}[u^x_i - u^y_i + u^x_{i+10} + u^y_{i+10} - u^x_{i+01} - u^y_{i+01} - u^x_{i+11} - u^y_{i+11}],
\]

Instead of \( t_x \) and \( t_y \), the following \( t_+ \) and \( t_- \) modes can be also used.

\[
t_+(\vec{i}) = \frac{1}{\sqrt{2}}[t_x(\vec{i}) + t_y(\vec{i})] \] (4.21)

\[
t_-(\vec{i}) = \frac{1}{\sqrt{2}}[t_x(\vec{i}) - t_y(\vec{i})] \] (4.22)

**Figure 4.5** Three rigid mode in the two-dimensional square lattice.
The first two modes, \( t_x \) and \( t_y \) correspond to the rigid translation of the motif along \( x \) and \( y \) direction, and \( r \) represents a rigid rotation of the motif. Straight-forward expansion shows that the kinetic energy of the lattice can be expressed in terms of eight symmetry modes in the following quadratic form, where \( M \) is the mass of the atom.

\[
T_{\text{sq.lat}} = \sum_i \frac{1}{2} M [\dot{u}_x(\vec{i})^2 + \dot{u}_y(\vec{i})^2]
\]

\[
= \sum_i \frac{1}{2} \left( \frac{M}{4} \right) [\dot{e}_1(\vec{i})^2 + \dot{e}_2(\vec{i})^2 + \dot{e}_3(\vec{i})^2 + \dot{s}_x(\vec{i})^2 + \dot{s}_y(\vec{i})^2 + \dot{t}_x(\vec{i})^2 + \dot{t}_y(\vec{i})^2 + \dot{r}(\vec{i})^2].
\]

As discussed in Ahn et al. (2003), constraint equations can be found by representing the relations between symmetry modes and displacement variables in the reciprocal space. For example, by inverting the relations between \([s_x(\vec{k}), s_y(\vec{k})]\) and \([u_x(\vec{k}), u_y(\vec{k})]\), one can represent \([u_x(\vec{k}), u_y(\vec{k})]\) in terms of \([s_x(\vec{k}), s_y(\vec{k})]\), which leads to the following six constraint equations.\(^1\)

\[
\sin \frac{k_x}{2} \cos \frac{k_y}{2} s_x(\vec{k}) + \cos \frac{k_x}{2} \sin \frac{k_y}{2} s_y(\vec{k}) - \sqrt{2}i \sin \frac{k_x}{2} \sin \frac{k_y}{2} e_1(\vec{k}) = 0,
\]

\[
\cos \frac{k_x}{2} \sin \frac{k_y}{2} s_x(\vec{k}) + \sin \frac{k_x}{2} \cos \frac{k_y}{2} s_y(\vec{k}) - \sqrt{2}i \sin \frac{k_x}{2} \sin \frac{k_y}{2} e_2(\vec{k}) = 0,
\]

\[
\sin \frac{k_x}{2} \cos \frac{k_y}{2} s_x(\vec{k}) - \cos \frac{k_x}{2} \sin \frac{k_y}{2} s_y(\vec{k}) - \sqrt{2}i \sin \frac{k_x}{2} \sin \frac{k_y}{2} e_3(\vec{k}) = 0,
\]

\[
\cos \frac{k_x}{2} \sin \frac{k_y}{2} s_x(\vec{k}) - \sin \frac{k_x}{2} \cos \frac{k_y}{2} s_y(\vec{k}) + \sqrt{2}i \sin \frac{k_x}{2} \sin \frac{k_y}{2} r(\vec{k}) = 0,
\]

\(^1\)It should be noted that inverting the relation between \( s_x(\vec{k}) \) and \( s_y(\vec{k}) \) versus \( u_x(\vec{k}) \) and \( u_y(\vec{k}) \) is not possible for certain wave vectors, for example, wave vectors with \( k_x=0 \) or \( k_y=0 \). In those cases, new constraint equations should be found from the definition of the modes.
\[
\cos \frac{k_x}{2} \cos \frac{k_y}{2} s_x(\vec{k}) + \sin \frac{k_x}{2} \sin \frac{k_y}{2} t_x(\vec{k}) = 0, \tag{4.29}
\]
\[
\cos \frac{k_x}{2} \cos \frac{k_y}{2} s_y(\vec{k}) + \sin \frac{k_x}{2} \sin \frac{k_y}{2} t_y(\vec{k}) = 0. \tag{4.30}
\]

For a potential energy \( V \) represented in terms of symmetry modes, the Lagrangian is
\[
\tilde{L} = T - V + \sum_{n=1}^{6} \sum_k \lambda_{n,k} f_{n,-k}, \tag{4.31}
\]
where \( \lambda_{n,k} \) are Lagrange multipliers and \( f_{n,k} = 0 \)'s are the six compatibility equations, Equations (4.25)-(4.30). By solving the Lagrangian equations, the dynamic properties of the lattice can be analyzed.

In the next two subsections, the two applications of description of lattice dynamics using atomic-scale symmetry-modes developed in this subsection are presented.

### 4.2.3 Comparison With Continuum Description of Lattice Dynamics

In Lookman et al. (2003), continuum description of lattice dynamics has been presented in the context of ferroelastic dynamics, with the lattice kinetic energy, Equation (3.12a) in Lookman et al. (2003), represented in terms of strain modes, \( e_1 \) and \( e_3 \) (\( e_2 \) in the notation of Lookman et al. (2003)). The atomic-scale theory developed in the previous subsection is compared with the existing continuum theory. Either by using Equations (4.11) and (4.13) or by using the constraint equations, the kinetic energy in terms of \( e_1 \) and \( e_3 \) can be obtained,
\[
T = \sum_{\vec{k}} \sum_{s=1,3} \sum_{s'=1,3} \frac{1}{2} M \gamma_{ss'}(\vec{k}) \dot{e}_s(\vec{k}) \dot{e}_{s'}(-\vec{k}), \tag{4.32}
\]
where
\[
\gamma_{11}(\vec{k}) = \gamma_{33}(\vec{k}) = \frac{1 - \cos k_x \cos k_y}{\sin^2 k_x \sin^2 k_y}, \tag{4.33}
\]
\[
\gamma_{13}(\vec{k}) = \gamma_{31}(\vec{k}) = \frac{\cos k_x - \cos k_y}{\sin^2 k_x \sin^2 k_y}. \tag{4.34}
\]
By taking the long wavelength limit, one obtains the following leading order term for $\gamma_{ss'}$, 

\[ \gamma^{(0)}_{ss'}(\vec{k}) = \begin{bmatrix} k_x^2 + k_y^2 & k_y^2 - k_x^2 \\ 2k_x^2k_y^2 & 2k_x^2k_y^2 \\ k_y^2 - k_x^2 & k_x^2 + k_y^2 \\ 2k_x^2k_y^2 & 2k_x^2k_y^2 \end{bmatrix}, \] (4.35)

which is identical\(^2\) to the result in Lookman et al. (2003). It shows that the approach is a natural extension of continuum theory, and is suitable for multiscale description of lattice dynamics within a single theoretical framework. The next order correction to the above continuum results is as follows.

\[ \gamma^{(1)}_{ss'}(\vec{k}) = \begin{bmatrix} 1 + \frac{k_x^4 + k_y^4}{8k_x^2k_y^2} & \frac{k_y^4 - k_x^4}{8k_x^2k_y^2} \\ \frac{k_y^4 - k_x^4}{8k_x^2k_y^2} & 1 + \frac{k_x^4 + k_y^4}{8k_x^2k_y^2} \end{bmatrix}. \] (4.36)

Specifically, in the long wavelength limit, the definition of symmetry modes are as follows.

\[ e_1(\vec{j}) = \frac{1}{\sqrt{2}}[\nabla_x u_x(\vec{j}) + \nabla_y u_y(\vec{j})], \] (4.37)
\[ e_2(\vec{j}) = \frac{1}{\sqrt{2}}[\nabla_x u_y(\vec{j}) + \nabla_y u_x(\vec{j})], \] (4.38)
\[ e_3(\vec{j}) = \frac{1}{\sqrt{2}}[\nabla_x u_x(\vec{j}) - \nabla_y u_y(\vec{j})], \] (4.39)
\[ r(\vec{j}) = \frac{1}{\sqrt{2}}[\nabla_x u_y(\vec{j}) - \nabla_y u_x(\vec{j})], \] (4.40)
\[ s_x(\vec{j}) = \frac{1}{2}\nabla_x \nabla_x u_x(\vec{j}), \] (4.41)
\[ s_y(\vec{j}) = \frac{1}{2}\nabla_x \nabla_y u_x(\vec{j}), \] (4.42)
\[ t_x(\vec{j}) = 2u_x, \] (4.43)
\[ t_y(\vec{j}) = 2u_y, \] (4.44)

which shows that in $k \rightarrow 0$ limit,

\[ t_x, t_y \sim u, \]

\(^2\)The difference in the pre-factor with Equation (3.12a) in Lookman et al. (2003) is due to the typographical error in Lookman et al. (2003).
\[
e_1, e_2, e_3, r \sim ku, \quad (4.45)
\]
\[
s_x, s_y \sim k^2 u.
\]

It is noteworthy that even if rotation is a rigid mode, it is related to displacement in the order of \( k \), unlike translation modes, \( t_x \) and \( t_y \).

### 4.2.4 Phonon Mode Analysis in Terms of Symmetry Modes

In this subsection, the analysis of phonon modes in terms of atomic scale symmetry modes is presented. Specifically, a harmonic potential energy with a square lattice ground state (Ahn et al. 2003) is considered, as shown below.

\[
V_{sq.lat} = \sum_i \frac{1}{2} A_1 e_1(\vec{r}_i)^2 + \frac{1}{2} A_2 e_2(\vec{r}_i)^2 + \frac{1}{2} A_3 e_3(\vec{r}_i)^2 + \frac{1}{2} B [s_x(\vec{r}_i)^2 + s_y(\vec{r}_i)^2]. \quad (4.46)
\]

By solving the Lagrangian equations, Equation (4.31), the dispersion relations are found,

\[
M \omega^2 = B (1 - \cos k_x)(1 - \cos k_y)
+ \frac{1}{2} (1 - \cos k_x \cos k_y)(A_1 + A_2 + A_3)
\pm \left[ \frac{1}{4} (\cos k_x - \cos k_y)^2 (A_1 - A_2 + A_3)^2
+ \frac{1}{4} \sin^2 k_x \sin^2 k_y (A_1 + A_2 - A_3)^2 \right]^{1/2}. \quad (4.47)
\]

Furthermore, the square of normalized amplitude of each symmetry mode within phonon modes can be found. Their general expressions are shown in the second column in Table 4.1, where \( \beta_1 = 1 - \cos k_x \cos k_y, \beta_2 = -\sin k_x \sin k_y, \beta_3 = \cos k_x - \cos k_y, \beta_4 = (1 - \cos k_x)(1 - \cos k_y), \beta_5 = (1 + \cos k_x)(1 + \cos k_y), \) and \( a = (A_1 - A_2 + A_3)/(A_1 + A_2 - A_3). \) First, the mode amplitude does not depend on the short wavelength mode modulus \( B \), but depends only on the long wavelength mode moduli, \( A_1, A_2, \) and \( A_3 \), through the parameter \( a \). Comparison of general expressions for the
mode amplitudes between upper and lower branches shows that the amplitudes of the $e_1$ mode in the upper[lower] branch are identical to that of $r$ mode in the lower[upper] branch. Similar relations exist between $e_2$ and $e_3$, between $s_x$ and $s_y$, between $t_x$ and $t_y$, between $s_+$ and $s_-$, and between $t_+$ and $t_-$. Furthermore, mode amplitudes for the short wavelength modes, $s_x$, $s_y$, $s_+$, and $s_-$, at $\vec{k}$ are identical to those for the translational modes, $t_x$, $t_y$, $t_+$, and $t_-$ at $(\pi, \pi) - \vec{k}$.

For special cases of $a = 0$ (i.e., $A_1 + A_3 = A_2$), $a = 1$ (i.e., $A_2 = A_3$), and $a = \infty$ (i.e., $A_1 + A_2 = A_3$), the general expressions can be simplified, which is also shown in the Table 4.1. It is noteworthy that, if $a = 1$, or $A_2 = A_3$, the upper phonon branch includes no rotational mode, $r$, and the lower branch no area-changing mode, $e_1$, which can be explained in the following way. If the two shape changing modes, $e_2$ and $e_3$, have identical moduli, the lattice sustains isotropic phonon dispersion in the long wavelength limit, in which the lattice behaves like an isotropic continuum medium. Such medium would support longitudinal phonon mode in the upper branch and transverse phonon modes in the lower branch: the former rotationless and the latter locally area-preserving. For finite wavelengths, the phonon dispersion is not exactly isotropic, and the phonon modes are not exactly longitudinal nor transverse. However, the upper and lower branch phonon modes remain locally rotationless and area-preserving, even for finite wavelength, if the two shape changing modes have an identical modulus.

Squared mode amplitudes for the upper branches within the first Brillouin zone are plotted in Figures 4.6-4.10 for $a = 0$, 0.1, 1, 10, and $\infty$, which reveals that different regions in k-space are dominated by different modes. For all values of $a$, the phonons around the Brillouin zone center, $\vec{k} = 0$, have mostly the translational modes, $t_x$, $t_y$, or $t_+$, $t_-$, [Figures 4.6-4.10 (e),(f),(i), and (j)] consistent with Equation (4.45). In contrast, the short wavelength modes, $s_x$, $s_y$, $s_+$, and $s_-$ contribute dominantly near the corners of the first Brillouin zone [Figures 4.6-4.10 (g),(h),(k), and (l)].
upper and lower branch phonon modes at $\vec{k} = (\pi, 0)$ are longitudinal and transverse, as shown in Figures 4.11(a) and 4.11(b) respectively. Therefore, the phonon at $\vec{k} = (\pi, 0)$ in the upper branch consists of $e_1$ and $e_3$ modes, and that in the lower branch of $e_2$ and $r$ modes, which explains the large contribution of these modes near $\vec{k} = (\pi, 0)$ and, equivalently, near $\vec{k} = (0, \pi)$ [Figures 4.6-4.10(a) and (c)]. The contribution of $e_2$ mode in the upper branch and, equivalently, $e_3$ mode in the lower branch, for $a = 0, 1, 10, \infty$ [Figures 4.7-4.10(b)] is relatively weak, except near $\vec{k} = (\pm \pi/2, \pm \pi/2)$. Rotational mode $r$ in the upper branch and, equivalently, $e_1$ mode in the lower branch are very small except for $a = 0$ [Figures 4.7-4.10(d)], and, in particular, vanish for $a = 1$ as discussed above [Figure 4.8(d)]. For $a = 0$, or $A_1 + A_3 = A_2$, the two phonon modes at $\vec{k} = (\pi, 0)$ and $(0, \pi)$ shown in Figure 4.11 have the same moduli and, therefore, are degenerate, which give rise to the equal contribution of the four modes, $e_1$, $e_2$, $e_3$ and $r$ at these $k$ points, as shown in Figure 4.6(a), (b), (c), and (d). Understanding how different modes contribute different parts in the $k$-space could be useful, for example, to gain insight into materials with electron-phonon coupling, such as, manganites, phonon-mediated superconductors, and materials near structural phase transition.

4.3 Quantum Mechanical Formalism

4.3.1 One Dimensional Lattice With a Monatomic Basis

The symmetry-based atomic-scale description of lattice dynamics is further extended to the quantum mechanical formalism for the one-dimensional chain. In particular, quantum mechanical commutation relations can be found among modes and conjugate momenta. Conjugate momenta for the two modes, $P_e(i)$ and $P_t(i)$, are

$$P_e(i) = \frac{\partial L}{\partial \dot{e}(i)} = \frac{M}{2} \dot{e}(i) = \frac{1}{2\sqrt{2}} (p_{i+1} - p_i), \quad (4.48)$$

$$P_t(i) = \frac{\partial L}{\partial \dot{t}(i)} = \frac{M}{2} \dot{t}(i) = \frac{1}{2\sqrt{2}} (p_{i+1} + p_i), \quad (4.49)$$
Table 4.1 Mode Amplitudes

<table>
<thead>
<tr>
<th>Mode</th>
<th>General expression</th>
<th>$a = 0$</th>
<th>$a = 1$</th>
<th>$a = \infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a = 0$</td>
<td>$a = 1$</td>
<td>$a = \infty$</td>
</tr>
<tr>
<td>$</td>
<td>e_1</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm \frac{\beta_1^2 + a \beta_1^2}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} (\beta_1 \pm</td>
</tr>
<tr>
<td>$</td>
<td>e_2</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm \frac{\beta_1^2 - a \beta_1^2}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} (\beta_1 \pm</td>
</tr>
<tr>
<td>$</td>
<td>e_3</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm \frac{-\beta_1^2 + a \beta_1^2}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} (\beta_1 \mp</td>
</tr>
<tr>
<td>$</td>
<td>r</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm \frac{-\beta_1^2 - a \beta_1^2}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} (\beta_1 \mp</td>
</tr>
<tr>
<td>$</td>
<td>s_x</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( 1 \pm \frac{-a \beta_1}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm</td>
</tr>
<tr>
<td>$</td>
<td>s_y</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( 1 \pm \frac{a \beta_1}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm</td>
</tr>
<tr>
<td>$</td>
<td>t_x</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( 1 \pm \frac{-a \beta_1}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm</td>
</tr>
<tr>
<td>$</td>
<td>t_y</td>
<td>^2$</td>
<td>$\frac{1}{8} \left( 1 \pm \frac{a \beta_1}{\beta_1^2 + a^2 \beta_1^2} \right)$</td>
<td>$\frac{1}{8} \left( \beta_1 \pm</td>
</tr>
</tbody>
</table>

85
Figure 4.6 Squared phonon mode amplitudes for the upper branch for $a = 0$:
(a)$|e_1|^2$, (b)$|e_2|^2$, (c)$|e_3|^2$, (d)$|r|^2$, (e)$|t_x|^2$, (f)$|t_y|^2$, (g)$|s_x|^2$, (h)$|s_y|^2$, (i)$|t_+|^2$, (j)$|t_-|^2$, (k)$|s_+|^2$, (l)$|s_-|^2$. [For the lower branch, they correspond to (a)$|r|^2$, (b)$|e_3|^2$, (c)$|e_2|^2$, (d)$|e_1|^2$, (e)$|t_y|^2$, (f)$|t_x|^2$, (g)$|s_y|^2$, (h)$|s_x|^2$, (i)$|t_-|^2$, (j)$|t_+|^2$, (k)$|s_-|^2$, (l)$|s_+|^2$.]

where $p_i$ represent the momentum of the atom at the site $i$. From the usual commutation relations between momentum and displacement operators, $\hat{p}_i$ and $\hat{u}_j$, the following commutation relations between the mode and the conjugate momentum are found with the same site index $i$.

\[
[P_e(i), e(i)] = [P_t(i), t(i)] = \frac{1}{2} \hbar \delta_{i,j},
\]

\[
[P_e(i), t(i)] = [P_t(i), e(i)] = 0.
\]

Since the nearest neighbor modes share an atom, the commutation relation between them can be non-zero, as shown below.

\[
[P_e(i), t(i + 1)] = [P_t(i), t(i + 1)] = \frac{\hbar}{4i},
\]

\[
[P_e(i), e(i + 1)] = [P_t(i), e(i + 1)] = -\frac{\hbar}{4i},
\]

\[
[P_e(i), e(i - 1)] = [P_e(i), t(i - 1)] = -\frac{\hbar}{4i},
\]

\[
[P_t(i), e(i - 1)] = [P_t(i), t(i - 1)] = \frac{\hbar}{4i}.
\]

The commutation relations between the momentum and the mode defined at the plaquettes farther than the nearest neighbors vanish.
Figure 4.7 Squared phonon mode amplitudes for the upper branch for $a = 0.1$. Mode for each panel is identical to Figure 4.6.

Figure 4.8 Squared phonon mode amplitudes for the upper branch for $a = 1$. Mode for each panel is identical to Figure 4.6.

The above relations can also be established graphically. For example, $[P_e(i), t(i + 1)]$ can be found from the drawing in Figure 4.12, where $P_e(i)$ and $t(i + 1)$ are represented with arrows. The arrows are then treated as unit vectors, and it can be found that the sum of scalar products of unit vectors defined for the same atom, which multiplied by $(h/i)(1/2)^2$, leads to the commutation relation. From the graphical rule, the following relation can be understood, where $a$ and $b$ represent $e$ or $t$.

$$[P_a(i), b(i + 1)] = [P_b(i), a(i - 1)]$$  \hspace{1cm} (4.50)
Similarly, using the fact that $e$ and $t$ have even and odd point reflection symmetry respectively and the scalar product in the graphic rule is invariant under the point reflection symmetry operation, the following relation is obtained.

$$[P_e(i), t(j)] = -[P_t(i), e(j)]$$ (4.51)

Using the commutation relation in the reciprocal space for the displacement variables and their momenta, the commutation relations in the reciprocal space for modes and their conjugate momenta are obtained, $[P_e(k), b(k')]$, which vanish for $k' \neq -k$. The commutation $[\frac{1}{\hbar} P_a(k), b(-k)]$ is shown in Table 4.2.
dependent prefactors of the commutation relations reflect the fact that the modes and conjugate momenta at neighboring plaquettes are defined in terms of shared atoms.

4.3.2 Two-Dimensional Square Lattice With a Monatomic Basis

The quantum mechanical commutation relations for the two-dimensional square lattice can be found as follows. Conjugate momenta of atomic scale modes are obtained by the same method as in the one-dimensional case, and are written as

\[
P_{e_1}(i) = \frac{1}{8\sqrt{2}} \left[ -p^x_i - p^y_i + p^x_{i+10} - p^y_{i+10} \
- p^x_{i+01} + p^y_{i+01} + p^x_{i+11} + p^y_{i+11} \right],
\]

\[
P_{e_2}(i) = \frac{1}{8\sqrt{2}} \left[ -p^x_i - p^y_i - p^x_{i+10} + p^y_{i+10} \
+ p^x_{i+01} - p^y_{i+01} + p^x_{i+11} + p^y_{i+11} \right],
\]

Table 4.2 Commutation Relation in the 1D Reciprocal Space, \([P_e(k), b(k')]\)

| \(e(-k)\) | \(\frac{1}{2}(1 - \cos k)\) | \(-\frac{i}{2}\sin k\) |
| \(t(-k)\) | \(\frac{i}{2}\sin k\) | \(\frac{1}{2}(1 + \cos k)\) |
\[
P_{e_{3}}(i) = \frac{1}{8\sqrt{2}} \left[ -p_{i}^{x} + p_{i+10}^{y} + p_{i+10}^{z} + p_{i+11}^{y} + p_{i+11}^{z} - p_{i+01}^{x} - p_{i+01}^{y} + p_{i+11}^{x} - p_{i+11}^{y} \right],
\]
\[
P_{r}(i) = \frac{1}{8\sqrt{2}} \left[ p_{i}^{x} - p_{i+10}^{y} + p_{i+10}^{z} - p_{i+01}^{x} + p_{i+01}^{y} + p_{i+11}^{x} - p_{i+11}^{y} \right],
\]
\[
P_{s_{x}}(i) = \frac{1}{8} \left[ p_{i}^{x} - p_{i+10}^{y} - p_{i+01}^{x} + p_{i+11}^{y} \right],
\]
\[
P_{s_{y}}(i) = \frac{1}{8} \left[ p_{i}^{y} - p_{i+10}^{x} - p_{i+01}^{y} + p_{i+11}^{x} \right],
\]
\[
P_{t_{x}}(i) = \frac{1}{8} \left[ p_{i}^{x} + p_{i+10}^{y} + p_{i+10}^{z} + p_{i+11}^{x} + p_{i+11}^{z} \right],
\]
\[
P_{t_{y}}(i) = \frac{1}{8} \left[ p_{i}^{y} + p_{i+10}^{x} + p_{i+10}^{z} + p_{i+11}^{y} + p_{i+11}^{z} \right].
\]

From the fundamental commutation relations for displacement operators and usual momentum operators,

\[
[p_{i}^{x}, u_{j}^{y}] = [p_{i}^{y}, u_{j}^{x}] = \frac{\hbar}{i} \delta_{ij}
\]

\[
[p_{i}^{x}, u_{j}^{y}] = [p_{i}^{y}, u_{j}^{x}] = 0
\]

the commutation relations between modes and their conjugate momenta are calculated in a straightforward way. Alternatively, one can use graphical method, explained for one-dimensional chain in the previous subsection.

The above fundamental commutation relations for \(i = j\) have the form of

\[
\hat{x} \cdot \hat{x} = \hat{y} \cdot \hat{y} = 1
\]

\[
\hat{x} \cdot \hat{y} = \hat{y} \cdot \hat{x} = 0
\]

except for the factor \(\hbar/i\), where \(\hat{x}\) and \(\hat{y}\) represent unit vectors, not operators. Therefore, the commutation relation \([P_{a}(\vec{i}), b(\vec{j})]\), where \(a\) and \(b\) represent eight atomic-scale modes, can be found from the drawings of \(a\) and \(b\) modes on the square lattice.

The sum of the scalar products of the unit vectors at the sites shared by the two modes, multiplied by \((\hbar/i)(1/4)^{2}\), gives the commutation of the two operators. The multiplication factor after \(\hbar/i\) is associated with the number of atoms in the motif,
that is, 4 for the monatomic 2D square lattice and 2 for the monatomic 1D chain. For example, from Figure 4.13, \([P_{e1}(\vec{i}), e_2(\vec{i} + 11)]\) can be found as follows.

\[
[P_{e1}(\vec{i}), e_2(\vec{i} + 11)] = \frac{\hbar}{i} \cdot \left( \frac{1}{4} \right)^2 \cdot (-1) \tag{4.52}
\]

Figure 4.13 Commutation relation of \(P_{e1}(i)\) and \(e_2(i + 11)\).

Graphical method is also useful to find symmetry related properties of the commutation relations. From the orthogonality of modes, the commutation relation between a conjugate momentum and a mode at the same motif vanishes except for the case that the two modes are identical, as follows.

\[
[P_a(i), b(i)] = \frac{1}{4} \frac{\hbar}{i} \delta_{ab}. \tag{4.53}
\]

Also, from the symmetry under point inversion, the following equations are obtained, where \(even\) and \(odd\) represent the even modes, namely, \(e_1, e_2, e_3, r\), and the odd modes, namely, \(s_x, s_y, t_x, t_y\), respectively.

\[
[P_{even}(i), even'(j)] = [P_{even'}(i), even(j)], \tag{4.54}
\]
\[
[P_{even}(i), odd(j)] = -[P_{odd}(i), even(j)], \tag{4.55}
\]
\[
[P_{odd}(i), odd'(j)] = [P_{odd'}(i), odd(j)]. \tag{4.56}
\]

The commutation relations in the reciprocal space are calculated from the usual reciprocal space commutation relations for displacement variables. The commutation relations in modes in the reciprocal space are given in Table 4.3.
Table 4.3 Commutation Relation in the 2D Reciprocal Space, $[\frac{\hbar}{i} P_a(k), b(-k)]$

<table>
<thead>
<tr>
<th>$a$</th>
<th>$\frac{\hbar}{i} P_{x1}(k)$</th>
<th>$\frac{\hbar}{i} P_{x2}(k)$</th>
<th>$\frac{\hbar}{i} P_{x3}(k)$</th>
<th>$\frac{\hbar}{i} P_t(k)$</th>
<th>$\frac{\hbar}{i} P_{xx}(k)$</th>
<th>$\frac{\hbar}{i} P_{xy}(k)$</th>
<th>$\frac{\hbar}{i} P_{lx}(k)$</th>
<th>$\frac{\hbar}{i} P_{ly}(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_1(-k)$</td>
<td>$\frac{1-C_{kx} C_{ky}}{4}$</td>
<td>$\frac{S_{kx} S_{ky}}{4}$</td>
<td>$-C_{kx} + C_{ky}$</td>
<td>0</td>
<td>$\frac{i(1-C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
<td>$\frac{i(1-C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
</tr>
<tr>
<td>$e_2(-k)$</td>
<td>$\frac{S_{kx} S_{ky}}{4}$</td>
<td>$\frac{1-C_{kx} C_{ky}}{4}$</td>
<td>0</td>
<td>$-C_{kx} + C_{ky}$</td>
<td>$\frac{i(1-C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
<td>$\frac{i(1-C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
</tr>
<tr>
<td>$e_3(-k)$</td>
<td>$\frac{-C_{kx} + C_{ky}}{4}$</td>
<td>0</td>
<td>$\frac{1-C_{kx} C_{ky}}{4}$</td>
<td>$-S_{kx} S_{ky}$</td>
<td>$\frac{i(1-C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
<td>$\frac{i(1-C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
</tr>
<tr>
<td>$r(-k)$</td>
<td>0</td>
<td>$\frac{-C_{kx} + C_{ky}}{4}$</td>
<td>$-S_{kx} S_{ky}$</td>
<td>$\frac{1-C_{kx} C_{ky}}{4}$</td>
<td>$\frac{i(1-C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
<td>$\frac{i(1-C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{ky}) S_{kx}}{4\sqrt{2}}$</td>
<td>$\frac{i(1+C_{kx}) S_{ky}}{4\sqrt{2}}$</td>
</tr>
</tbody>
</table>

$C_{kx}, C_{ky}, S_{kx},$ and $S_{ky}$ represent $\cos k_x, \cos k_y, \sin k_x,$ and $\sin k_y,$ respectively.
4.4 Conclusions

In this chapter, the mode-based atomic-scale description of the lattice dynamics is presented in detail. It is found that not only the potential energy but also the kinetic energy can be described in terms of the atomic-scale modes, for which the inclusion of the rigid modes is essential. Further, the atomic-scale mode-based approach is demonstrated for the dynamics of the one-dimensional chain and two-dimensional square lattice with a mono-atomic basis. By using the constraint equations, the modified Lagrangian equations are obtained in terms of atomic-scale modes only, without explicit use of the displacement variables. This approach to quantum mechanics is then extended, and the conjugate momenta and the commutation relations in real and reciprocal space are obtained. This approach becomes useful in describing systems with strong anharmonicity.
APPENDIX

4.A 2D Phonon Spectrum of the Uniform Phase

4.A.1 Potential Energy in 2D Lattice

Consider six symmetry modes, namely $e_1(\vec{j})$, $e_2(\vec{j})$, $e_3(\vec{j})$, $s_+(\vec{j})$, $s_-(\vec{j})$ and $r(\vec{j})$. Every mode defined by four atoms, which in turn defined by two coordinate components $u_x(\vec{j})$ and $u_y(\vec{j})$. Remaining two symmetry modes of translation have no direct relevance in this work. For example, mode $e_1(\vec{j})$ is defined as

$$e_1(\vec{j}) = \frac{1}{2\sqrt{2}} \left[ -u_x(\vec{j}) + u_x(\vec{j} + 10) - u_x(\vec{j} + 01) + u_x(\vec{j} + 11) + u_y(\vec{j}) - u_y(\vec{j} + 10) + u_y(\vec{j} + 01) + u_y(\vec{j} + 11) \right],$$

where $\vec{j}$ is the position of every atom in the desired domain. For simplicity of notation, the reference to $\vec{j}$ is dropped with every symmetry mode.

The goal is to derive a general mathematical expression of two-dimensional phonon spectrum for a lattice with rectangular unit base. To accomplish this, start with the shape of a square unit cell. With idealized two-dimensional square lattice, consider potential expression of the following form

$$V_{sq} = \sum_j \left[ \frac{A_1}{2} e_1^2 + \frac{A_2}{2} e_2^2 + \frac{A_3}{2} e_3^2 + \frac{F_3}{4} e_3^4 + \frac{A_3}{2} (s_+^2 + s_-^2) + C_{12} e_1^2 e_2^2 + C_{13} e_1 e_3^2 + C_{14} e_1 (s_+^2 + s_-^2) + C_{24} e_2 (s_+^2 - s_-^2) + C_{34} e_3 s_+ s_- + C_{23} r e_2 e_3 r + \frac{F_{3r}}{2} e_3^2 r^2 \right], \quad (4.57)$$

with selection of constants as

$$A_1, A_2, F_3, F_{3r} > 0 \quad \text{and} \quad A_3, C_{12}, C_{13}, C_{14}, C_{24}, C_{34}, C_{3s} < 0.$$

Various denominator constants selected to simplify further form of algebraic expressions. The choice of mixed modes comprising in third order with $C$-type pre-factors is due to invariance of symmetry operations over six modes used. There are eight possible symmetry group operations for a square unit cell, which are reflection with
respect to horizontal, vertical and both diagonal bisectors passing through center of
the cell, and rotations around 0, $\pi/2$, $\pi$, and $3\pi/2$ with cell center being the pivot
point. Note that the most obvious and allowed third order term $e_1^3$ is omitted from
Equation (4.57) to simplify the point of expansion that is further introduced. There
are two forth order terms, from which $F_3 e_3^4$ is essential to introduce two non-zero mini-
mums in the expansion for $e_3$ mode, and $F_3r^2 e_3^2 r^2$ to reduce degeneracy of eigenvalues
obtained later on.

To arrive to a rectangular type lattice, point of expansion must be chosen
with consideration of modes $e_1$ and $e_3$, whereas other resulting geometries can be
considered in analogous fashion.

Consider point of expansion $p(e_1, e_2, e_3, s_+, s_-, r) = (\tilde{e}_1, 0, \tilde{e}_3, 0, 0) = p_0$. To
establish values for $\tilde{e}_1$ and $\tilde{e}_3$, set $\nabla V_{sq} = 0.$

$$\frac{\partial V}{\partial e_1} = A_1 e_1 + C_{12} e_2^2 + C_{13} e_3^2 + C_{1s}(s_+^2 + s_-^2) \quad (4.58)$$
$$\frac{\partial V}{\partial e_2} = A_2 e_2 + 2C_{12} e_1 e_2 + C_{2s}(s_+^2 - s_-^2) + C_{2r} e_3 r \quad (4.59)$$
$$\frac{\partial V}{\partial e_3} = A_3 e_3 + F_3 e_3^3 + 2C_{13} e_1 e_3 + C_{3s} s_+ s_- + C_{23r} e_2 r + F_3 e_3 r^2 \quad (4.60)$$
$$\frac{\partial V}{\partial s_+} = A_s s_+ + 2C_{1s} e_1 s_+ + 2C_{2s} e_2 s_+ + C_{3s} e_3 s_- \quad (4.61)$$
$$\frac{\partial V}{\partial s_-} = A_s s_- + 2C_{1s} e_1 s_- - 2C_{2s} e_2 s_- + C_{3s} e_3 s_+ \quad (4.62)$$
$$\frac{\partial V}{\partial r} = C_{23r} e_2 e_3 + F_3 e_3^2 r \quad (4.63)$$

From Equations (4.58) and (4.60) it can be found that

$$A_1 \tilde{e}_1 = -C_{13} \tilde{e}_3^2 \quad \text{and} \quad A_3 + F_3 \tilde{e}_3^2 = -2C_{13} \tilde{e}_1$$

and therefore

$$\tilde{e}_1 = \frac{A_3 C_{13}}{A_1 F_3 - 2C_{13}^2} \quad (4.64)$$
$$\tilde{e}_3 = \pm \sqrt{\frac{-A_1 A_3}{A_1 F_3 - 2C_{13}^2}} = \pm \sqrt{\frac{-A_3}{F_3 - \frac{2C_{13}^2}{A_1}}} \quad (4.65)$$
Since \( A_3 < 0 \), a numerical constraint on \( C_{13} \) is then obtained, eg.

\[
|C_{13}| < \sqrt{\frac{A_1 F_3}{2}}.
\]  

(4.66)

Now consider non-zero second order derivative terms

\[
\left. \frac{\partial^2 V}{\partial e_1^2} \right|_{p_0} = A_1, \\
\left. \frac{\partial^2 V}{\partial e_2^2} \right|_{p_0} = A_2 + 2C_{12} \tilde{e}_1, \\
\left. \frac{\partial^2 V}{\partial e_3^2} \right|_{p_0} = A_3 + 3F_3 \tilde{e}_3^2 + 2C_{13} \tilde{e}_1, \\
\left. \frac{\partial^2 V}{\partial s_+^2} \right|_{p_0} = \left. \frac{\partial^2 V}{\partial s_-^2} \right|_{p_0} = A_s + 2C_{1s} \tilde{e}_1, \\
\left. \frac{\partial^2 V}{\partial r^2} \right|_{p_0} = F_3 r \tilde{e}_3^2, \\
\left. \frac{\partial^2 V}{\partial e_1 \partial e_3} \right|_{p_0} = 2C_{13} \tilde{e}_3, \\
\left. \frac{\partial^2 V}{\partial s_+ \partial s_-} \right|_{p_0} = C_{3s} \tilde{e}_3, \\
\left. \frac{\partial^2 V}{\partial e_2 \partial r} \right|_{p_0} = C_{23r} \tilde{e}_3.
\]

(4.67) to (4.79)

This allows us to form the second order expansion

\[
V_{sq} \approx \sum_j \left[V_0 + \frac{1}{2} \left[ A_1 (e_1 - \tilde{e}_1)^2 + (A_2 + 2C_{12} \tilde{e}_1) e_2^2 \\
+ (A_3 + 3F_3 \tilde{e}_3^2 + 2C_{13} \tilde{e}_1)(e_3 - \tilde{e}_3)^2 + (A_s + 2C_{1s} \tilde{e}_1)(s_+^2 + s_-^2) \\
+ (F_3 e_3^2) r^2 + 2(2C_{13} \tilde{e}_3)(e_1 - \tilde{e}_1)(e_3 - \tilde{e}_3) + 2(C_{3s} \tilde{e}_3) s_+ s_- \\
+ 2(C_{23r} \tilde{e}_3) e_2 r \right] \right]
\]

(4.75)

To further simplify the notation, one must re-normalize the constant terms

\[
\tilde{A}_1 = A_1, \quad \tilde{A}_2 = A_2 + 2C_{12} \tilde{e}_1, \\
\tilde{A}_3 = A_3 + 3F_3 \tilde{e}_3^2 + 2C_{13} \tilde{e}_1, \\
\tilde{A}_s = A_s + 2C_{1s} \tilde{e}_1, \\
\tilde{A}_r = F_3 \tilde{e}_3^2.
\]

(4.76) to (4.79)
\[ \hat{C}_{13} = 2C_{13} \bar{e}_3, \quad (4.80) \]
\[ \hat{C}_s = C_{3s} \bar{e}_3, \quad (4.81) \]
\[ \hat{C}_{2r} = C_{23r} \bar{e}_3, \quad (4.82) \]

which brings us to expression
\[ V_{rec} = \sum_j \left[ \frac{\hat{A}_1}{2} (e_1 - \bar{e}_1)^2 + \frac{\hat{A}_2}{2} e_2^2 + \frac{\hat{A}_3}{2} (e_3 - \bar{e}_3)^2 + \frac{\hat{A}_s}{2} (s_+^2 + s_-^2) + \frac{\hat{A}_r}{2} r^2 \right. \]
\[ + \hat{C}_{13} (e_1 - \bar{e}_1)(e_3 - \bar{e}_3) + \hat{C}_s s_+ s_- + \hat{C}_{2r} e_2 r \] \[ \left. + \hat{C}_{13} (e_1 - \bar{e}_1)(e_3 - \bar{e}_3) + \hat{C}_s s_+ s_- + \hat{C}_{2r} e_2 r \right] \quad (4.83) \]

that is suitable to describe vibrational dynamics of rectangular base lattice.

4.A.2 Formalizing Extraction of Pure Vibrational Modes

In order to construct suitable expressions for evaluation of the Lagrange equation, one must extract non-vibrational equilibrium part of the expansion, namely \( \bar{e}_1 \) and \( \bar{e}_3 \). Also, analytically it is desirable since this equilibrium contribution is non-Fourier transformable. The outline of bases is introduced in (Ahn)\(^3\). Directional displacements can be written as follows

\[ u_x(\vec{i}) = u_{x,eq}(\vec{i}) + \delta u_x(\vec{i}), \quad \text{and} \quad u_y(\vec{i}) = u_{y,eq}(\vec{i}) + \delta u_y(\vec{i}) \]

where \( \delta \) terms represent the vibrational term. Hence, the procedure follows

\[ \frac{\varepsilon_{xx}^0 + \varepsilon_{yy}^0}{\sqrt{2}} = \bar{e}_1, \quad \frac{\varepsilon_{xy}^0}{\sqrt{2}} = 0, \quad \frac{\varepsilon_{xx}^0 - \varepsilon_{yy}^0}{\sqrt{2}} = \bar{e}_3, \]

which implies

\[ \varepsilon_{xx}^0 = \frac{1}{\sqrt{2}}(\bar{e}_1 + \bar{e}_3), \quad \varepsilon_{yy}^0 = \frac{1}{\sqrt{2}}(\bar{e}_1 - \bar{e}_3), \quad \varepsilon_{xy}^0 = 0. \]

Since

\[ u_{x,eq}(\vec{i}) = \varepsilon_{xx}^0 i_x + \varepsilon_{xy}^0 i_y = \frac{1}{\sqrt{2}}(\bar{e}_1 + \bar{e}_3) i_x \]
\[ u_{y,eq}(\vec{i}) = \varepsilon_{xy}^0 i_x + \varepsilon_{yy}^0 i_y = \frac{1}{\sqrt{2}}(\bar{e}_1 - \bar{e}_3) i_y \]

\(^3\)K. H. Ahn, T. Lookman and A. R. Bishop. Model for strain-induced metal-insulator phase coexistence in perovskite manganites
it can be readily show that

\[ e_1(\vec{i}) = \tilde{e}_1 + \delta e_1, \quad \text{and} \quad e_3(\vec{i}) = \tilde{e}_3 + \delta e_3 \]

and therefore (4.83) is re-written as

\[ V_{rec} = \sum_j V_{rec}(\vec{j}) \]

\[ = \sum_j \left[ \frac{\hat{A}_1}{2} \delta e_1^2 + \frac{\hat{A}_2}{2} e_2^2 + \frac{\hat{A}_3}{2} \delta e_3^2 + \frac{\hat{A}_s}{2} (s_+^2 + s_-^2) + \frac{\hat{A}_r}{2} r^2 + \tilde{C}_{13} \delta e_1 \delta e_3 + \tilde{C}_s s_+ s_- + \tilde{C}_2 e_2 r \right]. \quad (4.85) \]

which is a somewhat an obvious result. From this point on, the \( \delta \) prefix will be dropped for simplicity of notation, otherwise all symmetry modes should be prefixed with \( \delta \) for rigor.

**4.4.3 Lagrange Equation**

With kinetic energy term defined as

\[ T = \sum_j \frac{M}{2} \left[ \dot{u_x}(\vec{j})^2 + \dot{u_y}(\vec{j})^2 \right] \]

where \( M \) being a unit of mass and (4.85) being included in \( L = T - V_{rec} \), one can write Lagrange equation of motion

\[ \frac{d}{dt} \frac{\partial L}{\partial \dot{u}_{x,y}(\vec{i})} - \frac{\partial L}{\partial u_{x,y}(\vec{i})} = 0, \quad (4.86) \]

with indication that derivatives in \( u_x \) and \( u_y \) are taken independently from each other. With

\[ \frac{\partial}{\partial \dot{u}_x(\vec{i})} \left( \sum_j \frac{M}{2} \dot{u}_x(\vec{j})^2 \right) = \sum_j M \dot{u}_x(\vec{j}) \delta_{i,j} = M \ddot{u}_x(\vec{i}) \]

where \( \delta_{i,j} \) is Kronecker delta, while (4.86) can be re-written as

\[ -M \ddot{u}_{x,y}(\vec{i}) = \frac{\partial V_{rec}(\vec{j})}{\partial u_{x,y}(\vec{i})} \]

\[ \quad (4.87) \]
where \( \vec{j} \) remains a reference to every atom inside of summation, and \( \vec{i} \) being a reference to every atom regardless of summation. This leads to us to relation between \( \vec{i} \) and \( \vec{j} \), e.g.

\[
\vec{j} \in \vec{i} + \{11, 01, 11, 00, 10, 11, 01, 11\}
\]

**Figure 4.14** Figure (a) shows labeling of atoms with respect to \( \vec{i} \), whereas (b) shows references to a symmetry group containing atom \( \vec{i} \) and its identifying (lower left) atom, both pointed to by curvy line.

The goal is to evaluate the derivative (4.87) of \( V_{rec} \) on the right side. Define an arbitrary symmetry mode \( a(\vec{i}) \) as

\[
a(\vec{i}) = \xi_a \left[ s_{1a}^x u_{00}^x + s_{2a}^x u_{10}^x + s_{3a}^x u_{01}^x + s_{4a}^x u_{11}^x \\
+ s_{1a}^y u_{00}^y + s_{2a}^y u_{10}^y + s_{3a}^y u_{01}^y + s_{4a}^y u_{11}^y \right]
\]

(4.88)

with \( s_{ka}^{x,y} \in \{-1, +1\} \). For example, for symmetry mode \( e_1(\vec{i}) \), \( \xi_{e_1} = \frac{1}{2\sqrt{2}} \) and \( s_{e1} = (-1, +1 - 1, +1, -1, -1, +1, +1) \). Now consider most general second order potential term with an arbitrary constant \( A \)

\[
V_{ab} = \sum_{\vec{j}} A a(\vec{j}) b(\vec{j})
\]

(4.89)
so that with the help of Figure 4.14 (a) and (b)

\[
\frac{\partial V_{ab}}{\partial u_{x,y}(\vec{i})} = \frac{\partial}{\partial u_{x,y}(\vec{i})} \sum_{\vec{j}} Aa(\vec{j})b(\vec{j})
\]

(4.90)

\[
= A \left[ a(\vec{j}) \frac{\partial b(\vec{j})}{\partial u_{x,y}(\vec{i})} + b(\vec{j}) \frac{\partial a(\vec{j})}{\partial u_{x,y}(\vec{i})} \right] \quad \text{for} \quad \vec{j} \in \{10, 00, 11, 01\}
\]

(4.91)

\[
= A \left[ a(\vec{i}) \xi_b s_{2b} x_{1b} + b(\vec{i}) \xi_a s_{1a} x_{1a} + a(\vec{i}) \xi_b s_{2b} x_{1b} + b(\vec{i}) \xi_a s_{1a} x_{1a} \right] + A \xi_a \left[ s_{2a} x_{1a} b(\vec{i} + 10) + s_{1a} x_{1a} b(\vec{i} + 11) + s_{2a} x_{1a} b(\vec{i} + 01) \right]
\]

(4.92)

\[
\sum_{\vec{j} \in \{10, 00, 11, 01\}} Aa(\vec{j})b(\vec{j}) = A \xi_b \left[ s_{2b} x_{1b} a(\vec{i} + 10) + s_{1b} x_{1b} a(\vec{i}) + s_{2b} x_{1b} a(\vec{i} + 11) + s_{1b} x_{1b} a(\vec{i} + 01) \right] + A \xi_a \left[ s_{2a} x_{1a} b(\vec{i} + 10) + s_{1a} x_{1a} b(\vec{i} + 11) + s_{2a} x_{1a} b(\vec{i} + 01) \right]
\]

(4.93)

Since (4.93) consist of two parts mutually symmetrical with respect to a and b, consider taking a closer look at one part. From this point on, the direct use of actual mode is no longer required, since underlying u_{x,y} notation is used, which in turn has a group of nine neighboring atoms as shown in Figure 4.14(a). Now first part of (4.93) can be re-written as

\[
\sum_{\vec{j} \in \{10, 00, 11, 01\}} Aa(\vec{j})b(\vec{j}) = A \xi_b \left[ s_{2b} x_{1b} a(\vec{i} + 10) + s_{1b} x_{1b} a(\vec{i}) + s_{2b} x_{1b} a(\vec{i} + 11) + s_{1b} x_{1b} a(\vec{i} + 01) \right] + A \xi_a \left[ s_{2a} x_{1a} b(\vec{i} + 10) + s_{1a} x_{1a} b(\vec{i} + 11) + s_{2a} x_{1a} b(\vec{i} + 01) \right]
\]
where \( u^x_{10} = u^x(\bar{i} + 10) \), for example. Lets denote

\[
\mathbf{u}_x(\bar{i}) = (u^x_{11}, u^x_{01}, u^x_{11}, u^x_{10}, u^x_{00}, u^x_{11}, u^x_{01}, u^x_{11})
\]

\[
\mathbf{u}_y(\bar{i}) = (u^y_{11}, u^y_{01}, u^y_{11}, u^y_{10}, u^y_{00}, u^y_{11}, u^y_{01}, u^y_{11})
\]

so that using inner product, one can compactly write

\[
\sum_j Aa(\bar{j}) \frac{\partial \mathbf{b}(\bar{j})}{\partial \mathbf{u}_x(\bar{i})} = A\zeta_a \zeta_b (s_{1,ab}, s_{2,ab}) \begin{pmatrix} \mathbf{u}_x \\ \mathbf{u}_y \end{pmatrix} \quad (4.96)
\]

\[
\sum_j Aa(\bar{j}) \frac{\partial \mathbf{b}(\bar{j})}{\partial \mathbf{u}_y(\bar{i})} = A\zeta_a \zeta_b (s_{3,ab}, s_{4,ab}) \begin{pmatrix} \mathbf{u}_x \\ \mathbf{u}_y \end{pmatrix} \quad (4.97)
\]

where

\[
s_{1,ab} = \begin{pmatrix} s^x_{4b} s^x_{1a} + s^x_{4b} s^x_{2a} + s^x_{3b} s^x_{1a} + s^x_{3b} s^x_{2a}, \\
 s^x_{2b} s^x_{1a} + s^x_{4b} s^x_{3a}, s^x_{2b} s^x_{2a} + s^x_{16} s^x_{1a} + s^x_{4b} s^x_{4a} + s^x_{3b} s^x_{3a}, s^x_{1b} s^x_{2a} + s^x_{3b} s^x_{4a}, \\
 s^x_{2b} s^x_{3a}, s^x_{2b} s^x_{4a} + s^x_{16} s^x_{3a}, s^x_{1b} s^x_{4a} \end{pmatrix}
\]

\[
s_{2,ab} = \begin{pmatrix} s^x_{4b} s^y_{1a} + s^x_{4b} s^y_{2a} + s^y_{3b} s^y_{1a} + s^y_{3b} s^y_{2a}, \\
 s^y_{2b} s^y_{1a} + s^y_{4b} s^y_{3a}, s^y_{2b} s^y_{2a} + s^y_{16} s^y_{1a} + s^y_{4b} s^y_{4a} + s^y_{3b} s^y_{3a}, s^y_{1b} s^y_{2a} + s^y_{3b} s^y_{4a}, \\
 s^y_{2b} s^y_{3a}, s^y_{2b} s^y_{4a} + s^y_{16} s^y_{3a}, s^y_{1b} s^y_{4a} \end{pmatrix}
\]

\[
s_{3,ab} = \begin{pmatrix} s^y_{4b} s^x_{1a} + s^y_{4b} s^x_{2a} + s^x_{3b} s^x_{1a} + s^x_{3b} s^x_{2a}, \\
 s^x_{2b} s^x_{1a} + s^x_{4b} s^x_{3a}, s^x_{2b} s^x_{2a} + s^x_{16} s^x_{1a} + s^x_{4b} s^x_{4a} + s^y_{3b} s^y_{3a}, s^x_{1b} s^x_{2a} + s^y_{3b} s^y_{4a}, \\
 s^y_{2b} s^y_{3a}, s^y_{2b} s^y_{4a} + s^y_{16} s^y_{3a}, s^y_{1b} s^y_{4a} \end{pmatrix}
\]
\( s_{4,ab} = (s^y_{4b}s^y_{1a}, s^y_{4b}s^y_{2a}, s^y_{4b}s^y_{3a}, s^y_{4b}s^y_{2a}, s^y_{3b}s^y_{1a}, s^y_{3b}s^y_{2a}) \\
= s^y_{2b}s^y_{1a} + s^y_{4b}s^y_{3a}, s^y_{2b}s^y_{2a} + s^y_{4b}s^y_{4a} + s^y_{3b}s^y_{3a}, s^y_{1b}s^y_{1a} + s^y_{4b}s^y_{4a}, s^y_{2b}s^y_{3a}, s^y_{2b}s^y_{4a} + s^y_{3b}s^y_{3a}, s^y_{2b}s^y_{4a}) \\
= s^y_{2b}s^y_{3a}, s^y_{2b}s^y_{4a} + s^y_{3b}s^y_{3a}, s^y_{2b}s^y_{4a}) \\
\)

Note that for \( b = a \), which implies a square term in the expression for potential, the middle elements of \( s_1 \) and \( s_4 \) automatically equal to largest possible integer 4 that corresponds to the center atom at \( \vec{i} \). This can be observed in the table below.

To summarize this chapter, let’s rewrite

\[
\left( \frac{\partial}{\partial u_x(\vec{i})} \right) \sum_j Aa(j)b(j) = A\xi_{ab}\xi_{ba}\left( \begin{array}{c} s_{1,ab} \\ s_{3,ab} \\ s_{4,ab} \end{array} \right) \left( \begin{array}{c} u_x \\ u_y \end{array} \right) \\
+ \left( \begin{array}{c} s_{1,ba} \\ s_{3,ba} \\ s_{4,ba} \end{array} \right) \left( \begin{array}{c} u_x \\ u_y \end{array} \right)
\]

(4.98)

where \( s_{n,ab} \neq s_{n,ba} \), or less generally for \( b(\vec{i}) = a(\vec{i}) \)

\[
\left( \frac{\partial}{\partial u_x(\vec{i})} \right) \sum_j Aa(j)^2 = 2A\xi^2\left( \begin{array}{c} s_{1,aa} \\ s_{3,aa} \\ s_{4,aa} \end{array} \right) \left( \begin{array}{c} u_x \\ u_y \end{array} \right)
\]

(4.99)

where upper matrix row corresponds to derivative in \( u_x \), while lower corresponds to derivative in \( u_y \).

Also, for all the symmetry modes of interest

\( \xi_{e_1} = \xi_{e_2} = \xi_{e_3} = \xi_{s_+} = \xi_{s_-} = \xi_v = \frac{1}{2\sqrt{2}} \).

4.A.4 Matrix Elements

From previously derived results summarized in (4.98) and (4.99), quantities for all \( s \) values relevant to Equation (4.87) can be calculated. These quantities appear in the following table
To interpret this table of coefficients, recall

\[ u_x(t) = (u^{x}_{11}, u^{x}_{01}, u^{x}_{11}, u^{x}_{10}, u^{x}_{00}, u^{x}_{11}, u^{x}_{01}, u^{x}_{11}) = e^{i\omega t} e^{-i(\vec{k} \cdot \vec{r})} U_{0x} \cdot \vec{v}(\vec{k}) \]

\[ u_y = (u^{y}_{11}, u^{y}_{01}, u^{y}_{11}, u^{y}_{10}, u^{y}_{00}, u^{y}_{11}, u^{y}_{01}, u^{y}_{11}) = e^{i\omega t} e^{-i(\vec{k} \cdot \vec{r})} U_{0y} \cdot \vec{v}(\vec{k}) \]
where $U_{0x}$ and $U_{0y}$ are diagonal matrices with corresponding initial displacements along the diagonal, and

$$\mathbf{v}(\vec{k}) = \left( e^{i(k_x + k_y)}, e^{ik_y}, e^{-i(k_x + k_y)}, e^{ik_x}, e^{-ik_x}, e^{i(k_x + k_y)}, e^{-ik_y}, e^{-i(k_x + k_y)} \right)$$

As an example consider a case:

$$\mathbf{s}_{1,e_{1}e_{1}} = \begin{pmatrix} -1 & 2 & -1 & -2 & 4 & -2 & 1 & 2 & -1 \end{pmatrix} \Rightarrow \mathbf{s}_{1,e_{1}e_{1}} \cdot \mathbf{v}$$

$$\mathbf{s}_{1,e_{1}e_{1}} \cdot \mathbf{v} = -e^{i(k_x + k_y)} + 2e^{ik_y} - e^{i(-k_x + k_y)} - 2e^{-ik_x} + 4 - 2e^{-ik_x} - e^{-i(k_x + k_y)} + 2e^{-ik_y} - e^{-i(k_x + k_y)}$$

$$= -(e^{ik_x} - 2 + e^{-ik_x})(e^{ik_y} + 2 + e^{-ik_y})$$

$$= 4(1 - \cos k_x)(1 + \cos k_y).$$

Total of four unique pattern-cases (using intermediate roman numeral notation) can be identified, down to ±:

$$\mathbf{I}: \begin{pmatrix} -1 & 2 & -1 & -2 & 4 & -2 & 1 & 2 & -1 \end{pmatrix} \Rightarrow 4(1 - \cos k_x)(1 + \cos k_y) \quad (4.100)$$

$$\mathbf{II}: \begin{pmatrix} -1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & -1 \end{pmatrix} \Rightarrow 4 \sin k_x \sin k_y \quad (4.101)$$

$$\mathbf{III}: \begin{pmatrix} -1 & -2 & -1 & 2 & 4 & 2 & -1 & -2 & -1 \end{pmatrix} \Rightarrow 4(1 + \cos k_x)(1 - \cos k_y) \quad (4.102)$$

$$\mathbf{IV}: \begin{pmatrix} 1 & -2 & 1 & -2 & 4 & -2 & 1 & -2 & 1 \end{pmatrix} \Rightarrow 4(1 - \cos k_x)(1 - \cos k_y) \quad (4.103)$$

$$\frac{\partial e_{1}^2}{\partial u_{x,y}} = \frac{2}{(2\sqrt{2})^2} \begin{pmatrix} \mathbf{I} & \mathbf{II} \\ \mathbf{II} & \mathbf{III} \end{pmatrix} = \frac{1}{4} \begin{pmatrix} \mathbf{I} & \mathbf{II} \\ \mathbf{II} & \mathbf{III} \end{pmatrix} \quad (4.104)$$

$$\frac{\partial e_{2}^2}{\partial u_{x,y}} = \frac{2}{(2\sqrt{2})^2} \begin{pmatrix} \mathbf{III} & \mathbf{II} \\ \mathbf{II} & \mathbf{I} \end{pmatrix} = \frac{1}{4} \begin{pmatrix} \mathbf{III} & \mathbf{II} \\ \mathbf{II} & \mathbf{I} \end{pmatrix} \quad (4.105)$$

$$\frac{\partial e_{3}^2}{\partial u_{x,y}} = \frac{2}{(2\sqrt{2})^2} \begin{pmatrix} \mathbf{I} & -\mathbf{II} \\ -\mathbf{II} & \mathbf{III} \end{pmatrix} = \frac{1}{4} \begin{pmatrix} \mathbf{I} & -\mathbf{II} \\ -\mathbf{II} & \mathbf{III} \end{pmatrix} \quad (4.106)$$

$$\frac{\partial (s_{1}^2 + s_{2}^2)}{\partial u_{x,y}} = \frac{2}{(2\sqrt{2})^2} \begin{pmatrix} \mathbf{IV} & \mathbf{IV} \\ \mathbf{IV} & \mathbf{IV} \end{pmatrix} + \frac{2}{(2\sqrt{2})^2} \begin{pmatrix} -\mathbf{IV} & -\mathbf{IV} \\ -\mathbf{IV} & \mathbf{IV} \end{pmatrix}$$
\[
\frac{\partial^2 v}{\partial u_{x,y}} = \frac{2}{(2\sqrt{2})^2} \begin{pmatrix}
\III & \II \\
-\II & \I
\end{pmatrix} = \frac{1}{4} \begin{pmatrix}
\III & \II \\
-\II & \I
\end{pmatrix}
\]

(4.108)

\[
\frac{\partial (e_1 e_3)}{\partial u_{x,y}} = \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
\I & \II \\
-\II & -\III
\end{pmatrix} + \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
\I & -\II \\
II & -\III
\end{pmatrix}
\]

(4.109)

\[
\frac{\partial (s_+ s_-)}{\partial u_{x,y}} = \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
\IV & \IV \\
-\IV & -\IV
\end{pmatrix} + \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
\IV & -\IV \\
IV & -\IV
\end{pmatrix}
\]

(4.110)

\[
\frac{\partial (r e_2)}{\partial u_{x,y}} = \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
-\III & \II \\
-\II & \I
\end{pmatrix} + \frac{1}{(2\sqrt{2})^2} \begin{pmatrix}
-\III & -\II \\
II & \I
\end{pmatrix}
\]

(4.111)

Now with corresponding normalized coefficients, the full expression for potential term of Lagrange Equation can be written as

\[
\frac{\partial V_{rec}}{\partial u_{x,y}} = \frac{\tilde{A}_1}{8} \begin{pmatrix}
\I & \II \\
II & \III
\end{pmatrix} + \frac{\tilde{A}_2}{8} \begin{pmatrix}
\III & \II \\
II & \I
\end{pmatrix} + \frac{\tilde{A}_3}{8} \begin{pmatrix}
\I & -\II \\
-\II & \III
\end{pmatrix}
\]

\[
+ \frac{\tilde{A}_s}{4} \begin{pmatrix}
\IV & 0 \\
0 & \IV
\end{pmatrix} + \frac{\tilde{A}_r}{8} \begin{pmatrix}
\III & -\II \\
-\II & \I
\end{pmatrix} + \frac{\tilde{C}_{13}}{4} \begin{pmatrix}
\I & 0 \\
0 & -\III
\end{pmatrix}
\]

\[
+ \frac{\tilde{C}_s}{4} \begin{pmatrix}
\IV & 0 \\
0 & -\IV
\end{pmatrix} + \frac{\tilde{C}_{2r}}{4} \begin{pmatrix}
-\III & 0 \\
0 & \I
\end{pmatrix}
\]

(4.112)

\[
= \begin{pmatrix}
D_{xx}(\tilde{k}) & D_{xy}(\tilde{k}) \\
D_{yx}(\tilde{k}) & D_{yy}(\tilde{k})
\end{pmatrix}
\]

(4.113)

with individual matrix elements written as

\[
D_{xx}(\tilde{k}) = \frac{1}{8} \left[ (\tilde{A}_1 + \tilde{A}_3 + 2\tilde{C}_{13}) \I + (\tilde{A}_2 + \tilde{A}_r - 2\tilde{C}_{2r}) \III + (2\tilde{A}_s + 2\tilde{C}_s) \IV \right]
\]

(4.114)

\[
D_{xy}(\tilde{k}) = \frac{1}{8} \left[ (\tilde{A}_1 + \tilde{A}_2 - \tilde{A}_3 - \tilde{A}_r) \II \right]
\]

(4.115)
\[ D_{yx}(\vec{k}) = \frac{1}{8} \left[ (\hat{A}_1 + \hat{A}_2 - \hat{A}_3 - \hat{A}_r) \right] \quad (4.116) \]
\[ D_{yy}(\vec{k}) = \frac{1}{8} \left[ (\hat{A}_2 + \hat{A}_r + 2\hat{C}_{2r}) \right] + (\hat{A}_1 + \hat{A}_3 - 2\hat{C}_{13}) \quad (4.117) \]

In case of the kinetic term of Lagrange Equation (4.87), one can write

\[ \sum_j -M \ddot{u}_{x,y}(\vec{j}) = \begin{pmatrix} -M \ddot{u}_x(\vec{i}) \\ -M \ddot{u}_y(\vec{i}) \end{pmatrix} = M\omega^2 \begin{pmatrix} u_x(\vec{k}) \\ u_y(\vec{k}) \end{pmatrix} \]

and therefore

\[ M\omega^2 \begin{pmatrix} u_x(\vec{k}) \\ u_y(\vec{k}) \end{pmatrix} = \begin{pmatrix} D_{xx}(\vec{k}) & D_{xy}(\vec{k}) \\ D_{yx}(\vec{k}) & D_{yy}(\vec{k}) \end{pmatrix} \begin{pmatrix} u_x(\vec{k}) \\ u_y(\vec{k}) \end{pmatrix} \quad (4.118) \]

4.A.5 Phonon Spectrum

It can be easily shown that for any 2x2 matrix the eigenvalues can be calculated as

\[ \text{eigenvalues} \left( \begin{pmatrix} a & b \\ c & d \end{pmatrix} \right) = \frac{1}{2} \left[ (a + d) \pm \sqrt{(a - d)^2 + 4bc} \right] \quad (4.119) \]

which can be applied to the right side of (4.118).

\[ D_{xx} + D_{yy} = \frac{1}{8} (\hat{A}_1 + \hat{A}_2 + \hat{A}_3 + \hat{A}_r + 2\hat{C}_{13} + 2\hat{C}_{2r}) \quad (4.118) \]
\[ + \frac{1}{8} (\hat{A}_1 + \hat{A}_2 + \hat{A}_3 + \hat{A}_r - 2\hat{C}_{13} - 2\hat{C}_{2r}) \quad (III) \]
\[ + \frac{1}{2} \hat{A}_s \quad (IV) \]

\[ = (\hat{A}_1 + \hat{A}_2 + \hat{A}_3 + \hat{A}_r)(1 - \cos k_x \cos k_y) \]
\[ + (2\hat{C}_{13} + 2\hat{C}_{2r})(\cos k_y - \cos k_x) \]
\[ + 2\hat{A}_s(1 - \cos k_x)(1 - \cos k_y) \]

\[ \left[ D_{xx} - D_{yy} \right]^2 = \left[ \frac{1}{8} (\hat{A}_1 - \hat{A}_2 + \hat{A}_3 - \hat{A}_r + 2\hat{C}_{13} - 2\hat{C}_{2r}) \right] \quad (4.118) \]
\[ + \frac{1}{8} (-\hat{A}_1 + \hat{A}_2 - \hat{A}_3 + \hat{A}_r + 2\hat{C}_{13} - 2\hat{C}_{2r}) \quad (III) \]
\[ + \frac{1}{4} 2\hat{C}_s \quad (IV) \]
\[ = (\hat{A}_1 - \hat{A}_2 + \hat{A}_3 - \hat{A}_r)(\cos k_y - \cos k_x) \]
\[ 4D_{xy}D_{yx} = \frac{1}{16}(\tilde{A}_1 + \tilde{A}_2 - \tilde{A}_3 - \tilde{A}_r)^2 \left[ \frac{\sin^2 k_x \sin^2 k_y}{4} \right] \]

The two-dimensional phonon spectrum or dispersion relation based on (4.85) can be finalized as

\[ \omega(\vec{k})^2 = \frac{1}{2M} \left[ E_1(\vec{k}) \pm \sqrt{E_2(\vec{k})^2 + E_3(\vec{k})^2} \right] \]  

(4.120)

where

\[ E_1(\vec{k}) = (\tilde{A}_1 + \tilde{A}_2 + \tilde{A}_3 + \tilde{A}_r)(1 - \cos k_x \cos k_y) + \\
+ (2\tilde{C}_{13} + 2\tilde{C}_{2r})(\cos k_y - \cos k_x) + \\
+ 2\tilde{A}_s(1 - \cos k_x)(1 - \cos k_y), \]  

(4.121)

\[ E_2(\vec{k}) = (\tilde{A}_1 - \tilde{A}_2 + \tilde{A}_3 - \tilde{A}_r)(\cos k_y - \cos k_x) + \\
+ (2\tilde{C}_{13} - 2\tilde{C}_{2r})(1 - \cos k_x \cos k_y) + \\
+ 2\tilde{C}_s(1 - \cos k_x)(1 - \cos k_y), \]  

(4.122)

\[ E_3(\vec{k}) = (\tilde{A}_1 + \tilde{A}_2 - \tilde{A}_3 - \tilde{A}_r) \sin k_x \sin k_y. \]  

(4.123)

### 4.A.6 Verifying and Plotting Results

Consider a set of initial values

\begin{align*}
\text{INPUT PARAMETERS:} & \quad A_1 = 5, \ A_2 = 4, \ A_3 = -4, \ As = 5 \\
& \quad C_{12} = -3, \ C_{13} = -5, \ C_{1s} = -7, \ C_{3s} = 2, \ C_{23r} = 0.5 \\
& \quad F_3 = 50, \ F_{3r} = 0.5 \\
\text{EXPANSION POINT:} & \quad e_{0.1} = 0.1, \ e_{0.3} = 0.316228 \\
\text{NORMALIZED PARAMETERS:} & \quad A_1 = 5, \ A_2 = 3.4, \ A_3 = 10, \ As = 3.6, \ Ar = 0.05 \\
& \quad C_{13} = -3.16228, \ C_s = 0.632456, \ C_{2r} = 0.158114
\end{align*}
Note that $\tilde{e}_3$ (computer: $e_{0, 3}$) chosen as a positive value.

Plot of both branches can be seen in Figure 4.17. The plotted continuous spectrum is superimposed with eigenvalues of discrete system of 4x4 atoms. Calculations for discrete system are done independently to make a verification case for obtained analytical dispersion relation (4.120). Points in $k$-space are placed on 4x4 grid with

$$k_x, k_y \in \left\{-\frac{\pi}{2}, 0, \frac{\pi}{2}, \pi\right\}.$$ 

Increasing set of eigenvalues for discrete system produced following eigenvalues

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</thead>
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<tr>
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<td>11.5987</td>
<td>17.1404</td>
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<tr>
<td>0</td>
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<td>11.5987</td>
<td>17.1404</td>
</tr>
<tr>
<td>3.1338</td>
<td>9.7013</td>
<td>11.8702</td>
<td>17.3509</td>
</tr>
<tr>
<td>3.1338</td>
<td>9.7013</td>
<td>15.6367</td>
<td>21.3246</td>
</tr>
<tr>
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<td>10.0133</td>
<td>15.6367</td>
<td>21.3246</td>
</tr>
<tr>
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<td>27.2596</td>
</tr>
<tr>
<td>6.2675</td>
<td>10.0133</td>
<td>15.6367</td>
<td>27.2596</td>
</tr>
<tr>
<td>7.5325</td>
<td>10.0133</td>
<td>16.9298</td>
<td>42.6491</td>
</tr>
</tbody>
</table>

shown in increasing order. On the other hand, continuous spectrum (4.120) generated following results

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Upper Branch:</td>
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<td></td>
</tr>
<tr>
<td>27.2596</td>
<td>42.6491</td>
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<td>16.9298</td>
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<tr>
<td>15.6367</td>
<td>21.3246</td>
<td>15.6367</td>
<td>17.1404</td>
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<tr>
<td>8.6754</td>
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<td>17.3509</td>
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<tr>
<td>15.6367</td>
<td>21.3246</td>
<td>15.6367</td>
<td>17.1404</td>
</tr>
<tr>
<td>Lower Branch:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.5987</td>
<td>6.2675</td>
<td>11.5987</td>
<td>11.8702</td>
</tr>
<tr>
<td>10.0133</td>
<td>3.1338</td>
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<td>9.7013</td>
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<td>3.7662</td>
<td>7.5325</td>
</tr>
<tr>
<td>10.0133</td>
<td>3.1338</td>
<td>10.0133</td>
<td>9.7013</td>
</tr>
</tbody>
</table>

at the corresponding $k$-points, as seen on the plots of Figure 4.17. Accuracy of 4 significant digits is sufficient to observe one-to-one comparison of both sets. Closer observation indicates a perfect match.
Figure 4.15 (Color) Sample eigenmode corresponding to eigenvalue of 6.2675 on 4x4 system, with the point located at $k_x = 0, k_y = \pi$ on the phonon spectrum.
Figure 4.16 (Color) Figure (a) shows upper branch of phonon spectrum squared, whereas (b) shows lower branch. Labeled points are discrete values of 4x4 system of atoms with corresponding values superimposed.
Figure 4.17 (Color) Figure (a) shows upper branch of phonon spectrum, whereas (b) shows lower branch. Labeled points are discrete values of 4x4 system of atoms with corresponding values superimposed.
Strongly momentum-dependent local charge screening dynamics is presented in CE-type charge, orbital, and spin ordered La$_{0.5}$Sr$_{1.5}$MnO$_4$, based on Mn K-edge resonant inelastic x-ray scattering data. Through a comparison with theoretical calculations, it is shown that the observed momentum dependence reflects highly localized, nearest neighbor screening of the transient local charge perturbation in this compound with an exciton-like screening cloud, rather than delocalized screening. The size of the screening cloud is estimated to be about 0.4–0.5 interatomic distances.

From the analysis of a Keating energy expression expanded in terms of the atomic-scale symmetry-modes, it is found that the effect of small RE ion size, known as chemical pressure effect, is significant in stabilizing the long range Jahn-Teller distortion in undoped perovskite manganites. Good agreement with the experimental data is obtained on the Jahn-Teller ordering temperature and the substantial increase of the Jahn-Teller ordering temperature from LaMnO$_3$ to PrMnO$_3$ and NdMnO$_3$. It is proposed that similar effects need to be considered to understand the phase diagram for doped perovskite manganites. The appearance of the uniform shear distortion below the Jahn-Teller ordering temperature is also explained in terms of the coupling between coherent shear, buckling, and deviatoric distortions within the Jahn-Teller energy. Moreover, the ratio between these distortions at low temperature is estimated, and good agreement with experimental data for LaMnO$_3$, PrMnO$_3$, and NdMnO$_3$ is found, which confirms the coupling proposed between them in the model.

The mode-based atomic-scale description of the lattice dynamics is also presented. It is established that not only the potential energy but also the kinetic energy can be described in terms of the atomic-scale modes, for which the inclusion of the rigid modes is essential. The atomic-scale mode-based approach for the dynamics of
the one-dimensional chain and two-dimensional square lattice with a mono-atomic basis is demonstrated. By using the constraint equations, the modified Lagrangian equations are obtained in terms of atomic-scale modes only, without explicit use of the displacement variables. This approach is extended to quantum mechanics, to obtain the conjugate momenta and commutation relations in real and reciprocal space. It is expected that this approach would be useful in describing systems with strong anharmonicity.
Many computer programs have been created during the course of theoretical formalism development for K-edge RIXS, applied to La$_{0.5}$Sr$_{1.5}$MnO$_4$ crystal structure.

In this chapter, it is noteworthy to present small fraction with two programs detailed in Sections 6.1 and 6.3, as they describe the central algorithms behind calculations, whereas Section 6.2 describes inclusion of physical parameters.

### 6.1 Code for Setting Up Hamiltonian Matrices with Hartree-Fock Approximation

Following computer code is related to the discussion in Chapter 2 and was developed for Matlab.\(^1\) Program sets up all the necessary Hamiltonian matrices and evaluates total Hamiltonian described in Equation (2.18), with inclusion of Hartree-Fock approximation. All the related figure plotting routines are omitted for compactness and clarity.

\footnote{MATLAB\textsuperscript{\textregistered} (matrix laboratory) is a numerical computing environment and fourth-generation programming language, developed by MathWorks\textsuperscript{\textregistered}. At the time of code development Matlab version R2012a (7.14.0.739) on 64-bit multi-core platform was used.}
if nargin < 3
  % 0: start from scratch, 1: reload from last state, 2: plot quickly
  bReloadLastState = 0;
end

maxSteps = 300;
%
% INITIALIZATION:
% if bReloadLastState
% STARTING FROM SAVED DATA:
  CmdTitle('RE-LOADING SAVED DATA FOR LaSrMnO4');
  LoadLastState(N,CH);
  fprintf('%sSYSTEM: N=%i, CH=%i\n\n', StageId(), N,CH);
else
  % STARTING FROM SCRATCH:
  CmdTitle('LaSrMnO4 HAMILTONIAN CALCULATION');
  Initialize(N,CH);
  fprintf('%sSYSTEM: N=%i, CH=%i\n', StageId(), N,CH);
  fprintf('%sCONSTRUCTING OPERATORS:... \n\n', StageId());
  Set_nOper_All(); % set all n operators for entire i-Space
  Set_H_nonint();
  Set_H_corehole();
end

if bReloadLastState < 2
  %-------------------------------
  % CORE ALGORITHM:
  % converging toward stable <n> values
  ConvergeData(maxSteps, bReloadLastState);
  %-------------------------------
  % SAVE MISC DATA
  SaveLastState(); % save all the final data
  fprintf('%sSAVING TABLES: ...
', StageId());
  Table_nXpt();
  Table_SysParams();
  %-------------------------------
  % EXPORT DATA:
  %(-
  fprintf('%sEXPORTING DATA FOR RIXS AND nDIFF: ...\n\n', StageId());
  Save_nDiff(); % For nDiff analysis
  Save_RIXS(); % For RIXS analysis
  Save_Hcoloumb_Bands();
  %}
end

% use ONLY for Uch estimation:
%ExtractDataForUch();
GetEocc();
%
%-------------------------------
% PLOTS:
%(%-
  fprintf('%n\nPILOTING VARIOUS DATA: ...
', StageId());
  Plot_Energies();
  Plot_Tracking();
  Plot_NetSpin();
  Plot_NetCharge();
%}
end
%
% KEY ALGORITHMIC COMPONENTS:
function Set_nOper_All()
% ACCESS:
global GL

% Gather all n_Operators and save them for later use
nPt = size(GL.iPoints,1);
for iPt = 1:nPt
    szFile = sprintf(GL.file_nOper, iPt);
    if exist(szFile, 'file') ~= 2
        c_nOper = cell(1,2);
        % Eg:
        nOper_eg = Oper_n_eg( GL.iPoints(iPt,:) );
        for i=1:2
            c_nOper{i} = sparse(nOper_eg(:,:,i));
        end
        % saving file:
        save(szFile,'c_nOper');
    end
end

% Construct H_nonint matrices with block-diagonal values
function Set_H_nonint()
% ACCESS:
global GL

nk = size(GL.kPoints,1);
GL.H_nonint_eg = zeros(16*nk,16*nk,2);
for i=1:nk
    i1 = (i-1)*16+1;
    GL.H_nonint_eg(i1:i1+15,i1:i1+15,:) = Oper_Hnonint_eg( GL.kPoints(i,:) );
end

% Construct H_1s3d matrices with core hole
function Set_H_corehole()
% ACCESS:
global GL Eg

% Core-Hole site:
switch GL.CH
    case 0
        return;
    case 1
        site = [0 0];
    case 2
        site = [1 0];
    case 3
        site = [1 1];
    case 4
        if GL.N == 4
            site = [-1 0];  % this is due to iPoints choice
        else
            site = [3 0];
        end
    case 5
        site = [1 -1];
    case 6
        site = [2 -1];
    case 7
        site = [2 0];
    case 8
        site = [2 1];
    otherwise
        error('ERR: Erroneous CH value! CH can only be {0,1,...,8}');
end
GL.Track_iPoint = find(GL.iPoints(:,1)==site(1) & GL.iPoints(:,2)==site(2));
if isempty(GL.Track_iPoint); error('ERR: Suggested tracking (CH) site is not within the domain of iPoints.'); end;

site = GL.iPoints(GL.Track_iPoint,:);

% Eg CASE:
GL.H_corehole_eg = Eg.C.Uch * sum( Oper_n_eg(site), 3 );
GL.H_corehole_eg(:,:,2) = GL.H_corehole_eg(:,:,1); end

% Update nXpt table
function Update_nXpt()
  % ACCESS:
  global GL
  % extract eigen vectors
  [vEg_up, eEg_up] = eig(GL.H_tot_eg(:,:,1)); eEg_up = diag(eEg_up);
  [vEg_dn, eEg_dn] = eig(GL.H_tot_eg(:,:,2)); eEg_dn = diag(eEg_dn);
  nnEg = size(vEg_up,1) / 8;
  
  % count number of spins/orbitals for all occupied electrons
  ii = [1 1];
  while sum(ii)-2 < 2*nnEg
    [~,ind] = min([ eEg_up(ii(1),1), eEg_dn(ii(2),1) ]); ii(ind) = ii(ind) + 1;
  end
  nEg_up = ii(1) - 1;
  nEg_dn = ii(2) - 1;
  
  %{ 
    % Make spins even
    nEg_up = nnEg;
    nEg_dn = nnEg;
    %}
    
    % just to keep an eye on the count
    if nEg_up ~= nnEg || nEg_dn ~= nnEg
      fprintf('!!! Split for %i electrons: [UP:eg|DN:eg]=[%i|%i]

    2*nnEg, nEg_up, nEg_dn);
    end

  nPt = size(GL.iPoints,1);
  nXpt_list_new = zeros(nPt,4);
  c_nOper = cell(1,2);
  for iPt = 1:nPt
    load(sprintf(GL.file_nOper, iPt)); % load nOper into: c_nOper
    n_xpt = [ ... 
      sum( sum( (LL1_up' * c_nOper{1}).' .* LL1_up, 1)), ... 
      sum( sum( (LL1_up' * c_nOper{2}).' .* LL1_up, 1)), ... 
      sum( sum( (LL1_dn' * c_nOper{1}).' .* LL1_dn, 1)), ... 
      sum( sum( (LL1_dn' * c_nOper{2}).' .* LL1_dn, 1)) ];
      ]
    %}
    
    n_xpt = zeros(1,4);
    % Eg spin UP case:
    for iv = 1:nEg_up
      L = vEg_up(:,iv);
      n_xpt(1:2) = n_xpt(1:2) + [L' * c_nOper{1} * L, L' * c_nOper{2} * L];
    end
    % Eg spin DOWN case:
    for iv = 1:nEg_dn
      L = vEg_dn(:,iv);
      n_xpt(3:4) = n_xpt(3:4) + [L' * c_nOper{1} * L, L' * c_nOper{2} * L];
    end
  end

load(sprintf(GL.file_nOper, 1)); % load nOper into: c_nOper
n_xpt = [ ... 
  sum( sum( (LL1_up' * c_nOper{1}).' .* LL1_up, 1)), ... 
  sum( sum( (LL1_up' * c_nOper{2}).' .* LL1_up, 1)), ... 
  sum( sum( (LL1_dn' * c_nOper{1}).' .* LL1_dn, 1)), ... 
  sum( sum( (LL1_dn' * c_nOper{2}).' .* LL1_dn, 1)) ];
  %}
  
  n_xpt = zeros(1,4);
  % Eg spin UP case:
  for iv = 1:nEg_up
    L = vEg_up(:,iv);
    n_xpt(1:2) = n_xpt(1:2) + [L' * c_nOper{1} * L, L' * c_nOper{2} * L];
  end
  % Eg spin DOWN case:
  for iv = 1:nEg_dn
    L = vEg_dn(:,iv);
    n_xpt(3:4) = n_xpt(3:4) + [L' * c_nOper{1} * L, L' * c_nOper{2} * L];
  end
nXpt_list_new(iPt,:) = real(n_xpt);

% Pullay Mixing segment:
if GL.isPullay == 1
    if GL.Track.Size(1) >= 2
        alpha = GL.alphaPullay;
        nXpt_list_new = alpha .* nXpt_list_new + ...
                        (1-alpha) .* GL.nXpt_list_old;
    else
        GL.nXpt_list_old = GL.nXpt_list;
    end
    elseif GL.isPullay == 2
        nXpt_list_new = GL.alphaPullay .* nXpt_list_new + ...
                        GL.betaPullay .* GL.nXpt_list_old + ...
                        (1-GL.alphaPullay-GL.betaPullay) .* GL.nXpt_list_old2;
    end
end
GL.nXpt_list = nXpt_list_new;

% this is for data tracking and stopping criteria
Eocc = sum(eEg_up(1:nEg_up)) + sum(eEg_dn(1:nEg_dn));
GL.Track.Add([Eocc, nXpt_list_new(GL.Track_iPoint,:)], 1:5);

% Calculate total Hamiltonian
function Update_Htot()
    % ACCESS:
    global GL Eg
    % Create U-based list for Hartree-Fock
    U_list = zeros(size(GL.nXpt_list));
    nXpt_sum = Eg.C.U * sum(GL.nXpt_list(:,1:4),2);
    for ic = 1:4
        U_list(:,ic) = nXpt_sum - Eg.C.U * GL.nXpt_list(:,ic);
    end
    % Create H_coulomb due to Hartree-Fock
    nPt = size(GL.iPoints,1);
    H_coulomb_eg = zeros(2*nPt,2*nPt, 2);
    c_nOper = cell(1,2);
    for iPt = 1:nPt
        load(sprintf(GL.file_nOper, iPt)); % load nOper into: c_nOper
        U = U_list(iPt,:);
        H_coulomb_eg(:,:,1) = H_coulomb_eg(:,:,1) + U(1)*c_nOper{1} + U(2)*c_nOper{2};
        H_coulomb_eg(:,:,2) = H_coulomb_eg(:,:,2) + U(3)*c_nOper{1} + U(4)*c_nOper(2);
    end
    GL.H_tot_eg = GL.H_nonint_eg + H_coulomb_eg;
    if GL.CH ~= 0
        GL.H_tot_eg = GL.H_tot_eg + GL.H_corehole_eg;
    end
end

function bval = isStopping()
    % ACCESS:
    global GL
    choice = 1; % {1,2}
    bval = false;
    switch choice
        case 1
            del_Eocc = abs(GL.Track.GetLast(1) - GL.Track.GetLast(1,-1));
            if del_Eocc < 1e-4
                bval = true;
            end
        case 2
            del_Eocc = abs(GL.Track.GetLast(1) - GL.Track.GetLast(1,-1));
            if del_Eocc < 1e-4
                bval = true;
            end
        otherwise
            bval = false;
    end
case 2
    del_n = max(abs(GL.Track.GetLast(2:5) - GL.Track.GetLast(2:5,-1)));
    if del_n < 1e-3
        bval = true;
    end
end

% Converging Loop
function ConvergeData(maxSteps, bReloadLastState)
    global GL
    ...
end

% PRINTING / SAVING:
function SaveLastState()
    ...
end

function LoadLastState(N,CH)
    ...
end

function szId = StageId()
    ...
end
szId = sprintf('## % 3i ## - ', stage_id);
end

function Table_nXpt()
global GL

cType = {'Mn3x', 'Mn4+', 'Mn3y'};
net_spin = GL.nXpt_list * [1 1 -1];
data = [GL.iPoints(:,1:3), GL.nXpt_list(:,1:4), net_spin, sum(GL.nXpt_list(:,1:4), 2)];

file = sprintf('%s__nXptTable.txt', GL.file_tables);
id = fopen(file, 'w');
fprintf(fid, '-----------------------------------------------------------
|
N = %2i: ELECTRON NUMBER TABLE (CH = %i) |
+------+------+-----------------------------+--------+------+
| i-pos | orb. | eg case: < n_{..} > | net | sum(n)
-------+------+-----------------------------+--------+-------

for i = 1:size(data,1)
    fprintf(fid, ' %i %i | %s | %6.4f %6.4f %6.4f %6.4f | %+5.3f | %6.4f ', ...
               data(i,1:2), cType{data(i,3)}, data(i,4:9) );
end
fprintf(fid, '-----------------------------------------------------------
|

CHECK: Sum(n)/N^2 = %5.3f |
+-----------------------------------------------------------
|

* File [%s] have been generated.

end

function Table_SysParams()
global GL Eg

nxpt = [GL.nXpt_list(GL.iPoints(:,1)==0 & GL.iPoints(:,2)==0,:); ...
       GL.nXpt_list(GL.iPoints(:,1)==1 & GL.iPoints(:,2)==0,:); ...
       GL.nXpt_list(GL.iPoints(:,1)==1 & GL.iPoints(:,2)==1,:); ...
       GL.nXpt_list(GL.iPoints(:,1)==-1 & GL.iPoints(:,2)==0,:) ... ];
cTF = {'false', 'true'};
cCH = {'n/a', ...
      'Mn3x+ up', 'Mn4+ up', 'Mn3y+ up', 'Mn4+ up', ...
      'Mn3x+ dn', 'Mn4+ dn', 'Mn3y+ dn', 'Mn4+ dn',};

file = sprintf('%s__SysParams.txt', GL.file_tables);
id = fopen(file, 'w');
fprintf(fid, '----------------------------------------------
|
SIMULATION SYSTEM PARAMETERS |
+------------+---------------------------------+
| System: | N = %2i, Ni = %03i, Nk = %03i |
+------------+---------+---------+-------------+
| Parameters | Eg | T2g | Units |
+------------+---------+---------+-------------+
| Q_1s | % 6.4f | - | angstrom |
| Q_2s | % 6.4f | - | angstrom |
| Q_3u | % 6.4f | - | angstrom |
| Q_3s | % 6.4f | - | angstrom |
| t0 | % 6.4f | - | eV |
| beta | % 6.4f | - | |
| lambda | % 6.4f | - | eV/angstrom |
| JhSc | % 6.4f | - | eV |
| U | % 6.4f | - | eV |
| Uch | % 6.4f | - | eV |
| shift | % 6.4f | - | eV |
+------------+---------+---------+-------------+

* File [%s] have been generated.

end
\[ Q_{33} = (E_{g, C, Q_{3u}} + E_{g, C, Q_{3s}}); \]
\[ Q_{34} = (E_{g, C, Q_{3u}} - E_{g, C, Q_{3s}}); \]
\[ \text{Gap}_{br} = 2 \cdot E_{g, C, \lambda} \cdot E_{g, C, \beta} \cdot E_{g, C, Q_{1s}}; \]
\[ \text{Gap}_{jt} = E_{g, C, \lambda} \cdot (\sqrt{4 \cdot E_{g, C, Q_{2s}}^2 + Q_{33}^2}) - \text{abs}(Q_{34}); \]
\[ \text{Gap}_{tot} = \text{Gap}_{br} + \text{Gap}_{jt}; \]
\[ \text{Gap}_{jt, Mn3} = 2 \cdot E_{g, C, \lambda} \cdot (\sqrt{4 \cdot E_{g, C, Q_{2s}}^2 + Q_{33}^2}); \]
\[ \text{fprintf}(\text{fid}, '| \text{Gap: br} | %6.4f | - | eV |\n'); \]
\[ \text{fprintf}(\text{fid}, '| \text{Gap: JT} | %6.4f | - | eV |\n'); \]
\[ \text{fprintf}(\text{fid}, '| \text{Gap: Tot} | %6.4f | - | eV |\n'); \]
\[ \text{fprintf}(\text{fid}, '| \text{Gap: JT Mn3} | %6.4f | - | eV |\n'); \]
\[ \text{fprintf}(\text{fid}, '+------------+---------+---------+-------------+\n'); \]
\[ \text{fprintf}(\text{fid}, '| Select Eg n_{xpt} Values: |
\]
\[ \text{fprintf}(\text{fid}, '| ix iy : -,up +,up -,dn +,dn |
\]
\[ \text{fprintf}(\text{fid}, '| 0 0 : %6.4f %6.4f %6.4f %6.4f |
\]
\[ \text{fprintf}(\text{fid}, '| 1 0 : %6.4f %6.4f %6.4f %6.4f |
\]
\[ \text{fprintf}(\text{fid}, '| 1 1 : %6.4f %6.4f %6.4f %6.4f |
\]
\[ \text{fprintf}(\text{fid}, '| -1 0 : %6.4f %6.4f %6.4f %6.4f |
\]
\[ \text{fprintf}(\text{fid}, '+------------+---------------------------------+\n'); \]
\[ \text{fprintf}(\text{fid}, '| C-H Type | %s |
\]
\[ \text{fprintf}(\text{fid}, '| C-H Site | %s |
\]
\[ \text{fprintf}(\text{fid}, '| isPullay | %s |
\]
\[ \text{fprintf}(\text{fid}, '| alpha Pull. | %3.2f |
\]
\[ \text{fprintf}(\text{fid}, '| Calc. Time | %s |
\]
\[ \text{fprintf}(\text{fid}, '| Cycles | %32i |
\]
\[ \text{fprintf}(\text{fid}, '| Time Stamp | %s |
\]
\[ \text{fclose}(\text{fid}); \]
\[ \text{fprintf}(\text{fid}, '* File [%s] have been generated.\n'); \]
\[ \text{fclose}(\text{fid}); \]
\[ \text{function Plot_Energies() \%
\]
\[ \text{global GL Eg} \%
\]
\[ \text{E1 = sortrows([eig(GL.H_nonint_eg(:,:,1)); eig(GL.H_nonint_eg(:,:,2))]);} \]
\[ \text{E2 = sortrows([eig(GL.H_tot_eg(:,:,1)); eig(GL.H_tot_eg(:,:,2))]);} \]
\[ \text{ind = 1:size(E1,1);} \]
\[ \text{szCH} = '\'; \]
\[ \text{if GL.CH =\n}
\]
\[ \text{szCH} = sprintf('%i,%i',GL.iPoints(GL.Track_iPoint,1:2));} \]
\[ \text{end} \]
\[ \text{hold on; \%}
\]
\[ \text{plot(ind,E1, '.','MarkerSize',5, 'Color',[.2 .8 1]);} \]
\[ \text{plot(ind,E2, '.','MarkerSize',5, 'Color',[0 0 1]);} \]
\[ \text{minNN = min( E1 );} \]
\[ \text{maxNN = max( E2 );} \]
\[ \text{szTitle = sprintf('N=%i, CH=%i: Energy Profile for H_{eg}%s',GL.N,GL.CH,szCH);} \]
\[ \text{GL.figId = FigId(GL.figId, szTitle);} \]
\[ \text{hold on; \%}
\]
\[ \text{plot(ind,E1, '.', 'MarkerSize',5, 'Color',[.2 .8 1]);} \]
\[ \text{plot(ind,E2, '.', 'MarkerSize',5, 'Color',[0 0 1]);} \]
\[ \text{minMN = min( E1 );} \]
\[ \text{maxMN = max( E2 );} \]
\[ \text{title(szTitle);} \]
\[ \text{ylabel('Energy - E_F (eV)');} \]
\[ \text{legend('E_{nonint}^{eg}','E_{tot}^{eg}','Location','SouthEast');} \]
NN = size(E1,1);
plot([1 NN], [0 0], ':k');
fermi = size(E1,1) / 8 + 0.5;
plot([fermi fermi], [minNN maxNN], ':k');
text(fermi,maxNN-.1,'occupied', ... 
'Rotation',90, 'HorizontalAlignment','right', 'VerticalAlignment','bottom');
text(fermi,maxNN-.1,'unoccupied', ... 
'Rotation',90, 'HorizontalAlignment','right', 'VerticalAlignment','top');
hold off;
end

function Plot_Tracking()
global GL Eg

data = GL.Track.GetData();
n = size(data,1);
Eocc = data(:,1);
Sp_up = data(:,[2 3]);
Sp_dn = data(:,[4 5]);
clrE = [0 .6 0];
clrEg = [0 0 1];

GL.figId = FigId(GL.figId, 'Evolution of various parameters.');

subplot(3,1,1);
plot(Eocc,'.-', 'Color',clrE);
szCH = ''; 
if GL.CH == 1
szCH = sprintf(', U_{CH}=%4.1f_{eg} (eV)', Eg.C.Uch);
end
title(sprintf('N=%i, CH=%i: E_{tot}^{OCC} Tracking, E = %.2f (eV)%s', GL.N,GL.CH, Eocc(n), szCH ));
xlabel('Steps');
ylim([min(Eocc)-5, max(Eocc)+5]);

szSite = sprintf('(%i,%i)', GL.iPoints(GL.Track_iPoint,1:2));

subplot(3,1,2); hold on;
plot(Sp_up(:,1),'.-', 'Color',clrEg);
plot(Sp_up(:,2),'.--', 'Color',clrEg);
hold off;
title(sprintf('Spin \uparrow n-Values at site %s',szSite));
ylabel('Steps');
ylim([0 -0.1, 1.1]);
legend(sprintf('n^{eg}_{-,\uparrow} = %5.3f',Sp_up(n,1)),... 
strftime('n^{eg}_{+,\uparrow} = %5.3f',Sp_up(n,2)),'
'Location','NorthWest');

subplot(3,1,3); hold on;
plot(Sp_dn(:,1),'.-', 'Color',clrEg);
plot(Sp_dn(:,2),'.--', 'Color',clrEg);
hold off;
title(sprintf('Spin \downarrow n-Values at site %s',szSite));
ylabel('Steps');
ylim([0 -0.1, 1.1]);
legend(sprintf('n^{eg}_{-,\downarrow} = %5.3f',Sp_dn(n,1)),... 
strftime('n^{eg}_{+,\downarrow} = %5.3f',Sp_dn(n,2)),'
'Location','NorthWest');

end

function Plot_ColoredAtoms(data_c, minmax_c, szTitle)
global GL
MS = 40; % marker size limits
nPt = size(GL.iPoints,1);

% define orbital loops
orb_size = 0.5;
th = 0:0.1:2*pi+0.1;
r_hor = orb_size * cos(th).^2;
r_ver = orb_size * sin(th).^2;
xy_hor = [r_hor.*cos(th); r_hor.*sin(th)];
xy_ver = [r_ver.*cos(th); r_ver.*sin(th)];
cirCH = [1 .9 .9];
cirOrb = [1 1 1]*.8;
cirZig = [1 1 1]*.95;

GL.figId = FigId(GL.figId, szTitle);

hold on;

% draw CH site
if GL.CH ~= 0
    CH_site = GL.iPoints(GL.Track_iPoint,:);
    plot(CH_site(1),CH_site(2),'.', 'Color',clrCH, 'MarkerSize',MS*4);
end

% draw zig-zag and orbitals
for iPt = 1:nPt
    x = GL.iPoints(iPt,1);
    y = GL.iPoints(iPt,2);
    switch GL.iPoints(iPt,3)
    case 1
        plot(x+[1 -1],y+[0 0],'-', 'Color',clrZig,'LineWidth',3);
        plot(x+xy_hor(1,:),y+xy_hor(2,:),'-', 'Color',cirOrb);
    case 3
        plot(x+[0 0],y+[-1 1],'-', 'Color',clrZig,'LineWidth',3);
        plot(GL.iPoints(iPt,1)+xy_ver(1,:),GL.iPoints(iPt,2)+xy_ver(2,:),'-',
             'Color',cirOrb);
    end
end

% draw color dots
nc = 64;
cmap = colormap( jet(nc) );
for iPt = 1:nPt
    q = (data_C(iPt) - minmax_C(1)) ./ (minmax_C(2) - minmax_C(1));
    iColor = max( 1, min(nc, round((nc-1)*q+1) ) );
    plot(GL.iPoints(iPt,1),GL.iPoints(iPt,2),'.', 'MarkerSize',MS,
         'Color',cmap(iColor,:));
end

hold off;
colorbar;
caxis(minmax_C);
minmax_xy = [min(GL.iPoints(:,:1)), max(GL.iPoints(:,:1))];
xlim(minmax_xy + [-.6, .6]);
ylim(minmax_xy + [-.6, .6]);
title(szTitle);
xlabel('i_x');
ylabel('i_y');
set(gca,'XTick',minmax_xy(1):.1:length(minmax_xy(1)), 'YTick',minmax_xy(1):.1:length(minmax_xy(1)), ...
     'DataAspectRatio',[1 1 1]);

function Plot_NetSpin()
global GL

net_spin = GL.nXpt_list * [1 1 -1 -1]';
msp = max(abs(net_spin));
minmax_C = [-msp,msp];
Plot_ColoredAtoms(net_spin, minmax_C, ...
612     sprintf('N=%i, CH=%i: Atomic Net Spin',GL.N,GL.CH));
613 end
614 function Plot_NetCharge()
615     global GL
616     net_charge = sum(GL.nXpt_list(:,1:4), 2);
617     minmax_C = [0,max(net_charge)];
618     Plot_ColoredAtoms(net_charge, minmax_C, ... 
619         sprintf('N=%i, CH=%i: Atomic Net Charge',GL.N,GL.CH));
620 end
621 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
622 % EXPORT DATA FOR FURTHER ANALYSIS:
623 function Save_nDiff()
624     global GL Eg
625     data.nXpt_list = GL.nXpt_list;
626     data.U_eg = Eg.C.U;
627     data.Uch_eg = Eg.C.Uch;
628     data.C = Eg.C;
629     if GL.CH == 0
630         % data file without Core Hole, used as a basis
631         data.N = GL.N;
632         data.figId = 20;
633         data.iPoints = GL.iPoints;
634     else
635         data.CH_site = GL.iPoints(GL.Track_iPoint,:);
636     end
637     eval( sprintf('CH%d = data;',GL.CH) );
638     save(GL.file_ndiff, sprintf('CH%d',GL.CH));
639 end
640 function Save_RIXS()
641     global GL Eg
642     data.H_eg = GL.H_tot_eg;
643     data.N = GL.N;
644     data.CH = GL.CH;
645     data.C = Eg.C;
646     if GL.CH == 0
647         % data without Core Hole, used as a basis
648         data.kPoints = GL.kPoints;
649         CHO = data;  %#ok
650         save(GL.file_rixs, 'CHO');
651     else
652         % data with Core Hole
653         data.CH_site = GL.iPoints(GL.Track_iPoint,1:2);
654         CH1 = data;  %#ok
655         save(GL.file_rixs, 'CH1');
656     end
657 end
658 function Save_Hcoulomb_Bands()
659     global GL
660     if GL.CH ~= 0; return; end;
661     file = sprintf('%.nXpt_list.mat', GL.file_main);
662     iPoints = GL.iPoints;
663     nXpt_list = GL.nXpt_list;
664     save(file, 'iPoints','nXpt_list');
665 end
666 function ExtractDataForUch()
667     global GL Eg
668     fid = fopen(sprintf('DataForUch_N%02d_t%.2f.txt', GL.N, Eg.C.t0), 'a');
ch = [0.0; 1.0; 1.1; -1.0];
if GL.CH == 0
    for i=1:2
        indCH = find(GL.iPoints(:,1)==ch(i,1) & GL.iPoints(:,2)==ch(i,2));
        S = sum(GL.nXpt_list(indCH,:));
        fprintf(fid, '%d %d %d %.4f %.4f
', GL.CH, ch(i,1), ch(i,2), Eg.C.Uch, S);
    end
else
    i = GL.CH;
    indCH = find(GL.iPoints(:,1)==ch(i,1) & GL.iPoints(:,2)==ch(i,2));
    S = sum(GL.nXpt_list(indCH,:));
    fprintf(fid, '%d %d %d %.4f %.4f
', GL.CH, ch(i,1), ch(i,2), Eg.C.Uch, S);
end
fclose(fid);

function GetEocc()
    global GL
    Eup = eig(GL.H_tot_eg(:,:,1));
    Edn = eig(GL.H_tot_eg(:,:,2));
    nF = size(Eup,1) / 8;
    Eocc = [Eup(1:nF), Edn(1:nF)];
    Eocc = sum(sum(Eocc));
end

%===============================================

6.2 Code for Initialization of Variables

Following computer code written for Matlab, provides initialization for the system described in previous Section 6.1 and specifically related to the physical parameters of a crystal La$_{0.5}$Sr$_{1.5}$MnO$_4$, which is related to the discussion in Chapter 2. Additional purpose for this code is to provide initialization for band structure calculation, not included in this chapter.
function Initialize(N,CH)
    if nargin < 0; error('ERR: Initialize(..) must have input parameters.'); end;
    if nargin == 1; isCluster = false; else isCluster = true; end;
    %------------------------------------------------------
    % DEFINE COMMON GLOBAL STRUCTURE
    %------------------------------------------------------
    global GL
    GL.path = MakeDir(sprintf('_N%02i_data_',N));
    % do not define GL for band plots
    if isCluster
        if mod(N,4) ~= 0 || N<4; error('ERR: System prameter N must be a positive integer divisible by 4. '); end;
        if mod(round(CH),9) ~= CH; error('ERR: Core-Hole parameter CH must be one of: {0,1,...,8}.'); end;
        GL.N = N;
        GL.CH = CH;
        GL.kPoints = GetAll_kPoints(GL.N); % create all k-points in reduced Bruloin zone (N^2/8)
        GL.iPoints = GetAll_iPoints(GL.N); % create all i-space points (N^2)
        GL.nXpt_list = zeros(GL.N^2, 4); % allocate table for <n..>: 1:4->eg
        % constant matrices
        GL.H_nonint_eg = []; GL.H_corehole_eg = [];
        GL.H_tot_eg = [];
        GL.R_eg = Get_kDiff_eg(); GL.R_eg = Get_kDiff_eg(); % used in Oper_n_eg() (see init below..)
        GL.nXpt_list(:,1) = 0.25; GL.nXpt_list(:,3) = 0.25;
        GL.nXpt_list_old = GL.nXpt_list; % allocate table for <n..>
        % create/verify directory/file prefix for: {n-Operators, main data, tables}
        GL.file_nOper = sprintf('%s/nOper_%%04i.mat', MakeDir(sprintf('_nOper_N%02i_',GL.N)));
        GL.file_main = sprintf('%s/N%02i_CH%i', MakeDir([GL.path,'/_main_']), GL.N, GL.CH);
        GL.file_tables = sprintf('%s/N%02i_CH%i', MakeDir([GL.path,'/_tables_']), GL.N, GL.CH);
        GL.file_ndiff = sprintf('%s/N%02i_CH%i', MakeDir([GL.path,'/_nDiff_']), GL.N, GL.CH);
        GL.file_rixs = sprintf('%s/N%02i_CH%i', MakeDir([GL.path,'/_RIXS_']), GL.N, GL.CH);
    end
    % miscellaneous
    GL.figId = 1; % starting figId
    GL.timecpu = cputime; % cpu time to calculate GL.timediff
    GL.timediff = 0; % time that already ellapsed in sec
    GL.Track = clDataTrack(5); % tracking data: [E_occ, nXpt(0,0,0)]
    GL.Track_iPoint = find(GL.iPoints(:,1)==0 & GL.iPoints(:,2)==0);
    if isempty(GL.Track_iPoint); error('ERR: Suggested tracking (CH) site is not within the domain of iPoints. ');end;
    %(-
    if GL.isPullay == 0; % (0,1,2)
        if mod(CH,2) == 1
            GL.isPullay = 2;
        else
            GL.isPullay = 0;
        end
    end
    %)
    if GL.isPullay == 1
        GL.alphaPullay = 0.1;
        if GL.alphaPullay > 1.0; error('ERR: alpha > 1, must be < 1. '); end;
        GL.nXpt_list(:,1) = 0.25;
        GL.nXpt_list(:,3) = 0.25;
        GL.nXpt_list_old = GL.nXpt_list; % allocate table for <n..>
    end
    else
        GL.alphaPullay = 0.3;
        GL.betaPullay = 0.3;
if (GL.alphaPullay+GL.betaPullay) > 1.0; error('ERR: alpha+beta > 1, must be < 1.1'); end;
GL.nXpt_list(:,1) = 0.25;
GL.nXpt_list(:,3) = 0.25;
GL.nXpt_list_old = GL.nXpt_list;
GL.nXpt_list_old2 = GL.nXpt_list;
end
end

%------------------------------------------------------
% DEFINE Eg GLOBAL STRUCTURE
%------------------------------------------------------
global Eg
% Physical Constants:
Eg.C.lambda = sqrt(3/2)*1.38*0.4/0.228; % (eV/angstrom), J-T param, (= 2.9652)
% Eg.C.lambda = 1.69; % (eV/angstrom), J-T param
Eg.C.JhSc = 2.47 / 2; % (eV), Hund's param, (= 1.235)
% Eg.C.U = 1.6; % (eV), Coulomb potential
Eg.C.Uch = -2.6; % (eV), core-hole potential

% Experimentally determined:
Eg.C.Q_1s = 0.05311622; % (A) distortion parameter
Eg.C.Q_2s = 0.05444722; % (A) distortion parameter
Eg.C.Q_3u = 0.10736930; % (A) distortion parameter
Eg.C.Q_3s = -0.01183920; % (A) distortion parameter

% Resonance parameters (used in RIXS model only):
Eg.C.omega_in = 0.0; % (eV), calculated later
Eg.C.Gamma1 = 0.75; % (eV), set here for Mn3 C-H
Eg.C.Gamma2 = 0.75; % (eV), set here for Mn4 C-H

% CHOSEN PARAMETERS:
Eg.C.beta = 2.0; % (unitless) breathing parameter
Eg.C.t0 = 1.2;
Eg.C.lambda = 4.566; % 5.953;
Eg.C.U = 0.95 * 1.6; % (= 1.52)
Eg.C.JhSc = 1.8 * 2.47 / 2; % (=2.2230)
Eg.C.Uch = -2.0;
Eg.C.shift = 4.17279306; % value for N16 t0 = 0.9

% beta t0 lambda U Uch
%----------------------------------------
Params = [...
1.5, 0.1, 10.79, 3.5, -4.0, 4.64902695; ...
1.5, 0.6, 9.606, 3.5, -4.0, 4.50117621;
1.5, 0.9, 7.407, 3.5, -4.0, 4.17279306;
1.5, 1.1, 4.810, 3.5, -4.0, 3.73921945;
1.5, 1.3, 3.800, 3.5, -4.0, 3.6194785;
1.5, 1.32, 3.760, 3.5, -4.0, 3.6173608;
1.5, 1.33, 3.748, 3.5, -4.0, 3.6193650;
1.5, 1.35, 3.725, 3.5, -4.0, 3.62362752;
1.5, 1.40, 3.650, 3.5, -4.0, 3.62999964;
1.5, 1.5, 3.509, 3.5, -4.0, 3.64416614;
]

% beta t0 lambda U Uch
%----------------------------------------
params(pCase,1); pCase = 3;

Eg.C.beta = Params(pCase,1);
Eg.C.t0 = Params(pCase,2);
Eg.C.lambda = Params(pCase,3);
Eg.C.U = Params(pCase,4);
Eg.C.Uch = Params(pCase,5);
Eg.C.shift = Params(pCase,6);
% Enable ONLY for running: run_Uch() and Uch_Estimation()
% Eg.C.Uch = -1 * load(’_temp_.txt’);

%------------------------------------------------------
% Hamiltonians 16x16:
Eg.H_hund = SetHund_eg(Eg.C.JhSc);
Eg.H_jt = SetJahnTeller_eg(Eg.C.lambda, Eg.C.Q_3u, Eg.C.Q_3s, Eg.C.Q_2s);
Eg.H_brtng = SetBreathing_eg(Eg.C.lambda, Eg.C.beta, Eg.C.Q_1s);
Eg.H_shift = Eg.C.shift .* eye(16);

if isCluster
    GL.R_eg = Set_R_eg(Eg.C.Q_3u, Eg.C.Q_3s, Eg.C.Q_2s);
end

%------------------------------------------------------
% FOR BANDS ONLY
%------------------------------------------------------
if not(isCluster)
    Eg.H_coloumb = SetCoulomb_Bands_eg(N);
end
end

%==========================================================
function kPoints = GetAll_kPoints(N)
    kPoints = zeros(N*N/8, 2);
    dk = 2*pi/N;
kx = dk*(-N/4+1:N/4);
kx = length(kx);
i = 1;
kPoints(i:i+nkx-1,1) = kx';
i = i+nkx;
ky = dk;
while nkx > 2
    kx = kx(2:nkx-1);
kx = length(kx);
kPoints(i:i+nkx-1,1) = kx';
    kPoints(i:i+nkx-1,2) = ky;
i = i+nkx;
kPoints(i:i+nkx-1,1) = kx';
    kPoints(i:i+nkx-1,2) = -ky;
i = i+nkx;
ky = ky+dk;
end
kPoints = sortrows(kPoints, [2 1]);
end

% Function creates an array of N^2 equally spaced (in 3D) i-points symmetrical w.r.t (0,0).
% All dimensions run from -N/2+1 to N/2 with increments of 1.
% NOTE: 3-rd dimension (3-rd column) are orbital id labels: {1,2,3}, not z-coordinate
%}
function iPoints = GetAll_iPoints(N)
iPoints = zeros(N^2, 3);
    nx = -N/2+1:N/2;
    ny = nx;
nn = length(nx);
    iy = 1:nn
    i = (iy-1)*nn+1;
iPoints(i:i+nn-1,1) = nx';
iPoints(i:i+nn-1,2) = ny(iy);
end

% create orbital id labels: 1: Mn^{3+}_-, 2: Mn^{4+}, 3: Mn^{3+}_+
for i = 1:size(iPoints,1)
    switch mod(-iPoints(i,2) - iPoints(i,1), 4)
    case 0
        iPoints(i,3) = 1;
    case 1
        iPoints(i,3) = 2;
    case 2
        iPoints(i,3) = 3;
    case 3
        iPoints(i,3) = 3;
    end
iPoints(i,3) = 2;

case 2  \% Mn^{3+}+
    iPoints(i,3) = 3;
    case 3  \% Mn^{4+}
        iPoints(i,3) = 2;
    end
end

function m16 = SetHund_eg(JhSc)
    Z = zeros(2);
    G = (JhSc / 2) * eye(2);
    m16 = [ ...
        Z, G, -G, Z, -G, Z, -G, Z, ...
        G, Z, Z, -G, Z, Z, -G, Z, ...
        -G, Z, Z, G, Z, Z, -G, Z, ...
        Z, -G, G, Z, -G, G, Z, ...
        -G, Z, Z, -G, Z, Z, -G, Z, ...
        -G, Z, Z, -G, Z, -G, Z, ...
        Z, -G, -G, Z, -G, -G, Z, ...
        Z, -G, -G, Z, -G, -G, Z, ...
    ];
    m16(:,:,2) = -m16(:,:,1);
end

function m16 = SetJahnTeller_eg(lambda, Q_3u, Q_3s, Q_2s)
    Z = zeros(2);
    A = -lambda * Q_3u * [ 1, 0; 0, -1];
    B = -lambda * Q_3s * [ 1, 0; 0, -1];
    C = -lambda * Q_2s * [ 0, -1; -1, 0];
    m16 = [ ...
        A, Z, Z, B, C, Z, Z, C, ...
        Z, A, B, Z, C, Z, C, Z, ...
        Z, B, A, Z, Z, C, C, Z, ...
        B, Z, Z, A, C, Z, Z, C, ...
        C, Z, Z, C, A, Z, Z, B, ...
        Z, C, C, Z, Z, A, B, Z, ...
        Z, C, C, Z, Z, B, A, Z, ...
end

function m16 = SetBreathing_eg(lambda, beta, Q_1s)
    Z = zeros(2);
    A = -lambda * beta * Q_1s * [1, 0; 0, 1];
    m16 = [ ...
        Z, Z, Z, A, Z, Z, Z, Z, ...
        Z, Z, A, Z, Z, Z, Z, Z, ...
        Z, A, Z, Z, Z, Z, Z, Z, ...
        Z, Z, Z, Z, Z, Z, A, Z, ...
        Z, Z, Z, Z, Z, A, Z, Z, ...
        Z, Z, Z, Z, Z, A, Z, Z, ...
end

function m16z2 = Get_kDiff_eg()
    m16z2 = zeros(16,16,2);
    m2 = ones(2);
    del_kx = [0, pi, 0, pi, -pi/2, pi/2, -pi/2, pi/2, pi/2];
    del_ky = [0, 0, pi, pi, -pi/2, -pi/2, pi/2, pi/2, pi/2];
    for ir = 1:8
        iir = (ir-1)*2+1;
        for ic = 1:8
            iic = (ic-1)*2+1;
    end
end

%==========================================================
%{  
%  Creates a pair of 16x16 matrices used in Oper_n() 
%  First 16x16 matrix is for kx component, second is for ky 
%}
%function m16z2 = Get_kDiff_eg()
function m16_R = Set_R_eg(Q_3u, Q_3s, Q_2s)
    if abs(Q_2s) > eps
        Q_33 = Q_3u + Q_3s;
        th0 = atan(( -Q_33 + sqrt(Q_33^2 + 4*Q_2s^2)) / (2*Q_2s));
        theta = [-th0, 0, th0];
    else
        theta = [0, 0, 0];
    end
    % 1-2 dim is 16x16
    % 3-rd dim is atom type based on theta {1,2,3} => {Mn3_x, Mn4, Mn3_y}
    % 4-th dim is orbital {1,2} => {-,+}
    m16_R = zeros(16,16,3,2);
    c2 = cos(theta).^2;
    s2 = sin(theta).^2;
    cs = cos(theta).*sin(theta);
    ind = 1:2:16;
    for i = 1:3
        m16_R(ind,ind, i,1) = c2(i);
        m16_R(ind,ind+1, i,1) = cs(i);
        m16_R(ind+1,ind, i,1) = cs(i);
        m16_R(ind+1,ind+1, i,1) = s2(i);
        m16_R(ind,ind, i,2) = s2(i);
        m16_R(ind,ind+1, i,2) = -cs(i);
        m16_R(ind+1,ind, i,2) = -cs(i);
        m16_R(ind+1,ind+1, i,2) = c2(i);
    end
end
% FOR BANDS ONLY:
function H_coulomb = SetCoulomb_Bands_eg(N_base)
    global GL Eg
    NN = N_base^2;
    iPoints = [];
    load(sprintf('%s/_main_/N%02d_CH0__nXpt_list',GL.path,N_base));
    nP = size(iPoints,1);
    U_list = zeros(size(nXpt_list));
    nXpt_sum = Eg.C.U * sum(nXpt_list(:,1:4),2);
    for ic = 1:4
        U_list(:,ic) = nXpt_sum - Eg.C.U * nXpt_list(:,ic);
    end
    m16_R = Set_R_eg(Eg.C.Q_3u, Eg.C.Q_3s, Eg.C.Q_2s);
    kDiff_eg = Get_kDiff_eg();
    spUp = 1; spDn = 2;
    oMn = 1; oPl = 2;
    H_coulomb = zeros(16,16,2);
    for i = 1:nP
        U = U_list(:,i);
        vi = iPoints(i,1:2);
6.3 Code for RIXS Spectrum Calculation with Kramers-Heisenberg Formula

Further, presented is Matlab code segment for calculation of RIXS intensity based upon exact diagonalization approach, applied to calculated Hamiltonian operators. This code is related to the discussion in Chapter 2. RIXS spectrum is calculated using Equation (2.26), that have been derived from Kramers-Heisenberg formula. All the related figure plotting routines are omitted for compactness and clarity.

```matlab
function run2_rixs_calc(N,minmax_E)
    clc; addpath('_functions_','../__common__');
    if nargin < 1
        clear all;
        N = 8; % must be divisible by 4
    end;
    fprintf('## SETTING GLOBAL PARAMS... 
');
    tic; SetGlobals(N); toc;
    fprintf('
## CALCULATING RIXS... 
');
    tic; SetRIXS(minmax_E); toc;
    fprintf('
## SAVING CALCULATED RIXS: ... 
');
    SaveCalcRixs();
end
```
fprintf('## SAVING DATA TABLES: ...
');
TableEnergy();
TableIntensity();
TableSumIntensity();
Table_Matrix_kMap();

fprintf('
FINISHED... 
');
end

%============================================
% PREPARE DATA FROM CH CORE-HOLE SITES:
% Collect all the extended points for the reduced Brillouin zone and
% their indexes mapped to the kPoints
function [kPoints_ext, ind_ext] = GetExtended_kPoints(kPoints)
sq = 1/sqrt(2);
ROT = [sq sq; -sq sq]; % +45 rotation
kR = kPoints * ROT;

del = 1e-10;
v1 = pi / 2 / sqrt(2);
v2 = pi / sqrt(2);

% stage 1: x
ind1 = find(abs(kR(:,1)-v1) < del);
kR_ext1 = kR(ind1,:);
% stage 2: y
ind2 = find(abs(kR(:,2)-v1) < del);
kR_ext2 = kR(ind2,:);
% stage 3: x & y
ind3 = find(abs(kR(:,1)-v1) < del & abs(kR(:,2)-v1) < del);
kR_ext3 = kR(ind3,:);

kR_ext = [kR_ext1, ind1; kR_ext2, ind2; kR_ext3, ind3];
kPoints_ext = kR_ext(:,1:2) * ROT';
ind_ext = kR_ext(:,3);
end

function [kPoints, kPointsExt, kIndexExt] = GetFull_kPoints(N)
dk = 2*pi/N;
kPoints = zeros(N^2, 2);
kx = dk*(-N/2+1:N/2);
ky = kx;
nn = length(kx);
for iy = 1:nn
  i = (iy-1)*nn+1;
kPoints(i:i+nn-1,1) = kx';
kPoints(i:i+nn-1,2) = ky(iy);
end

kSet = [kx', 0.*kx']; kSet(:,2) = -pi;
kPointsExt = [kPointsExt; kSet];
kIndexExt = [kIndexExt; (N^2-N+1:N^2)'];

kSet = [0.*kx', kx']; kSet(:,1) = -pi;
kPointsExt = [kPointsExt; kSet];
kIndexExt = [kIndexExt; (N:N^2)'];
end

function [V_CH0, MAP_CH0] = GetBaseCH0(H_CH0)

global GL
% allocate space
nk = size(GL.kPoints,1);
nE = size(H_CHO,1);    % # of electorns, total (per spin)
V_CHO = zeros(nE,nE, 2); % storage for column eigen-vectors
MAP_CHO = zeros(nE, 6, 2); % storage for [E,kPoint_index,band_index, E-H index,kx,ky]
iBands = (1:16)';
% go through every k-point
jj = 1:16;
for ik = 1:nk
    % k-point
    k = GL.kPoints(ik,:);
    % spin up/down
    for spin = 1:2
        [V,E] = eig(H_CHO(jj,jj,spin) ); E = diag(E);
        MAP_CHO(jj,1,spin) = E; % energies
        MAP_CHO(jj,2,spin) = ik; % kPoint index
        MAP_CHO(jj,3,spin) = iBands; % band index
        MAP_CHO(jj,4,spin) = k(1); % k_x
        MAP_CHO(jj,5,spin) = k(2); % k_y
    end
    % iteration
    jj = jj + 16;
end
% sort everything with increasing energy
for spin = 1:2
    MAP_CHO(:,1,spin) = ReNormalize(MAP_CHO(:,1,spin));
end
% set E-H index, used in RIXS table
MAP_CHO(:,4, 1) = 1:2:2*nE-1;
MAP_CHO(:,4, 2) = 2:2:2*nE;
end
function [Beta_occ, CoF, Beta_unc, Z, CH_iPoint, Eocc] = SetBetaMatrices(inv_V_CH0,MAP_CHO, file_CH, CH)
load( file_CH );
if CH1.CH ~= CH
  disp('ERR: Core hole input data file mismatch.');
end
[V_up,E_up] = eig(CH1.H_eg(:,:,1));
[V_dn,E_dn] = eig(CH1.H_eg(:,:,2));
BetaFull_up = inv_V_CH0(:,:,1) * V_up;
BetaFull_dn = inv_V_CH0(:,:,2) * V_dn;

% allocate space
nE = size(MAP_CHO,1);
nF = nE / 8;
Beta_occ = zeros( nF,nF,2);
CoF = zeros( nF,nF,2);
Beta_unc = zeros(nE-nF,nF,2);

% extract return values
Beta_occ(:,:,1) = BetaFull_up(1:nF,1:nF);
Beta_occ(:,:,2) = BetaFull_dn(1:nF,1:nF);
Z = [det(Beta_occ(:,:,1)), det(Beta_occ(:,:,2))];
CoF(:,:,1) = ( Z(1) .* inv(Beta_occ(:,:,1)) ).';
CoF(:,:,2) = ( Z(2) .* inv(Beta_occ(:,:,2)) ).';
Beta_unc(:,:,1) = BetaFull_up(nF+1:nE,1:nF);
Beta_unc(:,:,2) = BetaFull_dn(nF+1:nE,1:nF);
CH_iPoint = CH1.CH_site;
134
E_occ = sum(sum([E_up(1:nF), E_dn(1:nF)]));
end

function SetGlobals(N)

global GL
if mod(N,4)~=0 || N<4
    error('ERR: N must be divisible by 4, and N >= 4.);
end

GL.path = sprintf('_N%02i_data_',N);
load( sprintf('%s/_RIXS_/N%02i_CH0.mat', GL.path, N) );

GL.N = N;
GL.C = CH0.C;

% DELETE:
%GL.U_eg = CH0.C.U;
%GL.Uch_eg = CH0.C.Uch;

% DELETE:
%GL.figId = 30;
GL.dir_tables = [GL.path,'/_tables_'];
GL.kPoints = CH0.kPoints;
% DELETE:
%GL.figPref = sprintf('N=%i',N);

% extended kPoints and indexes connecting with GL.kPoints
[kPoints_ext, ind_ext] = GetExtended_kPoints(GL.kPoints);
GL.kPointsExt = kPoints_ext;
GL.kIndexExt = ind_ext;

% k-points for extended Brillouin zone
[GL.kPointsFull, GL.kPointsFullExt, GL.kIndexFullExt] = GetFull_kPoints(N);

% return data from base Hamiltonian (CH0) ordered in increasing energy
[V_CH0,MAP_CH0] = GetBaseCH0(CH0.H_eg);
GL.MAP_CH0 = MAP_CH0;

classname = 'TFS NOTES:

TFS NOTES:

beta matrices

nCH = 8;
nE = size(CH0.H_eg,1);

define beta_occ
GL.beta_occ = zeros( nF, nF, 2, nCH);

define beta unc
GL.beta_unc = zeros(nE-nF, nF, 2, nCH);

define Z
GL.Z = zeros(nCH,2);

define CH_iPoint
GL.CH_iPoint = zeros(nCH, 2);

for CH = 1:nCH
    file_CH = sprintf('%s/_RIXS_/N%02i_CH%i.mat', GL.path,N,CH);

SetBetaMatrices(inv_V_CH0,MAP_CH0, file_CH, CH); 

GL.Beta_occ(:,:,CH) = Beta_occ;
GL.Cof(:,:,CH) = Cof;
GL.Beta_unc(:,:,CH) = Beta_unc;
GL.Z(CH,:) = Z;
GL.CH_iPoint(CH,:) = CH_iPoint;
vEocc_CH(CH,1) = E_occ;

% calculating resonant term for each CH case
Eocc_CH0 = sum(sum([GL.MAP_CH0(1:nF,1,1), GL.MAP_CH0(1:nF,1,2)]));
omega_in = (vEocc_CH(2)-Eocc_CH0 + vEocc_CH(1)-Eocc_CH0) / 2;
g1 = GL.C.Gamma1;
g2 = GL.C.Gamma2;
vGamma = 1i *[g1,g2, g1,g2, g1,g2, g1,g2];
GL.RES = 1.0 ./ (omega_in - (vEocc_CH - Eocc_CH0) + vGamma);

%(-
% adding distortions at Mn4+ sites:
ds = 0.01871;
dd = [ 0,0; ...
ds,-ds;... 
0,0; ...
ds, ds;... 
0,0; ...
ds,-ds;... 
0,0; ...
ds, ds ];
GL.CH_iPoint = GL.CH_iPoint + dd;
)

function SetRIXS(minmax_E)

nE = size(GL.MAP_CH0,1);
nF = nE / 8;
k = size(GL.kPoints, 1);
nRows = 8*nk*nk * 14*2 * 2; % same as: (nE-nF)*nF * 8 * 2
iRow = 1;

% RixsData Columns:
% 1-hole id, 2-electron id, 3-intensity, 4-energy
% 5:6-momentum, 7-spin, 8-indexes of k-points
RixsData = zeros(nRows,8);
DK = [0,0; pi,0; 0,pi; -pi,0; -pi/2,-pi/2; pi/2,-pi/2; -pi/2,pi/2; pi/2,pi/2];
mapOCC = GL.MAP_CH0(1:nF,:); 
mapUNC = GL.MAP_CH0(nF+1:nE,:);
rowUNC = zeros(8,nF, 2);

% amplitude calculation terms, for every {ke,le,kh,lh, spin,K}:
PH = zeros(8,1); % phase
X1 = zeros(8,1); % one CH excitation
X0 = conj(GL.Z(:,1)).* conj(GL.Z(:,2)); % no excitation
RES = GL.RES; % resonance denominator
for iUNC = 1:(nE-nF)
rowUNC(:,:,1) = GL.Beta_unc(iUNC,:,1,CH);
rowUNC(:,:,2) = GL.Beta_unc(iUNC,:,2,CH);
end

% extract rows for use with CoF
for CH = 1:8 
rowUNC(CH,:, 1) = GL.Beta_unc(iUNC,:, 1,CH);
rowUNC(CH,:, 2) = GL.Beta_unc(iUNC,:, 2,CH);
end

% populate RIXS table
for iOCC = 1:nF
for spin = 1:2
% excitation contribution
% example for spin up: Z_dn * DETERMINANT^{Beta(SwapedRow)_up}
spin_neg = mod(spin,2)+1;
for CH = 1:8
    X1(CH,1) = GL.Z(CH,spin_neg) .* (rovUNC(CH,:, spin) * (GL.CoF(iOCC,:, spin,CH)).');
end

% TEST DETERMINANT:
CH = 1;
r = GL.Beta_unc(iUNC,:, spin,CH);
B = GL.Beta_occ(:,:, spin,CH);
B(iOCC,:) = r;
d1 = det(B);
d2 = (rovUNC(CH,:, spin) * (GL.CoF(iOCC,:, spin,CH)).');
err = abs(d1 - d2);
if err > 1e-15
    err
end

% k-indexes, band-indexes
ik_h = mapOCC(iOCC,2, spin); ik_e = mapUNC(iUNC,2, spin);
% il_h = mapOCC(iOCC,3, spin); il_e = mapUNC(iUNC,3, spin);
iH = mapOCC(iOCC,4, spin); iE = mapUNC(iUNC,4, spin);
% momentum change in 1-st BZ
dk = GL.kPoints(ik_e,:) - GL.kPoints(ik_h,:);
% energy
v = mapUNC(iUNC,1, spin) - mapOCC(iOCC,1, spin);

for iDK = 1:8
    % momentum change in the extended BZ
    [q, iq] = CorrectQpt(-dk - DK(iDK,:));
    % phase
    PH = exp(-1i * (GL.CH_iPoint * q') );
    % amplitude for all CH
    A = sum(PH .* X1 .* X0, 1);
    % one data row for rixs table
    RixsRow = [ iH, ... % hole id
                iE, ... % electron id
                A*conj(A), ... % rixs intensity
                w, ... % w energy
                q(1), ... % q_x momentum
                q(2), ... % q_y momentum
                spin, ... % spin
                iq ... % q-index
                ];
    RixsData(iRow,:) = RixsRow;
iRow = iRow+1;
end % iDK
end % iUNC
if iRow-1 ~= nRows
    disp('ERR: RIXS Table - number of processed rows mismatched.');
end

% RixsData = RixsData(1:iRow-1,:);
% reduce table to given energy bounds
RixsData = RixsData(RixsData(:,4) <= minmax_E(2), :);
RixsData = RixsData(RixsData(:,4) >= minmax_E(1), :);

% set new k-points for extended BZ
GL.kPoints = GL.kPointsFull;
GL.kPointsExt = GL.kPointsFullExt;
GL.kIndexExt = GL.kIndexFullExt;

% set new k-points for extended BZ

% Averaging w.r.t. qx <-> -qx:
% create swap array for ik
N = GL.N;
nk = size(GL.kPoints,1);
ind_swap = (1:nk)';
for iOff = 0:N-1
    for i = 1:N-1
        ind_swap(iOff*N + i) = iOff*N + N-i;
    end
end
%
% process new table
RixsData_qxNeg = RixsData;
for i = 1:size(RixsData_qxNeg,1)
    ik = ind_swap( RixsData_qxNeg(i,8) );
    RixsData_qxNeg(i,8) = ik;
    RixsData_qxNeg(i,5) = GL.kPoints(ik,1);
end
%
% merge with existing table, and averaging intensity
RixsData = [RixsData; RixsData_qxNeg];
RixsData(:,3) = RixsData(:,3) / 2;
%
% sort by descending intensity and pass to global
GL.RIXS = sortrows(RixsData, -3);
%
% integrate all intensities, separately per spin
nk = size(GL.kPoints,1); % must be recalculated, now for extended BZ
SumIrixs = zeros(nk,2);
for ik = 1:nk
    SumIrixs(ik,1) = sum( RixsData(RixsData(:,8) == ik & RixsData(:,7) == 1, 3) );
    SumIrixs(ik,2) = sum( RixsData(RixsData(:,8) == ik & RixsData(:,7) == 2, 3) );
end
if abs(sum(sum(SumIrixs)) - sum(RixsData(:,3))) > 1e-12
    disp('ERR: Sum Irixs mismatch. See SetRIXS().');
end
GL.RIXS_SUM = SumIrixs;
%
% cleanup GL
GL = rmfield(GL, 'kPointsFull');
GL = rmfield(GL, 'kPointsFullExt');
GL = rmfield(GL, 'kIndexFullExt');
GL = rmfield(GL, 'Beta_occ');
GL = rmfield(GL, 'CoF');
GL = rmfield(GL, 'Beta_unc');
GL = rmfield(GL, 'Z');
GL = rmfield(GL, 'CH_iPoint');
end

%==========================================================================
% This is necessary to eliminate 14/15-th significant
digit discrepancy in degenerate values
function EE = ReNormalize(E)
    [EE, ind] = sortrows(E,1);
dig_eps = 1000*eps(E(1));
igr = 1;
groups(igr,1) = 1;
val = EE(1);
for i = 2:size(EE,1)
    if values are not close
if abs(EE(i) - val) > dig_eps
val = EE(i);
groups(igr,2) = i-1;
igr = igr+1;
groups(igr,1) = i;
end
end

groups(igr,2) = i;

% fixing values
for i = 1:size(groups,1)
a = groups(i,1);
b = groups(i,2);
avg = mean( EE(a:b,1) );
EE(a:b,1) = avg;
end

EE = sortrows([EE, ind],2);
EE = EE(:,1);
end

% map new q-value onto extended BZ
function [q, iq] = CorrectQpt(q)
global GL
Eps = 1e-10;
% kx values
if q(1) > pi
q(1) = q(1) - 2*pi;
elseif q(1) <= -pi + Eps
q(1) = q(1) + 2*pi;
end
% ky values
if q(2) > pi
q(2) = q(2) - 2*pi;
elseif q(2) <= -pi + Eps
q(2) = q(2) + 2*pi;
end
% indexes
kk = (GL.kPointsFull(:,1) - q(1)).^2 + (GL.kPointsFull(:,2) - q(2)).^2;
q = GL.kPointsFull(iq,:);
end

% SAVING DATA:
function TableEnergy()
global GL

file = sprintf('%s/N%02i__RIXS_Energies.txt',GL.dir_tables,GL.N);
fid = fopen(file, 'w');
fprintf(fid, '+--------------------------------------------+
');
fprintf(fid, '| N = %2i: ELECTRON ENERGY SPECTRUM |
',GL.N);
fprintf(fid, '------+-----------+-----------------+----+----
');
fprintf(fid, 'iE/iH | Energy |BZ: kx ky |band| sp |
');
fprintf(fid, '------+-----------+-----------------+----+----
');

nT = size(GL.MAP_CH0,1);
NF = nT/8;
cSp = {'u ', 'd'};
for i = nT:-1:1:
% spin down/up
for spin = [2,1]
v = GL.MAP_CH0(:,i,spin);
fprintf(fid, ' %4i | %9.4f |%s%s | %2d | %s\n', Num2Latex(v(4),0,[8,4]), Num2Latex(v(6),0,[8,4]), v(3), cSp{spin});
end

end
% fermi level separator
if i == nRs
    fprintf(fid, '------------------------------- FERMI LEVEL -------------------------------\r\n');
end
fprintf(fid, '-------------------------------\r\n');
fclose(fid);
fprintf(' * File [%s] have been generated.\n',file);
end

function TableIntensity()
    global GL
    file = sprintf('%s/N%02i__RIXS_Intensity.txt',GL.dir_tables,GL.N);
    fid = fopen(file, 'w');
    fprintf(fid, '+----------------------------------------------------------------+
');
    fprintf(fid, '| N = %2i: RIXS CALCULATION - PARTIAL TABLE |
', GL.N);
    fprintf(fid, '------+------+--------------------+---------+-----------------+---
');
    fprintf(fid, ' H_id | E_id | I_RIXS | del_w | del_q(x,y) | sp
');
    fprintf(fid, '------+------+--------------------+---------+-----------------+---
');
    nR = min(size(GL.RIXS,1), 170); % limit to about 3 pages in PDF
    cSp = {'u ',' d'};
    for i = 1:nR
        fprintf(fid, ' %4i | %4i | %.16f |%8.4f |%s%s | %s
', GL.RIXS(i,1:4), ... 
        Num2Latex(GL.RIXS(i,5),0,[8,4]), Num2Latex(GL.RIXS(i,6),0,[8,4]),
        cSp{GL.RIXS(i,7)});
    end
    fprintf(fid, ' ... | ... | ... | ... | ... ... | ..
');
    fprintf(fid, '------+------+--------------------+---------+-----------------+---
');
    fclose(fid);
    fprintf(' * File [%s] have been generated.\n',file);
end

function TableSumIntensity()
    global GL
    file = sprintf('%s/N%02i__RIXS_SumIntensity.txt',GL.dir_tables,GL.N);
    fid = fopen(file, 'w');
    fprintf(fid, '+--------------------------------------------------------------+
');
    fprintf(fid, '| N = %2i: Integrated I_RIXS |
', GL.N);
    fprintf(fid, '-----+--------------------+--------------------+----------------
');
    fprintf(fid, 'k_id | Sum I_RIXS_up | Sum I_RIXS_dn | kx ky
');
    fprintf(fid, '-----+--------------------+--------------------+----------------
');
    Nk = size(GL.kPoints,1);
    for ik = 1:Nk
        fprintf(fid, ' %2i | %.16f | %.16f |%s%s
', ik, GL.RIXS_SUM(ik,:), ... 
        Num2Latex(GL.kPoints(ik,1),0,[8,4]), Num2Latex(GL.kPoints(ik,2),0,[8,4])
        );
    end
    fprintf(fid, '-----+--------------------+--------------------+----------------
');
    fclose(fid);
    fprintf(' * File [%s] have been generated.\n',file);
end

function Table_Matrix_kMap()
    global GL
    sPref = sprintf('%s/N%02i__kMap',GL.dir_tables,GL.N);
    % export coordinate layout
    kxy = GL.kPoints(1:GL.N,1);
    file = sprintf('%s_kx-ky.txt',sPref);
    fid = fopen(file, 'w');
    fprintf(fid, 'kx values:
');
    fprintf(fid, '% .16f ',kxy);
    fprintf(fid, ' 
');
    fprintf(fid, 'ky values:
');
    fprintf(fid, '% .16f ',flipud(kxy));
fclose(fid);

% export k-map matrix values
nD = sum(GL.RIXS_SUM, 2);
nD2 = flipud(reshape(nD, GL.N, GL.N)');
file = sprintf('%s_matrix_rixs.txt',sPref);
fid = fopen(file, 'w');
for ir = 1:size(nD2,1)
    fprintf(fid, ' % .16f', nD2(ir,:));
    fprintf(fid, '
');
end
fclose(fid);

fprintf(' * Table file [%s] have been generated.
',file);

%=====================================
% SAVING/LOADING:
function SaveCalcRixs()
% ACCESS to save
global GL
save(sprintf('%s/_RIXS_/N%02i_CalcRixs.mat',GL.path,GL.N), 'GL');
end

%=====================================
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