

Jahn–Teller coupling and double exchange in the two-site Van Vleck–Kanamori model

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The effect of the dynamical Jahn–Teller coupling on the Anderson–Hasegawa double exchange (DE) in the manganites is studied in a two-site model taking into account the double degeneracy of the e_g orbitals and their coupling to the three MnO_6 vibrational modes (Q_1 , Q_2 , and Q_3). Both exact diagonalization and the Lang–Firsov approach are used. We find that coupling to the Q_2 and Q_3 modes reduces the DE, while the Q_1 mode is ineffective. The isotope dependence of the DE interaction is consistent with recent experiments. © 1999 American Institute of Physics. [S0021-8979(99)48008-9]

It is well-known that the lanthanum manganites are mixed valence systems with a mixture of Mn^{3+} which is a Jahn–Teller (JT) ion and Mn^{4+} which is not. The electron therefore has the tendency of carrying the local JT distortion of the MnO_6 octahedron along with it as it moves about in the lattice. The way this coupled motion affects the phenomenology of the manganites has been addressed by several authors.¹

The recent discovery of the isotope effect indicates the involvement of the lattice in the magnetic properties.² The isotope effect requires for its explanation the quantum-mechanical nature of the nuclear wave function. In fact, we have shown earlier³ from a simple model with nondegenerate electron states that the double exchange (DE) interaction^{4,5} is modified in two important ways by coupling to the lattice: (1) the magnitude of the DE is reduced sharply from the Anderson–Hasegawa $t \cos(\theta/2)$ value and (2) the coupling to the oxygen motion leads to an oxygen-mass-dependent DE.

On the other hand, the double degeneracy of the e_g electrons and their characteristic coupling to the JT distortions of the MnO_6 octahedron has been shown to lead to interesting consequences. In this paper, we include the effects of double degeneracy and the appropriate JT coupling within a two-site Van Vleck–Kanamori Hamiltonian,^{6,7} which we solve by Lanczos diagonalization.

The relevant orbitals for the itinerant electron motion in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ are the $\text{Mn}(e_g)$ orbitals, which couple to the vibrational mode of the MnO_6 octahedra via the JT interaction. There are three important vibrational modes as indicated in Fig. 1, viz.: (i) the breathing mode Q_1 , (ii) the in-plane distortion mode Q_2 , and (iii) the apical stretching mode Q_3 . Taking the symmetric MnO_6 octahedron with the average Mn–O bond length as the reference, the amplitudes of the Q_2 and the Q_3 distortions in LaMnO_3 are 0.20 and

0.02 Å, respectively, resulting in the three Mn–O bond lengths of 1.91, 2.19, and 1.96 Å.⁸ The amplitude of the Q_1 distortion is zero by definition.

The Hamiltonian for the coupled system is given by

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{\text{ph}} + \mathcal{H}_{\text{JT}}, \quad (1)$$

$$\mathcal{H}_e = \sum_{\langle ij \rangle, \sigma} \sum_{ab} t_{ij}^{ab} c_{ia\sigma}^\dagger c_{jb\sigma} + \text{h.c.} - J_H \sum_{i,a} S_i \cdot \sigma_{ia}, \quad (2)$$

$$\mathcal{H}_{\text{ph}} = \sum_{i\alpha} -\frac{\hbar^2}{2M} \frac{d^2}{dQ_{i\alpha}^2} + \frac{K}{2} Q_{i\alpha}^2, \quad \mathcal{H}_{\text{JT}} = \sum_i h_{\text{JT}}^i, \quad (3)$$

and

$$h_{\text{JT}} = g' Q_1 I - g(Q_2 \tau_x + Q_3 \tau_z). \quad (4)$$

Here i is the lattice site index, $\langle ij \rangle$ denotes nearest neighbors (NN), the a, b summation is over the two e_g orbitals, and the α summation is over the three vibrational modes. The spin of the electron is denoted by σ , while the two e_g orbitals $|z^2 - 1\rangle$ and $|x^2 - y^2\rangle$ are described by the pseudospin τ . M is the mass of the oxygen atom. The t_{2g} core spin S is treated as classical and we take the Hund's energy J_H to be ∞ as ap-

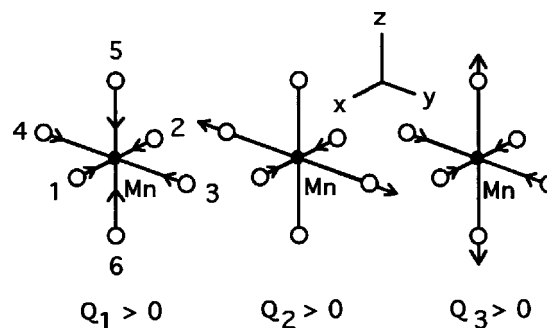


FIG. 1. The three relevant normal modes of vibration for the MnO_6 octahedron with their eigenvectors: $|Q_1\rangle = (-X_1 + X_2 - Y_3 + Y_4 - Z_5 + Z_6)/\sqrt{6}$, $|Q_2\rangle = (-X_1 + X_2 + Y_3 - Y_4)/2$, and $|Q_3\rangle = (-X_1 + X_2 - Y_3 + Y_4 + 2Z_5 - 2Z_6)/\sqrt{12}$, where X_1 denotes the x coordinate of the first atom, etc.

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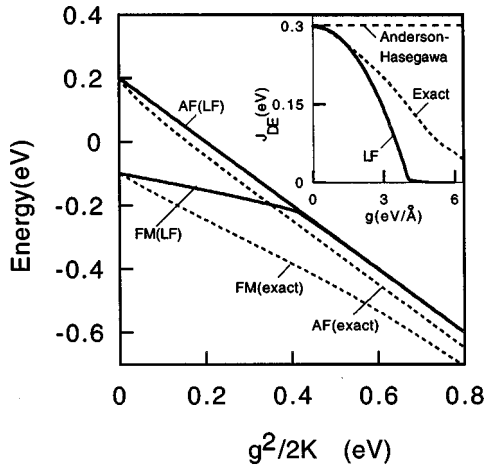


FIG. 2. Comparison between the exact and the variational Lang-Firsov (LF) ground-state energies for the ferromagnetic (FM) or antiferromagnetic (AF) alignment of the Mn core spins. The inset shows the reduction of J_{DE} from the Anderson-Hasegawa result due to the lattice coupling. Both Q_2 and Q_3 modes were retained in the calculations. Parameters used in all figures are: $V_{dd\sigma} = -0.30$ eV and $\hbar\omega$ for $^{16}\text{O} = 0.1$ eV.

appropriate for the manganites. The hopping matrix t depends on the relative positions of the NN. For NN along x , we have

$$t^{ab} = \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & 3 \end{pmatrix} \times \frac{V_{dd\sigma}}{4} \cos(\theta/2), \quad (5)$$

where $\cos(\theta/2)$ is the Anderson-Hasegawa factor, θ being the angle between the two (classical) core spins on the neighboring sites. The JT coupling term h_{JT} , Eq. (4), originally derived by Van Vleck⁶ and Kanamori⁷ has been widely used for octahedral ligand systems including the manganites.^{9,10}

We estimate the Hamiltonian parameters as follows: (i) $V_{dd\sigma} \approx -0.3 - -0.4$ eV from the calculated bandwidth taking into account the appropriate orbital ordering.¹¹ (ii) The electron-phonon coupling $g \approx 3-4$ eV/Å as estimated from tight-binding fits to the density-functional e_g bands with varying octahedral distortions.¹² (iii) The stiffness constant is then estimated from $K = g/\sqrt{Q_2^2 + Q_3^2}$ to be about 15-20 eV/Å², where Q_2 and Q_3 are the magnitudes of the distortions. These values result in a JT energy gain of $\Delta_{JT} = -g^2/(2K) \approx -0.35 - -0.5$ eV, which is in rough agreement with the density-functional result of -0.63 eV.¹³

Quantizing the vibrational modes, Eq. (1) becomes

$$\begin{aligned} \mathcal{H} = & \sum_{\langle ij \rangle, ab} t^{ab} (c_{ia}^\dagger c_{jb} + \text{h.c.}) + \sum_{j\nu} \hbar\omega (b_{j\nu}^\dagger b_{j\nu} + 1/2) \\ & + \sum_j [\xi'(b_{j1}^\dagger + b_{j1})n_j + \xi(b_{j2}^\dagger + b_{j2})(c_{j1}^\dagger c_{j2} + \text{h.c.}) \\ & + \xi(b_{j3}^\dagger + b_{j3})(n_{j1} - n_{j2})], \end{aligned} \quad (6)$$

where $b_{j\alpha}^\dagger$ is the creation operator corresponding to the $Q_{j\alpha}$ vibrational mode, $c_{j\alpha}^\dagger$ is the same for the orbital a at the j th site, $n_{j\alpha}$ is the number operator, $n_j \equiv n_{j1} + n_{j2}$ is the total number of electrons at the j th site, $\xi \equiv g \times \sqrt{\hbar}/(2m\omega)$, and ξ' is similarly defined. The electron spin is omitted as it is always parallel to the core spin, J_H being ∞ . The DE energy

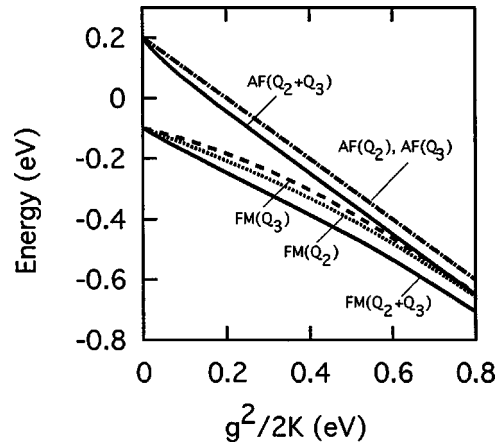


FIG. 3. Exact ground-state energies as a function of the JT coupling. Energies for the Q_2 and Q_3 cases are shifted up by $\hbar\omega$ for clarity of presentation.

is defined as $J_{DE} = E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$, where $E_{\uparrow\downarrow}$ ($E_{\uparrow\uparrow}$) is the ground-state energy for the parallel (antiparallel) alignment of the two Mn core spins.

Note from the ξ' term in Eq. (6) that the coupling to the Q_1 mode merely produces a shift in the total energy by the amount $-g'^2/2 K \times N_e$ (displaced simple harmonic oscillator), where N_e is the total number of electrons. The energy shift is independent of the hopping t^{ab} and therefore is the same for both the ferromagnetic and the antiferromagnetic cases. The Q_1 mode therefore contributes nothing to J_{DE} and is omitted in the rest of the paper. This would not be the case if the hopping t depended on the octahedral distortions, which in turn depended on θ .

We now restrict our discussion to a two-site model with one electron present in the system in the spirit of the original Anderson-Hasegawa treatment of double exchange. Unlike the case of the infinite solid, the two-site problem can be accurately solved and it is, at the same time, illustrative of the physics involved. The ground-state energy of the Hamiltonian, Eq. (6), is obtained by diagonalization, with the basis set $|ia, \nu_1, \nu_2, \nu_3, \nu_4\rangle$, where i, a are the site, orbital indices for the electron, and the ν_i s denote the vibrational quantum numbers of the Q_2 and the Q_3 modes at the two sites. We retain a total of 20 phonons, $\nu_{\text{tot}} \equiv \sum_{i=1}^4 \nu_i \leq 20$, in cases

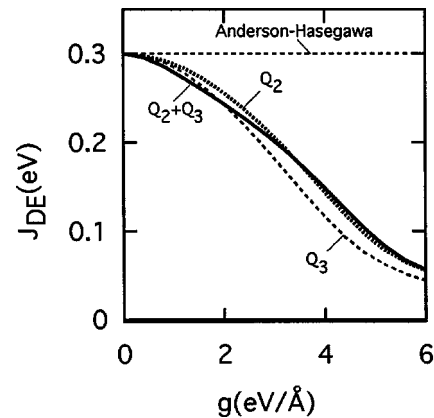


FIG. 4. Variation of J_{DE} with the electron-phonon coupling strength g , obtained from Fig. 3.

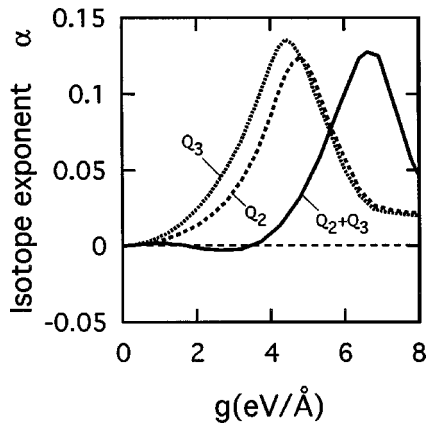


FIG. 5. Dependence of the isotope exponent α on the electron-phonon coupling strength g .

where both Q_2 and Q_3 modes were included, and a total of 50 phonons in cases where only the Q_2 or the Q_3 mode was kept. The resulting Hamiltonian of size up to $10^6 \times 10^6$ is diagonalized by the Lanczos method. We have verified that our results have converged with respect to ν_{tot} . Thus the results are essentially ‘‘exact.’’

It is illustrative to compare the exact results with the Lang–Firsov¹⁴ variational approach. We make the transformation $\tilde{\mathcal{H}} = e^{-S} \mathcal{H} e^S$, where $S = -\sqrt{\Delta_{JT}/\hbar\omega} \times \sum_i n_i [\gamma_1 (b_{i2}^\dagger - b_{i2}) + \gamma_2 (b_{i3}^\dagger - b_{i3})]$, γ_1 and γ_2 being variational parameters. Approximating the eigenstates $|\tilde{\Psi}\rangle$ of $\tilde{\mathcal{H}}$ by a variational state $|\tilde{\Psi}_V\rangle = |\tilde{\Psi}_{\text{ph}}\rangle \otimes |\tilde{\Psi}_{\text{el}}\rangle$ and averaging over the transformed phonon vacuum, $\tilde{\mathcal{H}} = \langle \tilde{\Psi}_{\text{ph}}^0 | \tilde{\mathcal{H}} | \tilde{\Psi}_{\text{ph}}^0 \rangle$, we get the effective hamiltonian,

$$\begin{aligned} \tilde{\mathcal{H}} = & e^{-(\Delta_{JT}/\hbar\omega)} (\gamma_1^2 + \gamma_2^2) \sum_{\langle ij \rangle, ab} t^{ab} (c_{ia}^\dagger c_{jb} + c_{jb}^\dagger c_{ia}) \\ & + \sum_i [\hbar\omega + \Delta_{JT}(\gamma_1^2 + \gamma_2^2)n_i^2] - 2\Delta_{JT} \\ & \times \sum_i [\gamma_1(c_{i1}^\dagger c_{i2} + \text{h.c.}) + \gamma_2(n_{i1} - n_{i2})]. \end{aligned} \quad (7)$$

The Lang–Firsov ground-state energy is obtained from minimization with respect to the variational parameters. Figure 2 shows a comparison between the exact and the Lang–Firsov ground-state energies for the ferromagnetic (FM) and the antiferromagnetic (AF) cases. Notice that the Lang–Firsov energies are higher than the corresponding exact re-

sults as they should be. The inset of Fig. 2 shows that the DE interaction is considerably reduced by the lattice coupling, which is a central point of the paper.

Figure 3 shows the variation of the ground-state energies with coupling g , obtained from diagonalization of the full Hamiltonian Eq. (6). When the coupling is zero, the energy for the AF case is simply the zero-point energy of the normal modes, while for the FM case, the energy is reduced from the AF value by $V_{dd\sigma}$ (the Anderson–Hasegawa result). The corresponding energy difference J_{DE} is plotted in Fig. 4.

The quantum-mechanical treatment of the nuclear motion leads to an isotope effect since the nuclear wave function is changed with the isotope mass. The isotope exponent α ($T_c \propto M^{-\alpha}$) is defined from the relation: $\alpha = -d \ln T_c / d \ln M = -d \ln J_{\text{DE}} / d \ln M$, where we have used the relationship $T_c \propto J_{\text{DE}}$. The variation of α with the coupling strength g is shown in Fig. 5. The calculated α is ~ 0.1 , in rough agreement with the measured value of $\alpha \approx 0.15$ – 0.2 in the manganites.²

In conclusion, we have studied the effect of the dynamical JT interaction on double exchange, taking into account the degeneracy of the Mn(e_g) electrons and their coupling with the MnO₆ octahedral modes. A key result was that the JT coupling drastically reduces the Anderson–Hasegawa double exchange. Both the in-plane distortion and the apical stretching modes were found to be important. Our work illustrates the dynamical JT effect and provides insight into the origin of the oxygen isotope effect.

The authors thank the Research Board of the University of Missouri for partial financial support.

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