

Magnetic model for alkali and noble metals: From diatoms to the solid state

J. P. Malrieu, D. Maynaud, and J. P. Daudey

*Laboratoire de Physique Quantique**[Equipe de Recherche (No. 821) associée au Centre National de la Recherche Scientifique],
Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France*

(Received 1 September 1983)

An effective Hamiltonian of the Heisenberg type is derived from the alkali-metal diatom potential curves. Its qualitative relevance is exemplified on small clusters. Approximate solutions for the metal in various types of crystallization are obtained by consideration of one of the most-ordered spin distributions and by perturbation under its coupling with the less-ordered spin distributions. The results for Na are in good agreement with experiment for the lattice parameter (4.27 Å, experiment 4.225 Å at 5 K), the cohesive energy (1.19 eV, experiment 1.113 eV), and for the bulk modulus (0.0065×10^{12} dyn/cm², experiment 0.0068×10^{12} dyn/cm²). The close-packed fcc and hcp structures are nearly degenerate, which explains the low-temperature martensitic transformation. The model may be extended to noble metals, provided that diabatic ($d^{10}s^1$)² potential curves are used for the $^3\Sigma_u^+$ state of the diatoms, as illustrated for copper, giving reliable results. The connection of the present model with band models, and possible extensions to open d shells, are discussed.

INTRODUCTION

The alkali metals are frequently presented as the basic example of the delocalized description of metals, "the valence electrons are taken away from each alkali atom to form a community electron sea in which the positive ions are dispersed."¹ The resulting theoretical approach rests upon the electron gas zeroth-order approximation, the use of plane waves, and results in the band-structure description. This dominant description has brought a lot of successes, and seems to receive, for instance, experimental confirmation from photoelectron spectroscopy. The electron correlation may be introduced later to this noncorrelated scheme, but its treatment remains rather difficult to achieve. Moreover the direct calculation of the cohesive properties of the crystal from this approach remains rather difficult.

On a completely opposite side of this delocalized picture, one finds the Heisenberg description,² especially valid for Mott insulators. In this description the valence electrons are no longer delocalized, they remain each on its site, and are weakly coupled through exchange interactions. As demonstrated by Anderson,³ these effective interactions actually reflect the possible short-range delocalization of electrons from their own site to the neighbor sites. Both the band description and the Heisenberg approach suppose that for one valence electron per atom, each atom has a mean electronic population of one electron, but the fluctuation is large in the band description (this fluctuation being reduced by the electron correlation treatment), while it is supposed to be very weak in the Anderson approach, the resulting effective Heisenberg Hamiltonian dealing with situations without any charge fluctuation.

The contrast between these two descriptions is so strong that they seem to apply to completely different physical situations. The first purpose of this paper is to show that

Heisenberg Hamiltonians may be derived and applied to typical conducting metals as well, and may be very efficient. A very crude effective Heisenberg Hamiltonian is deduced from the alkali diatoms and introduced in the solid-state problem, resulting in surprisingly good agreement with the cohesion properties of the metal.

In such an unusual and risky attempt, we have been directed by our experience on molecules. Following a way opened by Ovchinnikov,⁴ Bulaewskii,⁵ and Klein,⁶ the most delocalized chemical systems, i.e., the π electronic systems of conjugated molecules, have been treated⁷ through the quasidegenerate many-body perturbation theory (QDPT),⁸ choosing the neutral determinants (in the sense of valence-bond theory), i.e., the basis of N -electronic functions relevant for the Heisenberg treatment, as the model space. The solutions of the full π electron configuration interaction, i.e., the exact solutions of a Hubbard,⁹ or Pariser-Parr-Pople¹⁰ (PPP) type Hamiltonian have been obtained to a high accuracy⁷ by building effective spin (i.e., magnetic) Hamiltonians which are a simple generalization to higher orders of the Anderson-Heisenberg Hamiltonian. Some important collective operators involving four or six sites and electrons were shown to play a role in cyclic structures, but the simplest Heisenberg Hamiltonian introducing only effective exchange between nearest neighbors already gives a qualitative estimate of the molecular electronic energy. The model was applied to aromatic compounds which are supposed to be the most metal-like molecules, suggesting that its validity is not restricted to the case of weak interactions (i.e., near degeneracies between singlet and triplet situations).

The effective magnetic-type Hamiltonian was first derived by perturbing the degenerate subspace of neutral configurations under the influence of the ionic ones, but it may be shown that its structure remains the same besides the radius of convergence of this perturbative develop-

ment. Other (nonperturbative) approaches¹¹ may be used to derive the effective Hamiltonian for the case of strong couplings between neutral and ionic states (i.e., for the case of highly delocalizable systems), and the resulting effective operators keep the same form,¹² with larger amplitudes.

In a later stage of work,^{13,14} a two-body Heisenberg operator for conjugated molecules has been extracted from accurate *ab initio* calculations on the ethylene molecule, involving extended basis sets and large configuration interactions (CI's). The operators were geometry dependent and the resulting Hamiltonian allowed us to perform geometry optimizations of medium size conjugated molecules; the results¹³ for the ground-state geometries were in surprising agreement with experiment (agreement within 0.015 Å with experimental bond lengths) for linear, branched, (poly)cyclic, aromatic or nonaromatic, alternant or nonalternant molecules; the Jahn-Teller distortions were correctly treated. The model was able to treat neutral excited-state geometries of linear polyenes; it also allowed a discussion of the *cis-trans* photoisomerization mechanism and a correlated treatment of the soliton deformations.¹⁴

Our experience on molecular problems therefore convinced us that effective Heisenberg-type Hamiltonians might be obtained and successfully used on typically delocalized systems. Our hypothesis may be related to an early suggestion of a "resonating valence bond" description of metals formulated by Pauling,¹⁵ the relationship of this model with the Heisenberg Hamiltonian and Néel antiferromagnetic state had been discussed by Anderson.¹⁶

I. THE EFFECTIVE MAGNETIC HAMILTONIAN

A. The effective Hamiltonian approach

For a molecular problem, assuming the Born-Oppenheimer approximation, i.e., reducing the Hamiltonian to its electronic part in the field of fixed nuclei, the numerical calculations are generally done using a finite set of mono-electronic functions X_i (usually atomic orbitals centered on the nuclei). For an n -electronic problem, one may build a finite space of N electronic determinants from these mono-electronic functions,

$$\phi_K = |K\rangle = \mathcal{A} \prod_{i=1}^n X_j(i), \quad (1)$$

or from orthogonal combination of the X_j (the molecular orbitals). The exact Hamiltonian is projected into this finite space Σ . If one defines the projector P on these determinants,

$$P = \sum_{K \in \Sigma} |K\rangle \langle K|, \quad (2)$$

the numerical problem of the full CI is the search for the eigenvalues of a projected Hamiltonian

$$H' = PHP, \quad (3)$$

$$(H' - E_m) |\Psi_m\rangle = 0.$$

For nonminimal basis sets, this projected problem is al-

ready a formidable task for polyatomic problems.

The basic idea of the effective Hamiltonian strategy is to reduce the problem through a further reduction of the number of determinants. One may choose a certain number of determinants K , i.e., a subspace S (hereafter called model space) included in Σ but of much smaller dimension, on which one may hope that the few searched states have large components. One defines the projector

$$P_0 = \sum_{K \in S} |K\rangle \langle K| \quad (4)$$

and looks for an effective Hamiltonian defined on S only satisfying the two basic equations

$$P_0 H^{\text{eff}} P_0 |\psi_m\rangle = E_m |\psi_m\rangle, \quad (5)$$

$$|\psi_m\rangle = P_0 |\Psi_m\rangle. \quad (6)$$

If p is the dimension of the model space, the effective Hamiltonian is p dimensional and its p (nonzero) eigenvalues are p eigenvalues of H' , the corresponding eigenvectors ψ_m of H^{eff} being the projections of p eigenstates Ψ_m of H' . The philosophy of the effective Hamiltonian approach is (i) to reduce the dimension of the matrix to be diagonalized, and (ii) to project the information of the exact Hamiltonian into a reduced space of n -electronic wave functions. The counterpart of this second statement is necessarily the increased complexity of the effective Hamiltonian. Starting from the exact Hamiltonian (which only deals with bielectronic r_{ij}^{-1} operators) in a huge basis of determinants one wants to obtain the lowest states energies from diagonalization of moderate size matrices, but the price to pay for that is the introduction of unusual many-electron operators.¹⁷

Two ways may be followed to reach H^{eff} once P_0 has been chosen. The first consists in using one of the various perturbative expansions of the quasideterminant (many-body) perturbation theory (QDPT).⁸ One may also follow the wave operator formalism, starting from Bloch's equations,¹⁸ in an iterative nonperturbative scheme,¹¹ which converges for larger couplings between the model space and the complementary space.¹²

The most famous application of the effective Hamiltonian approach concerns magnetism, and introduces directly the Heisenberg spin Hamiltonian. One considers a set of n atoms I , every one bringing one electron and one atomic orbital i (i.e., two spin orbitals i and \bar{i}). One may suppose that the lowest states of the problem have large components on the so-called neutral or covalent configurations in which each atom bears one electron

$$\phi_{\text{neutral}} = |(a)(b)(c) \cdots (n)|, \quad (a) = a \text{ or } \bar{a}$$

with all possible spin distributions.

The neutral determinants only differ by the spin distribution. Their number is $C_n^{n/2}$ if one considers the $S_z = 0$ or $\frac{1}{2}$ problem, while the total number of determinants for this minimal basis set problem is $(C_n^{n/2})^2$. Then the model space may be chosen as spanned by the neutral determinants, and one may treat perturbatively their interaction with ionic determinants such as $A^- B^+$,

$$\phi_{\text{ionic}} = |a\bar{a}(c) \cdots (n)|$$

in which one atom (or k atoms) bears a negative charge (two electrons) while another one (or k other atoms) has no electron. The resulting effective Hamiltonian transforms this delocalization effect into effective exchange operators coupling the different neutral determinants, i.e., the various spin distributions. The simplest of these effective Hamiltonians is the Heisenberg Hamiltonian; the effective exchange operator is typically antiferromagnetic (i.e., negative) since it results from a second-order coupling with the ionic terms, as explained by Anderson.³ The effective operator reduces drastically the size of the CI problem through a projection into the subspace of the various spin distributions.

One should notice that the well-known diatomics in molecules (DIM) method¹⁹ is identical, for the case of atoms containing one electron per center in one basic atomic orbital (AO), to the simple Heisenberg Hamiltonian

$$H^{\text{eff}} = \sum_{p,q} \tilde{K}_{pq} \vec{S}_p \cdot \vec{S}_q + f(R) \quad (7)$$

[$f(R)$ being a scalar functional depending on the geometry], as will be evident later. The relative successes and some failures of the DIM method for small clusters of hydrogen molecules H_n are summarized in the excellent review by Tully.²⁰ The derivation of the DIM method is based on a partition of the Hamiltonian, the choice of specific configurations and specific approximations, and it is an amazing fact that such entirely different derivations lead to the same effective Hamiltonian. The connection between the two formalisms is evident from the equations given in a recent work.²¹

B. The diatomic problem

Let us consider a diatomic molecule built from two alkali-like atoms A and B , each one bearing one valence electron only in an s -type atomic orbital (a' and b' , respectively). These two AO's may be orthogonalized first into a and b , and the CI ($S_z=0$) problem restricted to the minimal basis set may be seen as a matrix in a basis of four determinants, two of them being neutral ($a\bar{b}, \bar{a}b$), the two other ones ($a\bar{a}$ and $b\bar{b}$) being ionic in the sense of the valence bond (VB) theory. The neutral determinants are much lower in energy and the QDPT may be applied to build an effective 2×2 Hamiltonian

$$\begin{pmatrix} a\bar{b} & \bar{a}b & a\bar{a} & b\bar{b} \\ E_1 & -K_{ab} & F_{ab} & F_{ab} \\ -K_{ab} & E_1 & -F_{ab} & -F_{ab} \\ F_{ab} & -F_{ab} & E_1 + \Delta E & K_{ab} \\ F_{ab} & -F_{ab} & K_{ab} & E_1 + \Delta E \end{pmatrix} \rightarrow \text{QDPT} \rightarrow \begin{pmatrix} a\bar{b} & \bar{a}b \\ E'_1 & -g \\ -g & E'_1 \end{pmatrix},$$

where the diagonal terms E' and off-diagonal term g may be approximated by a second-order development as

$$E'_1 = E_1 - \frac{2F_{ab}^2}{\Delta E}, \quad (8)$$

$$g = -K_{ab} + \frac{2F_{ab}^2}{\Delta E}, \quad (9)$$

where g is an effective exchange operator.

The resulting eigenvalues are necessarily for the triplet

$$(a\bar{b} + \bar{a}b)/\sqrt{2}: E(^3\Sigma_u^+) = E_1 - K_{ab} \quad (10)$$

and for the singlet

$$(a\bar{b} - \bar{a}b)/\sqrt{2}: E(^1\Sigma_g^+) = E_1 + K_{ab} - 2g \\ = E(^3\Sigma_u^+) - 2g. \quad (11)$$

The same kind of treatment might be applied to larger basis sets. One might introduce, for instance, other s orbitals to allow for the change of the s distribution in the molecule, or p orbitals to make possible the hybridization. These supplementary AO's should be orthogonalized first to the basic a and b AO's by projection into the orthogonal subspace, then orthogonalized among themselves.²² The resulting s'_a or p'_a AO's would be involved in $|s'_a s'_b|$ determinants (for the molecular contraction), $|s'_a s'_a|$ determinants (introducing the radial correlation of ionic structures), $|p'_a p'_a|$ determinants (for the angular correlation of the ionic structures), $|p'_a p'_b|$ determinants (for the van der Waals dispersion forces), etc.

The resulting 2×2 effective Hamiltonian would keep the same form and would incorporate these second- and fourth-order effects in the effective g operator. As a limit the effective Hamiltonian would allow us to reach the exact energies of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states. If one knows then the potential curves of these two states, it becomes possible to introduce an essentially repulsive function of the interatomic distance r , $R(r)$, which reduces to the $^3\Sigma_u^+$ energy,

$$R(r) = E(^3\Sigma_u^+). \quad (12)$$

This function incorporates the van der Waals dispersion energies and may exhibit a long distance weak minimum. The amplitude of the effective exchange operator $g_{ab}(r)$ is given by

$$g_{ab}(r) = [E(^3\Sigma_u^+) - E(^1\Sigma_g^+)]/2 \quad (13)$$

as noticed by Poshusta and Klein for the H_2 problem²³ and its extension to the H_n cyclic situations.

To go to larger systems involving more than two atoms, one might proceed in an analogous way. But in principle the orthogonalized AO's for a three-atom problem are different from the orthogonalized AO's of the two-atom problem, and the effective exchange operator g_{12} is not transferable from one system to a larger one. It is well known that the orthogonalization tails are rather large and extend on a series of atoms for alkali clusters and solids. This lack of transferability would result in a serious problem if the effective operator formalism had to be developed on these orthogonalized AO's. Two approaches may be followed, which should ensure a better transferability. The first one consists in building the effective operator in a basis of nonorthogonal determinants, built from local nonorthogonal AO's; the model space then defined from the neutral VB nonorthogonal determinants, and the resulting effective operator problem would turn to be

$$|H^{\text{eff}} - ES| \varphi = 0, \quad (14)$$

where S is an overlap matrix of scalar products between the nonorthogonal neutral determinants. To reach H^{eff} in such a problem, one should develop a nonorthogonal version of the quasidegenerate (Rayleigh-Schrödinger) perturbation theory, as has been done for the usual nondegenerate expansion.²⁴

A simpler procedure might be found by another choice of the P_0 model subspace in Eqs. (5) and (6). Instead of using the best valence atomic orbitals s of the atom, i.e., the s solutions of the atomic ground-state Hartree-Fock problem, one might introduce nonoverlapping \tilde{s} -type orbitals such that

$$\begin{aligned} \langle \tilde{s}_a | \tilde{s}_b \rangle &= 0, \\ \langle \tilde{s}_a | s_a \rangle &= \text{maximum}, \end{aligned}$$

or such that if

$$\tilde{\psi} = |1\bar{1}, \dots, n\bar{n}\tilde{s}|$$

is the determinant built from the core AO's and the \tilde{s} orbital,

$$\frac{\langle \tilde{\psi} | H | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} \cong \text{minimum}.$$

The zero overlap conditions might be fulfilled in different ways, either by cutting the long-range side of the orbital, in a smooth or in a discontinuous manner, or by compelling the wave function to be limited in a finite box; cf. Fig. 1.

Neutral orthogonal determinants would be built from these \tilde{s} contracted s orbitals, and "virtual" orthogonal sup-

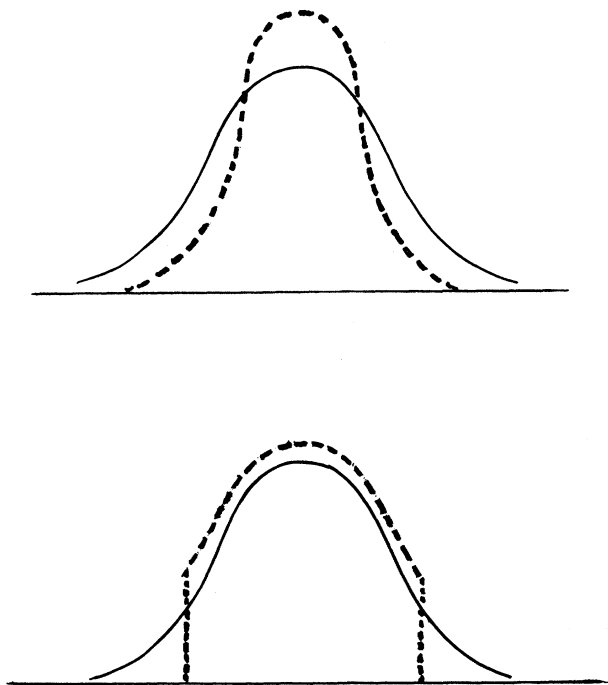


FIG. 1. Possible spatial contraction (a) or truncation (b) of the atomic orbitals (schematic view). Solid lines, s Hartree-Fock atomic orbital; dotted lines, \tilde{s} concentrated atomic orbital.

plementary orbitals should be added to the basis set to correct the artificial defect of the \tilde{s} orbitals. The \tilde{P}_0 modified model space spanned by the neutral determinants built from \tilde{s} orbitals would be used to build the effective Hamiltonian. For a two-atom problem,

$$\tilde{P}_0 = |\tilde{a}\tilde{b}\rangle\langle\tilde{a}\tilde{b}| + |\tilde{a}\tilde{b}\rangle\langle\tilde{a}\tilde{b}|$$

while for a three-atom problem

$$\tilde{P}_0 = |\tilde{a}\tilde{b}\tilde{c}\rangle\langle\tilde{a}\tilde{b}\tilde{c}| + |\tilde{a}\tilde{b}\tilde{c}\rangle\langle\tilde{a}\tilde{b}\tilde{c}| + |\tilde{a}\tilde{b}\tilde{c}\rangle\langle\tilde{a}\tilde{b}\tilde{c}|.$$

The resulting effective Hamiltonian would be identical to the one obtained from $S^{-1/2}$ orthogonalized atomic orbitals. This comment illustrates the fact that the effective Hamiltonian is not strictly dependent on the choice of the model space: different model spaces (i.e., different projectors P_0) may lead to the same effective Hamiltonian in its operatorial form (i.e., same matrices) but spanned by different (isomorphic) model spaces.

If one uses such a basis of intrinsically orthogonal AO's, the transferability of the matrix elements from the two-atom problem to a three-atom problem or to larger clusters or to the solid is less questionable. Of course, in the three-atom problem the effective ab exchange operator

$$g_{ab(c)} = \langle |\tilde{a}\tilde{b}\tilde{c}\rangle | H_{(3)}^{\text{eff}} | |\tilde{a}\tilde{b}\tilde{c}\rangle \rangle$$

should be different from the ab exchange operator in the two-atom problem

$$g_{ab} = \langle |\tilde{a}\tilde{b}\rangle | H_{(2)}^{\text{eff}} | |\tilde{a}\tilde{b}\rangle \rangle$$

even for identical R_{ab} distances since the presence of the third atom C should modify the energies of the excited determinants outside of P_0 , and should allow some perturbative travels through \tilde{c} . But the effective exchange operator between a and b in ABC may be expanded as

$$g_{ab(c)} = g_{ab} + \delta g_{ab(c)}, \quad (15)$$

where the three-body increment $\delta g_{ab(c)}$ may be hoped to be small. Such a development has been explicitly derived elsewhere^{7,12} for a Hubbard-type Hamiltonian and it has been shown through a perturbative expansion that $\delta g_{ab(c)}$ is much smaller than g_{ab} , in the



or



geometries. In the same way it has been shown that the through-bonds $g_{ac(b)}$ exchange in the



cluster remains very small.

As a first attempt, the present paper will reduce the effective Hamiltonian, which should in principle involve three-atom, four-atom, etc., operators to the effective two-atom interactions. The possible strategy to include these many-body corrections will be discussed in the final section. For the present time the effective Hamiltonian simply includes

(a) two-center repulsive diagonal or scalar operators, which disregard the spin attribution of the electrons on two interacting atoms

$$R_{ij} = R(r_{ij}),$$

and which are extracted from the diatomic problem

$$R(r_{ij}) = E(^3\Sigma_u^+(r_{ij})), \quad (16)$$

(b) two-center effective exchange operators occurring on atom pairs which present a spin alternation. These exchanges take place on both diagonal

$$g_{ij}^d = -g(r_{ij})(a_i^\dagger a_j^\dagger a_{\bar{j}} a_i + a_{\bar{i}}^\dagger a_j^\dagger a_i a_{\bar{j}}) \quad (17)$$

and off-diagonal operators of opposite signs and equal amplitude

$$g_{ij}^{nd} = g(r_{ij})(a_i^\dagger a_j^\dagger a_j a_{\bar{i}} + a_{\bar{i}}^\dagger a_j^\dagger a_j a_i) \quad (18)$$

also extracted from the diatomic problem

$$g(r_{ij}) = [^3\Sigma_u^+(r_{ij}) - ^1\Sigma_u^+(r_{ij})]/2.$$

The effective Hamiltonian is bielectronic

$$H_{\text{eff}} = \sum_{ij} R_{ij} + g_{ij}^d + g_{ij}^{nd}. \quad (19)$$

As an example one may illustrate its construction on three- and four-atom clusters, which may give some estimate about its qualitative relevance since such clusters have been rather accurately studied through *ab initio* well-correlated treatments. Let us specify before the origin of the potential curves used hereafter in the calculations.

Numerical assumptions about the diatomic potential curves. The $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves of the diatomic X_2 molecules have to be known not only near the equilibrium distances of the ground state [$r_e(X_2)$] but at the larger interatomic distance r of the metal [$r/r_e(X_2) \cong 1.2$] and at the metallic second-neighbor distance $r = r\sqrt{2}$ or $r(2/\sqrt{3})$ since the second neighbors will play an important role. Even for the ground state Morse curves or polynomials fitted on the spectroscopic constants would not give reliable values for these distances and accurate *ab initio* curves have been preferred when available. For the triplet excited state, *ab initio* calculations are necessary to get some information on the very important repulsive wall. As a consistent choice, the curves proposed by Konowalow and co-workers have been utilized for Li_2 (Refs. 25 and 26) and Na_2 .²⁷ For Li_2 the agreement with experiment is almost perfect [for $^1\Sigma_g^+ r_e = 2.69 \text{ \AA}$ (experimental, 2.67 \AA), $D_e = 1.04 \text{ eV}$ (experimental, 1.06 eV)]. For Na the core valence correlation begins to play a role, and the calculations did not include this effect, resulting in a somewhat too long [$r_e = 3.172 \text{ \AA}$ (experimental, 3.079 \AA)] and too weak [$D_e = 0.715 \text{ eV}$ (experimental, 0.748 eV)] bond. As a result of this slight lack of attraction, the calculation of the Na solid should present a slight overestimation of the lattice parameter and a slight underestimation of the cohesion energy with respect to what would be obtained from the use of the exact diatomic potential curves.

For K and heavier atoms the lack of reliable potential curves seems to prohibit calculations for the present time.

[One of the best calculations on K_2 (Ref. 22) (including a core-valence correlation correction) is in error of 0.03 eV on the dissociation energy.]

C. Three- and four-atom clusters

The three-atom problem reduces to a three-dimensional matrix since three ($S_z = \frac{1}{2}$) determinants may be built, namely $\bar{a}bc$, $a\bar{b}c$, and $ab\bar{c}$ (a proper approach should use the nonoverlapping \bar{a} orbitals, but for the sake of simplicity the tilde is omitted hereafter) and the effective Hamiltonian is

$$\begin{pmatrix} \bar{a}bc & a\bar{b}c & ab\bar{c} \\ \sum R - g_{ab} - g_{ac} & g_{ab} & g_{ac} \\ g_{ab} & \sum R - g_{ab} - g_{bc} & g_{bc} \\ g_{ac} & g_{bc} & \sum R - g_{ac} - g_{bc} \end{pmatrix}$$

where $\sum R = R_{ab} + R_{ac} + R_{bc}$.

For isocelc geometries



[$r_{ab} = r_{bc}$] this three-dimensional matrix splits into symmetric and antisymmetric parts by considering the vectors $(\bar{a}bc \pm ab\bar{c})/\sqrt{2}$. The combination $(\bar{a}bc - ab\bar{c})/\sqrt{2}$ is a symmetrical 2A_1 eigenvector, the corresponding eigenvalue of which

$$E_{2A_1} = 2R(r_1) + R(r_2) - g(r_1) - 2g(r_2)$$

may be transformed in terms of the potential curves

$$\begin{aligned} E_{2A_1} &= E(^1\Sigma_g^+(r_2)) + [3E(^3\Sigma_u^+(r_1)) + E(^1\Sigma_g^+(r_1))]/2 \\ &= E_0(X_2) + [3E(^3\Sigma_u^+(r_1)) + E(^1\Sigma_g^+(r_1))]/2 \end{aligned}$$

which is identical to the DIM result.

The minimum corresponds to the diatomic ground-state r_2 distance and a somewhat larger r_1 distance, i.e., to the interaction between a diatom and a weakly attracted atom. The association energy between X_2 and X (i.e., $E(X_3) - [E(X_2) + E(X)]$) is a first crucial test for the model. The resulting energies reported in Table I are in reasonable agreement with the best *ab initio* estimates. The interaction energy is somewhat too weak and the r_1 distance is somewhat too large but the qualitative properties of the 2A_1 surface minimum are well reproduced without introducing three-body operators.

The 2B_2 antisymmetrical eigenvectors are solutions of the 2×2 matrix

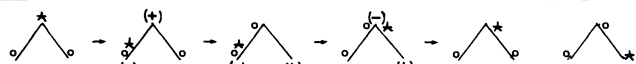
$$\begin{pmatrix} a\bar{b}c & (\bar{a}bc + ab\bar{c})/\sqrt{2} \\ \sum R - 2g(r_1) & g(r_1)\sqrt{2} \\ g(r_1)\sqrt{2} & \sum R - g(r_1) \end{pmatrix}$$

The lowest eigenvalue of which is

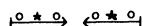
$$E(^2B_2) = 2R(r_1) + R(r_2) - 3g(r_1).$$

The potential surface of this state exhibits a valley for a certain value of r_1 slightly larger than the equilibrium distance of the diatom (6.3 a.u. for Na_3), with a minimum for an obtuse geometry. The r_2 optimal distance corre-

sponds to the minimum of the ${}^3\Sigma_u^+$ dimer. This minimum is slightly below the linear configuration which represents a saddle point, as in the *ab initio* calculation. The 2B_2 minimum is slightly below the 2A_1 minimum [$E({}^2A_1) - E({}^2B_2) = 1.6$ kcal/mole for Li_3 , 0.7 for Na_3 , instead of 1.3 and 0.7, respectively, in the *ab initio* calculations].



(where 0 and * represent α and β spins, respectively) resulting in attractive diagonal



and off-diagonal



operators. These corrections involve A^-C^+ intermediate states for which the electrostatic interaction would tend to shorten the $A-C$ distance between the nonbonded atoms. This interaction would lower the energy of the 2B_2 minimum with respect to the linear 2B_2 saddle point, which is underestimated in our two-body treatment. Nevertheless its results are surprisingly good.

As a further test the X_4 problem has been analyzed. Six ($S_z=0$) determinants span the effective Hamiltonian

$$\begin{array}{cccccc} |abc\bar{d}| & |a\bar{b}c\bar{d}| & |\bar{a}bc\bar{d}| & |a\bar{b}c\bar{d}| & |\bar{a}bc\bar{d}| & |\bar{a}b\bar{c}d| \\ \left[\begin{array}{cccccc} \sum R - g_{ac} - g_{ad} - g_{bc} - g_{bd} & g_{bc} & g_{ac} & g_{bd} & g_{ad} & 0 \\ g_{bc} & \sum R - g_{ab} - g_{ad} - g_{bc} - g_{cd} & g_{ab} & g_{cd} & 0 & g_{ad} \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \end{array} \right] \end{array}$$

TABLE I. X_3 conformations (in Å) and binding energies (in kcal/mol) relative to $X+X_2$.

Li_3			
DIM ^a or HH	$r=2.74$	$\alpha=50^\circ$ $r_1=2.66$ $r_2=3.17$	$\alpha=101^\circ$ $r_1=2.75$ $r_2=4.24$
	$\Delta E=9.8$	$\Delta E=10.1$	$\Delta E=11.7$
CI ^b	$r=2.91$	$\alpha=52^\circ$ $r_1=2.70$ $r_2=3.07$	$\alpha=69^\circ$ $r_1=2.80$ $r_2=3.17$
	$\Delta E=9.8$	$\Delta E=9.2$	$\Delta E=9.2$
CI ^c		$\alpha=54^\circ$ $r_1=2.78$ $r_2=3.08$	$\alpha=73^\circ$ $r_1=2.78$ $r_2=3.30$
	$\Delta E=4.6$	$\Delta E=9.1$	$\Delta E=10.4$
Na_3			
DIM ^d or HH	$r=3.4$	$\alpha=51^\circ$ $r_1=3.06$ $r_2=3.56$	$\alpha=89^\circ$ $r_1=3.16$ $r_2=4.47$
	$\Delta E=7.8$	$\Delta E=7.1$	$\Delta E=7.8$
CI ^d	$r=3.38$	$\alpha=52^\circ$ $r_1=3.22$ $r_2=3.72$	$\alpha=73^\circ$ $r_1=3.31$ $r_2=3.95$
	$\Delta E=5.5$	$\Delta E=7.8$	$\Delta E=8.5$

^aReference 28.

^bReference 29.

^cReference 30.

^dReference 31.

These results summarized in Table I show that the qualitative features of the two lowest potential surfaces of the X_3 problem are nicely predicted from this very simple model. The main defect concerns the shape of the 2B_2 minimum configuration, for which our r_2 value is too large. Some three-body contributions are lacking, especially some fourth-order contributions

[One may notice that the sum of the elements of a line (or column) is equal to $\sum R = \sum_{ij} R_{ij}$, as demonstrated previously.⁷] This 6×6 matrix may be diagonalized explicitly if sufficient symmetry is introduced. The minima are known to correspond to planar D_{2h} geometries (square or rhombus or distorted tetrahedron geometries), for which the solutions may be found explicitly in function of three interdependent distances, the perimetric one r_1 and the two diagonal ones r_2 and r_3 .

The lowest solution is a symmetrical singlet state

$${}^1E^{(1)} = \sum_{ij} R_{ij} - 6g(r_1),$$

$$\psi_1 = \alpha(\bar{a}b\bar{c}d + \bar{a}b\bar{c}d) + \beta(\bar{a}b\bar{c}d + \bar{a}b\bar{c}d + \bar{a}b\bar{c}d + \bar{a}b\bar{c}d)$$

which is dominated by the spin alternating perimetric distributions $\bar{a}b\bar{c}d$ and $\bar{a}b\bar{c}d$. The energy minimum corresponds to a planar square configuration with a rather long interatomic distance (2.77 Å for Li_4 , 3.16 Å for Na_4).

The second singlet state solution is

$${}^1E^{(2)} = \sum_{ij} R_{ij} - 2g(r_1) - 2g(r_2) - 2g(r_3)$$

which may be expressed from the energy of the diagonal diatomics as

$${}^1E^{(2)} = E_{AC}^{(r_3)} + E_{BD}^{(r_2)} + 4R(r_1) - 2g(r_1).$$

It is clear that the corresponding minimum is obtained for a distorted tetrahedron representing the interaction between the AC and BD molecules in their ground-state geometry. This intermolecular configuration is less stable than the square. Surprisingly enough this interaction has

been found to be repulsive in early *ab initio* CI calculations³² and recent works have not reexplored it.

The best CI calculations³³ find (see Table II) a slightly bonded square (2 kcal/mol for Li_4) which distorts into a rhombus [stable by about 15 kcal/mol with respect to 2Li_2 , 9.4 kcal/mol with respect to 2Na_2 (this ordering being rather unexpected)]. The rhombic solution should belong to the ${}^1E^{(2)}$ surface, but the Heisenberg-type Hamiltonian or DIM Hamiltonian suggest that the planar rhombus is a BD singlet molecule surrounded by two weakly interacting atoms A and C . The stabilization of the rhombus comes from specific large interaction with the dionic configuration $A^+B^-C^+D^-$. The CI predicts the triplet lowest configuration to be a bent square. This would agree with the DIM solution

$$\begin{aligned} {}^3E^{(2)} &= \sum R - 2g_1 - 2g_2 \\ &= E^3(AC) + E^1(BD) + 4R(r_1) - 2g(1) \end{aligned}$$

which represent the interaction between the BD singlet molecule and the long AC triplet molecule.

The conflict concerning the DIM or Heisenberg Hamiltonian predictions and present CI results reflects the lack of important four-body contributions in the Heisenberg Hamiltonian which had been noticed in the study of the π systems.⁷ However, as will be explained below, the four-body terms should play a less important role in the metal than in the small clusters.

II. SOLID STATE

The solution of the Heisenberg Hamiltonian for the three-dimensional crystal cannot be obtained exactly, and specific approximations must be proposed to reach an estimate of the cohesive energy E_{coh} (i.e., the total energy per

TABLE II. X_4 conformations (in Å) and energies (in kcal/mol) relative to $2X_2$.

	square	rhombus	distorted tetrahedron
	r	r_1 r_2	r_1 r_2
Li_4			
DIM ^a	$r=2.77$	$r_1=2.67$ $r_2=3.18$	$r_1=2.67$ $r_2=3.18$
CI ^b	$\Delta E=23.4$	$r_1=2.74$ $r_2=3.04$ $\Delta E=15.4$	$\Delta E=20.1$
Na_4			
DIM ^a	$r=3.16$	$r_1=3.08$ $r_2=3.56$	$r_1=3.08$ $r_2=3.56$
CI ^b	$\Delta E=15.7$	$r_1=3.15$ $r_2=3.48$ $\Delta E=9.4$	$\Delta E=13.8$

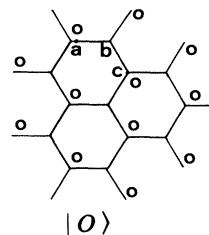
^aReference 28.

^bReference 33.

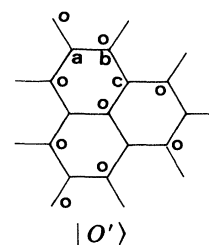
atom minus the energy of the isolated atom). From our experiment on molecules, one may suggest a perturbative procedure, which allows a deductive approach to the cohesive energy and properties.

A. Method: example

Let us consider a well-behaved graph, such that it allows one or several perfectly alternative spin distributions. For instance, the graphitlike hexagonal planar structure allows one to write two equivalent perfectly alternating spin distributions where the open circles indicate β spins,



and



The corresponding determinants $|O\rangle$ and $|O'\rangle$ necessarily have the lowest energy on the diagonal of the magnetic-type Hamiltonian since they present spin alternations on all the chemical bonds, i.e., between all the nearest neighbors. In this specific example each atom is engaged in three alternating bonds, and neglecting the long range 1-4 interactions, the energy of $|O\rangle$ and $|O'\rangle$ is

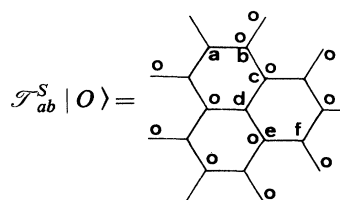
$$\langle O | H^{\text{eff}} | O \rangle = \langle O' | H^{\text{eff}} | O' \rangle = n(3R - 3g)/2, \quad (20)$$

where R is the repulsion between nearest neighbors and g the corresponding attractive effective exchange. The $\frac{1}{2}$ coefficient avoids counting each interaction twice. This gives a zeroth-order estimate of the cohesive energy,

$$E_{\text{coh}}^{(0)} = (3R - 3g)/2.$$

But these perfectly spin-ordered determinants interact with less ordered distributions. They interact first with the determinants which result from $|O\rangle$ or $|O'\rangle$ under a single spin interchange \mathcal{F}_{ab}^S between bonded atoms a and b ,

$$\langle O | H | a_a^\dagger a_b^\dagger a_b a_a | O \rangle = \langle O | H | \mathcal{F}_{ab}^S | O \rangle = g_{ab},$$



Such a determinant is less ordered than $|O\rangle$, and its energy is much higher, since four spin alternations have been lost by this single spin exchange

$$\langle \mathcal{T}_{ab}^S O | H^{\text{eff}} | \mathcal{T}_{ab}^S O \rangle - \langle O | H^{\text{eff}} | O \rangle = 4g .$$

It is clear that $\mathcal{T}_{ab}^S |O\rangle$ and $|O'\rangle$ do not interact since the spins still differ on $n-2$ atoms

$$\langle \mathcal{T}_{ab}^S O | H^{\text{eff}} | O' \rangle = 0 .$$

One may therefore be tempted to forget the spin degeneracy between $|O\rangle$ and $|O'\rangle$ and to perturb $|O\rangle$ only, as if it was not degenerate. The resulting second-order estimate would be

$$\begin{aligned} \epsilon_0^{(2)} &= \sum_{\text{bonded } ab} \frac{|\langle O | H^{\text{eff}} | \mathcal{T}_{ab}^S O \rangle|^2}{\langle O | H^{\text{eff}} | O \rangle - \langle \mathcal{T}_{ab}^S O | H^{\text{eff}} | \mathcal{T}_{ab}^S O \rangle} \\ &= - \sum_{\text{bonded } ab} \frac{g_{ab}^2}{4g} = - \sum_{\text{bonded } ab} \frac{g}{4} \end{aligned} \quad (21)$$

and the second-order contribution to the cohesive energy will be

$$\Delta E_{\text{coh}}^{(2)} = -\frac{3g}{8} \rightarrow E_{\text{coh}}^{(2)} = [3R - 3(1 + \frac{1}{4})g] \frac{1}{2} . \quad (22)$$

The perturbation expansion may be pushed to fourth order (the third-order contribution being zero). The general expression of the fourth-order energy is

$$\begin{aligned} \epsilon_0^{(4)} &= \sum_{IJK} \frac{\langle O | H | I \rangle \langle I | H | J \rangle \langle J | H | K \rangle \langle K | H | O \rangle}{\Delta E_{OI} \Delta E_{OJ} \Delta E_{OK}} \\ &\quad - \epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle , \end{aligned} \quad (23)$$

$$\epsilon^{(2)} \langle \psi^1 | \psi^1 \rangle = \left[\sum_I \frac{\langle O | H | I \rangle}{\Delta E_{OI}} \right] \left[\sum_J \left(\frac{\langle O | H | J \rangle}{\Delta E_{OJ}} \right)^2 \right] .$$

It is clear that in the triple summation I and K must result from one spin exchange on two different bonds, ab and ef for instance, and that J is then necessarily obtained by performing both spin exchanges.

The triple summation actually reduces to a double summation, and important cancellations occur between the two double summations, as is well known for the many-body problem, where the cancellations are expressed in terms of the linked cluster theorem.³⁴ In the present case, the cancellations are easily understood by considering two independent (nonconnected) bonds ab and ef . Then these two spin exchanges give rise to four possibilities in the "triple" summation

I	J	K
$\mathcal{T}_{ab}^S O\rangle$	$\mathcal{T}_{ab}^S \mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ef}^S O\rangle$
$\mathcal{T}_{ab}^S O\rangle$	$\mathcal{T}_{ab}^S \mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ab}^S O\rangle$
$\mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ab}^S \mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ef}^S O\rangle$
$\mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ab}^S \mathcal{T}_{ef}^S O\rangle$	$\mathcal{T}_{ab}^S O\rangle$

and to a negative energy contribution

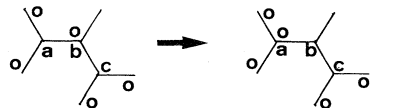
$$\begin{aligned} - \frac{4g_{ab}^2 g_{ef}^2}{(4g_{ab})(4g_{ef})4(g_{ab} + g_{ef})} &= - \frac{g_{ab} g_{ef}}{16(g_{ab} + g_{ef})} \\ &= - \frac{g}{32} \end{aligned}$$

while the two bonds also contribute to the double summation $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$ by

$$\begin{aligned} \frac{g_{ab}^2}{4g_{ab}} \left[\frac{g_{ef}}{4g_{ef}} \right]^2 + \frac{g_{ef}^2}{4g_{ef}} \left[\frac{g_{ab}}{4g_{ab}} \right]^2 &= \frac{1}{64} (g_{ab} + g_{ef}) \\ &= \frac{g}{32} . \end{aligned}$$

For equal bond lengths the two contributions cancel, and with them the fourth-order contributions varying as the square of the number of atoms, as physically desired.

Such a cancellation cannot occur when two bonds are *connected*; if they have a common atom such as ab and bc , the double spin exchange on ab and bc cannot occur, the bc exchange becomes impossible after the ab exchange



and there is no contribution from the $ab+bc$ pair of bonds to the "triple" summation, while that pair of bonds contribute to $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$. Each of these pairs of connected bonds gives a repulsive contribution

$$\frac{1}{64} (g_{ab} + g_{bc}) .$$

Moreover in the double summation of $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$ I and J may be equal and since each bond has four correction bonds, the repulsive fourth-order correction may be taken as

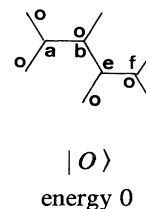
$$\epsilon^{(4)} = \sum_{ab} g \frac{5}{64}$$

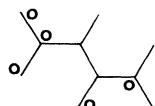
and the fourth-order contribution to the cohesive energy is

$$\Delta E_{\text{coh}}^{(4)} = \frac{15g}{128} \rightarrow E_{\text{coh}}^{(4)} = [3R - 3(1 + \frac{1}{4} - \frac{5}{64})g] / 2 . \quad (24)$$

The perturbation expansion seems to be nicely converging.

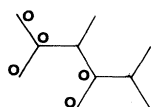
An improved expression of $\epsilon^{(4)}$ might be found by noticing that while the $\mathcal{T}_{ab}^S \mathcal{T}_{ef}^S |O\rangle$ intermediate state J in the triple summation actually lies $8g$ above $|O\rangle$ if ab and ef are sufficiently remote, its relative energy is only $6g$ if ab and ef are nonconnected neighbor bonds, such as in





$$|I\rangle = \mathcal{T}_{ab}^S |O\rangle$$

4g



$$|J\rangle = \mathcal{T}_{ef}^S \mathcal{T}_{ab}^S |O\rangle$$

6g

This prevents a strict cancellation with the corresponding contributions in $\epsilon^{(2)}\langle\psi^{(1)}|\psi^{(1)}\rangle$; the resulting negative contribution would slightly diminish the preceding fourth-order estimate.

However, one must remember that the perturbation expansion from $|O\rangle$ only cannot converge strictly since after a certain number of permutations one should approach or even reach the degenerate $|O'\rangle$ determinant. But for a well spin-ordered cluster $|O'\rangle$ can only be reached after a spin exchange on all bonds, i.e., at a high order of perturbation if the number of bonds (or of atoms) is sufficiently large. The divergence should occur at a very high order of perturbation. In other words, the perturbation should be asymptotically convergent.

Another more rigorous approach would consist in applying the quasidegenerate perturbation theory again, choosing now $\{|O\rangle, |O'\rangle\}$ as the model space. The resulting effective 2×2 Hamiltonian \mathcal{H} on the most spin-ordered distribution would give the lowest states of the problem. In practice for sufficiently large clusters this QDPT approach will lead to the same low-order energies as the independent perturbation of $|O\rangle$ or $|O'\rangle$ since the effective coupling between $|O\rangle$ and $|O'\rangle$ ($\langle O|\mathcal{H}|O'\rangle$) can only be reached through a travel

$$\langle O|H|I\rangle\langle I|H|J\rangle\cdots\langle K|H|O'\rangle$$

which changes the whole spin distribution and which can only appear at a very high order of perturbation. The direct perturbation of $|O\rangle$ only may be considered as the construction of the diagonal part $\langle O|\mathcal{H}|O\rangle$ of the new 2×2 effective Hamiltonian. The difference between the nondegenerate and quasidegenerate approaches is zero at the fourth order (except for the four-atom cluster



for which the exact diagonalization of H^{eff} is easy work).

The preceding example of the graphite-type hexagonal planar lattice has been treated explicitly in detail for a pedagogic purpose; the handling of the same method for tridimensional lattices is a bit more difficult, but may be achieved similarly by hand.

B. The alkali metals: Derivation and results

Three (or four) types of crystallizations have been analyzed. One is the simple cubic system which will be shown to be very high in energy. The body-centered-cubic (bcc) system is shown to give correct estimates of the lattice parameter and cohesive energy, and the perturbation converges quite well for both cases, due to the possibility of introducing a highly ordered zeroth-order spin distribution. The compact packings [namely the face-centered-cubic (fcc) and hexagonal-close-packed (hcp) systems] do not suggest such a highly ordered zeroth-order spin distribution and the perturbation expansion is less nicely convergent, exhibiting some oscillations from the zeroth to the fourth order. Nevertheless these compact packings appear to give a nearly degenerate cohesive energy and a correct lattice parameter, in agreement with low-temperature experiments.

The basic distance parameter r will be the distance between nearest neighbors. Owing to the rapid decrease of the effective exchange parameter g it is clear that the choice of the zeroth-order spin ordering must determine the spin alternation between nearest neighbors. However, for three-dimensional lattices the distance r' to the second neighbors is rather small ($2/\sqrt{3}r = 1.155r$ for bcc crystals), and we decided to include it in the calculation of the energies. More remote atoms have been disregarded in the calculation but their neglect does not mean that our approach only includes short-range effects since the introduction of highly ordered spin distributions and their stabilization are collective effects.

1. The simple-cubic crystallization

The highest spin ordering is given in Fig. 2 and corresponds to a perfectly ordered distribution in the three perpendicular planes; each atom i has six neighbors, all of them of opposite spins and the eight second neighbors at $r' = r\sqrt{2}$ all have the same spin as i . The zeroth-order cohesive energy is then (remembering that each interaction must be counted once only)

$$E_{\text{coh}}^{(0)} = 3R(r) + 4R(r') - 3g(r). \quad (25)$$

The second-order correction results from the coupling

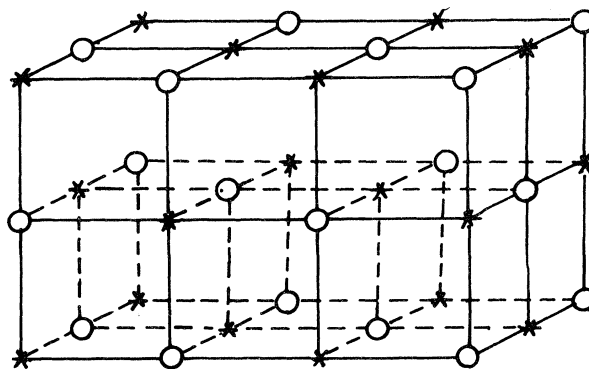


FIG. 2. Zeroth-order spin distribution on the simple cubic lattice. The circles (stars) represent α (β) spins.

with $\mathcal{S}_{ab}^S | O \rangle$, i.e., from one spin exchange on bonds; the resulting determinant loses 10 spin alternations between nearest neighbors and restores 16 spin alternations with the second neighbors. The second-order energy is then

$$\Delta E_{\text{coh}}^{(2)} = -3 \frac{g(r)^2}{10g(r) - 16g(r')} = 3g(r)f(r) \quad (26)$$

(with $f(r) = g(r)/[10g(r) - 16g(r')]$)

$$E_{\text{coh}}^{(2)} = 3R(r) + 4R(r') - 3g(r)[1 + f(r')] . \quad (27)$$

The fourth-order correction will result from the processes in $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$ [cf. Eq. (23)] which concern the same or connected bonds. Each bond has 10 spin alternant connected bonds and the repulsive fourth contribution to the cohesive energy will be

$$\begin{aligned} \Delta E_{\text{coh}}^{(4)} &= 3 \times 11 \frac{g(r)^4}{[10g(r) - 16g(r')]^3} \\ &= 3g(r) \times 11 f^3(r) \end{aligned}$$

TABLE III. Structural properties of metallic lattices.

	r_e (a.u.)	E_{coh} (eV)	Bulk modulus (10^{12} dyn/cm 2)
(a) Li			
bcc			
Order 0	5.87	1.789	0.122
Calc. order 2	5.66	2.150	0.153
Calc. order 4	5.83	1.979	0.152
Expt. ^a	5.71	1.63	0.116
fcc or hcp			
Order 0	6.01	1.728	
Calc. order 2 ^b			
Calc. order 4	6.2	1.876	
Expt. ^c fcc	5.85	$\cong 1.63$	
Expt. hcp	5.88		
Simple cubic			
Order 0	5.68	1.46	
Calc. order 2 ^b			
Calc. order 4	5.69	1.63	
(b) Na			
bcc			
Order 0	7.18	1.06	0.053
Calc. order 2	6.97	1.253	0.065
Calc. order 4	7.07	1.191	0.065
Expt. ^a	6.99	1.113	0.068
hcp or fcc			
Order 0	7.35	0.993	
Calc. order 2	6.18	1.34	
Calc. order 4	7.20	1.164	
Expt. ^c	7.19	$\cong 1.11$	
Cubic			
Order 0	7.02	0.866	
Calc. order 2	6.61	1.020	
Calc. order 4	6.82	1.015	

^aReference 1.

^bThe second-order results are meaningless.

^cReference 36.

resulting in

$$E_{\text{coh}}^{(4)} = 3R(r) + 4R(r') - 3g(r)(1 + f - 11f^3) \quad (28)$$

which will be nicely converging if $f \leq 0.3$.

The resulting variation of the cohesive energy, as calculated to the various orders of perturbation, is given in Table III. The best estimate (fourth order with second neighbors) of the cohesive energy (1.03 eV for Na) is significantly lower than the corresponding estimates for the bcc and compact crystals. If it existed, the simple cubic crystal would exhibit shorter interatomic distances than experiment. The repulsive fourth-order term increases significantly the interatomic distance.

2. The body-centered-cubic (bcc) lattice

The lattice also makes possible a perfect pairing between nearest neighbors. Figure 3 pictures the projection of the maximum spin ordering, represented by alternation of fully α and fully β spin planes, defining some sort of planar spin wave. Each atom is surrounded by eight nearest neighbors of opposite spin. The six second neighbors of i , which lie at a distance $r' = (2/\sqrt{3})r$, all have the same spin as i . The zeroth-order cohesive energy is then

$$E_{\text{coh}}^{(0)} = 4R(r) + 3R(r') - 4g . \quad (29)$$

The second-order correction results from all $\mathcal{S}_{ab}^S | O \rangle$. Any exchange between two planes of Fig. 3 leads to a determinant in which 14 bond exchanges between nearest neighbors have been lost, but 12 exchanges with second neighbors have been introduced, i.e., to a determinant which lies at $14g(r) - 12g(r')$ above the reference perfectly spin-ordered zeroth-order determinant $| O \rangle$. The second-order contribution to the cohesive energy is

$$\Delta E_{\text{coh}}^{(2)} = - \frac{4g(r)^2}{14g(r) - 12g(r')} = -4g f(r)$$

with

$$f(r) = \frac{g(r)}{14g(r) - 12g(r')} \quad (30)$$

and

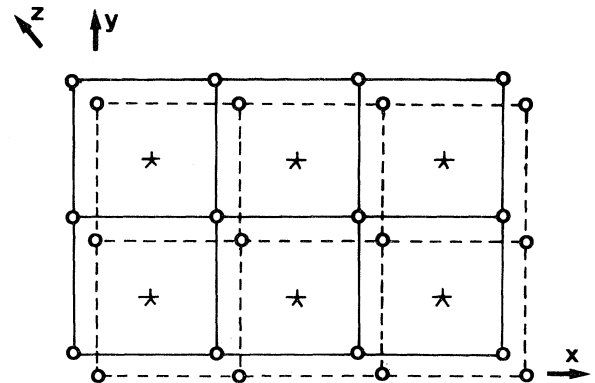


FIG. 3. Zeroth-order spin distribution on the bcc lattice. Solid lines: upper xy plane. Dotted lines: lower xy plane.

$$E_{\text{coh}}^{(2)} = 4R(r) + 3R(r') - 4g(r)[1 + f(r)]. \quad (31)$$

The fourth-order correction may be easily obtained by considering the 15 (i.e., 14 + 1) spin permutations which become impossible after a first spin exchange between nearest neighbors. The resulting correction

$$\Delta E_{\text{coh}}^{(4)} = \frac{4 \times 15g^4(r)}{[14g(r) - 12g(r')]^3} = 4g(r)15f^3(r)$$

leads to

$$E_{\text{coh}}^{(4)} = 4R(r) + 3R(r') - 4g(r)[1 + f(r) - 15f^3(r)] \quad (32)$$

and the perturbation seems to behave nicely if $f(r)$ remains smaller than 0.2. The calculated values for $f(r)$ would be $14^{-1} = 0.071$ if one neglected the role of the second neighbors and varies from 0.165 to 0.136 for Na when r goes from 6.5 to 7.5 a.u. when the second neighbors are taken into account.

The resulting energies at the various orders are given in Table III. The most complete evaluation ($E_{\text{coh}}^{(4)}$ including second neighbors) is somewhat exaggerated (1.98 eV for Li, 1.19 eV for Na₂), but becomes very reasonable. The bond distances are in good agreement with experiment, although a bit too long.

3. The compact hcp or fcc lattices

The compact hcp lattice is rather difficult to visualize simply, while the fcc lattice may be represented simply through the square containing planes (Fig. 4). Each atom has 12 nearest neighbors (distance r) and 6 second neighbors at distance $r' = \sqrt{2}r$. It becomes now impossible to find a total spin ordering between nearest neighbors. One can introduce a full spin ordering in two perpendicular square planar lattices, but in the third direction, one will find successions of fully α and fully β planes. The best spin ordering $|O\rangle$, as pictured in Fig. 4, is of course six-fold degenerate (instead of twofold degenerate in the preceding problems), and one may predict that the convergence behavior of our treatment will be more questionable.

Each atom i is then surrounded by eight atoms of opposite spins (four in the xy plane of Fig. 4, two above and two below in the xz plane), while four nearest neighbors (in the yz plane) have the same spin as i . The six second neighbors all have the same spin as i . The zeroth-order cohesive energy is then

$$E_{\text{coh}}^{(0)} = 6R(r) + 3R(r') - 4g(r). \quad (33)$$

Comparing this expression to that relative to the bcc lattice [Eq. (29)] one sees that the fcc lattice exhibits the same stabilizing spin exchange but larger repulsions and should be less stable than the bcc. This zeroth-order statement will be balanced by higher-order corrections, which necessarily will be larger in a less ordered situation.

The second-order correction actually goes through

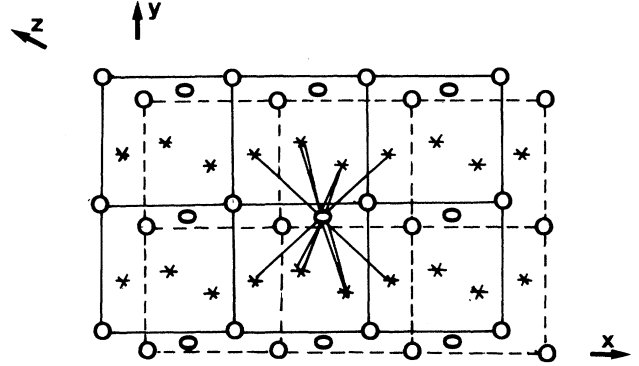


FIG. 4. Zeroth-order spin distribution on the fcc lattice. Solid lines: upper xy plane. Dotted lines: lower xy plane.

$\mathcal{F}_{ab}^S |O\rangle$ determinants in which the a and b atoms have lost six spin alternations. If the ab exchange occurs in the xy plane, for instance, for the a atom three spin alternations are lost in the xy plane, and four in the xz plane, but four new spin alternations are obtained in the yz plane. If the spin exchange occurs in the xz plane the conclusions are identical. In both cases the spin exchange results in the building of 12 spin alternations between second neighbors. The spin permuted determinants $\mathcal{F}_{ab}^S |O\rangle$ lie at $6g(r) - 12g(r')$ above the $|O\rangle$ reference determinant, and

$$\Delta E_{\text{coh}}^{(2)} = \frac{-4g^2(r)}{6g(r) - 12g(r')} = -4g(r)f(r), \quad (34)$$

where

$$f(r) = \frac{g(r)}{6g(r) - 12g(r')}, \quad (35)$$

$$E_{\text{coh}}^{(2)} = 6R(r) + 3R(r') - 4g(r)[1 + f(r)].$$

The denominator appearing in $f(r)$ (which is characteristic of the perturbation ratio) is likely to be small due to the appearance of new spin alternations when some disorder is introduced in the maximum spin alternation. Actually the quantity $6g(r) - 12g(r')$ becomes very small for $r < 6$ a.u. for Na resulting in meaningless second-order cohesive energies for this distance.

One may go now to the fourth-order energy correction, but one must notice that in that case, where the zeroth-order wave function is not perfectly spin alternating, the first \mathcal{F}_{ab}^S spin exchange in the xy or xz planes makes possible connected spin alternations in the yz planes which were previously impossible, and which have no counterpart in $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$.

Referring to Fig. 4 one should take into account that after an ab (in xy plane) spin permutation 15 bc or ac spin permutations become impossible in the xy or xz planes, resulting in a repulsive contribution from $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$, 8 bc or ac spin permutations become possible in the yz plane which contribute to the general fourth-order triple summation, without canceling with repulsive contributions in $\epsilon^{(2)} \langle \psi^{(1)} | \psi^{(1)} \rangle$. The resulting fourth-order correction will be

$$\begin{aligned}\Delta E_{\text{coh}}^{(4)} &= 4 \frac{7g^4(r)}{[6g(r) - 12g(r')]^3} \\ &= 4g(r) \frac{7g^3(r)}{[6g(r) - 12g(r')]^3} \\ &= 4g(r)7f^3(r),\end{aligned}\quad (36)$$

$$E_{\text{coh}}^{(4)} = 6R(r) + 3R(r') - 4g(r)[1 + f(r) - 7f^3(r)].$$

If one considered only nearest neighbors f would be $\frac{1}{6}$ and the perturbation would seem to converge nicely but the inclusion of the second neighbors introduces large values of f (for Na, $f=0.346$ for $r=6.5$ a.u., 0.233 for $r=7.5$ a.u.) and the oscillations from zeroth to second and from second to fourth orders are important.

The highest spin alternation for the hcp lattice is more difficult to picture, but it also consists in the introduction of eight spin alternations over the 12 nearest neighbors of a given atom, while the six second neighbors (also at distance $r'=r\sqrt{2}$) have opposite spins. A careful examination of the lattice shows that the fcc and hcp lattice remain degenerate to the present level of treatment. This degeneracy might only be broken by considering third neighbors and/or higher orders of perturbation.

In the present treatment the compact hcp and fcc lattices appear to be lower in energy than the bcc at the second-order perturbation level which becomes meaningless for Li ($r_e \cong 5$ a.u., $E_{\text{coh}} \cong 4.7$ eV). This estimate of the cohesive energy is significantly overestimated, and the fourth-order treatment brings the cohesive energy of the compact lattices to a slightly smaller value (1.16 eV for Na, 1.88 eV for Li) than the analogous value for the bcc lattice (1.19 eV for Na, 1.98 eV for Li) but the oscillatory behavior of the series for the compact lattices allows one to consider the compact and bcc lattices as nearly degenerate.

These results would be discouraging if one considered only the room-temperature bcc crystallization. But it is known that at low temperature [< 70 K for Li, 35 K for Na (Ref. 37)] a transformation occurs, and an hcp phase appears. This transformation is not total; bcc remains present [20% for Li (Ref. 38), 50% for Na (Refs. 38 and 39)]. For the lithium, a new fcc phase is obtained at low temperature under deformation,⁴⁰⁻⁴² which confirms the near degeneracy of the bcc, hcp, and fcc lattices. The lowest energy lattice at low temperature seems to be compact and their disappearance at higher temperature is evidently due to the vibrational properties; since every atom has a larger number of neighbors in compact lattices, for a given temperature, i.e., a given number of quanta, the vibrational energy will be larger in compact lattices than in the less dense bcc lattice.

The experimental bond distances in the compact forms [$r=5.85$ a.u. (fcc) or 5.88 a.u. (hcp) for Li,³⁶ 7.12 a.u. for Na (hcp)] are slightly larger than for the bcc lattice, as expected, and in good agreement with our calculated values, which are about 0.1 Å larger.

The bcc form having a lower density than the compact lattices, a phase change occurs under pressure from bcc to compact forms,⁴² but the value of this pressure is tem-

perature dependent and its calculation would require the knowledge of the vibrational energies which is beyond the scope of this preliminary work.

The curvature of the cohesive energy near the minimum should give us the compressibility or the bulk modulus

$$B = V \frac{\partial^2 E_{\text{coh}}}{\partial V^2}$$

and the calculated values agree very well with the experimental one.¹

Extension to noble metals. For noble metals, the relevant atomic configuration to build the crystal is $d^{10}s^1$. This configuration is nearly degenerate with the d^9s^2 configuration (which is 1.5 eV above the preceding one on the Cu atom). This second configuration should not play a role in the crystal building since the s^2 distribution is rather diffuse and would induce large repulsive interactions with the neighbor atoms. In other words, the d^9s^2 configuration would lie very high in energy in the solid. This configuration does not play a significant role in the Cu_2 dimer ground state.⁴³ However, it is involved in the ${}^3\Sigma_u^+$ minimum recently studied by Bondybey,⁴⁴ which appears to occur at a very short interatomic distance. This minimum should be essentially $(d^9s^2)(d^{10}s^1)$ in nature, due to the construction of a three-electron ($s_A^2 - s_B$) bond of about 1.6 eV depth. The study of the copper clusters and solid require the knowledge of a diabatic ${}^3\Sigma_u^+$ potential curve remaining $(d^{10}s^1)^2$ at all distances. The lowest ${}^3\Sigma_u^+$ adiabatic potential curve, as grossly calculated by Witko and Beckmann⁴⁵ actually appears as dominated by an avoided crossing between the ${}^3\Sigma_u^+(d^{10}s^1)^2$ configuration and the ${}^3\Sigma_u^+(d^9s^2)(d^{10}s^1)$ configuration. To obtain the former essentially repulsive diabatic potential curve, the Cu_2 dimer has been calculated as a two-electron problem, the d^{10} electrons being kept in the core and treated through a nonempirical pseudopotential extracted from atomic Hartree-Fock (HF) calculations⁴⁶ according to the technology of Barthelat and Durand.⁴⁷ The effect of the high polarizability of this "core" is treated through the core-valence correlation method recently proposed by Jeung *et al.*⁴⁸ This method gives the following characteristics for the ground ${}^1\Sigma_g^+$ and excited ${}^3\Sigma_u^+$ potential curves:

$$\begin{aligned}X {}^1\Sigma_g^+(\text{calc})r_e &= 2.14 \text{ \AA}, \quad D_e = 1.54 \text{ eV}, \\ X {}^1\Sigma_g^+(\text{expt})r_e &= 2.21 \text{ \AA}, \quad D_e = 2.05 \text{ eV}, \\ a {}^3\Sigma_u^+(\text{calc})r_e &= 3.49 \text{ \AA}, \quad D_e = 0.111 \text{ eV}.\end{aligned}$$

The ground-state well depth is underestimated. However, we decided to use the calculated potential curves to study the copper solid; the main interest of this exploratory work comes from the fact that the noble metals crystallize in the fcc lattice,¹ and it was a challenge to see whether our model might reproduce this qualitative difference with the alkali metals. The results are given in Table IV. In the present case the fcc results are lower than the bcc ones; while the reverse was true for the alkali atoms. If one remembers that the series is poorly convergent for the fcc lattice, the fourth-order cohesive energy is underestimated for this lattice and the energy difference between the fcc and bcc lattices should be larger than the calculat-

TABLE IV. Structural properties of copper solid.

	r_e (a.u.)	D_e (eV)	Bulk modulus (10^{12} dyn/cm 2)
fcc			
Order 0	2.567	2.568	0.086
Calc. ^a order 2	2.324	3.257	0.048
Calc. order 4	2.545	2.920	1.689
Expt. ^b	2.55	3.49	1.37
bcc			
Order 0	2.527	2.606	
Calc. ^a order 2	2.454	3.015	
Calc. order 4	2.490	2.88	

^aFrom calculated $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves (Ref. 46).

^bReference 1.

ed 0.04-eV fourth-order difference (and smaller than the 0.24-eV second-order estimate).

III. DISCUSSION

The rather unexpected success of this very simple scheme for the ground-state properties of the solid state of alkali metals deserves a few comments concerning (i) the possible refinements of the model for alkali metal, (ii) the relation between this model and the apparent contradictory band model, and (iii) the possible extension to other types of metals involving either p or d open shells besides the s electron contribution.

A. Possible refinements of the model for alkali and noble metals

1. Improvement of the effective Hamiltonian

As mentioned previously the effective Hamiltonian used in this work kept the simplest possible form since it remained a bieletronic two-body Hamiltonian. The numerical success of the model may be partly fortuitous as the result of canceling errors since the effective Hamiltonian should include at least three-body and four-body terms. *Ab initio* calculations already show that the repulsion between three atoms is not strictly additive; specific three-body repulsive terms contribute up to 20% of the two-body contributions in three-body clusters of rare gas.⁴⁹ Such three-body repulsive terms should be extracted from the study of X_3 in its $S_z = \frac{3}{2}$ quadruplet state as a function of the geometry of the cluster A, B, C in a non-symmetrical geometry ($r_1 = AB$, $r_2 = BC$, $\theta = \{ABC\}$)

$$V_{(A,B,C)}^3 = 4A'(r_1, r_2, \theta) - R(AB) - R(AC) - R(BC).$$

The same methodology should be applied (and will be applied) to extract the three-body magnetic operators such as the three-body contribution (involving C) to the exchange operator between A and B $g_{ab}^{(C)}$ in the ABC cluster

$$\delta g_{AB(C)} = g_{ab}^{(C)} - g_{ab}$$

which will be geometry dependent.

Previous work on π systems have shown the importance

of cyclic four-body terms which for instance perform a cyclic spin permutation

$$\left\langle \begin{array}{|c|c|} \hline a & \bar{b} \\ \hline d & c \\ \hline \end{array} \middle| H^{\text{eff}} \middle| \begin{array}{|c|c|} \hline \bar{a} & b \\ \hline d & c \\ \hline \end{array} \right\rangle = \frac{10g^2}{\Delta E},$$

where ΔE is a transition energy to ionic structures, and which should contribute significantly to the cubic lattice energies. These four-body operators should in general depend on six geometric parameters and their extraction and handling may become rather expensive for nonregular clusters. The situation would become worse if n -body terms ($n > 4$) are required to get a reasonable estimate of the energy and of the stable conformations. The involvement of very collective operators would prohibit the present strategy for the study of medium size clusters. For solid-state studies where the relative positions are well defined, the approach would remain practicable even if eight-body terms were important.

Two types of four-body operators should be distinguished. The first type concerns the operators which act on two spin only (in presence of other spins on the two other atoms) and which modify the g_{ij} two-body operator by a cyclic increment

$$\left\langle \begin{array}{|c|c|} \hline a & \bar{b} \\ \hline d & \bar{c} \\ \hline \end{array} \middle| H^{\text{eff}} \middle| \begin{array}{|c|c|} \hline \bar{a} & b \\ \hline d & \bar{c} \\ \hline \end{array} \right\rangle = g_{ab} + {}^c g_{ab}.$$

This modification of the g_{ij} operator for cyclic situations should be easy to handle. The second type of operators changes the spins of four atoms simultaneously, such as the operator mentioned above, or

$$\left\langle \begin{array}{|c|c|} \hline a & \bar{b} \\ \hline d & \bar{c} \\ \hline \end{array} \middle| H^{\text{eff}} \middle| \begin{array}{|c|c|} \hline \bar{a} & b \\ \hline d & c \\ \hline \end{array} \right\rangle.$$

One should notice that when one starts the perturbative treatment from the most alternant $|O\rangle$ spin ordering, the four body cyclic operators

$$\left| \begin{array}{|c|c|} \hline \bar{a} & b \\ \hline d & \bar{c} \\ \hline \end{array} \right\rangle \left\langle \begin{array}{|c|c|} \hline a & \bar{b} \\ \hline d & c \\ \hline \end{array} \right| = k_{abcd}$$

acting on $|O\rangle$ lead to a determinant $|I\rangle$ in which a lot of bond alternations between nearest neighbors have been broken. The excitation energy from $|O\rangle$ to $|I\rangle$ should be

$$\begin{aligned} \Delta E_{OI} &= \langle I | H^{\text{eff}} | I \rangle - \langle O | H^{\text{eff}} | O \rangle \\ &= 4 | (n_v^{\text{alt}} - 2) - n_v^{\text{nalt}} | g, \end{aligned}$$

where n_v^{alt} is the number of spin alternant neighbors and n_v^{nalt} is the number of non-spin-alternant neighbors. The excitation energy is then equal to $16g$ for simple cubic systems, $24g$ for body-centered-cubic systems, $8g$ for compact systems, and the second-order contribution of these four-body terms

$$\Delta E_{\text{coh}}^2 = \frac{k_{abcd}^2}{\Delta E_{OI}}$$

should remain rather small, at least for bcc systems.

In the present stage, the success may be due to cancellations between many-body repulsive and collective magnetic contributions and/or higher orders of the perturbation theory. This will be studied in future work. Nevertheless some extensions might be attempted to analyze the vibrational properties of the solid, the effect of a local defect.

We shall discuss later (Sec. III B) the possible extensions of the model to non-ground-state properties, namely the possible extraction of electrons (photoelectron spectroscopy) and spectral properties.

2. Improvement of the calculation

The perturbative expansion used in this work might be replaced by variational procedure which would avoid the divergence problem. Among these, one should mention the results obtained by Anderson^{16,50} and Kubo⁵¹ calculating the zero point correlation energy of spin waves. One might also use a cluster expansion from $|O\rangle$, using a trial wave function of the form

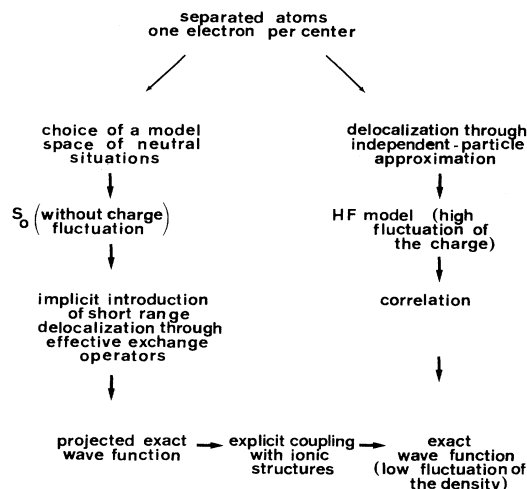
$$\psi_{(S)} = \prod_{\substack{ab \\ \text{nearest} \\ \text{neighbors}}} (1 - \lambda \mathcal{T}_{ab}^S) |O\rangle, \quad (37)$$

where λ would be a unique parameter to determine by minimization.

Such cluster expansions have been proposed for the correlation problem⁵² (where $|O\rangle$ represents the Hartree-Fock determinant and \mathcal{T}_{ab}^S is replaced by double excitations), and also for solution of effective magnetic Hamiltonians for the linear polyenes by Klein and Garcia-Bach,⁵³ and for treatment of correlation in molecules and solids by Stolhoff and Fulde.⁵⁴ Another promising approach might consist in using statistical methods.

B. Connection with the band model

In some sense our treatment is strictly opposite to the basic assumptions of the band model. Instead of being delocalized in plane waves, the electrons are kept on the atoms, without fluctuation of the charge per atom, the fluctuation concerning only the spin distribution. It is well known that the band or Hartree-Fock models (i.e., the independent particle descriptions) overestimate grossly the charge fluctuation, and the correlation treatment introduced later on diminishes this fluctuation and the weight of the ionic instantaneous structure through the self-repulsion of the electrons (the Hubbard Hamiltonian simply introduces the self-repulsion U of two electrons on the same center). The present procedure avoids the first delocalized step, keeps on the one electron per center hypothesis as the basic assumption, and treats the delocalization implicitly through effective exchange operators which actually reflect short-range ionic instantaneous situations.



The two strategies are summarized above. The obtainment of the exact wave functions from the projected wave-function solution would require an explicit treatment of the coupling between the neutral and ionic structures.

One should keep in mind that the magnetic effective Hamiltonian can only reproduce the lowest part of the spectrum of the n -atom, n -electron problem, i.e., the n -electron states of the n -atom problem which have large components on the neutral determinants. One cannot ask this model to give the lowest allowed transition energy, since the dipole transition would lead to a state which is essentially ionic in nature, and which cannot be given through this effective Hamiltonian. Its obtainment would require the production and solution of a different effective Hamiltonian built for the (lowest) ionic states.

The magnetic effective Hamiltonian is unable to treat the problem of the positive or negative ions [i.e., the problem of $(n \pm 1)$ electrons on n centers]. The treatment of this problem (i.e., of the photoelectron spectra) requires the construction of a specific effective Hamiltonian, as shown by Gad ea *et al.* for the π electron problem.⁵⁵ This effective Hamiltonian is defined on a model space of all the determinants which involve one hole only (all the atoms except one bear *one* electron); this model space is analogous to the space of the neutral states in the Heisenberg Hamiltonian, since it represents the most neutral states. The coupling with more "ionic" situations (with two positive centers and a negative one) leads to the construction of an effective $H_{\text{eff}}^{(\pm)}$ Hamiltonian for a positive ion which involves both $F_{ij} a_i^\dagger a_j$, mono-electronic operators introducing the delocalization (or hopping) of the hole from one site to another and $g_{ij} a_i^\dagger a_j a_j a_i$, effective exchanges between atoms bearing different spins, already present in Heisenberg Hamiltonians.

The purely magnetic Hamiltonian is a special case, a particular and extreme case of a much more general class of effective Hamiltonians which involve both the delocalization hopping integrals and the effective exchanges. In fact, the Heisenberg Hamiltonian is only valid for the case of the exactly half-filled band (one electron per center or AO). The treatment of $H_{\text{eff}}^{(\pm)}$ is not easy (the number of one-hole neutral states in the positive ion problem is larger

than the number of the neutral states for the ground-state system).

However, an illuminating remark makes easier the understanding of the connection between the Heisenberg model and the band model. Let us assume that a given spin ordering dominates the projected ground-state eigenfunction, which may be kept as $|O\rangle$ or as the cluster expansion $\psi_{(\lambda)}$ of Eq. (37). Then one may think that the spin ordering factors will be active also in the positive ion. The one-hole determinants of lowest energy are obtained from $|O\rangle$ by the annihilation of one electron on any site

$$\phi_p^\dagger = a_p |O\rangle,$$

the energy of which is easily obtained from the energy E_0 of $|O\rangle$,

$$\langle \phi_p^\dagger | H^{\text{eff}} | \phi_p^\dagger \rangle - \langle O | H^{\text{eff}} | O \rangle = I + n_p^p g,$$

where I is the atomic ionization energy and n_p^p is the number of neighbors of the atom p presenting a spin alternation with p . Other one-hole determinants of higher energies are obtained from the ϕ_p^\dagger by spin permutations $\mathcal{T}_{ab}^S \phi_p^\dagger$.

One may guess that a set of low-energy functions for the positive ion are obtained from the local ionizations of the cluster expansion of Eq. (37) which introduces the spin ordering and its relative disorder

$$\psi_p^\dagger = a_p \psi_\lambda = a_p \prod_{ab} (1 - \lambda \mathcal{T}_{ab}^S) |O\rangle,$$

and a reasonable approximation for the positive ion lowest states will be given by the interaction between these locally ionized states, i.e., by solving the $n \times n$ submatrix of H^{eff} reduced to the ψ_p^\dagger functions

$$\langle \psi_p^\dagger | H^{\text{eff}} | \psi_q^\dagger \rangle = \langle O | a_p H^{\text{eff}} a_q | O \rangle - \lambda \langle O | a_p H a_q \mathcal{T}_{ab}^S | O \rangle + \dots,$$

and the matrix element between $a_p |O\rangle$ and $a_q |O\rangle$ is of course the hopping F_{pq} integral which allows for the delocalization of the hole

$$\langle \psi_p^\dagger | H^{\text{eff}} | \psi_q^\dagger \rangle = F_{pq}.$$

The ionization problem is then reduced to a $n \times n$ matrix, the off-diagonal elements of which are the interatomic hopping integral. This matrix, which is an *approximation*

of the N -electron Hamiltonian is identical to the mono-electronic Hückel or Fock matrix, the solutions of which are the band functions.

The conclusion of this remark is that the effective Hamiltonian approach, which rests on the hypothesis of one electron per center, and which allows simply for interatomic spin permutations in the neutral state, is not in contradiction with the band structure for the positive ion. If the wave function is dominated by the spin ordering and its fluctuations, this stabilizing spin ordering will be maintained in the positive ion for the regions which are sufficiently far from the hole, but the hole is delocalized.

The present magnetic treatment is not strictly limited to the systems involving one electron and one atomic orbital per atom; it might be generalized to atoms involving several electrons in several atomic orbitals on each atom (such as polyacetylenic chains, or transition-metal atoms) provided that the monocentric ferromagnetic coupling (expressing the atomic Hund rules) is explicitly treated. Work is in progress along this direction.

One should notice that the present model is related to an early suggestion by Pauling¹⁵ of a resonating valence-bond description of metals. This description kept the localization of the electrons on the atoms and assumed that the metal might be described as a resonance between various diatomic couplings in random arrangements. This possible description of the metal, as well as its connection with the Heisenberg model has been discussed by Anderson.¹⁶ The present perturbative procedure allows us to reach better estimates of the energy and to take into account the repulsive components. As already noticed by Pauling and as emphasized by Anderson, a purely neutral state could not explain the electric conductivity. However, one must recall that the Heisenberg model is obtained through a truncation of the wave function to its neutral components, chosen as model space in the quasidegenerate perturbation theory. The eigenfunction of H^{eff} is not an eigenstate of the exact Hamiltonian; the latter involves ionic situations as well and possibly long-range charge fluctuations. The truncated wave function, which may give the correct energy through the corresponding effective Hamiltonian, cannot explain by itself the electric conductivity but one cannot say that it corresponds to an insulating state since the part of the wave function which would be relevant to the understanding of conductivity has been deleted at the very beginning of the model. A perturbation of the truncated wave function would be necessary to restore the full wave function.

¹C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), p. 72.

²C. Herring, in *Magnetism*, edited by C. T. Rado and M. Suhl (Academic, New York, 1966), Vol. IIB.

³P. W. Anderson, *Phys. Rev.* **115**, 2 (1959); in *Magnetism*, edited by C. T. Rado and H. Suhl (Academic, New York, 1963), p. 25.

⁴A. O. Ovchinnikov, *Theor. Chim. Acta* **47**, 297 (1978).

⁵L. N. Bulaevskii, *Zh. Eksp. Teor. Fiz.* **51**, 230 (1966) [Sov.

Phys.—JETP **24**, 154 (1967)].

⁶D. J. Klein and M. A. Garcia-Bach, *Phys. Rev. B* **19**, 877 (1979); M. A. Garcia-Bach and D. J. Klein, *Int. J. Quantum Chem.* **12**, 273 (1977); D. J. Klein, *J. Chem. Phys.* **77**, 3098 (1982); D. J. Klein, C. J. Nelin, S. Alexander, and F. Matsen, *ibid.* **77**, 3101 (1982).

⁷J. P. Malrieu and D. Maynau, *J. Am. Chem. Soc.* **104**, 3021 (1982); D. Maynau and J. P. Malrieu, *ibid.* **104**, 3029 (1982).

⁸J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929); *J. des Cloizeaux*,

- Nucl. Phys. **20**, 321 (1960); B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967); B. Kirtman, J. Chem. Phys. **49**, 3890 (1968); P. R. Certain and O. Hirschfelder, *ibid.* **52**, 5977 (1970); G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1979); I. Shavitt and L. Redmon, J. Chem. Phys. **73**, 5711 (1980).
- ⁹J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 283 (1963).
- ¹⁰P. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953); **21**, 767 (1953); J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953); I. Fischer Hjalmar, Adv. Quantum Chem. **2**, 25 (1965).
- ¹¹Ph. Durand, J. Phys. Lett. **43**, 1461 (1982); Phys. Rev. A **28**, 3184 (1983).
- ¹²D. Maynau, Ph. Durand, J. P. Daudey, and J. P. Malrieu, Phys. Rev. A **28**, 3193 (1983).
- ¹³M. Sald, D. Maynau, J. P. Malrieu, and M. A. Garcia-Bach, J. Am. Chem. Soc. **106**, 571 (1984).
- ¹⁴M. Sald, D. Maynau, and J. P. Malrieu, J. Am. Chem. Soc. J. Am. Chem. Soc. **106**, 580 (1984).
- ¹⁵L. Pauling, Proc. Natl. Acad. Sci. **39**, 551 (1953); *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), p. 334.
- ¹⁶P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
- ¹⁷K. F. Freed, J. Chem. Phys. **60**, 1765 (1974); S. Iwata and K. F. Freed, *ibid.* **61**, 1500 (1974); Y. S. Lee, H. Sun, M. G. Sheppard, and K. F. Freed, *ibid.* **74**, 6842 (1981).
- ¹⁸C. Bloch, Nucl. Phys. **6**, 329 (1958).
- ¹⁹F. O. Ellison, J. Am. Chem. Soc. **85**, 3540 (1963).
- ²⁰J. C. Tully, in *Modern Theoretical Chemistry Semiempirical Methods of Electronic Structure Calculations*, edited by G. A. Segal (Plenum, New York, 1977), Vol. 7A, p. 173.
- ²¹S. C. Richtsmeler, M. L. Hendewerk, D. A. Dixon, and J. L. Gole, J. Phys. Chem. **86**, 3922 (1982). The identity between DIM and Heisenberg Hamiltonians breaks down when ionic states are used in the DIM algorithm.
- ²²G. H. Jeung, J. P. Daudey, and J. P. Malrieu, J. Phys. B **16**, 699 (1982).
- ²³R. D. Poshusta and D. J. Klein, Phys. Rev. Lett. **48**, 1555 (1982).
- ²⁴S. M. Blinder, J. Chem. Phys. **32**, 111 (1960).
- ²⁵D. Konowalow and M. L. Olson, J. Chem. Phys. **71**, 450 (1979).
- ²⁶M. L. Olson and D. D. Konowalow, Chem. Phys. **21**, 333 (1977).
- ²⁷D. D. Konowalow, M. E. Rosenkrantz, and M. L. Olson, J. Chem. Phys. **72**, 2612 (1980).
- ²⁸S. C. Richtsmeler, D. A. Dixon, and J. L. Gole, J. Phys. Chem. **86**, 3937 (1982); see, as a previous work, A. L. Companion, Chem. Phys. Lett. **56**, 500 (1978).
- ²⁹J. Kendrick and I. H. Hillier, Mol. Phys. **33**, 635 (1977).
- ³⁰W. H. Gerber and E. Schumacher, J. Chem. Phys. **69**, 1692 (1978).
- ³¹R. L. Martin and E. R. Davidson, Mol. Phys. **35**, 1713 (1978).
- ³²H. O. Beckmann, J. Koutecky, P. Botschwina, and R. Meyer, Chem. Phys. Lett. **67**, 119 (1979).
- ³³H. O. Beckmann, J. Koutecky, and V. Bonacic-Koutecky, J. Chem. Phys. **73**, 5182 (1980).
- ³⁴K. A. Brueckner, *The Many Body Problem* (Wiley, New York, 1959).
- ³⁵J. Goldstone, Proc. R. Soc. London, Ser. A **239**, 267 (1959).
- ³⁶C. S. Barrett, Phys. Rev. **72**, 245 (1947); Acta Crystallogr. **9**, 671 (1956); *Phase Transformations in Solids* (Wiley, New York, 1950).
- ³⁷C. S. Barrett, Trans. Am. Soc. Met. **49**, 53 (1957).
- ³⁸J. D. Filby and D. L. Martin, Proc. R. Soc. London, Ser. A **276**, 157 (1963).
- ³⁹D. Hull and H. M. Rosenberg, Phys. Rev. Lett. **2**, 205 (1959).
- ⁴⁰V. Hovi, E. Mantysalo, and K. Tuisanen, Acta Mater. **14**, 67 (1966).
- ⁴¹I. A. Ginotin, B. G. Lazarev, and I. R. Khveduck, Fiz. Met. Metallov. **16**, 793 (1963); **16**, 794 (1963).
- ⁴²B. Olinger and J. W. Shaner, Science **219**, 1071 (1983).
- ⁴³M. Pelissier, J. Chem. Phys. **75**, 775 (1981); C. W. Bauschlicher, S. P. Walch, and P. M. Siegbahn, *ibid.* **78**, 3347 (1983).
- ⁴⁴V. E. Bondybey, J. Chem. Phys. **77**, 3771 (1982).
- ⁴⁵M. Witko and M. O. Beckmann, Mol. Phys. **47**, 945 (1982).
- ⁴⁶G. H. Jeung and J. C. Barthelat, J. Chem. Phys. **78**, 2097 (1983). The same treatment of copper as a one-electron atom has been applied with better success by H. Stoll, P. Fuentealba, M. Dolg, J. Flad, Y. L. Szentpaly, and H. Preuss, J. Chem. Phys. **79**, 5532 (1983).
- ⁴⁷J. C. Barthelat and Ph. Durand, Gazz. Chim. Ital. **108**, 225 (1978).
- ⁴⁸G. H. Jeung, J. P. Malrieu, and J. P. Daudey, J. Chem. Phys. **77**, 3571 (1982); G. H. Jeung, J. P. Daudey, and J. P. Malrieu, J. Phys. B **16**, 699 (1983).
- ⁴⁹J. P. Daudey, O. Novaro, W. Kolos, and M. Berrondo, J. Chem. Phys. **71**, 4297 (1979).
- ⁵⁰P. W. Anderson, Phys. Rev. **86**, 694 (1952).
- ⁵¹R. Kubo, Rev. Mod. Phys. **25**, 344 (1953).
- ⁵²J. Cizek, J. Chem. Phys. **45**, 4256 (1966); J. Cizek and J. Paldus, Int. J. Quant. Chem. **5**, 359 (1971).
- ⁵³D. J. Klein, Mol. Phys. **31**, 811 (1976); I. Nebenzahl, Phys. Rev. **177**, 1001 (1969). M. A. Garcia-Bach and D. J. Klein, Int. J. Quant. Chem. **12**, 273 (1977).
- ⁵⁴G. Stolhoff and P. Fulde, Z. Phys. B **26**, 257 (1971); **29**, 231 (1978), J. Chem. Phys. **73**, 4548 (1980).
- ⁵⁵X. Gadea, D. Maynau, and J. P. Malrieu, Int. J. Quantum Chem. (to be published).