Impurity-induced magnetic coupling in narrow band semiconductors

D. Hone, P. Lederer, M. Heritier

IMPURITY-INDUCED MAGNETIC COUPLING IN NARROW BAND SEMICONDUCTORS

D. HONE (*) (**), P. LEDERER and M. HÉRITIER

Laboratoire de Physique des Solides (***), Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France

Résumé. — Nous étudions les propriétés électroniques de semi-conducteurs dopés à bande étroite. Nous utilisons le modèle de Hubbard pour une bande à moitié remplie dans la limite des corrélations fortes. Nous examinons de quelle façon la self-énergie de l'impureté dépend de la configuration magnétique de l'hôte.

Nous trouvons comment varie le couplage ferromagnétique induit par l'état lié en fonction de l'énergie de l'état lié et de la distance à l'impureté. La possibilité d'appliquer les méthodes mathématiques que nous avons utilisées à des problèmes d'interaction entre impuretés et lacunes dans des semi-conducteurs conventionnels est discutée dans l'appendice.

Abstract. — We consider the electronic properties of impure narrow band magnetic semiconductors, using the Hubbard model for nearly half filled bands in the strong correlation limit. We examine the dependence of the impurity self-energy on the magnetic configuration of the host.

We find the energy and range dependence of the ferromagnetic coupling induced by the impurity bound state. The results are related to experiments in Ca doped $LaMnO_3$ and In doped $CdCr_2Se_4$. The relevance of the mathematical methods we use to problems dealing with vacancy impurity interactions in conventional semiconductors is discussed in the Appendix.

1. Introduction. — The physical properties of a number of magnetic semiconductors depend rather sensitively on the presence of a small concentration of specific impurities. For example, $CdCr_2 Se_4$ doped with In exhibits a sort of metal insulator transition [1]. $LaMnO_3$ is an antiferromagnetic insulator, which becomes ferromagnetic and metallic when doped with Ca [2]. A number of other doped magnetic semiconductors exhibit large variations of the extrinsic activation energies below and above the magnetic transition temperature [3]. In those systems it is essential to take into account the electronic structure of the 3-d band, since the impurities introduce extra-particles (or holes) which propagate in those bands [3]. Coulomb correlations play a central role in determining the magnetic and transport properties in such narrow band systems. In fact the intra atomic correlation energies are large compared to the bandwidth. Thus we must study the strongly interacting electron gas in order to understand the properties of the

compounds mentioned above. The effect of a point scattering potential on the electronic structure of a nearly half filled narrow energy-band has been investigated in the limit of infinite intra atomic Coulomb repulsion [4]. This model exhibits the main electronic features of a magnetic insulator, although it neglects orbital degeneracy and superexchange effects which lead to a magnetic coupling between spins. It was found that the potential needed to localize a state depends on the spin configuration. Thus, by varying the spin configuration, one may pass from localized to extended states; the magnetic and transport properties are intimately connected. Furthermore a localized hole was shown to stabilize a ferromagnetic polarization within a few atomic distances from the impurity. The strength of this coupling, as well as its dependence on distance were evaluated in a rough way [4].

In the present paper, we present a more detailed study of this coupling effect, although again in an approximate fashion. We give an upper limit for the strength of the coupling, and we present arguments to show that the range of the coupling becomes large when the bound state energy approaches the edge of the band. For simplicity the main calculation is

restricted to a square two dimensional lattice; it is clear that the results are qualitatively valid for a three dimensional lattice. Our work provides better theoretical tools to understand and to study doped magnetic semiconductors; also it is an example of calculations where the use of generating functions, as explained below, is seen to be helpful in a perturbation method in a discrete lattice. For instance our calculation applies to the problem of impurity activation energies in a conventional semiconductor in the presence of vacancies. The reason is that in this problem too, it is crucial to evaluate the number of paths starting from a point in the lattice, (i.e. the impurity center) passing through another point in the lattice (i.e. the vacancy site) which return to the origin for the first time (see Appendix).

An interesting implication is that the experimental evidence obtained from the study of vacancy impurity interaction in a conventional semiconductor should be correlated with the magnetic coupling we study in magnetic semiconductors in the same crystal structure. The present state of the art (in particular the fact that we are limited to two dimensional lattices for our present calculation) does not allow us any quantitative estimate at this stage. However it will be useful to do this in the future.

In section 2 we describe the model and recall earlier results abouth the single impurity problem. In section 3 we discuss the technique used for our calculation, which is outlined in details in Appendix I. Section 4 is a physical discussion of our results. The application to the problem of vacancy-impurity interaction in a conventionnal semi-conductor is discussed in Appendix II.

2. **The model.** — The model is that of a nearly half filled tightly bound s-band, with infinite intra atomic Coulomb repulsion between electrons of opposite spins. Thus we have almost one electron per atom, occupying unfilled atomic shells, with wave functions which overlap those on neighbouring sites.

The Hamiltonian is

$$\mathcal{H} = P \left\{ t_0(n_{0\uparrow} + n_{0\downarrow} - 1) + t \sum_{ij} c_{i\sigma}^+ c_{j\sigma} \right\} P \quad (1)$$

where t_0 is the impurity potential, t is the transfer energy between sites. $n_{0\sigma} \equiv c_{0\sigma}^+ c_{0\sigma} \cdot c_{i\sigma}^+$ is a creation operator for an electron of spin σ on site i. P projects on the subspace of wave functions

$$\varphi_{i\alpha_i} = (-1)^i c_{1\sigma_1}^+ c_{2\sigma_2}^+ \ldots c_{i-1\sigma_{i-1}}^+ \times$$

$$\times \; c_{i+1\sigma_{i+1}}^+ \ldots c_{N\sigma_N}^+ \mid 0 \rangle \quad (2)$$

where $\mid 0 \rangle$ is the vacuum and α_i denotes the spin configuration $\sigma_1, \sigma_2, \ldots, \sigma_N$. Transitions between these states are conveniently regarded in terms of motion on a superlattice labelled by the indices (i, α_i).

In order to find the energy levels of this Hamiltonian, we study the Green's function

$$G_{ij}^{\alpha_i \beta_j}(\omega) \equiv (j\beta_j \mid i\alpha_i)_\omega \equiv \left\langle \varphi_{j\beta_j} \left| \frac{1}{\omega - \mathcal{H}} \right| \varphi_{i\alpha_i} \right\rangle \quad (3)$$

where ω is a complex number in general. The poles of

$$G_i^{\alpha_i}(\omega) \equiv (i\alpha_i \mid i\alpha_i)_\omega$$

lie on the real axis and give the energy eigenvalues of the states ' with

$$S > \frac{\mid N_\uparrow - N_\downarrow \mid}{2} .$$

Using the identity

$$\frac{1}{\omega - \mathcal{H}} = \frac{1}{\omega} + \frac{1}{\omega} \mathcal{H} \frac{1}{\omega - \mathcal{H}} .$$

We can derive an expression for $G_{ij}^{\alpha_i \beta_j}(\omega)$,

$$\omega G_{ij}^{\alpha_i \beta_j}(\omega) = \delta_{ij} \, \delta_{\alpha_i \beta_j} + \left\langle \varphi_{j\beta_j} \mid \mathcal{H}(\omega - \mathcal{H})^{-1} \mid \varphi_{i\alpha_i} \right\rangle$$

whence

$$G_0^{\alpha_0}(\omega)^{-1} \cong \omega + t_0 - \Sigma_0^{\alpha_0}(\omega) \quad (4)$$

with

$$\Sigma_0^{\alpha_0}(\omega) = \omega \sum_{p=2}^{\infty} \left(\frac{A_p^{\alpha_0}}{z^p} \right) \left(\frac{-zt}{\omega} \right)^p$$

where z is the coordination number.

$A_p^{\alpha_0}$ is the number of paths in which a particle starts from $(0 \; \alpha_0)$ in the superlattice and comes back to the same site after p nearest neighbour steps without passing $(0 \; \alpha_0)$ on the way.

It was shown in reference [4] that the lowest energy pole (i.e., the lower limit of the branch cut in the thermodynamic limit : $N \to \infty$) in $G_0^{\alpha_0}(\omega)$ is obtained when the spin configuration is ferromagnetic, a generalization of a theorem due to Nagaoka [5]. In the ferromagnetic configuration, all paths returning to the origin restore the spin configuration; on the contrary when the spin configuration is not completely ferromagnetic, a number of paths which contributed to the self-energy in the ferromagnetic state no longer do so. Such is the case for closed loops which do not leave the spin configuration unchanged (Fig. 1). On the other hand paths which are completely retraceable leave the spin configuration unchanged in all cases. In fact the single particle density of states in the antiferromagnetic (AF) configuration can be obtained in an approximate fashion by retaining only Retraceable Paths in the calculation of the Green's function [6].

Suppose one studies the change in the bound state energy when one flips a spin nearest neighbour to the impurity in an otherwise completely ferromagnetic configuration. If the bound state lies deep below the
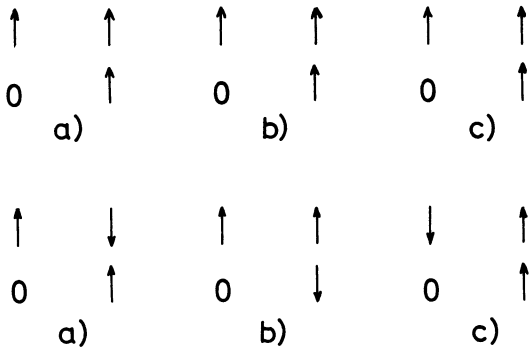
FIG. 1. — Upper row : spin configuration a) is left unchanged by moving the hole once b) or twice c) around the smallest closed loop. Lower row : spin configuration a) is altered by moving the hole once b) on twice c) around the loop. It is restored by moving it a third time.

band edge, the factor $(- zt/\omega)$ in the series of eq. (4) is small and it is a good approximation to retain only , the lowest order terms in the change of the self-energy. The leading term correspond to the smallest suppressed closed loop as shown on figure 1. Thus the approximate change in the bound state energy from its value for the fully ferromagnetic state to the value with one spin flip at a site nearest neighbour to the origin is of the order of

$$\delta E_{\mathrm{B}} \simeq \frac{8\,t}{z^3}\left|\frac{zt}{E_{\mathrm{B}}^{\mathrm{F}}}\right|^3\left(1 + 0\left(\frac{zt}{E_{\mathrm{B}}^{\mathrm{F}}}\right)^2\right). \qquad (5)$$

Similarly when the flipped spin is at a distance $R = la_0$ from the impurity site.

$$\delta E_{\mathrm{B}} = E_{\mathrm{B}}\,z^{-2\left(\frac{R}{a_0}+1\right)}\left(\frac{-zt}{E_{\mathrm{B}}}\right)^{+2\left(\frac{R}{a_0}+1\right)} \simeq$$

$$\simeq E_{\mathrm{B}}\exp\left[-2\frac{R}{a_0}\left(\ln z + \ln\frac{zt}{E_{\mathrm{B}}}\right)\right]. \qquad (5')$$

Expression (5) is equivalent to a ferromagnetic coupling between spins nearest neighbour to the impurity. This effect is largest when the bound hole sits nearest to the band edge. In that case, one must carefully evaluate all suppressed closed loops, since the correcting terms are all of comparable magnitude when $zt/E_{\mathrm{B}}^{\mathrm{F}} \sim 1$. Such an evaluation is complicated. In the following we describe an approximate method to deal with the path problem when the bound state sits initially near the band edge.

3. **Approximate method.** — As was done previously we shall consider the change in the bound state energy compared to the completely ferromagnetic configuration when a spin is flipped at a distance $R = la_0$ from the impurity center.

The equation for the bound state energy in the completely ferromagnetic configuration is

$$E_{\mathrm{B}}^0 = t_0 + E_{\mathrm{B}}^0\sum_{p=2}^{\infty} A_p^0\left(\frac{t}{E_{\mathrm{B}}^0}\right)^p. \qquad (6)$$

The equation for the bound state when one spin is flipped a distance R away from the impurity center is

$$E_{\mathrm{B}} = -t_0 + E_{\mathrm{B}}\sum_{p,i} A_p^{(i)}\left(\frac{t}{E_{\mathrm{B}}}\right)^{p-i}\left(\frac{t}{E_{\mathrm{B}}+t_0}\right)^i \qquad (7)$$

In eq. (7) the superscript i is the number of times a path of p steps passes at the impurity site without restoring the initial spin configuration, before it returns to the original superlattice site.

It is essential to notice that eq. (7) has E_{B}^0 as its lowest root. The reason is simply that the spin configuration $|\,\mathrm{s.f.R.}\,\rangle$ obtained by flipping one spin a distance R away from the impurity center in an otherwise ferromagnetic configuration has a small overlap, of order $1/\sqrt{N}$, with the state

$$|\,s = s_T, s_z = s_T - 1\,\rangle$$

which we know has the eigenvalue E_{B}^0.

Compared to the ferromagnetic A_p^0, the new numbers $A_p^{(i)}$ may be smaller when $i = 0$, corresponding then to suppressed loops of order p, or larger when $i \neq 0$, corresponding then to *added* loops ; let us separate out the negative parts δA_p and the positive one $A_p^{(i)}$ $(i \neq 0)$. We can then write an identity relating those two parts by using the fact that E_{B} is a root of eq. (7)

$$E_{\mathrm{B}}^0 = -t_0 + E_{\mathrm{B}}^0\sum_{p}(A_p^0 - \delta A_p)\left(\frac{t}{E_{\mathrm{B}}^0}\right)^p +$$

$$+ E_{\mathrm{B}}^0\sum_{p,i\neq 0} A_p^{(i)}\left(\frac{t}{E_{\mathrm{B}}^0}\right)^{p-i}\left(\frac{t}{E_{\mathrm{B}}^0+t_0}\right)^i. \qquad (8)$$

Substracting out eq. (6) we obtain the identity

$$\sum_{p}\delta A_p\left(\frac{t}{E_p^0}\right)^p = \sum_{p,i\neq 0} A_p^{(i)}\left(\frac{t}{E_p^0}\right)^{p-i}\left(\frac{t}{E_{\mathrm{B}}^0+t_0}\right)^i.$$

Thus the effect of added paths passing out the impurity site is to cancel out the effect of suppressed loops in the trivial case of a rotation of the total spin of the system away from the z axis.

We are interested in evaluating the *change* in bound state energy when the total spin of the system is effectively lowered. From what we know in the pure magnetic insulator problem [6]. the main effect of spin disorder is the suppression of closed loops compared to the ferromagnetic case. In fact, for the Antiferromagnetic configuration, the approximation which consists in neglecting all closed loops (the Retraceable Path Approximation) has been shown to be relatively correct by comparing it with a moment calculation based on the first 12 moments [6].

In the following parts, we shall assume that the essential effect of the flipped spin is to suppress closed loops which were present in the Ferromagnetic configuration. We neglect all added loops, thereby finding an upper limit for the energy change of the

bound state. Thus the approximate equation for the bound state when one spin is flipped a distance R away from the impurity center is

$$E_B = - t_0 + E_B \sum_{p=i}^{\infty} (A_p^0 - \delta A_p) \left(\frac{t}{E_B}\right)^p . \quad (8')$$

Thus, writing $E_B = E_B^0 + \delta E_B$, we obtain by substracting (8') from (8)

$$\delta E_B = \frac{E_B^0 \sum_p \delta A_p \left(\frac{-t}{E_B^0}\right)^p}{- \dfrac{t_0}{E_B^0} + \dfrac{\partial}{\partial \omega} \left(\sum_p A_p^0 \left(-\dfrac{t}{\omega}\right)^p\right)\Big|_{\omega = E_B}} \quad (9)$$

where $\delta A_p = A_p - A_p^0$.

We can express eq. (9) in a different way by using the familiar Slater Koster expression for the Green's function of the impurity problem [4]

$$1 + \frac{\partial}{\partial \omega} \left(\sum_p A_p^0 \left(-\frac{t}{\omega}\right)^p\right)\Big|_{\omega = E_B^0} \equiv - \frac{\partial F_0(\omega)/\partial \omega}{F_0^2(\omega)} \quad (10)$$

with

$$F_0(\omega) = \frac{1}{N} \sum_k 1/(\omega - \varepsilon_k)$$

where ε_k is the dispersion relation corresponding to the transfer integral t in a given lattice. Putting eq. (10) into (9) we obtain

$$\delta E_B = - \frac{E_B^0 \sum_p \delta A_p (- t/E_B^0)^p}{1 + \dfrac{t_0}{E_B^0} + \left(\dfrac{\partial}{\partial \omega} F_0(\omega)/F_0^2(\omega)\right)\Big|_{\omega = E_B^0}} . \quad (11)$$

Eq. (11) is the basis of our calculation for E_B. The denominator in (11) depends only on the energy once the crystal structure is known. On the contrary, in the numerator, the variation in the number A_p of closed loops of given length pa_0 depends on distance as well as on energy. In particular $\delta A_p = 0$ for $p < (2 l + 2)$ since the smallest closed loop passing through the site of the flipped spin has $(2 l + 2)$ steps. There are $(z - 2)(l - 1)$ loops of this size, where z is the coordination number of the lattice (number of nearest neighbours to a given site) giving a contribution to the numerator of eq. (11) of

$$(z - 2)(l - 1) E_B^0 \, e^{-(2l + 2)\ln(-E_B^0/t)} . \quad (12)$$

Thus the coupling decreases essentially exponentially with distance l in this approximation. This result was obtained in reference (4).

In the following part of this section we examine to what extent higher order corrections modify either the amplitude of the exponential, or, more impor-

tantly, the rate of exponential decay. We will examine various approximations for corrections to eq. (12). Eventually we will use a formulation in terms of generating functions [7] which has the drawback of mathematical complexity, but the advantage of being fairly general for problems connected with path-counting in a lattice.

We can consider first additionnal loops which manifestly result in a spin configuration different from the original one. These form a subset of the (positive definite) contributions to the sum over p in eq. (11) and provide, therefore, a lower limit to the correction. For example one can include all paths of the type shown in figure 2b by renormalizing each step of the path in figure 2a as shown in figure 2c. The result is to multiply E_B^0/t in the exponent of eq. (10) by a factor $(1 - (t/E_B^0)^2)$, which increases the range only by a small amount even for $E_B^0 \cong - zt$. The source of more important corrections is suggested by considering the renormalization of each vertex in the above paths by including the set of all completely retraceable excursions from the vertex, which return to that vertex for the first time at the final step (see Fig. 2d). The effect is simply to replace E_B^0 by $E_B^0 - \Sigma^R(E_B^0)$ in eq. (10), where

$$\Sigma^R(\omega) = \frac{z\omega}{2(z - 1)} \left(1 - \left(1 - \frac{4(z - 1) \, t^2}{\omega^2}\right)^{1/2}\right) .$$

The superscript R on $\Sigma^R(\omega)$, denotes the inclusion of retraceable paths only [4, 6]. This does modify the range of the exponential in eq. (10), but since the solutions of $\omega - \Sigma^R(\omega) = 0$ extend over a narrower band than the ferromagnetic one, $- zt < \omega < zt$, there are no dramatic changes even when $E_B^0 \to - zt$. On the other hand we know that the inclusion of closed loops in vertex renormalization (see Fig. 2e) replace ω by $\omega - \Sigma^F(\omega)$. Furthermore we have for the bound state energy the equation

$$E_B^0 + t_0 - \Sigma^F(E_B^0) = 0$$

so that the exponential in eq. (10) becomes

$$\exp(- 2 l + 2) \ln | t_0/t |$$

which modifies significantly the range of the coupling since $t_0 < zt$. (In three dimensions $t_0 = 0.65 \ zt$.) This reflects the fact that the wave functions become extended rather than localized at the band edge. This discussion shows that the renormalization of the coupling can be significantly altered by the inclusion of a number of paths generated from the smallest suppressed closed loop. However the class of paths we considered above is clearly too restrictive. In the following we consider a scheme based on generating functions which provides an upper limit to the energy correction. Clearly all suppressed paths must pass through this position (which return to the origin only at the last step) then we include some which restore the initial spin configuration. However we
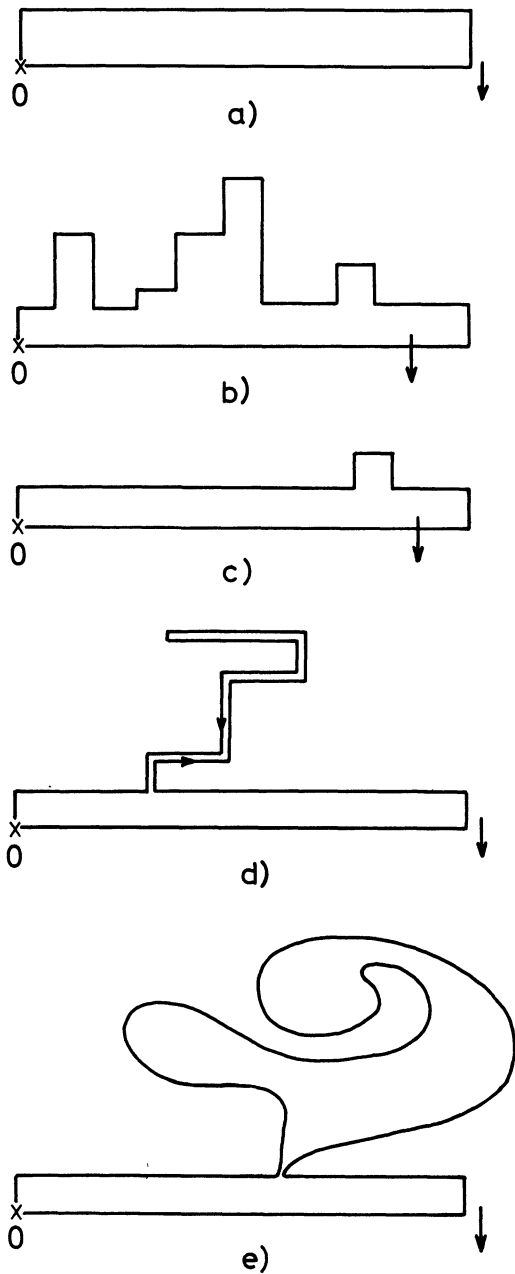
FIG. 2. — a) Smallest suppressed closed loop associated with the flipped spin (indicated by ↓) a distance R away from impurity site at 0. b) Example of a class of suppressed loops. c) Elementary line decoration of the loop shown on figure 2a. Iteration of this along the path yields the class of corrections indicated in b). d) Typical vertex decoration with Retraceable Paths only. e) Typical vertex decoration including closed loops.

argue that these constitute only some small fraction of the total, particularly when the flipped spin is relatively far from the origin, so that we expect this technique to give a reasonable estimate of δE_B.

Generating function technique. — Let us define the generating function [7] for a class of paths as

$$R(z) = \sum_p A_p z^p$$

where A_p is the number of paths of p steps for an element of the class. In order to compute the renor-

malization in an exact fashion, one would have to find the generating function [7] $T_t(z)$ for paths which leave the origin, pass the flipped spin any number of times and return to the origin once without restoring the initial spin configuration. One would then have to substract from $T_t(z)$ the generating function for paths which pass the flipped spin and the origin more than once and restore the spin configuration after a number of travels through the origin. Such paths are added to the self energy when the spin is flipped. We have solved this problem approximately in the following way : first we evaluate the generating function $R_{0t}(z)$ for paths which go from the origin to the flipped spin, then find the generating function for a first return to the origin. This procedure certainly yields an upper limit for the generating functions, since it includes a number of paths which should be left out : for instance paths such that the last steps to the flipped spin are retraced ; such paths leave the spin configuration unchanged. Similarly some paths pass the flipped spin a sufficient number of time to restore the spin configuration before returning to the origin (Fig. 3).
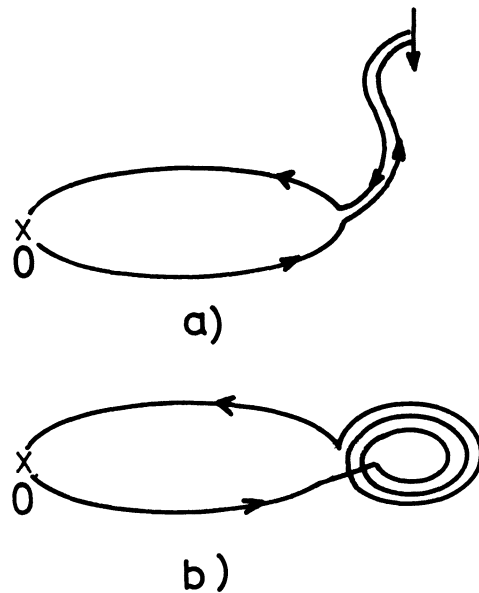

FIG. 3. — Example of paths which should be omitted because they restore the initial spin configuration. a) The last steps before the flipped spin are retraced. b) The multiple loop passing the flipped spin site restores the spin configuration.

Consider a simple cubic crystal. The dispersion relation in the tight binding approximation is

$$\varepsilon_k = 2\ t(\cos k_x\ a_0 + \cos k_y\ a_0 + \cos k_z\ a_0)\ .$$

The desired generating function is directly related to the well-studied Green's function [11] :

$$G_{lmn}(\omega) = \sum_q \frac{e^{iq_0 \cdot r_{lmn}}}{\omega - \varepsilon(q)}\ . \tag{13}$$

This corresponds to the Green's function of the unperturbed problem when the spin configuration is ferromagnetic

$$= \frac{1}{\omega} \sum_{\mathbf{q}} \frac{e^{i\mathbf{q}_0 \mathbf{r}_{lmn}}}{1 - 2\,y(\cos q_x\,a_0 + \cos q_y\,a_0 + \cos q_z\,a_0)}$$

where (lmn) is a lattice point and

$$y = \frac{t}{\omega}.$$

The bandedge defines

$$y_B = \frac{t}{\omega_B} = \frac{1}{6}$$

$$\omega_B = 6\,t.$$

When ω is outside the band of width $12\,t$, $G_{lmn}(\omega)$ is purely real and we can expand the denominator so that

$$G_{lmn}(\omega) = \frac{1}{\omega} \sum_{\mathbf{q}p} y^p\,e^{i\mathbf{q}_0 \mathbf{r}_{lmn}}(e^{iq_x a_0} + e^{-iq_x a_0} +$$

$$+ e^{iq_y a_0} + e^{-iq_y a_0} + e^{iq_z a_0} + e^{-iq_z a_0}).\quad (14)$$

Any term resulting form expanding the bracket on right hand side of this equation can be cast in the form $e^{i\mathbf{q}\cdot\mathbf{R}(p)}$ where $\mathbf{R}(p)$ is a vector joining the origin to some point in the lattice which can be reached in p steps. $e^{\pm iq_x a_0}$ corresponds to a step in the positive (negative) x direction, $e^{\pm iq_y a_0}$ corresponds to a step in the positive (negative) y direction, etc... Therefore one can write, when $(l, m, n) \ne (0, 0, 0)$

$$G_{lmn}(\omega) = \frac{1}{\omega} \sum_p C_p(lmn)\,y^p \quad (15)$$

where $C_p(lmn)$ is the number of ways of going from the origin $(0, 0, 0)$ to (l, m, n) in p steps [11], without restrictions, i.e. it may include paths with many returns to the origin or many passages through the final site.

In Appendix I, we derive an expression for the generating function $T_1(z)$ in terms of the Green's function $G_{lmn}(\omega)$ (eq. (15)). In Appendix II we transform $G_{lmn}(\omega)$ to express it in terms of special functions, which yield analytic expressions in the two simple limits : a) bound state very near the band edge, i.e. shallow hole limit, or b) deep bound state, or deep hole limit. Unfortunately we have not been able to find analytic expressions for the shallow hole case in three dimensions. Although the procedure we use is independant of the dimension of the lattice, the explicit result we exhibit below is quantitatively valid for dimension two only. We expect it to be qualitatively valid for three dimensions.

4. Results and discussion. — 4.1 DEEP HOLE LIMIT.
— In this limit the bound hole energy is low compared to the band edge :

$$| E_B^0/zt | \gg 1.$$

Then we expect perturbations expansions to converge well, and renormalization effects to vanish; indeed, as shown in Appendix I, one finds back the results of reference [4].

4.2 SHALLOW HOLE LIMIT. — In this limit, the bound hole energy becomes nearly equal to the band edge energie, i.e.

$$E_B^0 = -4\,t(1 + \varepsilon) \quad \text{with} \quad \varepsilon \ll 1$$

(as stated above explicit results are obtained for a two-dimensional (square) lattice.) When $\varepsilon \to 0$, the bound state merges into the band and becomes infinitely extended; its radius varies like $(1/\varepsilon)^{1/2}$. At the same time the bound state amplitude goes to zero on each site as its spatial extent becomes infinite. One finds

$$\delta E_B = 4\,zt\left(\frac{\varepsilon}{\ln \varepsilon}\right)\left(1 - \frac{1}{z}\right)^2 (ln(1/l\sqrt{2\,\varepsilon}) - \gamma)^2 \times$$

$$\times \exp - 20\,l^2\,\varepsilon \quad (16)$$

where γ is Euler's constant.
This expression exhibits two interesting properties of the coupling :

a) As the bound state moves near the band edge, the amplitude of the coupling decreases, irrespective of the distance, as $\varepsilon/(\ln \varepsilon)$. This is due to the decrease of the bound state amplitude per site as its spatial extent grows. In other words, since the bound state spreads over a larger and larger volume, local perturbations are less and less effective to change its energy.

b) The range of the coupling increases as $1/\sqrt{20\,\varepsilon}$, i.e. proportional to the inverse square root of the activation energy. This, again, reflects the growing spatial extent of the bound state as it moves near the band edge. Expression (31) also indicates the presence of a logarithmic term $\ln^2 4/l\eta$ which is related to the range of the coupling.
We have no indication for δE_B when $l\sqrt{\varepsilon} > 1$ so that the gaussian behaviour in expression (16) is only interesting in so far as it allows a comparison with the exponential behaviour in eq. (5'). Eq. (16) exhibits the important effect of the renormalization of the paths : not only does it alter the amplitude of the coupling in a significant way; it changes also the exponential behaviour to a gaussian one, at least for $l\sqrt{8\,\varepsilon} < 1$.

— Angular dependence of the coupling. — We can easily find the angular dependence of the coupling by considering a spin tilted at an angle θ from the z axis and asking what the average energy of that

state is compared with the ferromagnetic state. Supposing we know the ground state wave function for the completely ferromagnetic case $\varphi_F \mid F \rangle$ and the ground state wave function for the state

$$\mid S_T = S_{max} - 1, S_{ZT} = S_{max} - 1 \rangle \,,$$

i.e. $\psi_{sf} \mid R \rangle$ we can write the wave function describing a state with a spin tilted at angle θ :

$$\mid \psi(\theta) \rangle = \cos \frac{\theta}{2} \psi_F \mid F \rangle + \sin \frac{\theta}{2} \psi_{sf} \mid R \rangle \,.$$

Then the average energy of that state, compared with the ferromagnetic ground state, is

$$\delta E_B(\theta) = \delta E_B \sin^2 \frac{\theta}{2} = \delta E_B \frac{(1 - \cos \theta)}{2} \,.$$

5. **Discussion.** — We believe that our results may help to understand the interesting situation which arises in Ca doped $LaMnO_3$. Matsumoto [2] has observed that in this compound, which is antiferromagnetic at low concentrations of Ca, there seem to arise ferromagnetic clusters (magnetic polarons) around the Ca impurities. At first those clusters are uncoupled and the material exhibits no net magnetization in zero field. At a concentration $C_0 > 0.1$, the material becomes ferromagnetic, as if a percolation limit had been reached, allowing all clusters to form a macroscopic ordered ferromagnetic state. For the critical concentration C_0, the size of the clusters may be estimated to be about two lattice spacings. It must be remembered that our model is too crude to account for a macroscopically ordered ferromagnetic state, since Izuyama's theorems [12] apply irrespective of the number of impurity centers, i.e. the ferromagnetic state for our Hamiltonian has zero exchange stiffness coefficient. Therefore in $LaMnO_3$ doped with Ca, additional mechanisms not contained in our model must be invoked to account for the stabilization of the ferromagnetic state for $C > C_0$. However we do account for the formation of ferromagnetic clusters around impurities. It has been argued [2] that this could also be interpreted as a double exchange mechanism, the mobile hole favouring ferromagnetic alignment of spins at sites where it has a finite amplitude. At present we cannot rule out this explanation. However there is no doubt that the kinetic polaron effect we invoke is present too, with sizeable interaction strength. It is quite possible that both effects coexist there, the double exchange mechanism accounting for the long range ferromagnetic order for $C > C_0$. The situation is somewhat different in $CdCr_2Se_4$ [1] doped with In. This compounds is a paramagnetic insulator above $T_c = 77$ K. The impurity activation energy is $E_B \sim 0.2$ eV for $T > T_c$. Below T_c, In doped $CdCr_2Se_4$ is ferromagnetic, and the activation energy drops to zero, so that the conductivity becomes metallic. The interpretation [3] relies on the theory

of impurity states in Mott insulators given in reference [4] : the band edge moves towards the impurity energy level. With decreasing temperature, eventually absorbing the level somewhere below the ferromagnetic ordering temperature. In this interpretation, the ferromagnetic transition is driven by some exchange field which is not taken explicitly into account in the theory of the electronic structure. Our theory predicts that an additional ferromagnetic coupling is operative in the neighbourhood of In impurities, with a range which becomes infinite when the impurity level collapses into the band. Experiments investigating the neighbourhood of In impurities in $CdCr_2Se_4$ would help in checking the validity of our analysis.

APPENDIX I

Let us define

$$R_{01}(y) = \sum_p C_p(1) \, y^p \,.$$

Then define iR_{01} as the generating function for paths going from 0 to 1 without passing i on the way. Similarly $_{ij}R_{01}$ is the generating function for paths going form 0 to 1 without passing i and j on the way.

Then it is clear that

$$R_{01} = (1 + R_{00})_0 \, R_{01} \,. \qquad (A.1)$$

This equation simply expresses the fact that the most general path from 0 to 1 is the sum of paths going from 0 to 1 without passing the origin on the way, plus all paths going through the origin any number of times.

We are going to compute the upper limit for δE_B by summing all paths from the origin to the flipped spin and back again without going to the origin in the middle. This is an upper limit since it includes paths which do not change the spin configuration : for instance paths which pass many times through the flipped spin and manage to restore the spin configuration in the end. Or paths such that the last step to the flipped spin is immediately retraced.

In order to find the generating function corresponding to this upper limit, we must find the generating function $_{01}R_{10}$.

Now, obviously

$$_{01}R_{10}(_0R_{11} + 1) = _0R_{10} \equiv _0R_{01} = \frac{R_{01}}{R_{00} + 1} \,. \qquad (A.2)$$

Furthermore

$$R_{11} = (R_{10}) (_0R_{01}) + _0R_{11}$$

so that

$$_0 R_{ll} = R_{00} - (R_{l0})(_0 R_{0l}) = R_{00} - \frac{R_{ll}^2}{1 + R_{00}}.$$
(A.3)

Therefore

$$_{0l} R_{l0}(y) = \frac{R_{0l}(y)}{(1 + R_{00}(y))(_0 R_{ll}(y) + 1)} =$$

$$= \frac{R_{0l}}{(1 + R_{00})^2 - R_{l0}^2}.$$
(A.4)

The total generating function is

$$T(y) = (_0 R_{0l}(y))(_{0l} R_{l0}(y)) =$$

$$= \frac{R_{0l}^2(y)}{(1 + R_{00}(y))((1 + R_{00}(y))^2 - R_{0l}^2(y))}.$$
(A.5)

In order to improve on this evaluation, one should subtract all paths which do not change the spin configuration. An important class of such paths is represented in figure 3. The simplest to evaluate is the class of totally retraceable paths. The generating function for such paths is

$$_0 R_{0l}(y^2) = \frac{R_{0l}(y^2)}{1 + R_{00}(y^2)}.$$

One can approximate the contribution of all paths of the type shown in figure 3a by noting that the sum of all paths such that the last step to the flipped spin is retraced is of the order of

$$T(y) \times z \times (t/\omega)^2 = T(y) zy^2$$

in particular, when the bound state energy is near the band edge, $y \sim 1/z$, so that the total correction is

$$T(y)(1 - 1/z)$$
(A.6)

1. Calculation of the renormalized coupling. —
Let us now proceed to the actual calculation. Our aim is to evaluate the various elements in eq. (7) with the help of the generating function $T(y)$, suitably corrected by eq. (A.6).

In order to find $T(y)$, we shall first transform $G_{lmn}(y)$ to express it in terms of known functions, then study those expressions for appropriate limits, especially when the bound state energy is very close to the band edge.

Consider

$$G_{lmn}(y) = \frac{1}{2t} \int_{-\pi}^{+\pi} \frac{dq_x\, dq_y\, dq_z}{(2\pi)^3} \times$$

$$\times \frac{e^{i(q_x l + q_y m + q_z n)}}{\dfrac{1}{2y} - (\cos q_x + \cos q_y + \cos q_z)}$$

(we have set $a_0 = 1$) write

$$\frac{1}{2y - (\cos q_x + \cos q_y + \cos q_z)} = -i \int_0^\infty ds \times$$

$$\times \exp\left[is\left(\frac{1}{2y} - \cos q_x - \cos q_y - \cos q_z\right)\right]$$

$$\left(\text{Im } \frac{1}{2y} > 0\right).$$

Then

$$G_{lmn}(y) = -\frac{i}{2t} \int_0^\infty ds\, e^{is/2y} \int_{-\pi}^{\pi} \frac{dq_x}{2\pi} e^{i(lq_x - s \cos q_x)} \times$$

$$\times \int_{-\pi}^{+\pi} \frac{dq_y}{2\pi} e^{i(mq_y - s \cos q_y)} \int_{-\pi}^{+\pi} \frac{dq_z}{2\pi} e^{i(nq_z - s \cos q_z)}.$$

Now

$$J_l(s) = \frac{1}{2\pi} \int_\alpha^{2\pi + \alpha} d\theta \cos(l\theta - s \sin \theta)$$

$$= \frac{1}{2\pi} \int_{-\pi+\alpha}^{\pi+\alpha} d\theta \cos(l(\theta + \pi) + s \sin \theta) \quad \text{(any } \alpha\text{)}$$

where $J_l(s)$ is a Bessel function of order l. (See for example ref. [8].) We have

$$J_l(s) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} d\theta \cos(l\theta - s \sin \theta)$$

$$= \frac{1}{2\pi} \int_{-\pi}^{+\pi} d\theta\, e^{i(l\theta - s \sin \theta)}.$$

Since the integrand has periodicity 2π, we can write

$$\int_{-\pi}^{+\pi} \frac{dq}{2\pi} e^{i(lq - s \cos q)} = (-i)^l J_l(s)$$

whence

$$G_{lmn}(y) = \frac{(-i)^{l+m+n+1}}{2t} \int_0^\infty ds\, e^{is/2y} J_l(s) J_m(s) J_n(s)$$

In particular, if $1/2y \equiv i\zeta$ with $\zeta > 0$

$$G_{lmn}\left(-\frac{i}{2\zeta}\right) = \frac{(-i)^{l+m+n+1}}{2t} \times$$

$$\times \int_0^\infty ds\, e^{-\zeta s} J_l(s) J_m(s) J_n(s). \quad \text{(A.7)}$$

Eq. (A.7) is in general quite difficult to handle except numerically. However, it turns out to be enormously simplified, and to lead to tractable analytical expressions, in a two dimensional space. For that reason, the remainder of this paper applies strictly to a

2-dimensional problem. Let us recall that the problem is meaningless in one dimension, since all paths are then retraceable. The possibility of closed loops which do not restore the initial spin configuration arises in 2 as in 3 dimensions. The number of such paths of a given length increases, of course, from 2 to 3 dimensions. Qualitatively one expects at least equally strong influence of impurities (e.g., effective ferromagnetic coupling) in 3 dimensions as in 2.

In two dimensions, one can use the identity [8]

$$\int_0^\infty e^{-at} J_n^2(t)\, dt = \frac{1}{\pi} Q_{n-\frac{1}{2}}\left(\frac{a^2 + 2}{2}\right) \quad (A.8)$$

where $Q_{n-\frac{1}{2}}(x)$ is a Legendre polynomial of the 2nd kind

Thus

$$R_{01} = \frac{+1}{2y} \frac{1}{\pi} Q_{n-\frac{1}{2}}\left(\frac{\zeta^2 + 2}{2}\right). \quad (A.9)$$

Thus we are going to investigate the renormalized coupling for a flipped spin located at $\mathbf{R} = l a_0$ with $l_x^2 = l_y^2 = l^2$. It is quite obvious that the asymptotic results one obtains for this site are also valid for lattice sites such that

$$|R|^2 = (l_x^2 + l_y^2)\, a_0^2$$
$$= 2\, l^2\, a_0^2 \quad (A.10)$$

$$R_{01}\left(-\frac{i}{2\zeta}\right) = \sum_p \left(\frac{-i}{\zeta}\right)^p B(l, p)$$

$$= \sum_p \left(\frac{-i}{\zeta^2}\right)^p B(l, 2p)$$

since all possible paths have an even number of steps.

Now we need $\zeta = \frac{-i}{2y} + \eta$ with $\eta = 0^+$ to get $\sum_p y^{2p} B(l, 2p)$.

Thus we have

$$Q_{l-\frac{1}{2}}\left(\frac{\zeta^2 + 2}{2}\right) = Q_{l-\frac{1}{2}}\left(1 - \frac{1}{8\, y^2}\right).$$

Since we are dealing with bound states, we always have $y^2 = (t/E_B^0)^2 < (1/4)^2$. Thus the argument of $Q_{l-\frac{1}{2}}\left(1 - \frac{1}{8\, y^2}\right)$ is always smaller than or equal to -1.

In that range of values for the argument of $Q_{l-\frac{1}{2}}$, we can use the following expression [9]

$$Q_{l-\frac{1}{2}}(g) = \frac{1}{l!} \sqrt{\pi}\left(\Gamma\left(l + \frac{1}{2}\right)(g - \sqrt{g^2 - 1})^2\right)^{l+\frac{1}{2}} \times$$

$$\times F\left(\frac{1}{2}, l + \frac{1}{2}, l + 1, (g - \sqrt{g^2 - 1})^2\right) \quad (A.11)$$

where F is a hypergeometric function [9].

Then using the identity :

$$F\left(\frac{1}{2}; l + \frac{1}{2}; l + 1; (g - \sqrt{g^2 - 1})^2\right) =$$

$$= \frac{1}{\sqrt{1 - z}} F\left(\frac{1}{2}, \frac{1}{2}, l + 1; \frac{z}{z - 1}\right)$$

with $z = (g - \sqrt{g^2 - 1})^2$.

We have

$$Q_{l-\frac{1}{2}}(g) = \frac{\sqrt{\pi}}{l!\sqrt{2}} \Gamma\left(l + \frac{1}{2}\right) \frac{(g - \sqrt{g^2 - 1})^l}{\sqrt{2}(g^2 - 1)^{1/4}} \times$$

$$\times F\left(\frac{1}{2}, \frac{1}{2}; l + 1; \frac{\sqrt{(g^2 - 1)^2}}{2(g^2 - 1)^{1/2}}\right). \quad (A.12)$$

— Shallow hole-limit.

In this limit, the bound hole energy becomes nearly equal to the band edge energy i.e.

$$E_B^0 = -4\, t(1 + \varepsilon) \quad \text{with} \quad \varepsilon \ll 1.$$

In that case

$$g = \frac{1}{8}\left(\frac{E_B^0}{t}\right)^2 - 1 = 1 + 4\varepsilon + 2\varepsilon^2.$$

It is convenient to define the small parameter

$$\eta = \frac{2\sqrt{g^2 - 1}}{g - \sqrt{g^2 - 1}}, \quad (A.13)$$

η is proportional to $\sqrt{\varepsilon}(1 + 0(\varepsilon))$.

We can now use the asymptotic expansion [10]

$$F\left(\frac{1}{2}, \frac{1}{2}; l + 1; -\frac{1}{\eta}\right) =$$

$$= \frac{l!}{\sqrt{\pi}\Gamma(l + \frac{1}{2})}\, \eta^{1/2} \sum_{n=0}^\infty \frac{\Gamma(n + \frac{1}{2})\Gamma(n - l + \frac{1}{2})}{\sqrt{\pi}\Gamma(-l + \frac{1}{2})(n!)^2} \times$$

$$\times \eta^n(- \ln\eta + 2\psi_{(n+1)} - \psi_{(n+\frac{1}{2})} - \psi_{(l-\frac{1}{2}-n)})$$

where $\psi(x)$ is the digamma function.

We keep only the first few terms, using exact results for $\psi(n)$ for small n and the approximation $\psi(l - \frac{1}{2} - n) = \ln l$ for large l and small n.

Then

$$F\left(\frac{1}{2}, \frac{1}{2}; l + 1; -\frac{1}{\eta}\right) =$$

$$= \frac{l!}{\sqrt{\pi}\Gamma(l + \frac{1}{2})}\sqrt{\eta}(\ln(1/l\eta) + 2\ln 2 - \gamma) \times$$

$$\times \left(1 + \frac{1}{2}\left(l - \frac{1}{2}\right)\eta + \frac{3}{16}\left(l - \frac{1}{2}\right)\right)$$

$$\times \left(l - \frac{3}{2}\right)\eta^2 + 0(\eta^3)\right) \quad (A.14)$$

where γ is the Euler's constant.

This expansion is useful for $l\eta < 1$. From eq. (A.12) and (A.9),

$$R_{01}(y) = \frac{1}{2\pi y} Q_{n-\frac{1}{2}}\left(1 - \frac{1}{8 y^2}\right) = \frac{1}{2\pi y} \frac{\sqrt{\pi}}{l!} \times$$

$$\times \Gamma\left(l + \frac{1}{2}\right) \frac{(\eta + 1)^{-l/2 + 1/4}}{\eta^{1/2}} F\left(\frac{1}{2}, \frac{1}{2}; l + 1; -\frac{1}{\eta}\right) \simeq$$

$$\simeq \frac{1}{2\pi y}\left(1 - \frac{5}{16}(l\eta)^2 + 0(\eta^2) + 0(l^3 \eta^3)\right)\times$$

$$\times \left(l\eta \frac{1}{l\eta} + 2 l\eta 2 - \gamma\right).$$

As expected this expression diverges when $\eta \to 0$ for fixed l, as it should since the bound state then merges into the band, and its spatial extent then becomes infinite.

In order to obtain the full expression for the renormalized coupling, one must also evaluate the energy dependent terms in eq. (A.5), i.e. $R_{00}(y)$.

In two dimensions we see easily that

$$R_{00}(y) = \omega_B \sum_k \frac{1}{\omega_B - \varepsilon_k}$$

$$R_{00}(y) \sim \frac{\omega_B}{8\pi t} \ln \varepsilon = \frac{\omega_B}{8\pi t} \ln |1 + 1/zy|.$$

This logarithmic divergence is linked to the dimensionality two in the tight binding approximation.

In the final expression, eq. (9), there also appears an energy dependent term

$$\frac{\partial}{\partial\omega} F_0(\omega)\bigg|_{\omega = E_B{}^0}.$$

In the two dimensional case considered here

$$\frac{\partial}{\partial\omega} F_0(\omega)\bigg|_{\omega = E_B{}^0} = - \sum_k \frac{1}{(\omega - \varepsilon_k)^2}\bigg|_{\omega = E_B{}^0} = \frac{1}{8\pi} \frac{1}{t^2} \frac{1}{\varepsilon}.$$

This divergence simply expresses the fact that the bound state amplitude goes to zero on each site as its spatial extent becomes infinite.

Finally we obtain

$$\delta E_B = 16 \frac{t\omega_B}{zt + \varepsilon}\left(\frac{\varepsilon}{\ln \varepsilon}\right) \times (ln(4/l\eta) - \gamma)^2 \times$$

$$\times \left(1 - \frac{5}{8}(l\eta)^2 + 0(\eta^2) + 0(l^3 \eta^3)\right)\left(1 - \frac{1}{z}\right)^2$$
(A.15)

$$= \frac{4 \varepsilon}{\ln \varepsilon} zt(ln(4/l\eta) - \gamma)^2 \times$$

$$\times \left(1 - \frac{5}{8}(l\eta)^2 + 0(\eta^2) + 0(l^3 \eta^3)\right)\left(1 - \frac{1}{z}\right)^2.$$

Provided we keep in mind the condition $l\eta < 1$, we can rewrite eq. (A.15) as

$$\delta E_B = 4 zt\left(\frac{\varepsilon}{\ln \varepsilon}\right)\left(1 - \frac{1}{z}\right)^2 (ln(1/l \sqrt{2 \varepsilon}) - \gamma)^2 \times$$

$$\times \exp - 20 l^2 \varepsilon. \quad (A.16)$$

— Deep-hole limit.

In this limit, the bound hole energy is very low compared to the band edge, and

$$g = \frac{1}{8}\left(\frac{E_B{}^0}{t}\right)^2 - 1 \approx \frac{1}{8}\left(\frac{E_B{}^0}{t}\right)^2 \gg 1.$$

Then we can approximate

$$F\left(\frac{1}{2}; l + \frac{1}{2}; l + 1; 4\left(\frac{t}{E_B}\right)^2\right) \simeq \frac{\Gamma(l + 1)}{\Gamma(\frac{1}{2}) \Gamma(l + \frac{1}{2})}$$

and we obtain straightforwardly

$$R_{01} = \frac{E_B{}^0}{2\pi t} \times \exp - 2\left(l + \frac{1}{2}\right) \ln E_B/t \quad (A.17)$$

as was obtained previously [4].

Eq. (A.17) simply means that renormalization becomes unimportant in the deep hole limit.

APPENDIX II

Consider a semi-conductor, well described within the usual one-electron theory of solids, where the valence band and the conduction band are treated in the tight-binding approximation. Then introduce an impurity which creates a bound state in the gap. The bound state energy is a solution of the equation

$$E_B + t_0 - \sum_p A_p\left(\frac{t}{E_B}\right)^p = 0$$

where the same notations as in the body of this paper hold.

Now suppose a vacancy is created at a distance $R = la_0$ from the impurity center. Assume that the vacancy simply amounts to annuling the transfer matrix element t between the vacancy site and the nearest neighbour sites. (This is not quite correct, since in a number of semi-conducting compounds, the vacancy seriously distorts the lattice, thereby changing the value of t over a noticeable range (12).) Then we can ask :

1) How is the bound state energy changed by the vacancy ?

2) How is the vacancy creation energy changed by the presence of the bound state ?

The answer to the first question may be of interest when a very accurate energy definition of the bound state is needed with respect to the edge of the valence (or conduction) band. This answer is given by the calculation described in this paper. Indeed, the modification of the self energy of the bound state

is due to the variation $\delta A p$ of the number of walks from the impurity and back for the first time in p steps. All paths passing through the vacancy are suppressed (including retraceable paths). Thus we can evaluate the change in the bound state energy with the same method used in this paper. The generating function for all paths passing through the vacancy is

$$T(y) = \frac{R_{01}^2(y)}{(1 + R_{00}(y)) \, ((1 + R_{00}(y))^2 - R_{01}^2(y))} \; .$$

In this problem this expression is exact and no correction need be made since retraceable paths are included in this expression, as they should.

In the deep hole limit, the smallest suppressed path is the completely retraceable one, so that the energy change is given by

$$\delta E_{\mathrm{B}} = - E_{\mathrm{B}}^0 \left(- \frac{t}{E_{\mathrm{B}}^0} \right)^{2l} \times \frac{F_0^2(E_{\mathrm{B}}^0)}{\left. \dfrac{\partial}{\partial \omega} F_0(\omega) \right|_{\omega = E_{\mathrm{B}}^0}}$$

as can be seen from eq. (11).

In the shallow hole limit, an expression similar to eq. (A.16) holds in a square two-dimensional lattice, i.e.

$$\delta E_{\mathrm{B}} \sim 4 \, zt(\varepsilon/(\ln \varepsilon)) \, (lnl \sqrt{2} \, \varepsilon + \gamma)^2 \times (1 - 20 \, l^2 \, \varepsilon) \, .$$

The answer to the second question is, in this model, identical to the first : the change δE_{B} is the change of energy of the system formed by the vacancy and the impurity.

This question is of interest in the discussion of vacancy-impurity interaction problems, even though the model used here is very crude. In particular we have ignored dangling bonds, lattice distortions, and Coulomb interaction between impurity and vacancy [13], so that we can only discuss qualitatively the kinetic effect due to the suppression of all the paths passing through the vacancy site.

In this appendix, we shall not go into this matter in more detail. A complete paper is in preparation, with comparison with experiments in Si.

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