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Two-site interaction model for a ferromagnetic metal

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A model Hamiltonian is obtained for the itinerant electrons in an elemental ferromagnetic metal, based on two-site interactions derivable from Coulomb fields. The energy parameters are expressed as matrix elements of ferromagnetic band states derived from local-density-functional theory. For a special case of the model, a single-orbital half-filled band, a systematic perturbation theory is developed for the elementary excitations. The character of the spin waves and Stoner modes is discussed.

I. INTRODUCTION

Two approaches can be distinguished in current theoretical work on itinerant-electron ferromagnetism. Much the older of the two is the *model Hamiltonian.* It is assumed that the metal can be described by a small number of energy parameters, sometimes by just one parameter, as in the isotropic nearest-neighbor Heisenberg or Ising model.

These parameters characterize the processes that are presumed to be the most important, for the properties studied. The origin of the interactions derives in most cases from a selected part of the Coulomb repulsion between the electrons, together with static Coulomb fields from a rigid lattice.

Because of its simplicity, a rich array of results have been obtained for the ground-state and thermodynamic properties. However, it is often not clear what part of the Coulomb interactions should be selected to define the model; further, the parameters generally need to be taken as adjustable parameters.

Recently, electron *band theory* has provided good results for some of the ground-state properties of ferromagnetic nickel. Using the local-density-functional theory in the form provided by Hohenberg and Kohn,[1] and by Kohn and Sham,[2] various studies have enabled the computation of energy bands for ferromagnetic nickel and iron, often without the need for any adjustable parameters.

The local-exchange approximation (LEA) prescribes a *spin*-dependent exchange interaction, for nonzero magnetization. Band studies based on this concept have been performed by Connolly,[3] Wakoh and Yamashita,[4] Gunnarsson,[5] and others.

The LEA work of Wang and Callaway[6] takes electron correlation into account by the method of von Barth and Hedin,[7] to obtain bands for ferromagnetic nickel. A magneton number of 0.58 is obtained; this agrees closely with the observed value of 0.56. Also, the Fermi surface predicted by their results is in quite good agreement with empirical data, except for a small region near the zone edge in the $\langle 100 \rangle$ directions.

The experiments of Eastman, Himpsel, and Knapp[8] do indicate that the theoretical exchange splitting at the top of the $3d$ band is about twice the actual value. The theoretical bandwidth is about 30% larger than that observed.

The LEA has been used by Janak and Williams[9] and by Andersen *et al.*[10] to compute various properties of ferromagnetic nickel and iron. The agreement is good for the lattice constant and fair for the compressibility. Kleinman[11] has analyzed the photoelectron spin polarization by the functional theory with very good results.

More recently, some work has appeared for the purpose of computing the elementary excitations of a ferromagnetic metal by band-theory concepts. The transverse dynamic susceptibility has been calculated by Callaway and Wang[12] using the LEA. A formula is obtained for the susceptibility which requires the computation of the inverse of an infinite matrix. The poles of the susceptibility yield a secular equation whose solution contains the spin-wave dispersion relation.

Applying their result for the susceptibility, Callaway and Wang[13] obtained an explicit result for the spin-wave stiffness constant D. All that is required as input to their formula are the ferromagnetic band states and their energies. For nickel, their result is only 10% smaller than the observed value.

An independent calculation of the transverse susceptibility by Edwards and Rahman[14] also uses the LEA and expresses the susceptibility as a sum over band-state matrix elements. In addition to the band states, the input needed to apply their formula is the precession angle of the local magnetization due to a time-dependent magnetic field perpendicular to the magnetization. Their result for D generalizes that of Callaway and Wang,[12] displaying an additional term that accounts for local-field effects. Work by Liu and Vosko[15] obtains similar results.

If band theory is to be employed to obtain thermodynamic properties, it would be judicious to make use of results from model Hamiltonians; that is, it would be desirable to bridge the gap between the two approaches.

For this purpose, the present study begins by deriving a model Hamiltonian whose parameters are matrix elements of the spin-split band states (Secs. II, III, and IV). A special case of the model (single-orbital half-filled band) is then solved for the elementary excitations (Secs. V, VI, VII, and VIII). While the special case is not applicable to a real material, it demonstrates that the original model is tractable.

In Sec. II, the electron Hamiltonian is written in the Wannier representation. A truncation procedure deletes terms in the electron Coulomb repulsion involving more than two sites; this defines the model.

Included in the model are the Hubbard and Heisenberg Hamiltonians, intra-atomic exchange and some less familiar pair-site iteractions. The various parts of the model are examined in Sec. III and inequalities obeyed by the parameters are displayed in Sec. IV.

In Sec. V, the problem of finding the elementary excitations is reduced to simple perturbation theory. The ionic states can also be viewed as exciton modes and possess the properties generally ascribed to Stoner modes.

The spin-wave states and their energies are computed for the first few orders of perturbation theory in Sec. VI. In Sec. VII the stability against spin reversal of the saturated magnetic state is examined. The energies of the Stoner modes are considered in Sec. VIII.

Finally, Sec. IX contains a comparison with work of other authors. Some concluding remarks are given in Sec. X.

II. MODEL

Assuming a rigid Bravais lattice of N ions, the electronic Hamiltonian is

$$H = H_{\text{kinetic}} + H_{\text{ion}} + H_{\text{Coulomb}} + H_{\text{spin}} \ . \tag{2.1}$$

The kinetic energy is

$$H_{\text{kinetic}} = \frac{1}{2} m \sum_s v_s^2 \ , \tag{2.2}$$

where m is the electron mass and

$$\vec{v}_s = [\vec{p}_s + (e/c)\vec{A}(\vec{r}_s)]/m \tag{2.3}$$

is the velocity operator for the sth electron. Here, e is the absolute value of the electron charge, $\vec{p}_s$ is the momentum operator for electron s, and $\vec{A}(\vec{r})$ is a vector potential for the external magnetic field $\vec{B}$. In this study, the field will be chosen as uniform, static, and in the direction of the magnetization.

The second term in Eq. (2.1) is the electron-ion interaction

$$H_{\text{ion}} = \sum_s V_{\text{ion}}(\vec{r}_s) \ . \tag{2.4}$$

Here, $V_{\text{ion}}(\vec{r})$ denotes the potential energy of an electron at $\vec{r}$ due to all the ions.

The repulsion between the electrons is

$$H_{\text{Coulomb}} = \frac{1}{2} \sum_s \sum_{t \neq s} V_c(\vec{r}_s, \vec{r}_t) \ , \tag{2.5}$$

with

$$V_c(\vec{r}, \vec{r}\,') = e^2/|\vec{r} - \vec{r}\,'| \ . \tag{2.6}$$

The last term in Eq. (2.1) is the interaction that involves the electron spin explicitly

$$H_{\text{spin}} = -\frac{1}{2}\mu_{\text{B}} g \sum_s \vec{\sigma}_s \cdot \vec{B} + \sum_s H_{\text{S.O.}}(\vec{r}_s, \vec{p}_s, \sigma_s) \ . \tag{2.7}$$

Here, σ_s is the Pauli spin operator for the sth electron, g is the Landé factor, and μ_{B} is the Bohr magneton. The up direction is selected as antialigned with the field and is the direction of majority spin.

The second term in Eq. (2.7) is the spin-orbit coupling

$$H_{\text{S.O.}}(\vec{r}, \vec{p}, \sigma) = \left(\frac{\hbar}{4m^2c^2}\right) \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{p}) \ , \tag{2.8}$$

where $V(\vec{r})$ is the self-consistent potential field on an electron at $\vec{r}$ due to the ions and all the other electrons. By writing the second term of Eq. (2.7) as a sum of one-electron operators, it is tacitly assumed that the interaction is a static, local field.

The dipole-dipole interactions have been omitted from Eq. (2.7).

A convenient basis of one-electron states is obtained from the eigenstates of the one-electron Hamiltonian

$$H_\sigma = p^2/2m + V_\sigma(\vec{r}) \ . \tag{2.9}$$

The second term $V_\sigma(\vec{r})$ is the net interaction on an electron of spin σ, due to the ions and the other electrons. Thus, we have

$$V_\sigma(\vec{r}) = V_{\text{ion}}(\vec{r}) + V_\sigma^{\text{scf}}(\vec{r}) \ , \tag{2.10}$$

where $V_\sigma^{\text{scf}}(\vec{r})$ is a self-consistently determined field on the electron, obtained by the methods of the LEA. For example, the choice

$$V_\sigma^{\text{scf}}(\vec{r}) = V^{\text{Hartree}}(\vec{r}) + V_\sigma^{\text{exch}}(\vec{r}) + V_\sigma^{\text{corr}}(\vec{r}) \tag{2.11}$$

can be made. The first and second terms are the Hartree and exchange operators. The last term accounts for correlations omitted in the Hartree-Fock approximation and can be chosen, for example, in the form proposed by von Barth and Hedin.[7]

The spin-averaged potential

$$V(\vec{r})=\tfrac{1}{2}[V_\uparrow(\vec{r})+V_\downarrow(\vec{r})] \qquad (2.12)$$

can be chosen for the potential in the spin-orbit coupling, Eq. (2.8).

The bandstates $|n\vec{k}\sigma\rangle$ solve

$$H_\sigma|n\vec{k}\sigma\rangle=\epsilon_{n\vec{k}\sigma}|n\vec{k}\sigma\rangle \quad . \qquad (2.13)$$

The wave vector $\vec{k}$ is restricted to the Brillouin zone, n is the band index and $\epsilon_{n\vec{k}\sigma}$ denotes the band energies. Equation (2.13) or (2.9) is the local exchange approximation (LEA) used in Refs. 3–6. However, from the viewpoint of the present study, the LEA is not an approximation but just a choice of a convenient basis, as many-electron effects will not be discarded.

The Wannier states are defined by

$$|nj\sigma\rangle=(N)^{-1/2}\sum_{\vec{k}}\exp(-i\vec{k}\cdot\vec{R}_j)|n\vec{k}\sigma\rangle \quad , \qquad (2.14)$$

where $\vec{R}_j$ is the location of the jth lattice site. The phases of $|n\vec{k}\sigma\rangle$ are chosen so that $|nj\sigma\rangle$ is real and positive at the origin. Then $|nj\sigma\rangle$ will decay exponentially with $|\vec{r}-\vec{R}_j|$ for large $|\vec{r}-\vec{R}_j|$ and will be symmetric under inversion. Also, the spatial part $\psi_{ni\sigma}(\vec{r})$ of $|ni\sigma\rangle$ will satisfy the translation property

$$\psi_{ni\sigma}(\vec{r}-\vec{R}_i)=\psi_{nj\sigma}(\vec{r}-\vec{R}_j) \quad . \qquad (2.15)$$

Using Greek indices (α,β, etc.) to denote Wannier states, the electron Hamiltonian Eq. (2.1) can be written in Wannier representation as follows:

$$H=H_{\mathrm{ssh}}+H_Z+H_{\mathrm{S.O.}}+H_{\mathrm{Coulomb}} \quad . \qquad (2.16)$$

Here, the "simple single-hop" Hamiltonian is

$$H_{\mathrm{ssh}}=\sum_{\alpha,\beta}T_{\alpha\beta}c_\alpha^\dagger c_\beta \qquad (2.17)$$

and contains all static interactions except for the Zeeman energy and spin-orbit coupling. The operator c_α is the absorption operator for Wannier state α.

The amplitudes $T_{\alpha\beta}$ are defined by

$$T_{\alpha\beta}=\langle\alpha|H-V_{\mathrm{scf}}+H_{\mathrm{mag}}|\beta\rangle \quad , \qquad (2.18)$$

with the orbital part of the magnetic field interaction given by

$$H_{\mathrm{mag}}(\vec{r},\vec{p})=\frac{eB}{2mc}L_z+\frac{e^2B^2}{8mc^2}(x^2+y^2) \quad . \qquad (2.19)$$

The z direction is that of the field, $\vec{L}$ is the orbital angular momentum operator and the vector potential choice $\vec{A}=(\tfrac{1}{2})(\vec{B}\times\vec{r})$ has been made.

The second term in Eq. (2.16) is the Zeeman energy

$$H_Z=-\tfrac{1}{2}g\,\mu_{\mathrm{B}}B\sum_\alpha s_\alpha n_\alpha \quad . \qquad (2.20)$$

Here, $n_\alpha=c_\alpha^\dagger c_\alpha$ is the number operator for state α. Also, s_α is defined as 1 or -1, for α corresponding to up or down spin, respectively.

The third term is the spin-orbit coupling

$$H_{\mathrm{S.O.}}=\sum_{\alpha,\beta}Y_{\alpha\beta}c_\alpha^\dagger c_\beta \quad , \qquad (2.21a)$$

$$Y_{\alpha\beta}=\left(\frac{\hbar}{4m^2c^2}\right)\langle\alpha|\vec{\sigma}\cdot(\vec{\nabla}V\times\vec{p})|\beta\rangle \quad . \qquad (2.21b)$$

Finally, the Coulomb repulsion energy is

$$H_{\mathrm{Coulomb}}=\frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V_c|\gamma\delta\rangle \times c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma \quad . \qquad (2.22)$$

To construct a tractable model, a truncation can be made on Eq. (2.22). Note that $\langle\alpha\beta|V_c|\gamma\delta\rangle$ is

$$e^2\int\int\frac{d^3r\,d^3r'}{|\vec{r}-\vec{r}\,'|}\psi_\alpha{}^*(\vec{r}) \times\psi_\beta{}^*(\vec{r}\,')\psi_\gamma(\vec{r})\psi_\delta(\vec{r}\,') \qquad (2.23)$$

if $\sigma(\alpha)=\sigma(\gamma)$ and $\sigma(\beta)=\sigma(\delta)$; $\sigma(\alpha)$ denotes the spin index for state $|\alpha\rangle$. Otherwise, $\langle\alpha\beta|V_c|\gamma\delta\rangle$ is zero.

If the band indices of $\alpha,\beta,\gamma,\delta$ are all the same, the largest integral occurs when all four site indices are also identical. This can be termed the *zero-order overlap term;* integrals that contain two distinct site indices are *first order in overlap,* etc.

Mattheiss[16] has performed numerical calculations of these integrals for the sites comprising the six vertices of a regular hexagon. The Wannier states are orthogonal linear combinations of hydrogen atom $1s$ wave functions, each centered on a vertex. Calculations are performed for nearest-neighbor separation between three and five Bohr radii; the largest 3-site integral is less than one half of the smallest 2-site integral. Practically all of the 3-site integrals are an order of magnitude smaller than the nearest-neighbor 2-site integral. Hence, transitions second order in the overlap are much less important than those first order in the overlap.

When the band indices are not all identical, it is reasonable to expect that integrals containing two distinct bands will dominate the 3-band and 4-band terms. Herring[17] has tabulated nearest-neighbor integrals for cobalt, using atomic $3d$ wave functions obtained from the Hartree-Fock approximation; shielding effects of the $4s$ electrons are not included. Integrals from wave functions involving only one $3d$

state are at least ten times the size of integrals between $3d$ states of differing magnetic quantum numbers.

The foregoing evidence suggests the utility of defining "order of overlap" as follows: First, let the term "center" denote the spatial part of the Wannier state. If letters f, g, etc. denote centers, then $f=(n,i)$ where i denotes the site. Then the *order of overlap* of the integrals Eq. (2.23) is defined as one less than the number of distinct *centers* in the quartet of Wannier states $\alpha, \beta, \gamma, \delta$.

Let H_{model} denote that part of H which includes terms to first order in the overlap

$$H = H_{\text{model}} + H_{3\text{-center}} + H_{4\text{-center}} \ . \tag{2.24}$$

The last two terms comprise the second- and third-order overlap terms

$$H_{3\text{-center}} + H_{4\text{-center}} = \sum_{\alpha\beta\gamma\delta}{}' \langle\alpha\beta|V_c|\gamma\delta\rangle \times c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma \ . \tag{2.25}$$

The prime on the sum prescribes that only 3-center and 4-center terms are to be included.

The result for H_{model} is conveniently expressed as a breakup into the seven terms

$$H_{\text{model}} = H_{\text{Hubbard}} + H_{\text{Heisenberg}} + H_N + H_{\text{Csh}} + H_{\text{Cdh}} + H_{\text{S.O.}} + H_Z \ . \tag{2.26}$$

The first two terms have the familiar Hubbard and Heisenberg forms, respectively, although interband transitions are included as well as intraband processes. The third term H_N is that part of the Coulomb repulsion between electrons that can be written as Wannier-state number operators (excluding number operators already included in the two preceding terms).

The fourth and fifth terms are the Coulomb single-hop and Coulomb double-hop terms, respectively, and also arise from the mutual electron repulsion. The last two terms are the spin-orbit coupling and Zeeman energies. In Sec. III, the terms will be defined formally.

III. TERMS IN THE MODEL HAMILTONIAN

A. Hubbard term

The Hubbard term is

$$H_{\text{Hubbard}} = H_{\text{ssh}} + \sum_f U(f)\, n_{f\uparrow} n_{f\downarrow} \ . \tag{3.1}$$

The simple single-hop Hamiltonian H_{ssh} is

$$H_{\text{ssh}} = H_{\text{band}} - H_{\text{scf}} + H_{\text{mag}} \ . \tag{3.2}$$

The band Hamiltonian is the sum of Eq. (2.9) over all the electrons. Formally, we have

$$H_{\text{band}} = \sum_{f,g,\sigma} \epsilon_{fg\sigma} c_{f\sigma}^\dagger c_{g\sigma} \ . \tag{3.3}$$

The amplitudes $\epsilon_{fg\sigma}$ are

$$\epsilon_{fg\sigma} = \langle f\sigma|H_\sigma|g\sigma\rangle \ . \tag{3.4}$$

The self-consistent-field term in Eq. (3.2) is

$$H_{\text{scf}} = \sum_{f,g,\sigma} V_{fg\sigma}^{\text{scf}} c_{f\sigma}^\dagger c_{g\sigma} \ , \tag{3.5}$$

with

$$V_{fg\sigma}^{\text{scf}} = \langle f\sigma|V_\sigma^{\text{scf}}|g\sigma\rangle \ . \tag{3.6}$$

The last term in Eq. (3.2) is the contribution of the orbital effects of the magnetic field

$$H_{\text{mag}} = \sum_{f,g,\sigma} M_{fg\sigma} c_{f\sigma}^\dagger c_{g\sigma} \ , \tag{3.7}$$

with

$$M_{fg\sigma} = \langle f\sigma|H_{\text{mag}}|g\sigma\rangle \ . \tag{3.8}$$

The three terms of Eq. (3.2) can be succinctly written

$$H_{\text{ssh}} = \sum_{fg\sigma} T_{fg\sigma} c_{f\sigma}^\dagger c_{g\sigma} \ , \tag{3.9}$$

$$T_{fg\sigma} = \epsilon_{fg\sigma} - V_{fg\sigma}^{\text{scf}} + M_{fg\sigma} \ . \tag{3.10}$$

The second term of the Hubbard Hamiltonian, Eq. (3.1) is the Coulomb repulsion of electrons of opposite spin on the same center. $U(f)$ is the average Coulomb repulsion

$$U(f) = \langle f\uparrow;f\downarrow|V_c|f\uparrow;f\downarrow\rangle \ . \tag{3.11}$$

This term arises from the choice $\alpha=\gamma$, $\beta=\delta$ with α and β referring to the same center, but opposite spin.

The Hamiltonian, Eq. (3.1) is identical to that of Hubbard[18] and Kanamori,[19] except that it is generalized beyond the single-orbital case; also, the hopping amplitudes $T_{fg\sigma}$ depend on the spin σ.

To conclude this subsection, the band energies $\epsilon_{n\vec{k}\sigma}$ are related to $T_{fg\sigma}$ by

$$T_{fg\sigma} = \delta_{mn}\epsilon_{n\sigma}(\vec{1}_{ij}) + N^{-1}\sum_{\vec{k},\vec{k}'} e^{i(\vec{k}\cdot\vec{R}_i - \vec{k}'\cdot\vec{R}_j)} \langle m\vec{k}\sigma|H_{mag} - V_\sigma^{\text{scf}}|n\vec{k}'\sigma\rangle \ . \tag{3.12}$$

Here, we have $f=(m,i)$ and $g=(n,j)$. Also, we have $\vec{1}_{ij}=\vec{R}_i-\vec{R}_j$ and

$$\epsilon_{n\sigma}(\vec{1})=\frac{1}{N}\sum_{\vec{k}}e^{i\vec{k}\cdot\vec{1}}\epsilon_{n\vec{k}\sigma} \quad . \tag{3.13}$$

B. Heisenberg Hamiltonian

The second term of Eq. (2.26) is

$$H_{\text{Heisenberg}}=-\sum_{f}\sum_{g\neq f}J(fg)\,\vec{S}_f\cdot\vec{S}_g \quad . \tag{3.14}$$

The exchange integral J is given by

$$J(fg)=\langle f\uparrow;g\downarrow|V_c|g\uparrow;f\downarrow\rangle \tag{3.15}$$

and the spin operators $\vec{S}_f$ have components

$$S_f^x=\tfrac{1}{2}(S_f^+ + S_f^-) \quad , \tag{3.16}$$

$$S_f^y=\tfrac{1}{2}(S_f^+ - S_f^-) \quad , \tag{3.17}$$

$$S_f^z=\tfrac{1}{2}(n_{f\uparrow}-n_{f\downarrow}) \quad . \tag{3.18}$$

In the preceding equations, the raising and lowering operators S_f^+ and S_f^- are defined via

$$S_f^+=C_{f\uparrow}^+C_{f\downarrow} \quad , \tag{3.19}$$

$$S_f^-=C_{f\downarrow}^+C_{f\uparrow} \quad . \tag{3.20}$$

The Hamiltonian Eq. (3.14) is of the familiar Heisenberg form when the pairs f and g correspond to the same band; the terms with distinct band and identical sites represent intra-atomic exchange.

C. Number-operator term

Formally, the third term of Eq. (2.26) constitutes the contributions in H_{Coulomb}. Eq. (2.22) that are bilinear in the number operators, but excluding the single-center Coulomb repulsion (2nd term of H_{Hubbard}) and the $S_f^zS_g^z$ terms of $H_{\text{Heisenberg}}$. The result is

$$H_N=\frac{1}{2}\sum_{f,g\neq f}\sum_{\sigma,\sigma'}N(f\sigma,g\sigma')n_{f\sigma}n_{g\sigma'} \quad . \tag{3.21}$$

Here, we have

$$N(f\sigma,g\sigma')=W(f\sigma,g\sigma')-\tfrac{1}{2}J_{\sigma\sigma'}(fg) \quad , \tag{3.22}$$

with

$$W(f\sigma,g\sigma')=\langle f\sigma;g\sigma'|V_c|f\sigma;g\sigma'\rangle \tag{3.23}$$

denoting the average repulsion between electrons in states $|f\sigma\rangle$ and $|g\sigma\rangle$. Also, we have

$$J_{\sigma,-\sigma}(fg)=J(fg) \tag{3.24}$$

and

$$J_{\sigma\sigma}(fg)=2J(fg:\sigma)-J(fg) \quad , \tag{3.25}$$

with

$$J(fg:\sigma)=\langle f\sigma;g\sigma|V_c|g\sigma;f\sigma\rangle \quad . \tag{3.26}$$

The exchange integrals $J(fg)$, $J_{\sigma\sigma}(fg)$, and $J(fg:\sigma)$ are identical if the basis corresponds to the paramagnetic case. That is, if the spatial part of $|f\sigma\rangle$ is independent of σ. In general, the exchange integrals will differ in value; however, it is easy to show that the difference between any two of these exchange integrals is second order in the overlap. In fact, the difference between *any* two energy parameters will be one order higher than the parameters themselves if the following condition holds: the two integrals only differ in that a spatial function in one has a different spin-index than the corresponding function in the other. A proof is given in the Appendix.

The two terms $H_{\text{Heisenberg}}$ and H_N together arise from terms of Eq. (2.22) with

$$f(\alpha)=f(\delta),\quad f(\beta)=f(\gamma),\quad f(\alpha)\neq f(\beta)$$

plus the terms

$$f(\alpha)=f(\gamma),\quad f(\beta)=f(\delta),\quad f(\alpha)\neq f(\beta) \quad .$$

The notation $f(\alpha)$ refers to the center described by Wannier state $|\alpha\rangle$. In particular, the transverse terms of $H_{\text{Heisenberg}}$ arise from

$$f(\alpha)=f(\delta),\quad f(\beta)=f(\gamma) \quad ,$$

$$f(\alpha)\neq f(\beta),\quad \sigma(\alpha)\neq\sigma(\beta) \quad .$$

D. Coulomb single-hop term

The fourth term of Eq. (2.26) is

$$H_{\text{Csh}}=\sum_{f,g\neq f}\sum_{\sigma}I_\sigma(fg) \times c_{g,-\sigma}^{\dagger}c_{f,-\sigma}n_{g\sigma}+\text{H.c.} \quad , \tag{3.27}$$

where H.c. denotes Hermitian conjugate and

$$I_\sigma(fg)=\langle g,\sigma;g,-\sigma|V_c|g,\sigma;f,-\sigma\rangle \quad . \tag{3.28}$$

The first term of H_{Csh} describes two electrons initially on centers f and g with opposite spin. The electron on f is transferred to g. The second term is the time-reversed process. H_{Csh} arises when

$$f(\alpha)=f(\beta)=f(\gamma),\quad f(\delta)\neq f(\alpha),$$

$$\sigma(\delta)\neq\sigma(\alpha)$$

plus the three other sets of terms obtained by permuting α, β, γ, and δ.

E. Double-hop term

The third-from-last term of Eq. (2.26) describes a pair of opposite spin on the same center, both scattered to a vacant center. Formally, we have

$$H_{\mathrm{Cdh}} = -\sum_{f,g\neq f} J_{\mathrm{dh}}(fg)\, c^{\dagger}_{f\uparrow} c_{g\downarrow} c^{\dagger}_{f\downarrow} c_{g\uparrow} \quad . \tag{3.29}$$

Here, $J_{\mathrm{dh}}(fg) = J(fg)$ and the subscript dh is inserted only to distinguish effects of the double hops from those of simple exchange.

H_{Cdh} is obtained from $f(\alpha) = f(\beta)$, $f(\gamma) = f(\delta)$ with $f(\alpha) \neq f(\gamma)$ and $\sigma(\alpha) \neq \sigma(\beta)$.

F. Spin-orbit coupling

The next-to-last term of Eq. (2.26) can be obtained from Eqs. (2.20) and (2.21) yielding

$$H_{\mathrm{S.O.}} = \sum_{fg} \sum_{\sigma\sigma'} Y(f\sigma|g\sigma')\, c^{\dagger}_{f\sigma} c_{g\sigma'} \quad , \tag{3.30}$$

with

$$Y(f\sigma|g\sigma) = \langle f\sigma|b_z|g\sigma\rangle \quad , \tag{3.31}$$

$$\vec{b}(\vec{r},\vec{p}) = (\hbar/4m^2c^2)\,\vec{\nabla} V(\vec{r}) \times \vec{p} \quad . \tag{3.32}$$

For $\sigma \neq \sigma'$, the element $Y(f\sigma|g\sigma')$ is defined by

$$Y(f\downarrow|g\uparrow) = (f\downarrow|b_x|g\uparrow) + i(f\downarrow|b_g|g\uparrow) \quad , \tag{3.33a}$$

$$Y(f\uparrow|g\downarrow) = (f\uparrow|b_x|g\downarrow) - i(f\uparrow|b_g|g\downarrow) \quad , \tag{3.33b}$$

and with the scalar products in Eqs. (3.33) denoting a spatial integration only.

The last term in Eq. (2.26) is the spin-field interaction already defined in Eq. (2.20).

IV. SIZE OF ENERGY PARAMETERS

A. Inequalities

The Schwarz inequality

$$(\phi_1,\phi_1)(\phi_2,\phi_2) \geqslant |(\phi_1,\phi_2)|^2$$

can be applied to yield several inequalities connecting the energy parameters.

First, let

$$\phi_1(\vec{r},\vec{r}') = \psi_{f\uparrow}(\vec{r})\psi_{f\downarrow}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

$$\phi_2(\vec{r},\vec{r}') = \psi_{g\uparrow}(\vec{r})\psi_{g\downarrow}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

with

$$h(\vec{r},\vec{r}') = |\vec{r}-\vec{r}'|^{-1/2}$$

to obtain

$$U(f)\,U(g) \geqslant |J(fg)|^2 \quad . \tag{4.1a}$$

If the band indices of f and g are the same, then $U(f)$ is independent of the site index so that Eq. (4.1a) simplifies to

$$U(n) \geqslant J(ni;nj) \quad . \tag{4.1b}$$

Here, n is the band index and i and j denote any pair of sites.

Similarly, let

$$\phi_1(\vec{r},\vec{r}') = \psi_{f\sigma}(\vec{r})\psi_{g\sigma}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

$$\phi_2(\vec{r},\vec{r}') = \psi_{g\sigma}(\vec{r})\psi_{f\sigma}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

to obtain

$$W(f\sigma;g\sigma) \geqslant J(fg:\sigma) \quad . \tag{4.2a}$$

A similar inequality relating W and J follows from the choice

$$\phi_1(\vec{r},\vec{r}') = \psi_{f\uparrow}(\vec{r})\psi_{g\downarrow}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

$$\phi_2(\vec{r},\vec{r}') = \psi_{g\uparrow}(\vec{r})\psi_{f\downarrow}(\vec{r}')h(\vec{r},\vec{r}') \quad ,$$

yielding

$$W(f\uparrow;g\downarrow)\,W(f\downarrow;g\uparrow) \geqslant J^2(fg) \quad . \tag{4.2b}$$

Finally, let

$$\phi_1(\vec{r},\vec{r}') = \psi_{f\sigma}(\vec{r})\psi_{g,-\sigma}(\vec{r}')h(\vec{r},\vec{r}')$$

$$\phi_2(\vec{r},\vec{r}') = \psi_{f\sigma}(\vec{r})\psi_{f,-\sigma}(\vec{r}')h(\vec{r},\vec{r}')$$

to obtain

$$W(f\sigma;g,-\sigma)\,U(f) \geqslant |I_{\sigma}(fg)|^2 \quad . \tag{4.3}$$

Two more inequalities between parameters arises from the demand that appropriately chosen Coulomb self-energies be positive. Let the charge density $\rho(\vec{r})$ be

$$\rho(\vec{r}) = |\psi_{f\uparrow}(\vec{r})|^2 - |\psi_{g\uparrow}(\vec{r})|^2 \quad .$$

The inequality

$$U(f) + U(g) \geqslant 2\,W(fg) \tag{4.4a}$$

follows.

If f and g correspond to the same band, then we have

$$U(n) \geqslant 2\,W(ni;nj) \tag{4.4b}$$

for any pair i and j.

The remaining inequality can be obtained from the choice

$$\rho(\vec{r}) = \psi_{f\uparrow}(\vec{r})\psi_{g\uparrow}(\vec{r})\psi_{g\uparrow}(\vec{r}) \quad ,$$

yielding

$$\sum_{\sigma} J_{\sigma\sigma}(fg) \geqslant 2J(fg) \quad . \tag{4.5}$$

B. Relative size of the energy parameters

Watson[20] has calculated wave functions for a free cobalt ion (no $4s$ electrons present). From the results, Freeman and Watson[21] have computed the Coulomb integrals U, W, J, and I, except that the Wannier states are replaced by atomic states. For W, J, and I, the separation $|\vec{1}| = 2.51$ Å (nearest-neighbor distance of metallic cobalt) was used. A summary is given by Herring[17] and by Freeman, Nesbet, and Watson.[22]

The results imply that the parameters are ordered (in decreasing size) as U, $W(\vec{1})$, $I(\vec{1})$, and $J(\vec{1})$. The intra-atomic exchange is comparable to $I(\vec{1})$.

For a set of six hydrogen atoms at the vertices of a regular polygon, Mattheiss[16] obtains the same ordering for U, W, I, and J.

From their definitions, U, W, and J are positive. The sign of I is determined by the detailed character of the states. Mattheiss[16] obtains a positive value with free-atom states and a negative value with Wannier states. Freeman and Watson[21] also obtain $I(\vec{1}) > 0$ with free-atom functions. If their functions are orthogonalized, it is easy to show that $I(\vec{1})$ becomes negative.

The parameter $T_{fg\sigma}$ can be estimated from Eq. (3.12) for the case where f and g correspond to neighboring sites and identical bands. Assume that the second term of Eq. (3.12) is small, and that $\vec{1}$ corresponding to nearest neighbors provides the dominant $\epsilon_{n\sigma}(\vec{1})$. Then, Eq. (3.13) yields a band energy at $\vec{k} = 0$ that is $12\epsilon_{n\sigma}(\vec{1})$ above the band energy at the [111] zone edge for a face-centered-cubic (fcc) lattice.

A bandwidth of 0.55 eV in the [111] direction for the highest $3d$ band of majority spin ($\Lambda_{3\uparrow}$ band) is obtained from the photoemission experiments of Eastman, Himpsel, and Knapp.[8] Hence, we have $T_{fg\uparrow} = -0.046$ eV for $\Lambda_{3\uparrow}$, when f and g correspond to nearest neighbors. This indicates that $T_{fg\sigma}$ is comparable to $J(\vec{1})$ using estimates of the latter from Ref. 21.

V. SINGLE-ORBITAL HALF-FILLED BAND

A special case of the model of Eq. (2.26) (the single-orbital half-filled band) is of interest in its own right, although it needs generalization before it can apply to a ferromagnetic metal. It may be remarked that the hypothetical spin-aligned hydrogen crystal may be well described by this special case, provided the electron-phonon interaction is added to Eq. (2.26).

Henceforth, band indices will be suppressed; the center indices f and g will be replaced by site indices i and j. Spin-orbit coupling will be omitted.

A. State of magnetic saturation

The state $|\psi_0\rangle$ that is a Slater deteminant of Wannier states with one electron of spin up on each site is an eigenstate of H_{model} with eigenvalue

$$E_0 = E_{0\ \text{Hubbard}} + E_{0\ \text{Heisenberg}} + E_{0N} + E_{0Z} \quad . \tag{5.1}$$

The terms denote the contributions from the Hubbard, Heisenberg, number-operator, and the Zeeman Hamiltonians, respectively:

$$E_{0\ \text{Hubbard}} = \sum_j T_{jj\uparrow} \quad , \tag{5.2}$$

$$E_{0\ \text{Heisenberg}} = -\frac{1}{4} \sum_{i,j \neq i} J(ij) \quad , \tag{5.3}$$

$$E_{0N} = \frac{1}{2} \sum_{i,j \neq i} N(i\uparrow, j\uparrow) \quad , \tag{5.4}$$

$$E_{0Z} = -\frac{1}{2} g \mu_B N \quad . \tag{5.5}$$

Letting the total spin S_z and total square spin S^2 be defined by

$$S_{x,y,z,} = \sum_j S_j^{x,y,z} \quad ,$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 \quad ,$$

it follows that $|\psi_0\rangle$ has S_z and S^2 well defined with values of $\frac{1}{2}N$ and $(\frac{1}{2}N)(1 + \frac{1}{2}N)$, respectively.

B. Single reversed spin: basic equations

Letting E be the energy of any one of the N^2 stationary states of the model that have S_z well defined at value $(\frac{1}{2}N) - 1$, then

$$E \geqslant E_0 \tag{5.6}$$

is the condition for stability of $|\psi_0\rangle$ against spin reversal.

A basis for the vector space of these states is the set of N^2 states

$$|ij\rangle = c_{j\downarrow}^{\dagger} c_{i\uparrow} |\psi_0\rangle \quad .$$

For $i = j$, the state has one electron per site; the reversed spin is at i. For $i \neq j$, $|ij\rangle$ is the state with i vacant, j doubly occupied (ionic configuration).

The N^2 solutions of $H_{\text{model}}|\psi\rangle = E|\psi\rangle$ are of the form

$$|\psi\rangle = \sum_{i,j} D_{ij} |ij\rangle \tag{5.7}$$

if the constants D_{ij} satisfy

$$\underline{H}_{\text{model}} \underline{D} = E \underline{D} \quad . \tag{5.8}$$

Here, $\underline{D}$ is the one-column vector of elements D_{ij}, while $\underline{H}_{\text{model}}$ is the matrix of order N^2 representing H_{model} in the vector space for the representation $|ij\rangle$.

A straightforward calculation for

$$\underline{H}_{\text{model}} = \underline{H}_{\text{Hubbard}} + \underline{H}_{\text{Heisenberg}} + \underline{H}_N + \underline{H}_{\text{Csh}} + \underline{H}_{\text{Cdh}} + \underline{H}_Z$$

yields the following results for the six terms: First, we have

$$\underline{H}_{\text{Hubbard}} = \underline{H}_{\text{ssh}} + \underline{H}_U \quad . \tag{5.9}$$

The single-hop Hamiltonian is

$$(\underline{H}_{\text{ssh}}\underline{D})_{ij} = E_{0\text{ Hubbard}} D_{ij} - \sum_l T_{li\uparrow} D_{lj} + \sum_l T_{jl\downarrow} D_{il} \tag{5.10}$$

and the single-site repulsion term H_U is given by

$$(\underline{H}_U \underline{D})_{ij} = U(1-\delta_{ij}) D_{ij} \quad . \tag{5.11}$$

For the Heisenberg Hamiltonian, the result is

$$(\underline{H}_{\text{Heisenberg}}\underline{D})_{jj} = \tilde{E}_{0\text{ Heisenberg}} D_{jj} - \sum_{l\neq j} J(jl) D_{ll} \quad , \tag{5.12}$$

$$(\underline{H}_{\text{Heisenberg}}\underline{D})_{ij} = [\tilde{E}_{0\text{ Heisenberg}} - \tfrac{1}{2} J(ij)] D_{ij} \quad , \tag{5.13}$$

the last relation valid for $i \neq j$. The notation

$$\tilde{E}_{0\text{ Heisenberg}} = E_{0\text{ Heisenberg}} + \sum_{h\neq 0} J(\vec{h}) \tag{5.14}$$

has been used. In Eq. (5.14), $J(\vec{h})$ is the exchange $J(ij)$ for two sites i and j separated by the translation vector $\vec{h}$. A similar notation will be used for the energy parameters $T_{ij\sigma}$, $N(i\sigma;j\sigma')$, $I_\sigma(i,j)$, etc.

The number operator Hamiltonian has the representation

$$(\underline{H}_N \underline{D})_{jj} = \tilde{E}_{0N} D_{jj} \quad , \tag{5.15}$$

with

$$\tilde{E}_{0N} = E_{0N} + \sum_{l\neq j} O(jl) \quad ; \tag{5.16}$$

$$O(jl) = N(j\downarrow;l\uparrow) - N(j\uparrow;l\uparrow) \quad . \tag{5.17}$$

For $i \neq j$, we have

$$(\underline{H}_N \underline{D})_{ij} = [E_{0N} - N(j\uparrow;i\uparrow) + \sum_{l\neq i,j} O(jl)] D_{ij} \quad . \tag{5.18}$$

For the Coulomb single-hop Hamiltonian, we have

$$(\underline{H}_{\text{Csh}}\underline{D})_{jj} = \sum_{l\neq j} [I_\uparrow(lj) D_{jl} - I_\downarrow(jl) D_{lj}] \quad , \tag{5.19}$$

while for $i \neq j$,

$$(\underline{H}_{\text{Csh}}\underline{D})_{ij} = I_\uparrow(ji) D_{ii} - I_\downarrow(ji) D_{jj} + 2 \sum_{l\neq i,j} I_\uparrow(lj) D_{il} \quad . \tag{5.20}$$

Finally, the Coulomb double-hop Hamiltonian has the representation

$$(\underline{H}_{\text{Cdh}}\underline{D})_{ij} = -(1-\delta_{ij}) J_{\text{dh}}(ij) D_{ji} \quad . \tag{5.21}$$

and the Zeeman term is

$$\underline{H}_Z = -\tfrac{1}{2} g \mu_{\text{B}} B (N-2) 1 \quad , \tag{5.22}$$

where 1 is the identity matrix.

Imposing periodic boundary conditions, the requirement

$$D_{ij} = D_{lj} \tag{5.23a}$$

must be met whenever $\vec{R}_l - \vec{R}_i = N_t \vec{a}_t$ for $t = 1$, 2, or 3. Here, $\vec{a}_t$ is one of a trio of basis vectors of the lattice, while N_t is the number of sites in the crystal in the direction $\vec{a}_t$.

Similarly, we have

$$D_{ij} = D_{il} \tag{5.23b}$$

if $\vec{R}_l - \vec{R}_j = \vec{N}_t \vec{a}_t$ for $t = 1$, 2, or 3.

C. Single reversed spin: reduction of the equations

To simplify the eigenvalue problem, Eq. (5.8), let

$$\vec{R}_{ij} = \tfrac{1}{2}(\vec{R}_i + \vec{R}_j) \quad , \tag{5.24}$$

$$\vec{l}_{ij} = \vec{R}_i - \vec{R}_j \quad , \tag{5.25}$$

define the center of mass and relative coordinates.

A convenient basis for the one-column vector $\underline{D}$ is the N^2 one-column vectors $D(\vec{Q},\vec{q})$ defined by

$$D_{ij}(\vec{Q},\vec{q}) = \exp(i\vec{Q}\cdot\vec{R}_{ij} + i\vec{q}\cdot\vec{l}_{ij}) \quad . \tag{5.26}$$

The wave vector $\vec{Q}$ runs over N nonequivalent wave vectors in the zone of the form

$$\vec{Q} = \sum_{t=1}^{3} n_t \vec{b}_t / N_t \quad , \tag{5.27}$$

where $\vec{b}_t$ solves $\vec{a}_s \cdot \vec{b}_t = 2\pi\delta_{st}$ and where n_t is an integer.

The boundary condition Eq. (5.23) is obeyed if $\vec{q}$ is any one of N nonequivalent wave vectors in the zone of the form

$$\vec{q} = \sum_{s=1}^{3} m_s \vec{b}_s / N_s \quad , \tag{5.28}$$

with m_s integral if n_s is even, and m_s half integral if n_s is odd.

Since $J(ij)$, $N(ij)$, etc. depend on $\vec{l}_{ij}$ but not on $\vec{R}_{ij}$, Bloch's theorem can be applied to Eq. (5.8); a complete set of solutions exist in the form

$$D_{ij}=(N)^{-1/2}e^{i\vec{Q}\cdot\vec{R}_{ij}}d_{\vec{Q}}(\vec{l}_{ij}) \quad . \tag{5.29}$$

The remaining problem is to find $d_{\vec{Q}}(\vec{l}_{ij})$, a one-column vector of N components which is independent of $\vec{R}_{ij}$. The subscript $\vec{Q}$ on $d_{\vec{Q}}(\vec{l}_{ij})$ will be omitted henceforth.

The boundary conditions are comprised by

$$d(\vec{l}+N_t\vec{a}_t)=\pm d(\vec{l}) \quad . \tag{5.30}$$

The upper and lower signs apply when n_t is even or odd, respectively. Clearly, $d(\vec{l})$ is a linear combination of the N exponentials $\exp(i\vec{q}\cdot\vec{l})$.

The eigenvalue problem for $d(\vec{l})$ is

$$\underline{\hat{H}}_{\text{model}}\underline{d}=E\underline{d} \quad , \tag{5.31}$$

obtained by combining Eqs. (5.29) and (5.8); d is the N-component vector $d(\vec{l})$. The matrix $\underline{\hat{H}}_{\text{model}}$ represents H_{model} in the subspace of the vectors $\underline{d}$ with fixed $\vec{Q}$.

After some computation, the result for $\underline{\hat{H}}_{\text{model}}$ is

$$\begin{aligned}\underline{\hat{H}}_{\text{model}}=\underline{\hat{H}}_{\text{Hubbard}}&+\underline{\hat{H}}_{\text{Heisenberg}}\\&+\underline{\hat{H}}_{N}+\underline{\hat{H}}_{\text{Csh}}+\underline{\hat{H}}_{\text{Cdh}}+\underline{\hat{H}}_{Z} \quad .\end{aligned} \tag{5.32}$$

Here, we have

$$\underline{\hat{H}}_{\text{Hubbard}}=\underline{\hat{H}}_{\text{ssh}}+\underline{\hat{H}}_{U} \quad , \tag{5.33}$$

with the simple single-hop Hamiltonian defined by

$$\begin{aligned}(\underline{\hat{H}}_{\text{ssh}})_{\vec{l}\,\vec{h}}=&E_{0\ \text{Hubbard}}\delta(\vec{h};\vec{l})\\&-T_{\uparrow}(\vec{h}-\vec{l};\vec{Q})+T_{\downarrow}(\vec{l}-\vec{h};\vec{Q}) \quad .\end{aligned} \tag{5.34}$$

The notation

$$A_{\sigma}(\vec{h};\vec{Q})=A_{\sigma}(\vec{h})e^{i(\vec{Q}\cdot\vec{h}/2)} \tag{5.35}$$

is used for any parameter $A_{\sigma}(\vec{h})$.

In Eq. (5.33), $\hat{H}_U$ is the diagonal matrix

$$(\underline{H})_{\vec{h}\,\vec{h}}=U[1-\delta(\vec{h})] \quad , \tag{5.36}$$

with $\delta(\vec{h})$ equal to unity if $\vec{h}=0$ and equal to zero for the other $N-1$ translation vectors.

The Heisenberg Hamiltonian is the diagonal matrix

$$(\underline{\hat{H}}_{\text{Heisenberg}})_{00}=E_{0\ \text{Heisenberg}}+J_0-J_{\vec{Q}} \quad , \tag{5.37}$$

$$(\underline{\hat{H}}_{\text{Heisenberg}})_{\vec{l}\,\vec{l}}=E_{0\ \text{Heisenberg}}+J_0-\tfrac{1}{2}J(\vec{l}) \quad , \tag{5.38}$$

for $\vec{l}\neq 0$. The notation

$$A_{\vec{Q}}=\sum_{\vec{h}\neq 0}A(\vec{h})e^{-i\vec{Q}\cdot\vec{h}} \tag{5.39}$$

defines $A_{\vec{Q}}$ for an energy parameter $A(\vec{h})$.

For $\underline{\hat{H}}_N$, the representation is the diagonal matrix

$$(\underline{\hat{H}}_N)_{00}=E_{0N}+\sum_{\vec{h}\neq 0}O(\vec{h}) \quad , \tag{5.40}$$

and

$$(\underline{\hat{H}}_N)_{\vec{l}\,\vec{l}}=E_{0N}-N(0\uparrow;\vec{l}\uparrow)+\sum_{\vec{h}\neq 0,\vec{l}}O(\vec{h}) \quad , \tag{5.41}$$

for $\vec{l}\neq 0$.

The Coulomb single-hop Hamiltonian is

$$(\underline{\hat{H}}_{\text{Csh}})_{0\vec{h}}=I_{\uparrow}(\vec{h};-\vec{Q})-I_{\downarrow}(\vec{h};\vec{Q}) \quad , \tag{5.42}$$

for $\vec{h}\neq 0$. Also, we have

$$(\underline{\hat{H}}_{\text{Csh}})_{\vec{l}\,\vec{h}}=2I_{\uparrow}(\vec{l}-\vec{h};\vec{Q}) \quad , \tag{5.43}$$

for $\vec{l}\neq 0$, $\vec{h}\neq 0$, $\vec{l}\neq\vec{h}$. The diagonal elements vanish.

The nonzero elements of $\underline{\hat{H}}_{\text{Cdh}}$ are

$$(\underline{\hat{H}}_{\text{Cdh}})_{\vec{l},-\vec{l}}=-J_{\text{dh}}(\vec{l}) \quad , \tag{5.44}$$

for $\vec{l}\neq 0$. Finally, we have

$$(\underline{\hat{H}}_Z)_{\vec{l}\,\vec{h}}=-\delta(\vec{l};\vec{h})(\tfrac{1}{2}g\mu_{\text{B}}B)(N-2) \quad . \tag{5.45}$$

The last term of Eqs. (5.40) and (5.41) is second order in the overlap, from Appendix A and Eq. (5.17). Also, $T_{\uparrow}(0)-T_{\downarrow}(0)-g\mu_{\text{B}}B$ is second order in the overlap for the same reason. Since H_{model} is derived by keeping only those terms first order in the overlap, these second-order overlap terms will be dropped, henceforth.

D. Single reversed spin: perturbation theory

If $\vec{Q}=0$, Eq. (5.31) is solved by

$$d(\vec{l})=\delta(\vec{l}) \quad , \tag{5.46a}$$

$$E=E_0+g\mu_{\text{B}}B \quad . \tag{5.46b}$$

The boundary condition Eq. (5.30) extends the solution to translation vectors other than the N vectors defining the crystal parallelpiped. This solution has S^2 well defined with value $(\frac{1}{2}N)(\frac{1}{2}N+1)$.

When $\vec{Q}\neq 0$, Eq. (5.31) cannot be solved exactly; a perturbation theory is desirable, consistent with the results of Sec. IV that indicate that U and $W(\vec{l})$ are the largest energy parameters. Hence, it is convenient to define one power of a perturbation parameter λ for each factor of J, T_{σ}, I_{σ}, or J_{dh} in the solution for E and $d(\vec{l})$. Thus,

$$d(\vec{l})=d^{(0)}(\vec{l})+d^{(1)}(\vec{l})+\cdots \quad , \tag{5.47}$$

$$E=E^{(0)}+E^{(1)}+\cdots \tag{5.48}$$

is the expansion of the solution in powers of λ. The

Hamiltonian $\underline{\hat{H}}_U + \underline{\hat{H}}_N$ is chosen as the unperturbed Hamiltonian, except for an additive constant which is the energy E_0 of the saturated state.

Hence, we have

$$\underline{\hat{H}}_{\text{model}} = \underline{\hat{H}}^{(0)} + \underline{\hat{H}}' \ , \qquad (5.49)$$

with

$$\underline{\hat{H}}^{(0)} = E_0 + \underline{\hat{H}}_U + \underline{\tilde{H}}_N + g\mu_{\text{B}}B \ . \qquad (5.50)$$

Here, we have

$$\underline{\tilde{H}}_N = \underline{\hat{H}}_N - E_{0N} \ . \qquad (5.51)$$

The perturbation in Eq. (5.49) is

$$\underline{\hat{H}}' = \underline{\tilde{H}}_{\text{Heisenberg}} + \underline{\tilde{H}}_{\text{hop}} \ , \qquad (5.52)$$

with the total hopping Hamiltonian as

$$\underline{\hat{H}}_{\text{hop}} = \underline{\hat{H}}_{\text{ssh}} + \underline{\hat{H}}_{\text{Csh}} + \underline{\hat{H}}_{\text{Cdh}} \ , \qquad (5.53\text{a})$$

and

$$\underline{\tilde{H}}_{\text{hop}} = \underline{\hat{H}}_{\text{hop}} - E_{0\ \text{Hubbard}} \ . \qquad (5.53\text{b})$$

Also, we have

$$\underline{\tilde{H}}_{\text{Heisenberg}} = \underline{\hat{H}}_{\text{Heisenberg}} - E_{0\ \text{Heisenberg}} \ . \qquad (5.54)$$

An alternative choice is to take advantage of the fact that $\underline{\tilde{H}}_{\text{Heisenberg}}$ is diagonal and add it to the right-hand side of Eq. (5.51) while removing it from Eq. (5.52). Then Heisenberg exchange is included in the zero-order results; however, there is no gain in the speed of convergence of the perturbation theory since $\underline{\hat{H}}_{\text{ssh}}$ and $\underline{\hat{H}}_{\text{Csh}}$ cannot be handled exactly and includes transitions as strong or stronger than those of Heisenberg exchange.

For fixed $\vec{Q}$, the unperturbed eigenvalue equation

$$\underline{\hat{H}}^{(0)}\underline{d}^{(0)} = E^{(0)}\underline{d}^{(0)} \qquad (5.55)$$

has N solutions; the lowest-energy solution is nondegenerate and is given by

$$\underline{d}^{(0)} \equiv d^{(0)}(\vec{l};0) \equiv 0\rangle = \delta(\vec{l}) \ , \qquad (5.56)$$

with energy $E^{(0)} \equiv E^{(0)}(0)$ given by

$$E^{(0)}(0) = E_0 + g\mu_{\text{B}}B \ , \qquad (5.57)$$

independent of $\vec{Q}$.

The corresponding solution for the constants D_{ij} of Eqs. (5.7) and (5.8) is

$$D_{ij}^{(0)} = \delta_{ij}N^{-1/2}e^{i\vec{Q}\cdot\vec{R}_j} \ , \qquad (5.58)$$

describing simple spin waves. Double occupation of any site is precluded by the δ_{ij} factor.

Applying first-order perturbation theory yields the familiar result

$$E^{(1)}(0) = 2\sum_{\vec{h}} J(\vec{h})\sin^2(\tfrac{1}{2}\vec{Q}\cdot\vec{h}) \ , \qquad (5.59)$$

for the first-order spin-wave energies.

The remaining $N-1$ solutions of Eq. (5.55) for $d^{(0)}(\vec{l})$ are

$$d^{(0)}(\vec{l}) \equiv d^{(0)}(\vec{l};\vec{h}) \equiv |\vec{h}\rangle = \delta(\vec{l};\vec{h}) \ , \qquad (5.60)$$

where $\vec{h}$ distinguishes the solutions and runs over the $N-1$ nonzero translation vectors. The corresponding energies $E^{(0)} \equiv E^{0}(\vec{h})$ are given by

$$E^{(0)}(\vec{h}) = E_0 + U(\vec{h}) \ , \qquad (5.61)$$

with excitation energy

$$U(\vec{h}) = U - N_{\uparrow}(\vec{h}) + g\mu_{\text{B}}B \ , \qquad (5.62\text{a})$$

$$N_{\uparrow}(\vec{h}) = N(0\uparrow;\vec{h}\uparrow) \ . \qquad (5.62\text{b})$$

The solution for $D_{ij}^{(0)}$ is $D_{ij}^{(0)} = D_{ij}^{(0)}(\vec{h})$, with

$$D_{ij}^{(0)}(\vec{h}) = N^{-1/2}\delta(\vec{l}_{ij};\vec{h})\exp(i\vec{Q}\cdot\vec{R}_{ij}) \qquad (5.63)$$

describing an ionic state with fixed separation $\vec{h}$ between vacant and doubly occupied sites. The center of mass $\vec{R}_{ij}$ of the pair propagates with wave vector $\vec{Q}$; all other sites have one electron of up spin.

By varying $\vec{Q}$ and $\vec{h}$, a total of $N(N-1)$ ionic states are obtained in addition to the N spin-wave states. Together they comprise a basis of N^2 states.

The zero-order excitation energy $U(\vec{h})$ given by Eq. (5.62) is

$$U - W_{\uparrow}(\vec{h}) + (\tfrac{1}{2})J_{\uparrow\uparrow}(\vec{h}) + g\mu_{\text{B}}B \ ,$$

with $W_{\uparrow}(\vec{h}) = W(0\uparrow;\vec{h}\uparrow)$. It represents the cost to reverse an up spin on a singly occupied site, and transfer it to a site displaced by $\vec{h}$; energy U is gained by the double occupation; but $W_{\uparrow}(\vec{h})$ is lost. The ionic states of lowest energy are those of largest W; i.e., smallest $|\vec{h}|$; the degeneracy will be the coordination number for the lattice, if the field is zero. As $|\vec{h}|$ increases, $U(\vec{h})$ increases; for large $|\vec{h}|$, $U(\vec{h}) \rightarrow U$ and a quasicontinuum of ionic states is realized (Stoner modes).

The ionic states Eq. (5.63) have S^2 with value $(\tfrac{1}{2}N)(\tfrac{1}{2}N-1)$; from general symmetry arguments it can be shown that this remains true for the exact solution of Eq. (5.31).

A schematic picture of the zero-order energies of the spin waves and ionic states is given in Fig. 1.

VI. PERTURBED SPIN-WAVE ENERGIES

The effects of the hopping terms will be examined here; formally, the first-order states and the second- and third-order energies will be obtained.

Perturbation theory yields the result

$$d^{(1)}(\vec{l};0) = -2i\frac{L(\vec{l})}{U(\vec{l})}\sin\tfrac{1}{2}\vec{Q}\cdot\vec{l} \qquad (6.1)$$

for the first-order spin-wave coefficients for $d(\vec{1})$. Here,

$$L(\vec{1}) = T(\vec{1}) + I(\vec{1}) \ , \tag{6.2}$$

and

$$A = \tfrac{1}{2}(A_{\uparrow} + A_{\downarrow}) \tag{6.3}$$

for any energy parameter A_σ.

The admixture of ionic states onto the simple spin-waves is displayed in Eq. (6.1); inhibiting the hopping is the single-site Coulomb repulsion U.

For the second-order energy, a computation yields

$$E^{(2)}(0) = -4 \sum_{\vec{h}} \hat{L}(\vec{h}) \sin^2 \tfrac{1}{2}\vec{Q}\cdot\vec{h} \ , \tag{6.4}$$

where

$$\hat{L}(\vec{h}) = L^2(\vec{h})/U(\vec{h}) \ . \tag{6.5}$$

The lowering of the spin-wave energy by $E^{(2)}(0)$ can be interpreted as follows: starting from magnetic saturation, an electron at the top of the band is placed at the bottom with spin reversed. A large bandwidth [i.e., $|T(\vec{h})|$ large] yields a large reduction in energy. Since U inhibits the hopping processes, a large U enhances the stability of the saturated state; however, stability cannot occur without the exchange effects of J, since $E^{(2)}(0)$ is negative.

Double-hop effects first appear in third order. The standard formula[23] yields, after a lengthy computation, the result

$$E^{(3)}(0) = E^{(3)}_{\mathrm{dh}} + E^{(3)}_{\mathrm{Heisenberg}} + E^{(3)}_{\mathrm{sh}} \ . \tag{6.6}$$

The double-hop contribution is

$$E^{(3)}_{\mathrm{dh}} = 4 \sum_{\vec{h}} J_{\mathrm{dh}}(\vec{h}) \tilde{L}^2(\vec{h}) \times \sin^2(\tfrac{1}{2}\vec{Q}\cdot\vec{h}) \ , \tag{6.7}$$

$$\tilde{L}(\vec{h}) = L(\vec{h})/U(\vec{h}) \ . \tag{6.8}$$

Comparing Eqs. (6.7) and (5.59) shows that $E^{(3)}_{dh}$ differs from the simple spin-wave energy only by the factor $2\tilde{L}^2(\vec{h})$ in the sum on $\vec{h}$. This result can be interpreted by noting that the combination of single hop, followed by double hop, followed by single hop is equivalent to a mutual spin flip of electrons of opposite spin on the pair of sites. Hence, it is to be expected that $E^{(3)}_{\mathrm{dh}}$ has the same sign and form as the lowest-order exchange result $E^{(1)}(0)$.

The middle term of Eq. (6.6) is defined by

$$E^{(3)}_{\mathrm{Heisenberg}} = 4J_{\vec{Q}} \sum_{\vec{h}} \tilde{L}^2(\vec{h}) \sin^2(\tfrac{1}{2}\vec{Q}\cdot\vec{h}) \tag{6.9}$$

and is positive for $\vec{Q}$ near zero.

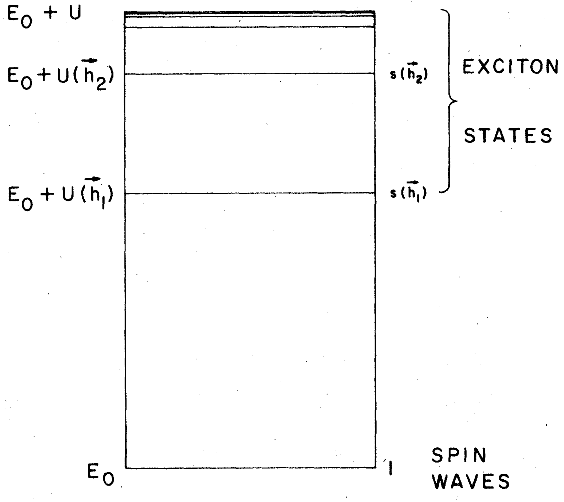

FIG. 1. Drawing (schematic) of the zero-order energies of the elementary excitations for the special case of the model, in zero external field. The energies of the spin waves and excitons are independent of the wave vector $\vec{Q}$ characterizing the propagation of the reversed spin. For fixed $\vec{Q}$, the spin-wave state is nondegenerate and has the energy E_0 of the saturated magnetic state. Each length $|\vec{h}|$ defines an exciton level of energy $E_0 + U(\vec{h}) = E_0 + U(\vec{h}) + (\tfrac{1}{2})J(\vec{h})$. The relevant relations are Eqs. (5.57), (5.61), (5.62), and (3.22).

The last term is due to single hops only

$$E^{(3)}_{\mathrm{sh}} = 4 \sum_{\vec{h}\neq 0} \sum_{\vec{1}\neq 0,\vec{h}} G(\vec{1},\vec{h}) f(\vec{h},\vec{1},\vec{Q}) \ , \tag{6.10}$$

with

$$G(\vec{h},\vec{1}) = \tilde{L}(\vec{h}) \tilde{L}(\vec{1}) I(\vec{1}-\vec{h}) \ , \tag{6.11}$$

$$f(\vec{h},\vec{1},\vec{Q}) = \cos^2 \tfrac{1}{2}\vec{Q}\cdot(\vec{h}-\vec{1}) - \tfrac{1}{2}\cos\vec{Q}\cdot\vec{h} - \tfrac{1}{2}\cos\vec{Q}\cdot\vec{1} \ . \tag{6.12}$$

The speed of convergence can be ascertained by noting that the third-order spin wave energy $E^{(3)}_{\mathrm{dh}}$, Eq. (6.7), is of identical form to $E^{(1)}$, except for the additional factor $2L^2(\vec{h})/U^2(\vec{h})$. Estimates of $T(\vec{h})$, $I(\vec{h})$, and U discussed in Sec. IV, indicate that $\tilde{L}(\vec{h}) = L(\vec{h})/U(\vec{h})$ is small so that terms beyond the second-order terms are likely not to be significant. Similar remarks hold for the other two contributions to the third-order energy in Eq. (6.6).

VII. STABILITY OF THE SATURATED STATE

A. Criterion to second order

From Eqs. (5.57), (5.59), and (6.4), the spin-wave energy is

$$E(0) \doteq E_0 + g\mu_B B + 2\sum_{\vec{h}} F(\vec{h})\sin^2\tfrac{1}{2}\vec{Q}\cdot\vec{h} \tag{7.1}$$

to second order in λ, with

$$F(\vec{h}) = J(\vec{h}) - \hat{L}(\vec{h}) \ . \tag{7.2}$$

Then, for zero field, the stability condition, Eq. (5.6) is that

$$J_0 - J_{\vec{Q}} \geqslant 2(\hat{L}_0 - \hat{L}_{\vec{Q}}) \ , \tag{7.3}$$

using the notation of Eq. (5.39). Stability must occur if $F(\vec{h}) > 0$ for all $\vec{h}$.

B. Stiffness constant

Expanding about $\vec{Q}=0$ yields

$$E(0) = E_0 + g\mu_B B + \sum_{s=1}^{3} D_s Q_s^2 \ , \tag{7.4}$$

omitting terms cubic in $\vec{Q}$ or higher, and including terms to second order in λ. The indices $s = 1, 2, 3$, denote Cartesian components of $\vec{Q}$. The stiffness constants D_s are defined by

$$D_s = \tfrac{1}{2}\sum_{\vec{h}} F(\vec{h}) h_s^2 \ . \tag{7.5}$$

For a cubic crystal, $D_1 = D_2 = D_3 \equiv D$ so that

$$D = \tfrac{1}{6}\sum_{\vec{h}} F(\vec{h}) |\vec{h}|^2 \ . \tag{7.6}$$

C. Short-range interactions

Assuming that nearest-neighbor energy parameters dominate those of more distant neighbors, Eq. (5.59) reduces to the result

$$E^{(1)}(0) = 16J\sin^2(\tfrac{1}{4}Qa) \tag{7.7}$$

for a fcc lattice of cubic side a. Here, J is the Heisenberg exchange parameter for nearest neighbors, and $\vec{Q}$ is chosen along a crystal axis.

Similarly, Eq. (6.4) reduces to

$$E^{(2)}(0) = -32\hat{L}\sin^2(\tfrac{1}{4}Qa) \ . \tag{7.8}$$

Hence, stability holds (up to second order in λ) if $J > 2\hat{L}$, for zero field.

VIII. IONIC STATES

A. First-order energies

Following the reasoning at the end of Sec. V, the zero-order ionic states are linear combinations of the $s(\vec{h})$ states $|\vec{h}\rangle$ with identical $|\vec{h}|$. For the triclinic or monoclinic lattices, $s(\vec{h}) = 2$, corresponding to linear combinations of $|\vec{h}\rangle$ and $|-\vec{h}\rangle$.

In general, a partial diagonalization of the perturbation matrix may be achieved from the two linear combinations

$$|\vec{h}_\pm\rangle^{(0)} = 2^{-1/2}(e^{i\beta}|\vec{h}\rangle \pm e^{-i\beta}|-\vec{h}\rangle) \ . \tag{8.1}$$

Then, we have

$$\langle\vec{h}_+|\underline{H}'|\vec{h}_-\rangle = 0 \tag{8.2}$$

provided the angle β is defined by

$$(\underline{H}')_{\vec{h},-\vec{h}} = |(\underline{H}')_{\vec{h},-\vec{h}}| e^{2i\beta} \ . \tag{8.3}$$

From the matrix elements of H', an equivalent definition of β is

$$\tan 2\beta = 2[L(2\vec{h})/\Gamma(\vec{h})]\sin\vec{Q}\cdot\vec{h} \ . \tag{8.4}$$

where

$$\Gamma(\vec{h}) = 2I(2\vec{h})\cos\vec{Q}\cdot\vec{h} - J_{\mathrm{dh}}(\vec{h}) \ . \tag{8.5}$$

The angle β will be chosen $-\pi < 2\beta \leqslant \pi$, so that $\beta(-\vec{h}) = -\beta(\vec{h})$. In Eq. (8.1), $\vec{h}$ varies over the $\frac{1}{2}(N-1)$ nonzero translation vectors in a selected half parallepiped of the crystal.

The combinations Eq. (8.1) form the correct zero-order states in the following circumstances: (i) when $s(\vec{h}) = 2$; (ii) when the single-hopping interactions are short range [i.e., $I(\vec{l}) = 0 = T(\vec{l})$ for $|\vec{l}|$ greater than the nearest-neighbor distance]; (iii) in the limit of strong magnetic field. [Orbital effects then produce $\frac{1}{2}s(\vec{h})$ doublets of the form Eq. (8.1).]

In the remainder of this section, it will be assumed that one of these three cases applies. Then standard degenerate perturbation theory yields the first-order energies

$$E_\pm^{(1)}(\vec{h}) = J_0 \pm \sigma(\vec{h}) \ , \tag{8.6}$$

with

$$\sigma(\vec{h}) = [4L^2(2\vec{h})\sin^2(\vec{Q}\cdot\vec{h}) + \Gamma^2(\vec{h})]^{1/2} \ , \tag{8.7}$$

defining the resonance energy for oscillations between $|\vec{h}\rangle$ and $|-\vec{h}\rangle$.

For $\vec{Q}=0$, the value of $\sigma(\vec{h})$ is

$$\sigma_0(\vec{h}) = |2I(2\vec{h}) - J_{\mathrm{dh}}(\vec{h})| . \tag{8.8}$$

As $|\vec{Q}|$ increases from zero, $\sigma(\vec{h})$ increases if

$$\sigma_1(\vec{h}) = [2L^2(2\vec{h}) - I(2\vec{h})\Gamma_0(\vec{h})]/\sigma_0(\vec{h}) \tag{8.9}$$

is positive; if it is negative, $\sigma(\vec{h})$ decreases. Also, $\Gamma_0(\vec{h})$ is the value of $\Gamma(\vec{h})$ when $\vec{Q}=0$. An extremum is reached when

$$\cos(\vec{Q}\cdot\vec{h}) = -I(2\vec{h})/G(\vec{h}) \tag{8.10}$$

for a given direction, with

$$G(\vec{h}) = [L^2(2\vec{h}) - I^2(2\vec{h})]/J_{\mathrm{dh}}(\vec{h}) \ . \tag{8.11}$$

The extremum is a maximum (minimum), if $\sigma_1(\vec{h})$ is positive (negative). The value of $\sigma(\vec{h})$ at the extremum is

$$\sigma_{\mathrm{extr}}(\vec{h}) - 2|L(2\vec{h})||1+(\tfrac{1}{4}J_{\mathrm{dh}}(\vec{h})G^{-2}(\vec{h})| \ . \tag{8.12}$$

Figure 2 provides a schematic picture of the spin-wave and ionic-state energies.

B. Exciton character of the ionic states

The extra electron on the doubly occupied site can be viewed as bound to the vacant site. From Eqs. (5.61) and (5.62), the zero-order energy is

$$U(\vec{h}) = U - W(\vec{h}) + (\tfrac{1}{2})J_{11}(\vec{h}) + g\mu_{\mathrm{B}}B \tag{8.13}$$

above that of the saturated state. The ground excitonic state (nearest-neighbor $\vec{h}$) has ionization energy $W(\vec{h}) - (\frac{1}{2})J_{11}(\vec{h})$. As $|\vec{h}|\to\infty$, the exciton levels approach the energy $E_0+U+g\mu_{\mathrm{B}}B$.

Letting $|\vec{h}_\pm\rangle$ be the actual solutions for the ionic (or exciton) states, then

$$|\vec{h}_\pm\rangle = |\vec{h}_\pm\rangle^{(0)} + |\vec{h}_\pm\rangle^{(1)} + \cdots \tag{8.14}$$

denotes its expansion in powers of λ. The result for the first-order contribution is

$$|\vec{h}_\pm\rangle^{(1)} = |\vec{h}_\pm\rangle_{\mathrm{sw}} + |\vec{h}_\pm\rangle_{+} + |\vec{h}_\pm\rangle_{-} \ . \tag{8.15}$$

The first term is the admixture of the spin wave onto the ionic state

$$|\vec{h}_\pm\rangle_{\mathrm{sw}} = K_\pm(\vec{h})|0\rangle \ , \tag{8.16}$$

$$K_+(\vec{h}) = 2^{3/2}\tilde{L}(\vec{h})(\sin\tfrac{1}{2}\vec{Q}\cdot\vec{h})\sin\beta \ , \tag{8.17a}$$

$$K_-(\vec{h}) = 2^{3/2}\tilde{L}(\vec{h})(\sin\tfrac{1}{2}\vec{Q}\cdot\vec{h})\cos\beta \ . \tag{8.17b}$$

The second term in Eq. (8.15) is the admixture of "symmetric" states $|\vec{l}_+\rangle^{(0)}$ onto $|\vec{h}_\pm\rangle^{(0)}$ and is given by

$$|\vec{h}_\pm\rangle_+ = \sum_{\vec{l}\neq 0,\vec{h}} K^{+}_{\pm}(\vec{h},\vec{l})|\vec{l}_+\rangle^{(0)} \ , \tag{8.18}$$

$$K^{+}_{\pm}(\vec{h},\vec{l}) = \frac{1}{2}\frac{K(\vec{h},\vec{l})+K(\vec{h},-\vec{l})}{W(\vec{h})-W(\vec{l})} \pm \text{c.c.} \tag{8.19}$$

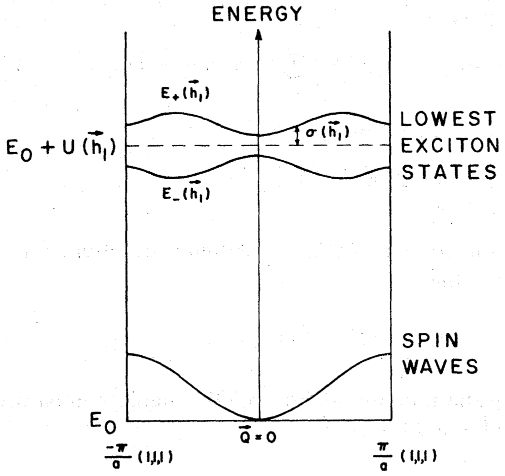

FIG. 2. Energies of the spin waves and the lowest exciton level to first order, in zero external field (schematic). The drawing applies to a fcc crystal with $\vec{Q}$ in the [111] direction. The spin-wave energies are given by Eq. (5.59). The sketch for the lowest pair of exciton levels is for the short-range interaction case. Then Eqs. (8.1) and (8.6) give the correct zero-order states and first-order energies. The splitting of the pair is due to hopping processes.

with c.c. denoting complex conjugate. The energy parameter $K(\vec{h},\vec{l})$ is defined by

$$K(\vec{h},\vec{l}) = S(\vec{h}+\vec{l})e^{i[\beta(\vec{h})+\beta(\vec{l})]} \ , \tag{8.20}$$

with

$$S(\vec{l}) = 2I(\vec{l})\cos(\tfrac{1}{2}\vec{Q}\cdot\vec{l}) - 2iL(\vec{l})\sin\vec{Q}\cdot\vec{l} \ . \tag{8.21}$$

In Eq. (8.18), the sum on $\vec{l}$ is over the half parallelpiped.

Finally the last term in Eq. (8.15) is the admixture of "antisymmetric states" $|\vec{l}_-\rangle^{(0)}$ onto $|\vec{h}_\pm\rangle^{(0)}$,

$$|\vec{h}_\pm\rangle_- = \sum_{\vec{l}} K^{-}_{\pm}(\vec{h},\vec{l})|\vec{l}_-\rangle^{(0)} \ , \tag{8.22}$$

$$K^{-}_{\pm}(\vec{h},\vec{l}) = \frac{1}{2}\frac{K(\vec{h},-\vec{l})-K(\vec{h},\vec{l})}{W(\vec{h})-W(\vec{l})} \pm \text{c.c.} \ . \tag{8.23}$$

The admixture of $|\vec{l}_+\rangle^{(0)}$ and $|\vec{l}_-\rangle^{(0)}$ onto $|\vec{h}_\pm\rangle^{(0)}$ varies as $|W(\vec{h})-W(\vec{l})|^{-1}$. For nearest neighbor $\vec{h}$ and large $|\vec{l}|$, this approaches $|W(\vec{h})|^{-1}$ showing the small admixture of such $|\vec{l}\rangle$.

C. Second-order energy

Standard perturbation theory gives the result

$$E^{(2)}_{\pm}(\vec{h}) = E^{(2)}_{\pm}(\vec{h},0) + 2\sum_{\vec{l}\neq 0,\vec{h}} E^{(2)}_{\pm}(\vec{h},\vec{l}) \tag{8.24}$$

for the second-order energy of the ionic states. Here, we have

$$E_{+}^{(2)}(\vec{h},0)=8\frac{L^2(\vec{h})}{U(\vec{h})}\sin^2(\tfrac{1}{2}\vec{Q}\cdot\vec{h})\sin^2\beta\ , \tag{8.25a}$$

$$E_{-}^{(2)}(\vec{h},0)=\frac{8L^2(\vec{h})}{U(\vec{h})}\sin^2(\tfrac{1}{2}\vec{Q}\cdot\vec{h})\cos^2\beta\ , \tag{8.25b}$$

and

$$E_{\pm}^{(2)}(\vec{h},\vec{l})=\frac{1}{2}\frac{|K(\vec{h},\vec{l})\mp K(-\vec{h},\vec{l})|^2}{W(\vec{l})-W(\vec{h})}\ , \tag{8.26}$$

with the sum in Eq. (8.24) taken over the half parallelpiped.

The energy denominators in Eqs. (8.25) and (8.26) indicate that $|E_{\pm}^{(2)}(\vec{h},\vec{l})|$ will exceed $|E_{\pm}^{(2)}(\vec{h},0)|$. For small $|\vec{Q}|$, $E_{\pm}^{(2)}(\vec{h},\vec{l})$ will be negative, while $E_{\pm}^{(2)}(\vec{h},0)$ is always positive. Hence, it is to be expected that $E_{\pm}^{(2)}(\vec{h})$ is a parabolic function of $\vec{Q}$ with a maximum at $\vec{Q}=0$.

D. Short-range interactions

If simple hopping parameters involving separations greater than nearest neighbors are discarded, Eq. (8.4) yields $\beta=\frac{1}{2}\pi$ and Eq. (8.1) represents simple symmetric and antisymmetric combinations of $|\vec{h}\rangle$ and $|-\vec{h}\rangle$. The resonance energy $\sigma(\vec{h})$ is $J_{\mathrm{dh}}(\vec{h})$.

The resonance effect can be viewed as a pair of electrons jumping simultaneously back and forth from one site to a site displaced by $\vec{h}$, with period $2\pi\hbar/J_{\mathrm{dh}}(\vec{h})$, analogous to the jumping back and forth of the electron in the ionized hydrogen molecule.

The symmetric state $|\vec{h}_{+}\rangle^{(0)}$ has energy $2J_{\mathrm{dh}}$ above the antisymmetric state $|\vec{h}_{-}\rangle^{(0)}$. The lower energy of $E_{-}^{(1)}(\vec{h})$ is due to the fact that $|\vec{h}_{-}\rangle$ corresponds to a smaller probability for the electron pair to be close together; there is a resultant reduction in the Coulomb repulsion between the pair.

E. Entry of spin waves into the exciton modes

Consider a fcc lattice, with $\vec{Q}$ along the [111] direction and only short-range interactions present. To second order in λ, the spin-wave energy is a maximum at the zone edge, with value

$$E(0)=E_0+g\mu_{\mathrm{B}}B+12(J-2\hat{L})\ . \tag{8.27}$$

The ground-state exciton energy at the zone edge is

$$E_{-}(\vec{h})=E_0+U-W-(\tfrac{1}{2})J+g\mu_{\mathrm{B}}B \tag{8.28}$$

to first order in λ, using $J_{\mathrm{dh}}=J$.

The spin waves enter the exciton region before the zone edge is reached if

$$U<W+(\tfrac{25}{2})J-24\hat{L}\ .$$

This requires a large stiffness constant and that U be not too much larger than W.

IX. COMPARISON WITH OTHER WORK

A. Ruijgrok

Ruijgrok's study[24] is closest to that of Secs. II and III. He specializes to a one-band model at the outset and gives a complete derivation of all two-site interactions obtainable from the Coulomb repulsion.

The reduced Hamiltonian [his Eq. (3.8)] is equivalent to the model Hamiltonian Eq. (2.26) here, except that intra-atomic exchange is absent in his one-band model, and he uses a paramagnetic basis.

A molecular-field approximation is made on the reduced Hamiltonian, replacing terms quartic in creation and absorption Wannier operators by quadratic terms. The result is a simplification of the reduced Hamiltonian corresponding to noninteracting electrons with spin-dependent energies. Thus, many-electron effects are not present, but the scheme can serve as a first-principles derivation of spin-split bands, alternative to the LEA.

At the end of the paper, a different simplification of the reduced Hamiltonian is given. The parameters U, I, J_{dh}, and W are set to zero and spin waves are found from the Heisenberg Hamiltonian and the simple hopping terms. However, the dropping of U prevents the spin-wave energies from having the correct dependence on the hopping effects (second order in λ terms in the present study).

B. Chen and Bailyn

Nearest to the special case of the model considered in Secs. V to VIII is the one-band model of Chen and Bailyn.[25] A one-dimensional lattice has a half-filled band; the electrons interact via nearest-neighbor two-site Wannier integrals. Their model is identical to the special case of this study if the latter is specialized to one dimension and if only nearest-neighbor interactions are included for all energy parameters.

Analytic results are found for the spin-wave energies when I, J_{dh}, and $J'\equiv W-(\frac{1}{2}J)$ all vanish and with the additional assumption $U>>|T|$ and $U>>J$ [see their Eq. (5.10)]. Their results are similar to Eqs. (5.59) and (6.4) of the present study, when the latter results are applied to their conditions. An exact correspondence with their results is obtained if the modification in the perturbation theory discussed after Eq. (5.54) is used.

Chen and Bailyn also obtain numerical results for the spin-wave energies for nonzero I, J_{dh}, and J. The double-hop processes increase the energy (their Fig. 12) in harmony with the analytic result Eq. (6.6). Single hops due to Coulomb repulsion decrease the energy (their Fig. 13), agreeing with Eq. (6.4). The energies increase with W in their numerical results (Fig. 11), which is consistent with Eq. (6.4) of the present work.

For the ionic states, they find simple symmetric and antisymmetric combinations of electron-hole states whose translation vectors differ in sign. This agrees with the short-range interaction result of Sec. VIII D. They find that J_{dh} serves to split the energies of the symmetric and antisymmetric states, agreeing with the explicit analytic results in Eqs. (8.5), (8.6), and (8.7) of the present study. In addition, the latter equations show that longer-range effects of the Coulomb single hops [characterized by $I(2\vec{h})$] also contribute to the splitting.

In a later paper, Chen and Bailyn[26] generalize their work to include long-range interactions, with I and J_{dh} set to zero. Some of the new features found parallel the results in the present paper, such as the existence of a set of discrete exciton levels above the ground exciton level.

C. Paul

Prior to the work of Chen and Bailyn, Paul[27] had considered the same one-dimensional model and had obtained some results similar to theirs. He also obtains some general results for arbitrary number of reversed spins.

For one reversed spin, his difference equations [Eq. (13)] are equivalent to Eq. (5.8) if the latter is applied to one dimension. His result for the spin-wave energy [Eq. (32)] is similar to Eq. (7.1).

X. CONCLUSION

A model Hamiltonian [Eq. (2.26)] has been derived that contains all two-site interactions arising from the Coulomb repulsion between electron pairs; it generalizes many earlier models in the inclusion of intra-atomic exchange. The parameters of the model are expressed as matrix elements of spin-split band states derived from the LEA, enabling inequalities between parameters to be found, as listed in Sec. IV.

A special case of the model (half-filled single band) is considered. Consistent with the inequalities, it is shown in Secs. V–VIII that finding the elementary excitations can be reduced to Rayleigh-Schrödinger perturbation theory. The perturbation parameter λ is proportional to the strength of the exchange and/or hopping parameters.

Explicit analytic results are obtained for the spin-wave energies (up to third order) and the ionic-state or exciton energies (up to second order) in Secs. VII and VIII. These results generalize those of other studies (Sec. IX) to three dimensions and long-range interactions. Analytic results of this study complement numerical results of Chen and Bailyn[24] when the former are applied to one dimension.

To complete the bridge connecting the model Hamiltonian approach to LEA band theory, work is necessary in two directions:

(i) Special cases of the model such as that examined in Secs. V–VIII need to include intra-atomic exchange and arbitrary filling of the band.

(ii) The optimum choice for the local self-consistent potential [Eq. (2.11)] needs to be considered such that the 3-center and 4-center terms [Eq. (2.25)] and the terms of higher order in λ have the smallest possible effect for the property to be calculated.

APPENDIX

It is desired to verify the statement made at the end of Sec. III C concerning two integrals that differ only in that a spin index in a wave function of one differs from the spin index in the corresponding wave function of the other.

To show that the order of overlap of the difference is one order higher than that of the integrals themselves, it is sufficient to cite an example. Consider

$$P(fg) \equiv W(f\uparrow;g\uparrow) - W(f\uparrow;g\downarrow) \ . \tag{A1}$$

Each term on the right-hand side is first order in the overlap.

The set of *spatial* wave functions $\psi_{d\sigma}(\vec{r})$, (with the center index d varying) forms a complete set of spatial functions for either choice of the spin σ.

The spatial function $\psi_{f\downarrow}(\vec{r})$ can then be expanded in the set of states $\psi_{d\uparrow}(\vec{r})$. Letting b_d denote the expansion coefficients, one can write

$$\psi_{f\downarrow}(\vec{r}) = \sum_d b_d \psi_{d\uparrow}(\vec{r}) \ . \tag{A2}$$

While b_f is zero order in the overlap, all the other b_d are first order. Insertation of Eq. (A2) into Eq. (A1) readily yields the result that $P(fg)$ is second order.

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