Theory of Paramagnetic Impurities in Semiconductors*

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(Received 21 February 1966)

In this paper, a model of a paramagnetic impurity in a semiconductor (or of an F' center in an alkali halide) is proposed. It is an exactly soluble form of the quantum-mechanical 3-body problem. Specifically, we deal with 2 interacting particles in any number of dimensions in an attractive external potential, and present the qualitative features of the resulting eigenvalues and eigenfunctions. We find algebraically the conditions for a magnetic moment to appear (e.g., for an F' center to become unstable with respect to an F center) and discover that even a large 2-body electronic repulsion U does not cause a moment to appear when the one-electron bound state orbits about the impurity are sufficiently great. Conversely, in the case of small, tightly bound orbits, beyond a certain value of U, the impurity does in fact become magnetic in the ground state. Using the exact ground-state solution, we show that a perturbation-theoretic expansion in powers of U has a finite radius of convergence.

1. INTRODUCTION

THE problems associated with magnetic impurities in metals have received a great deal of attention,[1] but are still far from reaching a rigorous solution. By contrast, we have readily found an exactly soluble model of paramagnetic (donor or acceptor) impurities in semiconductors, which can be rigorously analyzed over an entire range of parameters with rather interesting results. The present paper is the first report on the theory of this model,
giving features of the eigenstates and of the magnetic properties. Quantitative numerical results as well as transport properties (i.e., scattering cross section), statistical mechanics, and other features of this model will be reported later.

It has long been known that the Coulomb repulsion among electrons in impurity states of a semiconductor cannot be safely neglected. More than eleven years ago Brooks[2] wrote, "... band (i.e., Bloch) states have the property that the corresponding wavefunctions are spread throughout the crystal. Thus there is practically no price, in terms of extra electrostatic interaction, for putting two electrons in the same (Bloch) state. This is the condition for the applicability of Fermi statistics in its simple form. In the case of localized states, however, a very different situation obtains. Even though an

[1] The quantum- and statistical-mechanical aspects have been discussed by P. W. Anderson, Phys. Rev. **124**, 41 (1961), and recently extended by, among others, A. C. Hewson, Phys. Rev. **144**, 420 (1966), and by J. R. Schrieffer and D. C. Mattis, *ibid.* **140**, A1412 (1965). Transport properties have been analyzed by J. Friedel, *Metallic Solid Solutions* (W. A. Benjamin, Inc., New York, 1963), and most recently by D. J. Kim, Phys. Rev. (to be published).

[2] H. Brooks, *Advances in Electronics and Electron Physics*, L. Marton, Ed. (Academic Press Inc., New York, 1955), Vol. VII. See also C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 359.

electron may be allowed two directions of spin in a localized state, once the state is occupied by an electron of either spin, it cannot then be occupied by an electron of opposite spin, because the electrostatic repulsion of the two localized charge distributions would raise the energy of the second electron. . .". If only a single electron can be bound to the impurity, the latter is perforce a paramagnetic impurity of one Bohr magneton. The present model is designed to explain precisely how this single binding may or may not occur.

Several superficial difficulties have to be overcome in the process, for, in general, the problem of two interacting particles in an attractive potential well (such as the two electrons in helium atom or in the hydrogen molecule) has no solution in closed form. Fortunately for us, the present calculation for the solid is more tractable than the usual two-electron problems, and it *is* possible to obtain an explicit solution in closed form, as we show below.

In all such problems involving two electrons, one readily proves[3] that the ground-state wavefunction is nodeless; it then must be symmetric under interchange of the spatial coordinates of the two particles, and it must belong to spin $S = 0$. Does this preclude magnetic behavior? The answer, surprisingly is no, provided the 2-particle repulsion U exceeds a critical magnitude U_c. In that case, one of the electrons is ionized and the energy splitting between the ground state and the lowest $S = 1$ state ceases to be finite and becomes $O(N^{-2})$, where N = number of atoms in the crystal. The ground state can then be taken as an arbitrary combination of triplet and singlet, so that, in effect, there is one Bohr magneton localized on the impurity, and one uncorrelated Bohr magneton on the second, wandering, particle. The net localized spin of the impurity is then $1\mu_B$, the largest value attainable in the present model. One of the results obtained below is an expression for U_c in terms of the one-electron parameters (viz., band structure and binding energy of the impurity potential well). When U_c is infinite, then the impurity is always entirely nonmagnetic.

[3] E. Lieb and D. Mattis, Phys. Rev. 125, 164 (1962). This theorem and its consequences are discussed also in D. Mattis, *The Theory of Magnetism* (Harper and Row, Publishers, Inc., New York, 1965), Chap. 4. The 2-electron problem considered earlier by J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. 91, 1323 (1953), also indicated that, without Hund's rule coupling, the ground state belongs to $S = 0$, on the basis of a model similar to the present model with $v \equiv 0$. A different but also exactly soluble model of two electrons in an harmonic oscillator potential, interacting by Coulomb repulsion, was solved by N. Kestner and O. Sinanoglu, Phys. Rev. 128, 2687 (1962). Their interesting result cannot be directly compared with ours, however, because it has no scattering state, no unbound solution, and no magnetism.

After the present manuscript was essentially completed, strong experimental evidence for the existence of such paramagnetic impurities in n-type InSb was reported by Katayama and Tanaka[4] (viz., the existence of a resistance-minimum anomaly such as have been commonly observed in metals containing paramagnetic impurities, but much larger than in these metals). An earlier indication of this was provided by work on the thermoelectric power by Khosla and Sladek.[4] Both series of experiments were preceded by a theory due to Toyozawa,[5] based on the Hartree–Fock approximation. As we see below, this approximation can only be valid for very deep donor levels.

As another application, we recall that the F center consists of an electron bound to a vacancy in an alkali–halide crystal, whereas the F' center consists of *two* electrons bound to the same vacancy. The energetic stability and capture cross section of the F' center for the second electron may also in principle be calculated by the present methods, extending recent approximation schemes.[6]

2. DESCRIPTION OF THE MODEL

In this section, we describe the general model and its general solutions, explaining the steps whereby the latter are obtained. In the following section a one-dimensional example is explicitly worked out using this method.

For definiteness, we discuss a donor-type impurity and 2 electrons in the conduction band of a semiconductor. (The analysis for an acceptor-type impurity and 2 holes in the valence band is, *mutatis mutandis*, formally identical.) The electrons move from one Wannier site to the next, with overlap matrix elements $K(R_i - R_j)$. The band structure, given by the Bloch energies $\epsilon(k)$ (the Fourier transforms of the K's) is therefore

$$\epsilon(k) = \frac{1}{N} \sum_{i,j} K(R_i - R_j) \cos k \cdot R_{ij}. \qquad (2.1)$$

In addition, there is the potential of an impurity at the origin: $-v(R_i)$ which is assumed to be deep enough to have *one and only one* bound state.

[If the potential has *no* bound state there can be no localized spin, as the probability that either of the two electrons is in the vicinity of

[4] Y. Katayama and S. Tanaka, Phys. Rev. Letters 16, 129 (1966); R. Khosla and R. Sladek, Phys. Rev. Letters 15, 1521 (1965).

[5] Y. Toyozawa, J. Phys. Soc. Japan 17, 986 (1962). [See parenthetical statement after Eq. (2.22).]

[6] S. Y. La and R. H. Bartram, Phys. Rev. 144, 670 (1966), and references therein.

the impurity is just $O(1/N) \sim$ zero. (This is quite different from the cases of interest in a metal, where electrons are always available in the vicinity of any site.) When the potential has two or more bound states, the analysis becomes more complicated than envisaged in the present calculation but it can be done. A summary of our findings in the more complicated situation is this: if the bound states are a *degenerate set*, then the 2-electron ground state of the impurity is likely to be a triplet or doublet magnetic state, in agreement with Hund's rule. Otherwise, the impurity is generally a nonmagnetic singlet *for all values of the two-electron repulsion*. This situation, descriptive of multilevel traps such as gold in germanium, can in fact be handled by the present methods although we do not further consider it in the present paper.[7]]

Before introducing the two-particle interaction, let us solve for the one-electron eigenstates for the band structure (2.1) in the presence of the impurity potential $-v$. This can always be done by straightforward methods (an explicit solution in the one-dimensional case is displayed in the following section) and results in a set of orthonormal eigenfunctions labeled by an ascending quantum number $r = 0, 1, 2, \cdots$ and spin quantum number $m = \pm\frac{1}{2}$:

$$\phi_{r,m} = \sum_i f_r(R_i)c_{i,m}^* \mid 0) \qquad (2.2)$$

with energy eigenvalues: e_r;

$r = 0$ for the bound state, $r = 1, 2, \cdots$ for continuum states, arranged in the sequence $e_r \leq e_{r+1}$, and interlacing the Bloch energies ϵ_r. $\qquad (2.3)$

Two-particle states are merely antisymmetrized product states,

$$\Phi_{r,m;r',m'}^0 = 2^{-\frac{1}{2}}\{[\sum_i f_r(R_i) \sum_j f_{r'}(R_j)$$
$$\pm \sum_j f_r(R_j) \sum_i f_{r'}(R_i)]\}c_{i,m}^* c_{j,m'}^* \mid 0) \qquad (2.4)$$

with energy eigenvalues:

$E(r, r') = e_r + e_{r'}'; r = r' = 0$ for the two-particle bound state, $r = 0$ and $r' \neq 0$ (or vice-versa) for the one-particle bound state, and $r \neq 0$ and $r' \neq 0$ for the completely ionized states of the impurity. $\qquad (2.5)$

Of all these two-particle states, *only the one-particle bound states possess a localized magnetic moment* of one Bohr magneton, the others having a localized magnetic moment which is either identically zero (two-particle bound states) or virtually zero, $O(1/N)$, (for the completely ionized states).

The two-particle eigenstates in presence of the two-particle interaction can be written as

$$\Phi = \sum_{i,j} F(R_i, R_j)c_{i,m}^* c_{j,m'}^* \mid 0), \qquad (2.6)$$

and are antisymmetric or symmetric under the interchange of R_i and R_j according to whether they belong to eigenvalue $S = 1$ or $S = 0$ of total spin.

We obtain the correct F's by a Green's function technique. First we write the complete two-body Green's function,

$$G_E(ij \mid i'j') = \sum_{r,r'} \frac{f_r^*(i)f_{r'}^*(j)f_r(i')f_{r'}(j')}{E - e_r - e_{r'}} \qquad (2.7)$$

and then, in terms of the repulsive two-body interaction $U(R_i, R_j) \geq 0$, we obtain

$$F(ij) = \sum_{i',j'} U(i', j')G_E(i'j' \mid ij)F(i'j'), \qquad (2.8)$$

a system of linear coupled equations which are to be solved for the wavefunction F and the energy eigenvalue E. If U is nonvanishing over the entire crystal, this poses an intractable problem which must be solved by any of the variety of approximate techniques used in scattering theory. Although it is justified to neglect this long-range interaction, there are good reasons, outlined by Anderson,[1] not to neglect the Coulomb repulsion *near the impurity*. There, the atomic orbitals, hence the Wannier orbitals, tend to be more compact, and the electrostatic repulsion cannot be ignored, particularly in the case of magnetic atoms. If U is nonvanishing over Z distinct sites in the neighborhood of the impurity (located at the origin), the solution of (2.8) reduces to a $Z^2 \times Z^2$ determinantal equation. In what follows, we assume the simplest model,[8] i.e., an interaction only at the origin [i.e., $Z = 1$, with $U(0, 0) \equiv U$, and $U(i, j) = 0$ for R_i and R_j not both at the origin].

With the assumption of such a local repulsion, the wavefunctions are explicitly given as

$$F(ij) = UG(00 \mid ij)F(00). \qquad (2.9)$$

We immediately note that all the antisymmetric solutions (i.e., the triplet states, in addition to those

[7] For more background into the one-electron problem, the nature of the bound states, etc., we refer to G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); *ibid.* **96**, 1208 (1954); and M. Lax, *ibid.* **94**, 1391 (1954). Interaction with field bands is discussed by L. J. Sham, Phys. Rev. **150**, 720 (1966).

[8] The simplest model displays the qualitative features of the general model; we have also determined that Anderson's model[1] yields similar results in the present context, when a one-particle bound state exists.
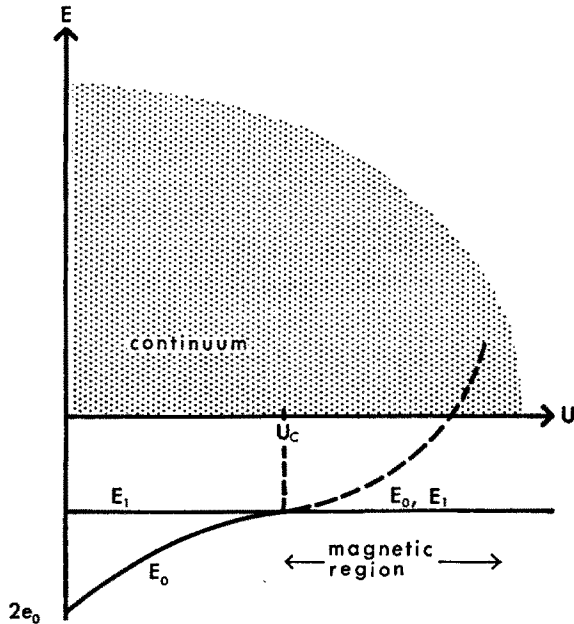
FIG. 1. Energy eigenvalues as functions of repulsive 2-body interaction U. Lowest singlet solution E_0 and triplet solution E_1 merge for $U \geq U_c$, resulting in a localized moment of $1 \ \mu_B$. The dotted line (spurious) indicates solution of Eq. (2.17) in range $U > U_c$. Note that, although curve shown does not indicate it, $dE_0/dU = 0$ when $U = U_c$. Range of energies above E_1 is 1-particle scattering states continuum. Shaded range labeled "continuum" refers to the 2-particle scattering states.

singlet states which have a node at the origin) have the unperturbed energy eigenvalues

$$E = e_r + e_{r'} \qquad (2.10)$$

thus compensating the vanishing numerator in (2.9) by a vanishing denominator. These wavefunctions are given in (2.4). Excluding such trivial solutions from present considerations, let us now consider those solutions for which $F(00) \neq 0$. First, we calculate the magnitude of this parameter required to normalize the wavefunctions:

$$1 = \sum_{i,j} |F(ij)|^2 = |F(00)|^2 \ U^2 \sum_{r,r'} \frac{|f_r(0)f_{r'}(0)|^2}{(E - e_r - e_{r'})^2},$$

i.e.,

$$F(00) = \left\{ U^2 \sum_{r,r'} \frac{|f_r(0)f_{r'}(0)|^2}{(E - e_r - e_{r'})^2} \right\}^{-\frac{1}{2}}, \quad (2.11)$$

where we have made use of the orthogonality relation,

$$\sum_i f_r^*(i)f_{r'}(i) = \delta_{r,r'}. \qquad (2.12)$$

Next, we solve for the eigenvalues E by setting $R_i = R_j = 0$ in the eigenvalue equation (2.9) and obtain:

$$\frac{1}{U} = \sum_{r,r'} \frac{|f_r(0)f_{r'}(0)|^2}{E - e_r - e_{r'}}. \qquad (2.13)$$

This is a standard eigenvalue equation with the usual *interlacing* properties: there is an eigenvalue E between each pair of neighboring unperturbed energy levels $E(r, r')$ given in (2.5). Thus all *but one* of the energy levels may be displaced by at most $O(1/N)$, no matter how large U is allowed to become. The exception is the 2-particle bound state, which corresponded to $r = r' = 0$ for the unperturbed electrons. If we denote its energy eigenvalue by E_0, we must have

$$2e_0 < E_0 < e_0 + e_1 \equiv E_1. \qquad (2.14)$$

The first inequality reflects the fact that a repulsive interaction can only raise the energy,[9] and the second is proved by setting $E_0 = e_0 + e_1 - x$. As x is varied from the value $e_1 - e_0$ to zero, the right-hand side of (2.13) varies from $+\infty$ to $-\infty$, which ensures that at some intermediate value a solution to the equation *must* exist.

What we are to discover is that, in the limit $N \to \infty$ *the range of* x required to change the right-hand side of (2.13) from some finite positive value to $-\infty$ *is only* $O(1/N)$. Consequently, the solution E_0 of (2.13) must have the general features shown in Fig. 1: it is an increasing function of U below a certain value denoted U_c. For values of U larger than this, $E_0 = e_0 + e_1 = $ const, in the limit $N \to \infty$. As a result, the ground-state energy is a nonanalytic, albeit continuous, function of U at $U = U_c$, which *defines* U_c as: precisely the magnitude of the repulsive potential required to singly ionize the impurity. Thus, for $U \geq U_c$, the impurity possesses a magnetic moment of one Bohr magneton.

The above is not a general property of the above eigenvalue equation, but follows, rather, from detailed consideration of both numerator and denominator in this equation. We find it important to consider the normalization of the unperturbed states $f_r(i)$, so as to find their amplitudes at the origin, and we find that the continuum states behave differently from the bound state in one very significant way.

Thus, we note that, while the bound-state amplitude at the impurity site is $f_0(0) \sim O(1)$, the scattering-state amplitudes are $O(N^{-\frac{1}{2}})$, and we therefore write

$$|f_r(0)|^2 \equiv n^2(r)/N, \qquad r \geq 1, \qquad (2.15)$$

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[9] Differentiating (2.13) with respect to U yields $dE/dU \geq 0$ for *all* eigenvalues E.

which defines $n(r)$ a quantity $O(1)$. The eigenvalue equation (2.13) now reads

$$\frac{1}{U} = \frac{|f_0(0)|^4}{E - 2e_0} + |f_0(0)|^2 \frac{2}{N} \sum_{r \geq 1} \frac{n^2(r)}{E - e_0 - e_r}$$
$$+ \left(\frac{1}{N}\right)^2 \sum_{\substack{r \geq 1 \\ r' \geq 1}} \frac{n^2(r)n^2(r')}{E - e_r - e_{r'}}. \quad (2.16)$$

In solving this equation for E_0, it is permissible to proceed to the limit $N \to \infty$ and replace sums by integrals, provided E_0 does not exceed $E_1 \equiv e_0 + e_1$. Let us define U_e as that value of U for which $E_0 = E_1$. Then, $E_0 = E_1$ for the entire range $U_e \leq U \leq \infty$, whereas for $U < U_e$ the correct solution is obtained from the equation

$$\frac{1}{U} = \frac{|f_0(0)|^4}{E_0 - 2e_0} + 2|f_0(0)|^2 \int dr \frac{g(r)n^2(r)}{E_0 - e_0 - e(r)}$$
$$+ \iint dr\, dr' \frac{g(r)g(r')n^2(r)n^2(r')}{E_0 - e(r) - e(r')}, \quad U \leq U_e, \quad (2.17)$$

where $g(r) \equiv$ density of states factor required to change a sum to an integral.

If we interpret the integrals as principal parts integrations, this equation also has a (spurious) solution for E_0 in the range $U > U_e$, indicated by the dotted line in Fig. 1, which merely shows that *the limiting process $N \to \infty$ must be taken carefully*, for we have already seen that the correct solution in this range is $E_0 = E_1$.

We may also examine the results of perturbation theory, by expanding the exact solution in powers of U. Letting

$$E_0 = 2e_0 + y$$

define the energy shift y, we readily solve for this quantity in (2.17):

$$y = |f_0(0)|^4 U(1 - UQ)^{-1}$$
$$= |f_0(0)|^4 U(1 + UQ + \cdots),$$

where Q, the correlation terms in (2.17), are given by

$$Q = 2|f_0(0)|^2 \int dr \frac{g(r)n^2(r)}{E_0 - e_0 - e(r)}$$
$$+ \iint dr\, dr' \frac{g(r)g(r')n^2(r)n^2(r')}{E_0 - e(r) - e(r')}$$

and, in the Rayleigh–Schrödinger perturbation theory, may be evaluated using approximate values of y, computed to the desired order in powers of U. Clearly, the expansion ceases to exist, and perturbation theory becomes meaningless, once

$$U |Q| \geq 1.$$

The Brillouin–Wigner perturbation theory, in which Q is not approximated, appears to have a somewhat larger radius of convergence. Further examination of this point would be of interest, but is outside the scope of the present investigation.

We now proceed to a very useful simplification, which enables the double integral in (2.17) to be formally eliminated from the theory. This is especially valuable for numerical computations.

Simplification of some Integrals

We define $I_N(W_0)$ as

$$I_N(W_0) \equiv -\frac{1}{N} \sum_{r \geq 1} \frac{n^2(r)}{W_0 - e_r}, \quad W_0 \leq e_1, \quad (2.18)$$

and the limiting function $I(W_0) \equiv I_\infty(W_0)$ as

$$I(W_0) = -\int dr \frac{g(r)n^2(r)}{W_0 - e(r)}. \quad (2.19)$$

The negative signs are introduced to make $I > 0$. Next, we consider the *ground-state eigenvalue* W_0 of the *one-electron* Hamiltonian with the *original* impurity potential $-v(R_i)$ *plus* a perturbing *one*-body potential $\lambda \delta_{i,0}$ *added thereto*, resulting in $-v(R_i) + \lambda \delta_{i,0}$. It may be assumed[7] that we know W_0 as a function of λ, or conversely, that we know $\lambda(W_0)$ [this is of course easiest if $v(R_i)$ itself was nonvanishing only at the origin, as in the example of the following section]. At any rate, we know $W_0 \leq e_1$. We may use the one-body Green's function to obtain the integral equation,

$$\frac{1}{\lambda(W_0)} = \frac{|f_0(0)|^2}{W_0 - e_0} + \frac{1}{N} \sum_{r \geq 1} \frac{n^2(r)}{W_0 - e_r} \quad (2.20)$$

by complete analogy to the preceding calculation. But now we have the advantage of knowing W_0 and $\lambda(W_0)$, and thus can solve for

$$I_N(W_0) = \frac{|f_0(0)|^2}{W_0 - e_0} - \frac{1}{\lambda(W_0)} \quad (2.21)$$

and we may also easily take the limit $N \to \infty$ to obtain $I(W_0)$ therefrom. Substitution into (2.17) yields the following, simplified, equation[10]

$$\frac{1}{U} = \frac{|f_0(0)|^2}{\lambda(E_0 - e_0)} + \int dr\, g(r) \frac{n^2(r)}{\lambda(E_0 - e_r)}, \quad (2.22)$$

[10] For comparison with other results and recent theories, the following references may be useful: L. D. Fadeev, *Mathematical Aspects of the Three-Body Problem in the Quantum Scattering Theory* (Danial Davey & Company, Inc., New York, 1965); J. Callaway, J. Math. Phys. **5**, 783 (1964), and Phys. Rev. **140**, A618 (1965); G. V. Skorniakov and K. A. Ter-Martirosin, Zh. Eksperim. i Teor. Fiz. **31**, 775 (1956) [English transl.: Soviet Phys.—JETP **4**, 648 (1957)]; L. Eyges, J. Math. Phys. **6**, 1320 (1965).

which is the desired alternate, and fully equivalent version of (2.17).

[Equation (2.22) may be (crudely) interpreted as an effective, Hartree–Fock type, one-body repulsion, given by a constant $\lambda(W)$,

$$\lambda = U \, |f_0(0)|^2$$

with the integral in (2.22) representing the effects of *correlations*. We see that the Hartree–Fock approximation would be exact if U were replaced by a smaller interaction (the integral can be shown to be negative)

$$\tilde{U} = \left\{ U^{-1} - \int dr \, g(r)n^2(r)/\lambda(E_0 - e(r)) \right\}^{-1} < U,$$

but since this involves an integral over the "effective coupling constant" λ, $\tilde{U}$ is in general just as difficult to obtain as an exact solution to the problem. Note that, when v is much larger than the band width, the correlation energy becomes negligible and the Hartree–Fock theory is correct for all values of U.]

3. LINEAR CHAIN AS EXPLICITLY SOLUBLE EXAMPLE

The appearance of a localized magnetic moment in the one-dimensional case is all the more striking because of the theorems[3] that the ground-state magnetic moment vanishes. For this reason, it would be of great interest to generalize the present analysis to examine the case of more than two electrons, but we have not completely succeeded in this as yet.

We consider the nearest neighbor coupling, i.e., $K(0) = 1$ and $K(\pm a) = -\frac{1}{2}$ corresponding to the band structure

$$\epsilon(k) = 1 - \cos ka, \tag{3.1}$$

and an attractive potential localized at the origin

$$-v(R_i) = -v\delta_{i,0}, \qquad v \geq 0. \tag{3.2}$$

The one-particle eigenfunctions with a node at the impurity are simply

$$f_r(n) = \left(\frac{2}{N+1} \right)^{\frac{1}{2}} \sin k_r n \tag{3.3}$$

with energies independent of the interaction,

$$e_r = 1 - \cos k_r, \tag{3.4}$$

where periodic boundary conditions imposes

$$\sin k_r(\tfrac{1}{2}N + 1) = \sin k_r(-\tfrac{1}{2}N),$$

which results in

$$k_r = 2\pi r/(N+1), \qquad r = 1, 2, \cdots, \tfrac{1}{2}N. \tag{3.5}$$

Precisely because of the vanishing amplitude at the impurity, however, these functions do not appear in the equations for the ground state of the interacting system. The even eigenfunctions are of course derived from the cosine functions and, introducing the phase shifts φ_r, may be written as

$$f_r(n) = C_r^{-\frac{1}{2}} \cos (k_r \, |n| + \varphi_r). \tag{3.6}$$

The energy is also given by (3.4), but the wave vectors k_r must be recalculated. This is done by studying the $n = 0$ amplitude equation

$$e_r \cos \varphi_r = \cos \varphi_r - \cos (k_r + \varphi_r) - v \cos \varphi_r. \tag{3.7}$$

We use (3.4) to eliminate e_r and obtain

$$\tan \varphi_r = v/\sin k_r, \qquad 0 \leq \varphi_r \leq \pi. \tag{3.8}$$

Periodic boundary conditions give a second relation between φ and k

$$k_r = (2\pi r - 2\varphi_r)/(N+1), \quad r = 1, 2, \cdots, \tfrac{1}{2}N. \tag{3.9}$$

In the limit $N \to \infty$ the normalization constants C_r are independent of r, and are given by

$$C_r = \tfrac{1}{2}N. \tag{3.10}$$

So far we have N out of the total $N + 1$ eigenfunctions; the missing one is the bound-state solution, which decays exponentially from the origin and is therefore independent of boundary conditions for large N. For an infinite chain, it has the form

$$f_0(n) = C_0^{-\frac{1}{2}} \exp -\alpha \, |n|, \qquad \alpha \geq 0, \tag{3.11}$$

hence an energy,

$$e_0 = 1 - \cosh \alpha \tag{3.12}$$

a finite amount below the continuum. The eigenvalue is once more determined by the $n = 0$ amplitude equation

$$e_0 = 1 - \exp (-\alpha) - v, \tag{3.13}$$

which, combined with the preceding, yields

$$\sinh \alpha = v \qquad \text{(meaningful only for } v \geq 0\text{)} \tag{3.14}$$

or

$$e_0 = 1 - (1 + v^2)^{\frac{1}{2}} \quad \text{(note that } e_0 < 0\text{)}. \tag{3.15}$$

Finally one determines the normalization constant

$$C_0 = 1 + 2 \sum_{n>0} \exp -2\alpha n = \coth \alpha. \tag{3.16}$$

All these formulas are valid to within an error $O(\exp -\alpha N)$, and so should hold, with a reasonable choice of parameters, for all but the shortest chains.

Equations (3.6) and (3.8)–(3.10) yield $f_r^2(0)$ [i.e.,

$n^2(r)$] for the continuum states $r \geq 1$. The bound-state amplitude at $n = 0$ is given by Eqs. (3.11), (3.14), and (3.16). The results are

$$|f_0(0)|^2 = v/(1 + v^2)^{\frac{1}{2}}$$

$$\text{and} \quad n^2(r) = 2\left[1 + \frac{v^2}{\sin^2 k_r}\right]^{-1}. \quad (3.17)$$

Finally, we can readily obtain $\lambda(W_0)$ required for the simplified form (2.22) of the eigenvalue equation, and find

$$\lambda(W_0) = v - [(1 - W_0)^2 - 1]^{\frac{1}{2}}. \quad (3.18)$$

The eigenvalue equation in question now reads

$$\frac{1}{U} = \frac{v}{(1 + v^2)^{\frac{1}{2}}(v - \{[2 - (1 + v^2)^{\frac{1}{2}} - E_0]^2 - 1\}^{\frac{1}{2}})}$$

$$+ \frac{1}{\pi} \int_0^\pi \frac{dk \, (1 + v^2/\sin^2 k)^{-1}}{v - [(2 - \cos k - E_0)^2 - 1]^{\frac{1}{2}}} \quad (3.19)$$

and must be solved for E_0 only in the range

$$2 - 2(1 + v^2)^{\frac{1}{2}} \leq E_0 \leq 1 - (1 + v^2)^{\frac{1}{2}}. \quad (3.20)$$

As U is increased from zero to a value U_c, E_0 increases from the left-hand value of the inequality
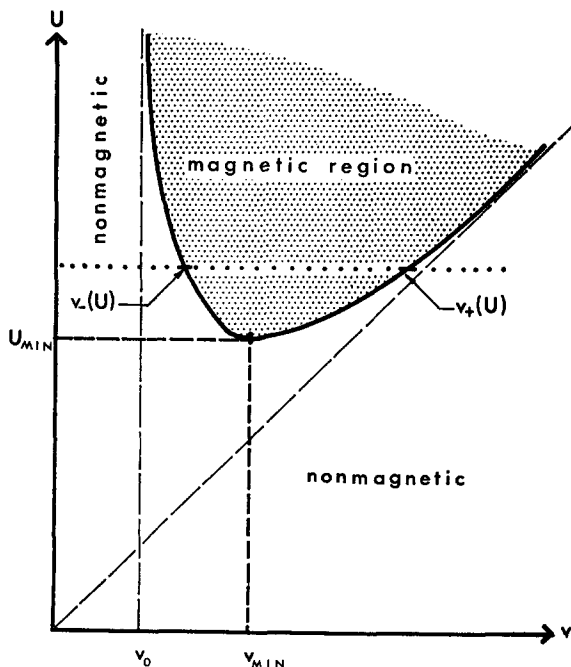

FIG. 2. Schematic solution of Eq. (3.22) for one-dimensional model. For $v \leq v_0$ no finite 2-body repulsion can magnetize the impurity ground state, which will always have a 2-body $S = 0$ bound state. For $v > v_0$, the impurity can be ionized (acquiring 1 Bohr magneton in the ground state) by $U > U_c$, where U_c is the solid line shown. (Dashed lines indicate the asymptotes.) Region of magnetic behavior is indicated by shaded region above the curve U_c, which has its minimum value U_{min} at v_{min}. The points $v_\pm(U)$ are defined in Fig. 3.
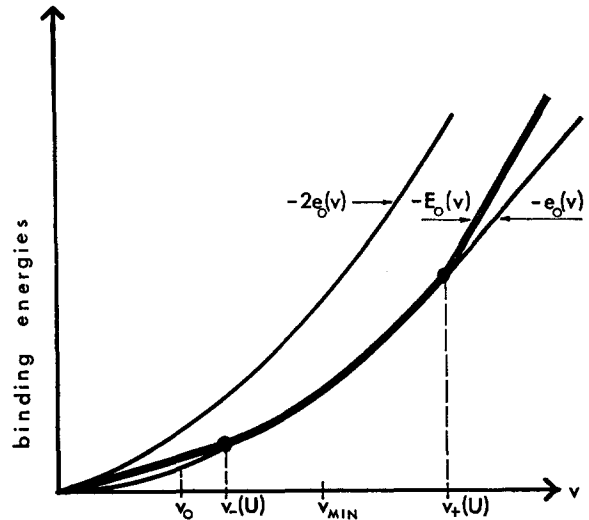

FIG. 3. Schematic solution of Eq. (3.22) for fixed inter-particle repulsive potential, U, and variable attractive potential, v. Compare with Fig. 2, especially the points $v_-(U)$ and $v_+(U)$. Note that $v_-(U)$ is always greater than the fixed point v_0, regardless of the magnitude of U, and that v_+ and v_- straddle v_{min}. Finally, note that one can easily prove that dE_0/dv, as well as E_0, is a *continuous* function of v, and therefore $(dE_0/dv) = (de_0/dv)$ at $v = v_\pm$.

to the right-hand value. For U greater than U_c, Eq. (3.19) is no longer valid and we have,

$$E_0 \equiv 1 - (1 + v^2)^{\frac{1}{2}}(\text{ind}' \text{ of } U \text{ for } U \geq U_c). \quad (3.21)$$

[This is but repeating the observations made following Eq. (2.14.).]

To obtain the magnitude of U_c, we replace E_0 in (3.19) by the upper bound in (3.20):

$$\frac{1}{U_c} = \frac{1}{(1 + v^2)^{\frac{1}{2}}} + \frac{1}{\pi}$$

$$\times \int_0^\pi \frac{dk \, (1 + v^2/\sin^2 k)^{-1}}{v - \{[1 - \cos k + (1 + v^2)^{\frac{1}{2}}]^2 - 1\}^{\frac{1}{2}}}. \quad (3.22)$$

The solution is shown in Fig. 2. From this figure, it is clear that, if v is smaller than a certain value (denoted v_0), then the right-hand side of (3.22) is negative, signifying that no value of the interparticle repulsion will ionize the impurity. This is further illustrated in Fig. 3.

4. SUMMARY

In examining the ground state of two interacting electrons about an attractive impurity, we found a variety of possible behavior (as summarized in the first two figures). Generally, there exists a finite critical repulsive interaction U_c such that, if U exceeds U_c, the two electrons cannot be simultaneously bound in the neighborhood of the impurity, and one of them spontaneously ionizes in the ground

state. When this is the case, only one electron, with its single Bohr magneton, is found in this neighborhood. For U not exceeding U_c, however, the electrons are *both* bound to the impurity which therefore has net spin $S = 0$ in the ground state.

However, for the linear chain, we have also found that, when the attractive impurity potential v is *sufficiently small* (less than an amount v_0, as shown in Fig. 2), no finite electronic repulsion can ionize the impurity, i.e., $U_c = \infty$. The reason for this is intuitively obvious; when the impurity potential is weak, the bound-state orbits are very large so that the charge clouds of the two electrons have very little interaction. It then requires little correlation energy to keep the two particles out of each other's way in this limit, and the result is a nonmagnetic ground state for *all values* of the interaction U. In the opposite limit of very large attractive impurity potential v, the electrons become very tightly bound and require $U \gtrsim v$ to be ionized. (Here the approximate Hartree–Fock theory[5,6] should be most reliable.) There exists an *optimum* magnitude of v (denoted by $v_{\min}$, Fig. 2) requiring a minimal interaction energy U (denoted by min) to become magnetic. The detailed nature of these results must be modified somewhat if they are to

apply to three dimensions, as bound states do not exist for arbitrarily small v, but otherwise qualitatively similar comments can be made in three dimensions on the basis of our exact results, Eqs. (2.13) or (2.16) and (2.17), or (2.22).

Considering the simplicity of the present model, such a variety of behavior is truly surprising, and illustrative of the virtue of exactly soluble models in the analysis of the complex phenomena of electronic magnetism. Extensions of the present model which have some appeal might include the extension to more than two particles and/or more than one impurity, and, closer to the present analysis, an *explicit* quantitative calculation of the eigenvalues and eigenfunctions in three dimensions, and a calculation of the anomalous scattering cross section[4] in the magnetic case when $U > U_c$.

The capture cross section of traps may also be related to the two-body interaction, which provides a mechanism whereby one electron may become bounded by releasing its energy to a second carrier. The scattering properties in our model are, in any event, expected to have considerably more structure than in the one-electron theory of solids because of the two distinct continua, Fig. 1. We hope to return to these topics subsequently.