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Bond-Orbital Model and the Properties of Tetrahedrally Coordinated Solids

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The recent application of tight-binding models of the Coulson-Hall type to semiconductors by Harrison and co-workers is discussed critically.

Several years ago Van Vechten and I developed an algebraically simple yet numerically very accurate ($\sim 1\%$) model of chemical bonding in $A^N B^{8-N}$ compounds, including specifically the tetrahedrally coordinated semiconductors.¹ The obvious qualitative trends in properties have, over the years, tempted many authors to propose specific quantitative models of binary bonds, but most of them have had little success. For this reason I took some care to review in detail¹ what I regarded as the two models (Pauling and Coulson) which, prior to our model, had been most successful (errors of order 10%). In the review I attempted to identify, insofar as possible, the differences between the three theories. The chemical theories of Pauling and Coulson concentrate primarily on the energies of charge transfer between cation A and anion B , which were estimated either from Pauling's famous table of elemental electronegativities, where the parameters were derived in turn from heats of formation, or in Coulson's case from atomic ionization energies (Mulliken's definition of electronegativities).

By contrast, our theory derives its parameters from chemical trends in the dielectric constants of $A^N B^{8-N}$ compounds. That the dielectric constants could actually contain information of this kind was no doubt unexpected. Traditionally, oscillator strengths were thought to be very difficult to calculate from quantum mechanics, and the large variations in calculated values in small molecules suggested that the oscillator strengths might be sensitive to many factors. However, those who had studied the fundamental optical spectra of semiconductors in some detail² noticed that conventional chemical trends were qualitatively evident in many features of the spectra, notably the energy of the largest peak (conven-

tionally denoted by E_2) in $\epsilon_2(\omega)$, the imaginary part of the frequency-dependent dielectric constant. This led to discovery of the relation for isoelectronic sequences (e.g., diamond, cubic BN, BeO, or Ge, GaAs, ZnSe) that $[\epsilon_1(0) - 1]^{-1}$ was proportional to E_g^{-2} , i.e., to $a + b(4 - N)^2$ in all cases.³ The appearance of the valence number N is what makes possible the development of a chemical theory; this relation is as basic to the success of the dielectric theory of chemical bonding as the fact that most heats of formation depend quadratically on electronegativity differences is to Pauling's approach.⁴

Harrison and co-workers, in a series of recent papers,^{5,6} have attempted to marry dielectric theory to an atomic-orbital model of the Coulson-Hall type. However, it is well known that atomic orbitals yield very poor conduction bands. This is recognized by Harrison, who omits the conduction levels altogether from his energy-band plots. (In fact, the tight-binding models make the conduction band much narrower than the valence band, whereas it should be at least as wide.) For many applications (e.g., to dangling- and back-bond surface states with energies near or below the top of the valence band⁷), the tight-binding method can give results of even quantitative value, provided one is interested in the valence band *only*. However, the dielectric constant involves valence and conduction bands symmetrically, and a method which is good for valence bands and poor for conduction bands cannot derive satisfactory values for chemical parameters from the starting point of dielectric constants. In particular, the valence dependence of $[\epsilon_1(0) - 1]^{-1}$, which is the cornerstone of the dielectric theory, is not explained by Harrison's model, which gives instead of $a + b(4 - N)^2$ an en-

tirely unsuitable result $[a + b(4 - N)^2]^{3/2}$ if Harrison's parameter V_3 is to be proportional to $4 - N$. On the other hand, if V_3 is not made proportional to $4 - N$, then the experimental fact that $[\epsilon_1(0) - 1]^{-1}$ is proportional to $a + b(4 - N)^2$ is relegated by Harrison to an accident which just "happens" to describe trends in seven isoelectronic series. (The same trends are observed in the cohesive energy.¹)

It is, of course, a surprising fact that chemical trends in $\epsilon_1(0)$ can be represented by a single-oscillator model, with small corrections for d -electron effects in elements from the Ge, Sn, and Pb periods.¹ However, it is even more surprising that Harrison should, after the success of the dynamical dielectric model, introduce a static model in which the energy gap $E_g = (V_2^2 + V_3^2)^{1/2}$ enters the polarizability as $|E_g|^{-3}$, i.e., as an odd power.⁵ In general $\epsilon_2(\omega)$ contains odd powers of ω and $\epsilon_1(\omega)$ contains even ones, in accordance with the Kramers-Kronig relations. Although Harrison does not discuss the frequency dependence of $\epsilon(\omega)$, it is difficult to see what can be gained from a physical model which is mathematically so restricted and at the same time does not explain the salient chemical trends.

Several realistic studies have been made of the charge densities of valence- and conduction-band states. These show² that while there is progressive localization of the valence-band charge density on the anions, this is not accompanied by corresponding localization of conduction-band charge density on the cations, as one would have expected from the tight-binding model. [Decoupling through localization can be used to explain the addition factor of E_g^{-1} that occurs in Harrison's expression for $\epsilon_1(0)$.] On the contrary, with increasing ionic character the conduction states remain delocalized and the oscillator strengths are nearly constant (for fixed electron density), as implied by experiment and as incorporated into the dielectric model.¹

Classical models for dielectric functions give the result⁸

$$\epsilon_1(0) = 1 + \omega_p^2 \sum_{j,j'} \frac{f_{jj'}}{(\omega_j - \omega_{j'})^2}, \quad (1)$$

where j and j' are ground and excited states, $\hbar\omega_p$ is the plasma energy associated with the valence electrons, and the dimensionless oscillator strength $f_{jj'}$ satisfies the f -sum rule⁸

$$\sum_{j,j'} f_{jj'} = 1. \quad (2)$$

For a single transition $\omega_j - \omega_{j'} \equiv \omega_g$, and from (1) and (2) one obtains

$$\epsilon_1(0) = 1 + \omega_p^2 / \omega_g^2, \quad (3)$$

which is a simplified version of the equations basic to the dielectric model. From (1) and (2) it is clear that, although it contains only one energy gap, Harrison's model is inconsistent with the single-oscillator approximation, because his $f_{jj'}$ contains a factor which assigns increasing weight to $f_{jj'}$ for larger values of $|\omega_j - \omega_{j'}|$ with increasing values of ω_g . For example $\langle f \rangle \propto \omega_p / \omega_g$ would give $\epsilon_1(0) - 1 \propto \omega_g^{-3}$, but this is not consistent with (2).

There is no doubt that the decoupling effect described by $\langle f \rangle \propto \omega_p / \omega_g$ does occur in the tight-binding approximation, and vestiges of it can be seen in one-electron calculations where interband momentum matrix elements in an isoelectronic series remain nearly constant with increasing ionicity (see Table I). However, to satisfy Eq. (2) one must assume that there are corresponding corrections to f of an excitonic nature. (These are the final-state Coulomb interactions between electrons and holes, which dominate the spectra of ionic crystals like NaCl.) These corrections rather completely cancel the one-electron decoupling effect. In almost all cases this cancelation actually occurs to a surprisingly accurate extent (as can be seen from the very small scatter in Fig. 4 of Ref. 8).

For a single isoelectronic sequence (e.g., Ge, GaAs, ZnSe) where ω_p is constant, the difference between Harrison's model and ours can be indicated explicitly (if rather unrealistically) by arbitrarily assuming that there are two separa-

TABLE I. Chemical trends in interband oscillator strengths between band 4 (the highest valence) and band 5 (the lowest conduction band) at two k points with interband energies close to the E_2 energy. These results were kindly supplied by M. L. Cohen, and are based on his most recent nonlocal pseudopotentials.

k	Compound	$E(4-5)$ (eV)	$ (a/2\pi)\langle 4 \nabla 5\rangle ^2$
X(100)	Ge	4.42	0.76
	GaAs	5.01	0.71
	ZnSe	6.61	0.66
$K(\frac{3}{4}\frac{3}{4}0)$	Ge	4.39	1.59
	GaAs	5.07	1.56
	ZnSe	6.67	1.50

ble contributions to the sum in (1), interband and excitonic, with $\omega_j - \omega_{j'} = \omega_g$ in both cases, and with oscillator strengths f_1 and f_2 , respectively, given by

$$f_1 = \omega_g(\text{Ge})/\omega_g, \quad (4)$$

$$f_2 = 1 - f_1. \quad (5)$$

Harrison's model retains only f_1 , whereas our model includes $f_1 + f_2$. From an inductive viewpoint the cancelation of the two effects, as required by the sum rule, is a great simplification. It is just this cancelation which makes possible a chemical theory, i.e., one which explicitly exhibits effects dependent on size and on the valences N and $8 - N$ or the valence difference $8 - N - N = 2(4 - N)$.

At present there are no complete deductive treatments in semiconductors of excitonic effects (sometimes called local-field corrections) which would explain the observed cancelation. There have been several efforts on the subject recently,⁹ but none of them has attempted to establish broad chemical trends of the kind required to differentiate between Harrison's and our own models. Because our model incorporates the sum rule (2) in the simplest possible manner, and because it is both classical and chemical (in the previous sense) I believe it is the one to be preferred in most cases.

In view of the above, I recommend caution in considering the use of Harrison's model. There has been solid work extending and refining our ideas, e.g., the derivation of orbitally dependent electronegativities,¹⁰ which resolves the discrepancies between Pauling's table of electronegativities and our table, as well as work on ionic

contributions to structural energies in intermetallic compounds.¹¹ Because of this excellent work the entire field of theories of electronegativity will soon be ripe for review again.

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Reply to Phillips's Comment on the Bond-Orbital Model

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The central question of Phillips's Comment, that concerning the dependence of dielectric constant on band gap in polar semiconductors, is extracted and answered theoretically and in terms of experiments. My conclusion differs from his.

I agree that the variation of oscillator strengths in isoelectronic series of increasing polarity, such as Ge, GaAs, ZnSe, CuBr, is very important. This is particularly true for Phillips's ion-

icity theory¹ since the cornerstone of the work is the assumption that the dimensionless oscillator strength can be taken as constant in going from Eq. (1) to Eq. (3) in Phillips's Comment²; that