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ELECTRONIC STRUCTURE OF SEMICONDUCTORS

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Abstract. — Problems that can be solved with large, fast computers are discussed. Special emphasis is laid on structural questions, which are expected to provide an exacting test of different approaches to the electronic structure of covalent systems.

Before the advent of large-scale computers many quantum theorists felt that the central obstacle preventing a deeper understanding of the electronic structure of molecules and crystals was the computational complexity of the wave equation. The availability of large, fast computers has partially confirmed and partially disproved this viewpoint. On the one hand, many important results have been obtained from the solutions of large matrix equations which would have been too tedious to solve with a desk calculator. On the other hand, most young theorists have become increasingly involved in the mechanics of programming the new computers, to such an extent that they have lost sight of the original goal. The result is the publication of many papers containing undigested and unrelated computer outputs, the assessment of the significance of the results being left as an exercise for the reader. With much of the relevant material either unpublished, unprocessed, or even never printed out by the computer, such assessments are usually not feasible, even for those that know what the problems are.

This situation is not a new one, and my description of it is not particularly original. However, I have some practical remedies to propose, which may be especially suitable for discussion at this « Colloqium on Perspectives ». Perhaps we can arrive at some agreement on these remedies or on some others, that will rescue the subject, and save it from deteriorating entirely into an exercise in programming. That this is a real possibility was demonstrated at a well-attended conference held in the U. S. in the Spring of 1971, entirely devoted to technical problems (such as phase-space sampling), at which discussion of physical questions was specifically excluded.

My remedies emphasize the first step, which is the choice of problem to be solved. The impression seems to be widespread that the one-electron wave equation, apart from the determination of one or two parameters to describe many-electron effects, constitutes a complete prescription for answering all physical questions. One has only to program the equation and photograph the computer output to produce a valuable addition to our physical understanding. The approach is equally suited to a single atom or to hemoglobin. Each calculation is presented in isolation, and the connection between internal electronic structure and physical variables of interest to experimentalists is never made, because nothing is varied. Each calculation is a « one-shot » effort, with its format fixed by the standard program, which is seldom, if ever, varied.

To go beyond mere demonstration of computer capability requires, of course, some prior insight into the nature of the physical problem. It may even require us to anticipate the answer before we begin our calculations. Such insights are often chemical in nature, and rely on structural similarities that are known experimentally. As examples of such behavior in structurally homologous systems, I will discuss three structural problems of current interest in semiconductor physics: pure compounds, pseudobinary mixed crystals, and amorphous systems.

The largest family of structurally homologous semiconductors consists of the tetrahedrally coordinated compounds with formulae $A^N B^{8-N}$ or $A^{N-1} B^{N+1} C_2^{2-N}$ or mixed crystals such as $A_2 B_1^{N-1} C^{8-N}$ or $(A^{N-1} B^{N+1} C_2^{2-N})_{1-x}$.

The simplest compounds, the $A^N B^{8-N}$ ones, have either cubic (sphalerite) structures or hexagonal (wurtzite) ones, and there are about forty such binary compounds with tetrahedral coordination (Phillips,
The ternary compounds $\text{A}^{N-1}\text{B}^{N+1}\text{C}^{2-}\text{N}$ usually have the chalcopyrite structure, which is tetragonal. The A-B interactions, which are responsible for the deviations from cubic symmetry, are second neighbor ones, and hence alter the axial ratio $c/a$ from the ideal value (cubic) by as much as 10%. This may be compared with deviations from ideal of $c/a$ in wurtzite crystals (third neighbor interactions) of order 1%.

There are a number of structural questions concerning this family of compounds that deserve attention. Of course, a calculation of the one-electron energy levels of a crystal does not by itself determine the total energy of the crystal, because of double counting of electron-electron interaction energies, as well as local and static approximations to exchange and correlation energies. However, experience with a number of molecular calculations of the extended Hückel type and the CNDO method has shown that molecular configurations at constant bond length (corresponding to constant crystal density) can be determined by minimizing the sum of the one-electron energies of occupied states. Moreover, changes in structure, achieved by varying bond angles and conformation configurations, most strongly affect electron energy levels near the Fermi energy, and have almost no effect on the energy of the totally symmetric $I_g$ state at the bottom of the valence band. Thus all energies can be referred to $E(I_g) = 0$.

With this prescription we can try to carry out calculations to answer substantive questions such as the following:

1) What are the factors that determine the phase transformation from sphalerite to wurtzite? This question has already been discussed briefly by Van Vechten (1969), but it deserves more systematic, quantitative analysis. The same calculations can be used to determine the $c/a$ ratio and the birefringence of compounds with the wurtzite structure. I would like to see calculations of these quantities carried out for at least twenty $\text{A}^8\text{B}^8\text{C}^8\text{N}$ tetrahedrally coordinated compounds, in order to see whether the calculations are actually accurate enough to answer these questions. Previous workers on wurtzite compounds, such as Bergstresser (1967), encountered convergence difficulties. These arose because of the presence of four atoms per unit cell, instead of the two that are found in the cubic sphalerite structure. These difficulties are certainly removable with large, fast computers. Moreover, the discipline imposed by having some real structural questions to answer might help us to find a way of introducing the differences between wurtzite and sphalerite in a systematic, more rapidly convergent way. By this I mean a separation of the effects of longer-range forces (third neighbors) from shorter-range ones (bond-bending and deviations from tetrahedral coordination).

2) What are the factors that cause the A and B atoms in $\text{A}^{N-1}\text{B}^{N+1}\text{C}^{2-}\text{N}$ compounds to order on sublattices, and produce a tetragonal distortion as well as determine the internal coordinates (bond angles and lengths) in the unit cell? Here again calculations should be carried out for ten or twenty compounds, in order to identify unambiguously the factors responsible for structural trends. If the approach is a good one, and the crystal potential is sufficiently accurate, we should be able to answer these questions.

Let us now turn to a somewhat more difficult problem that of the pseudobinary compounds such as $\text{A}_x\text{B}_y\text{C}^8\text{N}$. Thermodynamically many of these alloys behave as regular solutions, and even at room temperature some of them are stable for all values of $x$, i.e., they are miscible in all proportions. The energy bands are correspondingly nearly linear in $x$ and only a small downward "bowing", or depression, proportional to $x(1 - x)$, is observed in many cases (Van Vechten, 1970). Nevertheless the energy band structure of these crystals is not accessible by brute force, and some averaging procedure, based on scattering theory (perturbation relative to the average potential) is ordinarily employed to obtain the energy levels.

The great weakness in most of the averaging procedures is that they do not obtain a self-consistent potential for the system, either in terms of the electron distribution, or in terms of the nuclear coordinates, which are generally assumed to lie on a virtual lattice. Moreover, the averaging procedures are so cumbersome, and are expressed in such general terms, that it is virtually impossible to carry the calculations through to a self-consistent conclusion.

With large, fast computers now becoming available, it is possible to attack this problem in a way that is flexible and imaginative, and which is suited specifically to the problem at hand, and not to some other problem, such as quantum electrodynamics. The way that I would use is the following. Represent each atomic potential by a pseudopotential, determined semiempirically to fit the energy bands of the pure $\text{A}^8\text{B}^8\text{N}$ compounds. (In determining this pseudopotential, one must take care to introduce a suitable high-energy cutoff into the wave equation. This avoids certain spurious effects connected with charge transfer from the core of the cation to the core of the anion. See Phillips, 1970.) Having determined the pseudopotentials in this manner, one should obtain good results for the energy bands of the mixed crystal by making a virtual crystal approximation and averaging making a virtual crystal approximation and averaging making a virtual crystal approximation and averaging the pseudopotentials of the cations, $V_{av} = V_A + (1 - x) V_B$ for an $\text{A}_x\text{B}_y\text{C}^8\text{N}$ system. One can then test the validity of the averaging procedure for $x = 1/2$ by studying the energy levels of a periodically repeated cube containing four A and four B atoms, together with eight C atoms, and comparing the energy levels of this system against that of the same cube with $V_{av} = (V_A + V_B)/2$ on the cation.
sites. The energy levels of the latter at $k = \Gamma$ are of course the same as those of the virtual crystal with two atoms per unit cell, and $k = \Gamma, X$ and $L$. However, the wave functions of the former can be used to diagonalize rapidly the secular equation of the large cube, where no virtual crystal approximation has been made. For the latter one can also make a self-consistent study of distortion effects, using the same methods as were used for the chalcopyrite compounds.

The question of breakdown of the virtual lattice approximation leads us naturally into the problem of the electronic structure and optical properties of amorphous semiconductors. Here we encounter the problem that we do not know how to characterize the atomic configurations of the amorphous state, even in the elemental case of amorphous Ge. From experiment it appears that the amorphous state is stabilized by interlocking strain fields associated with vacancies or cavities in a concentration of 0.1 to 1 atomic per cent. The vacancies need not all be monatomic, but if they are, a realistic model of the amorphous state would have to contain of order 100 atoms or more, arranged in such a way that no spatial axes are apparent. (Even the topological problem of how many atoms are needed to accomplish this, for a given distribution of bond angles about tetrahedral, has not been discussed, to my knowledge.) We do know, however, from optical experiments that the band edges of the valence and conduction bands are sharp to within about a Debye energy (i.e., $0.03-0.05$ eV). This strongly suggests that an attempt to model the amorphous state using fewer than 100 atoms is bound to generate spurious « band tailing » effects of the same kind that are found in inhomogeneous amorphous films. (Some theorists have asserted that these tailing effects are characteristic of the amorphous state, but I believe that they are indicative experimentally of inhomogeneities, and theoretically of improper ansätze about « randomly » distributed atoms, self-consistency effects.)

If my description of the amorphous state is correct, the absence of long-range crystalline order is explained in terms of rather weak vacancy-vacancy interactions. This suggests that it may be appropriate to consider the problem of an isolated vacancy first, and settle for a level of computational accuracy of order 0.5 eV, rather than the 0.05 eV needed to describe the amorphous state. Watkins (1970) has calculated the energy levels of a nitrogen impurity surrounded by 35 carbon atoms, using an extended Hückel (LCAO-MO) method. The calculations are successful in the sense that they exhibit Jahn-Teller effects of a reasonable magnitude. It is unsuccessful in the sense that the LCAO approach (as well as the semiempirical Hückel method) works well only for first row atoms, and cannot account for the electronic structure trends in true semiconductors composed of atoms from the Si, Ge, Sn and Pb rows of the periodic table.

Of course, it is just these compounds which have been treated so successfully by the pseudopotential method, and one may reasonably suppose that the energy levels of a large cluster containing 34 pseudo-atoms plus one vacancy should be attainable with modern computers. The four valence levels of diatomic Si require about 60 plane waves for a description accurate to 0.1 eV, but 40 of these can be treated by block perturbation theory (Bergstresser, 1967). Therefore the size of the secular matrix for the large cluster should be about 350, with an additional 700 plane waves treated by block perturbation theory. The cluster in question is an octahedron, to which periodic boundary conditions can be applied, thus ensuring that the wave functions represent propagating waves. The localized states associated with the defect will have a small bandwidth (associated with vacancy-vacancy « image » interactions) which measures directly the uncertainty in the defect energy levels. The pseudo-atoms adjacent to the vacancy are in the interior of the octahedron, and so can be allowed to relax (possible Jahn-Teller effect) without affecting the boundary conditions. Again the equilibrium configuration is determined approximately by summing the energies of the occupied one-electron levels, including different charge states of the vacancy. (A similar approach can be used for studying the mechanism of self-compensation in II-VI semiconductors (Mandel, 1964).)

In the preceding paragraphs I have given a number of examples of important problems in electronic structure of semiconductors that are soluble with the latest large, fast computers but which would have been prohibitively expensive to solve on smaller machines. I have tried to indicate methods for attacking structural problems in covalent crystals which do not exclude important features of the electronic structure where covalent interactions are dominant. The two most noteworthy features which are commonly neglected are the sharpening of band edges by self-consistent adjustment of atomic coordinates, and the formation of bond charges (Phillips, 1968; Walter, 1971), which characterize covalent bonding in dense matter. (The latter electrostatic manifestation of covalency is not conveniently treated either by atomic orbital methods or by means of sphericalized (muffin-tin) potentials.)

In conclusion, I should stress again the importance of using new computer facilities to solve physical problems. The temptation simply to do an elaborate calculation is always great, but it is greatest when a new generation of larger and faster computers becomes available. By now the capabilities of the new machines are well known, so that calculations containing larger clusters of atoms than have hitherto been attempted are not by themselves of great value. Instead we should look for problems where self-consistency can really be tested, as it is in structural questions. These may well provide the most exacting tests of different approaches to understanding electronic structure.
References