

Table 3—cont.
(b) The valence band

	A	B	C	L	M	N
Our values ($\hbar^2/2m$)	-13.0	-8.9	10.3	-31	-4	-32.3
Experimental ($\hbar^2/2m$)	-13.0 ± 0.2	$\pm 8.9 \pm 0.1$	10.3 ± 0.2	—	—	—

acceptable structures. The quantities that we used to determine this band structure are listed in Table 3 in comparison with the experimental values⁽⁷⁾ derived by cyclotron resonance. As is shown in the Table, we have had to take the value of the longitudinal effective mass m_l a little smaller and the value of the transverse effective mass m_t considerably larger than the cyclotron resonance data, respectively.

We can refine our theory by taking into account more distant resonance integrals. But in view of the fact that our available data are confined to effective mass data derived from cyclotron resonance experiments and a few data concerning energy gaps derived by optical absorption experiments, such an attempt may be impractical.

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N.2 ON THE CONNECTION BETWEEN BONDS AND BANDS IN METALS AND SEMICONDUCTORS

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THESE last years, various investigators in semiconductor and metal physics have expressed the need for a chemical approach to solid state problems. This means an approach using the localized electron picture and the valence bond scheme. They take as an example PAULING's "resonating valence bond theory of metals". The interest of this theory seems to justify a further investigation into its nature and its connection with the band

theory. We shall illustrate how one might attempt this by using a theorem of LÖWDIN and formulating the resonances in terms of configuration interaction.

A chemical approach to solid state problems implies, as must any correct description of cohesive, magnetic or electric properties of solids, an appropriate treatment of electron-electron correlation due mainly to Coulomb interaction. This

fact has led SLATER to develop the method of configuration interaction by which he was able to show the equivalence of valence bond and molecular orbital treatment of the hydrogen molecule, where three configurations were necessary. Later LÖWDIN demonstrated that this equivalence could be extended to the N electron problem, showing that a sufficient condition was realized if one started from two complete sets of orbitals φ_K and ψ_e related by an infinite unitary matrix:

$$\varphi_K = \sum_{e=1}^{\infty} U_{Ke} \cdot \psi_e$$

For our purpose however, we will discuss and use a practical version of this theorem in choosing appropriate bases of one-electron wave functions.

For the sake of simplicity let us consider from now on a simple case of the N electron problem, namely the linear chain consisting of N atoms with one electron per atom. This model is not only of academic interest but also of practical interest since such properties as electrical properties may be handled one-dimensionally. The representation suited for molecular orbital treatment is naturally the Bloch representation whereas the one most suited for a valence bond treatment will be the Wannier representation. The Bloch functions $b_q(K, x)$ and Wannier functions $a_q(x-R)$ are connected by the known relation:

$$b_q(\mathbf{K}, \mathbf{x}) = N^{-\frac{1}{2}} \sum_{\mathbf{R}} [\exp(i\mathbf{KR})] a_q(\mathbf{x}-\mathbf{R})$$

By this selection, the infinite unitary matrix gets a simple physical meaning in being reduced to a direct sum of unitary matrices enumerated along the diagonal by the quantum number q . The matrix elements are:

$$N^{-\frac{1}{2}} [\exp(i\mathbf{KR})] \delta_{qq'}$$

From the structure of the unitary matrices we notice that a necessary condition for equivalence is contained in the simple requirement of at least one orbital per electron. Generally the same number, say M of orbitals is required in both representations in order to treat both schemes to the same order of approximation, that means taking into account a specific number of bands. The minimum of one band corresponds to $M_{\min} = N$.

Let us enumerate the number of ways we may distribute the N electrons over M orbitals taking into consideration the exclusion principle but forgetting for a moment the spin variables. First we have the number of ways of distributing $N/2$ doubly filled orbitals, then $N/2-1$ doubly filled orbitals multiplied by the number of distributions of two electrons over the rest of $M-(N/2-1)$ orbitals and so on, until the number of distributions of N singly occupied orbitals. So we have:

$$\mathcal{N} = \binom{M}{N/2} + \binom{M}{N/2-1} \times \\ \times \binom{M-(N/2-1)}{2} + \dots + \binom{M}{N}$$

Whatever the spin configuration one imposes on the electrons, any determinantal wave function of the N electrons expressed in one scheme becomes, via the unitary transformation, a linear combination of determinantal wave functions in the other scheme—the number of which is never larger than \mathcal{N} . So a configuration in one scheme is a superposition of configurations in the other scheme with definite coefficients given by the unitary transformation.

Next we consider the spin degeneracy. We must specify further the state of the chain and say for instance that it is diamagnetic, characterized therefore by $S_z = S^2 = 0$. Then the total number of singlets will be given by

$$C = \binom{M}{N/2} \rho_0 + \dots + \binom{M}{N/2-K} \times \\ \times \binom{M-(N/2-K)}{2K} \cdot \rho_{2K} + \dots \binom{M}{N} \cdot \rho_{NA}$$

where

$$\rho_{2K} = \frac{1}{K+1} \binom{2K}{K}$$

is Rumer's number.

These singlet states, antisymmetric in spin and symmetric in space variables are linear combinations of configurations with $S_z = 0$; in order to be eigenvectors of $S^2 = 0$, they are produced for example by the projection operator method of LÖWDIN or by the bond configuration method of EYRING. EYRING's bond configurations involve

each $2^{N/2}$ of the $\binom{N}{N/2}$ spin configurations having $S_z = 0$ and are conventionally known under SLATER-PAULING's form. LÖWDIN's singlets are orthogonal whereas EYRING's are not, but the latter have a simple interpretation in terms of bond diagrams. The relation between both descriptions has recently been given by LÖWDIN but only for small values of N . For our purpose we keep the bond configuration description since even in the Bloch scheme they may be constructed by the simple device of placing on Rumer's circle the N values of the wave vector \mathbf{K} instead of the N positions of the atoms. Equivalence is achieved if one writes the solution ψ of the N electron problem as linear combinations of all C singlets in both schemes.

We shall now illustrate how PAULING's resonances may be formulated.

Synchronized resonance

According to PAULING, this resonance implies a change of at least two bonds. It requires the same number of orbitals as electrons: in particular this will be our chain made of hydrogen-like atoms with $M = N$. In principle all the singlet states enumerated above contribute to the resonance but as an illustration of the prototype of this resonance which in fact has not been treated by PAULING, we shall consider only the bond configurations A_1, A_2 given by the diagrams

$$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \begin{pmatrix} 3 \\ 4 \end{pmatrix} \dots \begin{pmatrix} N-1 \\ N \end{pmatrix} \text{ and } \begin{pmatrix} N \\ 1 \end{pmatrix} \begin{pmatrix} 2 \\ 3 \end{pmatrix} \dots \begin{pmatrix} N-2 \\ N-1 \end{pmatrix}$$

and the N bond configurations B_ν given by the diagrams

$$\begin{pmatrix} 1 \\ 2 \end{pmatrix} \dots \begin{pmatrix} \nu \\ \nu+3 \end{pmatrix} \begin{pmatrix} \nu+1 \\ \nu+2 \end{pmatrix} \dots \begin{pmatrix} N-1 \\ N \end{pmatrix}$$

These bond configurations are not stationary but if we impose the cyclic condition to the chain, we may, as in the Bloch scheme, form bases for irreducible representations of the cyclic group by the transformations

$$\mathcal{A}_N = A_1 + A_2 \quad \mathcal{A}_{N/2} = A_1 - A_2$$

$$\mathcal{B}_\mu = \sum_{\nu=1}^N \left[\exp\left(\frac{2\pi i \mu \nu}{N}\right) \right] B_\nu \quad \mu = 1, 2, \dots, N$$

$\mathcal{A}_{N/2}$ interacts with $\mathcal{B}_{N/2}$, \mathcal{A}_N with \mathcal{B}_N since they belong to the same representation $\Gamma_{N/2}, \Gamma_N$. In this example the ground state is given by the following ansatz

$$\psi_N = c_A(A_1 + A_2) + c_B(B_1 + B_2 + \dots + B_N)$$

from which we get two solutions. The same is true for $\psi_{N/2}$ whereas the others $\psi_\mu = \mathcal{B}_\mu$ are unaffected. Since the ψ belong to different representations, they are stationary states. Having found the $N+2$ values E_λ of the energy spectrum, we may easily deduce the behaviour in time of the original bond configurations A and B , imposing a definite configuration at an initial time $t = 0$, and formulate in this way the resonance theory of synchronized type. This procedure may be generalized to include all the sets of N Rumer's bond configurations and in principle also the ionic configurations, but for those it might be advisable to take into account their participation by introducing new orbitals which are linear, but not orthogonal combinations of the basic Wannier functions and calculating the mixing parameters by minimization of the energy.

Pivoting resonance

This resonance occurs for example when there are reasons to attribute two orbitals on at least one or a certain number n of foreign atoms, such as lithium atoms, placed on the chain so that no two such atoms are nearest neighbours. If some superlattice is obtained by this arrangement, we may apply the same procedure as described before with $M_{\min} = N + n$. Here n is the number of PAULING's metallic orbitals.

Uninhibited resonance

This is obtained in the case of a chain of lithium-like atoms in which one has two orbitals per atom, that means $M = 2N$. In treating this resonance, PAULING has however reduced the N electron problem to a one-electron approximation. He assumes that the resonance energy depends on hybridization as binding energy depends on hybridization in a diatomic molecule.

One may recall the connection between resonance-type and conductivity character: uninhibited resonance is responsible for the metallic character of solids, whereas pivoting and synchronized resonances are characteristic of semiconductors, as MOOSER and PEARSON have shown.

In conclusion we may say that PAULING's scheme

is equivalent to the molecular orbital scheme. If the calculations are pursued far enough both theories will give the same result since solid state properties are invariant with respect to unitary transformation applied to one of their description. However, further work must be carried out on simple models in order to obtain these results.

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N.3

ENERGY BANDS OF SILICON AND GERMANIUM*

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IN recent years there has been a great increase in both theoretical and experimental knowledge of the electronic energy bands of Si and Ge. The following information can be deduced from various experiments (energy values are measured relative to the top of the valence band):

(1) The direct energy gap at the center of the Zone, as determined optically by DASH and NEWMAN⁽¹⁾ (0.18 and 0.06 Ryd., for Si and Ge, respectively);

(2) The indirect energy gaps to the conduction-band minima along the (100) and (111) directions in Si and Ge, respectively;

(3) The obverse values, as determined from extrapolating optical measurements^(2,3) on Ge-Si alloys; together with the results of (2) this yields⁽⁴⁾ $E(X_1^{(2)}) = 0.09$ and 0.08 Ryd., and $E(L_1^{(2)}) = 0.22$ and 0.045 Ryd., respectively, for Si and Ge; and

(4) The location of the minimum in the (100) direction in the lowest conduction band in Si at $k_0 = (0.86 \pm 0.06)2\pi a^{-1}$, as determined from the hyperfine structure of donor spin resonance.⁽⁵⁾

In addition the curvatures (effective masses) of the top of the valence and bottom of the conduction bands are known from cyclotron resonance experiments.^(6,7) These curvatures can be used to

estimate certain term values, as will be discussed presently.

On the theoretical side the calculations of HERMAN⁽⁸⁾ for Ge and WOODRUFF⁽⁹⁾ and BASSANI⁽¹⁰⁾ for Si have shown that an orthogonalized plane wave calculation can yield results that are in good qualitative agreement with experiment. Indeed, HERMAN⁽¹¹⁾ has recently emphasized that the qualitative features of the energy bands of semiconductors can be understood in terms of a nearly free electron picture.

Since the plane wave formalism gives a good qualitative account of the variation of energy with wave-vector, the author constructed an interpolation scheme based on the plane-wave formalism which replaced the orthogonalization terms by a repulsive pseudopotential.⁽¹²⁾ The basic assumption here is that the core has relatively little effect on the variation of energy with wave vector for bands near the energy gap. This assumption can be justified by noting that the orthogonalization terms related to the core are chiefly represented by high Fourier components, and the latter are not important in determining effective masses, although they may affect the overall convergence of the levels. If the energy gaps at a few points of the Zone are fitted correctly by a suitable choice of the parameters the latter difficulty is eliminated. In this way 3-parameter pseudopotentials were constructed for Ge and Si that agreed very well with

* The calculations presented in this paper were carried out at Bell Telephone Laboratories, Murray Hill, New Jersey.