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STUDY OF ELECTRONIC STRUCTURES OF SOLIDS WITH STRONGLY INTERACTING ELECTRONS

By

Yen-Sheng Su

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

Study Of Electronic Structures Of Solids With Strongly Interacting Electrons

By

Yen-Sheng Su

This work contains studies of two classes of perovskite transition metal oxides. The first class is the layered perovskite cuprates and the related nickelate. The second class is the three dimensional perovskite manganites. Both model and *ab initio* calculations are carried out for the two classes of systems. The dissertation is therefore divided into the following four parts.

The first part is about the 3-band Hubbard model. The model is commonly used for describing the electronic properties of the important CuO₂ layers in the crystals of high-T_c superconducting cuprates, such as doped La₂CuO₄ and YBa₂Cu₃O₇. The straightforward perturbation expansion on the model taking t_{pd}/ε_{pd} (~0.36 for the cuprates) as the small parameter does not converge. In this work, I show that there exist canonical transformations on the model Hamiltonian such that the perturbation expansion based on the transformed Hamiltonians converges.

In the second part, crystal Hartree-Fock calculations are carried out for La_2NiO_4 and La_2CuO_4 . The results predict correctly that these two materials are antiferromagnetic insulators, in contrast to the wrong predictions made by the density functional calculations using the local spin density approximation (LSDA). The spin form factors of the materials are also calculated. The results agree with previous theoretical works using an embedded cluster model. The calculated spin form factor of La_2CuO_4 is consistent with the few experimental data currently available, while the results for La_2NiO_4 show a large discrepancy between theory and experiment. We question the accuracy of the experimental results of La_2NiO_4 and call for more experiments to settle the issue.

In the third part, crystal Hartree-Fock calculations are carried out for LaMnO₃. Our main focus is on the magnetic and orbital orderings, the effect of the crystal distortion from the cubic perovskite structure, and the analysis of the projected density of states. In addition, we also find unexpected charge associated with the Mn ions. The effective spin Hamiltonian obtained by mapping the energies of different magnetically ordered states is consistent with experimental data of the spin wave dispersion, while it is qualitatively different from that of a LSDA calculation which was also claimed to be consistent with the experiment. We show that the current experimental accuracy is not enough to distinguish these two theories.

In the fourth part, I report a study on possible extensions of the double-exchange (DE) model for the doped manganites in the hope of understanding the recently observed softening of the spin wave dispersion near the Brillouin zone edge. I also argue that most models in the literature are flawed by assuming uncoupled normal mode vibrations of the MnO₆ octahedral clusters in the crystal. As a first trial, I consider several possible electron-phonon couplings based on the single-band DE model. The results show that the spin wave states are robust and the spin wave dispersion gets very slightly hardened in the presence of the electron-phonon couplings. This suggests that the observed softening of the spin wave dispersion may be beyond the scope of the single-band DE model.



To My Parents and My Wife

To My Parents and My Wife

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It has been six years since I came to Michigan State University, East Lansing, in 1994. This is a bit longer than I would have liked to get my Ph.D. study done. But the delay is mostly caused by a pleasant reason: The life here in East Lansing is so cheerful that I simply lost the motivation to rush for the degree. ©

I was very fortunate to join the group of Profs. T. A. Kaplan, S. D. Mahanti in Physics and J. F. Harrison in Chemistry departments. All the three professors are outstanding scholars and excellent teachers. They are all very knowledgeable in Physics in general but they each also have their own specialties. The discussion in our weekly group meeting is often full of sparks of intelligence. That I can learn from the best the various subjects of physics is truly the most wonderful thing about my study here. I would like to express my deep gratitude to them. They are essentially all my advisors, although my formal advisor is nominally only Prof. Kaplan.

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Chapter 1

Introduction

The fundamental physical law at the atomic length scale and above has long been known; namely, the Schrödinger Equation with Coulomb interaction between charged particles plus secondary relativistic corrections like spin-orbit coupling. For electronic systems, a wonderful feature of the theory is that often the electrons can be treated as non-interacting particles moving in an effective potential to a good approximation, provided the proper statistics are obeyed. This approximation is a kind of mean-field theory and is often called a single-particle picture, where the electron-electron interaction is treated in an average way. In this picture, one first calculates the energy levels of an electron in the presence of an effective potential. Then the states of a system with N electrons will be just all possible configurations obtained by filling the N electrons in the set of energy levels in different ways obeying the Pauli exclusion principle. For example, the band theory of solids with periodic structures and the interpretation of the atomic emission/absorption spectra by transitions of electrons between energy levels are two of the most well known and successful single-particle theories.

Corrections to the single-particle picture are often called correlation or many-body effects and cause only quantitative changes in many physical systems. However, in some circumstances electron correlation can surprise us by leading systems to unexpected new states or phases. The Mott insulator [1] and the fractional Quantum Hall effect [2] are two of the famous examples. Simply put, correlation is probably the very source of most of the radically new physics at the atomic level that we are still discovering everyday even after the fundamental physical law was discovered so long ago in 1926 by E. Schrödinger.

In this dissertation, I study the perovskite La-cuprate (and isostructural Lanickelate) and La-manganite. Both have been the focus of intensive studies by many researchers [3-4]. When properly doped with some elements, the cuprate reveals high- T_c superconductivity and the manganite reveals the so-called colossal magnetoresistance. The interesting physics of the two systems is generally believed to be dictated by the strong interaction among the transition metal (Cu, Ni, Mn) 3d electrons and the oxygen 2p electrons. To understand the observed physical properties of these systems, correlation effects must be taken into account to some extent. For both systems, I study model Hamiltonians commonly used in the literature and also carry out *ab initio* calculations using the crystal Hartree-Fock (HF) method. For the latter we use the unrestricted HF method, which allows a sensible treatment of the ground state even when correlation effects are large. The detailed motivation for the selection of different models and the calculation methods will be given in the respective chapters.

In Chapter 2, I study the 3-band Hubbard model for cuprate and nickelate using a perturbation approach called the effective Hamiltonian method. In Chapter 3, I carry out crystal HF calculations for the cuprate and nickelate and compare various physical quantities obtained with those from the Local Spin Density Approximation (LSDA) [5] and those from an embedded cluster approximation [6]. In Chapter 4, I carry out the crystal HF calculation for the manganite and compare the results with those of LSDA calculations. Some quantities, like the order of the oxygen p band and the manganese d

band, and the charge of the manganese ions in the crystal, are found to be dramatically different from those of LSDA calculations or those of the commonly conceived picture. The significance of the discrepancy will be discussed. In Chapter 5, I report a study on modified Double-Exchange models for the doped manganite motivated by the recent intriguing experimental observation of phonon-induced softening of the spin wave dispersion near Brillouin zone boundaries. In Chapter 6, some concluding remarks of the work of this dissertation are given.

Chapter 2

Small-Bandwidth Perturbation Theory for Highly-Covalent Mott Insulators^{*}

2.1 Introduction

The question of how to set up a perturbation theory for Mott insulators like NiO, $KNiF_3$, Fe_2O_3 , was considered in 1959 by P. W. Anderson [7]. The object was to take advantage of the obviously localized property of the magnetic electrons to construct the theory, where the interatomic overlap of localized orbitals is treated as the small parameter. Such a theory leads to low-lying states that are governed by the Heisenberg spin Hamiltonian, in leading order. At the time, it was known that most of the low-temperature properties of these materials could be understood on the basis of such a Hamiltonian.

Anderson, on considering how to determine the localized orbitals, stated that there exist "exact" localized orbitals (orthogonal, and thus called Wannier functions) which will make the perturbation theory converge well. These orbitals were required to be nonmagnetic (spin-up and -down orbitals the same), as is natural, since the magnetic properties were to be derived from the spin Hamiltonian resulting from the perturbation theory (p.t.). Anderson gave an explicit prescription, namely Wannier functions derived

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from Hartree-Fock theory in which the spins of the magnetic ions were all parallel. It was noted some time later [8] that there was an inconsistency with this, since Hartree-Fock eigenstates with up and down spins differ in such a situation. [9] An alternative approach was studied [8] based on the so-called Thermal Single Determinant Approximation (TSDA) [10], a variational generalization of thermal Hartree Fock theory. Solving this TSDA for non-magnetic localized solutions at sufficiently low temperature amounted to minimizing the mean determinantal energy, averaged over all spin configurations of the magnetic ions, an approach adopted by Gondaira and Tanabe [11]. It was shown for a small cluster model [8,11] which we can call H-He-H (hydrogenhelium-hydrogen) and for a 1-D crystal model [8] (the corresponding H-He chain) that this TSDA choice indeed improved, quite dramatically, the convergence rate of perturbation theory for the Heisenberg exchange parameter *J*, through 4th order in the H-He overlap.

The overlap, or more precisely, the amplitude for cation-anion hopping, is small in the highly ionic materials considered at the time, e.g. NiO, $KNiF_3$, so the p.t. was expected to converge rapidly. For this reason higher order perturbations were not investigated. However, materials that have recently become of interest in connection with high-temperature superconductivity, namely the cuprates and the related La_2NiO_4 , are thought to be much more covalent. Doubts about the validity of perturbation theory in this connection, specifically for the 3-band Hubbard model of a CuO₂ plane (Fig. 2.1), have been expressed [12-14]. And, in fact, later we have shown [15] that straightforward perturbation theory does **not** converge, specifically for the version of the 3-band model due to Hybertsen *et al.* [12], which is rather realistic for many physical observables [16], and is quite similar to other versions of the 3-band model [17-20].



Figure 2.1: CuO_2 plane.

Clearly then it is of interest to try the TSDA approach to find new localized orbitals, and to test the implied new perturbation expansion for convergence. In fact, the question of convergence of p.t. within the 3-band model has been addressed [13,14], and rapid convergence of a new p.t. was claimed. But the transformation in these works involved both 1- and 2-body transformations. (Finding new localized orbitals is an 1-body transformation.) It is important to understand how far one can go with the 1-body transformation alone, because of its relative conceptual simplicity and its historical interest. This is the content of this chapter.

We have been motivated to explore these questions by difficulties in connection with calculating the ground state spin density in the cuprates and La_2NiO_4 [21,22]. The type of perturbation theory discussed above, which in effect separates the spin and space (or charge) degrees of freedom, might be the only hope at present of making tractable *ab* *initio* calculations of this observable. This is due to the fact that the reduction of the ordered spin due to zero-point or quantum spin fluctuations (QSF), which is large in these cases, constitutes a macroscopic correlation effect. That is, (i) in principle it requires the thermodynamic limit for its very existence, and therefore one needs very large systems to estimate the QSF [23], and (ii) the wave function representing such a state requires a linear combination of many Slater determinants. Thus, even with the remarkable advances in computational many-body physics (e.g. Refs. 24 and 25), the present problem is still beyond the reach of those approaches. Also, standard band-theoretic approaches fail to capture essential physics (the local spin density approximation misses the antiferromagnetism and insulating property of La_2CuO_4 [26], and the Hartree-Fock method (unrestricted) misses the QSF).

Since the work reported here involves calculations only for a small cluster, the spin density of a crystal can't be addressed (the spin density in a finite cluster with an even number of electrons is zero, since the ground state is a singlet). Instead we will be investigating the Heisenberg exchange parameter J as an indicator of convergence of the perturbation expansions. In Sec. 2.2 we define the Hamiltonian to be considered, review effective-Hamiltonian perturbation theory, and the TSDA. In Sec. 2.3 we describe the three types of single-particle transformations considered, which we call *site localization*, *cell localization*, and *no localization* (the names are after the transformed ligand p orbitals surrounding the magnetic cations), and find the best in each case according to the TSDA. Also in this section, J is calculated to high order in p.t. to examine its convergence properties. In Sec. 2.4 we carry out the particular 2-body transformation suggested by the work of Ref. 13, for the special model they considered, as a check; we

also carry this out for the model of Hybertsen *et al.* [16]. A summary and conclusions are given in Sec. 2.5. A brief overview of the results obtained can be seen by glancing at Figs. 2.3, 2.5, 2.7, 2.9, 2.10 which show the non-convergent series of straightforward p.t., and the rather dramatic improvement obtained in each of the four modifications, respectively.

2.2 The model, effective-Hamiltonian perturbation theory, and TSDA

2.2.1 Model Hamiltonian

We consider the 3-band Hubbard Hamiltonian (sometimes referred to as the Anderson lattice model) as parametrized by Hybertsen *et al.* [12,16]:

$$H = H_1 + H_U + H_K \tag{2.1}$$

where

$$H_{1} = \varepsilon \sum_{i} n_{i}^{p} + t_{pd} \sum_{\langle il \rangle \sigma} (c_{i\sigma}^{d+} c_{l\sigma}^{p} + \text{h.c.}) + t_{pp} \sum_{\langle ll' \rangle \sigma} (c_{l\sigma}^{p+} c_{l'\sigma}^{p} + \text{h.c.}), \qquad (2.1a)$$

$$H_{U} = U_{d} \sum_{i} n_{i\uparrow}^{d} n_{i\downarrow}^{d} + U_{p} \sum_{l} n_{l\uparrow}^{p} n_{l\downarrow}^{p} + U_{pd} \sum_{\langle il \rangle} n_{i}^{d} n_{l}^{p} , \qquad (2.1b)$$

and

$$H_{K} = K_{pd} \sum_{\langle il \rangle \sigma \sigma'} c_{i\sigma}^{d} c_{l\sigma'}^{d} c_{l\sigma'}^{p} c_{l\sigma}^{p} + K_{pp} \sum_{\langle ll' \rangle \sigma \sigma'} c_{l\sigma'}^{p} c_{l\sigma'}^{p} c_{l\sigma'}^{p} c_{l\sigma'}^{p} c_{l\sigma'}^{p} .$$
(2.1c)

 $c_{i\sigma}^{v*}$ creates a hole in a Wannier function w_{vi} of type v at site i with spin σ , $n_i^v = \sum_{\sigma} n_{i\sigma}^v$, $n_{i\sigma}^v = c_{i\sigma}^{v*} c_{i\sigma}^v$. The orbital at a copper site is $d_{x^2-y^2}$; at each oxygen site there is one p orbital. The parameter values are $\varepsilon = 3.6$, $t_{pd} = -1.3$, $t_{pp} = -0.65$, $U_d = 10.5$, U_p = 4, $U_{pd} = 1.2$, $K_{pd} = -0.18$, $K_{pp} = -0.04$, all in eV [27]. Note that for the convenience of having the d-p hopping parameters all the same, and similarly for the p-p hopping, as in Eq. (2.1a), one has to set up the underlying Wannier functions in the way that they may change signs under the crystal or cluster symmetry. The signs corresponding to orbital phases are chosen as follows: if $d_{x^2-y^2}$ exists at a particular Cu, then at the O's immediately to its right and left (along the x-axis) the orbitals are p_x and $-p_x$ respectively; similarly, the orbitals at the nearest O's below and above are p_y and $-p_y$ overlap always negative. We limit ourselves to the case where the number of holes equals the number of Cu sites, i.e. the Mott insulator limit.

2.2.2 Formal perturbation theory

The form of the perturbation theory used involves an effective Hamiltonian. Given

$$H\Psi = E\Psi, \tag{2.2}$$

then the effective Hamiltonian Heff satisfies

$$H_{eff}(E)P\Psi = EP\Psi, \qquad (2.3)$$

namely

$$H_{eff}(E) = P\{H + H[Q(E - H)Q]^{-1}H\}P.$$
(2.3a)

Here, P = 1-Q is a projection operator which projects Ψ onto a given subspace. The "inverse of the corner" [28] $G(E) \equiv [Q(E-H)Q]^{-1}$ has to be understood as the matrix with zeroes everywhere except in the Q-subspace, where the matrix is the inverse of the Qprojection of E - H. Similarly, $Q \equiv Q^{-1}$ is the matrix with zeroes everywhere except for the Q-subspace, where it is the unit matrix. We choose the P-subspace as that defined by the ground states of some chosen unperturbed Hamiltonian H_0 , with eigenvalue E_0 . Then $PHQ = P(H_0+V)Q = PVQ$, and Eq. (2.3) can be rewritten as

$$P\{V + VG(E)V\}P\Psi = \delta E P\Psi, \qquad (2.4)$$

where $\delta E = E - E_0$. Expanding G(E) in powers of $\delta E - V$, and substituting the full lefthand side of Eq. (2.4) for $\delta E P \Psi$ everywhere it appears in the expansion, Eq. (2.4) becomes [29]

$$P\{H_{0} + V + VG_{0}V + (VG_{0}VG_{0}V - VG_{0}^{2}VPV) + \cdots\}P\Psi = EP\Psi.$$
(2.5)

where

$$G_0 = [Q(E_0 - H_0)Q]^{-1}.$$

Straightforward perturbation theory takes the terms in H that involve hopping $(t_{pd}$ and $t_{pp})$ plus the exchange terms (H_K) as the perturbation V (and $H_0 = H - V$). We studied [15] this p.t. in the case of a crystal (infinite CuO₂ plane), where we obtained the first three terms (3rd, 4th and 5th order) for the nearest Cu-Cu exchange parameter in the Heisenberg Hamiltonian [30]. We also studied this p.t. on the cluster Cu₂O₇, using the

embedding scheme described in Ref. 16, and showed that the corrections to J increase in magnitude and oscillate in sign through 14th order [15]. See Fig. 2.3 below.

2.2.3 TSDA

To help in choosing transformations which are to define new p.t.'s (i.e. new choices of V), we will appeal to the TSDA [10] which, essentially, finds the "best" 1-particle wave functions according to the free energy variational principle (for the canonical ensemble)

$$F(\rho) \equiv tr(\rho H) + \beta^{-1} tr(\rho \ln \rho) \geq -\beta^{-1} \ln tr \exp(-\beta H).$$
(2.6)

Here ρ is any density operator and β^{-1} is Boltzmann's constant times absolute temperature. Writing $\rho = Z_a^{-1} \exp(-\beta H_a)$ with $Z_a = tr \exp(-\beta H_a)$, one can consider H_a as an approximate Hamiltonian. The TSDA is defined by taking H_a as a general real function of the occupation number operators for some complete orthonormal set of oneparticle wave functions ψ_v and then varying the functional form of H_a and the ψ_v 's to minimize F. A complete set of eigenstates of H_a can be chosen as single Slater determinants with all the various subsets of the ψ_v 's occupied. It turns out [10] that the best function H_a for a given set of ψ_v is simply the determinantal energy of the exact Hamiltonian H with respect to that set of ψ_v . In other words, if H is expressed with respect to an arbitrary complete orthonormal set of one-particle wave functions ψ_v as

$$H = \sum_{\nu\mu} h_{\nu\mu} c_{\nu}^{\dagger} c_{\mu} + \frac{1}{2} \sum_{\nu\mu\lambda\kappa} \nu_{\nu\mu\lambda\kappa} c_{\nu}^{\dagger} c_{\mu}^{\dagger} c_{\kappa} c_{\lambda}, \qquad (2.7)$$

where the subscripts v, μ , .. each label both the spatial and spin quantum numbers and the quantities $h_{\nu\mu}$ and $\nu_{\nu\mu,\lambda\kappa}$ are matrix elements (which, by properly choosing the phase factors of the ψ_{ν} 's, are taken to be real in this paper), respectively, of the one- and two-body terms in the exact Hamiltonian *H*, then H_a will be

$$H_{a} = \sum_{\nu} h_{\nu\nu} n_{\nu} + \frac{1}{2} \sum_{\nu\mu} (\nu_{\nu\mu,\nu\mu} - \nu_{\nu\mu,\mu\nu}) n_{\nu} n_{\mu}$$
(2.8)

which contains terms linear and quadratic in the occupation-number operators n_v corresponding to the ψ_v 's. (The distinction between this and thermal Hartree Fock theory is that in the latter, H_a is restricted to be linear in the occupation numbers, i.e. a oneelectron operator.) H_a turns out to be equal to the diagonal part of H with respect to the single-determinantal states constructed from having the one-particle states μ , ν , ... occupied in all possible ways. As an example, for the particular model Eq. (2.1) the determinants with the original Wannier functions occupied in all possible ways have energies given by

$$H_a = \varepsilon \sum_i n_i^p + H_U + K_{pd} \sum_{\langle il \rangle \sigma} n_{i\sigma}^d n_{l\sigma}^p + K_{pp} \sum_{\langle ll' \rangle \sigma} n_{l\sigma}^p n_{l'\sigma}^p, \qquad (2.9)$$

the values of the occupation numbers being defined by the determinant being considered. Furthermore, stationarity of $F(\rho)$ with respect to the ψ_v 's implies [10]

$$< n_{\nu} - n_{\mu} > h_{\nu\mu} + \sum_{\lambda} < (n_{\nu} - n_{\mu})n_{\lambda} > (\nu_{\nu\lambda,\mu\lambda} - \nu_{\nu\lambda,\lambda\mu}) = 0,$$
 (2.10)

where the brackets $\langle ... \rangle$ mean average over the canonical ensemble with H_a as Hamiltonian, i.e. for any operator A, $\langle A \rangle$ means

$$\langle A \rangle \equiv \frac{tr(e^{-\beta H_a} A)}{tr(e^{-\beta H_a})}.$$
(2.11)

A physical interpretation of Eq. (2.10) is presented in Appendix A.

It should be noted that TSDA allows localized solutions in crystals, or analogously in molecules with high symmetry, in contrast to thermal HF approximation [10,31]. This distinction is important in the Mott insulators we are considering. Further, the form of the localized orbitals in TSDA is dictated by the Hamiltonian, H. As far as we are aware TSDA is the only variational theory in the literature with this formal property.

It would be natural to ask here why not simply use the TSDA as a variational approximation to the Hamiltonian *H* of Eq. (2.1)? The answer is that it is known to give a poor description of the low-energy physics when the hopping is very small (actually, specifically in the case of the single-band Hubbard model), so that the low-lying energies are accurately given by the Heisenberg model. E.g., it gives a Curie law susceptibility rather than the correct Curie-Weiss law at temperatures above the antiferromagnetic transition temperature, and it gives the latter about an order of magnitude too large. [32] Thus in the present work we are not considering TSDA in this way. Rather we are using it as a formal device to help discover a 1-body transformation that (hopefully) will lead, via a rapidly convergent perturbation theory, to the proper effective Hamiltonian (it is the solution of the latter that will determine accurately the low-energy physics of the model). The early success of this approach discussed in the Introduction has motivated our present investigation.

Thus in our TSDA considerations here, β will be considered as a parameter whose optimum value β_0 would ideally give the "fastest" convergence of the perturbation expansion Eq. (2.5). As is apparent from the above TSDA equations, the solution, i.e. the ψ_{ν} 's, will depend on β_0 . If we take a finite number of terms in the perturbation expansion (as one would do), then the resulting effective Hamiltonian will thus depend on $\beta_{0}.\;$ For properties, e.g., β_0 would thermal then enter the partition function $\sum_{n} \exp[-E_{n}(\beta_{0})/k_{B}T]$ where $E_{n}(\beta_{0})$ are the eigenvalues of the spin Hamiltonian and T is the physical temperature. When working within the TSDA to find the ψ_v 's, we will think of β^{-1} intuitively as temperature to help find a "good" TSDA solution, i.e. a solution that gives rapid convergence of p.t.; in fact we will tend to consider large β , since the effective Hamiltonian is designed to give the low-energy states of H. (One could probably not explore the whole range of β in practice.)

One should realize that even for the small-basis-set model of the small cluster treated below, the 1-body Hilbert space is too large to explore completely. So one needs *some* guide. There are alternate approaches to determining localized orbitals, widely used in quantum chemistry; see Ref. 25 and references contained there, and Ref. 33. These conceivably could be useful in the magnetism problem considered here, and should probably be studied in this connection.

2.3 Achievement of convergence via 1-body transformations

As mentioned above, we applied [15] p.t. to the Hamiltonian in the original Wannier-function representation, i.e. Eq. (2.1), where the perturbation V incorporates all the hopping and exchange terms and H_0 , the rest. For the crystal (an infinite CuO₂ plane) we obtained the first 3 contributions to the nearest-neighbor exchange parameter J (they occur in 3rd, 4th and 5th order), with no sign of convergence [34]. We also calculated J to very high order for the embedded cluster Cu₂O₇, shown in Fig. 2.2, with two holes. The results of the latter work are given in Fig. 2.3. Plotted there is

$$J^{(m)} = \sum_{n=1}^{m} J_n, \qquad (2.12)$$

where J_n is the contribution to J (the splitting between the lowest singlet and triplet) from n-th order p.t.. The non-convergence is apparent, the result oscillating with increasing amplitude about the exact value (straight line) calculated by direct diagonalization.



Figure 2.2: The cluster Cu_2O_7 . The symbols at each site serve both as labels and as orbitals.



Figure 2.3: The *n*th approximation to J vs n according to straightforward perturbation theory. The horizontal line shows the exact value of J. From Ref. 15.

To follow up on the idea [7] that an appropriate change of 1-electron basis states, with its consequent change in the partition of H into unperturbed and perturbed pieces, might improve the convergence, we consider the unitary linear transformation,

$$c'_{i\sigma} = \sum_{j} A_{ij} c_{j\sigma} \,. \tag{2.13}$$

An essential assumption we make about this transformation is that it maintains localization and symmetry of the *d* states and that all states should be nonmagnetic. The reason for this is that we want to maintain the property of the straightforward p.t. that the low-lying energies are governed by a Heisenberg Hamiltonian with the symmetry of the nuclear structure. A_{ij} is a unitary matrix, which we take as real, since we assume the new Wannier functions are real. The spin independence of A_{ij} embodies the assumption that the new Wannier functions are nonmagnetic (they are each a product of a spatial orbital times a spin function, α or β , the spatial orbital being the same for either spin). These properties are assumed of course to hold for the original Wannier functions, i.e. those created by the $c_{i\sigma}^{*}$.

2.3.1 Site localization

We begin with our first scheme which we call *site localization*, defined by the requirement that the new Wannier functions have the same symmetry properties as the original ones. Referring to Fig. 2.2, let σ_v and σ_h be reflections in the vertical and horizontal symmetry axes, respectively. Then the *d* states are taken to satisfy

$$d_1' = -\sigma_v d_2' \tag{2.14}$$

(a similar relation being assumed, of course, for the original, unprimed, orbitals; the sign choice follows the discussion in Sec. 2.2.1). Similarly, we require

$$p'_{2} = -\sigma_{v}p'_{5}, \quad p'_{3} = -\sigma_{v}p'_{6}, \quad p'_{1} = -\sigma_{v}p'_{1}, \quad \text{etc.}$$

$$p'_{2} = \sigma_{h}p'_{4}, \quad p'_{5} = \sigma_{h}p'_{7}, \quad p'_{3} = \sigma_{h}p'_{3}, \quad \text{etc.}$$
(2.15)

Eqs. (2.14) and (2.15), satisfied also by the unprimed Wannier functions, define "site localization".

One can see that these requirements plus orthonormality are not sufficient to completely determine the transformation. A simple example is the 3-site cluster $d_1 - p_1 - d_2$ or Cu₂O: Then the two symmetry requirements, Eq. (2.14) and $p'_1 = -\sigma_v p'_1$, give

$$d'_{1} = N_{1}(d_{1} + A_{1}d_{2} + A_{2}p_{1})$$

$$d'_{2} = N_{1}(A_{1}d_{1} + d_{2} + A_{2}p_{1}).$$

$$p'_{1} = N_{2}[B(d_{1} + d_{2}) + p_{1}]$$

The N_i are normalization constants, determined directly in terms of the three coefficients, A_1 , A_2 , and B. Orthogonality clearly gives two equations, leaving one independent coefficient. For the cluster Cu₂O₇, it turns out that there are 9 independent coefficients. It is useful to see this in detail. We can write the transformation as

$$d'_{1} = N_{1}[d_{1} + A_{1}d_{2} + A_{2}p_{1} + A_{3}(p_{2} + p_{4}) + A_{4}p_{3} + A_{5}(p_{5} + p_{7}) + A_{6}p_{6}]$$

$$p'_{1} = N_{2}[B_{1}(d_{1} + d_{2}) + p_{1} + B_{2}(p_{2} + p_{4} + p_{5} + p_{7}) + B_{3}(p_{3} + p_{6})]$$

$$p'_{2} = N_{3}(C_{1}d_{1} + C_{2}d_{2} + C_{3}p_{1} + p_{2} + C_{4}p_{3} + C_{5}p_{4} + C_{6}p_{5} + C_{7}p_{6} + C_{8}p_{7})$$

$$p'_{3} = N_{4}[D_{1}d_{1} + D_{2}d_{2} + D_{3}p_{1} + D_{4}(p_{2} + p_{4}) + p_{3} + D_{5}(p_{5} + p_{7}) + D_{6}p_{6}]$$
(2.16)

The first two and the last forms are dictated by the horizontal reflection symmetry; the remaining five primed orbitals are obtained from those given here by operating with σ_v

and σ_{h} . Aside from the N_{i} there are 23 coefficients A_{i} , B_{i} , C_{i} , D_{i} . One can see that there are 14 orthogonality conditions, leaving 9 free coefficients.

To determine these coefficients we turn to the TSDA. For every pair of states μ and ν , there is a corresponding TSDA equation (2.10) to be satisfied. Since both *h* and *v* are spin independent, the states labeled ν and μ in the TSDA equation (2.10) must correspond to the same spin, each such state also corresponding to an atomic site using the site-localized orbitals defined by Eq. (2.16). It is easy to see that if two sites are equivalent by symmetry, e.g. the two Cu sites or the two O sites labeled p_2 and p_5 , then the corresponding equation vanishes identically, giving no information. Thus from Eq. (2.10) the only equations with content are those where the sites in ν and μ are non-equivalent, e.g. a Cu and an oxygen, or p_2 - p_3 . The number of such non-equivalent pairs which are independent can be seen directly to be 9, the number of free variables to be determined, i.e. there is the correct number of equations to determine these unknowns.

Because we are looking for basis functions on which a perturbation theory will be based with the purpose of deriving a spin Hamiltonian which will yield the low-lying energies and magnetic properties, we look for low-temperature nonmagnetic solutions such that for every spin up state there is a spin down state with the same spatial orbital. In the same spirit, we consider $K_{dd} <<\beta^{-1} <<\varepsilon$, where K_{dd} is the splitting of the lowest levels within the single-determinantal energies (It was 0 for the original Hamiltonian, Eq. (2.1), but as we'll see later it has value of about 0.03 eV after the 1-body transformations). Unfortunately, the low temperatures of interest lead to large disparity in the sizes of different contributions to the thermal averages $<n_v>$, etc., this causing
serious numerical difficulties. An approximation has been introduced to get rid of the exponential factors in, and thus simplify, the TSDA equations. Details of the calculation and discussion about its validity are given in the Appendix B.

The results obtained after solving these approximate TSDA equations are shown in Fig. 2.4 which gives an idea of the "shape" of the new orbitals relative to the original ones. The Hubbard Hamiltonian, Eq. (2.1), is then rewritten in terms of the new orbitals and thus the parameters in the model get renormalized. Note that the price to pay for the transformation is mainly that the Hamiltonian, which was restricted up to nearestneighbor terms in Eq. (2.1), now resumes back to a general form like Eq. (2.7). We take together all those terms which are associated only with number operators as unperturbed Hamiltonian H_0 , and the rest of the transformed Hamiltonian as perturbation [35]. The exchange parameter obtained from the new perturbation expansion is seen in Fig. 2.5 to **converge** (to the exact value). The errors in 2nd and 4th order are 15.4% and 15.7%, respectively.

	.24]	00			.20		.20	
.24	.88	.22	02	02	15	28	.80	28	15
	.24		00			.20		.20	
		d'_1					p'_1		
							1		
	.73]	00			55		.03]
.57	.73	08	00 .03	.01	.52	55 .06	.34	.03 08	04
.57	.73 26 27	08	00 .03 00	.01	.52	55 .06 55	.34	.03 08 .03	04

Figure 2.4: TSDA orbitals within the *site localization* assumption--the numbers indicate the amplitudes of the transformed orbital at the original orbitals. (The positions of the numbers correspond to the Cu_2O_7 cluster in Fig. 2.2.)



Figure 2.5: Perturbation result for *site localization*.

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2.3.2 Cell localization

To see if we could do better, we considered another type of symmetry assumption, named *cell localization* with respect to the transformed p orbitals. This was inspired by the work of Zhang and Rice [36], which also played an important role in the work of Refs 13 and 14. Instead of demanding that each new p orbital is localized at a site, we require each of them, with the exception of the central p, to be localized either within the cell on the left (the d plus the 4 p's) or the one on the right, maintaining a certain symmetry, analogous to Eqs. (2.14) and (2.15). There is no distinction between *site* and *cell localization* for the d orbitals, so they obey Eq. (2.14):

$$d_1' = -\sigma_v d_2' \tag{2.17}$$

The distinction between *site* and *cell localization* is seen in the following symmetry requirements for the (*cell localization*) *p* orbitals:

$$p_{i}^{l} = -\sigma_{v} p_{i}^{r}, \quad p_{i}^{l(r)} = \sigma_{h} p_{i}^{l(r)}, \quad \text{with } i = 1, 2$$

$$p_{3}^{l} = -\sigma_{v} p_{3}^{r}, \quad p_{3}^{l(r)} = -\sigma_{h} p_{3}^{l(r)}, \quad (2.18)$$

$$p^{c} = -\sigma_{v} p^{c}, \quad p^{c} = \sigma_{h} p^{c}.$$

The superscripts l and r stand for left and right, and c for central. Thus, for example, rather than σ_h taking orbital p'_2 into an orthogonal orbital p'_4 , as in the *site localization*, it takes p'_1 into itself. The explicit transformation in this case is

$$d_{1}' = N_{1}[d_{1} + A_{1}d_{2} + A_{2}p_{1} + A_{3}(p_{2} + p_{4}) + A_{4}p_{3} + A_{5}(p_{5} + p_{7}) + A_{6}p_{6}]$$

$$p^{c} = B_{1}(d_{1} + d_{2}) + B_{2}p_{1} + B_{3}(p_{2} + p_{4} + p_{5} + p_{7}) + B_{4}(p_{3} + p_{6})$$

$$p_{1}' = C_{1}d_{1} + C_{2}d_{2} + C_{3}p_{1} + C_{4}(p_{2} + p_{4}) + C_{5}p_{3} + C_{6}(p_{5} + p_{7}) + C_{7}p_{6}$$

$$p_{2}' = p_{1}' \quad \text{with } C_{i} \text{ replaced by } D_{i}$$

$$p_{3}' = \frac{1}{\sqrt{2}}(p_{2} - p_{4})$$

$$(2.19)$$

Following a counting similar to that done in the *site localization* case, one can show that, for the *cell localization*, the number of free coefficients after orthonormalization and the number of independent nontrivial TSDA equations are equal, as in the previous case.

The analogous figures to the *site localization* case for the *cell localization* are shown in Fig. 2.6 and Fig. 2.7. The errors in the exchange parameter in 2nd and 4th order are 15.4% and 13.6%, respectively. It shows that the *cell localization* is a slightly better choice for the perturbation calculation than the *site localization*.



Figure 2.6: TSDA orbitals for cell localization.



Figure 2.7: Perturbation result for *cell localization*.

2.3.3 No localization

The third choice of the symmetry of the new orbitals is named *no localization*. The term means releasing any localization requirement on the new p orbitals (but still keeping the new d orbitals localized). This is analogous to the case in a crystal where the p orbitals may form a p-band while the d orbitals remain localized. The new orbitals are required to satisfy the following symmetry properties:

$$d_1' = -\sigma_y d_2' \tag{2.20}$$

which is the same as in the previous two cases, and

$$p_{i}^{-+} = -\sigma_{v} p_{i}^{-+}, \quad p_{i}^{-+} = \sigma_{h} p_{i}^{-+} \quad \text{with } i = 1, 2, 3$$

$$p_{i}^{++} = \sigma_{v} p_{i}^{++}, \quad p_{i}^{++} = \sigma_{h} p_{i}^{++} \quad \text{with } i = 1, 2$$

$$p^{--} = -\sigma_{v} p^{--}, \quad p^{--} = -\sigma_{h} p^{--}, \quad p^{+-} = \sigma_{v} p^{+-}, \quad p^{+-} = -\sigma_{h} p^{+-},$$
(2.21)

where the first sign in the superscripts denotes the symmetry under σ_v , and the second sign, the symmetry under σ_h . The explicit transformations for some of the orbitals are listed below

$$d_{1}' = N_{1}[d_{1} + A_{1}d_{2} + A_{2}p_{1} + A_{3}(p_{2} + p_{4}) + A_{4}p_{3} + A_{5}(p_{5} + p_{7}) + A_{6}p_{6}]$$

$$p_{1}^{-+} = B_{1}(d_{1} + d_{2}) + B_{2}p_{1} + B_{3}(p_{2} + p_{4} + p_{5} + p_{7}) + B_{4}(p_{3} + p_{6})$$

$$p_{2}^{-+}(p_{3}^{-+}) = p_{1}^{-+} \quad \text{with } B_{i} \text{ replaced by } C_{i}(D_{i})$$

$$p_{1}^{++} = E_{1}(d_{1} - d_{2}) + E_{2}p_{1} + E_{3}(p_{2} + p_{4} - p_{5} - p_{7}) + E_{4}(p_{3} - p_{6}) \qquad (2.22)$$

$$p_{2}^{++} = p_{1}^{++} \quad \text{with } E_{i} \text{ replaced by } F_{i}$$

$$p^{--} = \frac{1}{2}(p_{2} - p_{4} + p_{5} - p_{7})$$

$$p^{+-} = \frac{1}{2}(p_{2} - p_{4} - p_{5} + p_{7})$$

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The transformed orbitals and the perturbation results for the *no localization* case is shown in Fig. 2.8 and Fig. 2.9. The errors at 2nd and 4th order in the exchange parameter J are 15.5% and 14.8%, respectively, not as good as the *cell localization*.



Figure 2.8: TSDA orbitals for no localization.



Figure 2.9: Perturbation result for *no localization*.

2.3.4 Comments on the TSDA solutions for the three localization choices

Because the symmetry requirements in these three choices are different for p orbitals but the same for d orbitals, and since the lowest energy states in which only the d orbitals are occupied dominate at low T, it turns out that the transformed d orbitals for the three localization choices are the same. After TSDA transformation, the energies of the lowest two single-determinantal states of the half-filled Cu₂O₇ cluster are -2.7718 and -2.7430 (all in eV) for the spins of the two holes, one at each transformed d orbital, being parallel and antiparallel, respectively. This can be compared with the energies using the original orbitals, 0 for both parallel and antiparallel spin configurations, and with the exact eigen-energies from direct diagonalization of the Hamiltonian matrix, -2.7738 and -2.9000 for the triplet and the singlet, respectively.

After transformations, all parameters $h_{\nu\mu}$ and $\nu_{\nu\mu,\lambda\kappa}$ in the Hamiltonian get renormalized. For example, some new parameters resulted from the TSDA solutions are:

$$t'_{dd} = -0.403, \ U'_{d} = 6.910, \ U'_{dd} = 0.113, \ K'_{dd} = -0.029,$$
 (2.23)

where the 1st, 3rd and 4th ones were absent in the original form of the Hamiltonian, Eq. (2.1).

2.4 Further improvement via 2-body transformation

Although the TSDA guided 1-body transformations did lead to convergent perturbation expansions as we had hoped, we were somewhat disappointed about the relatively slow convergence rate compared to the achievement of Refs. 13 and 14, in which transformation is not restricted to be 1-body. An interesting question was then asked: What is the main factor which limits the convergence rate of 1-body-transformation-induced p.t.? The answer is given below and a minimal 2-body transformation is added to improve the convergence rate.

Our attempt to incorporate both 1- and 2-body transformations is inspired by the work of Zhang and Rice [36], as well as J. H. Jefferson *et al.* [13]. On the CuO₂ planes, a cell is defined as any one copper and its four surrounding oxygens. Turning on the perturbation (*p*-*d* hopping) will induce hybridization among the copper *d* orbital and the oxygen *p* orbitals. If the perturbation is small, the new orbitals would remain localized within a cell. The copper *d* orbital is expected, by symmetry, to equally hybridize with its four surrounding oxygen *p* orbitals. Let us define the symmetric *p* orbital of each cell as

$$p_i^s = \frac{1}{2} \sum_{l \in \{i\}} p_l \; ,$$

where the summation index indicates that l is taken over the (four) p sites in cell i. It is intuitive to expect that the largest hybridization will occur between the d_i and p_i^s . The symmetric p_i^s orbital has its analogue in our *cell localization* choice of the 1-body transformation for the Cu₂O₇ cluster, namely p_1^l and p_1^r , for the left cell and the right cell respectively. Therefore our following investigation is based on the *cell localization* choice.

Because the Hamiltonian of Eq. (2.1) conserves the total spin S and its projection on the z-axis S_z, the Hamiltonian matrix elements form isolated blocks for different values of S_z. From here to the end of this section we only consider the S_z = 0 case. Through the process of the 1-body transformations, the hybridization between the d and p orbitals are actually taken into account. Because of the expected large hybridization between the d and the symmetric p^{s} orbitals, we are interested in those states which consist of only d'_{1} (d'_{2}) and p'_{1} (p'_{1}). Among the total 81 states for the half-filled Cu₂O₇ cluster (i.e. only two holes on it) with S_z = 0, this means the states of interest are

$$\left|d_{1\uparrow}' p_{1\downarrow}' \right\rangle, \left|d_{1\downarrow}' p_{1\uparrow}' \right\rangle, \left|d_{1\uparrow}' d_{1\downarrow}' \right\rangle, \left|p_{1\uparrow}' p_{1\downarrow}' \right\rangle,$$

$$(2.24)$$

and four similar states for the right cell. Hereafter we consider only the left cell because the expressions for the right cell are exactly the same. After the 1-body transformation, the Hamiltonian submatrix in the basis set of Eq. (2.24) is

$$\begin{bmatrix} 5.483 & -1.149 & -2.239 & -0.148 \\ -1.149 & 5.483 & 2.239 & 0.148 \\ -2.239 & 2.239 & 4.055 & 0.984 \\ -0.148 & 0.148 & 0.984 & 11.922 \end{bmatrix}$$
(2.25)

(row and column indices correspond to the states in Eq. (2.24) in order). Two things are worth noting. First, the off-diagonal matrix elements are large. This is due to d'_1 and p'_1 being mainly strong mixtures of d_1 and p'_1 . This hybridization leads to large renormalized model parameters for hole-transfer terms (between d'_1 and p'_1) in the transformed Hamiltonian, and thus contributes to the off-diagonal matrix elements. It indicates that these four states are far from the eigenstates and may lead to slow convergence if adopted as unperturbed states in the perturbation calculation. Second, the energy of the state of double occupancy of the d orbital, 4.055, the third diagonal element of Eq. (2.25), is dramatically reduced from its original value 10.5, also a result of strong hybridization. Each new d orbital contains part of the original d orbital and part of the original p orbitals. Therefore double occupancy in the new d orbital only gains energy from a fraction of the large (original) U_d , and that causes the large change of this energy level. Direct diagonalization of the Hamiltonian matrix shows that the energy levels associated with double occupancy at the d orbitals remain high (~ 12.7). Thus, in spite of giving good approximate low-lying energy levels, the 1-body transformation also leads to some high-lying levels which are not at all good approximations of corresponding eigenstates, and these high-energy eigenstates do play am important role in the perturbation theory. In conclusion, it is the strong hybridization (covalence effect) and the large on-site Coulomb energy U_d (correlation effect) together that prevents a 1-body transformation from generating good approximation for the whole energy spectrum.

In order to take care of the above limitation, we diagonalize the matrix of Eq. (2.25) and use the 4 resulting eigenstates (the 2-body transformation comes in here), plus the 4 counterpart states for the right cell and the remaining 73 (unchanged) states, as the basis set to perform the perturbation calculation. In some sense, by this we allow relaxation in the intermediate states of the p.t., where one hole hops into the neighbor cell which has already been occupied by another hole. We call this scheme the *minimal 2-body* transformation where "minimal" means that, among the various p orbitals, only

 $p_1'(p_1')$ are involved in the 2-body transformation. The result is shown in Fig. 2.10. We have also tried including $p_2'(p_2')$ in the 2-body transformation $[p_3'(p_3')]$ are out of our consideration because they possess different symmetry from $d_1'(d_2')$. However, it only made a tiny change from that of the minimal 2-body transformation and so the result is omitted here.

In Ref. 13, J. H. Jefferson *et al.* described another transformation scheme, which is, in spirit, similar to our 1-body + minimal 2-body transformation, and demonstrated rapid convergence to 2nd order p.t. on a model with a restricted parameter set: $\varepsilon=3$, $t_{pd}=$ l, $t_{pp}=-0.5$, $U_d=\infty$, and all other parameters equal to zero. (The straightforward p.t. for this parameter set is divergent, too.) For comparison, we applied our method to the same parameter set. The result showed that the 1-body transformation alone fails to lead to a convergent perturbation expansion. This is not surprising since the renormalization in U_d , the double-occupation energy at *d* orbitals, caused by the 1-body transformation is fatal to the p.t. in the case of $U_d=\infty$ Nevertheless, we achieved similar precision as theirs after we added the minimal 2-body transformation to the p.t..



Figure 2.10: Perturbation result for *cell localization* 1-body + minimal 2-body transformation.

2.5 Summary and discussion

For simplicity, we sought 1-body transformations to convert the p.t. from divergent to convergent in the context of strongly covalent CuO2 planes. Taking TSDA as a guide, several 1-body transformations were found, in the Cu₂O₇ case, to achieve this goal, but the convergence rate in each case was rather slow. Besides those suggested by TSDA, we have also tried some other 1-body transformations, of which the best one gives errors of about 13% and 6% at 2nd and 4th order p.t., respectively, better than the best TSDA result (cell localization, where the errors at 2nd and 4th order p.t. are 15.4% and 13.6%). However, the convergence is still slow, particularly in higher order where the results oscillate with slowly decreasing amplitude, similarly to TSDA (see Fig. 2.5, 2.7, 2.9). The details of these other transformations are omitted here for the above reason and the fact that they were obtained in a rather *ad hoc* way, not as systematically as in TSDA. A striking difference between the best *ad hoc* trial and the *cell localization* TSDA is the following. Two of the transformed p-orbitals of the ad hoc trial (the one with errors 13% and 6%) were deliberately guided to be close to the Zhang-Rice-type orbital [36] (where a transformed orbital localized in a cell consists of four oxygen p-orbitals in the cell with equal weight). On the other hand, the p_1^l and p_1^r in the *cell localization* choice of TSDA are further from the Zhang-Rice-type orbital, which is a result of the low symmetry of the Cu_2O_7 cluster plus the free energy minimization. This suggests that being closer to the Zhang-Rice-type orbital helps the convergence. However, one can see that this issue becomes moot when the *cell localization* TSDA is applied to the crystal, where the 4-fold

symmetry at a Cu site holds and therefore the *cell localization* TSDA will give the Zhang-Rice-type orbital.

After all our considerations of 1-body transformations, we guess that we are close to their limit in connection with improving convergence. If one wants to do better, 2- or more-body transformation is probably necessary. It is the large covalence and strong correlation in the problem that limits the effect of 1-body transformations: a 1-body transformation designed to give some zero-order energy levels accurately will likely spoil other levels, all of which enter p.t. in high order.

We then found that a minimal 2-body transformation dramatically improved the convergence rate. Only transformed d_i -like and p_i^s -like orbitals are essential to be taken into account in extracting the Hamiltonian submatrix to solve for "good" two-particle basis states. In comparison, our cell-localization 1-body + minimal 2-body transformation scheme achieves similar (high) precision by second order p.t. as obtained in the work of Ref. 13.

Chapter 3

Crystal Hartree-Fock Calculations for La₂NiO₄ and La₂CuO₄^{*}

3.1 Introduction and Methods

La₂NiO₄ and La₂CuO₄, which have essentially the same crystal structure, have attracted considerable theoretical and experimental research efforts, especially since the latter was found to become a high-T_c superconductor when properly doped with Sr or Ba [37]. Above their respective structural transition temperatures T_s, both materials are in a tetragonal structure [space group D_{4h}¹⁷ (*I4/mmm*), see Fig. 3.1 below]. Below T_s, they are slightly distorted to an orthorhombic structure. Each of them is an antiferromagnetic (AFM) insulator below a Néel temperature T_N (< T_s), and is a paramagnetic (PM) insulator above T_N.

The past theoretical studies of these two materials can be broadly classified into two categories. The first one is density functional calculations executed on the crystals. This sort of approach only achieved partial success and failed to predict certain properties of the materials. For instance, local spin density approximation (LSDA) calculations incorrectly predicted La_2CuO_4 to be a PM metal [37] and La_2NiO_4 to be an AFM metal [38]. Since 1990, several modifications have been made to LSDA to produce AFM

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insulating solutions, like SIC-LSDA, LSDA+U [39,40]. However, since the modifications are somewhat *ad hoc*, whether the modified LSDA approaches still fall into the *ab initio* regime or not is arguable.

The second category is cluster calculations. This category itself can be further divided into two subsets: single-magnetic-ion cluster (SMIC) calculations and multi-magnetic-ion cluster (MMIC) calculations. The SMIC calculations were aimed at obtaining the neutron scattering form factors of the crystals [41] and hyperfine properties [42]. A more detailed description of this approach will be given in Sec. 3.2 when we come to the comparison of results of the SMIC calculations with the results of our present work. Note that, since the cluster in the SMIC calculations contains only one magnetic ion, the AFM ground state of the crystals must be assumed *a priori* and quantities such as the Heisenberg exchange parameter J cannot be extracted from the calculations. On the other hand, MMIC calculations [43-46] have given information about J.

The present calculations were done using the program *CRYSTAL95* [47], which is designed to do Hartree-Fock (HF) calculations on infinite crystalline materials, using linear-combination-of-atomic-orbital (LCAO) basis sets. Clearly, the crystal Hartree-Fock approximation (HFA) falls outside the two categories mentioned above and thus may provide useful supplementary information. The crystal HFA has recently been applied to a number of AFM Mott insulators including MnO, NiO [48], KNiF₃ [49], KCuF₃ [50], and CaCuO₂ [51]. These were successful in that they gave the materials to be insulators (vs. metals), to be antiferromagnets (vs. ferro- or paramagnets); also they gave energy differences between the various magnetic states in semiquantitative agreement with experiment. In this paper, in addition to these considerations, we will

compare the spin density with neutron diffraction experiments. Our major emphasis is on the ground state properties, although some discussion of band structure (1-electron energies, nature of 1-electron states) is presented.



Figure 3.1: The centered-tetragonal structure of La_2NiO_4 . La_2CuO_4 has the isosturcture of La_2NiO_4 (Ni atoms are replaced by Cu atoms). The NiO₆ octahedral cluster, an important signature of perovskite crystal structure, is marked by the dotted lines.

In this work, we use the centered tetragonal crystal structures with lattice constants taken from experimental data [52]: a=3.855, c=12.652 for La_2NiO_4 , and a=3.7793, c=13.226 for La_2CuO_4 (in units of Å). The basis sets of O, Ni and Cu are taken from Ref. 53, which are specially designed for crystal calculations. (Note that the usual basis sets used in molecular and cluster calculations are often too diffuse for crystal

calculations; they may cause nonconvergence or a very slow convergence rate with not much increment in the accuracy to the result one might get using tighter basis sets [47].) Since La is a heavy atom (atomic number 57), relativistic effects are not negligible for the inner shell electrons. Besides, an atomic basis set for La suitable for crystal calculation is not available in the literature. We thus used the effective core potential (ECP) calculated by Hay and Wadt [54] for the La^{+3} ion core [55], where the relativistic effect of the inner shell electrons is supposed to have been taken into account. In Hay and Wadt's papers, basis sets for valence electrons designed for use with the ECPs were also given. However, they are so diffuse that they cause a numerical problem in the crystal HF calculation. Thus, La was treated in the present work as a bare La⁺³ ion and represented by the Hay and Wadt large core ECP, no valence orbitals (therefore no valence electrons) being attached to it. We did test the significance of the bare La⁺³ core approximation to some extent by adding a d shell (consisting of a single, optimized, Gaussian exponent) to the La^{+3} and seeing how it affected the results. It turned out that about 0.45 electron per La gathered into the added shell. Accompanying that, the total energy per formula unit (including one Ni or Cu) changed by about 4.5 eV. However, the shape of the occupied bands and the spin density changed negligibly, and the energy difference between ferromagnetic (FM) and AFM solutions, which is around 36 meV, varied by only about 1.4 meV. The insensitivity of the FM-AFM energy difference to variation of the outer shells of basis sets was also observed for other materials [49]. The properties that are only slightly affected by the bare La⁺³ core approximation are the main focus in this paper.



3.2 Results

3.2.1 Heisenberg exchange parameter J

Our results show that both La_2NiO_4 and La_2CuO_4 are AFM insulators, in agreement with experiments. The FM solutions also exist for both materials, with higher energy. The energy difference per formula unit between FM and AFM states is 36.9 meV for La_2NiO_4 and 36.1 meV for La_2CuO_4 . It is a common and long-standing practice [56,57,48-50,43] to map energies of FM and AFM electronic states to the mean field approximation for the nearest-neighbor Heisenberg Hamiltonian H_{Heis} . This is done for materials such as these, where H_{Heis} is known to accurately describe the low-lying excitations [56,58], and leads to an estimate of the Heisenberg exchange parameter J. In Appendix C, we give a rationale for doing the mapping in HF calculations, while pointing out a potential inconsistency if the same procedure is used in approximate density functional theories.

To proceed then with the determination of J, the Heisenberg Hamiltonian is

$$H_{Heis} = J \sum_{\langle i,j \rangle} \vec{s}_i \cdot \vec{s}_j , \qquad (3.1)$$

the summation going over each nearest neighbor pair $\langle i, j \rangle$ of magnetic ions, taken once. We equate the calculated FM-AFM energy difference in the HFA to the corresponding FM-AFM energy difference in the mean field approximation of Eq. (3.1), and thus define the Heisenberg J in the HFA, J_{HF}, as follows

$$\Delta E_{HF} = \left(2J_{HF}s^2\right)\left(\frac{NZ}{2}\right). \tag{3.2}$$



 ΔE_{HF} is the FM-AFM energy difference for the whole crystal in the HFA, N is the number of magnetic ions, s is the spin of each site (1 for Ni and 1/2 for Cu), and Z is the coordination number. Eq. (3.2) (with J instead of J_{HF}) appears elsewhere [43-46] for dimers where N = 2, Z = 1, but the claim in some of the references that this gives the correct or exact J is not warranted in general (see Appendix C). Since the interactions within a CuO₂ plane are much stronger than the interplanar ones, we take Z = 4. It turns out that J is 9.2 meV for La₂NiO₄ and 36.1 meV for La₂CuO₄. The La₂CuO₄ result agrees with an embedded cluster calculation using HFA [43], which gives 37.8 meV, strengthening the suggestion [43-46] that J appears to be a rather local property. These values are to be compared with the experimental data, which give 18 meV for La₂NiO₄ [59,60], and 134 (neutron) or 128 (Raman) meV for La₂CuO₄ [61,62]. Although our results are about a factor of 3 too small, it actually is remarkable to be so close, since we are picking up the small difference between the FM and AFM energies with each on the order of 4000 Hartrees. (So it is at an accuracy of about one out of a million.) Similar underestimates for J using HFA were found for other materials [48-50].

3.2.2 Spin density and spin form factor

Spin density maps on the perovskite magnetic ion - oxygen layer [(001) plane] are given in Fig. 3.2 for both materials. The x-y plane of the graphs matches the NiO₂ (CuO₂) plane and includes 3×3 magnetic ion sites. The large peaks on the graphs coincide with the locations of the magnetic ions. The sign of the spin density alternates from one site to another, a manifestation of the AFM character of the systems. The

magnitudes of spin density around oxygens, which are half way between each nearest neighbor pair of magnetic ions, are extremely small as expected. Every peak in the graphs has an approximate 4-fold symmetric shape, a result of the singly occupied $d_{x^2-y^2}$ orbital. Although Fig. 3.2(a) (for La₂NiO₄) and Fig. 3.2(b) (for La₂CuO₄) resemble each other very much, a characteristic difference between the spin densities of these two materials does exist and can be seen in a tomograph of other directions. For instance, Fig. 3.3 shows the spin density tomographs of these two materials in the (100) plane passing through a magnetic ion. For this plane, the peak in the graph of La₂NiO₄ still has four lobes, while the peak in the graph of La_2CuO_4 has only two lobes aligned in the y direction. This is expected because each copper in La₂CuO₄ has only a singly occupied $d_{x^2-y^2}$, while each nickel in La₂NiO₄ has a singly occupied $d_{x^2-y^2}$ and a singly occupied $d_{3z^2-r^2}$ which together give a spin distribution with cubic symmetry (small distortions from cubic symmetry are caused by the surroundings). Later on we will see that this difference in spin densities leads to characteristically different spin form factors for these two materials.

It has been shown [41] that, for the single-band Hubbard model assuming small hopping t compared to the repulsion U, the Fourier transform of the spin density is

$$s(\vec{k}) = \langle s_z \rangle_{Heis} F(\vec{k}) f(\vec{k}) [1 + O((t_U')^2)].$$
(3.3)









Figure 3.2: The spin density in the magnetic ion - oxygen plane [(001) plane]: (a) La_3NiO_4 , AFM, (b) La_2CuO_4 , AFM. The range of the basal plane in the graphics is 2a (a is the lattice constant) in each direction and is centered at one magnetic ion. The vertical axis is in atomic units (same as Fig. 3.3 in the following).





Figure 3.3: The spin density in the (100) plane: (a) La_2NiO_4 , AFM, (b) La_2CuO_4 , AFM. The range of the basal plane in the graphics is *a* in each direction and is centered on one magnetic ion. The labels of the two axes of the basal plane refer to the y and z directions in the conventional tetragonal lattice coordinates.



Here $\langle s_z \rangle_{Heis}$ is the expectation value of the spin at a site (an up site) in the (spontaneously) symmetry-broken ground state of the corresponding Heisenberg model. $f(\vec{k})$, the form factor, is the Fourier transform of 1/s times the HF spin density over a nonmagnetic unit cell centered at a magnetic ion, where s is the spin quantum number for the free ion (1 for Ni⁺² and ¹/₂ for Cu⁺²). This implies f(0) = 1. $F(\vec{k})$ is given as

$$F\left(\vec{k}\right) = \sum_{\vec{k}} e^{-i\left(\vec{k} - \vec{k}_A\right)\vec{k}}$$
(3.4)

where \bar{R} runs over all the Bravais lattice vectors and \bar{k}_A is an antiferromagnetic wave vector (e.g. for the square lattice with lattice constant a, \bar{k}_A is $\left[\frac{\pi}{a}, \frac{\pi}{a}\right]$). The correction term $O\left(\left(f_U'\right)^2\right)$ is negligible for the cuprate [41] and, we expect, for the nickelate [63]. Although the derivation of Eq. (3.3) is somewhat lengthy, the result is physically understandable. $\langle s_z \rangle_{Heis}$ accounts for the quantum spin fluctuations (QSF) in the Heisenberg-model ground state and is just an overall scale factor. $F(\bar{k})$ accounts for the occurrence of the Bragg peaks. $f(\bar{k})$ gives the relative sizes of the Bragg peaks, and conveys detailed information about the spin density $s(\bar{r})$ in the unit cell. Eq. (3.3) is discussed further in Sec. 3.3.

In an earlier work [41] of our group, SMIC calculations on several AFM insulating compounds including La_2NiO_4 and La_2CuO_4 were carried out based on this formula. The results agreed extremely well for KNiF₃ and NiO; for La_2CuO_4 they gave rough overall agreement for the shape of $f(\vec{k})$ (for a sample well off stoichiometry). Only in the case of La_2NiO_4 did the results show a serious qualitative disagreement with

experiment [64]. This disagreement provided a strong part of our motivation for the present study.

Thus we calculated the Fourier transform of the spin density that we had obtained from the crystal HF calculations. The resulting form factors at the k-values for the magnetic Bragg peaks are shown in Fig. 3.4.

Note that if the spin density is spherically symmetric, all the data will fall on a smooth curve. In Fig. 3.4(b), the form factor of La₂CuO₄, the data separate into several branches, indicating that the form factor varies dramatically in different directions of \bar{k} . This is understood as due to the asphericity of the Cu $d_{x^2-y^2}$ orbital of the unpaired electron, as first pointed out by S. Shamoto *et al.* [65]. On the other hand, in the Ni compound both e_g states are singly occupied, giving a nearly cubic spin density; and thus $s(\bar{r})$ is closer to spherical. Indeed, the corresponding form factor [Fig. 3.4(a)] reveals no obvious branches.



Figure 3.4: The spin form factor: (a) La₂NiO₄, AFM, (b) La₂CuO₄, AFM. The horizontal axis is the magnitude of \vec{k} , in units of inverse Angstroms. The black stars are for the family of $(\frac{1}{2}, -\frac{1}{2}, l)$ Bragg peaks, diamonds for $(\frac{1}{2}, \frac{1}{2}, l)$, circles for $(\frac{1}{2}, \frac{3}{2}, l)$, empty stars for $(\frac{1}{2}, -\frac{3}{2}, l)$, triangles for $(\frac{3}{2}, -\frac{3}{2}, l)$ and squares for $(\frac{3}{2}, \frac{3}{2}, l)$, where the three components of the triple numbers are in units of $\frac{2\pi}{a}$, $\frac{2\pi}{a}$, $\frac{2\pi}{c}$, respectively. With our choice of coordinate system, for the Bragg peaks the sum of the three components of each triple number must be an even integer.

Our present results are compared to the previous cluster calculations and to experiment in Fig. 3.5. Note that Fig. 3.5(a) for the nickelate shows the Bragg scattering amplitude (in units of μ_B) and Fig. 3.5(b) for the cuprate shows the form factor. In Fig. 3.5(a), the Bragg scattering amplitude $g\langle s_z \rangle_{Heis} f(\vec{k})$ is calculated using g = 2.29 [66] and $\langle s_z \rangle_{Heis} = 0.8$ from the spin wave theory [67]. The two theoretical results agree with each other very well; however, both disagree qualitatively with experiment. In view of the very good agreement between theory and experimental results for several other compounds like KNiF₃ and NiO [41], it seems odd that the theory would be so far off from experiments for the case of La_2NiO_4 . The agreement between the cluster and the crystal calculations ensures that the theoretical results are calculation-error free, excluding one possible source of the discrepancy between theory and experiment. Then, logically, more independent experiments are called for to cross-check with the single existing experimental work on a presumably stoichiometric sample [64,68]. We should note that the plot in Fig. 3.5(a) is on an absolute scale; thus the agreement between theory and experiment at large k might be significant [69].




Figure 3.5: Comparison of the crystal and cluster calculations with experiments: (a) Bragg scattering amplitude for La_2NiO_4 . (b) spin form factor for La_2CuO_4 . The diamonds are for the crystal, stars for the cluster, and circles with error bars for the experimental data. Note that in (b) the experimental data has been scaled to make the least-square fit to the crystal results.

For the cuprate [Fig. 3.5(b)], the experimental form factor data [70] have been scaled to give the least-square fit to the crystal HF result. It has been argued [71, 41] that the moment (and Néel temperature) should be maximum at the stoichiometric compound; the main experimental question here is the oxygen content [72,73]. Since the experimental "moment" in Ref. 70 is appreciably smaller than that of other samples [72], we expect the one used to measure the form factor shown is far from being stoichiometric. Therefore, only comparison of the "shape" of the form factor might be sensible. It is seen that the overall shape is in rough agreement with theory.

For a test of the absolute value of our calculated spin density, we consider the sample with the highest "moment", 0.6 ± 0.05 Bohr magnetons (with Néel temperature of 298K) [72]. As discussed in Ref. 41, the "moment" (called moment in that reference) defined by the experimentalists is the amplitude $g\langle s(\vec{k}) \rangle$ at the Bragg peak with the smallest k, divided by 0.835 (the form factor of K_2CuF_4 , interpolated for the k-value appropriate for the cuprate being measured [72]); g is the usual g-factor, $\cong 2.2$ for the cuprate. Multiplying the above "moment" by 0.835 yields $g\langle s(\vec{k}) \rangle_{exp} = 0.50 \pm 0.04$. Using our calculated HF value of $f(\vec{k}) = 0.763$, $\langle s_z \rangle_{Heis} = 0.3$ for the square lattice (appropriate to a CuO₂ plane) [67], and g = 2.2, Eq. (3.3) gives $g\langle s(\vec{k}) \rangle_{\text{theo}} = 0.504$. This exact agreement is surely fortuitous. In fact a sample with a slightly higher T_N (325K) has been reported [74] as being highly stoichiometric. Unfortunately an absolute magnetic Bragg intensity measurement (which would yield e.g. a value of the "moment") was not reported on this sample. Judging from the increase in "moment" with T_N shown

in Ref. 72, the experimental amplitude will be larger than the 0.5 quoted above. Nevertheless, this agreement between theory and experiment suggests that the HF approach, corrected for quantum spin fluctuations, gives a very good account of the ground state spin density. It is clearly important to have the absolute intensities at several Bragg peaks measured on an excellent sample like that of Ref. 74, for comparison with our calculations.

It is noted that an appreciable discrepancy between the crystal and cluster HF results exists. This is interesting in view of the very good agreement between the two theoretical calculations for the nickelate as shown in Fig. 3.5(a). We believe that the larger covalence in the cuprate is the cause of this discrepancy. Indeed, we performed the integration of the HF spin density over a Wigner-Seitz cell on the magnetic ion sublattice, as a measure of the ordered spin per magnetic ion (without QSF), on both materials. We found 0.926 for the nickelate and 0.421 for the cuprate. In comparison with the free magnetic ion spin (1 for Ni⁺² and $\frac{1}{2}$ for Cu⁺²) we see a 7.36% reduction for the nickelate and 15.8% reduction for the cuprate [75]. This reduction is evidence of the covalence between Ni (Cu) and Oxygen [76,77]. The finding here of appreciably less covalence in the nickelate strongly suggests that the original explanation [64] of the extreme flattening of the form factor at small k as being due to strong covalence may not be correct [78].

As one further check on the accuracy of our crystal calculations, we considered another Ni compound, KNiF₃, where the cluster approach agreed excellently with experiment [41,66]. Taking $\langle s_z \rangle_{Heis} = 0.92$ from the spin wave theory [67], we summarize the results for the amplitude $\langle s(\vec{k}) \rangle$ at the three Bragg peaks measured in

Table 3.1. It is apparent that both the crystal and cluster results are slightly larger than the experimental data. However, if we took $\langle s_z \rangle_{Heis} = 0.9$, both of them predict the experimental data to within the error bars! It should be remembered that the spin wave theory of Ref. 67 is an approximation to the ground state of the Heisenberg model [79].

Table 3.1: Comparison of the crystal HF, the cluster HF and the experiment results of the spin form factor of $KNiF_3$. The first row shows the indices of the three Bragg peaks measured in experiments up to date. For the convention of the indexing, see the caption of Fig. 3.4.

	$\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$	$\left(\frac{3}{2}\frac{1}{2}\frac{1}{2}\right)$	$\left(\frac{3}{2}\frac{3}{2}\frac{1}{2}\right)$
Crystal HF	0.813	0.679	0.554
Cluster HF	0.807	0.683	0.564
Experiment	0.783 ± 0.018	0.672 ± 0.015	0.553 ± 0.013

3.2.3 Band structure

The band structures of the AFM solutions are given in Fig. 3.6. The results show a wide gap (~17 eV) for both materials; we also see a similar large gap for the FM solutions. The experimental (optical) gap for La_2CuO_4 is about 2.0 eV [80]. That the gap is much larger than the experimental gap has been found much more generally in the HFA; see the papers of Refs. 48-50 for examples and Ref. 48 for discussion. The results suggest that the insulating character of both materials is not strongly correlated with their



magnetic ordering, in agreement with experiment [81], and in contradiction to a bandtheory scheme proposed by Slater [51,82]. In the La₂NiO₄ AFM solution, the Γ point of the highest occupied band consists mainly of the Ni $3d_{x^2-y^2}$ and O(1) $2p_{x,y}$, and the Γ point of the lowest unoccupied band consists mainly of the O(1) 3s and O(2) 3s, plus a bit of Ni 4s and O(2) $3p_z$. In the La₂CuO₄ AFM solution, the Γ point of the highest occupied band consists mainly of the Cu $3d_{x^2-y^2}$ and O(1) $2p_{x,y}$, and the Γ point of the lowest unoccupied band consists mainly of the O(1) 3s and O(2) 3s, plus a bit of Cu 4s. For both materials, the Γ point is the minimum in the lowest unoccupied band but not the maximum in the highest occupied band, showing an indirect band gap. The width of the highest occupied band is about 1.6 eV for La₂NiO₄ and 0.6 eV for La₂CuO₄. The projected densities of occupied states (not shown) have many features in common with those previously reported for other Mott insulators [48-50]. Two of these features are that it is mainly anion p-states that exist near the Fermi energy, and that the bulk of the magnetic ion e_g states is lower in energy than the t_{2g} states. These results need further analysis and are suitable for a future publication.



Figure 3.6: The band structure: (a) La₂NiO₄, AFM, (b) La₂CuO₄, AFM (on next page). The band structures of the spin-up and spin-down states are the same (because of the antiferromagnetism), so the figure shown here is for either one. The (vertical) ε -axis is in units of Hartrees. The (horizontal) k-axis goes through two contiguous paths: $(\frac{1}{2}, \frac{1}{2}, 0) \rightarrow (000) \rightarrow (\frac{1}{4}, \frac{1}{4}, 0) \rightarrow (\frac{3}{4}, \frac{1}{4}, 0) \rightarrow (000) \rightarrow (001)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2}) \rightarrow (000) \rightarrow (\frac{1}{2}, 0, \frac{1}{2})$. For the convention of the triple numbers, see the caption of Fig. 3.4. The horizontal line inside each graph indicates the Fermi energy.



Figure 3.6 (continued from previous page)

3.3 Summary and Discussion

We have calculated the electronic structure of La_2NiO_4 and La_2CuO_4 using the crystal HF approach. The major emphasis has been on ground state properties, although some discussion of band structure has been given. The results provide supplementary information to that obtained from crystal LSDA and embedded cluster calculations in interpreting the experimental data. For both materials, our crystal HF results correctly predict an AFM insulating ground state. The calculated Heisenberg exchange parameter J is about a factor of 3 too small compared with experiments. This is consistent with the interpretation of Martin and Illas [43], and Towler et al. [48] that the HFA overestimates the on-site Coulomb interaction. The spin form factor $f(\vec{k})$ basically agrees with earlier cluster calculations. However, there is an appreciable discrepancy between the two theoretical calculations in the cuprate case, which we believe is due to the larger covalence in the cuprate. We found rough overall agreement with experiment for the shape of $f(\vec{k})$ vs. $|\vec{k}|$ for a poor sample of the cuprate, and excellent agreement for the absolute intensity of the one Bragg reflection measured on a good cuprate sample. However in the case of La₂NiO₄ the shape of the form factors in both the crystal and cluster calculations disagree seriously with experiment. The fact that we found the nickelate to be (appreciably) less covalent than the cuprate deepens the puzzling nature of this disagreement with the nickelate together with agreement for the cuprate. For a further check, we also calculated the form factor for KNiF, and found excellent agreement with experimental absolute intensities. These results should create strong motivation for performing more experiments on a stoichiometric sample of the nickelate;

it is also important to measure the absolute Bragg intensities at more than one Bragg peak for a stoichiometric sample of La_2CuO_4 for a more stringent test of our theory.

We conclude with a discussion of the procedure used to calculate the spin density. We used our earlier result calculated within the single-band Hubbard model as a guide. Namely, following that result, we took the spin density to be that in the HFA reduced by the ratio $\langle s_z \rangle_{Heis} / s$, the reduction from 1 being due to the quantum spin fluctuations in the Heisenberg AFM ground state. In fact we have shown [83] that this procedure is not exact for a model more general than the single-band Hubbard model. Thus we need to understand, e.g., why our present and previous [41] results are in excellent agreement with experiment for a number of cases using the HFA. Such studies are in progress. In any case, we want to emphasize that the QSF (which give large effects) cannot be ignored, as they were in Ref. 46 where a large moment reduction was attributed entirely to covalence. We note also that in Ref. 43, the large QSF correction was made, showing the confusion on this issue in the literature. The single-band Hubbard model result, Eq. (3.3), is a good starting point for clarification, and the generalization is clearly important.

Chapter 4

Electronic Structure of LaMnO₃ in the *Ab Initio* Crystal Hartree-Fock Approximation^{*}

4.1 Introduction

The divalent-metal doped rare-earth-manganites have received a great deal of attention in recent years largely due to the colossal magnetoresistance (CMR) in these compounds. The phase diagrams of these manganites are very rich; the magnetic and conducting properties, as well as crystallographic structure, can vary substantially with temperature and doping concentration [84]. These properties alone, aside from the CMR, constitute an interesting research area. La_{1-x}Ca_xMnO₃ is a typical family of these manganites, with the CMR occurring in the region near x = 1/3 [84]. Here we focus on LaMnO₃ (the x=0 end member of the above family). Its properties, which involve magnetic and orbital orderings plus strong Jahn-Teller distortion, are interesting in their own right.

There has been a great deal of work on $LaMnO_3$; the papers most directly relevant here are Refs. 85 – 90. Saitoh *et al.* [85] obtained experimental photoemission results and interpreted them through a cluster configuration-interaction model. LSDA (local spin

^{*} This work has been published in "Y-S Su, T. A. Kaplan, S. D. Mahanti, and J. F. Harrison, Phys. Rev. B 61, 1324 (2000)".

density approximation) band calculations were reported in Refs. 86-88. In all three of the band calculations, the experimentally observed ground state magnetic ordering was found. The observed orbital ordering was obtained by Satpathy *et al.* [87] (this property was not discussed in Refs. 86 and 88). The spin Hamiltonian, which governs the magnetic properties including the low-lying excitations (spin waves or magnons), was calculated by Solovyev *et al.* [89] within the LSDA. Hirota *et al.* [90] determined the magnon dispersion via inelastic neutron scattering measurements, and claimed it to be consistent with the theory of Ref. 89. Sarma *et al.* [86] found their LSDA density of states and calculated photoemission intensity to agree with the measurements of Saitoh *et al.* [85].

These facts would seem to have the theory of these properties of LaMnO₃ in satisfactory shape. However, the theories of Refs. 85 and 86, both of which apparently explain the photoemission data, disagree with each other. In Ref. 86 (in agreement with the other LSDA calculations of Refs. 87 and 88), the Mn d-band lies near the top of the valence band, with the O p-band lower than the d-band, while in Ref. 85 the opposite order occurs. Furthermore, an LSDA+U band calculation gave the Mn d-band below the O p-band [87]. Thus there are major differences between existing pictures, and they are of considerable importance, e.g. at stake is the nature of the band gap, O-p \rightarrow Mn-d or Mn-d \rightarrow Mn-d (the two possibilities have been called charge-transfer insulators or Mott-Hubbard insulators, respectively [91]). We were thereby motivated to carry out calculations on LaMnO₃ using the Hartree-Fock approximation (HFA). HFA is a wellestablished theoretical approach, independent of the above methods, and thus can provide valuable comparison with the other results. Also, it is known that for some 3d-transitionmetal oxides with perovskite-based structure, e.g. lanthanum cuprate and nickelate, LSDA failed [92] and the HFA succeeded [93] to predict correctly the ground state insulating property and the magnetic ordering.

Our HFA results show some surprising physical effects, and significant differences from LSDA. The correct magnetic and orbital orderings and insulating character are found in both theories. However, we find major differences in the occupied densities of states (e.g. the O p bands lie close to the top of the valence band in the HFA, more like the interpretation of Ref. 85 and the LSDA+U results of Ref. 87). There is also a major difference in the effective spin Hamiltonians; yet the magnon dispersion curves of both theories are consistent with the neutron scattering experiment [90], as we will explain. Also, in apparent contrast to LSDA [87,94], a large spinless charge backflow, $O^{-2} 2p \rightarrow Mn^{+3} 3d$, is found in HFA. Finally, the fundamental type of insulator differs in the two approximations: LSDA gives a band insulator (the gap doesn't exist for the cubic structure), HFA yields a Mott insulator (the gap exists for both the cubic and distorted structures).

4.2 Method

If there were no distortion, $LaMnO_3$ would be a perfect cubic perovskite crystal as shown in Fig. 4.1. Note that the MnO_6 octahedron marked in the figure is connected with every one of its neighboring octahedra by sharing a common oxygen, which is a key signature of the perovskite structure. In reality, the MnO₆ octahedra (denoted as [MnO₆]) are strongly distorted due to Jahn-Teller effect and rotate from the crystal axes by an appreciable amount, resulting in an orthorhombic crystal structure (space group *Pnma*) with four Mn per unit cell [95]. The unit cell of the orthorhombic structure is close to a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the undistorted cubic perovskite structure. The longest side of the unit cell is chosen as c-axis [96] and the MnO₂ planes perpendicular to it are called basal planes.



Figure 4.1: The cubic perovskite crystal structure. This is the structure for compounds like KNiF₃ and CaMnO₃. For LaMnO₃, large distortion exists. The atom at the center of the cube is Mn, the face centers are O₄ and the corners are La. The important MnO₆ octahedral cluster is marked by the dotted lines.

We carried out the calculations on both the observed orthorhombic structure and the fictitious iso-volume cubic structure in order to investigate the effect of the strong lattice distortion. To our knowledge, ours is the first *ab initio* HFA calculation for this material [97]. The calculation makes use of the program *CRYSTAL95* [98]. The basis sets of Mn and O are those optimized for CaMnO₃ [99]. La is treated as a bare La^{+3} ion and represented by an effective core potential [100]; a test of this approximation as well as other accuracy control parameters of the program will be discussed in Sec. 4.4.

4.3 Results

4.3.1 Magnetic properties

For the orthorhombic structure, it can be shown that there are five collinear magnetic orderings that maintain the size of the unit cell. They are ferromagnetic (FM), A-type, G-type, and C-type antiferromagnetic (AAF, GAF, and CAF), and ferrimagnetic (FI) orderings, defined as follows. AAF: the Mn spins are parallel in a basal plane and antiparallel from plane to plane. GAF: each nearest neighbor (n.n.) pair of Mn are antiparallel. CAF: each n.n. pair of Mn are antiparallel in a basal plane and parallel along the c-axis. FI: one of the four Mn in a unit cell is antiparallel to the other three. HFA results for these ordered states are listed in Table 4.1, together with LSDA results [88] for comparison. It is seen that HFA predicts the ground state of LaMnO₃ to be an AAF insulator, in agreement with experiment [101]. LSDA also makes the same prediction. In the cubic structure, both theories predict the FM state to have the lowest energy.

However, there are substantial differences between the theories. E.g., in HFA all states are insulating (for both cubic and orthorhombic structures), while in LSDA all states of the cubic structure are metallic [88]. The band gaps (not shown in the table) in HFA are much larger than those in LSDA. From the results in the AAF column, it is seen that the crystal distortion lowers the energy per Mn by \sim 1 eV in HFA, vs. 0.27 eV in LSDA. For the cubic case, it is seen that LSDA predicts much larger energy differences among the various magnetically ordered states.

Table 4.1: HFA and LSDA [88] energies of LaMnO₃ with various magnetic orderings. The energies shown are relative to the FM state of the cubic structure, in meV / Mn. (ins.=insulator, met.=metal.) The HFA energies are for the states with the observed orbital ordering (see text).

		FM	AAF	GAF	CAF	FI
HFA	cubic	0, ins.	0.4, ins.	34, ins.	32, ins.	16, ins.
	orth.	-1053, ins.	-1055, ins.	-1041, ins.	-1039, ins.	-1047, ins.
	cubic	0, met.	110, met.	365, met.		
LSDA	orth.		-156, ins.			

The HFA energies of the five magnetically ordered states for the orthorhombic structure are used to map to an effective spin Hamiltonian (see Refs. 93 and 99 for discussion of the mapping). We add 4-spin terms to the usual 2-spin terms in the spin Hamiltonian [102]

$$H = \text{constant} + \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{(i,j,k,l)} J_{ijkl} (4 - \text{spin terms}) + \cdots; \qquad (4.1)$$

where \bar{S}_i is the spin at (Mn) site i, J_{ij} and J_{ijkl} are exchange parameters, and each combination of summation indices is summed once. Since there are five energies, the mapping can determine four J's plus the constant in H. We choose the J's in the following way. We consider the one-band Hubbard model with n.n. intra- and inter-(basal) plane hopping t_1 , t_2 . Perturbation theory with the t_1 small implies the spin Hamiltonian of Eq. (4.1). Keeping through fourth order terms, more than four J's occur; however, only a particular subset of four can be determined by the five ordered states considered. This is the chosen set and is as follows: the intra-plane n.n. J_1 , the inter-plane n.n. J_2 , the inter-plane next n.n. J_3 , and the inter-plane 4-spin J_4 . Due to the distortion of the crystal structure, there are actually two types of J_3 and J_4 , denoted as $J_3^{(1)}$ and $J_3^{(2)}$ [89], and $J_4^{(1)}$ and $J_4^{(2)}$. In the mapping here, only the average values of the two types of J's are determined: J_3 is the average of $J_3^{(1)}$ and $J_3^{(2)}$, and similarly for J_4 . Note that the same mapping can also be done for the cubic case. This is possible because the existing orbital ordering (discussed later on) breaks the cubic symmetry and make, for example, J₁ not equal to J_2 .

The results of the mapping are listed in Table 4.2. In both the cubic and orthorhombic cases, J_3 and J_4 are negligible. This supports the neglect of further neighbor terms, expected *a priori* to be small. The signs of J_1 and J_2 reflect the ground state magnetic properties (FM for the cubic and AAF for the orthorhombic). LSDA calculations by Solovyev *et al.* for the orthorhombic case give a qualitatively different picture [89]. As shown in Table 4.3, LSDA gives a much bigger J_3 ; also J_1 and J_2 are both

ferromagnetic and they alone would yield a wrong magnetic state. It is the J_3 that turns the ground state from FM to AAF in the LSDA.

	J	J ₂	J ₃	J ₄
cubic	-2.1	-0.13	0.019	0.0049
orth.	-0.88	0.21	0.0036	0.00051

Table 4.2: HFA J's in the effective spin Hamiltonian of LaMnO₃, in meV.

The spin wave spectrum of the system has been measured in a recent inelastic neutron scattering experiment and was fitted very well using a 2-J (J_1 and J_2) spin Hamiltonian by Hirota *et al.* [90]. The results are also included in Table 4.3 for comparison. Our HFA results are smaller in magnitude than the experimental values by about a factor of 2 for J_1 and 6 for J_2 . At first glance one would say that the experiment shows a 2-J character of the system and thus favors the HFA picture. However, as we analyze further, we find that this conclusion is not solid enough yet. Hirota *et al.* state that their experimental results are consistent with those of Solovyev *et al.* in the following sense. If one maps the 3-J model by Solovyev *et al.* to the following effective 2-J model,

$$\begin{cases} J_1^{(2J)} = J_1^{(3J)} \\ J_2^{(2J)} = J_2^{(3J)} + 4J_3^{(3J)} \end{cases},$$
(4.2)

(the factor of 4 in the second equality comes from the coordination number involved with J_3), then $J_1^{(21)}$ and $J_2^{(21)}$ have the right signs and are both about a factor of 2 too large in magnitude compared with the experimental values. By Eq. (4.2), the 3-J model and its

effective 2-J model have identical spin wave dispersion along the c-axis. Dispersion along several other directions is shown in Fig. 4.2. It is seen that the spin wave spectra of the two models are quite close. The difference is estimated to be about the size of the error bars of the experimental data cited. So at this point, the LSDA picture is not definitely ruled out. The issue could be settled by somewhat more accurate measurements.

Table 4.3: Comparison of the HFA, LSDA [89] and experimental [90] J's in the spin Hamiltonian of LaMnO₃, in meV.

	J	J ₂	J ₃	
Exp.	-1.67	1.21	~ 0	
HFA	-0.88	0.21	~ 0	
LSDA	-2.28	-0.78	0.78	



Figure 4.2: The spin wave dispersions of the 3-J (solid line) and its effective 2-J (dashed) spin Hamiltonians, along four arbitrarily chosen directions. The values of J's are those given by Solovyev *et al.* [89]. The k-indexing follows the convention used in Ref. 90.

4.3.2 Spinless Charge Backflow and Density of States

To our surprise, Mulliken population analysis (MPA) on the HFA results gives charges that deviate substantially from the formal valence picture, although the spin values do not show such deviation. We find $Mn^{+2.2}$, $O_1^{-1.7}$ and $O_{11}^{-1.75}$, while the Mn spin is 1.98; the formal valence picture is Mn^{+3} , O^{-2} , with Mn spin of 2. (O_1 is the apical oxygen and O_{11} , the basal-plane oxygen.) We note that, due to the bare core approximation for La, these MPA results should only serve as an indication of deviation from the formal valence picture, not taken as being very accurate. A similar but more severe departure from the formal valence picture has been reported for an all-electron HFA calculation on CaMnO₃ [99], where Mn was found to be $Mn^{+2.17}$ with spin 3.25/2, compared with the nominal value Mn^{+4} with spin 3/2. That is, there is a large nearly spinless backflow of electrons from O^{-2} to Mn^{+3} or Mn^{+4} . Such large changes in ionic charges would have obviously important consequences, e.g., on Madelung energies, phonon spectra, dielectric constant. How they would affect current simplified models is obscure, but certainly their implications for such models would have to be considered.

It must be pointed out that the MPA is basis set dependent, and can be very misleading when in the basis set there are diffuse basis functions that are appreciably occupied [103,104]. However the following considerations suggest that the deviation from the formal valence picture found here cannot be explained solely by basis set dependence. (i) We repeated the calculation with the most diffuse Mn d and O sp basis functions omitted from the basis set. This gave a very small change in the MPA, the result actually being further from the formal valence picture. (ii) The way that the MPA

attributes an overlap charge to the two atoms involved is somewhat artificial and therefore results in an inherent uncertainty in the meaning of the MPA results. Moreover, when the MPA gives ridiculous results due to the presence of very diffuse basis functions in the basis set [103,104], there usually are large overlap charges. So smallness of the overlap charges is an indication of the reliability of the MPA results. In the present case, the overlap charges totally account for 0.06 electrons for Mn, considerably smaller than the deviation of the MPA charge of Mn from the formal charge. (iii) In contrast to MPA, the charge from the actual integration of the charge density over a reasonable volume (vide infra) around an atom is much more basis-set insensitive, and gives a realistic value of the HFA result (assuming a good basis set, of course). So this integration is a good check for verifying the correctness of MPA results. We didn't do the integration for $LaMnO_1$ since the precise numbers will not be useful due to the bare core approximation for the La, as mentioned in the previous paragraph. Instead, we redid the all-electron calculation of Ref. 99 for CaMnO₃, and then integrated the charge density over a cube around a Mn. The faces of the cube are perpendicular to the Mn-O bonds and pass through the minima of the charge density along the bonds, which gives the cube edge to be 1.8 Å (the cube is close in size to the Mn sphere of diameter 2.12 Å used in Ref. 88). The integrated charge for Mn was +2.52, close to the MPA result of +2.17. Further discussion of the La bare core approximation is given in Sec. 4.4, where it is suggested that a large deviation from formal valence, as found above, probably will hold true in more accurate HFA calculations.

The projected density of occupied states of $LaMnO_3$ is shown in Fig. 4.3. It is seen that a small amount of Mn-d projected density of states (DOS), both up and down,

exists in the range of 0 to 6.9 eV below the top of the valence bands, E_t , coinciding with the range of the O p bands and accounting for the nearly spinless backflow. The large peaks (spin up) in the Mn-d projected DOS in the 8.7-10.3 eV range below E_t are associated with the Mn d bands, which are spin polarized and give the moment of Mn close to that predicted by the formal valence picture.

This HFA picture is rather different from previous LSDA calculations. First, to our knowledge, no departure from the formal valence picture has been reported in LSDA studies of the system. In fact, Satpathy *et al.* [87] state that the charge states are close to nominal in their LSDA results. Second, the O p bands lie above the Mn d bands in HFA, opposite to what LSDA predicts [86-88,94]. The disagreement between HFA and LSDA in the order of O p and transition metal d bands has also been seen for other systems. [92,93,88,99]

We also note that LSDA+U calculations [87] show ordering of the O p and Mn d bands much like our HFA results. Those calculations were disparaged [88] on the grounds that the Mn spin turned out to be larger than the nominal value (3/2 for CaMnO₃). However, as far as we are aware, there is no theorem that the Mn spin must not be greater than nominal. In fact intra-atomic exchange would tend to increase the Mn spin by polarizing electron transfer from O; also, we find in HFA an increase in Mn spin (as determined by integration of the spin density within a suitable cube centered at the Mn) over the nominal value for CaMnO₃.



Figrue 4.3: The (projected) DOS of LaMnO₃, with AAF ordering. Positive and negative DOS are for up- and down-spin states, respectively. Energies are relative to the top of the valence band. The projected Mn-d and O_{II} -p DOS are for Mn and O on an up-spin basal plane. The projected O_I -p and total DOS are symmetric for up- and down-spin. The down-spin part of the total DOS is omitted from the figure.

The HFA predictions of the charges on ions and the characters of the valence bands are consistent with the interpretation of a recent experiment by Saitoh et al., who studied La_{1-x}Sr_xMnO₃ by photoemission and x-ray-absorption spectroscopy [85]. These authors determined that the character of the band gap of LaMnO₃ is of the p-to-d chargetransfer type while that of SrMnO₃ (corresponding to CaMnO₃ in our discussion) has considerable p-p character as well as p-d character. The HFA results (via the MPA) show that for LaMnO₃ and CaMnO₃, the Mn-d electron population is roughly equal, while the O-p population gets reduced for the latter. This implies that the valence bands of CaMnO₃ consist of a smaller amount of O-p character than LaMnO₃, which in turn suggests that there is a larger amount of O-p character in the conduction bands of CaMnO₃. Combining this with the other HFA prediction that the O p bands are the highest occupied bands can explain the above experimental observation. Saitoh et al. also reported that the Mn-d electron population is 4.5 for LaMnO₃ and 3.8 for SrMnO₃, a considerable deviation from the formal valence picture similar to (although not as severe as) that predicted by the HFA, which we find to be about 4.7 for both $LaMnO_3$ and The most surprising aspect of the Saitoh et al. work [85] is that their CaMnO₁. calculation showed a large reduction in photoemission intensity of the Mn d band as compared to the density of states (due to matrix-element effects). We intend to calculate that intensity using our HFA wave functions to check this.

4.3.3 Orbital Ordering

We now discuss orbital ordering – this is ordering of the single e_g orbital occupied at each Mn. In the observed structure, each [MnO₆] is stretched substantially along one axis and is rotated by 10-15° from its orientation in the cubic structure. Disregarding the rotation for simplicity, the stretched axes lie in the basal plane, alternating in direction by 90°, and this pattern repeats along the c-axis. The stretching, being driven by the Jahn-Teller splitting of the eg states, leads to an expected orbital ordering – the single occupied e_g orbital at each Mn is d(3z²-r²)-type with its axial symmetry along the stretched axis of the associated [MnO₆]. This orbital ordering is indeed found in our HFA solutions, by plotting the spin density. A combination of the three t_{2g} and one e_g electrons (nominally the only unpaired electrons in the system) dictates a unique shape in the spin density distribution, which therefore can be used to identify which e_g orbital is actually occupied. For example, Fig. 4.4 shows the spin density at a Mn with the $d(3x^2-r^2)$ orbital occupied (the z-direction is along the c-axis). This orbital ordering, which was predicted long ago by Goodenough [105], has also been obtained in LSDA calculations [87], and was recently confirmed in experiments [106].

Spin Density at $d(3x^2-r^2)-Mn$



Figure 4.4: The spin density on the xy-, yz- and zx-planes at a Mn with the $d(3x^2-r^2)$ and three t_{2x} orbitals occupied. The plotting region is about (3.9 Å)², centered at the Mn. The slightly off of the symmetry axes of the distribution from the x-, y- and z-axes is a result of the rotations of the [MnO₄] in the observed crystal structure.

In our study, we obtain the same orbital ordering for all trials with various magnetic orderings as well as initial conditions used to start the Hartree-Fock calculations, for the observed orthorhombic structure. However, for the cubic structure we find a variety of orbital orderings by starting with different initial conditions. This is probably due to the absence of the Jahn-Teller distortion which would stabilize the occupancy pattern of the e_g orbitals [107]. Table 4.4 lists the energies of the various states we have obtained in the cubic case. Roughly speaking, the results suggest that the energy scales associated with the change in crystal structure (cubic to orthorhombic), orbital ordering (in the cubic structure), and magnetic ordering are in the ranges of 1, 0.1 and 0.01 eV / Mn, respectively.

Table 4.4: HFA energies of different magnetic and orbital ordering states for the cubic structure. The symbol $d(3z^2-r^2)$ means that the e_g electron is of this type for all Mn, similarly for $d(x^2-y^2)$. The third one, $d(3x^2-r^2)/d(3y^2-r^2)$, is the observed ordering of the orthorhombic structure, as discussed in the text. Energies are relative to the AAF state of the orthorhombic structure, in meV / Mn.

	FM	AAF	GAF	CAF
$d(3z^2-r^2)$	-	1147.4	-	-
$d(x^2-y^2)$	-	1165.9	1145.0	1157.5
$d(3x^2-r^2)/d(3y^2-r^2)$	1054.8	1055.2	1088.9	1087.2

4.4 Discussion and Summary

The extreme smallness of the various energy differences between magnetic states requires a discussion of the numerical accuracy of our calculations. The sources of error are [98] the tolerance in the direct-space summations of Coulomb and exchange series (controlled in the program by five parameters called TOLINTEG), the number of sampling points for the Brillouin zone integration (controlled by a shrinking factor IS), and the finite basis sets used. The presented results of this work were calculated using TOLINTEG of (7, 7, 7, 7, 14) and IS of 6. IS = 6 translates to 80 asymmetric k-points in the Brillouin zone and is more than adequate for our need of accuracy; the total energy obtained from using IS = 4 (30 asymmetric k-points) deviated by less than 0.003 meV / Mn. The deviation of total energy due to change of TOLINTEG is much larger; by using (8, 8, 8, 8, 16) for TOLINTEG, we observed that the total energy changed by about 50 meV / Mn. However, the energy differences between various magnetic states in the test remained quite stable, typically only varying by $\sim 0.1 \text{ meV} / \text{Mn}$. Concerning the errors due to the finite basis sets, we expect the most severe should come from the La bare core approximation, which we now discuss.

The test of the bare La^{+3} ion approximation consisted of adding to the La^{+3} core an optimized d shell consisting of a single primitive Gaussian (0.32 Bohr⁻² is the optimized exponent). The total energy decreased by about 2 eV / Mn; however, the energy differences between the various magnetic states changed by only ~ 0.1 meV / Mn (a few %), and the change in the occupied band structure (not shown) is small. Similar behavior of the basis set dependence was also found in studies of other systems [93]. The charges

found in the test were $La^{+2.58}$, $Mn^{+2.14}$, $O_I^{-1.55}$ and $O_{II}^{-1.59}$. Interestingly, 0.42 electrons per La occupied the added La d shell, but these electrons were taken from oxygen, making the results even further from the formal valence picture.

To summarize, our HFA results on LaMnO, give a dramatically different picture from that of previous LSDA calculations, although for some properties, e.g. orbital and magnetic ordering, the two theories agree. This agreement is surprising in view of, but certainly not inconsistent with, the large differences. Some of the HFA predictions have been supported by experiment. In particular, the HFA spin Hamiltonian is consistent with a spin wave experiment, but the present accuracy of the experiment is not quite sufficient to distinguish conclusively between the HFA and LSDA results. The DOS in HFA is consistent with one interpretation [85] of a photoemission experiment [85]. However it is not consistent with another interpretation [86] of the same experimental results, based on LSDA. Further, the DOS in LSDA+U theory [87] is more like the HFA result, and is definitely inconsistent with the LSDA result. We can conclude that our HFA results have added weight to the picture where the top of the valence band consists predominantly of O-p states, as found in the LSDA+U [87] and the cluster model interpretation of photoemission results [85] (in contradiction to the LSDA results [86-88]).

Chapter 5

Effect of Oxygen Vibration on Spin Waves in the Double-Exchange Model

5.1 Introduction

In recent years, research activities on perovskite manganites such as $A_{1,x}B_xMnO_3$ (A represents a trivalent rare-earth element such as La, Pr or Nd; B represents a divalent alkali or transition element such as Ca, Sr, or Pb) have increased dramatically due primarily to the possibility of important technological applications of the colossal magnetoresistance observed in about the $0.2 \le x \le 0.4$ region. $A_{1,x}B_xMnO_3$ has the typical perovskite structure, where each Mn is surrounded by six oxygens forming an MnO₆ octahedron, and each MnO₆ octahedron shares one oxygen with each of its six nearestneighbor octahedra. Fig. 4.1 in Chap. 4 shows the basic cubic structure of $A_{1,x}B_xMnO_3$, while the actual crystal may exhibit distortion depending on the constituents and doping concentration.

When x = 0, each Mn carries charge of +3 with electronic configuration [Ar]3d⁴. The substitution of a divalent element for the trivalent element introduces holes and results in Mn⁺⁴ ([Ar]3d³) ions in the crystal. The electronic transport properties of these manganites are usually described by the so called double-exchange (DE) model [108]. In the model, only the d electrons of Mn's are considered. Due to the cubic (or near cubic) crystal field, the Mn d shell splits into t_{2g} (xy, yz, zx) and e_g (x²-y², 3z²-r²) levels with the former lower in energy. In the DE model, three electrons are assumed to be in the t_{2g} orbitals, localized at each Mn, constituting a local spin \vec{S}_i at i site, $S_i = 3/2$. All remaining d electrons, the number of them depending on the doping concentration, go into the e_g orbitals and can hop from Mn to Mn. The interactions between the t_{2g} and e_g electrons are governed by the strong intra-atomic exchange J (Hund's rule coupling) and Coulomb repulsion. Historically, people considered the simpler single-band DE model (assuming one e_g orbital per Mn), which reads:

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^{+} c_{j\sigma} + \text{h.c.}) - J \sum_{i} \vec{S}_{i} \cdot \vec{s}_{i} , \qquad (5.1)$$

where $\langle ij \rangle$ denotes nearest neighbors, $c_{i\sigma}^{+}(c_{i\sigma})$ creates (destroys) an e_g electron with spin σ at Mn of site i, $\vec{S}_i(\vec{s}_i)$ is the spin of the localized t_{2g} (conduction e_g) electrons, and t (J) is the hopping (exchange) parameter, both positive. In these materials, $J/t \gg 1$. This model can explain the concurrence of the metallic and ferromagnetic phases of the materials in the following way: if all of the local spins \vec{S}_i are parallel, then the conduction (e_g) electrons with the same spin direction can move most freely because there is no energy barrier (due to the exchange term) for them to hop between sites, thereby minimizing the kinetic, as well as the exchange energy.

The DE model of Eq. (5.1) also predicts a shape of the spin wave dispersion very much like that of the Heisenberg model with nearest neighbor spin-spin coupling in a broad range of doping concentration, $0.1 \le x \le 0.6$ [109]. This has been confirmed by experiments on high-T_c (Curie temperature) manganites, e.g. La_{0.7}Pb_{0.3}MnO₃ [110]. However, recent experiments on low-T_c manganites such as La_{0.7}Ca_{0.3}MnO₃ [111] showed strong softening of the dispersion near zone boundaries compared with that of the Heisenberg model with same spin wave stiffness. Moreover, results of Ref. 111 strongly suggest that this softening is phonon-induced and the magnon-phonon band crossing pattern is unusual and therefore intriguing. Under common circumstances, the spin wave dispersion is a steadily increasing curve from Brillouin zone (BZ) center to the zone boundary. (In one dimension, it is more or less close to an upside-down cosine curve.) On the other hand, an optical phonon band remains quite flat throughout the whole BZ. If these two bands happen to cross and there is some inter-band interaction present, usually we would expect that a gap opens up near the crossing and two new non-crossing bands are formed. This expectation turns out not to be the scenario observed in the low-T_c manganite experiment of Ref. 111. The experimental data show the following: The optical phonon band remains roughly constant all the way to the BZ edge. The spin wave band increases from zero at k = 0, but where it meets the optical phonon band, it flattens ("softens") and merges with the phonon band, out to the BZ edge. Thus there is no band above the phonon band near the BZ edge as would be expected in usual band-crossing situations. Based on the DE model, we have tried several possible schemes for the electron-phonon interaction to seek the mechanism which underlies the observed spin wave softening.

5.2 A flaw of popular models in the literature

In fact, even before the recently found spin wave softening many modifications of the DE model had been studied in the literature for various reasons, e.g. isotope effect [112]. Most of the works extended the DE model by including some form of the so called Jahn-Teller (JT) coupling. According to the well known Jahn-Teller theorem, it is energetically favorable to distort the MnO₆ octahedra to lift the degeneracy of the two e_g orbitals. This interplay between the electronic energy and the geometry of a MnO₆ octahedron is therefore called JT coupling and is introduced in many extensions of the original DE model. A typical model including the JT coupling is the following:

$$H = H_e + H_{ph} + H_{JT}, (5.2)$$

$$H_{e} = -\sum_{\langle ij \rangle,\sigma,ab} t_{ij}^{ab} (c_{ia\sigma}^{+} c_{jb\sigma}^{-} + \text{h.c.}) - J \sum_{i,a} \vec{S}_{i} \cdot \vec{s}_{ia}^{-} - \frac{U}{2} \sum_{i,\gamma} \tau_{i\gamma} \tau_{i\gamma}^{-} , \qquad (5.3)$$

$$H_{ph} = \frac{M}{2} \sum_{i,\alpha} \dot{Q}_{i\alpha}^2 + \frac{K}{2} \sum_{i,\alpha} Q_{i\alpha}^2 , \qquad (5.4)$$

$$H_{JT} = g' \sum_{i} Q_{i1} I_{i} - g \sum_{i} (Q_{i2} \tau_{ix} + Q_{i3} \tau_{iz}), \qquad (5.5)$$

This is a two-band model: it considers both the two e_g orbitals of each Mn, which are described by a pseudospin τ . Due to some technical details, only x and z components of τ are present in the model. The first two terms in Eq. (5.3) are just the direct generalization of the single-band DE model. The third term in Eq. (5.3) takes into account the on-site Coulomb repulsion between e_g electrons, which is irrelevant in the

single-band DE model in the large J/t limit but important in the two-band DE model. Eq. (5.4) is the Hamiltonian of the three relevant normal mode vibrations (with coordinates Q_1, Q_2 and Q_3 , respectively) of each MnO₆ octahedron [112]. Eq. (5.5) is the JT coupling (an electron-phonon interaction), where the Q modes affect the on-site energies of the two e_g orbitals in a specific way deduced from symmetry considerations (g' and g are two coupling constants). Note that there is a definite proportionality among the components of t_{ij}^{ab} , but the actual relation is not uniquely determined and its form may vary slightly from model to model [113].

By Eq. (5.4), this model assumes that the vibrations of MnO₆ octahedra of different sites are uncoupled, which we consider as a rather unphysical assumption. The fact that every pair of nearest-neighbor octahedra share a common oxygen implies that their individual vibrations cannot be uncoupled. In other words, there should be some cross terms (Q_iQ_j and $\dot{Q}_i\dot{Q}_j$ terms) in Eq. (5.4). Unfortunately, the significance of this assumption has not been discussed in most of the literature. [114]

One may speculate that maybe the cross terms are small in the first place. This turns out not to be the case. Furthermore, there are more complications than meet the eyes. To illustrate the point, consider a 1D chain of Mn-O as shown in Fig. 5.1:

 $\cdots \quad \bullet \quad O \quad \bullet \quad O \quad \bullet \quad O \quad \bullet \quad O \quad \cdots \\ \cdots \quad i-1 \quad u_{i-1} \quad i \quad u_i \quad i+1 \quad u_{i+1} \quad i+2 \quad u_{i+2} \quad \cdots \\ \bullet \text{ manganese } \quad O \text{ oxygen}$

Figure 5.1: The Mn-O linear chain
The manganese atoms are assumed heavy and therefore still. The u_i 's are displacements of the oxygens from their equilibrium positions. Suppose there are N unit cells with periodic boundary condition, i.e. $u_{N+i} = u_i$. The Hamiltonian of these vibrations can be written in terms of u_i 's and their conjugate momenta:

$$H_{ph} = \frac{1}{2M} \sum_{i=1}^{N} p_i^2 + \frac{K}{2} \sum_{i=1}^{N} u_i^2$$
(5.6)

In this 1D model, the relevant normal mode coordinate of each unit cell would be

$$Q_i = \frac{1}{\sqrt{2}} \left(u_i - u_{i-1} \right). \tag{5.7}$$

Now, can we transform the Hamiltonian to a form in terms of the Q variables? The answer is NO. Because of the periodic boundary conditions, we have

$$\sum_{i=1}^{N} Q_i = 0.$$
 (5.8)

This means that we only have N-1 truly independent Q variables. Therefore the transformation from the u variables to Q variables is impossible unless we add an arbitrarily chosen new variable to the Q set. A natural choice for the Nth variable (let's call it Q_0) will be

$$Q_0 \equiv \frac{1}{N} \sum_{i=1}^{N} u_i \tag{5.9}$$

Now we are able to proceed with the transformation of Eq. (5.6) from $\{u\}$ to $\{Q\}$. The result is not in a simple form and therefore is omitted here. But the general properties of the results can be described easily: After the transformation, terms Q_iQ_j with any i and j

are present. For i and j nonzero, the coefficients of Q_iQ_j (i \neq j) are of the same order of magnitude as those of the diagonal terms Q_i^2 when |i - j| are small, then their magnitudes decrease gradually with |i - j| and become near zero when |i - j| reach the maximum. Furthermore, cross terms not only occur in the potential energy part (the Q_iQ_j terms), but also in the kinetic energy part (the P_iP_j terms) with the same coefficients. This means that the neglect of cross terms in Eq. (5.4) is not justified.

There is actually a paper by G. Khaliullin and R. Kilian [115], which includes cross terms of nearest-neighbor Q's with the coefficient as an adjustable parameter, claiming to have solved the spin wave softening problem. However, there is a flaw in their model: cross terms of the kinetic energy part are missing.

5.3 Model Studied

In view of the question raised in the previous section, we suggest that the H_{ph} in Eq. (5.4) should be replaced by

$$H_{ph} = \frac{M}{2} \sum_{i,\alpha} \dot{u}_{i\alpha}^{2} + \frac{K}{2} \sum_{i,\alpha} u_{i\alpha}^{2} , \qquad (5.10)$$

where the u variables denote the displacements of individual oxygens. The H_{JT} in Eq. (5.5) remains unchanged but should be now written in terms of the u variables.

To seek the mechanism which underlies the spin wave softening near the zone boundaries, we explored several possible schemes of inclusion of electron-phonon interaction into the DE model. To get started, we considered the 1D single-band model

with only oxygen vibrations taken into account. The portion of the crystal structure of interest to the model is the Mn-O linear chain, as shown in Fig. 5.1. The Hamiltonian considered has the following form:

$$H = H_e + H_{ph} + H_{e-ph}, (5.11)$$

$$H_e = -t \sum_{i,\sigma} (c_{i\sigma}^+ c_{i+1,\sigma} + \text{h.c.}) - J \sum_i \vec{S}_i \cdot \vec{s}_i , \qquad (5.12)$$

$$H_{ph} = \frac{1}{2M} \sum_{i} p_{i}^{2} + \frac{K}{2} \sum_{i} u_{i}^{2} .$$
 (5.13)

The electronic part H_e is just the original single-band DE model. The phonon part H_{ph} represents the simple-harmonic oxygen vibrations (u_i and p_i are the displacement and corresponding momentum of oxygen at site i). $H_{e,ph}$ stands for the electron-phonon interaction part and hasn't been specified above. Which form of the electron-phonon interaction $H_{e,ph}$ would give rise to the spin wave softening is not known *a priori*. It could be that displacements of the neighboring oxygens would affect the local on-site energy ε of the e_g orbital. Assuming linear response $\varepsilon_i \propto (u_i-u_{i-1})$, then $H_{e,ph}$ would have the form:

$$H_{e-ph} = \sum_{i,\sigma} \varepsilon_i c_{i\sigma}^+ c_{i\sigma} = -g \sum_{i,\sigma} (u_i - u_{i-1}) c_{i\sigma}^+ c_{i\sigma} .$$
(5.14)

This is analogous to Eq. (5.4) for the two-band model. In addition, we have also considered another possibility where oxygen vibrations affect the local electron hopping parameter t (in both magnitude and phase). The results of the first scheme (changing on-site energy) are presented in next section, while the results of the other scheme will only

be mentioned briefly in Sec. 5.5, *Remarks and Conclusions*, since its results are not any better than those of the first scheme towards the explanation of the spin wave softening.

5.4 Results

We solved the Hamiltonian of Eq. (5.11) – (5.14) for a ring with 4 Mn's and 4 O's in the $S_z^{total} = S_{maximum} - 1$ manifold in two different approximate ways.

5.4.1 Pseudo-Born-Oppenheimer approximation

In this approximation, the oxygen is assumed heavy and H_{ph} is neglected. Each u_i in H_{e-ph} [Eq. (5.14)] is randomly taken from the interval [- $\delta/2$, $\delta/2$] with a uniform probability distribution. For a set of { u_i } randomly taken, $H_e + H_{e-ph}$ is solved exactly, giving a set of electronic eigenenergies. Then another set of { u_i } is chosen, and the procedure repeats. We ran many iterations to get a statistical distribution of the electronic eigenenergies. A typical case is shown in Fig. 5.2 with ground state energy set to 0.

Fig. 5.2(a) shows the energy levels of the ordered system. The lowest three peaks carry the wave vector quantum number k of 0, $\pm \pi/2$ (two-fold degeneracy) and π , respectively. These are excited sites due to creation of a single magnon, with wave vector k, from the ground state. For an infinite ring, these three levels will expand into a complete band and become the familiar spin wave dispersion. Thus we refer to the states associated with these three peaks as the spin wave states.



Fig. 5.2(b) shows clearly that each energy level of the ordered system is now broadened by the random electron-phonon interaction. Compared with the width of the random distribution of u_i (0.5 in this example), the broadening of the spin wave levels is surprisingly small. Other higher energy levels do have much larger broadening. The results suggest that the spin wave dispersion remains robust in the presence of the electron-phonon interaction of the form of Eq. (5.14). Moreover, we also calculated the distribution centers of the spin wave states in Fig. 5.2(b) and found that the ratio of the (averaged) $k=\pi$ magnon energy to the $k=\pi/2$ magnon energy increases slightly compared with that of the ordered system [Fig. 5.2(a)]. Therefore this model actually predicts a small hardening in the spin wave dispersion, opposite to the experimental observation.



Figure 5.2: Density of states of the DE model for a 4-site, 3-electron ring. $(t = 1, J = \infty, g = 1, \delta = 0.5)$

5.4.2 QM treatment of the oxygen vibrations with cut-off in the number of phonons

In the second approximation, we treated the oxygen vibrations fully quantummechanically but a cut-off in the number of phonons was imposed. This approximation was checked for convergence by using different cut-offs. The energies of the spin wave states are shown in Fig. 5.3, plotted as E versus k. The result is consistent with that of the first approximation; namely, the spin wave energies are very robust in the presence of the electron-phonon interaction Eq. (5.14) and the spin wave dispersion is actually slightly hardened in this model.



Figure 5.3: The spin wave dispersion of the DE model for a 4-site, 3-electron ring. (cutoff of phonon number = 4, t =1, J = ∞ , $\omega_{ph} = 0.15$)

5.5 Remarks and Conclusions

We have criticized the unphysical assumption of uncoupled vibrations of the MnO_6 octahedra in studies of the DE model with JT coupling, which unfortunately is prevalent in the literature. We suggest that the H_{ph} in question should be changed from Eq. (5.4) to Eq. (5.10).

In seeking the underlying mechanism of the recently observed spin wave softening in low-T_c manganites, we considered the simple 1D single-band DE model with electron-phonon coupling in the spirit of our suggestion mentioned above. Given the Hamiltonian of Eq. (5.11)-(5.14), the spin wave energies hardly change at all in the presence of the electron-phonon interaction. A study of the ratio of the energies of the k= π and $\pi/2$ magnons shows that the model actually predicts slightly hardening in the spin wave dispersion, contrast to the large softening found in experiments for low T_c manganites.

Although omitted here, another possible scheme for the H_{e-ph} , in which oxygen vibration can modify the local electron hopping, is also studied. Two cases in this regard are considered: One is

$$H_{e-ph} = \alpha \sum_{i\sigma} u_i^2 \left(c_{i\sigma}^+ c_{i+1,\sigma} + \text{h.c.} \right), \tag{5.15}$$

where α is an adjustable but positive parameter. Note that the sign of this term is opposite to that of the hopping term in Eq. (5.11); that is to say that the displacement of oxygen, u_i, can reduce the magnitude of the local electron hopping. The proportion to u_i²

is due to symmetry consideration; the reduction of the hopping magnitude shouldn't depend on which way the oxygen moves. The other case is

$$H_{e-ph} = -t \sum_{i\sigma} \left(e^{i\alpha u_i} - 1 \right) \left(c_{i\sigma}^+ c_{i+1,\sigma} + \text{h.c.} \right) \approx -i\alpha t \sum_{i\sigma} u_i \left(c_{i\sigma}^+ c_{i+1,\sigma} + \text{h.c.} \right).$$
(5.16)

This assumes that u_i can alter the phase of the local electron hopping. Despite the rather different mechanisms defined in Eqs. (5.14), (5.15) and Eq. (5.16), their effects are very similar for the spin wave states alone (while they make larger difference for other states). Namely, the spin wave states are robust and the dispersion gets very slightly hardened in the presence of these electron-phonon interactions.

This strongly indicates that the observed softening of the spin wave dispersion cannot be explained by the simple single-band model. A more realistic two-band model which incorporates the Jahn-Teller effect such as Eqs. (5.2), (5.3), (5.5) and (5.10) may be needed in this respect.

Chapter 6

Concluding Remarks

This work gives several new results which are likely to have a broader impact on the research community on these subjects. First, although the three-band Hubbard model with the model parameters fitted to high-T_c superconducting cuprates [12] has a large t_{pd}/ϵ_{pd} (~0.36) ratio, the perturbation expansion using the effective Hamiltonian method on this model for the undoped case is proved to converge well in the leading order. It explains why the low-lying states of the undoped cuprates are found to be governed by the nearest-neighbor Heisenberg spin Hamiltonian in a study of the model on small clusters [16]. However, the rapid convergence of the expansion doesn't come from the straightforward perturbation. In fact, the straightforward perturbation does not converge at all. To achieve convergence, one has to first perform a proper canonical transformation on the model Hamiltonian and then apply the perturbation method to the transformed Hamiltonian. In this work, it is shown that transformations involving only recombinations of the underlying single-particle orbitals (called 1-body transformations) lead only to a slow convergent expansion. The reason for the slow convergence is the following: 1-body transformations are usually aimed to reduce the hopping between the transformed orbitals. But at the same time, it also reduces the intra-atomic Coulomb repulsion in the new d orbitals due to the p-d orbital mixing (the Coulomb repulsion in the p orbitals is much less than that in the d orbitals). This repulsion energy occurs in the energy denominators of the perturbation expansion, associated with the intermediate

states where two holes occupy the same copper site. Thus the reduction of this repulsion energy has a negative impact on the convergence of the perturbation expansion. This is an inherent limitation of 1-body transformations. I have shown that an 1-body + minimal 2-body transformation can simultaneously reduce the hopping and retain the large repulsion energy, and leads to rapid convergence.

Second, the crystal Hartree-Fock (HF) calculations on the spin form factors of La_2NiO_4 , La_2CuO_4 and $KNiF_3$ in this dissertation confirm the results of Ref. 41 which explored the embedded cluster approximation. In both the works, Eq. (3.3) is used as the approximation to obtain the spin form factor. The authors of Ref. 41 actually have calculated spin form factors for a much broader range of Mott insulators. Their results all agree very well with experimental measurements except for the case of La_2NiO_4 in which a large discrepancy between the theory and an experiment [64] is observed. Based on the agreement between this work and Ref. 41, and the fact that Eq. (3.3) has been successfully applied to many other materials in Ref. 41, we cast doubt on the experimental results of La_2NiO_4 and call for more experiments to settle the issue.

Third, the crystal Hartree-Fock approximation (HFA) is proved to be valuable for the solids with strong interacting electrons. For example, the crystal HFA predicts correctly that La_2CuO_4 and La_2NiO_4 are both antiferromagnetic insulators, in contrast to the wrong prediction (paramagnetic metal for La_2CuO_4 and antiferromagnetic metal for La_2NiO_4) made by the local spin density approximation (LSDA) [37,38]. It is commonly perceived that, in general, the HFA overestimates band gap and the LSDA underestimates or predicts no band gap for insulators. However, there are other important differences in the predictions of the two theories which have not been tested by direct experimental

measurements yet. For example, the crystal HFA predicts the oxygen p band while the LSDA predicts the magnetic ion d band to be the top valence band for the perovskite Mott insulators. This is a fundamental problem in understanding the electronic structures of these systems, but has not yet been resolved by direct experimental measurement. Besides, it is found in the crystal HFA that the charge of the Mn ion is close to +2 for both LaMnO₃ and CaMnO₃, in contrast to the formal valence picture where it is Mn^{+3} for LaMnO₃ and Mn^{+4} for CaMnO₃. What makes the matter more intriguing is that the spin of the Mn ion predicted by the crystal HFA is very close to the value of the formal valence picture (2 for LaMnO₃ and 3/2 for CaMnO₃). Based on these results, we hypothesize that high charge ion states are not energetically favorable in reality and, for systems containing ions with large formal charges, there is a spinless charge backflow from the anion (such as O, F) p orbitals to the magnetic ion (such as Cr, Mn) d orbitals (thus it only changes the charge but not the spin of the magnetic ion). Since the formal valence picture has been a universal concept in general physics and chemistry, the importance of examining this hypothesis, which is a departure from the formal valence picture, is obvious.

Fourth, in this work it is argued that the common treatment of the doubleexchange (DE) model with Jahn-Teller (JT) coupling found in the literature [112] is seriously flawed. The DE model is commonly used in describing the electronic properties of the perovskite manganites. The point of concern here is the vibrations of the MnO_6 clusters in the crystal, which affect the electronic properties through the JT coupling. Obviously for the sake of convenience, most people treat the vibrations of the MnO_6 clusters as uncoupled. This leads to an approximation which essentially neglects all the cross terms in both the kinetic and the potential energy parts of the Hamiltonian for the MnO_6 vibrations. Using a simple example, I show that the coefficients of the cross terms are just as large as those of the diagonal terms. Thus the neglect of the cross terms is not justified.

Fifth, the energies of the spin wave states in the single-band DE model are found to be surprisingly robust in the presence of several trial electron-phonon couplings. Based on this, it is believed that the mechanism responsible for the recently observed phonon-induced softening of the spin wave dispersion near Brillouin zone boundaries in several low-T_c (Curie Temperature) manganites [111] lies beyond the simple single-band DE model. It remains to be seen whether the two-band DE model with JT coupling can explain this phenomenon satisfactorily.

APPENDICES

Appendix A

A physical interpretation of the TSDA equations

In the one-body terms of the Hamiltonian, $h_{\nu\mu}c_{\nu}^{+}c_{\mu}(\nu \neq \mu)$ is the so called hopping term which causes a particle initially in the one-particle state μ to hop to the oneparticle state ν , provided the one-particle state ν is empty initially. Therefore, for an arbitrary single-determinantal state $|\Psi\rangle$, the expectation value of the operator $h_{\nu\mu}n_{\mu}(1-n_{\nu})$ gives the amplitude of the hopping $\mu \rightarrow \nu$ when $|\Psi\rangle$ is operated on by the hopping terms of the Hamiltonian; i.e.,

$$\left\langle \Psi \left| h_{\nu\mu} n_{\mu} \left(1 - n_{\nu} \right) \right| \Psi \right\rangle = \left\langle \Psi' \left| H'_{1-\text{body}} \right| \Psi \right\rangle, \tag{A1}$$

where $H'_{1-body} \equiv (H - H_a)_{1-body} = \sum_{\alpha \neq \beta} h_{\alpha\beta} c^+_{\alpha} c_{\beta}$ and $|\Psi'\rangle$ is the single-determinantal state which differs from $|\Psi\rangle$ by replacing, if there is any, the one-particle state μ in $|\Psi\rangle$ with the one-particle state ν . For the same reason, the operator $h_{\nu\mu}n_{\nu}(1-n_{\mu})$ (note that $h_{\mu\nu}=h_{\nu\mu}$ are assumed to be real here) corresponds to the reverse hopping $\nu \rightarrow \mu$. The difference between these two operators:

$$h_{\nu\mu}n_{\nu}(1-n_{\mu})-h_{\nu\mu}n_{\mu}(1-n_{\nu})=h_{\nu\mu}(n_{\nu}-n_{\mu})$$
(A2)

reflects, in some sense, the "net" hopping $v \rightarrow \mu$. Therefore we define it as the net hopping operator due to the one-body terms of the Hamiltonian.

Now, let's turn to the two-body terms of the Hamiltonian. The analogous hopping terms which cause a particle in the one-particle state μ to hop to another one-particle state ν while other particles in the system don't move are $v_{\nu\lambda,\mu\lambda}c_{\nu}^{*}c_{\lambda}^{*}c_{\lambda}c_{\mu}$ and $v_{\nu\lambda,\lambda\mu}c_{\nu}^{*}c_{\lambda}^{*}c_{\mu}c_{\lambda}$. What's different from that of the one-body terms is that this hopping must occur in the presence of another particle in the orbital λ . Also keep in mind that the second term, $v_{\nu\lambda,\lambda\mu}c_{\nu}^{*}c_{\lambda}^{*}c_{\mu}c_{\lambda}$, introduces an extra minus sign in the final state from that of the first term, $v_{\nu\lambda,\mu\lambda}c_{\nu}^{*}c_{\lambda}^{*}c_{\lambda}c_{\mu}$. Analogous to the case of the one-body terms of the Hamiltonian, for an arbitrary single-determinantal state $|\Psi\rangle$ the expectation value of the operator $\sum_{\lambda} (v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu}) n_{\lambda}n_{\mu}(1-n_{\nu})$ gives the amplitude of the hopping $\mu \rightarrow \nu$ when $|\Psi\rangle$ is

operated on by the two-body terms of the Hamiltonian,

$$\left\langle \Psi \left| \sum_{\lambda} \left(v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu} \right) n_{\lambda} n_{\mu} \left(1 - n_{\nu} \right) \right| \Psi \right\rangle = \left\langle \Psi' \left| H'_{2\text{-body}} \right| \Psi \right\rangle$$
(A3)

where H'_{2-body} denotes the two-body terms of $H - H_a$ and $|\Psi'\rangle$ has the same meaning as in Eq. (A1); and correspondingly, $\sum_{\lambda} (v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu}) n_{\lambda} n_{\nu} (1 - n_{\mu})$ accounts for the reverse

hopping $\nu \rightarrow \mu$. The difference,

$$\sum_{\lambda} (v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu}) n_{\lambda} n_{\nu} (1 - n_{\mu}) - \sum_{\lambda} (v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu}) n_{\lambda} n_{\mu} (1 - n_{\nu})$$

$$= \sum_{\lambda} (v_{\nu\lambda,\mu\lambda} - v_{\nu\lambda,\lambda\mu}) n_{\lambda} (n_{\nu} - n_{\mu})$$
(A4)

is defined as the net hopping $\nu \rightarrow \mu$ due to the two-body terms of the Hamiltonian. Then it's natural that the total net hopping operator is

$$h_{\nu\mu}(n_{\nu}-n_{\mu})+\sum_{\lambda}(\nu_{\nu\lambda,\mu\lambda}-\nu_{\nu\lambda,\lambda\mu})n_{\lambda}(n_{\nu}-n_{\mu}), \qquad (A5)$$

which is just the left-hand side of the TSDA equation (2.10) without the thermal average acting on it. Thus we get another view of TSDA; namely, the solutions of TSDA give zero thermal average of the net hopping operator (again, note that here the thermal averages are not with respect to the exact Hamiltonian H but to the approximation H_a).

Appendix B

Solving the TSDA equations

Since the detailed use of the TSDA in the present context is not commonly seen, we present the details to aid in further pursuit of the matter. Because of the numerical difficulty mentioned in the text and explained later in this appendix, what we have actually solved are modified TSDA equations, where the modification is based on argument of the large β (or low temperature) region of interest. In the following, we consider *site localization* as an example to explain the difficulty and show how we circumvent it.

The TSDA equations are: [Eq. (2.10) of the text]

$$< n_{\nu} - n_{\mu} > h_{\nu\mu} + \sum_{\lambda} < (n_{\nu} - n_{\mu})n_{\lambda} > (\nu_{\nu\lambda,\mu\lambda} - \nu_{\nu\lambda,\lambda\mu}) = 0$$
(B1)

for any pair of orbitals labeled v, μ . The thermal average bracket, $\langle \cdots \rangle$, is defined as, for any operator A,

$$< A > \equiv \frac{tr(e^{-\beta H_a}A)}{tr(e^{-\beta H_a})} = \frac{\sum < \cdots, N_{\nu}, \cdots |e^{-\beta H_a}A| \cdots, N_{\nu}, \cdots >}{\sum < \cdots, N_{\nu}, \cdots |e^{-\beta H_a}| \cdots, N_{\nu}, \cdots >},$$
(B2)

where the summation is over all possible occupations. The subscripts in Eq. (B1) label both the spatial and spin quantum numbers of the one-particle states. In the Hubbard model, the one-body and two-body matrix elements, $h_{\nu\mu}$ and $\nu_{\nu\mu,\lambda\kappa}$, preserve spin (i.e. $h_{\nu\mu} \equiv h_{i\sigma,j\sigma'} = 0$ if $\sigma \neq \sigma'$; similarly $\nu_{\nu\mu,\lambda\kappa} \equiv \nu_{i\sigma js,k\sigma ls'} = 0$ if $\sigma \neq \sigma'$ or $s \neq s'$) and are spin independent (i.e. $h_{i\sigma,j\sigma} \equiv h_{ij}$; similarly, $v_{i\sigma js,k\sigma ls} \equiv v_{ij,kl}$). So the TSDA equations in this case can be written in the following form:

$$< n_{i\sigma} - n_{j\sigma} > h_{ij} + \sum_{k,\sigma'} < (n_{i\sigma} - n_{j\sigma})n_{k\sigma'} > (v_{ik,jk} - \delta_{\sigma\sigma'}v_{ik,kj}) = 0$$
(B3)

for any pair of spin-orbitals $_{i\sigma}$ and $_{j\sigma}$. In the large β regime in which we are interested, the exponential factors in the thermal averages of the number operators in Eq. (B3) cause numerical difficulty and need special treatment.

In viewing the diagram of the Cu_2O_7 cluster (Fig. 2.2), it is apparent that all the orbitals can be divided into four groups:

$$(d'_1, d'_2), (p'_1), (p'_2, p'_4, p'_5, p'_7), (p'_3, p'_6).$$
 (B4)

Each orbital is said to be equivalent by symmetry to any other orbital in the same group. Because no original orbital (unprimed) will occur in this discussion, the prime on the new orbitals will be suppressed hereafter for brevity. By symmetry requirements, it is easy to see that the TSDA equation (B3) for any pair of orbitals is automatically satisfied if the two orbitals of this pair are in the same group. These trivial equations give us no information in determining the new orbitals. Further, careful counting shows that, among those remaining non-trivial TSDA equations, there are precisely nine independent equations; they are the TSDA equations for the pairs

$$(d_{1}\uparrow, p_{1}\uparrow), (d_{1}\uparrow, p_{2}\uparrow), (d_{1}\uparrow, p_{3}\uparrow), (d_{1}\uparrow, p_{5}\uparrow), (d_{1}\uparrow, p_{6}\uparrow), (p_{1}\uparrow, p_{2}\uparrow), (p_{1}\uparrow, p_{3}\uparrow), (p_{2}\uparrow, p_{3}\uparrow), (p_{2}\uparrow, p_{6}\uparrow).$$
(B5)

(The corresponding equations for the down-spin pairs are identical to these.) If β^{-1} is far below the transfer energy $\varepsilon_p - \varepsilon_d$ but much larger than the parallel-antiparallel splitting of



the underlying states, i.e. $K_{dd} \ll \beta^{-1} \ll \varepsilon_p - \varepsilon_d$, then the states which have one hole in each of the Cu *d* orbitals will dominate the thermal averages and the weights they contribute to the thermal average are essentially equal no matter what their spin configurations are. For the Cu₂O₇ cluster this means

Because the TSDA equations for the last four pairs of Eq. (B5) only involve the thermal averages $\langle n_{p,\sigma} \rangle$ and $\langle n_{p,\sigma} n_{\nu} \rangle$, their numerical values for the left hand side of Eq. (B3) are very small. This causes difficulty in solving numerically the nine simultaneous TSDA equations resulting from Eq. (B5) since the computer program may only "see" the first five equations of Eq. (B5) and regard the last four as having been solved. To circumvent this problem, we keep only the leading terms in the thermal averages, substitute them into the TSDA equations, and then extract the limiting forms of the equations in the large β regime, as shown below.

The lowest energy group of the half-filled Cu_2O_7 cluster is the set of 4 single determinants

$$\Psi(d_1\sigma, d_2\sigma'),\tag{B7}$$

where σ and σ' are either \uparrow or \downarrow . The next three higher energy groups are

$$\Psi(d_1\sigma, p_1\sigma'), \quad \Psi(d_2\sigma, p_1\sigma')$$

$$2. \Psi(d_2\sigma, p_2\sigma'), \quad \Psi(d_2\sigma, p_4\sigma'), \quad \Psi(d_1\sigma, p_5\sigma'), \quad \Psi(d_1\sigma, p_7\sigma').$$

$$(B8)$$

$$3. \Psi(d_2\sigma, p_3\sigma'), \quad \Psi(d_1\sigma, p_6\sigma')$$

(We don't know the energy order of the three groups in Eq. (B8) before we solve the TSDA equations.) To circumvent the numerical difficulty mentioned above, we make two assumptions about β : (i) β^{-1} is sufficiently low such that in the thermal average the exponential weight due to a lower energy group numerically overwhelms the weights due to other higher energy groups. (ii) But at the same time β^{-1} is sufficiently high such that the parallel-antiparallel splittings are to be neglected and average energies (over 4 possible spin configurations) are to be used in substitution of real individual energies. For example, define $E(d_1\sigma, p_1\sigma')$ as the energy of state $\Psi(d_1\sigma, p_1\sigma')$ and $E(d_1p_1)$ as the average of $E(d_1\sigma, p_1\sigma')$ over the 4 possible spin configurations,

$$E(d_{1}p_{1}) = \frac{1}{4} \sum_{\sigma\sigma'} E(d_{1}\sigma, p_{1}\sigma')$$

$$= \frac{1}{4} \sum_{\sigma\sigma'} \left(h_{d_{1}d_{1}} + h_{p_{1}p_{1}} + v_{d_{1}p_{1},d_{1}p_{1}} - \delta_{\sigma\sigma'} v_{d_{1}p_{1},p_{1}d_{1}} \right).$$

$$= h_{d_{1}d_{1}} + h_{p_{1}p_{1}} + v_{d_{1}p_{1},d_{1}p_{1}} - \frac{1}{2} v_{d_{1}p_{1},p_{1}d_{1}}$$
(B9)

Because there is essentially no energy resolution among the different spin configurations by our assumption, we are to replace $E(d_1\sigma, p_1\sigma')$ with $E(d_1p_1)$ in our calculation. The energies of other states are similarly treated. We will come back to our assumption about β later. Some thermal averages of the number operators are listed below as examples:

$$< n_{d_{1}\sigma} > \cong \frac{1}{Z} \left(e^{-\beta E(d_{1}\sigma,d_{2}\uparrow)} + e^{-\beta E(d_{1}\sigma,d_{2}\downarrow)} \right) \cong 2 < n_{d_{1}\sigma} n_{d_{2}\sigma'} > \cong \frac{1}{2}$$

$$< n_{p_{1}\sigma} > \cong \frac{1}{Z} \left(e^{-\beta E(p_{1}\sigma,d_{1}\uparrow)} + e^{-\beta E(p_{1}\sigma,d_{1}\downarrow)} + e^{-\beta E(p_{1}\sigma,d_{2}\uparrow)} + e^{-\beta E(p_{1}\sigma,d_{2}\downarrow)} \right) \cong 4 < n_{p_{1}\sigma} n_{d_{1}\sigma'} > \cong 0$$

$$< n_{p_{2}\sigma} > \cong \frac{1}{Z} \left(e^{-\beta E(p_{2}\sigma,d_{2}\uparrow)} + e^{-\beta E(p_{2}\sigma,d_{2}\downarrow)} \right) \cong 2 < n_{p_{2}\sigma} n_{d_{2}\sigma'} > \cong 0$$

$$< n_{p_{3}\sigma} > \cong \frac{1}{Z} \left(e^{-\beta E(p_{3}\sigma,d_{2}\uparrow)} + e^{-\beta E(p_{3}\sigma,d_{2}\downarrow)} \right) \cong 2 < n_{p_{3}\sigma} n_{d_{2}\sigma'} > \cong 0$$

$$(B10)$$

where Z denotes the partition function. The TSDA equation for the pair $(d_1 \uparrow, p_1 \uparrow)$ therefore reduces approximately to a simple form in our assumed β regime:

$$(< n_{d_1\uparrow} > - < n_{p_1\uparrow} >) h_{d_1p_1} + \sum_{k,\sigma} (< n_{d_1\uparrow}n_{k\sigma} > - < n_{p_1\uparrow}n_{k\sigma} >) (v_{d_1k,p_1k} - \delta_{\uparrow\sigma}v_{d_1k,kp_1}) = 0$$

$$\Rightarrow (\frac{1}{2} - 0) h_{d_1p_1} + (< n_{d_1\uparrow}n_{d_2\uparrow} > -0) (v_{d_1d_2,p_1d_2} - v_{d_1d_2,d_2p_1}) + (< n_{d_1\uparrow}n_{d_2\downarrow} > -0) (v_{d_1d_2,p_1d_2}) = 0$$

$$\Rightarrow h_{d_1p_1} + (v_{d_1d_2,p_1d_2} - \frac{1}{2}v_{d_1d_2,d_2p_1}) = 0$$

The TSDA equations for the 2nd to 5th pairs in Eq. (A5) are similar in form to that for $(d_1 \uparrow, p_1 \uparrow)$. Now we examine the TSDA equation for the 6th pair $(p_1 \uparrow, p_2 \uparrow)$:

$$(\langle n_{p_{1}\uparrow} \rangle - \langle n_{p_{2}\uparrow} \rangle)h_{p_{1}p_{2}} + \sum_{k,\sigma} (\langle n_{p_{1}\uparrow}n_{k\sigma} \rangle - \langle n_{p_{2}\uparrow}n_{k\sigma} \rangle)(v_{p_{1}k,p_{2}k} - \delta_{\uparrow\sigma}v_{p_{1}k,kp_{2}}) = 0$$

$$\Rightarrow (\langle n_{p_{1}\uparrow} \rangle - \langle n_{p_{2}\uparrow} \rangle)h_{p_{1}p_{2}} + (\langle n_{p_{1}\uparrow}n_{d_{1}\uparrow} \rangle - 0)(v_{p_{1}d_{1},p_{2}d_{1}} - v_{p_{1}d_{1},d_{1}p_{2}}) + (\langle n_{p_{1}\uparrow}n_{d_{1}\downarrow} \rangle - 0)(v_{p_{1}d_{1},p_{2}d_{1}})$$

$$+ (\langle n_{p_{1}\uparrow}n_{d_{2}\uparrow} \rangle - \langle n_{p_{2}\uparrow}n_{d_{2}\uparrow} \rangle)(v_{p_{1}d_{2},p_{2}d_{2}} - v_{p_{1}d_{2},d_{2}p_{2}}) + (\langle n_{p_{1}\uparrow}n_{d_{2}\downarrow} \rangle - \langle n_{p_{2}\uparrow}n_{d_{2}\downarrow} \rangle)(v_{p_{1}d_{2},p_{2}d_{2}}) = 0$$

$$\Rightarrow (2 < n_{p_{1}\uparrow}n_{d_{1}\sigma} \rangle - \langle n_{p_{2}\uparrow}n_{d_{2}\sigma} \rangle)h_{p_{1}p_{2}} + \langle n_{p_{1}\uparrow}n_{d_{1}\sigma} \rangle(v_{p_{1}d_{1},p_{2}d_{1}} - \frac{1}{2}v_{p_{1}d_{1},d_{1}p_{2}})$$

$$+ (\langle n_{p_{1}\uparrow}n_{d_{1}\sigma} \rangle - \langle n_{p_{2}\uparrow}n_{d_{2}\sigma} \rangle)(v_{p_{1}d_{2},p_{2}d_{2}} - \frac{1}{2}v_{p_{1}d_{2},d_{2}p_{2}}) = 0$$

where in the last expression $d_{i\sigma}$ can be either $d_{1\uparrow}$, $d_{1\downarrow}$, $d_{2\uparrow}$, or $d_{2\downarrow}$. If $E(p_1d_1) < E(p_2d_2)$, then $\langle n_{p_1\uparrow}n_{d_i\sigma} \rangle >> \langle n_{p_2\uparrow}n_{d_2\sigma} \rangle$ by the former assumption about β and the previous equation reduces to

$$2h_{p_1p_2} + (v_{p_1d_1, p_2d_1} - \frac{1}{2}v_{p_1d_1, d_1p_2}) + (v_{p_1d_2, p_2d_2} - \frac{1}{2}v_{p_1d_2, d_2p_2}) = 0;$$

on the other hand, if $E(p_1d_1) > E(p_2d_2)$, then $\langle n_{p_1\uparrow}n_{d,\sigma} \rangle << \langle n_{p_2\uparrow}n_{d_2\sigma} \rangle$ and the equation reduces to

$$h_{p_1p_2} + (v_{p_1d_2,p_2d_2} - \frac{1}{2}v_{p_1d_2,d_2p_2}) = 0.$$

The limiting forms of the TSDA equations for the 7th to 9th pairs in Eq. (B5) can be obtained in a manner similar to that for $(p_1 \uparrow, p_2 \uparrow)$. All the nine equations are summarized below:

$$(d_{1} \uparrow, p_{i} \uparrow) : h_{d_{1}p_{i}} + (v_{d_{1}d_{2}, p_{i}d_{2}} - \frac{1}{2}v_{d_{1}d_{2}, d_{2}p_{i}}) = 0 \text{ for } i = 1,2,3,5,6$$

$$(p_{1} \uparrow, p_{2} \uparrow) : 2h_{p_{1}p_{2}} + (v_{p_{1}d_{1}, p_{2}d_{1}} - \frac{1}{2}v_{p_{1}d_{1}, d_{1}p_{2}}) + (v_{p_{1}d_{2}, p_{2}d_{2}} - \frac{1}{2}v_{p_{1}d_{2}, d_{2}p_{2}}) = 0 \text{ if } E(p_{1}d_{1}) < E(p_{2}d_{2})$$

$$h_{p_{1}p_{2}} + (v_{p_{1}d_{2}, p_{2}d_{2}} - \frac{1}{2}v_{p_{1}d_{2}, d_{2}p_{2}}) = 0 \text{ if } E(p_{1}d_{1}) > E(p_{2}d_{2})$$

$$(p_{1} \uparrow, p_{3} \uparrow) : 2h_{p_{1}p_{3}} + (v_{p_{1}d_{1}, p_{3}d_{1}} - \frac{1}{2}v_{p_{1}d_{1}, d_{1}p_{3}}) + (v_{p_{1}d_{2}, p_{3}d_{2}} - \frac{1}{2}v_{p_{1}d_{2}, d_{2}p_{3}}) = 0 \text{ if } E(p_{1}d_{1}) > E(p_{3}d_{2})$$

$$h_{p_{1}p_{3}} + (v_{p_{1}d_{2}, p_{3}d_{2}} - \frac{1}{2}v_{p_{1}d_{2}, d_{2}p_{3}}) = 0 \text{ if } E(p_{3}d_{2})$$

$$(p_{2} \uparrow, p_{3} \uparrow) : h_{p_{2}p_{3}} + (v_{p_{2}d_{2}, p_{3}d_{2}} - \frac{1}{2}v_{p_{2}d_{2}, d_{2}p_{3}}) = 0$$

$$(p_{2} \uparrow, p_{6} \uparrow) : h_{p_{2}p_{6}} + (v_{p_{2}d_{1}, p_{6}d_{1}} - \frac{1}{2}v_{p_{2}d_{1}, d_{1}p_{6}}) = 0 \text{ if } E(p_{2}d_{2}) > E(p_{3}d_{2})$$

$$(B11)$$

There are 3! = 6 possible orderings of the energies $E(p_1d_1), E(p_2d_2), E(p_3d_2)$. For each possible order, we solve Eq. (B11) and then check the consistency of the solutions with their respective presumed energy order. Those which are not self-consistent are, of course, dropped. Although the forms of Eq. (B11) are pretty simple, the transformed parameters $h_{\nu\mu}$ and $\nu_{\nu\mu,\lambda\kappa}$ in Eq. (B11) are each a polynomial function of the transformation coefficients defined in Eq. (2.16) of order 2 and 4, respectively. Therefore

there indeed exist many solutions. We solved Eq. (B11) numerically. By varying the starting point and length of searching steps, we got several solutions of Eq. (B11). These solutions were examined by comparing their resulting TSDA free energies and also by cross checking with the solutions obtained in the *cell localization* and *no localization* cases to confirm that the real TSDA solution (which means the one which, within the single-determinantal and the particular localization-choice framework, gives the lowest free energy) has been found and identified. It turns out $E(p_2d_2) < E(p_1d_1) < E(p_3d_2)$ for the real TSDA solution.

Now we examine the consistency of the solution with our assumption about β , which was made to simplify the TSDA equations and therefore circumvent the numerical difficulty it leads to. Based on the solution, we calculate the energies of various states. The average energies (over 4 possible spin configurations) of the first four lowest energy groups, i.e. those of Eqs. (B7) and (B8), are

The smallest energy gap among the above four groups is between the second and the third ones, which is about 0.41. For our assumption to be right, the β^{-1} must be well below 0.41 to make a lower energy group numerically overwhelm other higher energy groups in contributing the weight in thermal average. However, the parallel-antiparallel splittings, which we have neglected in order to replace the energy of every state of a group with the average energy of that group, for the four groups in Eq. (B12) are

$$\begin{array}{ccccc} K(d_1d_2) & K(p_1d_1) & K(p_2d_2) & K(p_3d_2) \\ 0.0288 & 0.7605 & 0.0097 & 0.0823 \end{array}$$
(B13)

(Note that the second one is big because the p_1 and d_1 are nearest neighbors to each other so that they are from strong hybridization of the original p_1 and d_1 , and that strong hybridization also leads to big exchange energy between the new p_1 and d_1 orbitals.) So β^{-1} must be much larger than 0.76 for the neglect of parallel-antiparallel splittings to be legitimate. An inconsistency thus occurs.

We have two reasons to believe that this inconsistency does no harm to our work here. First, in addition to what we presented so far (which we call the average case), we have done the same calculation on two artificial cases: one is to assume the spins of the two particles in the Cu_2O_7 cluster can only be parallel and the other, antiparallel. As a matter of fact, the parallel case is not really artificial because it is exactly the limiting situation when $\beta^{-1} \rightarrow 0$. (Note that a state with a pair of spin-parallel particles is always lower in energy than its antiparallel counterpart by an amount of the exchange energy Kbetween these two particles. When β^{-1} is sufficiently low, the parallel states will dominate the thermal average.) At first glance, the inconsistency suggests that we shouldn't assume β^{-1} is sufficiently high and neglect the parallel-antiparallel splittings. It turns out that the TSDA solution of the average case is somewhere between the TSDA solutions of the parallel and antiparallel cases, and, more importantly, they only slightly differ from each other. This suggests that the solution we obtained is close to the solution one might get by solving the exact (unsimplified) TSDA equations (for $\beta^{-1} \ll 0.4$). Second, the average case itself can also be viewed as the exact calculation for another

artificial case, namely, a system which has no spin degrees of freedom and has the average energies as the energies of its levels. Our purpose is to seek a definite guideline which can lead us to a good transformation on the basis set such that the perturbation converges rapidly. So the model which we use to derive the transformation may be closely related to the system of interest, but it doesn't have to be the same. Also, recall that β^{-1} here is rather a parameter than a physical temperature. Therefore, the inconsistency is not really our concern as long as we can obtain a suitable transformation.

Appendix C

On the determination of the Heisenberg J from electronic structure calculations

In this appendix, we discuss the theoretical justification behind the commonly used mapping scheme mentioned in Sec. 3.2.1 in estimating the Heisenberg exchange parameter J from *ab initio* electronic calculations. We assume that the problems under consideration have their low-lying states governed by a Heisenberg Hamiltonian. Of course, if a problem is simple enough, one can calculate J exactly (using standard quantum chemistry techniques such as configuration interaction). For example, if one were actually dealing with two magnetic electrons, with a limited number of non-magnetic electrons, one could in practice calculate the energies of the true lowest energy eigenstates, singlet and triplet. Equating their energy difference to the difference in eigenvalues of the Heisenberg Hamiltonian, would then yield J. This approach has been used [116-118,44-46].

However, for more complicated systems, we are forced to make approximations. The mapping scheme to estimate J in Sec. 3.2.1 has been used for years, in both Hartree-Fock and density functional calculations. We have shown [83] that for some special cases, e.g. a single-band Hubbard model, J_{HF} defined by Eq. (3.2) equals J to the leading order in perturbation with small hopping; but that does not hold in general (although one may get the contrary impression from some papers [46]). Still, J_{HF} serves as a reasonable and well-defined estimation of J.

We now discuss the determination of J within density functional theory (DFT) approaches, which invoke the following procedure [119,120]. One obtains a symmetrybroken (SB) solution for the Kohn-Sham determinant D_{KS} for the "antiferromagnetic" state and a triplet state (for simplicity we discuss the case of one magnetic electron per magnetic site in a two-magnetic-site cluster). The triplet energy minus the SB AFM state energy is equated to the triplet energy minus the (average) energy of the SB spin state $\alpha(1)\beta(2)$ for the Heisenberg model, thereby obtaining a number for J [121]. Although making the correspondence "SB electronic state \leftrightarrow SB spin state" sounds reasonable, one must realize that **there is not a unique SB spin state**, even in this simplest of cases. The following spin state is SB for all values of $\mu \neq 0$ or ∞ .

$$\Omega_{\mu} = \frac{1}{\sqrt{2(1+\mu^2)}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) + \mu[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \} .$$
(C1)

The expectation value of the Heisenberg energy is

$$J\langle \vec{S}_{1} \cdot \vec{S}_{2} \rangle = -\frac{J}{4} \frac{3 - \mu^{2}}{1 + \mu^{2}}.$$
 (C2)

If one used the *exact* density functional (DF), then the energies of the exact lowest triplet and singlet states would be obtained. The difference in these energies would be equated to the corresponding difference in Eq. (C2) with $\mu = 0$ and ∞ , and this would give the exact J. However, given an approximate DF, as in almost all applications, one is faced with the problem of what value of μ to use in Eq. (C2) for the SB AFM state. Many people [57,119,120] take $\mu = 1$ without giving a reason. But there is a potential inconsistency in doing so: as one's approximate DF gets closer to the exact DF, continued

use of $\mu = 1$ may lead to serious errors. Thus the appropriate value of μ to use is unknown.

A possible way out of this dilemma is as follows. From Eq. (C2) one gets

$$\mu = \sqrt{\langle \vec{S}^2 \rangle / (2 - \langle \vec{S}^2 \rangle)}, \tag{C3}$$

where $\vec{S} = \vec{S}_1 + \vec{S}_2$. One could demand that $\langle \vec{S}^2 \rangle$ be equal to the expectation value of the square of the total electronic spin in D_{KS} , thus determining μ via Eq. (C3). One should remember that there is no guarantee that D_{KS} is an eigenfunction of \vec{S}^2 or that the average value $\langle \vec{S}^2 \rangle$ in D_{KS} is correct, even for the exact D_{KS} , presenting a possible inconsistency in this approach. Also, how to generalize this mapping idea for determining the SB AFM spin state to more than two sites (two electrons) is not obvious and remains to be investigated.

Interestingly, this idea raises a question about the standard mapping used for the HFA where μ is taken to be 1 for the AFM spin state. For this two-site two-electron example, one can show easily that $\langle \vec{S}^2 \rangle_{D_{HF}} = 1 - \delta^2$, where D_{HF} is the HF determinant of the AFM state and δ is the overlap integral between the two localized orbitals. Since δ is usually quite small (< 0.1), it is seen that this probably would make little difference.

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