

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-

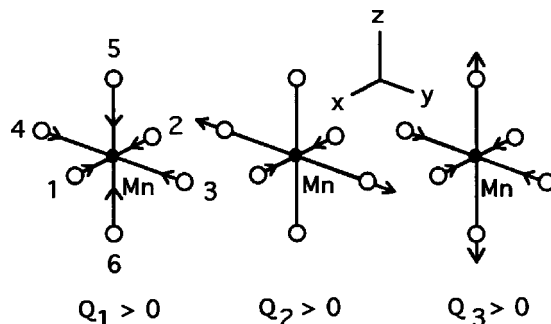


FIG. 1. The three relevant normal modes of vibration for the MnO_6 octahedron with their eigenvectors: $|Q_1\rangle = (-X_1 + X_2 - Y_3 + Y_4 - Z_5 + Z_6)/\sqrt{6}$, $|Q_2\rangle = (-X_1 + X_2 + Y_3 - Y_4)/2$, and $|Q_3\rangle = (-X_1 + X_2 - Y_3 + Y_4 + 2Z_5 - 2Z_6)/\sqrt{12}$, where X_1 denotes the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

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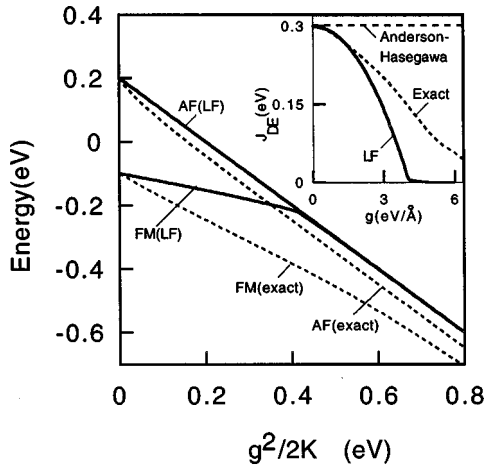


FIG. 2. Comparison between the exact and the variational Lang-Firsov (LF) ground-state energies for the ferromagnetic (FM) or antiferromagnetic (AF) alignment of the Mn core spins. The inset shows the reduction of J_{DE} from the Anderson-Hasegawa result due to the lattice coupling. Both Q_2 and Q_3 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_{ja}^\dagger is the creation operator corresponding to the Q_{ja} vibrational mode, c_{ja}^\dagger is the same for the orbital a at the j th site, n_{ja} 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

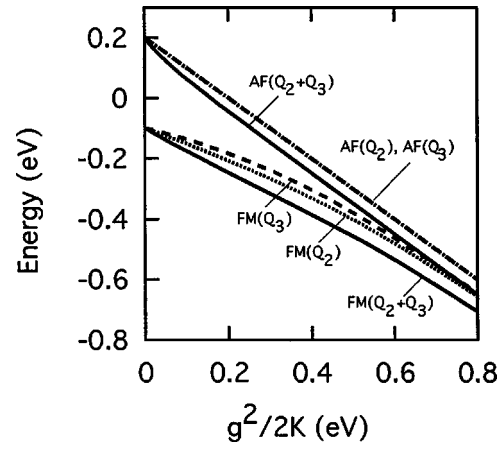


FIG. 3. Exact ground-state energies as a function of the JT coupling. Energies for the Q_2 and Q_3 cases are shifted up by $\hbar\omega$ for clarity of presentation.

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

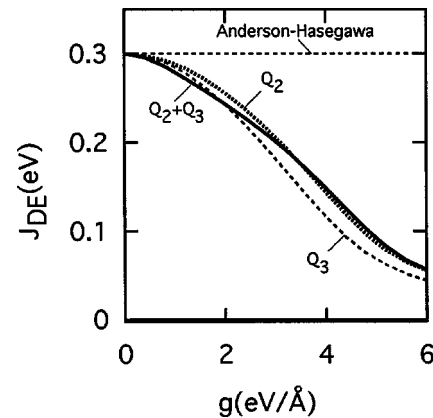


FIG. 4. Variation of J_{DE} with the electron-phonon coupling strength g , obtained from Fig. 3.

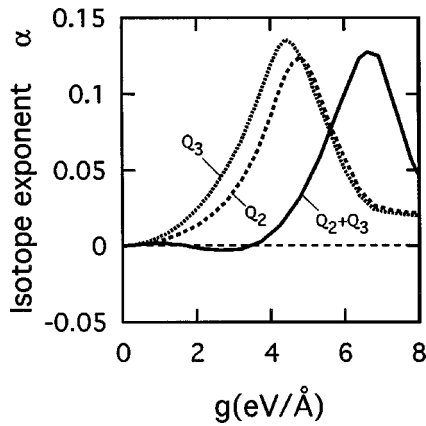


FIG. 5. Dependence of the isotope exponent α on the electron-phonon coupling strength g .

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 $\text{Mn}(e_g)$ electrons and their coupling with the MnO_6 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.

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