

**Problem 1. Exchange** Consider single-particle wavefunctions on two neighboring identical atoms  $\psi_A, \psi_B$ , which may be assumed real. These are to be used as the basis for a two-electron state. Show that the charge density in a singlet (triplet) state made out of the two orbitals is given by

$$\rho(r) = |\psi_A(r)|^2 + |\psi_B(r)|^2 \pm 2 \langle \psi_A | \psi_B \rangle \psi_A(r) \psi_B(r).$$

Explain why the singlet state will usually be lower in energy.

**Problem 2. One-dimensional spin waves** Assume a one-dimensional chain of spins, precessing according to Eq. (6.30). By considering two neighbors of the  $n$ th spin, as in Fig. 6.8, each at relative angles  $\theta$ , show that the rate of precession according to Eq. (6.30) is

$$\omega = \frac{4JS}{\hbar}[1 - \cos(\theta)].$$

Hence show that for a spin wave of wavevector  $q$ , the dispersion is

$$\hbar\omega = 4JS[1 - \cos(qa)].$$

**Solution.** Equation (6.30) in the lecture notes is

$$\delta\dot{\mathbf{S}}_n = \frac{2JS}{\hbar} \sum_{j=\text{n.n. of } n} (\delta\mathbf{S}_n - \delta\mathbf{S}_j) \times \hat{\mathbf{z}},$$

where  $\hat{\mathbf{S}}_n$  is a vector in the  $xy$  plane and  $\hat{\mathbf{S}}_n = S\hat{\mathbf{z}} + \delta\mathbf{S}_n$  by (6.29). For a one-dimensional chain, the only nearest neighbors are  $j \in \{n-1, n+1\}$ . Thus

$$\delta\dot{\mathbf{S}}_n = \frac{2JS}{\hbar} (2\delta\mathbf{S}_n - \delta\mathbf{S}_{n-1} - \delta\mathbf{S}_{n+1}) \times \hat{\mathbf{z}}.$$

Splitting into one equation for each component, we have

$$\delta\dot{S}_n^x = -\frac{2JS}{\hbar} (2\delta S_n^y - \delta S_{n-1}^y - \delta S_{n+1}^y), \quad \delta\dot{S}_n^y = \frac{2JS}{\hbar} (2\delta S_n^x - \delta S_{n-1}^x - \delta S_{n+1}^x), \quad \delta\dot{S}_n^z = 0, \quad (1)$$

since  $\hat{\mathbf{x}} \times \hat{\mathbf{z}} = -\hat{\mathbf{y}}$  and  $\hat{\mathbf{y}} \times \hat{\mathbf{z}} = \hat{\mathbf{x}}$ . By analogy with phonon waves, we make the ansatz that the solutions have the form

$$\delta S_n^x = ue^{i(j\theta - \omega t)}, \quad \delta S_n^y = ve^{i(j\theta - \omega t)}, \quad \delta S_n^z = 0, \quad (2)$$

where  $u$  and  $v$  are constants and  $j$  is an integer. Making this substitution, Eq. (1) becomes

$$\begin{aligned} -i\omega ue^{i(n\theta - \omega t)} &= -\frac{2JS}{\hbar} \left( 2e^{i(n\theta - \omega t)} - e^{i[(n-1)\theta - \omega t]} - e^{i[(n+1)\theta - \omega t]} \right) v, \\ -i\omega ve^{i(n\theta - \omega t)} &= \frac{2JS}{\hbar} \left( 2e^{i(n\theta - \omega t)} - e^{i[(n-1)\theta - \omega t]} - e^{i[(n+1)\theta - \omega t]} \right) u, \end{aligned}$$

or

$$\begin{aligned} -i\omega u &= -\frac{2JS}{\hbar} \left[ 2 - (e^{-i\theta} + e^{i\theta}) \right] v = -\frac{4JS}{\hbar} [1 - \cos(\theta)]v, \\ -i\omega v &= \frac{2JS}{\hbar} \left[ 2 - (e^{-i\theta} + e^{i\theta}) \right] u = \frac{4JS}{\hbar} [1 - \cos(\theta)]u. \end{aligned}$$

This system can be solved using the matrix equation

$$0 = \begin{vmatrix} -i\omega & 4JS[1 - \cos(\theta)]/\hbar \\ -4JS[1 - \cos(\theta)]/\hbar & -i\omega \end{vmatrix} = -\omega^2 + \frac{16J^2S^2}{\hbar^2} [1 - \cos(\theta)]^2,$$

which has the solutions

$$\omega = \frac{4JS}{\hbar} [1 - \cos(\theta)]$$

as we wanted to show [1, p. 332]. □

For a spin wave of wavevector  $q$ , the phonon waves have the form  $e^{i\mathbf{q} \cdot \mathbf{r}} e^{i\omega t}$  by (5.5) of the lecture notes. Assuming the distance between adjacent spins is  $a$ , then  $\mathbf{q} \cdot \mathbf{r} \rightarrow qa$  in one dimension and  $\theta = qa$  by inspection of Eq. (2). So the dispersion is

$$\hbar\omega = 4JS[1 - \cos(qa)]$$

as desired.

**Problem 3. Colossal magnetoresistance** In a material like that shown in Fig. 6.10 the magnetism arises from a mechanism called double exchange, which is a version of itinerant exchange but involving two types of d-bands. The prototype compound is  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , where the valence of La is 3+ and Sr is 2+. This is a cubic (perovskite) crystal structure where the Mn ions are nominally equidistant from six oxygen neighbors in three Cartesian directions.

**3(a)** Explain why the valence of Mn in the compound  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  is expected to be between 3+ and 4+ and that the occupancy of the d-levels is expected to be  $4 - x$  electrons per Mn ion.

**3(b)** The degeneracy of the 5 d-levels in the free ion is split by the cubic environment into a low energy three-fold degenerate subset (whose notation is  $t_{2g}$ ) and a higher energy doubly degenerate orbital set ( $e_g$ ). Explain why the spin configurations of these levels for the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions are expected to be as shown in Fig. 6.12.

**3(c)** The lowest three electron states can be regarded as forming a classical spin  $S = 3/2$  which has negligible hopping from site to site, whereas the highest state is potentially itinerant. Now consider two neighboring sites  $i, j$  in the solid, each having the same “core” spin  $S$ , and sharing a single itinerant  $e_g$  electron, that has a tight-binding matrix element

$$t = \langle \phi_{e_g}(\mathbf{r} - \mathbf{R}_i) | H | \phi_{e_g}(\mathbf{r} - \mathbf{R}_j) \rangle$$

for hopping from site to site.

Explain the origin of the terms

$$H_{\text{int}} = J \sum_i \hat{\mathbf{s}}_i \cdot \mathbf{S}_i + J_x \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j$$

in the total Hamiltonian ( $\hat{\mathbf{s}}_i$  is the spin of the  $e_g$  electron) and suggest relative magnitudes of  $U$ ,  $J$ , and  $J_x$ .

**3(d)** Consider two neighboring core spins  $\mathbf{S}_i, \mathbf{S}_j$  that are at a relative angle  $\theta_{ij}$ . By considering that the spin wavefunction of the itinerant electron must, for  $J \gg t$ , be always aligned with the local core spin  $\mathbf{S}$ , explain why the Schrödinger equation for the itinerant electron can be simplified to one in which the tight-binding hopping matrix element from site  $i$  to site  $j$  is replaced by

$$t_{\text{eff}} = r \cos\left(\frac{\theta_{ij}}{2}\right).$$

To do this, you may wish to note that under a rotation by an angle  $\theta$ , the spin wavefunction transforms as

$$\begin{pmatrix} |\uparrow'\rangle \\ |\downarrow'\rangle \end{pmatrix} = \begin{pmatrix} \cos(\theta/2) & \sin(\theta/2) \\ -\sin(\theta/2) & \cos(\theta/2) \end{pmatrix} \begin{pmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{pmatrix}.$$

**3(e)** Sketch the density of states of the itinerant electrons for different alignments of the core spins  $\mathbf{S}$ :

- (i) *ferromagnetic* (all core spins aligned),
- (ii) *antiferromagnetic* (all neighboring core spins anti-aligned),
- (iii) *paramagnetic* (core spins randomly aligned).

Discuss how the total free energies of these states differ, and suggest what is the magnetic ground state when  $x = 0$ , and when  $tx > J_x$ ; give rough estimates of the transition temperatures of the ordered magnetic states toward high temperature paramagnetism.

**3(f)** Figure 6.13 shows the resistivity as a function of temperature of several samples of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  with different concentrations  $x$ , as well as the magnetic field dependence of the resistivity (which gives rise to the label “colossal” magnetoresistance). Discuss this data in light of the results above.

## References

- [1] C. Kittel, “Introduction to Solid State Physics”. Wiley, 8th edition, 2005.
- [2] N. W. Ashcroft and N. D. Mermin, “Solid State Physics”. Harcourt College Publishers, 1976.