SOVIET PHYSICS JETP VOLUME 24, NUMBER 1 JANUARY, 1967

QUASIHOMOPOLAR ELECTRON LEVELS IN CRYSTALS AND MOLECULES

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Submitted to JETP editor January 24, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **51**, 230–240 (July, 1966)

Quasihomopolar states of a system with a half-filled band, which is narrow compared with the conductivity band of metals (copper salts, antiferromagnets such as iron-group transition-metal oxides, and hydrocarbons with conjugated bonds), are considered on the basis of perturbation theory for degenerate levels of a many-particle system. The low-energy levels of these systems belong to the quasihomopolar states. The Schrödinger equation can be projected on the spin-function space for the quasihomopolar states. Operators corresponding to physical quantities can also be defined in this space; in other words, the operators of the physical quantities can be projected on the spin-function space. A method is proposed for calculating the projected Hamiltonian and projected physical-quantity operators of the systems. Corrections of the Heisenberg Hamiltonian are obtained for antiferromagnets. The projected current operators and electron-density distribution are investigated. After calculation of the projected operators, the problem reduces to a solution of the Schrödinger equation with a spin Hamiltonian in spin-function space.

WE consider crystals or molecules made up of identical atoms with one electron (or hole) in the unfilled shell. Such systems include, for example, the antiferromagnetic VO_2 (electron in d-shell of the V^{4+} ion), copper salts with Cu^{2+} ion (hole in the d-shell), and molecules of hydrocarbons with conjugated bonds such as the polyenes or benzene (p_z-electron band). The electrons of the unfilled shells of these systems form a narrow (compared with metals) half-filled band. The behavior of electrons in such systems depends essentially on the Coulomb correlation energy of the electron interaction. We shall break up the Hamiltonian of the system of electrons into a zero-order Hamiltonian and a perturbation, such that the Coulomb correlation energy of the electron is already taken into account in the zero-order Hamiltonian. To this end we go over to a system of orthonormalized localized Wannier functions w_{nl}, where n is the number of the band and l is the number of the center on which the electron is localized. The Hamiltonian of the system, written with the aid of Wannier functions, is

$$H = H_0 + H', \qquad H' = H_1 + H_2,$$

$$H_0 = \frac{1}{2}\sum_{l_1 l_2} F(l_1 l_2 l_2 l_1)(N_{l_1} - 1)(N_{l_2} - 1) + E_0,$$

$$H_1 = \sum_{l,\, l',\, \sigma}{}' \beta(ll') \overset{+}{a}_{l\sigma} a_{l'\sigma},$$

$$H_2 = \sum_{\substack{l_1 l_3 \neq ll' \\ \sigma}} \beta(l_1 l_3) \overset{+}{a}_{l_1\sigma} a_{l_3\sigma} + \sum_{l,\, l_1 \neq l_2,\, \sigma}{}' F(l_1 l l l_2) \overset{+}{a}_{l_1\sigma}(N_l - 1) a_{l_2\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{l_1 \neq l_4,\, l_2 \neq l_3 \\ \sigma_1,\, \sigma_2}} F(l_1 l_2 l_3 l_4) \overset{+}{a}_{l_1\sigma_1} \overset{+}{a}_{l_2\sigma_2} a_{l_3\sigma_2} a_{l_4\sigma_1},$$

$$\beta(l_1 l_2) = \int d^3r w_{l_1}(r) \left[\frac{p^2}{2m} + V(r)\right] w_{l_2}(r) + \sum_l F(l_1 l l l_2),$$

$$F(l_1 l_2 l_3 l_4) = \int d^3r_1 d^3r_2 \frac{e^2}{|r_1 - r_2|} w_{l_1}(r_1) w_{l_2}(r_2) w_{l_3}(r_2) w_{l_4}(r_1),$$

$$N_l = \sum_\sigma a_{l\sigma}{}^+ a_{l\sigma}, \qquad \sum_l N_l = N. \tag{1}$$

We have retained in (1) terms pertaining only to the lowest half-filled band. Its Wannier functions are denoted $w_l(r)$. We shall discuss below the question of allowance for terms with Wannier functions of the higher energy bands. H_0 includes terms that do not contain overlaps of the Wannier functions from different centers, H_1 includes the overlap of only the nearest neighbors (the summation is over l'—the nearest neighbors of l), and H_2 contains the overlap of the nearest neighbor from the Coulomb energy and all the overlaps of the non-nearest centers.

The eigenfunctions of H_0 are functions with a definite number of electrons N_l at the center l. The ground state is 2^N-fold degenerate in the spins, and includes functions with a single electron at each center. The energy of such homopolar states is E_0; we shall henceforth denote their space by C. The excited (polar) states of H_0 are separated from the ground state by a gap $u_1 = F(llll) - F(ll'l'l)$. The perturbation H′ lifts the spin degeneracy of the homopolar states, and they go over into states called quasi-homopolar. We shall henceforth consider only the quasi-homopolar states. In crystals with transition-metal ions and in molecules, these include the ground and the lowest excited states of the Hamiltonian (1).

In copper salts, the coefficient $\beta(ll')$ in H_1 is two orders of magnitude smaller than the parameter of the zero-order Hamiltonian u_1, and the coefficients in H_1 constitute not more than $0.1\beta(ll')$. In antiferromagnets with iron-group transition-element ions $\beta(ll')u_1^{-1} \approx 0.1$ and H_2 is, as before, lower by one order than the term H_1. In such cases we can confine ourselves to perturbation theory for the degenerate states C. In the lower orders of perturbation theory, the secular equation for the determination of the stable combinations C_i and the energies corresponding to them was obtained by Bogolyubov for the polar model of metals[1] and by Andersen for antiferromagnets.[2] The secular equation has the form of a Schrödinger equation in which the Heisenberg spin Hamiltonian plays the role of the effective Hamiltonian in C-space. Bogolyubov also found a method of calculating the operator of any physical quantity, projected on the space C, in lowest orders of perturbation theory in H′ for quasi-homopolar states.

In molecules, H_1 is of the same order as H_0 ($\beta(ll')u_1^{-1} \approx 0.7$), and we cannot confine ourselves to the lowest order of perturbation theory in H_1. However, the parameters in H_2 do not exceed $0.1\beta(ll')$, and this circumstance enables us to find for molecules, too, the effective spin Hamiltonian and the projected (on the spin-function space) operators of the physical quantities of quasi-homopolar levels.

We shall construct below a perturbation-theory series in H′ for the exact secular equation of the degenerate levels C of the Hamiltonian (1). By using the perturbation-theory series, we shall show that in the approximation $H = H_0 + H_1$ the current operator on the space of the quasi-homopolar functions is equal to zero and that the electron density at each center is equal to unity. We shall subsequently propose a method for calculating the spin Hamiltonian and the projected operators of the physical quantities for molecules with conjugated bonds.

PERTURBATION THEORY FOR DEGENERATE LEVELS

Our problem is to obtain a perturbation theory series in H′ for the matrix h of the secular equation

$$(h-E)C = 0, \tag{2}$$

such as to obtain the exact stable combinations C_i and the energy E_i of the quasi-homopolar states. The methods of stationary perturbation theory[1-3] are not suitable for this purpose, since they give a secular equation (2) with h dependent on E. In [4, 5], the formalism of the S-matrix with adiabatic inclusion of the interaction was used for the construction of the perturbation-theory of the degenerate level. In the case of the zero-order quadratic Hamiltonian, the singularities arising in this case, of the type δ^{-n} as $\delta \to 0$, were eliminated by Morita[4] by a diagram technique. The diagram technique cannot be applied to a four-fermion zero-order Hamiltonian (1). Therefore, using Morita's main idea,[4] but without resorting to diagram technique, we shall construct a perturbation theory which is valid for any type of zero-order Hamiltonian. At the same time we improve the form of the exact secular equation obtained in [4], making the matrix h of this equation hermitian.

We shall use the S-matrix formalism with adiabatic switching of the interaction.[5] If C_i' are stable wave functions of the Hamiltonian H_0 with respect to the perturbation H′, then we have for them the Schrödinger equation

$$(H_0 + H' - E_i)S(0)C_i' = 0,$$

$$S(0) = T\exp\left[-i\int\limits_{-\infty}^{0} H_p'(\tau)\,d\tau\right],$$

$$H_p'(\tau) = \exp(iH_0\tau)H'\exp(-iH_0\tau + \delta\tau), \quad \delta \to 0. \tag{3}$$

Let P be the operator of projection on the space C. Acting with this operator from the left on (3) and recognizing that $H_0C_i' = E_0C_i$, we obtain

$$(PH'SP - E_i'PSP)C_i' = 0, \quad E_i' = E_i - E_0. \tag{4}$$

Here and below we shall denote S(0) simply by S. Integration with respect to τ transforms the matrix SP into

$$S = \sum_{n=0}^{\infty} S_n, \qquad S_0P = P,$$

$$S_n = (-1)^n \frac{1}{H_0 - E_0 - in\delta} H' \frac{1}{H_0 - E_0 - i(n-1)\delta}$$

$$\times H' \ldots \frac{1}{H_0 - E_0 - i\delta} H'P. \tag{5}$$

When (5) is substituted in (4) we obtain in the expressions for PSP and PH′SP singularities of the type δ^{-n} as $\delta \to 0$. It is shown in [4] that when H_0

is quadratic in the electron operators the matrix SP can be represented in the form

$$SP = S_R PSP = S_R V, \quad V \equiv PSP, \tag{6}$$

where the matrix S_R is regular when $\delta \rightarrow 0$, and all the singularities are contained in the matrix V. It is shown in the Appendix that (6) is valid for arbitrary H_0 and H'. We can then rewrite (4) in the form

$$(PH'S_R P - E_i')VC_i' = 0 \tag{7a}$$

or

$$(PH'S_R P - E_i')C_i = 0. \tag{7b}$$

Equation (7b), obtained in [4] for H_0 quadratic in the electron operators, has, however, an essential shortcoming. Inasmuch as V is not a unitary matrix, the effective Hamiltonian of the secular equation (4)

$$h' = PH'S_R P \tag{8}$$

is in general not hermitian, and its eigenfunctions are not orthonormal. From

$$PS^+SP = V^+PS_R^+ S_R PV = 1$$

it follows that the unitary matrix will be

$$U = (PS_R^+ S_R P)^{1/2} V = (VV^+)^{-1/2} V. \tag{9}$$

Denoting $(VV^+)^{1/2}$ by Γ, we obtain $V = \Gamma U$ and from (7a)

$$(h' - E_i')\Gamma U C_i' = 0. \tag{10}$$

Putting here $UC_i' = C_i$ and multiplying (10) from the left by Γ^{-1}, we obtain a secular equation with a hermitian effective Hamiltonian

$$(h - E_i')C_i = 0, \quad h = \Gamma^{-1} PH'S_R P\Gamma = \Gamma^{-1} h' \Gamma. \tag{11}$$

The exact wave function corresponding to the energy E_i' is

$$\Psi_i = SC_i' = S_R VC_i' = S_R \Gamma C_i.$$

Therefore the matrix elements of any operator G for states Ψ_i can be found with the aid of the functions C_i. The operator G projected on the space C is

$$g = \Gamma PS_R^+ GS_R P\Gamma. \tag{12}$$

To calculate the perturbation-theory series for the effective Hamiltonian h, it is convenient to use the somewhat different form given in [5] for the singular Hamiltonian h_s,

$$h_s = i\delta PS^{-1} \frac{\partial S}{\partial \lambda} P, \tag{13}$$

where λ is a parameter of H', which will be set equal to unity in the final results. Using (6) and separating from (13) the singularities with the aid of the unitary matrix (9), we obtain

$$h = Uh_s U^{-1} = i\delta\Gamma^{-1} \frac{\partial V}{\partial \lambda} V^{-1}\Gamma. \tag{14}$$

We write out the perturbation-theory series for (14) accurate to third order in H' inclusive:

$$\begin{gathered} h = h_1 - h_2 + h_3 - {}^1/_2(h_1 h_2' + h_2' h_1), \\ h_1 = PH'P, \qquad h_2 = PH' \frac{1-P}{H_0 - E_0} H'P, \\ h_2' = PH' \frac{1-P}{(H_0 - E_0)^2} H'P, \\ h_3 = PH' \frac{1-P}{H_0 - E_0} H' \frac{1-P}{H_0 - E_0} H'P. \end{gathered} \tag{15}$$

If $h_1 = 0$, then, accurate to fourth order in H'

$$\begin{gathered} h = -h_2 + h_4 - {}^1/_2(h_2 h_2' + h_2' h_2), \\ h_4 = PH' \frac{1-P}{H_0 - E_0} H' \frac{1-P}{H_0 - E_0} H' \frac{1-P}{H_0 - E_0} H'P. \end{gathered} \tag{16}$$

In the case of a quadratic zero-order Hamiltonian, the terms in h_3 and h_4, corresponding to nonconnective diagrams, cancel out similar terms in the last terms of (15) and (16). No complete cancellation takes place for H_0 from (1). The remaining terms are written out below (see (20)). If we deal with a nondegenerate level E_0 of the zero-order Hamiltonian, then (14) yields the perturbation-theory series for the energy in the Rayleigh-Schrödinger form.[3]

CURRENT AND ELECTRON DENSITY IN QUASI-HOMOPOLAR STATES

Let us investigate with the aid of the series for the effective Hamiltonian h and the projected operators the current and the electron density of the quasi-homopolar states in the approximation $H = H_0 + H_1$. Let the ion lattice be such that any closed line made up of segments joining the nearest neighboring centers contains only an even number of these segments (such are the lattices of most molecules and antiferromagnets). Then the series for h contains only even powers of H_1, and h is an even function of $\beta \equiv \beta(ll')$. Γ, E_i, and C_i will also be even functions of β. Let us consider the parity with respect to β of the operators of other quantities. It is clear that the electron density at the center l is $nl(\beta) = nl(-\beta)$, but if we project the current operator **J** on the space C in the nearest-neighbor approximation

$$\mathbf{J} = \sum_{l, l', \sigma} i\mathbf{I}(ll')(a_{l\sigma}^+ a_{l'\sigma} - a_{l'\sigma}^+ a_{l\sigma}), \tag{17}$$

then the projected operator is $\mathbf{j}(\beta) = -\mathbf{j}(-\beta)$.

We now proceed to the hole representation, choosing as vacuum the state in which all the localized states are occupied by two electrons. The homopolar functions $\tilde{C}$ in the new representations are obtained from the functions C by replacing the operators $a^+_{l\sigma}$ by the hole-creation operators $b^+_{l,-\infty}$. In the operators H_0, H_1, N_l, and $\mathbf{J}$ it is necessary to replace the electron operators by hole operators $b_{l\sigma} = a^+_{l\sigma}$ and $b^+_{l\sigma} = a_{l\sigma}$. It is easy to see that in H_0 and $\mathbf{J}$ this substitution is equivalent to the substitution $a_{l\sigma} \rightarrow b_{l,-\sigma}$ and $a^+_{l\sigma} \rightarrow b_{l,-\sigma}$, and in H_1 it is necessary in addition to reverse the sign of β. For the number of holes ν_l we have $\nu_l = 2 - n_l$. Denoting the operators G in the hole representation by $\tilde{G}$, we obtain for the current

$$\begin{aligned}\mathbf{j}(\beta) &= \tilde{\Gamma}\tilde{P}\tilde{S}_R{}^+\tilde{\mathbf{J}}\tilde{S}_R\tilde{P}\tilde{\Gamma}\\ &= \Gamma(-\beta)\,PS_R{}^+(-\beta)\,\mathbf{J}S_R(-\beta)\,\Gamma(-\beta)\\ &= \mathbf{j}(-\beta) = -\mathbf{j}(\beta) = 0. \end{aligned}\qquad (18)$$

The current for quasi-homopolar states becomes different from zero if allowance is made for H_2 in (1), and for the contribution of the non-nearest neighbors in the current operator $\mathbf{J}$. Apparently, Kohn did not take these terms into account and obtained $j = 0$ for the quasi-homopolar states.[6]

The momentum is proportional to the current, and therefore for molecules with conjugated bonds the result (18) shows that the matrix elements of allowed transitions between quasi-homopolar states in an electromagnetic field is determined by the terms H_2 and by the overlap of the non-nearest neighbors in the current operator. The corresponding absorption lines will be approximately two orders of magnitude weaker than the lines of other allowed transitions.

For the electron density at the center l we have

$$n_l(\beta) = 2 - \nu_l(\beta) = 2 - n_l(-\beta) = 2 - n_l(\beta) = 1. \qquad (19)$$

This result is nontrivial for those molecules for which the same conclusion does not follow from considerations of spatial symmetry.

SPIN HAMILTONIAN OF ANTI-FERROMAGNETS AND MOLECULES

The functions in the space C differ from one another only in the spin coordinates, therefore the effective Hamiltonian and all the operators (12) projected on C can be expressed in terms of the spin-$^1/_2$ operators $\mathbf{S}_l$.[1] For a cubic lattice with $H_2 = 0$, accurate to fourth order of perturbation theory in H', we obtain from (16)

$$\begin{aligned} h = {} & \sum_{l,l'}\mathcal{J}_1\left(\mathbf{S}_l\mathbf{S}_{l'} - \frac{1}{4}\right) + \sum_{l,l''}\mathcal{J}_2'\left(\mathbf{S}_l\mathbf{S}_{l''} - \frac{1}{4}\right)\\ & + \sum_{l,l_d'}\mathcal{J}_2''\left(\mathbf{S}_l\mathbf{S}_{l_d'} - \frac{1}{4}\right) + \sum_{ll' \neq l_1 l_1'} \frac{4\beta^4[u_1(\delta_1+\delta_2) - \delta_1\delta_2]}{u_1{}^3(2u_1+\delta_1)(2u_2+\delta_2)}\\ & \times\left(\mathbf{S}_l\mathbf{S}_{l'} - \frac{1}{4}\right)\left(\mathbf{S}_{l_1}\mathbf{S}_{l_1'} - \frac{1}{4}\right),\\ \mathcal{J}_1 = {} & \frac{2\beta^2}{u_1} - \frac{8\beta^4}{u_1{}^3} + \frac{8\beta^4}{u_1{}^2}\left(\frac{1}{u_2''} - \frac{1}{u_1}\right) + \frac{32\beta^4}{u_1{}^2}\left(\frac{1}{u_2'} - \frac{1}{u_1}\right),\\ \mathcal{J}_2' = {} & \frac{2\beta^4}{u_1{}^2}\left(\frac{2}{u_1} - \frac{1}{u_2'}\right), \qquad \mathcal{J}_2'' = \frac{4\beta^4}{u_1{}^2}\left(\frac{2}{u_1} - \frac{1}{u_2''}\right),\\ u_2' = {} & F(llll) - F(ll''l''l),\ u_2'' = F(llll) - F(ll_d'l_d'l). \end{aligned}\qquad (20)$$

The summation in the second term of (20) goes over l''—the neighbors of l next to the nearest neighbors l' along the directions (100), (010), and (001) of the lattice. In the third term, the summation is over l_d'—the nearest neighbors of l in the directions of the diagonal faces of the cube (the directions (110), (101), and (011)). δ_1 and δ_2 are the differences between the energies of the intermediate states with two pairs of electrons on the two holes at the centers l, l', l_1 and l_1' and the energies $2u_1$. For four centers located one behind the other along a line, $\delta_1 = -\delta_2 = 2u_2 - u_1 - u_3$, where u_3 is the energy of a state with a hole at the first center and a pair of electrons at the fourth center. The values of δ_1 and δ_2 decrease rapidly with increasing distance between centers (ll') and (l_1l_1'), and therefore the contribution of the last term of (20) to the energy is proportional to the total number of electrons N. The foregoing results are valid, with simple modifications, also for crystals containing ions with several electrons in the unfilled shell. In this case the space C consists of functions with higher spins.

In oxides of iron-group transition elements,[2] $\beta u_1^{-1} \approx 0.1$ and u_2' and u_2'' are close to u_1. Therefore the corrections to the Heisenberg spin Hamiltonian, calculated in second order of perturbation theory in H', are small, and the coefficients in them do not exceed $0.05\mathcal{J}_1$. The first non-vanishing contribution to the current $\mathbf{j}$, calculated from formula (12), is made only by the terms of second order in H', which contain H_2 or the overlap of the non-nearest neighbors in the current operator $\mathbf{J}$.[1,7] On the basis of the result (18) we can state that the corrections of next order perturbation theory contain an additional factor $\beta^2 u_1^{-2} \approx 0.01$.

In hydrocarbons with conjugated bonds, $\beta u_1^{-1} \approx 0.7$[8] and we cannot confine ourselves to lowest order of perturbation theory. However, for a perturbation $H' = H_1 + H_2$ with H_2 small it is possible to sum that infinite set of terms of perturbation-theory series which gives the main contribution to the effective Hamiltonian and the projected operators (12). To this end we calculate exactly the contribution made to h by the interaction of the nearest lattice points (ll'), summing in the series all the terms containing the operators of these two points only. The summation can be performed with the aid of the series for (14), but there is no need for this. The same result can be obtained by solving exactly the Schrödinger equation with Hamiltonian (1) for two centers (ll') and finding the energies E_i and the functions Ψ_i of the quasi-homopolar states of the two electrons. Projecting Ψ_i on the space C, we obtain a non-orthonormal system of functions $P\Psi_i = PS_R\Gamma C_i = \Gamma C_i$. Extracting the root of the matrix $(\Gamma^2)_{ik} = (\Gamma C_i)^+(\Gamma C_k)$, we get Γ and with the aid of the operation $\Gamma^{-1}(\Gamma C_i)$ we obtain the required system of eigenfunctions C_i of the secular equation (11). Knowledge of E_i and C_i allows us to find the spin Hamiltonian of the two centers:

$$h_{ll'} = \mathcal{J}_1(\mathbf{S}_l\mathbf{S}_{l'} - {}^1/_4),$$

$$\mathcal{J}_1 = {}^1/_2\{[[(u_1 - F(ll'll')]^2 + 16u_1^{-2}[\beta - F(llll')]^2]^{1/2} - u_1\} - {}^3/_2F(ll'll'). \tag{21}$$

Summing over all the centers (ll'), we obtain h(2)—the effective Hamiltonian in the nearest-neighbor approximation.

We now determine the contribution of those terms of the perturbation-theory series, which contain the operators of the three centers $(ll'l'')$. To this end it is necessary to solve the Schrödinger equation with Hamiltonian (1) for these three centers, obtain the spin Hamiltonian by the program indicated above, and subtract from it the contribution of the nearest neighbors (ll') and $(l'l'')$.[1)] If we disregard H_2, we get

$$h_{ll'l''} = -({}^2/_3\varepsilon' + \mathcal{J}_1)(\mathbf{S}_l\mathbf{S}_{l'} + \mathbf{S}_{l'}\mathbf{S}_{l''} - {}^1/_2) + ({}^1/_3\varepsilon' - \varepsilon'')(\mathbf{S}_l\mathbf{S}_{l''} - {}^1/_4),$$

$$\varepsilon'' = {}^1/_2(u_1 - \sqrt{u_1^2 + 8\beta^2}) \tag{22}$$

and ϵ' is the smallest root of the equation

$$\varepsilon^3 - \varepsilon^2(u_1 + u_2) + \varepsilon(u_1u_2 - 8\beta^2) + 6u_2\beta^2 = 0.$$

Summing over all triplets $(ll'l'')$, we obtain h(3)—the contribution made to h by the triple interactions. Continuing further, this process yields for h a series in the interactions of the pairs, triplets, etc.:

$$h = \sum_{n=2}^{N} h(n). \tag{23a}$$

The series (23a) contains the spin operators $\mathbf{S}_l$ in the following combinations:

$$(\mathbf{S}_{l_1}\mathbf{S}_{l_2} - {}^1/_4), \quad (\mathbf{S}_{l_1}\mathbf{S}_{l_2} - {}^1/_4)(\mathbf{S}_{l_3}\mathbf{S}_{l_4} - {}^1/_4), \ldots \tag{23b}$$

It is possible to obtain in similar fashion the series for the projected operator of any other physical quantity (12).

Let us investigate the convergence of the series (23a). If the centers are linearly arranged with $H_2 = 0$, and the parameters of H_0 and H_1 are those characteristic of conjugated hydrocarbons ($\beta u_1^{-1} = 0.65$, $u_2u_1^{-1} = 1.7$, $u_3u_1^{-1} = 2.2$), then the coefficients at the spin operators (23b) amount to $\approx 0.13\mathcal{J}_1$ in h(3) and to $0.03\mathcal{J}_1$ and $0.01\mathcal{J}_1$ in h(4) and h(5), respectively. In this case the main contribution to the spin Hamiltonian is made by the pair and triplet interactions of the centers. Allowance for H_2 changes the estimates significantly.

For a ring of six centers we obtain the same relation between h(2), h(3), and h(4). However, owing to the specific nature of this lattice, the terms h(4), h(5), and h(6) are approximately equal, and taken together make a contribution of the same order as h(3). The pair interactions h(2) remain decisive, as before. This circumstance was noticed by Mattheiss,[9] who carried out numerical calculations for a ring of six hydrogen atoms and chose empirically a spin Hamiltonian with interaction of neighboring spins, which describes sufficiently well the quasi-homopolar levels of the H_6 system at distances between centers $R \geq 2$ atomic units.

Antiferromagnets constitute that limiting case of Hamiltonian (1), in which the term H' is small compared with H_0. In this situation, the rapid convergence of the series (23a) is attributed to the fact that h(n) contains the perturbation H' raised to the power n. We investigate, for a linear lattice, another limiting case, when H_0 and H_2 are small. When $H_0 = H_2 = 0$ the spin Hamiltonian, in the approximation of paired and triple interactions is $(\beta = 1)$.

$$h = 1.88 \sum_l (\mathbf{S}_l\mathbf{S}_{l+1} + \mathbf{S}_{l+1}\mathbf{S}_{l+2} - {}^1/_2) + 0.47 \sum_l (\mathbf{S}_l\mathbf{S}_{l+2} - {}^1/_4). \tag{24}$$

The coefficients in h(4) amount approximately to 0.1. With the aid of the Hamiltonian (24) we can

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[1)] For two and three centers, the parameters of the spin Hamiltonian are determined only by the values of the energies E_i of the quasi-homopolar levels.

now find the energies of the quasi-homopolar states for a cyclic lattice with $N = 2(2n + 1)$ centers at $n \gg 1$. An exact solution for the one-dimensional spin Hamiltonian with the nearest-spin interaction is known.[10, 11] Estimating the contribution of the second term of (24) by the method proposed in [12], we obtain for the ground-state energy per center ϵ_0 and for the first-excitation energy ϵ_1:

$$\varepsilon_0 = -0.69\mathcal{J}_1 + \left(\frac{2}{\pi^2} - \frac{1}{4}\right)\mathcal{J}_2 \approx -1.23,$$

$$\varepsilon_1 = \frac{1}{2}\pi\left(\mathcal{J}_1 - \frac{8}{\pi^2}\mathcal{J}_2\right)\sin\frac{\pi}{2n+1} \approx \frac{2.16\pi}{2n+1}. \qquad (25)$$

The exact solution of the Schrödinger equation with Hamiltonian (1) yields for $H_0 = H_2 = 0$

$$\varepsilon_0 = -\frac{4}{\pi} \approx -1.27,$$

$$\varepsilon_1 = 2\cos\frac{\pi n}{2n+1} - 2\cos\frac{\pi(n+1)}{2n+1} \approx \frac{2\pi}{2n+1}. \qquad (26)$$

From a comparison of (25) with (26) we see that in this limiting case the series (23a) converges quite rapidly.

In all the cases under consideration the term H_2 is small, and this explains the rapid decrease of the terms of the series (23a). Indeed, H_1 couples by transitions only the neighboring centers of the lattice. This property is retained also in the projected Hamiltonian h—only the interaction of the nearest neighboring centers is large in the latter. The interaction H_0 decreases the role of the transitions for the quasi-homopolar states, and therefore the convergence of the series (23a) improves with increasing H_0. With increasing parameters in H_2, the terms of the series (23a) no longer decrease so rapidly. Therefore the approximation of paired and triple interactions is not applicable, for example, to metals or to the ring H_6 at distances between centers $R = 1$ atomic units (in this case $\beta = -0.67$, $\beta(l, l + 2) = 0.15$, and $\beta(l, l + 3) = -0.20$).[9]

Thus, if we are interested only in quasi-homopolar states of the Hamiltonian (1), then information concerning them can be obtained by solving the Schrödinger equation with spin Hamiltonian. At this stage, the proposed method is similar in form to the Heitler-London method. Essentially, however, they are different since the Heitler-London method is confined only to the space of homopolar functions, while the proposed method allows us to take into account, with the required degree of accuracy, the addition of polar states. As in the Heitler-London method, the solution of the Schrödinger equation with spin Hamiltonian becomes simpler if we use Young's scheme[13] for breaking down the space C into subspaces with definite total spin of the system.

In the scheme proposed above, the initial data for the numerical calculations can be the Wannier functions $w_{nl}(r)$. If they are known, then we can take into account, besides the transitions inside the lowest half-filled band, also transitions to higher energy bands. Such transitions change somewhat the values of the spin-Hamiltonian parameters. However, at the present time we cannot construct any complete system of single-electron wave functions of a crystal or molecule and find with its help the Wannier functions $w_{nl}(r)$. We can therefore follow a different path—determine the unknown parameters of the spin Hamiltonian and the projected operators from experiment. The rapid convergence of the series (23a) makes it possible to predict, from experimental data for molecules with a small number of centers, the properties of more complicated molecules made up of the same centers. Proceeding in this manner, we partially take into account also the contribution of transitions to higher energy bands.

The proposed method makes it possible to take into account the $\pi-\sigma$ electron interaction and can be extended to include molecules with heteroatoms in the conjugation chain.

The author is deeply grateful to D. A. Kirzhnits and G. M. Vagradov for a discussion of problems connected with perturbation theory for degenerate levels, and the participants of the seminars of V. L. Ginzburg and N. D. Sokolov for valuable remarks.

APPENDIX

It follows from the definition $SP = S_R PSP$ that $PS_R P = 1$, so that it is sufficient to show that $(1 - P)SP = (1 - P)S_R PSP$. If we expand S_R and S in a perturbation theory series in H', then

$$(1-P)S_n P = (1-P)\sum_{m=1}^{n}(S_R)_m P S_{n-m} P, \quad (S_R)_0 = 1. \quad (A.1)$$

From (5) we obtain

$$(1-P)S_n P = F_n{}^1 S_{n-1} P = F_n{}^1 P S_{n-1} P + F_n{}^1 (1-P) S_{n-1} P,$$

$$F_n{}^1 = -(1-P)(H_0 - E_0 - in\delta)^{-1} H'. \qquad (A.2)$$

Putting here $n = 1$, we obtain a matrix $(S_R)_1 = F_1^1$ which is regular in δ. We continue further

$$(1-P)S_n P = (S_R)_1 P S_{n-1} P + (F_n{}^1 - F_1{}^1) P S_{n-1} P$$

$$+F_n^1(1-P)S_{n-1}P=(S_R)_1PS_{n-1}P+F_n^2S_{n-2}P,$$

$$F_n^2=(F_n^1-F_1^1)\frac{1}{i(n-1)\delta}H'$$
$$-F_n^1(1-P)[H_0-E_0-i(n-1)\delta]^{-1}H'. \tag{A.3}$$

Putting n = 2 in (A.3), we obtain $(S_R)_2$. Continuing the process of separating $(S_R)_m$, we obtain the recurrence formula

$$F_n^{m+1}=(F_n^m-F_m^m)\frac{1}{i(n-m)\delta}H'-F_n^m(1-P)$$
$$\times[H_0-E_0-i(n-m)\delta]^{-1}H', \tag{A.4}$$
$$(S_R)_m=F_m^m.$$

Let us prove that F_n^m are regular operators. To this end it is sufficient to show that they are of the form (m ≤ n!)

$$F_n^m(\delta)=\sum_{k=0}^{n-m}A_{k,m}P_{k,m}(n)\delta^k+o(\delta^{n-m}), \tag{A.5}$$

where $P_{k,m}(n)$ is a polynomial of degree k in n, with coefficients that depend on m, and $A_{k,m}$ are operators of degree m in H′ and do not depend on n. The proof of (A.5) is by induction from the recurrence formula (A.4). Indeed, F_n^1 from (A.2) is of the same form as (A.5):

$$F_n^1=(1-P)\sum_{k=0}^{n-1}(E_0-H_0)^{-(k+1)}H'n^k\delta^k+o(\delta^{n-1}). \tag{A.6}$$

On the other hand, if F_n^m is of the form (A.5), then in F_n^{m+1} from (A.4) the second term contains δ and n only in the combination (n − m)δ, i.e., it increases simultaneously the powers δ and n without changing the form of (A.5), and the first term equal to

$$\sum_{k=0}^{n-m}(-i)A_{k,m}H'\frac{P_{k,m}(n)-P_{k,m}(m)}{n-m}\delta^{k-1}+o(\delta^{n-m-1})$$
$$=\sum_{k=1}^{n-m}(-i)A_{k,m}H'P_{k-1,m}\delta^{k-1}+o(\delta^{n-m-1})$$
$$=\sum_{k=0}^{n-m-1}(-i)A_{k+1,m}H'P_{k,m}(n)\delta^k+o(\delta^{n-m-1}),$$

inasmuch as $P_{0m}(n)-P_{0m}(m)=0$ and $P_{k-1,m}(n)=(n-m)^{-1}[P_{k,m}(n)-P_{k,m}(m)]$. We see that even the first term has the form (A.5). The regularity of F_n^m and consequently of $(S_R)_m=F_m^m$ is thus proved.

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Translated by J. G. Adashko
29