QUASIHOMOPOLAR ELECTRON LEVELS IN CRYSTALS AND MOLECULES

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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 VO₃ (electron in d-shell of the V⁴⁺ ion), copper salts with Cu²⁺ ion (hole in the d-shell), and molecules of hydrocarbons with conjugated bonds such as the polyenes or benzene (pₓ-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 \( \psi_{n,l} \), 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

\[
H = H₀ + H', \quad H' = H₁ + H₅,
\]

\[
H₀ = \frac{1}{2} \sum_{l,l'} \sum_{\sigma} F(l_{l}l_{l'}l_{l'}) (N_l - 1) (N_{l'} - 1) + E₀,
\]

\[
H₁ = \sum_{l,l',\sigma} \beta(l_{l}l_{l'}l_{l'}) a_{l_{l'}\sigma}^{+} a_{l_{l}\sigma},
\]

\[
H₂ = \sum_{l,l',\sigma} \beta(l_{l}l_{l'}l_{l'}) a_{l_{l'}\sigma}^{+} a_{l_{l}\sigma} + \sum_{l,l',\sigma} F(l_{l}l_{l'}l_{l'}) (N_l - 1) a_{l_{l'}\sigma}^{+} a_{l_{l}\sigma} + \frac{1}{2} \sum_{l,l',\sigma} \sum_{\sigma'} F(l_{l}l_{l'}l_{l'}) a_{l_{l'}\sigma}^{+} a_{l_{l}\sigma},
\]

\[
\beta(l_{l}l_{l'}l_{l'}) = \frac{\psi_{l_{l'}l_{l'}}(r)}{\psi_{l_{l}l_{l'}}(r)} + \frac{\psi_{l_{l'}l_{l'}}(r)}{\psi_{l_{l}l_{l'}}(r)} - \frac{\psi_{l_{l}l_{l'}}(r)}{\psi_{l_{l'}l_{l'}}(r)} - \frac{\psi_{l_{l'}l_{l'}}(r)}{\psi_{l_{l}l_{l'}}(r)} + \psi_{l_{l}l_{l'}}(r).
\]

We have retained in (1) terms pertaining only to the lowest half-filled band. Its Wannier functions are denoted \( \psi_{l}(r) \). We shall discuss below the question of allowance for terms with Wannier functions of the higher energy bands. \( H₀ \) includes terms that do not contain overlaps of the Wannier functions from different centers, \( H₁ \) includes the overlap of only the nearest neighbors (the summation is over \( l' \)—the nearest neighbors of \( l \)), and \( H₂ \) contains the overlap of the nearest neighbor from the Coulomb energy and all the overlaps of the non-nearest centers.

The eigenfunctions of \( H₀ \) 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 \( E₀ \); we shall henceforth denote their space by \( C \). The excited (polar) states of \( H₀ \) are separated from the ground state by a gap \( \Delta = F(lll') - F(ll'') \). 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 $\beta(H')$ in $H_1$ is two orders of magnitude smaller than the parameter of the zero-order Hamiltonian $u_i$, and the coefficients in $H_1$ constitute not more than 0.1$\beta(H')$. In antiferromagnets with iron-group transition-element ions $\beta(H')u_i^2 \approx 0.1$ 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 $C_1$ and the energies corresponding to them was obtained by Bogolyubov for the polar model of metals$^{[11]}$ 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 $C_i$ in lowest orders of perturbation theory in $H'$ for quasi-homopolar states.

In molecules, $H_1$ is of the same order as $H_0$ ($\beta(H')u_i^2 \approx 0.7$), 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$\beta(H')$, 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

$$ (h - E)C = 0, \quad (2) $$

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$^{[11-13]}$ are not suitable for this purpose, since they give a secular equation (2) with $h$ dependent on $E$. In $^{[14,5]}$, 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 $\delta^{-\infty}$ 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

$$ (H_0 + H' - E_0)S(0)C' = 0, $$

$$ S(0) = T \exp \left[ -i \frac{1}{\hbar} \int_{-\infty}^{\infty} H'_p(\tau) d\tau \right], $$

$$ H'_p(\tau) = \exp (iH_0)H' \exp (-iH_0+\delta\tau), \quad \delta \to 0. \quad (3) $$

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

$$ (PH'SP - E'_i PSP)C'_i = 0, \quad E'_i = E_i - E_0. \quad (4) $$

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

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

$$ S_n = (-1)^n \frac{1}{H_0 - E_0 - in\delta} H'_0 \frac{1}{H_0 - E_0 - i(n-1)\delta} \times H'_0 \ldots H'_0 \frac{1}{H_0 - E_0 - i\delta} \frac{1}{H_0 - E_0 - i\delta} H'_P. \quad (5) $$

When (5) is substituted in (4) we obtain in the expressions for PSP and PH'SP singularities of the type $\delta^{-n}$ as $\delta \to 0$. It is shown in $^{[4]}$ that when $H_0$
is quadratic in the electron operators the matrix
\[ SP = S_nPSP = S_nV, \quad V = PSP, \]
where the matrix \( S_n \) is regular when \( \delta \to 0 \),
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
\[ (PH'S_nP - E_{i'})VC_i' = 0 \quad (7a) \]
or
\[ (PH'S_nP - E_{i'})C_i = 0. \quad (7b) \]
Equation (7b), obtained in [4] for \( H_0 \) quadratic
in the electron operators, has, however, an essen­
tial shortcoming. Inasmuch as \( V \) is not a unitary
matrix, the effective Hamiltonian of the secular
equation (4)
\[ h' = PH'S_nP \]
is in general not hermitian, and its eigenfunctions
are not orthonormal. From
\[ PS+SP = V+PS_JiSnPV = 1 \]
it follows that the unitary matrix will be
\[ U = (PS^2_nPS_nP)^{1/2}V = (VV^*)^{-1/2}V. \]
Denoting \( (VV^*)^{1/2} \) by \( \Gamma \), we obtain \( V = \Gamma U \)
and from (7a)
\[ (h' - E_{i'})\Gamma UC_i' = 0. \]
Putting here \( UC_i' = C_i \) and multiplying (10) from
the left by \( \Gamma^{-1} \), we obtain a secular equation with a hermitian effective Hamiltonian
\[ (h' - E_{i'})C_i = 0, \quad h = \Gamma^{-1}PH'S_nP\Gamma = \Gamma^{-1}h\Gamma. \]
The exact wave function corresponding to the
energy \( E_i' \) is
\[ \Psi_i = SC_i' = S_nVC_i' = S_n\Gamma C_i. \]
Therefore the matrix elements of any operator \( G \)
for states \( \Psi_i \) can be found with the aid of the func­
tions \( C_i \). The operator \( G \) projected on the space \( C \) is
\[ g = TPS_nGSP\Gamma. \]
To calculate the perturbation-theory series for the
effective Hamiltonian \( h \), it is convenient to use
the somewhat different form given in [3] for the
singular Hamiltonian \( h_{s} \),
\[ h_{s} = i\delta S^{-1}\frac{\partial S}{\partial h}P, \]
where \( \lambda \) 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
\[ h = UhU^{-1} = i\delta V^{-1}\frac{\partial V}{\partial h}V^{-1} \Gamma. \]
We write out the perturbation-theory series for (14) accurate to third order in \( H' \) inclusive:
\[ h = h_1 - h_2 + h_3 - \frac{1}{2}(h_2h_2' + h_2' h_2), \]
\[ h_1 = PH'P, \quad h_2 = PH'1 - P \frac{H_0 - E_0}{H_0 - E_0} H'P, \]
\[ h_3 = PH'1 - P \frac{H_0 - E_0}{H_0 - E_0} H'P \frac{H_0 - E_0}{H_0 - E_0} H'P. \]
If \( h_1 = 0 \), then, accurate to fourth order in \( H' \)
\[ h = -h_2 + h_3 - \frac{1}{2}(h_2h_2' + h_2' h_2), \]
\[ h_4 = PH'1 - P \frac{1}{H_0 - E_0} H'1 - P \frac{H_0 - E_0}{H_0 - E_0} H'P. \]
In the case of a quadratic zero-order Hamiltonian,
the terms in \( h_3 \) and \( h_4 \) corresponding to non­
connective diagrams, cancel out similar terms in the
last terms of (15) and (16). No complete cancellation takes place for \( H_0 \) from (1). The remain­
ing 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 perturba­
tion-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 near­
est neighboring centers contains only an even num­
ber 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 \( \{3 \). Then \( \{3 \) will also be even functions of \( \{3 \).
It is clear that the electron den­
sity at the center \( l \) is \( n(l) = n(-l) \), but if we
project the current operator \( J \) on the space \( C \) in
the nearest-neighbor approximation
\[ J = \sum_{l',\sigma} a_{l,l'}^{\dagger}(a_{l\sigma}a_{l\sigma} - a_{l\sigma}^{\dagger}a_{l\sigma}), \]
then the projected operator is \( J(\beta) = -J(-\beta) \).

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 \( C \) in the new representations are obtained from the functions \( C \) by replacing the operators \( a_i^\dagger \) by the hole-creation operators \( b_i^\dagger \). It is easy to see that in \( H_0 \) and \( J \) this substitution is equivalent to the substitution \( a_i^\dagger \to b_i^\dagger \) and \( a_i^\sigma \to b_i^\dagger - \sigma \), and in \( H_1 \) it is necessary in addition to reverse the sign of \( \beta \). For the number of holes \( \nu_1 \) we have \( \nu_1 = 2 - n_1 \). Denoting the operators \( G \) in the hole representation by \( \bar{G} \), we obtain for the current

\[
\bar{J}(\beta) = \bar{\Gamma} \bar{P} \bar{S}_R \bar{3}_R \bar{P} \Gamma = \Gamma(\bar{-\beta}) \bar{P} \bar{S}_R (\bar{-\beta}) \bar{3}_R (\bar{-\beta}) \bar{P} \Gamma = J(-\beta) = -J(\beta) = 0. \tag{18}
\]

The current for quasi-homopolar states becomes different from zero if allowance is made for \( H_2 \) in \( K \), and for the contribution of the non-nearest neighbors in the current operator \( J \). Apparently, Kohn did not take these terms into account and obtained \( j = 0 \) for the quasi-homopolar states. \( ^{11} \)

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

\[
n_l(\beta) = 2 - n_l(\beta) = 2 - n_1(\beta) = 2 - n(\beta) = 1. \tag{19}
\]

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 \( S_l^z \). \( ^{11} \) For a cubic lattice with \( H_2 = 0 \), accurate to fourth order of perturbation theory in \( H' \), we obtain from (16)

\[
h = \sum_{i < j} J_i \left( S_i S_j - \frac{1}{4} \right) + \sum_{i < j} J_j' \left( S_i S_j' - \frac{1}{4} \right) + \sum_{i < j} 4\delta^4 \left[ a_i (b_i + \delta_1) - \delta_1 \delta_2 \right] \tag{20}
\]

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 \( (l \) along the directions \( (110), (131), \) and \( (011) \). \( \delta_1 \) and \( \delta_2 \) 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 \( l'_d \) 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 \( \delta_1 \) and \( \delta_2 \) decrease rapidly with increasing distance between centers \( (l''l') \) and \( (l'_dl'_d) \), 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, \( ^{21} \) \( \beta u_1^{-1} \approx 0.1 \) and \( u_2^0 \) and \( u_2^0 \) 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\( J_1 \). The first non-vanishing contribution to the current \( j \), 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 \( J \). \( ^{11, 73} \) On the basis of the result (18) we can state that the corrections of next order perturbation theory contain an additional factor \( \beta u_1^{-2} \approx 0.01 \).

In hydrocarbons with conjugated bonds, \( \beta u_1^{-1} \approx 0.7 \) \( ^{41} \) 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 ($U'$), 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 ($U''$) and finding the energies $E_i$ and the functions $\Psi_i$ of the quasi-homopolar states of the two electrons. Projecting $\Psi_i$ on the space $C$, we obtain a non-orthonormal system of functions $\mathbf{P}\Psi_i = \mathbf{P}\mathbf{S}\mathbf{R}\mathbf{C}_i = \mathbf{C}_i$. Extracting the root of the matrix $(\mathbf{C}_i^\dagger \mathbf{C}_i)$, we obtain $\Gamma$ and with the aid of the operation $\Gamma^{-1}(\mathbf{C}_i)$ we obtain the required system of eigenfunctions $\mathbf{C}_i$ of the secular equation (11). Knowledge of $E_i$ and $\mathbf{C}_i$ allows us to find the spin Hamiltonian of the two centers:

$$h_{II} = \mathbf{J}_i (\mathbf{S}_i \mathbf{S}_n - \frac{1}{4}),$$

$$\mathbf{J}_i = \frac{1}{2} \left[ \left( \mathbf{u}_{1} - \mathbf{F}(\mathbf{U''}) \right)^2 + 16 \mathbf{u}_{1}^2 \left[ \mathbf{\beta} - \mathbf{F}(\mathbf{U''}) \right] \right] - \frac{1}{6} \left[ \mathbf{F}(\mathbf{U''}) \right].$$

(21)

Summing over all the centers ($U''$), 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 ($U''''$). 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 ($U''$) and ($U'''$).\footnote{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.} If we disregard $H_2$, we get

$$h_{III} = - (\mathbf{J}_i' + \mathbf{J}_j') (\mathbf{S}_i \mathbf{S}_n + \mathbf{S}_j \mathbf{S}_n - \frac{1}{4})$$

$$+ (\mathbf{J}_i' + \mathbf{J}_j) (\mathbf{S}_i \mathbf{S}_n - \frac{1}{4}).$$

$$\mathbf{e}'' = \frac{1}{2} (\mathbf{u}_1 - \mathbf{Y} \mathbf{u}_2 + 8 \mathbf{p}^2)$$

and $\mathbf{e}'$ is the smallest root of the equation

$$\mathbf{e}^2 - \mathbf{e}^2 (\mathbf{u}_1 + \mathbf{u}_2) + \mathbf{e} (\mathbf{u}_1 \mathbf{u}_2 - 8 \mathbf{p}^2) + 6 u_2 \mathbf{p}^2 = 0.$$  

(22)

Summing over all triplets ($U''''$), 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.:

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

(23a)

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

$$(\mathbf{S}_i \mathbf{S}_n - \frac{1}{4}), \quad (\mathbf{S}_i \mathbf{S}_n - \frac{1}{4}) (\mathbf{S}_i \mathbf{S}_n - \frac{1}{4}), \ldots$$  

(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 ($u_3^3 = 0.65$, $u_3 u_1^2 = 1.7$, $u_3 u_1^2 = 2.2$), then the coefficients at the spin operators (23b) amount to $\approx 0.13 \mathbf{J}_i$ in $h(3)$ and to $0.03 \mathbf{J}_i$ and $0.01 \mathbf{J}_i$ 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,\footnote{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.} 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 ($\beta = 1$),

$$h = 1.88 \sum_i (\mathbf{S}_i \mathbf{S}_{i+1} + \mathbf{S}_{i+1} \mathbf{S}_{i+2} - \frac{1}{4}) + 0.47 \sum_i (\mathbf{S}_i \mathbf{S}_{i+2} - \frac{1}{4}).$$

(24)

The coefficients in $h(4)$ amount approximately to 0.1. With the aid of the Hamiltonian (24) we can
now find the energies of the quasi-homopolar states for a cyclic lattice with \( N = 2(2n + 1) \) centers at \( n \geq 1 \). An exact solution for the one-dimensional spin Hamiltonian with the nearest-spin interaction is known.\(^{[19,111]}\) Estimating the contribution of the second term of \((24)\) by the method proposed in \(^{[121]}\), we obtain for the ground-state energy per center, \( \epsilon_0 \) and for the first-excitation energy \( \epsilon_1 \):

\[
\begin{align*}
\epsilon_0 &= -0.69J_1 + \left( \frac{2}{\pi^2} - \frac{1}{4} \right) \mathcal{J}_2 \approx -1.23, \\
\epsilon_1 &= \frac{1}{2} \pi \left( \mathcal{J}_1 - \frac{8}{\pi^2} \mathcal{J}_2 \right) \sin \frac{\pi}{2n+1} \approx \frac{2.16\pi}{2n+1}.
\end{align*}
\]

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

\[
\begin{align*}
\epsilon_0 &= -\frac{4}{\pi} \approx -1.27, \\
\epsilon_1 &= 2 \cos \frac{\pi n}{2n+1} - 2 \cos \frac{\pi(n+1)}{2n+1} \approx \frac{2\pi}{2n+1}.
\end{align*}
\]

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 \( H_2 \) decreases the role of the transitions for the quasi-homopolar states, and therefore the convergence of the series \((23a)\) improves with increasing \( H_2 \). 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 \( H_5 \) at distances between centers \( R = 1 \) atomic units (in this case \( \beta = -0.67 \), \( \beta(l, l + 2) = 0.15 \), and \( \beta(l, l + 3) = -0.20 \), \((8)\)).

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\(^{[111]}\) for breaking down the space \( \mathcal{C} \) 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 \( w_n(l) \). 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 \( w_n(l) \). 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.

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**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

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

From \((5)\) we obtain

\[
(1 - P)S_nP = F_n S_{n-1} P = F_n P S_{n-1} P + P (1 - P) S_{n-1} P, \quad F_n = -(1 - P) (H_0 - E_0 - in \delta)^{-1} H'. \quad (A.2)
\]

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

\[
(1 - P) S_nP = (S_R)_1 P S_{n-1} P + (F_n - F_1) P S_{n-1} P
\]
Putting \( n = 2 \) in (A.3), we obtain \((SR)m\). Continuing the process of separating \((S\gamma)m\), we obtain the recurrence formula

\[
F_{nm+1} = (F_{nm} - F_{m}) \frac{1}{i(n-m)\delta} H' - F_{nm}(1 - P)
\]

(A.4)

\[
(S\gamma)m = F_{nm}.
\]

Let us prove that \( F_{nm} \) are regular operators. To this end it is sufficient to show that they are of the form \((m \geq n)\)

\[
F_{nm}(\delta) = \sum_{k=0}^{n-m} A_{k, m} P_{k, m}(n) \delta^k + o(\delta^{n-m}),
\]

(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, \( F_{n1} \) from (A.2) is of the same form as (A.5):

\[
F_{n1} = (1 - P) \sum_{k=0}^{n} (E_0 - H_0)^{-k+1} H' P_{k, 1}(n) \delta^k + o(\delta^{n-1}).
\]

(A.6)

On the other hand, if \( F_{nm} \) is of the form (A.5), then in \( F_{n1} \) from (A.2) the second term contains \( \delta \) and \( n \) only in the combination \((n-m)\delta \), i.e., it increases simultaneously the powers \( \delta \) and \( n \) without changing the form of (A.5), and the first term equal to

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

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

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

\[
\frac{(n-m)}{n-m-1} \]

inasmuch as \( P_{m}(n) - P_{m}(m) = 0 \) and \( P_{k-1, m}(n) = \frac{(n-m-1)!}{(n-m)\delta} \) we see that even the first term has the form (A.5). The regularity of \( F_{nm} \) and consequently of \((SR)m = F_{nm}\) is thus proved.

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Translated by J. G. Adashkevich