Problem 1. Exchange Consider single-particle wavefunctions on two neighboring identical atoms ψ_A, ψ_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.

Solution. The charge density $\rho(r)$ is equivalent to the electron density, which can be found by

$$\rho(r) = \langle \psi | \hat{\rho}(r) | \psi \rangle,$$

where

$$\hat{\rho}(r) = \sum_{i=1}^{N} \delta(r - r_i)$$

is the density operator [1]. For a two-electron state, the wavefunction is given by (6.9) of the lecture notes,

$$\psi(r_1, r_2) = \frac{\psi_A(r_1)\psi_B(r_2) \pm \psi_A(r_2)\psi_B(r_1)}{\sqrt{2}},$$

where the $+\,(-)$ is for the spin singlet (triplet) state. Since ψ_A and ψ_B are real, $\psi^* = \psi$. Then the density is

$$
\begin{aligned}
\rho(r) =\ & \langle \psi | [\delta(r - r_1) + \delta(r - r_2)] | \psi \rangle \\
=\ & \iint dr_1\, dr_2\, \psi(r_1, r_2)[\delta(r - r_1) + \delta(r - r_2)]\psi(r_1, r_2) \\
=\ & \int dr_2\, \psi(r, r_2)\psi(r, r_2) + \int dr_1\, \psi(r_1, r)\psi(r_1, r) \\
=\ & \frac{1}{2} \int dr_2\, [\psi_A(r)\psi_B(r_2) \pm \psi_A(r_2)\psi_B(r)]^2 + \frac{1}{2} \int dr_1\, [\psi_A(r_1)\psi_B(r) \pm \psi_A(r)\psi_B(r_1)]^2 \\
=\ & \frac{1}{2} \int dr_2 \left[|\psi_A(r)|^2|\psi_B(r_2)|^2 \pm 2\psi_A(r)\psi_B(r)\psi_A(r_2)\psi_B(r_2) + |\psi_A(r_2)|^2|\psi_B(r)|^2 \right] \\
& + \frac{1}{2} \int dr_1 \left[|\psi_A(r_1)|^2|\psi_B(r)|^2 \pm \psi_A(r)\psi_B(r)\psi_A(r_1)\psi_B(r_1) + |\psi_A(r)|^2|\psi_B(r_1)|^2 \right] \\
=\ & \frac{1}{2} \left(|\psi_A(r)|^2 \int dr_2\, |\psi_B(r_2)|^2 \pm 2\psi_A(r)\psi_B(r) \int dr_2\, \psi_A(r_2)\psi_B(r_2) + |\psi_B(r)|^2 \int dr_2\, |\psi_A(r_2)| \right. \\
& \left. + |\psi_B(r)|^2 \int dr_1\, |\psi_A(r_1)|^2 \pm 2\psi_A(r)\psi_B(r) \int dr_1\, \psi_A(r_1)\psi_B(r_1) + |\psi_A(r)|^2 \int dr_1\, |\psi_B(r_1)| \right) \\
=\ & \frac{1}{2} \left(|\psi_A(r)|^2 \pm 2\psi_A(r)\psi_B(r) \langle \psi_A | \psi_B \rangle + |\psi_B(r)|^2 + |\psi_B(r)|^2 \pm 2\psi_A(r)\psi_B(r) \langle \psi_A | \psi_B \rangle + |\psi_A(r)|^2 \right) \\
=\ & |\psi_A(r)|^2 + |\psi_B(r)|^2 \pm 2 \langle \psi_A | \psi_B \rangle \, \psi_A(r)\psi_B(r),
\end{aligned}
$$

where we have assumed both ψ_A and ψ_B are properly normalized. $\square$

The singlet state will usually be lower in energy because ψ_A and ψ_B are not orthogonal, as mentioned on p. 110 of the lecture notes. The singlet state has a higher charge density near $r = 0$, as shown in Fig. 1. Since the electrons are therefore more likely to be located between the two atoms, they tend to be less excited, and so less energetic.
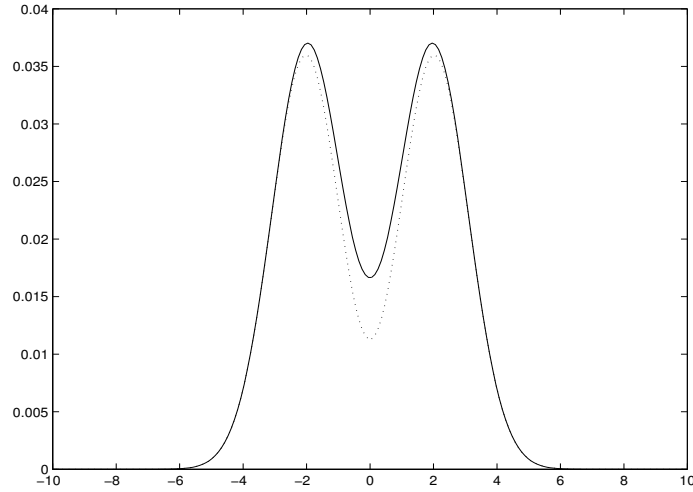
Figure 1: [Fig. 6.2 of the lecture notes] Charge density for the wavefunctions in a singlet state (solid line) and a triplet state (dotted line).

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 nth spin, as in Fig. 6.8, each at relative angles θ, 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

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

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 [2, p. 332]

$$\delta S_n^x = u e^{i(j\theta - \omega t)}, \qquad \delta S_n^y = v e^{i(j\theta - \omega t)}, \qquad \delta S_n^z = 0, \qquad (2)$$

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

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

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

or

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

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 [2, p. 332]. $\square$

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 $\mathbf{q}\cdot\mathbf{r} \to qa$ 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 $La_{1-x}Sr_xMnO_3$, 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 $La_{1-x}Sr_xMnO_3$ 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.

Solution.   write later

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 Mn^{3+} and Mn^{4+} ions are expected to be as shown in Fig. 6.12.

Solution.   write later

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.

Solution.   write later

3(d) Consider two neighboring core spins $\mathbf{S}_i, \mathbf{S}_j$ that are at a relative angle θ_{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

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

To do this, you may wish to note that under a rotation by an angle θ, 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 **S**:

   (i) *ferro*magnetic (all core spins aligned),

  (ii) *antiferro*magnetic (all neighboring core spins anti-aligned),

 (iii) *para*magnetic (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 $La_{1-x}Sr_xMnO_3$ 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

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[2] C. Kittel, "Introduction to Solid State Physics". Wiley, 8th edition, 2005.

[3] N. W. Ashcroft and N. D. Mermin, "Solid State Physics". Harcourt College Publishers, 1976.