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TWO-ELECTRON BOND-ORBITAL MODEL I.

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ABSTRACT

Harrison's one-electron bond-orbital model of tetrahedrally coord-
inated solids is generalized to a two-electron model, using an extension of
the method of Falicov and Harris for treating the hydrogen molecule. The
six eigenvalues and eigenstates of the two-electron anion-cation Hamiltonian
entering this theory can be found exactly even in the most general case.
In this first paper, however, the non-orthogonality of the anion and cation
$\underline{s}\,\underline{p}^3$ hybrids is neglected to simplify the treatment and to emphasize the
most essential features of the model. The two-electron formalism is shown
to provide a useful basis for calculating both non-magnetic and magnetic
properties of semiconductors in perturbation theory. As an example of the
former, we calculate expressions for the electric susceptibility and the
dielectric constant. In the limit of no electron correlation, our expres-
sion for the susceptibility agree with that found by
Harrison and by Harrison and Ciraci. As an example of the latter, we calcu-
late new expressions for the nuclear exchange and pseudo-dipolar coefficients.
A simple theoretical relationship between the dielectric constant and the
exchange coefficient is also found in the limit of no correlation. The
expressions for the exchange and pseudo-dipolar coefficients are quantita-
tively evaluated in the limit of no correlation for twenty elemental and
binary semiconductors, and the results are compared with existing experi-
mental data. Preliminary studies on the quantitative effects of correlation
on the various quantities considered here are also discussed.

I. INTRODUCTION

In a recent paper[1] Harrison has introduced what he calls the bond-orbital model of tetrahedrally-coordinated solids. This model is a generalization of the cruder linear-combination-of-atomic-orbitals (LCAO) model originally proposed by Hall[2] for elemental group IV semiconductors and subsequently considered by various others over the past twenty years or so. The LCAO or tight-binding basis set used in this model is made up of four $\underline{s}\,\underline{p}^3$ hybrids on each atom directed towards the four nearest neighbors in the solid. At most, only one-center integrals and two-center integrals linking nearest-neighbor anion-cation pairs are retained. In his first formulation, Harrison neglected the nonorthogonality of the anion and cation hybrids, although this was explicitly retained in the reformulated version of the model by Harrison and Ciraci[3] (hereafter referred to as HC). In any case, the few surviving matrix elements are fit to experiment and the emphasis of the bond-orbital model is on understanding a wide range of properties of semi-conductors and insulators in terms of a few parameters of the anion-cation bond.

While Harrison's bond-orbital model seems to be quite successful in achieving its objectives, there are further refinements one might consider incorporating into the theory. One such refinement is the effect of electron correlation in the bond. Conventional tight-binding theory, of course, is a one-electron method, yet the most fundamental property of the bond is that it contains two electrons. It is of interest, therefore, to consider what modifications a two-electron bond-orbital model implies. In Sec. II of this

paper we formulate such a model using a generalization of the method of Falicov and Harris[4] (hereafter referred to as FH) for treating the hydrogen molecule.

Our two-electron bond-orbital model has several noteworthy features. First, the conceptual simplicity of Harrison's original treatment is largely retained. In the one-electron bond-orbital method one relates crystal properties to the properties of the bonding and anti-bonding orbitals associated with the anion-cation pair. The latter orbitals and their energy eigenvalues can be found by diagonalizing a simple two by two matrix. In the two-electron bond-orbital method, the two by two matrix is replaced by a six by six, which can still be diagonalized analytically even in the most general case. For the sake of simplicity and clarity, however, we will confine our attention in this first paper to certain limiting forms of the general results. Clearly, all the results of our analysis can be used to determine how the predictions of the one-electron theory are modified in specific cases.

An equally important feature of the two-electron formulation is the appearance of the three triplet and two singlet excited states in addition to the singlet ground state. This allows one to perform, in a self-contained manner, perturbation calculations which involve either singlet-triplet or singlet-singlet coupling. An example of the former is the indirect interaction between nuclear spins via the bond electrons. In Sec. III expressions for the nuclear exchange and pseudo-dipolar interactions are obtained for the first time in terms of bond-orbital-model parameters. An example of singlet-singlet coupling is the induced polarization caused by an external electric field. This is the perturbation involved in the calculation of the

dielectric constant, which we also consider in Sec. III. The quantitative predictions of the formulas derived in Sec. III for real semiconductors are considered in Sec. IV, and in Sec. V we draw our conclusions.

II. FORMULATION OF THE TWO-ELECTRON MODEL

The two-electron bond-orbital model is most simply and elegantly formulated in the language of second quantization. In this treatment it is necessary to assume that the anion and cation $s\,p^3$ hybrids, e.g. $\phi_{a\uparrow}(\vec{r})$ and $\phi_{c\uparrow}(\vec{r})$, are orthogonal. While the actual overlap matrix element

$$S = \int \phi^*_{a\uparrow}(\vec{r})\, \phi_{c\uparrow}(\vec{r})\, d\vec{r} \tag{1}$$

may be quantitatively large, in conceptual terms the inclusion of overlap represents a refinement on the basic theory. This overlap may be incorporated into the theory without fundamental difficulty, and will be treated in the second paper of this series.

The Hamiltonian for a general many-electron system can be obtained in second-quantized form from the prescription

$$H = \int \psi^+(\vec{r}) \left[T + V_{ext}(\vec{r}) \right] \psi(\vec{r})\, d\vec{r}$$
$$+ \frac{1}{2} \iint \psi^+(\vec{r})\, \psi^+(\vec{r}')\, \frac{e^2}{|\vec{r}-\vec{r}'|}\, \psi(\vec{r}')\psi(\vec{r})\, d\vec{r}\, d\vec{r}' \tag{2}$$

where $\psi(\vec{r})$ and $\psi^+(\vec{r})$ are the usual field operators, T is the kinetic-energy operator and $V_{ext}(\vec{r})$ is the external potential arising from charges other than those of the electrons under consideration. We wish to focus our attention on the two electrons contained in a single anion-cation bond, so in our case

4

$$\psi(\vec{r}) = C_{a\uparrow}\phi_{a\uparrow}(\vec{r}) + C_{a\downarrow}\phi_{a\downarrow}(\vec{r}) + C_{c\uparrow}\phi_{c\uparrow}(\vec{r}) + C_{c\downarrow}\phi_{c\downarrow}(\vec{r})$$

$$\psi^{+}(\vec{r}) = C_{a\uparrow}^{+}\phi_{a\uparrow}^{*}(\vec{r}) + C_{a\downarrow}^{+}\phi_{a\downarrow}^{*}(\vec{r}) + C_{c\uparrow}^{+}\phi_{c\uparrow}^{*}(\vec{r}) + C_{c\downarrow}^{+}\phi_{c\downarrow}^{*}(\vec{r})$$

where $C_{a\uparrow}^{+}$ and $C_{a\uparrow}$, etc. are the usual Fermion creation and annihilation operators, and

$$V_{ext}(\vec{r}) = V_{a}(\vec{r}) + V_{c}(\vec{r}) + \sum_{i \neq a,c} V_{i}(\vec{r}) \qquad . \qquad (4)$$

The potentials $V_{a}(\vec{r})$ and $V_{c}(\vec{r})$ are centered on the anion and the cation, respectively. Each of these potentials includes a bare-ion potential due to the nucleus and the core electrons plus the potential associated with the three filled hybrids not involved in the bond in question. The potential $V_{i}(\vec{r})$ is that arising from the nucleus, core and four filled hybrids of the ith neighbor of the anion-cation pair.

Using Eq. (3) in Eq. (2) and setting $n_{a\uparrow} = C_{a\uparrow}^{+} C_{a\uparrow}$, etc., one obtains in a straight-forward manner

$$
\begin{aligned}
H = {} & \mathcal{E}_{a}'\,(n_{a\uparrow} + n_{a\downarrow}) + \mathcal{E}_{c}'\,(n_{c\uparrow} + n_{c\downarrow}) \\
& - V_{2}\,(C_{a\uparrow}^{+}C_{c\uparrow} + C_{a\downarrow}^{+}C_{c\downarrow} + C_{c\uparrow}^{+}C_{a\uparrow} + C_{c\downarrow}^{+}C_{a\downarrow}) \\
& + U_{a}\,n_{a\uparrow}n_{a\downarrow} + U_{c}\,n_{c\uparrow}n_{c\downarrow} \\
& + K\,(n_{a\uparrow}n_{c\uparrow} + n_{a\uparrow}n_{c\downarrow} + n_{a\downarrow}n_{c\uparrow} + n_{a\downarrow}n_{c\downarrow}) \quad,
\end{aligned}
\qquad (5)
$$

where $\mathcal{E}'_a$ and $\mathcal{E}'_c$ are the one-center energy expectation values:

$$\mathcal{E}'_a = \int \phi^*_{a\uparrow}(\vec{r}) \left[T + V_{ext}(\vec{r}) \right] \phi_{a\uparrow}(\vec{r}) \, d\vec{r} \qquad (6)$$

with a similar expression for $\mathcal{E}'_c$; V_2 is the two-center transfer or hopping integral (called the covalent energy by HC)

$$V_2 = - \int \phi^*_{a\uparrow}(\vec{r}) \left[T + V_{ext}(\vec{r}) \right] \phi_{c\uparrow}(\vec{r}) \, d\vec{r} \; ; \qquad (7)$$

$\mathcal{U}_a$ and $\mathcal{U}_c$ are the one-center Coulomb integrals:

$$\mathcal{U}_a = \iint \phi^*_{a\uparrow}(\vec{r}) \phi^*_{a\downarrow}(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{a\downarrow}(\vec{r}') \phi_{a\uparrow}(\vec{r}) \, d\vec{r}' d\vec{r} \qquad (8)$$

with a similar expression for $\mathcal{U}_c$; and K is the two-center Coulomb integral

$$K = \iint \phi^*_{a\uparrow}(\vec{r}) \phi^*_{c\uparrow}(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_{c\uparrow}(\vec{r}') \phi_{a\uparrow}(\vec{r}) \, d\vec{r}' d\vec{r}. \qquad (9)$$

The remaining two-center Coulomb integrals have been set to zero consistent with setting $S = 0$ in Eq. (1). In analogy with FH, the following identities can be derived from the fact that there are two electrons in our system:

$$n_{a\uparrow} + n_{a\downarrow} = 2 - (n_{c\uparrow} + n_{c\downarrow})$$

$$(n_{a\uparrow} n_{c\uparrow} + n_{a\uparrow} n_{c\downarrow} + n_{a\downarrow} n_{c\uparrow} + n_{a\downarrow} n_{c\downarrow}) = \qquad (10)$$

$$1 - (n_{a\uparrow} n_{a\downarrow} + n_{c\uparrow} n_{c\downarrow})$$

$$(n_{c\uparrow} + n_{c\downarrow}) = 1 + n_{c\uparrow} n_{c\downarrow} - n_{a\uparrow} n_{a\downarrow}$$

These results can be used in turn to simplify Eq. (5) to the form

$$H = \varepsilon_a' + \varepsilon_c' + K + V_2 H' \qquad , \qquad (11)$$

where the (dimensionless) Hamiltonian H' is

$$H' = X_a\, n_{a\uparrow}\, n_{a\downarrow} + X_c\, n_{c\uparrow}\, n_{c\downarrow} - \left(C_{a\uparrow}^{\dagger} C_{c\uparrow} + C_{a\downarrow}^{\dagger} C_{c\downarrow} \right. \qquad (12)$$
$$\left. + C_{c\uparrow}^{\dagger} C_{a\uparrow} + C_{c\downarrow}^{\dagger} C_{a\downarrow} \right) \qquad ,$$

where we have set

$$X_a = (U_a - K)/V_2 - (\varepsilon_c' - \varepsilon_a')/V_2$$
$$X_c = (U_c - K)/V_2 + (\varepsilon_c' - \varepsilon_a')/V_2 \qquad (13)$$

For $\varepsilon_a' = \varepsilon_c'$ and $U_a = U_c$, the Hamiltonian H given by Eq. (11) is formally equivalent to that considered by FH.

A. Eigenvalues of H

To find the eigenvalues and eigenfunctions of H , we need only consider diagonalizing H' , since $\varepsilon_a' + \varepsilon_c' + K$ and V_2 are constants. Again we follow FH. There are six linearly independent two-electron states in terms of which all the eigenstates of H can be expressed. Symbolically, these basis states are $|a\uparrow c\uparrow\rangle$, $|a\downarrow c\downarrow\rangle$, $|a\uparrow a\downarrow\rangle$, $|c\uparrow c\downarrow\rangle$, $|a\uparrow c\downarrow\rangle$ and $|c\uparrow a\downarrow\rangle$, where $|a\uparrow c\uparrow\rangle$ means $C_{a\uparrow}^{\dagger} C_{c\uparrow}^{\dagger} |0\rangle$, etc. If we denote these states simply as $|i\rangle$, where $i = 1, 2, \cdots 6$, then we can solve the Schroedinger equation

$$H |M\rangle = E_M |M\rangle, \qquad M = I, II. \quad \cdots VI \; ,$$

(14)

by making the expansion

$$|M\rangle = \sum_{i=1,6} a_{iM} |i\rangle \; .$$

(15)

In the usual way, one is led to the condition

$$\| \; H'_{ij} - E'_M \| = 0$$

(16)

for the eigenvalues

$$E_M = \varepsilon'_a + \varepsilon'_c + K + V_2 \, E'_M \; .$$

(17)

It is a straight-forward matter to determine the H'_{ij} and Eq. (16) is easily shown to be

$$
\begin{vmatrix}
-E'_M & 0 & 0 & 0 & 0 & 0 \\
0 & -E'_M & 0 & 0 & 0 & 0 \\
0 & 0 & X_a - E'_M & 0 & -1 & -1 \\
0 & 0 & 0 & X_c - E'_M & -1 & -1 \\
0 & 0 & -1 & -1 & -E'_M & 0 \\
0 & 0 & -1 & -1 & 0 & -E'_M
\end{vmatrix} = 0
$$

(18)

The six eigenvalues of Eq. (18) may be divided into three triplet-state energies, which are degenerate and equal to zero for all X_a and X_c :

$$E_M' = 0 \qquad \text{or} \qquad E_M = \mathcal{E}_a' + \mathcal{E}_c' + K, \quad M = I \dots \text{III} \quad (19)$$

and three singlet-state energies, which are solutions of the cubic equation

$$E_M'^3 - (X_a + X_c) E_M'^2 + (X_a X_c - 4) E_M' + 2(X_a + X_c) \quad (20)$$

The three roots of Eq. (20) may, of course, be written down immediately for arbitrary X_a and X_c , but it is more instructive to consider the special cases $X_a = X_c$ and $X_A = -X_c$. The former case corresponds to taking $\mathcal{U}_a$ and $\mathcal{E}_a' = \mathcal{E}_c'$ in Eq. (13) [or more generally $(\mathcal{U}_a - \mathcal{U}_c) = 2(\mathcal{E}_c' - \mathcal{E}_a')$]. This is the appropriate solution for the elemental group IV semiconductors, where the anion and cation are the same. We shall denote this as the Falicov-Harris limit. Dropping the subscripts a and c and defining

$$V_4 = (\mathcal{U} - K)/2 = V_2 X /2 \qquad (21a)$$

and

$$X = 2 V_4 / V_2 \qquad (21b)$$

one can immediately factor Eq. (20) and obtain

$$\begin{aligned} E_{IV} &= 2\mathcal{E}' + \mathcal{U} \\ &= 2\mathcal{E}' + K + 2V_4 \end{aligned}$$

$$\begin{aligned} E_{V, VI} &= 2\mathcal{E}' + K + \frac{V_2}{2}\left[X \pm \sqrt{X^2 + 16} \right] \\ &= 2\mathcal{E}' + K + V_4 \pm \sqrt{4 V_2^2 + V_4^2} \; . \end{aligned} \qquad (22)$$

Clearly, E_{III} is the ground state energy of the system for all values of V_2 and V_4. An energy-level diagram for the Falicov-Harris limit is shown in Fig. 1.

The other special case, $X_a = -X_c$, corresponds to $U_a = U_c \equiv \Lambda$ in Eq. (13) [or more generally to $U_a + U_c = 2K$]. We denote this as the Harrison limit, since one is led to the results of the one-electron bond-orbital model in this case. Defining

$$V_3 = (\mathcal{E}'_c - \mathcal{E}'_a)/2 = V_2 X/2 \qquad , \qquad (23a)$$

and

$$Y = 2V_3/V_2 \qquad (23b)$$

the three solutions of Eq. (20) are again easily found and one obtains

$$E_{IV} = \mathcal{E}'_a + \mathcal{E}''_c + K$$

$$E_{V, VI} = \mathcal{E}'_a + \mathcal{E}'_c + K \pm V_2 \sqrt{Y^2 + 4} \qquad (24)$$

$$= \mathcal{E}'_a + \mathcal{E}'_c + K \pm 2\sqrt{V_2^2 + V_3^2} \quad .$$

Again E_{VI} is the ground state energy for all V_2 and V_3. Also note that the state $|IV\rangle$ is degenerate with the three triplet states. The energy-level diagram for the Harrison limit is shown in Fig. 1.

Because E_{VI} is the total energy of two bond electrons, the proper relationship between E_{VI} and the one-electron bonding energy E_b of Harrison[1] is

$$E_{VI} = 2E_b - E_{ee} \qquad , \qquad (25)$$

where [from Eq. (9) of Ref. 1]

$$E_b = (\epsilon_a + \epsilon_c)/2 - \sqrt{V_2^2 + (\epsilon_c - \epsilon_a)^2/4} \qquad (26)$$

and E_{ee} is the electron-electron interaction energy, which is counted twice in $2E_b$. Using the bond orbital

$$\phi_b(\vec{r}) = \mu_a \phi_{a\uparrow}(\vec{r}) + \mu_c \phi_{c\uparrow}(\vec{r}) \qquad (27)$$

and the fact that $\mu_a^2 + \mu_c^2 = 1$, it is simple to show that E_{ee} in the limit that $\mathcal{U}_a = \mathcal{U}_c = K$. Equation (25) thus shows that

$$
\begin{aligned}
\epsilon_a &= \epsilon_a' + K \\
&= \int \phi_{a\uparrow}^*(\vec{r}) \left[T + V_a \right] \phi_{a\uparrow}(\vec{r}) \, d\vec{r} \\
&\quad + \int \phi_{a\uparrow}^*(\vec{r}) \left[V_c(\vec{r}) + \int \frac{e^2 \phi_{c\uparrow}^*(\vec{r}') \phi_{\uparrow}(\vec{r}') d\vec{r}'}{|\vec{r} - \vec{r}'|} \right] \phi_{a\uparrow}(\vec{r}) \, d\vec{r} \\
&\quad + \sum_{i \neq a,c} \int \phi_{a\uparrow}^*(\vec{r}) V_i(\vec{r}) \phi_{a\uparrow}(\vec{r}) \, d\vec{r}
\end{aligned} \qquad (28)
$$

with a similar expression for ϵ_c. The first integral on the right-hand-side of Eq. (28) is just the Hartree-Fock expectation value of [T + $V_a(\vec{r})$]. The second and third integrals, on the other hand, vanish identically in the limit that $\phi_{a\uparrow}(\vec{r})$ and $\phi_{c\uparrow}(\vec{r})$ do not overlap. In real materials, however, these latter terms may not be negligible.

Similarly, one can relate the other five two-electron eigenvalues in the Harrison limit to E_b and E_a, the one-electron anti-bonding energy level. This correspondence is illustrated graphically in Fig. 1. The six two-electron energy levels represent the six unique ways two electrons can occupy E_b and E_a. Thus E_{VI} corresponds to having two electrons (one with spin up and one with spin down) in E_b. The four degenerate levels E_I, E_{II}, E_{III} and E_{IV} arise from the four spin combinations one can have with one electron in E_b and the other in E_a. Finally, E_V corresponds to two electrons occupying E_a.

B. Eigenstates of H

Returning to Eqs. (14) and (15), one can determine the expansion coefficients a_{iM} using the calculated E_M in the usual way. For the three triplet states one obtains

$$
\begin{aligned}
|I\rangle &= |1\rangle = |a\uparrow c\uparrow\rangle \\
|II\rangle &= |2\rangle = |a\downarrow c\downarrow\rangle \\
|III\rangle &= \tfrac{1}{\sqrt{2}}(|5\rangle - |6\rangle) = \tfrac{1}{\sqrt{2}}\left(|a\uparrow c\downarrow\rangle - |c\uparrow a\downarrow\rangle\right)
\end{aligned}
\tag{29}
$$

for all X_a and X_c. The singlet states are given by

$$
\begin{aligned}
|M\rangle &= \frac{1}{D(E_M')}\Big[(X_c - E_M')|3\rangle + (X_a - E_M')|4\rangle + \tfrac{1}{2}(X_a - E_M')(X_c - E_M')(|5\rangle + |6\rangle)\Big] \\
&= \frac{1}{D(E_M')}\Big[(X_c - E_M')|a\uparrow a\downarrow\rangle + (X_a - E_M')|c\uparrow c\downarrow\rangle \\
&\qquad\qquad + \tfrac{1}{2}(X_a - E_M')(X_c - E_M')\left(|a\uparrow c\downarrow\rangle + |c\uparrow a\downarrow\rangle\right)\Big] ,
\end{aligned}
\tag{30}
$$

$$
M = IV,\ V,\ \text{and}\ VI ,
$$

where

$$D(E_M') = \left[(X_c - E_M')^2 + (X_a - E_M')^2 + \tfrac{1}{2}(X_c - E_M')^2 (X_a - E_M')^2 \right]^{\pm \frac{1}{2}}.$$

(31)

In the Falicov-Harris limit, $X_c = X_a = X$, the singlet states are found to be

$$|IV\rangle = \tfrac{1}{\sqrt{2}} \left(|a\uparrow a\downarrow\rangle - |c\uparrow c\downarrow\rangle \right)$$

$$|V, VI,\rangle = \left[X^2 + 16 \mp X\sqrt{X^2+16} \right]^{-\frac{1}{2}} \left[2\left(|a\uparrow a\downarrow\rangle + |c\uparrow c\downarrow\rangle \right) \right.$$

$$\left. + \tfrac{1}{2}\left(X \mp \sqrt{X^2+16} \right)\left(|a\uparrow c\downarrow\rangle + |c\uparrow a\downarrow\rangle \right) \right] ,$$

(32)

where X is given by Eq. (21). Note that in this case $|IV\rangle$ does not follow from Eq. (30), because $D(E_{IV}')$ vanishes. In the Harrison limit $X = X_c = Y$, on the other hand, Eq. (30) reduces to

$$|IV\rangle = (2Y^2+8)^{-\frac{1}{2}} \left[2\left(|a\uparrow a\downarrow\rangle - |c\uparrow c\downarrow\rangle \right) - Y\left(|a\uparrow c\downarrow\rangle + |c\uparrow a\downarrow\rangle \right) \right]$$

$$|V, VI\rangle = \tfrac{1}{2}(Y^2+4)^{-\frac{1}{2}} \left[\left(Y \mp \sqrt{Y^2+4} \right) |a\uparrow a\downarrow\rangle \right.$$

$$\left. - \left(Y \pm \sqrt{Y^2+4} \right) |c\uparrow c\downarrow\rangle + 2\left(|a\uparrow c\downarrow\rangle + |c\uparrow a\downarrow\rangle \right) \right]$$

(33)

where Y is given by Eq. (23b).

III. PERTURBATION THEORY

Just as in the one-electron bond-orbital method, one may now proceed to calculate a wide range of properties of the solid in terms of the eigenfunctions and eigenvalues obtained in Sec. II. In particular, if the bond is subject to a small perturbing potential, one can employ standard perturbation theory to calculate the energy shift induced by the potential. We consider here two such calculations. The first is the energy shift resulting from the application of an external electric field. This, of course, leads one to formulas for the electric susceptibility χ and the dielectric constant ϵ. The second calculation we consider is the energy shift induced by the magnetic interaction between the nuclear spins and the bond-electron spins. This calculation leads one to expressions for the nuclear exchange and pseudo-dipolar coefficients Γ_e and Γ'_{pd}.

A. External Electric Field

If we apply an electric field $\vec{\mathcal{E}}$ to our system, an electron will gain a potential energy $\mathcal{U}_{\mathcal{E}} = e \vec{r} \cdot \vec{\mathcal{E}}$. Following HC we chose the origin for $\vec{r}$ at the geometrical center of the bond and take $\vec{\mathcal{E}}$ in the $+\chi$ direction. This makes the calculation of the energy shift equivalent for all bonds in the solid and we thus need only consider the calculation for an isolated bond lying in the (111) direction. With this geometry $\mathcal{U}_{\mathcal{E}}$ becomes

14

$$u_{\mathcal{E}} = \left(-\frac{d}{2\sqrt{3}} + X_a\right) e \mathcal{E}$$

$$= \left(\frac{d}{2\sqrt{3}} + \chi_c\right) e \mathcal{E} \quad , \tag{34}$$

where X_a and X_c are X coordinates measured from the anion and the cation, respectively, and d is the bond length. The corresponding Hamiltonian in second-quantized form, $H_{\mathcal{E}}$, is found from Eqs. (2) and (3) with $V_{ext} = u_{\mathcal{E}}$. Using the first of the identities (10) and neglecting all overlap terms, one finds

$$H_{\mathcal{E}} = \left[-(\bar{X}_c - \bar{X}_a) - \frac{d\gamma'}{2\sqrt{3}}(n_{a\uparrow} + n_{a\downarrow}) + \frac{d\gamma'}{2\sqrt{3}}(n_{c\uparrow} + n_{c\downarrow})\right] e \mathcal{E} , \tag{35}$$

where $\bar{X}_a \equiv \langle \phi_{a\uparrow} | x_a | \phi_{a\downarrow} \rangle$, $\bar{X}_c \equiv -\langle \phi_{c\uparrow} | x_c | \phi_{c\downarrow} \rangle$ and

$$\gamma' = 1 - \frac{\sqrt{3}(\bar{X}_a + \bar{X}_c)}{d} \tag{36}$$

The definition of γ' given by Eq. (36) is the same as that made in Eq. (16) of HC. Also note $\bar{X}_a$ and $\bar{X}_c$ are expected to be positive quantities, because the $\underline{sp}^3$ hybrid on the anion is $\frac{1}{2}\left[|s^a\rangle + |P_x^a\rangle + |P_y^a\rangle + |P_3^a\rangle\right]$, while that on the cation is $\frac{1}{2}\left[|s^c\rangle - |P_x^c\rangle - |P_y^c\rangle - |P_3^c\rangle\right]$. Thus $\bar{X}_a = \frac{1}{2}\langle s^a | x_a | P_x^a \rangle$ and $\bar{X}_c = \frac{1}{2}\langle s^c | x_c | P_x^c \rangle$, which are both positive because the $\underline{s}$ and $\underline{p}$ wavefunctions will have the same sign at large . This implies $\gamma' < 1$ and we have confirmed this for the case of silicon, as discussed in Sec. IV below. Because $\bar{X}_c - \bar{X}_a$ is a constant, one can write

$$H_\varepsilon = -(\bar{X}_c - \bar{X}_a)e\varepsilon + H'_\varepsilon\, e\varepsilon , \tag{37}$$

so that the energy shift out of the ground state to second order in ε is

$$\Delta E = \left[-(\bar{X}_c - \bar{X}_a) + \langle G| H'_\varepsilon |G\rangle \right] e\varepsilon + \sum_{M=I,V} \frac{\langle G| H'_\varepsilon |M\rangle\langle M| H'_\varepsilon |G\rangle}{E_G - E_M}(e\varepsilon)^2, \tag{38}$$

where we have denoted $|VI\rangle$ as $|G\rangle$ and E_{VI} as E_G. From elementary electrostatics considerations, one has in each unit volume of the solid

$$\sum_{BONDS} \Delta E = -\sum_{BONDS} (\vec{P}_0 \cdot \vec{\varepsilon}) - \tfrac{1}{2}\chi \varepsilon^2 , \tag{39}$$

where $\vec{P}_0$ is the (zero-field) polarization of the bond. Comparing Eqs. (38) and (39) one has

$$\vec{P}_0 = -\frac{\sqrt{3}\,e}{d}\left[(\bar{X}_c - \bar{X}_a) - \langle G| H'_\varepsilon |G\rangle \right]\vec{d} \tag{40}$$

and

$$\chi = -Ne^2 \sum_{M=I,V} \frac{\langle G| H'_\varepsilon |M\rangle\langle M| H'_\varepsilon |G\rangle}{E_G - E_M} , \tag{41}$$

where N is the valence electron density in the solid. (Note that $N/2$ is the density of bonds, since there are two valence electrons per bond.) It is a straight-forward matter to work out the matrix elements $\langle M| H'_\varepsilon |G\rangle$ using Eqs. (29), (30), (35), and (37). As expected, the electric field does not couple the ground-state singlet to the three excited triplet states, so

$$\langle M | H'_\varepsilon | G \rangle = 0, \qquad M = I, II \text{ and } III \ . \tag{42}$$

On the other hand, the ground state is coupled, in general, to itself and to the two remaining singlet states:

$$\langle M | H'_\varepsilon | G \rangle = \frac{\gamma' d}{\sqrt{3}\, D(E'_M)\, D(E'_G)} \left[(X_a - E'_M)(X_a - E'_G) - (X_c - E'_M)(X_c - E'_G) \right], \tag{43}$$

$$M = IV, V, \text{ and } VI \ .$$

Let us now examine the above results in the Falicov-Harris and Harrison limits. In the former case, the only-non-zero matrix element is $\langle IV | H'_\varepsilon | G \rangle$ and using Eqs. (22), (32), (35), (37) and (40)-(42), one finds

$$\vec{P}_0 = 0 \tag{44}$$

and

$$\chi_1 = \frac{N(\gamma' e d)^2}{12} \frac{1}{V_2\, \beta} \ , \tag{45}$$

where

$$\beta = \left[X(X^2 + 16) + (X^2 + 8)\sqrt{X^2 + 16} \right] / 32 \tag{46}$$

$$= 1 + \frac{1}{2} X + \frac{5}{32} X^2 + \ - - - - -$$

Clearly, $\beta > 1$ for $\chi > 0$ and $\beta \to 1$ as $\chi \to c$. The dielectric constant in the Falicov-Harris limit is thus

$$\epsilon = 1 + 4\pi \chi$$
$$= 1 + \frac{\pi N (\gamma' e d)^2}{3} \frac{1}{V_2 \beta} \quad . \tag{47}$$

In the Harrison limit both $\langle \text{I\!V} | H_c' | G \rangle$ and $\langle G | H_\epsilon' | G \rangle$ are non zero. Using Eqs. (24) and (33) together with Eqs. (40)-(43), one obtains in this case

$$\vec{P}_0 = e \left[\frac{\sqrt{3}(\bar{X}_c - \bar{X}_a)}{d} + \gamma' \alpha_p \right] \vec{d} \quad , \tag{48}$$

where α_p is Harrison's polarity parameter[1]

$$\alpha_p = V_3 / \sqrt{V_2^2 + V_3^2} \quad , \tag{49}$$

and

$$\chi = \frac{N (\gamma' e d)^2}{12} \frac{V_2^2}{(V_2^2 + V_3^2)^{3/2}} \quad . \tag{50}$$

The dielectric constant is thus

$$\epsilon = 1 + \frac{\pi N (\gamma' e d)^2}{3} \frac{V_2^2}{(V_2^2 + V_3^2)^{3/2}} \quad . \tag{51}$$

Equation (51) for ϵ agrees with the corresponding result obtained by Harrison[1] and HC. In HC all corrections to Eq. (51) are adsorbed into γ' by fitting ϵ to experiment. This leads to values of γ' greater than one.

It is important to note that in both the Falicov-Harris and Harrison limits χ can be expressed entirely in terms of $E_G - E_{\overline{I\!V}}$ and matrix elements of $|G\rangle$. Any explicit reference to the eigenstate $|\overline{I\!V}\rangle$ can be removed by the identity

$$\langle G| (H_\epsilon')^2 |G\rangle = |\langle \overline{I\!V} | H_\epsilon' |G\rangle|^2 + |\langle G| H_\epsilon' |G\rangle|^2, \tag{52}$$

which follows from the completeness of the states $|M\rangle$, Eq. (42) and the fact that $\langle V| H_\epsilon' |G\rangle = 0$. This is consistent with the fact that Harrison and HC obtained their expressions for ϵ without reference to the one-electron anti-bonding orbital.

It is of interest to compare Eq. (45) with Eq. (50) in the case that $V_3 = 0$, that is, for the elemental group IV semiconductors. Clearly, for fixed γ' and V_2, χ is decreased by a factor of β^{-1} when electron correlation effects are included. It follows that $(\gamma')^2 / V_2$ will be increased by a factor of β if the dielectric function is fit to experiment with Eq. (47) instead of Eq. (51). In Sec. IV below we make some rough estimates of V_4 and β for the group IV elements.

It is also instructive to examine the polarity of the states $|\overline{I\!V}\rangle$ and $|\overline{V\!I}\rangle = |G\rangle$ which are coupled by $\vec{\epsilon}$. The polarity of state $|M\rangle$ is naturally defined as

$$\alpha_p^M = a_{3M}^2 - a_{4M}^2 \tag{53}$$

where α_{3M} and α_{4M} are expansion coefficients entering Eq. (15). In the Falicov-Harris limit $\alpha_p^M = 0$ for all six states, as one expects and as is obvious from Eqs. (29) and (30). In the Harrison limit, on the other hand, $\alpha_p^G = \alpha_p$ and $\alpha_p^W = 0$, as can be inferred from Eq. (33). (Also note that $\alpha_p^V = -\alpha_p$.) Thus for materials other than the elemental group IV semiconductors there is a shift in polarity, and hence a shift in the distribution of the wavefunction, between the excited and ground states. This important feature is absent in the more familiar Penn model[5] of the dielectric constant and partially explains the difference between that result and Eq. (51), thus verifying Harrison's speculation to this effect.[6]

B. Magnetic Interaction

An electron with spin $\frac{1}{2} \hbar \vec{\sigma}$ in the presence of a nucleus with spin $\vec{I}$ will change its potential energy by

$$\mathcal{U}_A = \vec{I} \cdot \vec{\vec{A}} \cdot \vec{\sigma} \quad , \tag{54}$$

where

$$\vec{\vec{A}} = \mu_B \hbar \gamma \left[\frac{8\pi}{3} \delta(\vec{r}) \vec{\vec{1}} + \frac{1}{r^3} \left(\frac{3\vec{r}\vec{r}}{r^2} - \vec{\vec{1}} \right) \right] . \tag{55}$$

In Eq. (55) μ_B is the Bohr magneton, γ is the gyromagnetic ratio and $\vec{r}$ is the position of the electron relative to the nucleus. Representing the cartesian coordinates of $\vec{\sigma}$ by the usual Pauli spin matricies and using Eqs. (2) and (3), the perturbing Hamiltonian is found to be

$$H_A = \Delta_a \left(n_{a\uparrow} - n_{a\downarrow} \right) + \Delta_c \left(n_{c\uparrow} - n_{c\downarrow} \right) + \delta_a c_{a\uparrow}^+ c_{a\downarrow}$$
$$+ \delta_a^* c_{a\downarrow}^+ c_{a\uparrow} + \delta_c c_{c\uparrow}^+ c_{c\downarrow} + \delta_c^* c_{c\downarrow}^+ c_{c\uparrow} \quad , \tag{56}$$

where again all overlap terms have been neglected and where we have set

$$\Delta_a = \vec{I}_a \cdot \vec{\vec{A}}_a \cdot \hat{z} \tag{57}$$

and

$$\delta_a = \vec{I}_a \cdot \vec{\vec{A}}_a \cdot (\hat{x} - i\hat{y}) \quad ,$$

with $\vec{\vec{A}}_a \equiv \langle \phi_{a\uparrow} | \vec{\vec{A}} | \phi_{a\uparrow} \rangle$ and similar expressions for Δ_c, δ_c and $\vec{\vec{A}}_c$. Using Eqs. (29) and (30) together with Eq. (56), one may again obtain the matrix elements $\langle M | H_A | G \rangle$ without difficulty. In this case, the perturbating Hamiltonian H_A couples the ground-state singlet only to the three degenerate triplet states:

$$|\langle I | H_A | G \rangle|^2 = |\langle II | H_A | G \rangle|^2 = -\tfrac{1}{2} V_2 E_G' (\delta_a - \delta_c)(\delta_a^* - \delta_c^*)/E_o$$
$$|\langle III | H_A | G \rangle|^2 = - V_2 E_G' (\Delta_a - \Delta_c)^2 / E_o \tag{58}$$

and

$$\langle M | H_A | G \rangle = 0 , \qquad M = IV, V \text{ and } VI \quad ,$$

where

$$E_o^{-1} = -\tfrac{1}{2} \frac{(X_a - E_G')^2 (X_c - E_G')^2}{V_2 E_G' D^2(E_G')} \quad . \tag{59}$$

(Note that E_o is a positive quantity, since $E_G' < 0$.) Because $E_M' = 0$ for the triplet states, $E_G - E_M = V_2 E_G'$ and the energy shift to second order in $\vec{A}$ is just

$$\Delta E' = \frac{2|\langle I | H_A | G \rangle|^2 + |\langle III | H_A | G \rangle|^2}{V_2 E_G'}$$

$$= - \left[(\delta_a - \delta_c)(\delta_a^* - \delta_c^*) + (\Delta_a - \Delta_c)^2 \right] / E_o \quad . \tag{60}$$

Note that the dependence of ΔE on the parameters of the bond-orbital model is contained entirely within the factor E_0^{-1}. This remains true even when overlap is included into the calculation of $|M\rangle$ and E_M, because $\langle M | H_A | G \rangle$ and $E_G - E_M$ for the triplet states can at most be altered by constant factors. Moreover, the only detail of the triplet states which affects E_0 is the triplet eigenvalue. Any explicit dependence of E_0 on the triplet eigenfunctions is removed by the identity

$$\langle G | H_A^2 | G \rangle = 2 |\langle I | H_A | G \rangle|^2 + |\langle II | H_A | G \rangle|^2 , \tag{61}$$

which follows from Eq. (58) and the completeness of the states $|M\rangle$.

Now using Eq. (57) in Eq. (60), one has

$$\Delta E = - \left[\vec{I}_a \cdot \vec{\vec{A}}_a - \vec{I}_c \cdot \vec{\vec{A}}_c \right] \cdot \left[\hat{x}\hat{x} + \hat{y}\hat{y} + \hat{3}\hat{3} \right] \cdot \left[\vec{\vec{A}}_a \cdot \vec{I}_a - \vec{\vec{A}}_c \cdot \vec{I}_c \right]$$

$$= - \left[\vec{I}_a \cdot \vec{\vec{A}}_a \cdot \vec{\vec{A}}_a \cdot \vec{I}_a + \vec{I}_c \cdot \vec{\vec{A}}_c \cdot \vec{\vec{A}}_c \cdot \vec{I}_c - 2 \vec{I}_a \cdot \vec{\vec{A}}_a \cdot \vec{\vec{A}}_c \cdot \vec{I}_c \right] / E_0 . \tag{62}$$

More explicit expressions for $\vec{\vec{A}}_a$ and $\vec{\vec{A}}_c$ can be obtained by directly inserting sp^3 hybrids for $|\phi_{a\uparrow}\rangle$ and $|\phi_{c\uparrow}\rangle$ and discarding all matrix elements which vanish by symmetry. Doing this, one finds

$$\vec{\vec{A}}_a = \tfrac{1}{2} \mu_B \hbar \gamma_a \left[\tfrac{1}{3} \delta_a^2 \vec{\vec{I}} + \tfrac{3}{5} P_a (3 \hat{r}_{ac} \hat{r}_{ac} - \vec{\vec{I}}) \right] \tag{63}$$

with a similar expression for $\vec{\vec{A}}_c$. In Eq. (63) $\hat{r}_{ac}$ is a unit vector directed from the anion to the cation and

$$\delta^2 = 4\pi \langle s | \delta(\vec{r}) | s \rangle = R_s^2(0) \tag{64}$$

where $R_S(o)$ is the $\underline{S}$ radial wavefunction evaluated at the origin, and

$$\rho = \langle P | r^{-3} | P \rangle, \qquad (65)$$

where $|P\rangle$ is any one of the three $\underline{P}$ states of the hybrid. If one writes ΔE as a sum of two chemical shifts and an interaction term,

$$\Delta E = - \Delta E_{aa} - \Delta E_{cc} + \Delta E_{ac} \qquad (66)$$

and uses Eq. (63) in Eq. (62), then

$$\Delta E_{aa} = \frac{1}{2} \Gamma_e^{aa} \vec{I}_a \cdot \vec{I}_a + \frac{1}{2} \Gamma_{pd}^{aa} \left[3 (\vec{I}_a \cdot \hat{r}_{ac})(\hat{r}_{ac} \cdot \vec{I}_a) - \vec{I}_a \cdot \vec{I}_a \right] , \qquad (67)$$

with a similar expression for ΔE_{cc} and

$$\Delta E_{ac} = \Gamma_e^{ac} \vec{I}_a \cdot \vec{I}_c + \Gamma_{pd}^{ac} \left[3 (\vec{I}_a \cdot \hat{r}_{ac})(\hat{r}_{ac} \cdot \vec{I}_c) - \vec{I}_a \cdot \vec{I}_c \right] . \qquad (68)$$

In Eqs. (67) and (68)

$$\Gamma_e^{ac} = \mu_B^2 \hbar^2 \gamma_a \gamma_c \left[\frac{1}{18} \delta_a^2 \delta_c^2 + \frac{9}{25} \rho_a \rho_c \right] / E_n \qquad (69)$$

and

$$\Gamma_{pd}^{ac} = \mu_B^2 \hbar^2 \gamma_a \gamma_c \left[\frac{1}{10} (\delta_a^2 \rho_c + \delta_c^2 \rho_a) + \frac{9}{50} \delta_a^2 \rho_c \right] / E_n \qquad (70)$$

with similar expressions for Γ_e^{aa}, Γ_{pd}^{aa}, Γ_e^{cc} and Γ_{pd}^{cc}. The quantities $\Gamma_e \equiv \Gamma_e^{ac}$ and $\Gamma_{pd} \equiv \Gamma_{pd}^{ac}$ are the nuclear exchange and pseudo-dipolar coefficients,

respectively. Note that Γ_{pd} is inherently positive and consequently the pseudo-dipolar interaction is of opposite sign from the direct dipole-dipole interaction, which is in broad agreement with experimental observation. In Sec. IV below we compare Γ_c and Γ_{pd} calculated from Eqs. (69) and (70) with experiment. Finally, we observe that Eqs. (69) and (70) are similar to the earlier results obtained by Clough and Goldberg[7] with a cruder model. For the case of tetrahedrally bonded solids,[8] the essential differences between our results and theirs are: (i) what we call E_0^{-1} is an arbitrary, unspecified constant 2λ in their treatment, (ii) they do not distinguish between either δ_a and δ_c nor ρ_a and ρ_c, and (iii) the term involving $(\delta_a^2 \rho_c + \delta_c^2 \rho_a)$ - in Eq. (70) is a factor of two larger than the corresponding term in their Eq. (24).

It only remains to evaluate the factor E_0^{-1} in Eqs. (69) and (70). In the Falicov-Harris limit, one obtains

$$ E_0^{-1} = \frac{1}{4V_2} \, \zeta \, , \tag{71} $$

where

$$ \zeta = \frac{1}{2} \left[X^2 + 8 + X \sqrt{X^2 + 16} \right] / \sqrt{X^2 + 16} $$
$$ = 1 + \frac{1}{2} X + \frac{3}{32} X^2 + \cdots \tag{72} $$

As with β defined in Eq. (46), $\zeta > 1$ for $X > 0$ and $\zeta \to 1$ as $X \to$. Thus for fixed V_2 the effect of correlation is to enhance both Γ_c and Γ_{pd}.

In the Harrison limit, on the other hand,

$$E_b^{-1} = \frac{1}{4} \frac{V_3^2}{(V_2^2 + V_3^2)^{3/2}}$$

$$= \frac{1}{4V_2} \alpha_c^3 \quad ,$$

(73)

where $\alpha_c = (1 - \alpha_p^2)^{1/2}$ is Harrison's covalency parameter.[1] It is very interesting to note that in this limit χ , Γ_e and Γ_{pd} all have the same dependence on V_2 and V_3 . Using this fact, one may obtain a simple relationship between the dielectric constant ϵ and Γ_e :

$$\epsilon - 1 = C \, \Gamma_e / d \quad ,$$

(74)

where $C = \sqrt{3}\, \pi \, (\gamma'e)^2 / \left[\mu_0^2 \hbar^2 \Gamma_a \Gamma_c \left(\frac{1}{18} \delta_a^2 \delta_c^2 + \frac{9}{25} \Gamma_a \Gamma_c \right) \right]$ and an analagous result linking $\epsilon - 1$ to Γ_{pd} . In deriving Eq. (74) we have used the fact that $N = \frac{2}{3}\sqrt{3}/d^3$ for a diamond or zinc-blende structure. The quantity ϵ here is not necessarily a constant, but it is a function of only intra-atomic parameters. The origin of the relationship (74) can be traced to the degeneracy of the singlet state $|\mathbb{V}\rangle$ and the three triplet states in the Harrison limit. The inclusion of overlap terms alone into the bond-orbital model will not lift this degeneracy, as can be inferred from Fig. 1. The inclusion of correlation into the bond-orbital model, on the other hand, will lift the degeneracy and hence modify the result. In the Falicov-Harris limit, for instance, the right-hand side of Eq. (74) should be multiplied by a factor of $\beta\gamma = 1 + \chi + \frac{1}{2}\chi^2 + \cdots$

IV. APPLICATIONS

In this section we briefly consider the quantitative predictions of the new formulas derived in Sec. III for real materials. Our analysis is necessarily incomplete because of our neglect of overlap terms in both the two-electron bond-orbital model and in the perturbation calculations. However, the above formulas are sufficiently realistic to expose significant trends and allow us to draw some tenative conclusions. In this regard, it should be mentioned that HC found that the effect of including the overlap matrix element S in the one-electron bond-orbital model was simply to renormalize V_2 by $(1-S^2)^{-1}$ and γ' and V_3 by $(1-S^2)^{-\frac{1}{2}}$. Since they eventually fit all three of these parameters to experiment, the effect of S on χ , ϵ , Γ_e and Γ_{pd} can, in fact, be implicitly included in Eqs. (50), (51) and (73).

A. Γ_e and Γ_{pd} in the Harrison Limit

In order to evaluate our expressions for Γ_e and Γ_{pd} in the Harrison limit one needs, in addition to V_2 and V_3 , values of the intra-atomic parameters δ and ρ . Relevant values for these quantities are available from the Hartree-Fock atomic structure calculations of Mann.[9] Mann's values of δ and ρ are listed in Table I for the group III, IV and V elements of interest here. It is convenient to calculate Γ_e and Γ_{pd} in units of $\Gamma_{dd} = \hbar^2 r_a r_c / d^3$, the direct dipole-dipole interaction coefficient. In terms of Γ_{dd} and the ratio

$$\mathcal{R} = \frac{4}{5}\, \mathcal{P}/\beta^2 \tag{75}$$

one has, using Eqs. (69) and (70),

$$\Gamma_e/\Gamma_{dd} = C_o\, \delta_i^2 \delta_c^2\, (1 + 2\, \mathcal{R}_a \mathcal{R}_c)\, d^3/E_o$$

$$\Gamma_{pd}/\Gamma_{dd} = C_o\, \delta_a^2 \delta_c^2\, (\mathcal{R}_a + \mathcal{R}_c + \mathcal{R}_a \mathcal{R}_c)\, d^3/E_o \tag{76}$$

and

$$\Gamma_{pd}/\Gamma_e = (\mathcal{R}_a + \mathcal{R}_c + \mathcal{R}_a \mathcal{R}_c)/(1 + 2\, \mathcal{R}_a \mathcal{R}_c) \quad,$$

where $C_o = \mu_B^2/18$. If $\mathcal{P}_a$ and $\mathcal{P}_c$ are expressed in a.u. , d is in $\overset{\circ}{A}$, and E_o is in eV , then $C_o = 1.362 \times 10^{-4}$. Using Eqs. (73) and (76) and the HC values of V_2 and V_3 , we have evaluated Γ_e/Γ_{dd}, Γ_{pd}/Γ_{dd}, and Γ_{pd}/Γ_e for a total of twenty of the group IV elements and the group IV and III-V compounds. These results are listed in Table II together with the small amount of relevant experimental data available in the literature. One can see from Table II that the theoretical Γ_e is consistently larger than the experimental value, while the reverse is true for Γ_{dd} . The theoretical values of Γ_e , however, correctly follow the experimental trend of increasing Γ_e with increasing mean atomic number and consequently with increasing bond length. This is more clearly illustrated in Fig. 2, where we have plotted both the theoretical and experimental values of Γ_e as a function of d . One additional interesting result that can be seen from Table II is the almost constant value we calculate for the ratio

Γ_{pd} / Γ_e . This result is quite clearly a consequence of the insensitivity of R to atomic number, but it is not in accord with the two experimental numbers we have for comparison.

The lack of detailed agreement here between theory and experiment is not unexpected, however, and a number of factors could be responsible. One important effect concerns the choice of S and P wavefunctions used in calculating the matrix elements δ and φ . The use of Hartree-Fock free-atom wavefunctions is not necessarily an optimum choice for the solid. To test the sensitivity of Γ_e and Γ_{pd} to this choice, we have calculated two other sets of atomic wavefunctions for silicon (one set for the ground state $3 \underline{S}^2 3 \underline{P}^2$ configuration of the free atom and one for the excited $3 \underline{S}^1 3 P^3$ configuration) using the Herman-Skillman approximation[10] to the Hartree-Fock potential field. These wavefunctions were used in turn to determine values of δ and φ and Γ_e and Γ_{pd} . The results of these calculations are compared with the Hartree-Fock results in Table III. Clearly the Herman-Skillman approximation has a large effect on the calculated magnitudes of Γ_e and Γ_{pd} , increasing these quantities by almost a factor of two over the Hartree-Fock values. On the other hand, the configuration change from $3 \underline{S}^2 3 \underline{P}^2$ to $3 \underline{S}^1 3 \underline{P}^3$ has a much smaller effect on Γ_e and Γ_{pd} separately, but a larger effect on the ratio Γ_{pd} / Γ_e . The obvious implication from this study is that small changes in the atomic potential can significantly alter the S and P wavefunctions of the $\underline{S}P^3$ hybrids, making experiment a sensitive check on first-principles calculations of Γ_e and Γ_{pd} .

A second obvious effect which could modify the results of Table II is, of course, two-electron correlation. As mentioned in Sec. III, however, correlation can at most alter the value of E_0 and consequently cannot affect

the ratio Γ_{pd}/Γ_e . The preliminary indication is, as discussed below, that correlation can significantly enhance the theoretical values of Γ_e and Γ_{pd} in the group IV elements. A similar effect in the III-V compounds would be in the right direction for Γ_{pd} , but not for Γ_e .

A third possible factor here is the overlap term $\langle \phi_a | \vec{A} | \phi_c \rangle$, which was dropped from consideration in deriving Eq. (56). Unlike the ordinary overlap and correlation corrections to the bond-orbital model, this term could lead to a change in the ratio of Γ_{pd}/Γ_e . For this reason, we shall want to include this term when we consider overlap effects in paper II.

The accumulation of additional experimental data will be important in clarifying this situation further. In particular, note that the chemical shifts ΔE_{aa} and ΔE_{cc} each contain an isotropic part with respective coupling constants Γ_e^{aa} and Γ_e^{cc} and an anisotropic part with coupling constants Γ_{pd}^{aa} and Γ_{pd}^{cc} . Since these interactions will have different angular dependences, they are separately measurable. Thus for binary compounds, including Γ_e and Γ_{pd} , there are six constants which can be measured in principle. Neglecting the overlap term $\langle \phi_a | \vec{A} | \phi_c \rangle$, these six measurables are a function of only five parameters of the solid, δ_a , δ_c , P_a , P_c and E_c , so that the latter can all be determined from experiment. When $\langle \phi_a | \vec{A} | \phi_c \rangle$ is included, the number of parameters will exceed six, although some of the additional parameters may be negligible. Thus an approximate determination of the largest parameters may still be possible. The situation is similar for the group IV elemental semiconductors, where $\Gamma_e^{aa} = \Gamma_e^{cc}$, etc. In this case there are four measurables, three theoretical parameters when the overlap term is neglected, and more than four parameters when the overlap term is included.

B. ε vs. Γ_e

An empirical determination of the factor C entering Eq. (74) for a given material is possible if corresponding values of ε and Γ_e are known. To examine any possible trends in C , we have plotted in Fig. 3 experimental values of ε versus experimental values of $\Gamma_e / I_{dd} d^4$ for the six III-V compounds for which we have data on both quantities. Remarkably, the points for InP , $InAs$ and $InSb$ fall on an almost perfect straight line. Clearly, however, more data is needed to determine whether or not this trend applies to other series of compounds as well.

C. Effects of Correlation

To examine the quantitative effects of correlation, one needs values for the Coulomb integrals U and K . Values for U are readily calculable from Mann's atomic structure results.[9] In terms of his two-electron F and G integrals, one finds for an sp^3 hybrid[11]

$$U = \tfrac{1}{16} \left[F^0(n0;n0) + 6 F^0(n0;n1) + 4 G^1(n0;n1) + 9 F^0(n1;n1) + \tfrac{36}{25} F^2(n1;n1) \right],$$ (77)

where n is the principal quantum number and $\ell = 0$ and $\ell = 1$ are the orbital angular-momentum quantum numbers of the s and p wavefunctions. The values of U so determined for the group III, IV and V elements are given in Table I.

Good estimates of K are more difficult to obtain, however, without detailed calculation. One can infer from Eqs. (8) and (9) that

$$\frac{e^2}{d} \leq K \leq U$$ (78)

for the group IV elements. The upper and lower limits on K are, respectively, the values for very small and very large separation of the two members

of the bond. Equivalently, one can view these limits as those of large

and small $(s \sim c)$ overlap of the $\hat{S} \hat{I}^3$ hybrids. Most calculated values[12]

of S lie in the range 0.5 - 0.7, so that neither limit is probably appro-

priate. One might expect a dependence on S like $K \sim S \mathcal{U} + (1-s) e^2/1$.

With $S = 0.6$ this leads to the formula $V_4 = (\mathcal{U} - e^2/d)/S$. For lack

of a better prescription, we have based the calculations discussed below on

this equation. The assumed value of K is clearly important, however, be-

cause of the large magnitude of $\mathcal{U}$.

For $\mathcal{U} \neq K$ it is desirable to obtain new empirical values of V'

before trying to estimate the quantitative effects of correlation. The HC

value of V_2 , which we now denote as $V_2{}^{Hc}$, was obtained by fitting

$E_a - E_b$ (the anti-bonding-bonding energy gap) to the principal experi-

mental optical absorption peak E_2 . In a two-electron theory $E_a - E_b$

is to be replaced by $E_{IV} - E_G$, as is obvious from Fig. 1. It readily

follows from Eq. (22) that one must have

$$V_2 = V_2{}^{Hc} \sqrt{1 - V_4/V_2{}^{Hc}}$$

(79)

in the Falicov-Harris limit to fit the experimental E_2 . Clearly, $V_2 <$

for $V_4 > 0$. In Table IV we list our refitted values of V_2 together

with other relevant parameters for the group IV elements. The quantity

$V_2{}^{Hc}/V_2 \beta$ is the factor by which the susceptibility χ is multiplied when

correlation effects are included. This factor tends to resist change as

$\mathcal{U} - K$ is increased, because V_2 is decreased while β is increased. For

the case of silicon one requires a value of $\gamma' = 1.44$ to fit the

experimental dielectric function if $V_4 = (\mathcal{U} - e^2/d)/5$. Not unexpectedly, this value of γ' is significantly greater than the values we have calculated from Eq. (36) using Herman-Skillman wavefunctions. (See Table III).

While the effect of correlation on $\mathcal{X}$ and ϵ is partly adsorbed into V_2^{HC}, the same is not true for Γ_e and Γ_{pd}. The quantity entering Eqs. (69) and (70) is increased by a factor of $V_2^{HC}\xi/V_2'$ when correlation effects are included for the group IV elements. From Table IV it is clear that this factor can be significantly greater than one if $\mathcal{U} \cdot \mathcal{K}$ is not small. In this case both ξ and V_2^{-1} are increased as $\mathcal{U} \cdot \mathcal{K}$ is increased.

Just as V_2^{HC} is replaced by Eq. (79) for V_2 in the group IV elements, V_3^{HC}, the HC value of V_3, must be altered for the binary compounds when correlation effects are included. In this regard, it should be noted that the V_3^{HC}, which were empirically determined by fitting to the experimental dielectric constant of each material, are consistently smaller (except possibly for SiC) than one would predict on the basis of the formula $V_3 = (\epsilon_c - \epsilon_a)/2$. (See, for example, Fig. 3 of HC) This situation is further aggravated when the renormalization factor of $(1 - S^2)^{-\frac{1}{2}}$ is included in V_2'. To see if correlation effects might help account for the small values of V_3^{HC}, we have made the following two calculations. First we have calculated $E_a = E_\Pi - E_q$ for eight binary compounds, using V_2^{HC}, V_3 determined from the Hartree-Fock values of ϵ_c and ϵ_a given in Table I, and $\mathcal{K} = \mathcal{U}_a = \mathcal{U}_c$ (i.e., no correlation). These calculations were then repeated using V_2 (as given by Table IV), the same V_3, and $\mathcal{K} = [\mathcal{U}, + \mathcal{U} - e^2/d]/5$. [In the latter calculations it was necessary to solve the cubic equation (20) with $X_a = (\mathcal{U}_a - \mathcal{K} - 2V_3)/V_2$ and

$X_c = (U_c - K + 2 V_3)/V_2$.] The results of both sets of calculations are plotted in Fig. 4 together with the experimental values of E_1 . The general tendency is for E_1 to increase with increasing V_3 and to decrease with increasing $|U_{a,c} - K|$. Except for SiC and BP, it would appear that our calculated effects of correlation have overcompensated for the larger values of V_3 . Of course, these results will most probably be modified when overlap effects are explicitly included. Note, for instance, that the $(1-S^2)^{-1/2}$ factor increases V_3 by 25% for $S = 0.6$.

V. CONCLUSIONS

We have attempted here to illustrate the essential features of a two-electron bond-orbital model by considering the simplest special case of a full theory. We have seen that several classes of problems can be readily treated using this model as a basis. In addition to the non-magnetic properties considered by Harrison[1] and HC, such as the electric susceptibility and the dielectric constant, magnetic properties, such as the nuclear exchange and pseudo-dipolar interactions, fall naturally into the scope of such a theory. Moreover, for each property it is possible to assess the quantitative effect of electron correlation in the anion-cation bond. It is clear that the empirical HC parameters V_2^{HC} and V_3^{HC} must be readjusted when correlation parameters such as V_4 are introduced. The preliminary indication is that $V_2 < V_2^{HC}$, while $V_3 > V_3^{HC}$ for $V_4 > 0$. In some properties the appearance of V_4 will partly compensate for these changes, such as appears to be the case in the electric susceptibility. In other cases, however, the effect may be cummulative, as seems to be true for the nuclear exchange and pseudo-dipolar coefficients.

There are, of course, a whole series of additional properties of tetrahedrally bonded solids which one can examine within the framework of our two-electron bond-orbital model. A natural extension of this method would be to the calculation of the magnetic susceptibility. Although we anticipate such applications in the future, it will first be desirable to generalize

the model to include overlap effects explicitly before proceeding further. This will be done in the second paper of this series. It will also be essential to obtain more accurate estimates of the correlation parameter V_4.

ACKNOWLEDGMENTS

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11. Equation (77) is most easily derived by directing the hybrid along the z axis so that it takes the form $\frac{1}{2} \left[|s\rangle + \sqrt{3} |V_j\rangle \right]$.

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TABLE I

Intra-atomic parameters of interest for the group III, IV and V elements inferred from the Hartree-Fock atomic structure calculations of Mann (Ref. 8). Values of $-\epsilon_{a,c}$ and U are given in eV, while δ and ρ are given in a.u.

Element	$-\epsilon_{a,c}$	U	δ	ρ	$\aleph = 9/5\,\rho/\delta^2$
B	9.68	13.96	4.21	0.776	0.0789
Al	6.96	9.27	5.44	1.09	0.0661
Ga	7.14	9.37	9.34	2.89	0.0596
In	6.56	8.43	11.1	4.46	0.0654
C	13.14	17.62	5.91	1.66	0.0856
Si	9.38	11.34	6.94	2.03	0.0759
Ge	9.28	10.96	11.0	4.73	0.0708
Sn	8.33	9.63	12.7	6.75	0.0758
N	16.92	21.20	7.78	3.02	0.0898
P	11.95	13.27	8.44	3.27	0.0825
As	11.46	12.36	12.5	6.85	0.0786
Sb	10.11	10.67	14.1	9.23	0.0832

TABLE II

Nuclear exchange and pseudo-dipolar coefficients for group IV elements and group IV and III-V compounds in units of the direct dipole-dipole interaction coefficient. The bond length d is given in $\overset{o}{A}$.

Element	d	Γ_e/Γ_{dd}		Γ_{pd}/Γ_{dd}		Γ_{pd}/Γ_e	
		Theory	Expt.	Theory	Expt.	Theory	Expt.
C	1.54	0.0253		0.00444		0.175	
Si	2.35	0.473		0.0735		0.155	
Ge	2.44	3.35		0.487		0.145	
Sn	2.80	11.1		1.72		0.155	
SiC	1.88	0.0828		0.0137		0.165	
BN	1.57	0.0177		0.00307		0.173	
BP	1.97	0.0909		0.0151		0.166	
BAs	2.07	0.234		0.0379		0.162	
AlN	1.89	0.0597		0.00958		0.160	
AlP	2.36	0.296		0.0451		0.152	
AlAs	2.43	0.768		0.114		0.148	
AlSb	2.66	1.17	~0.0[a]	0.180		0.154	
GaN	1.94	0.174		0.0267		0.153	
GaP	2.36	0.807		0.118		0.146	
GaAs	2.45	2.12	0.66[a]	0.301	0.47[c]	0.142	0.71
GaSb	2.65	4.17	1.89[a]	0.610		0.146	

TABLE II (Continued)

InN	2.15	0.347		0.0554		0.160	
InP	2.54	1.35	~ 0.55[b]	0.205	~ 1.0[b]	0.152	1.8
InAs	2.61	3.64	2.06[a]	0.?38		0.148	
InSb	2.81	6.82	5.28[a]	1.04		0.152	

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TABLE III

Sensitivity of various parameters of silicon to small changes in the atomic
$\underline{s}$ and $\underline{p}$ wavefunctions making up the $\underline{sp}^3$ hybrid. The symbols HF and HS denote results for Hartree-Fock and Herman-Skillman calculations, respectively. Values of $-\varepsilon_{a,c}$ are given in eV, while $\bar{x}$ is given in $\overset{\circ}{A}$.

	HF	HS	HS
Configuration	$3s^2 3p^2$	$3s^2 3p^2$	$3s^1 3p^3$
$-\varepsilon_{a,c}$	9.38	8.29	8.84
$\bar{x}$	0.359	0.388	0.333
γ'	0.471	0.501	0.509
$\mathscr{J}$	6.94	8.02	8.15
$\mathcal{P}$	2.03	2.69	2.90
$\mathcal{R}$	0.0759	0.0753	0.0787
Γ_e/Γ_{dd}	0.473	0.844	0.895
Γ_{pd}/Γ_{dd}	0.0735	0.130	0.145
Γ_{pd}/Γ_e	0.155	0.154	0.162

TABLE IV

Effect of correlation on the parameters of the two-electron bond-orbital model for the group IV elements based on the assumption that $V_4 = (U-e^2/d)/5$. The quantities V_2^{HC}, the Harrison-Ciraci value of V_2, our (refitted) value of V_2 and V_4 are given in eV.

Element	V_2^{HC}	V_2	V_4	$1/2X$	β	ξ	$V_2^{HC}/V_2\beta$	$V_2^{HC}\xi/V_2$
C	6.10	5.21	1.66	0.32	1.39	1.36	0.84	1.59
Si	2.20	1.59	1.04	0.66	2.01	1.81	0.69	2.51
Ge	2.15	1.56	1.01	0.65	1.99	1.80	0.69	2.48
Sn	1.76	1.23	0.90	0.73	2.18	1.92	0.66	2.75

FIGURE CAPTIONS

Fig. 1. Energy levels of Harrison's one-electron bond-orbital model and the present two-electron bond-orbital model in the Harrison and Falicov-Harris limits, as described in the text. Note that the six two-electron states derive from the six unique ways (including spin) that two electrons can occupy E_b and E_a.

Fig. 2. Theoretical and experimental values of Γ'_e/Γ'_{dd}, the ratio of the nuclear exchange coefficient to the direct dipole-dipole interaction coefficient, as a function of bond length in the group IV elements and various group IV and III-V compounds.

Fig. 3. Experimental values of $\epsilon -1$ versus experimental values of Γ'_e/Γ'_{dd} for III-V compounds on which data is available. This plot is suggested by the theoretical result given by Eq. (74). Note that
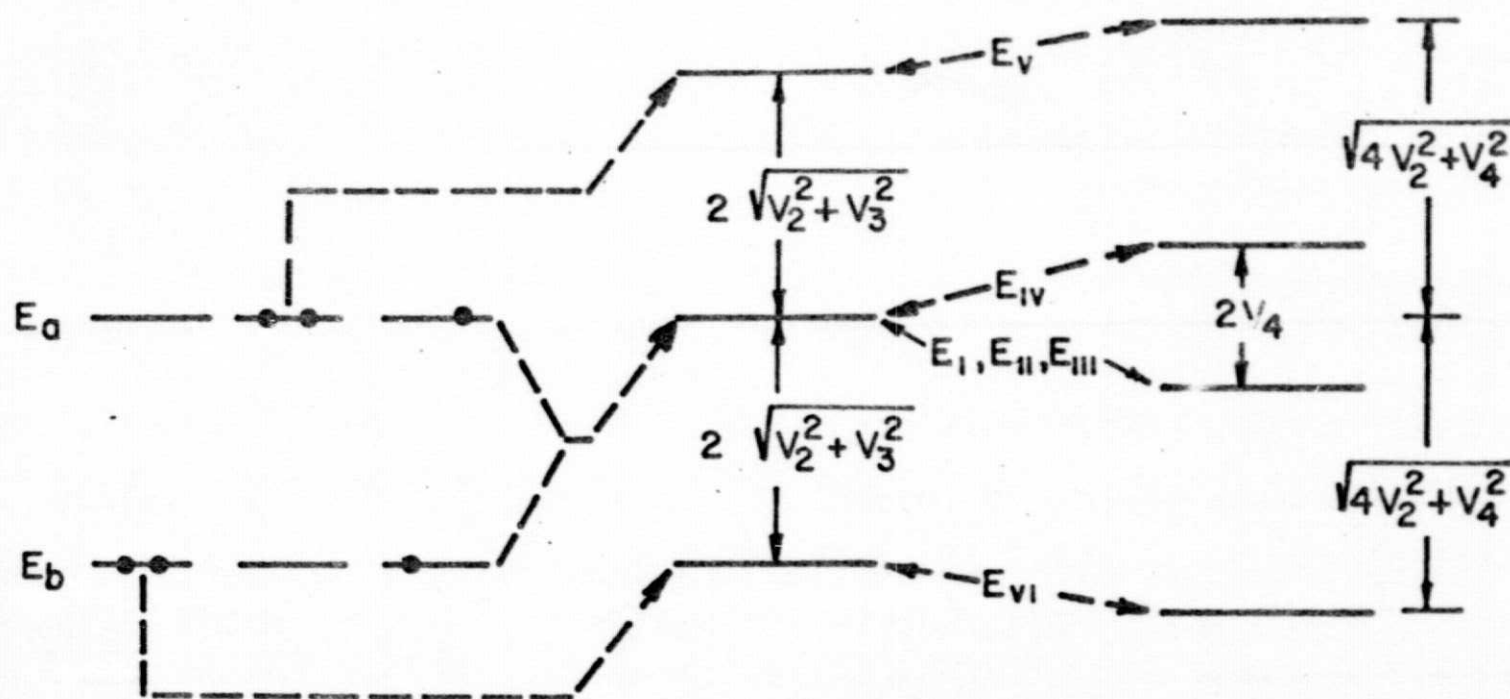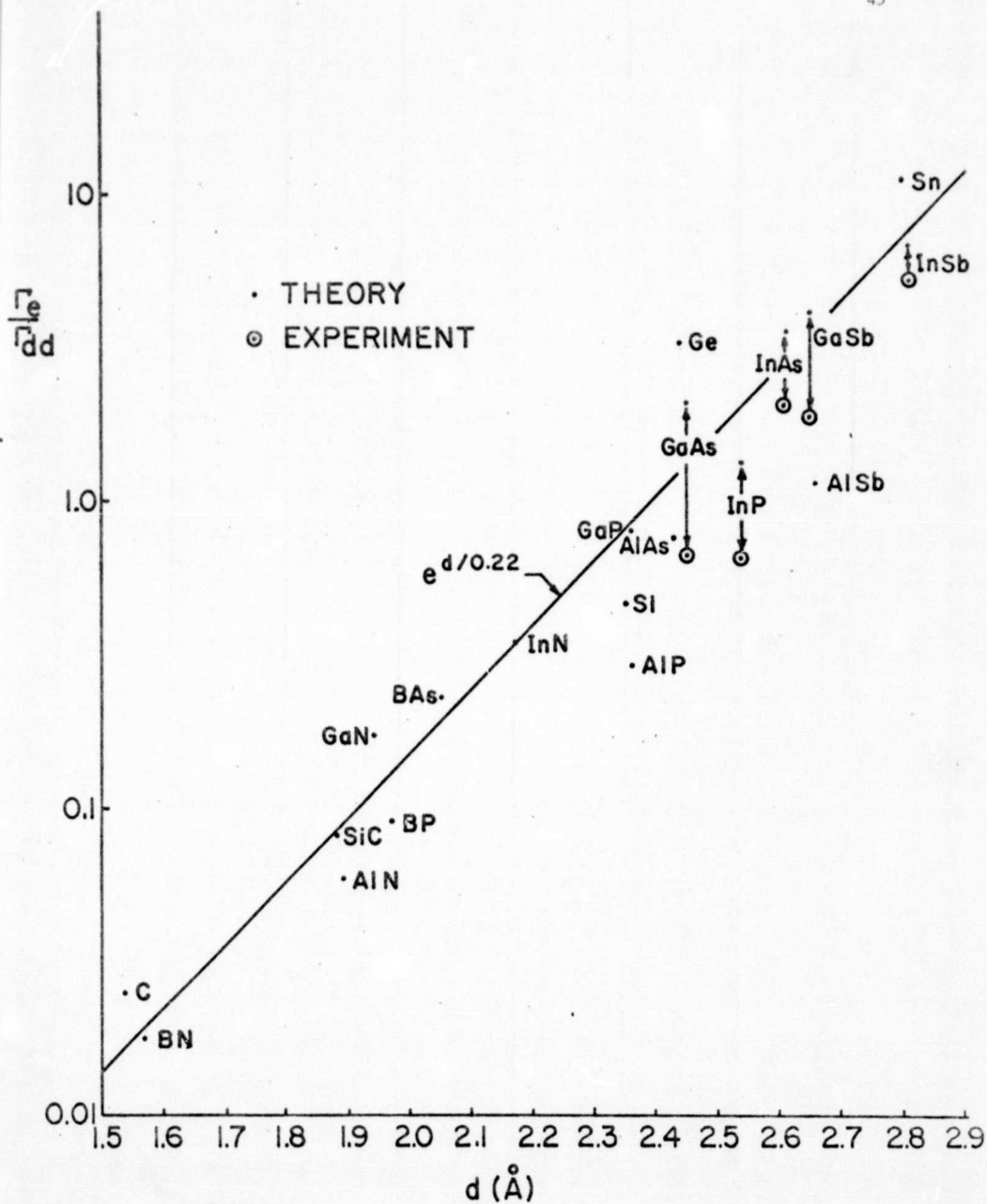
$$\Gamma_{dd} d^4 = \hbar^2 \gamma_a \gamma_c d$$

Fig. 4. Theoretical calculations of the energy gap $E_2 = E_{\pi} - E_q$ compared against the energy of the principal experimental optical absorption peak E_2 for eight binary compounds. The triangles indicate calculations done with V_2^{Hc}, $V_3 = (\epsilon_c - \epsilon_a)/2$, and $K = U_a - U_c$, while the dots denote calculations done with our refitted V'_2, the same V_3, and $K = [(U_a + U_c)/2 - e^2/d]/5$, as described in the text. The open circles for the group IV elements represent values fit to experiment.
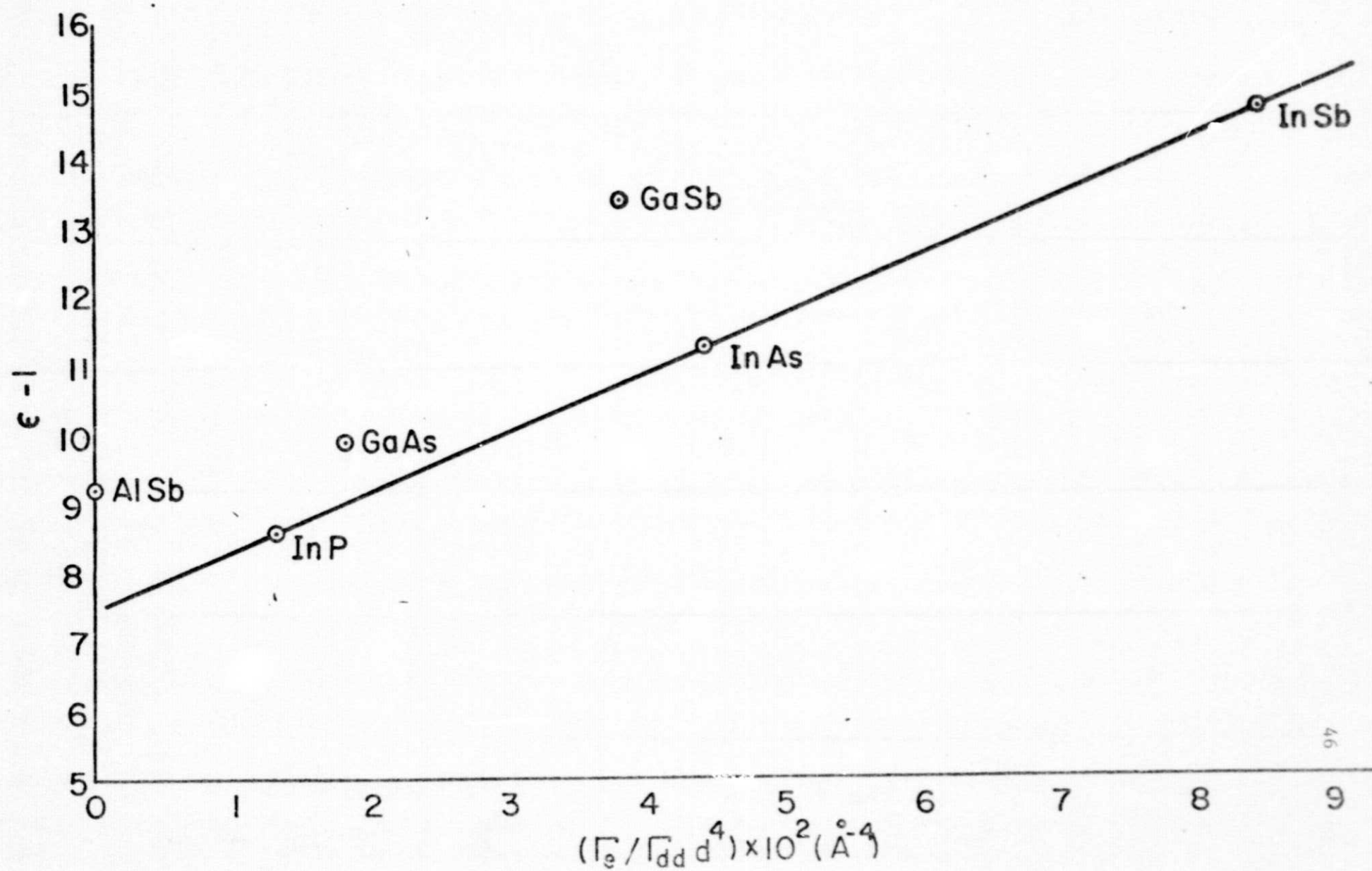
HARRISON ONE ELECTRON   HARRISON TWO ELECTRON   FALICOV-HARRIS TWO ELECTRON
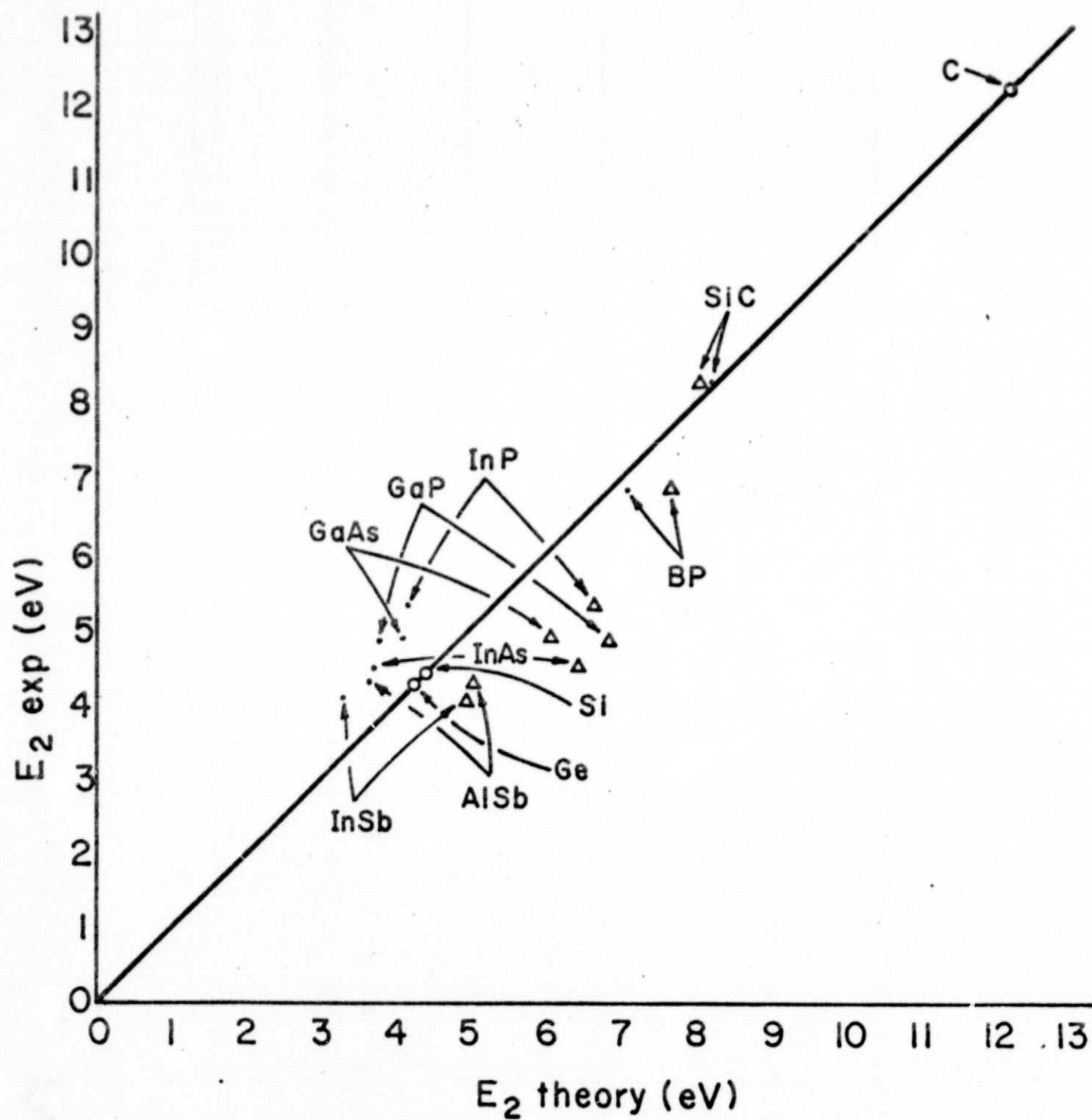
The y-axis is labeled $\epsilon - 1$ with values 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16.

The x-axis is labeled $(\Gamma_e / \Gamma_{dd} d^4) \times 10^2 (\mathring{A}^{-4})$ with values 0, 1, 2, 3, 4, 5, 6, 7, 8, 9.

Data points labeled: Al Sb, In P, GaAs, GaSb, In As, In Sb.

Fig. 4