PHYSICAL REVIEW B VOLUME 27, NUMBER 6 15 MARCH 1983

Theory of the two-center bond

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(Received 16 August 1982; revised manuscript received 24 August 1982)

Tight-binding theory, with universal parameters, provides direct prediction of bond energies, bond lengths, and force constants for ordinary molecular and solid-state two-center bonds. Corrections, which are dominated by nonorthogonality of orbitals on neighboring atoms, are included and are seen to be given approximately by a two-body repulsion proportional to the inverse fourth power of internuclear distance. The bond properties depend upon metallicity, increasing in a series such as C, Si, Ge, and Sn, and are strongly affected by the coupling between the bond and its environment at high metallicity. This effect, called metallization, is calculated in perturbation theory. The properties depend also strongly upon the polarity of the bond and upon the decrease in the effect of metallization with increasing polarity. Finally, the properties depend upon bond order. This effect is characterized by a π-bonding strength, which for a resonating bond is enhanced by a factor of the square root of the number of sites between which the bond resonates. Formulas are derived for the bond energies, lengths, and force constants in terms of these parameters and are compared with experiment.

I. INTRODUCTION

Virtually all of the properties of solids and molecules are determined by their electronic structure. In recent years it has become possible to calculate this electronic structure[1-3] and a number of related properties[4-7] from first principles. A central finding has been that most properties of solids and molecules are describable in terms of a one-electron framework, based upon density-functional theory.[8,9] There have also been efforts to simplify or parametrize these *ab initio* methods for simplicity of calculation or organization of trends.[10-15] There has also envolved a very much simpler, approximate, but meaningful, theory of all of the properties of nonmetallic systems which is based upon tight-binding theory with universal parameters.[16,17] It is interesting to apply this approach to the variety of properties of the two-center chemical bond which is traditionally discussed in terms of empirically based bonding theory.[18,19] Indeed, for many years semiempirical models have been introduced which attempted this.[20] However, the theory has now evolved into an essentially first-principles, though simple, theory with methods for estimating errors and systematically improving the estimates of properties. It now becomes possible to make direct elementary estimates of all of the bonding properties without the addition of empirical parameters. The theory takes a surprisingly simple and intuitively pleasing form. It provides a clear way to think about all of the trends from system to system, entirely in terms of concepts which arise within the simple formalism and are explicitly defined in terms of them. It is seen that most of these concepts appear already in Pauling's more empirical studies,[18] but these concepts now take on new and sharper meaning in terms of the tight-binding formalism and represent particular aspects of a quantitative estimate of the property in question.

We cannot expect that the new description will provide more accurate values for properties than the empirical methods. Since the tight-binding description is essentially from first principles, no new parameters are introduced when a new property is discussed; all input is based upon the ultimate electronic structure. It cannot hope to be more accuate than formulations such as ionicity theory which interpolate data. The goal here is a unification and simplification of the subject. This simplification may ultimately lead to more accurate empirical descriptions but that is not the goal here.

We begin in Sec. II with a summary of the tight-binding method and the universal tight-binding parameters. We then discuss the formation of hybrids and σ-bond orbitals and the metallic, covalent, and polar energies V_1, V_2, and V_3, which characterize them. We introduce also the interatomic repulsion arising from the overlap of atomic orbitals on neighboring atoms; it is seen to be proportional (approximately) to the inverse fourth power of internuclear distance, a form which considerably simplifies the theory. In terms of these quantities we can then directly estimate the bond energy (the sum of bond energies equals the cohesive energy of the system), a bond tension from which we can estimate the variation of bond length from system to system, and the force constant which determines the vibrational frequencies of the system.

In Sec. III we focus on the effect of the metallic energy and trends in the bond properties with metallicity, studying its effect by consideration of the series of elemental tetrahedral semiconductors: diamond, silicon, germanium, and gray tin. In Sec. IV we study the role of the polar energy in the series of polar semiconductors isoelectronic with the elemental semiconductors, e.g., diamond, boron nitride, and berillium oxide. In Sec. V we treat π bonding, considering the series C_2H_6, C_2H_4, and C_2H_2, with single, double, and triple bonds, respectively. We also consider resonant π bonding in graphite and benzene (C_6H_6). Section VI contains a summary of the results. A study of the nitrogen molecule in the Appendix provides an independent test for a number of the approximations used in this approach.

II. TIGHT-BINDING THEORY OF THE BOND

A. Formulation

We follow the procedure and notation of Ref. 16 as modified in Ref. 17. Our tight-binding description is formulated in terms of a minimal basis set of valence-electron orbitals, a single s state and three p states, in the systems considered which are taken to have energies equal to the Hartree-Fock atomic term values.[21] We use here recently revised values for all parameters,[17] though the results would not be greatly modified had we used earlier values.[16] These orbitals are coupled to those on neighboring atoms by universal matrix elements[17] $V_{ll'm}=\eta^2_{ll'm}/md^2$, where d is the internuclear distance, and the four universal coefficients are $\eta_{ss\sigma}=-1.32$, $\eta_{sp\sigma}=1.42$, $\eta_{pp\sigma}=2.22$, and $\eta_{pp\pi}=-0.63$.

Also incorporated in the recent formulation was a peripheral excited s state to be included in Louie's perturbation-theory approach[22,17]; this coupling shifts each σ-oriented p-state energy by $V^2_{s^*p\sigma}/(\epsilon_p-\epsilon^*_s)=\lambda_{sp\sigma}\hbar^2/md^2$ with $\lambda_{sp\sigma}=-0.40$. This is the only effect of the peripheral state in the present context. It is not difficult to include this effect in the present calculations, and we shall do it in the Appendix, but it complicates the discussion. We shall see that the energy levels of the σ states are typically shifted by an energy of order $3.26\hbar^2/md^2$ by the bonding, and this additional shift, a factor of 8 smaller and appearing in every system, is not important. We, therefore, drop it throughout our discussion of bonding.

It will also be necessary to include the nonorthogonality (overlap) of the orbitals on neighboring atoms. These will be related to the interatomic couplings using extended Hückel theory after we have characterized the bond orbitals.

This specifies all of the tight-binding parameters which are needed for the calculation of molecular levels (as in the Appendix), energy bands, dielectric properties, and the bonding properties being addressed here. We begin with the construction of bond orbitals.

B. Bond orbitals and hybrids

Semiconductors and insulators, like molecules, are characterized by an energy gap between the occupied and empty electronic states. The constituent atoms ordinarily do not have this feature; in the silicon atom, the highest occupied and lowest empty states are $3p$ states which have the same energy in our tight-binding representation. The solid, on the other hand, has occupied bond orbitals lying well below empty antibonding orbitals. In order to present a simple picture of the electronic structure it is essential to transform to such bonding and antibonding orbitals. This is simply a change of variables and has no effect on the final answer if an exact solution is to be made, but it is the step which allows a simple understanding and simple approximations to the properties of the bond.

The essential features of this transformation are quite familiar in cases, such as silicon, which can be described in terms of two-center bonds. We transform from s states and p states, each of which may have comparable coupling to each of the four neighbors, to sp^3 hybrids which are oriented each toward a particular neighbor. Then in a first approximation we may include only the coupling, called the covalent energy, between two hybrids directed at each other. Pantelides and Harrison[23] called this the *bond-orbital approximation*, an approximation which we use in this section and which contains the principal features of the bonding.

There are, in fact, two aspects to the bond-orbital approximation. First is the neglect of coupling between two hybrids on the same atom, but directed into different bonds. This matrix element is called the metallic energy and will be evaluated in Sec. II C. We shall see in Sec. III that it becomes quite important in heavier systems but can be accurately treated in perturbation theory. Second is the neglect of coupling between one hybrid and a hybrid on a neighboring atom, but directed into a different bond. Its effect will be seen to be negligible for the properties treated here, though Sokel[24,16] found it essential to the understanding of the elastic shear constants in polar semiconductors.

In cases such as graphite, with three neighboring atoms rather than four, it will be appropriate to construct sp^2 hybrids. There will still be a covalent energy and a metallic energy, and the theory proceeds in much the same way. Such a construction will also be appropriate in the analysis of molecules.

It is convenient to calculate the change in energy step by step as we go from the free atoms to the bonded solid or molecule. The first step, transforming to hybrids, gives the *promotion energy.* A general sp hybrid is a normalized sum of an s and a p state, which can be written

$$|h\rangle=\cos\beta\;|s\rangle+\sin\beta\;|p\rangle\;. \tag{1}$$

Writing the constant coefficients as sines and cosines makes the normalization automatic. The expectation value of the energy for such a hybrid is

$$\epsilon_h=\cos^2\beta\,\epsilon_s+\sin^2\beta\,\epsilon_p\;, \tag{2}$$

or $(\epsilon_s+3\epsilon_p)/4$ for an sp^3 hybrid with $\cos^2\beta=\frac{1}{4}$, $\sin^2\beta=\frac{3}{4}$.

In silicon the free atom has two electrons with ϵ_s and two with ϵ_p so transforming to four sp^3 hybrids costs $\epsilon_p-\epsilon_s$ per atom. This promotion energy is divided equally among the bonds for a promotion energy of $(\epsilon_p-\epsilon_s)/2$ per bond.

When we construct molecules such as C_2H_4 the promotion energy is again, by convention, equally divided among the bonds formed by each atom, with one-third in the C—C bond and two-thirds in the C—H bonds in the case of C_2H_4.

C. Covalent, metallic, and polar energies

The matrix element between two hybrids in the same bond (note the second has its p state oriented in the reverse direction, changing the sign of the matrix elements it enters) can be written down directly; it is the *covalent energy,*

$$V_2=\cos^2\beta\,V_{ss\sigma}-2\sin\beta\cos\beta\,V_{sp\sigma}$$
$$-\sin^2\beta\,V_{pp\sigma}=\eta_2\hbar^2/md^2\;. \tag{3}$$

η_2, of course, depends upon the hybrid mixture; it reaches its peak near the sp^2 hybrid but is rather constant over the entire range of interest, -3.19, -3.26, and -3.22, respectively, for sp, sp^2, and sp^3 hybrids. This variation will not be important in our analysis, but we shall use the appropriate value, -3.22, when we are discussing tetrahedral semiconductors. The fact that the matrix element is near its maximum makes the matrix elements with differently oriented hybrids small and, therefore, makes the interatomic aspect of our bond-orbital approximation more accurate. Two coupled hybrids form bonding and antibonding states of energy $\epsilon_h\pm V_2$ and the gain in energy, called the *σ-bonding energy,* is simply $2V_2$ per bond since there are two electrons for each bond.

The coupling between two hybrids on the same atom is also directly obtainable using Eq. (1). Both hybrids are of this form but with p states differently oriented. The matrix element, which we have called the *metallic energy,* is given by

$$V_1=\langle h'\,|\,H\,|\,h\rangle=(\epsilon_s-\epsilon_p)\cos^2\beta\;, \tag{4}$$

or $(\epsilon_s-\epsilon_p)/4$ for sp^3 hybrids.[16,17] It is the principal term giving the valence (bonding) bands and conduction (antibonding) bands their width, but it does not affect the total energy in the bond-orbital approximation. For this simple case it will be interesting to note that the promotion energy is simply $-2V_1$.

In Sec. IV we shall discuss compounds where the bond orbital is made up of two hybrids of different energy. We shall then introduce a polar energy V_3 equal to half this energy difference. These are the three energies which characterize the bond. In this section it will be simpler to take the polar energy equal to zero and postpone the generalization until Sec. IV.

D. Overlap interaction

There are other contributions to the total energy from the nonorthogonality of the basis states, self-energy corrections, and core-core interactions. In tight-binding theory these can be written approximately as a two-body central-force interaction, dominated by the excess electronic kinetic energy.[25] This is the term which keeps the system from collapsing under the attractive σ-bonding energy.

The approximate form of this repulsive term in the energy can be obtained by combining the universal-parameter theory with extended Hückel theory.[26] In both theories two coupled levels split into bonding and antibonding levels, at energy $\pm V_2$ in our notation. There is an additional shift in the average energy given[16] by $-SV_2$, where S is the overlap (nonorthogonality) of the coupled orbitals. This provides the repulsive two-body interaction in extended Hückel theory. In fact, the inclusion of overlap also increases the bonding-antibonding splitting by a factor $(1-S^2)^{-1}$, but since our interatomic elements are consistent with observed band gaps in semiconductors, that increase is already included in our interatomic matrix elements and in V_2.[16] The shift of the average is given by S times half the final splitting; so our use of $-SV_2$ is the correct shift and may be added directly to the bonding energies we obtained without explicit consideration of the overlap.

We note also that, in extended Hückel theory, the matrix element itself is written $V_2 = K\bar{\epsilon}S$, where $\bar{\epsilon}$ is the average term value and K is a constant, frequently taken as 1.75. For the case of tetrahedral semiconductors, $\bar{\epsilon}$ is the average hybrid energy and only the repulsion arising from the hybrids in the bond is included. With two electrons in the bond, the resulting *overlap interaction* becomes

$$V_0(d) = -2SV_2 = 2V_2^2/|K\epsilon_n| \,, \tag{5}$$

varying as d^{-4}. In π-bonded systems we could add also a term from the π-oriented states, but it would be quite negligible.

The value 1.75 for K was chosen by Hoffmann[26] to give good results for organic molecules, and indeed we shall see in the Appendix that using this value in our approach gives reasonable predictions for the equilibrium spacing in carbon-row compounds. However, different values of K would be needed for different rows, and all that will be required for our analysis is the d^{-4} dependence and that K be a constant in a series of varying polarity or bond orders.

E. Prediction of bond energy, bond length, and force constant

The term *bond energy* was used by Pauling[18] such that the sum of all bond energies is the energy to separate the system into isolated atoms. For a system with every bond identical, the calculation we have just outlined gives directly an estimate of the bond energy. We have also defined the distribution of promotion energy to make the bond-energy values specific when there are different kinds of bonds.

The bond energy consists, in the preceding discussion, of a promotion energy which is independent of spacing, a σ-bonding energy, $2V_2$, and an overlap interaction given by Eq. (5). At the equilibrium spacing these should be a minimum, or $\partial V_0/\partial d = -\partial(2V_2)/\partial d$. In other cases we shall treat there will be other terms in the bond energy, and it is convenient to define a *bond tension* T, which is the derivative of all terms but the overlap interaction with respect to internuclear distance. For the simple case at hand, $T = -4V_2/d$. The equilibrium condition (note that $\partial V_0/\partial d = -4V_0/d$) can be written

$$V_0(d_0) = Td_0/4 \,, \tag{6}$$

where d_0 is the equilibrium spacing. Thus the equilibrium contribution of the overlap interaction can be written entirely in terms of bond tension, requiring only the d^{-4} dependence. For the simple case at hand, $V_0(d_0) = -V_2(d_0)$, and the bond energy becomes $-2V_1 + V_2$.

When we consider two systems which are expected to have the same overlap interaction but a different tension we directly predict the change in bond length. The safest way is to fit K to obtain the correct spacing for the first system, and to use that K to predict the spacing for the second. For the specific case where both the change in bond tension and the original tension varied as d^{-3}, we may deduce from Eq. (6) that d varies as $T^{-1/2}$, or

$$d/d_0 = (T_0/T)^{1/2} \,. \tag{7}$$

The force constant for a bond is the second derivative of the bond energy with respect to d. The second derivative of the overlap interaction is $2OV_0/d^2$, so, using Eq. (6), the force constant k at equilibrium can be written

$$k = \frac{5T}{d} + \frac{\partial T}{\partial d} \,, \tag{8}$$

or $k = -8V_2/d^2$ for the case at hand where $T = -4V_2/d$.

Use of the equilibrium condition to eliminate the evaluation of K is accompanied by an ambiguity in the bond energy and force constant predicted when the predicted length, from Eq. (7), differs from the observed bond length. In the present analysis we shall use Eqs. (6) and (8), evaluated at the observed spacing, unless otherwise stated.

III. EFFECTS OF METALLICITY

We analyze first the simplest case, that of the tetrahedrally coordinated elemental semiconductors: diamond, silicon, germanium, and gray tin. The tight-binding parameters we are using give a good description of the energy-band structure.[17] We have outlined the transformation to bonding and antibonding orbitals in the preceding section and, if we were to retain all matrix elements coupling these, we would reproduce that band structure. We shall instead begin with the bond-orbital approximation used in the preceding section and then discuss the principal corrections to it.

A. Bond-orbital approximation to the bonding

We calculated the bond energy as containing the promotion energy $(\epsilon_p - \epsilon_s)/2 = -2V_1$ per bond, the σ-bonding energy $2V_2$, and the overlap interaction $-V_2$. In writing down the total it is convenient to define the *metallicity* by

$$\alpha_m = 2V_1/V_2 \ . \tag{9}$$

Then the bond energy becomes

$$E_{\text{bond}} = V_2(1-\alpha_m) \ . \tag{10}$$

This definition, Eq. (9), differs by a factor of 2 from an earlier definition,[16] but is clearly appropriate for discussion of the bonding. Furthermore, with the new parameters[17] it relates closely to the energy-band structure. For a homopolar semiconductor the optical gap is given by[27]

$$\begin{aligned} E_0 &= \epsilon_s - \epsilon_p - 4V_{ss\sigma} + 4V_{pp\sigma}/3 + 8V_{pp\pi}/3 \\ &= 2(2V_1 + 3.28\hbar^2/md^2) \\ &\approx -2V_2(1-\alpha_m) \ . \end{aligned} \tag{11}$$

In the last step we neglected the difference between -3.28 and -3.22 appropriate to V_2 for sp^3 hybrids. Thus the optical gap goes to zero at approximately $\alpha_m = 1$. This was also roughly true for the old α_m with the old parameters.

In the earlier analysis the metallicity was also generalized to polar systems in which the hybrids on the two atom types had different energies. However, the metallic energy then also differs on the different atoms, and a different average enters the optical gap than enters the bonding. It is not clear that a generalization different from Eq. (9) is useful.

The qualitative result seen in Eq. (10) is familiar. The bond energy decreases in a series of increasing metallicity such as diamond, silicon, germanium, and tin. This comes partly from the decrease in $1-\alpha_m$ and partly from the decrease in the magnitude of V_2 as the bond length increases.

Quantitatively, the trend is overestimated. The metallic energy is obtained by subtracting the atomic term values and the covalent energy from $V_2 = -3.22\hbar^2/md^2$ to obtain the results given in Table I. The error comes largely from the bond-orbital approximation, the neglect of coupling between hybrids in adjacent bond sites. We treat that effect, which we call *metallization,* next.

B. Metallization

Each bond orbital is the sum of two hybrids, divided by $\sqrt{2}$ for normalization, and each antibonding orbital is a difference divided by $\sqrt{2}$, so the coupling between neighboring bond oribtals, or neighboring bond and antibonding orbitals, is $V_1/2$. The coupling *among* bond orbitals broadens the levels into a band, but does not shift the average energy, so that, since they are all occupied, it does not change the energy. The metallization arises, then, from the coupling between bond and antibonding orbitals. Each bond orbital is, in fact, coupled to six antibonding orbtials, each higher in energy by $2V_2$, and so the total shift in bond energy for the two spin states is the *metallization energy*

$$E_{\text{met}} = 3V_1^2/2V_2 = 3V_2\alpha_m^2/8 \ . \tag{12}$$

There is also a decrease in bond tension $\delta T = \partial E_{\text{met}}/\partial d = 3V_1^2/V_2 d$. From Eq. (6) we obtain a change in overlap interaction $3V_1^2/4V_2$ which adds to Eq. (12) and

$$E_{\text{bond}} = V_2(1-\alpha_m + 9\alpha_m^2/16) \ , \tag{13}$$

where metallization is seen to give the third term in the expansion of energy in metallicity.

Its addition to the bond energy is seen in Table I to bring considerable improvement in the predictions; however, the predictions are still only semiquantitative. Hoffmann[26] has noted that the extended Hückel theory overestimates the binding energy of organic compounds by a factor of order 1.8, close to the discrepancy found here for diamond, though the error is smaller in the compounds of higher metallicity. The principal error presumably comes in the approximate manner in which the overlap interaction is treated. Even at that, the predictions are close enough to be useful.

We have indicated that there is also interatomic metallization. The coupling matrix elements in this case vary as d^{-2}, as do the energy denominators, so they add a term to the bond energy as a change in the magnitude of the leading term in Eq. (13). They were evaluated earlier,[28] found to be a 2% correction, and are quite negligible here.

TABLE I. Contributions to the bond energy in homopolar semiconductors (eV).

	α_m	$V_2(1-\alpha_m)$	$E_{\text{met}}+\frac{\delta T\, d}{4}$	Total	Expt.
C	0.40	-6.19	-0.94	-7.14	-3.68
Si	0.81	-0.84	-1.64	-2.49	-2.32
Ge	0.95	-0.20	-2.10	-2.30	-1.94
Sn	1.00	$+0.01$	-1.77	-1.76	-1.56

C. Variation of bond length

The essence of metallicity is the increase in bond length from material to material, and the corresponding decrease in covalent energy, while the metallic energy varies much less. We cannot predict the variation here since the appropriate value of K is expected to vary. In the Appendix we shall determine K for each row of the Periodic Table using the observed internuclear distance for the elemental semiconductors and $2V_2+V_0(d)$ for the energy; the result would have been slightly different if we had included metallization.

Though we cannot predict bond lengths for these systems, we can directly discuss the variation of properties for any of these systems under pressure. We expect K not to change with the change in bond length, so the formula derived here for the force constant [Eq. (8)] provides a direct prediction of the force constant as a function of bond length under pressure.

D. Force constants

We have written the force constant, in Eq. (8), in terms of the bond tension, which in this case includes the derivative of E_{met}, e.g., $T=-4V_2/d+3V_1^2/V_2d$. Evaluating Eq. (8) we obtain

$$k=-(8V_2/d^2)(1-9\alpha_m^2/16) . \tag{14}$$

The results of this evaluation are presented in Table II. The prediction for diamond is accurately given, but the decrease with metallicity is overestimated, the small metallization correction worsening the agreement with experiment.

TABLE II. Contributions to the force constant k for tetrahedral semiconductors (in units of 10^5 dyn/cm).

	From metallization	Total [Eqs. (14) and (17)]	Expt.[a]
C	−0.51	5.08	4.76
BN	−0.20	4.09	
BeO	+0.31	2.30	
Si	−0.38	0.65	1.60
AlP	+0.50	0.71	
Ge	−0.45	0.44	1.28
GaAs	+0.02	0.63	1.27
ZnSe	+0.15	0.43	1.01
Sn	−0.29	0.22	
InSb	+0.03	0.37	0.90
CdTe	+0.08	0.23	0.82

[a] From Ref. 16, p. 196.

IV. EFFECTS OF POLARITY

The effect of polarity (or ionicity) on the bond has been discussed extensively (e.g., Refs. 11, 16, and 20), but not with the effect of metallization included; we find that to be absolutely essential in understanding the general trends.

In a polar bond the two hybrids forming the bond have different energy. The *polar energy* is defined to be half the difference,

$$V_3=(\epsilon_h^c-\epsilon_h^a)/2 . \tag{15}$$

It is convenient in writing formulas to define also a polarity $\alpha_p=V_3(V_2^2+V_3^2)^{1/2}$ and a covalency $\alpha_c=-V_2/(V_2^2+V_3^2)^{1/2}$. A variational calculation for the bond orbital is made,[16] leading to a bond-orbtial energy $(V_2^2+V_3^2)^{1/2}$ below the average energy of the hybrids. It is straightforward to generalize the theory we have given here to such systems. We consider in particular the four series isoelectronic with diamond, silicon, germanium, and tin.

A. Bond energy

The promotion energy per bond is one-fourth of the energy to shift the electrons on a pair of atoms from the atomic configuration to a single electron in each of the eight hybrids; e.g., $(\epsilon_p^c-\epsilon_p^a+\epsilon_p^c-\epsilon_s^c+\epsilon_p^a-\epsilon_s^a)/4$ for a III-V compound such as BN. The σ-bonding energy is now $-2(V_2^2+V_3^2)^{1/2}$ and the overlap repulsion is obtained from Eq. (6).

In order to treat the metallization energy we must obtain the bond and antibond *states*, as well as their energies. The coefficient[16] of the anion hybrid for the bond orbital is $[(1+\alpha_p)/2]^{1/2}$, where α_p is the polarity defined above. The coefficient of the anion hybrid for the antibonding state is $[(1-\alpha_p)/2]^{1/2}$, so the coupling to a neighbor antibonding orbital through the anion is $V_1^a[(1-\alpha_p^2)/4]^{1/2}$. Similarly, the coupling through the cation hybrid is $V_1^c[(1-\alpha_p^2)/4]^{1/2}$, and for two spins we obtain a metallization energy of

$$E_{\text{met}}=3[(V_1^a)^2+(V_1^c)^2](1-\alpha_p^2)^{3/2}/4V_2 . \tag{16}$$

For the special case of the homopolar semiconductors with $\alpha_p=0$ and $V_1^a=V_1^c$, this reduces to Eq. (12). δT is obtained from this also.

These contributions and the total are listed in Table III for the four series in question. The noble-metal halides are not included. The bond energy for them predicted with this scheme reverses sign, while the observed bond energy actually increases; omission of the effects of the noble-metal d states is presumably responsible. For the other compounds, both theory and experiment are approximately equal

TABLE III. Contributions to the bond energy in compound semiconductors (in eV).

	α_c	E_{pro}	E_σ	V_0	$E_{\text{met}}+\frac{d\,\delta T}{4}$	Total	Expt.
C	1	4.15	-20.70	10.35	-0.94	-7.14	-3.68
BN	0.94	5.71	-21.18	9.95	-0.93	-6.45	-3.34
BeO	0.78	10.45	-23.19	9.01	-0.68	-4.41	-3.06
Si	1	3.61	-8.89	4.44	-1.64	-2.48	-2.32
AlP	0.81	4.63	-10.14	4.41	-0.94	-2.04	-2.13
Ge	1	3.91	-8.24	4.12	-2.10	-2.31	-1.94
GaAs	0.88	4.78	-9.25	4.09	-1.23	-1.61	-1.63
ZnSe	0.68	7.36	-11.96	4.09	-0.42	-0.93	-1.29
Sn	1	3.14	-6.26	3.13	-1.77	-1.76	-1.56
InSb	0.87	3.86	-7.16	3.11	-0.95	-1.14	-1.40
CdTe	0.66	5.98	-9.47	3.11	-0.29	-0.67	-1.03

to the homopolar value (C, Si, Ge, and Sn) times the covalency α_c, an empirical trend noted earlier.[16] Thus the discrepancies discussed in Sec. IV B for the homopolar semiconductors are reproduced here, but the trend with polarity is very well given.

Looking at the contributions, there would be little reason to expect the proportionality of the total to α_c. In particular, in the heavier compounds the variation of the metallization through each series is of the same sign and even larger than the trend in the total. An analysis of the bond-orbital approximation (no metallization) would give the wrong sign of the trend.

B. Bond length

A puzzle has arisen[25] in that the bond tension arising from the σ-bonding energy,

$$T=-2\frac{\partial(V_2^2+V_3^3)^{1/2}}{\partial d}=-4\alpha_c\frac{V_2}{d}\ ,$$

drops with increasing polarity while the repulsive force, $\partial V_0/\partial d$, does not, so that one would expect the bond length to increase in a series such as Ge, GaAs, and ZnSe. Experimentally, it is rather constant. The resolution comes from the metallization, which tends to expand the lattice, but which becomes weaker as the polarity increases. Thus the lack of dependence of the lattice distance on polarity in this series is from an accidental cancellation of the effects of the σ-bonding term and of metallicity.

We should not use Eq. (7) to predict the variation in length since the metallization force does not vary as d^{-3}. We should instead add $-2(V_2^2+V_3^2)^{1/2}$, E_{met} from Eq. (16) [with α_p written $V_3/(V_2^2+V_3^2)^{1/2}$], and the overlap interaction [Eq. (5)] in the form CV_2^2. We may then minimize this energy with respect to d (or equivalently to V_2) with d chosen to give the correct bond length when V_3 is taken equal to zero in the homopolar semiconductor, e.g., germanium. Almost the same result is actually obtained using Eq. (7). The results from the full calculation are listed in Table IV. The corresponding predictions without the metallization term would have been, for example, 1.59 and 1.83 Å for BN and BeO, respectively, and 2.64 Å and infinity for GaAs and ZnSe, respectively. Thus the inclusion of metallization has eliminated the main part of the discrepancy, but because the two canceling terms are rather different in origin, the net shift is rather poorly given.

C. Force constant

We may evaluate the contributions of both the σ-bonding and the metallization terms to Eq. (8) for the force constant. We obtain

$$k=-\frac{8V_2\alpha_c^3}{d^2}+\frac{9[(V_1^a)^2+(V_1^c)^2]}{V_2d^2}(5\alpha_c^2-4)\alpha_c^5\ , \qquad (17)$$

which reduces to Eq. (14) for the homopolar case.

TABLE IV. Dependence of bond length on polarity. Corrections for the effect of polarity on both σ bonding and metallization are included.

	Predicted d (Å)		Expt. (Å)
C	1.54	=	1.54
BN	1.58		1.57
BeO	1.74		1.65
Si	2.35	=	2.35
AlP	2.40		2.36
Ge	2.44	=	2.44
GaAs	2.42		2.45
ZnSe	2.70		2.45
Sn	2.80	=	2.80
InSb	2.76		2.81
CdTe	3.13		2.81

This has been evaluated for the series isoelectronic with the elemental semiconductors and listed in Table II. Again the discrepancies with the homopolar semiconductors remain and the trends with polarity appear to be reasonably described.

V. EFFECTS OF BOND ORDER

The tetrahedral semiconductors which we have discussed are the simplest case, with all four orbitals from each atom participating in a σ bond, and every bond is identical. In many solids, such as graphite, and in many molecules, not all orbitals participate in σ bonds and there is a possibility of π bonding between the same two centers. Such systems are described as having bond order greater than 1.[18]

The relevant matrix element $V_{pp\pi}$ was present in the tetrahedral semiconductors, but entered only through interatomic metallization. With every empty state lying $-2V_2$ above the occupied level, such a coupling lowers the bond-orbital energy by an amount of order $V_{pp\pi}^2/2V_2$, only 2% of the lowering, V_2, due to the σ bond. We were justified in neglecting it. On the other hand, if a π bond is formed, the corresponding electron's energy is lowered by $V_{pp\pi}$, which is 20% of the σ-bond lowering and far from being negligible.

The concept of bond order is perhaps most familiar in the series ethane, ethylene, and acteylene, and we shall treat that series, returning afterward to fractional bond order in graphite and benzene. In all of these cases it is carbon—carbon bonds under discussion and we may neglect the effects of metallization, though they can, of course, be treated straightforwardly.

A. C_2H_6, C_2H_4, and C_2H_2

In ethane (C_2H_6), each carbon atom is bonded to the other carbon and to three hydrogens at approximate tetrahedral angles. As in diamond we form tetrahedral hybrids, associate one-fourth of the promotion energy with the carbon bond, and add an overlap interaction proportional to d^{-4}, to again obtain a bond energy $[V_2+(\epsilon_p-\epsilon_s)/2]$, a bond length, and a force constant equal to that in diamond, as found experimentally to a very good approximation.

In ethylene (C_2H_4), carbon in bonded to only two hydrogen atoms in addition to the other carbon and all lie in the same plane. The angles are close to 120° and we should construct sp^2 hybrids. One-third of the promotion energy is associated with the carbon—carbon bond, and the coefficient for V_2 in the σ-bonding energy of $2V_2$ is increased from 3.22 to 3.26 (for sp^2 hybrids). However, now the p states oriented perpendicular to the plane of the molecule form bonding and antibonding levels at $\epsilon_p \pm V_{pp\pi}$, with only the bonding level occupied. Thus we must add a π-bonding energy to the energy associated with the carbon—carbon bond,

$$E_{\text{bond}} = 2(\epsilon_p-\epsilon_s)/3 - 2(3.26\hbar^2/md^2) - 2(0.63\hbar^2/md^2) + V_0(d) \ . \tag{18}$$

If we neglect the difference in 3.22 and 3.26, we see that the bond tension has been increased by a factor of $1+0.63/3.26=1.193$. This is a double bond and we may say that it has *π-bonding strength* of unity. Equation (7) tells us that the bond length should decrease to $(1.193)^{-1/2}\times 1.54$ Å$=1.41$ Å in fair agreement with the observed 1.33 Å. [The prediction is improved very slightly (1.40 Å) if we do not neglect the difference between the V_2 for sp^2 and sp^3 hybrids, but not significantly so and not enough to justify complicating the theory.] For the bond energy in Eq. (18) $V_0(d)$ is again equal to minus half of the bonding terms and the bond energy, evaluated at the observed spacing, is 11.23 eV, again about twice the accepted double-bond energy of 6.37 eV.

Acetylene (C_2H_2) is linear and one might guess that sp hybrids should be used. However, a molecular-orbital calculation suggests that an sp^2 hybrid is closer to correct, again maximizing V_2. It makes little difference, but the theory is simple if we use sp^2 hybrids for all of the π-bonded cases. Then, in comparison to Eq. (18), for acteylene the promotion energy increases to $\epsilon_p-\epsilon_s$, and the π-bonding energy is doubled. We may say that the π-bonding strength is $\xi_\pi=2$ and the bond tension is increased to $1+0.193\xi_\pi$. Equation (7) becomes

$$d/d_0=(1+0.193\xi_\pi)^{-1/2} \ , \tag{19}$$

where d_0 is the single-bond length, leading to a prediction of 1.31 Å in comparison to the observed 1.20 Å. The bond energy becomes 15.63 eV at the observed spacing, compared to the empirical 8.41 eV. We shall plot these results and treat the force constant after analyzing nonintegral bond orders.

B. Fractional bond order

Graphite is similar to ethylene in that again sp^2 hybrids are formed in the plane of the system and p states oriented perpendicular to the plane are coupled by $V_{pp\pi}$. However, in this case each p state is coupled equally to three others and there is only one pair of electrons available for each three bond sites so the simple bond picture fails; one notes that there is resonant bonding.[18] We must treat these π-like states in more detail.

The N coupled π levels (one per aton) form an energy band which could be obtained by diagonlizing the $N\times N$ Hamiltonian matrix H. The second moment of the band can also be obtained from that matrix,

$$\langle(\epsilon-\epsilon_p)^2\rangle=\sum_{i,j}(H_{ij}-\epsilon_p\delta_{ij})(H_{ji}-\epsilon_p\delta_{ji})/N$$
$$=3V_{pp\pi}^2\ . \qquad (20)$$

In the last step we noted that each level is coupled to three neighbors by $V_{pp\pi}$ and the diagonal terms are $H_{ii}=\epsilon_p$. The distribution of levels is symmetric around ϵ_p and only the lower half is filled. If we estimate the average shift by $\langle(\epsilon-\epsilon_p)^2\rangle^{1/2}$, we obtain $\sqrt{3}V_{pp\pi}$. This will always slightly overestimate the shift, but not by much. We shall be able to compare this approximate value with the exact value when we treat benzene and see that the error there is only 6%. Since there are two electrons for each three bonds, the lowering in energy per bond is $2\sqrt{3}\ V_{pp\pi}/3$, to be added to the σ-bonding energy of $2V_2$.

If we wish to describe this as a resonating bond we should say that *it contributes a π-bonding strength equal to the fraction of its presence in each bond* ($\frac{1}{3}$) *enhanced by the square root* ($\sqrt{3}$) *of the number of sites among which it resonates.* This was described by Pauling[18] earlier as a total bonding proportional to bond order ($\frac{4}{3}$) and the discrepancy in comparison to experiment called a resonance energy. Use of the π-bonding strength defined here includes this resonance energy automatically and allows direct prediction of the other properties as well.

In particular, Eq. (18) for the bond energy remains appropriate except for the reduction of the π-bonding energy by a factor of the π-bonding strength. Evaluation at the observed spacing gives 8.16 eV, compared to the observed 4.91 eV. The bond length predicted from Eq. (19) is 1.46 Å in comparison to the observed 1.42 Å.

The same analysis may be applied to benzene. There each carbon π state is coupled to two others for an average shift of $\sqrt{2}V_{pp\pi}$, and there is one pair of π electrons for each two bonds for a π-bonding strength of $\sqrt{2}/2$. This gives a bond energy of 10.33 eV, compared with the value (including resonance energy) of 5.25 eV given by Pauling,[18] and a predicted length of 1.44 Å, compared with the observed 1.40 Å.

For benzene we may also calculate the π-bonding energy exactly, in the tight-binding context. The six coupled π levels yield energies $\epsilon_p+2V_{pp\pi}\cos(n\pi/3)$ with integral n. These are filled for $n=0,\pm1$ giving an energy per bond of $4V_{pp\pi}/3$, or a π-bonding strength of $\frac{2}{3}$, only 6% less than the value $\sqrt{2}/2$ obtained above. The square-root formula is of more interest since it is more generally applicable, and the numerical difference is not important.

The same square-root factor is appropriate in other circumstances which are thought of as resonant bonding. In an ionic crystal such as rocksalt we might regard the coupling between the p states on the halogen and the s states on the six neighboring alkalis as giving rise to a covalent contribution to the bonding.[25] It is interesting that the nearest-neighbor band calculation in this case gives a bonding band which *at each wave number* is a combination of the s state and a p state of a *particular* orientation; in a sense the bond is resonating in wave-number space. Evaluation at a wave number called the Baldereschi point[29] gives an energy for the bonding state of

$$(\epsilon_s+\epsilon_p)/2-\{[(\epsilon_s-\epsilon_p)/2]^2+nV_{sp\sigma}^2\}^{1/2}\ ,$$

where n is the number of neighbors,[25] six for rocksalt, eight for cesium chloride, and four for zinc blende.[25] The coupling is again amplified by the square root of the number of sites among which the bond resonates.

The same effect is also reasonably familiar in metals where each atom may have eight or twelve nearest neighbors. The added binding energy in a transition metal due to the d bands is proportional to the width of the d band.[30] If the square root of the second moment is used as a measure of the width, an argument such as Eq. (20) indicates again a proportionality to the square root of the number of neighbors.[31] Thus one can formulate the same rule for the dd bond resonating among the eight or twelve nearest neighbors.

C. Force constant

In the cases of multiple bond order we have treated, the bond tension is given by $T=-4V(1+0.193\xi_\pi)/d$. This may be inserted in the equation for the force constant, Eq. (8), to obtain a form for the force constant,

$$k=26.08\frac{\hbar^2}{md^4}(1+0.193\xi_\pi)\ , \qquad (21)$$

or combined with the predicted bond-length variation, Eq. (19), to obtain

$$k=5.66(1+0.193\xi_\pi)^3\times10^5\ \text{dyn/cm}\ , \qquad (22)$$

where we have inserted 1.54 Å for the single-bond distance. Comparison of Eq. (21) with experiment indicates that the variation with bond length is not as rapid experimentally as d^{-4} and Eq. (22) fits better, simply because it underestimates the variation of d with ξ_π.

D. Dependence of the properties on π-bonding strength

We have found that the bond length and force constant are expected to vary smoothly with π-

bonding strength, not with bond order, for fractional bond orders. The bond energy itself has an additional variation because the promotion energy is different for single and triple bonds than for the others. However, it is appropriate to plot the experimental values as a function of π-bonding strength for which the predicted results are simple. This is done in Figs. 1–3.

The bond energy is surprisingly linear in ξ_π; the promotion energy variation is responsible for the fluctuations in the theoretical curve. The trend seen experimentally is quite well given by theory. Note that there is some arbitrariness in the experimental values for hydrocarbons since there may be different ways to assign the molecular cohesion among the bonds.

We have underestimated the change in bond length with π-bonding strength, but we should note that these are first-principles estimates and the accuracy should not be compared with empirical schemes. If, for example, we were to adjust the scale factor $V_{pp\pi}/V_2=0.193$ rather than take it from first principles the agreement would be very good.

The absolute predictions of the force constant are very close to experiment, but would not have been as close had we evaluated Eq. (21) at the observed spacing rather than using Eq. (22).

VI. SUMMARY

A two-center σ bond is characterized by three energies. The covalent energy V_2 is the matrix element between two hybrids extending into the bond. It is rather insensitive to the sp mixture and can be taken as $-3.26\hbar^2/md^2$. The polar energy V_3 is half the difference in energy (if any) between the two hybrids. Since the hybrid energies [e.g., $\epsilon_h=(\epsilon_s+3\epsilon_p)/4$ for sp^3 hybrids] are independent of internuclear distance, the energy of the bond, $\bar{\epsilon}_h-(V_2^2+V_3^2)^{1/2}$, depends on bond length only through V_2.

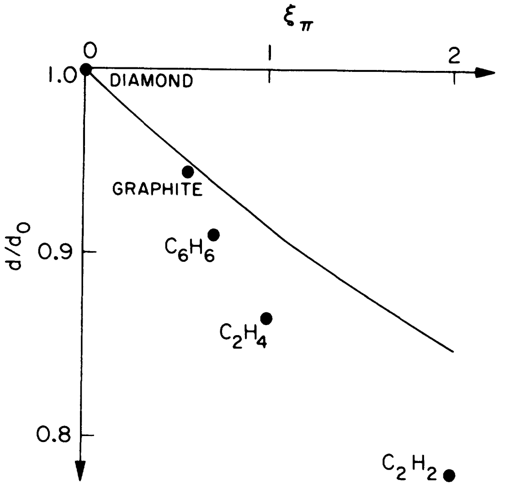

FIG. 2. Ratio of bond length to single-bond length as a function of π-bonding strength. The plotting scheme is as in Fig. 1.

The metallic energy V_1 is proportional to $\epsilon_p-\epsilon_s$ with a coefficient depending upon the sp mixture of the hybrid ($-\frac{1}{4}$ for sp^3 hybrids). It couples the bond orbital to the bonding and antibonding orbitals in the neighboring sites. Its effect, called metallization, is calculated in perturbation theory and has important effects on the bond properties in heavier compounds.

The variation of the bonding energy, through V_2, gives a bond tension which is balanced at equilibrium by an overlap repulsion, given approximately by $\hbar^4/(\epsilon_h m^2 d^4)$, with a numerical coefficient which

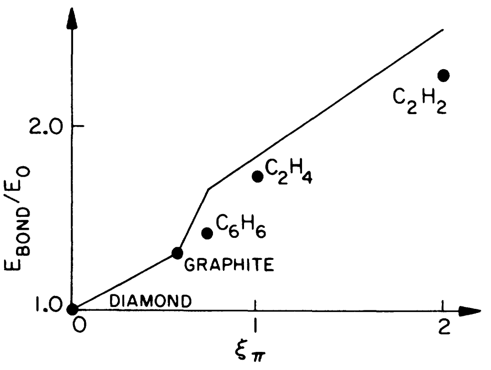

FIG. 1. Ratio of bond energy to single-bond energy as a function of π-bonding strength ξ_π. The line is predicted, the circles are from experiment from Ref. 18. The π-bonding strength is 0 for diamond, $\sqrt{3}/3$ for graphite, $\sqrt{2}/2$ for benzene, 1 for ethylene, and 2 for acetylene.

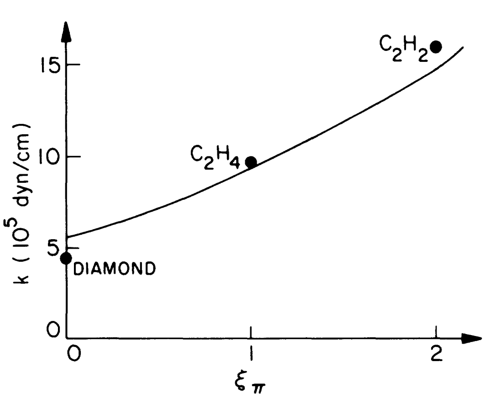

FIG. 3. Force constant, obtained as a function of π-bonding strength [Eq. (22)] using the predicted bond-length variation. Experimental values are from Ref. 16.

varies from system to system. The value of the repulsive energy can be obtained, given the equilibrium spacing, by setting its derivative equal to the bond tension. Variations in bond length and bond force constant can also be computed in terms of the bond tension, without knowing the numerical coefficient in the repulsion, within systems (e.g., carbon—carbon bonds) for which the repulsion is expected to be the same.

A change in tension δT produces a change in bond length δd given by $\delta d/d=(1+\delta T/T)^{-1/2}-1$. The metallicity, defined here by $\alpha_m=2V_1/V_2$ for a homopolar semiconductor, characterizes the importance of metallization. It is small for diamond, but approaches unity as the band gap corresponding to the optical threshold goes to zero at tin. The bond energy (cohesive energy per bond) in these singly bonded systems is $V_2(1-\alpha_m+9\alpha_m^2/16)$. The first term gives the energy gained in forming the bond, including the overlap repulsion energy. The second term is the promotion energy to form the hybrids, and the third is from metallization. In the heavy semiconductors the metallization dominates the bond energy, appreciably expands the lattice, but has little effect on the bond force constant (responsible for the vibrational frequencies). That force constant, neglecting metallization, is $-8V_2/d^2$.

In polar semiconductors the promotion energy, the energy gained in forming the bond, and the metallization are all modified. The theory correctly predicts a decrease in bond energy with increasing polarity. The weakening of the bond tension, $T=-4V_2^2/(V_2^2+V_3^2)^{1/2}d$, by the polar energy causes the bond length to increase with polarity in the series C, BN, BeO. In the heavier semiconductors the decrease in the metallization with increasing polarity cancels this effect and the bond length varies little with polarity.

If not all orbitals participate in σ bonds with neighbors, they can contribute π-bonding energy. A single π bond (here ethylene) contributes $2V_{pp\pi}=-1.26\hbar^2/md^2$ and is associated with a π-bonding strength $\xi_\pi=1$. A double π bond (here acetylene), $\xi_\pi=2$, contributes twice that amount. A fractional π bond (graphite, $\frac{1}{3}$; benzene, $\frac{1}{2}$) corresponding to fractional bond order contributes with a π-bonding strength equal to that fraction *multiplied by the square root of the number of bond sites between which it resonates* (graphite, 3; benzene, 2). The bond energy (neglecting metallization as appropriate for carbon-row compounds) becomes $V_2(1+0.193\xi_\pi)$ plus the promotion energy. The increased tension also modifies the bond length by $\delta d/d=(1+0.193\xi_\pi)^{-1/2}-1$ and the force constant by $\delta k/k=(1+0.193\xi_\pi)^3-1$. This same representation of the electronic structure and parameters gives also direct predictions of the bands and dielectric properties of these systems and other covalent and ionic systems.[16]

ACKNOWLEDGMENTS

This work was supported in part by the Alexander von Humboldt Foundation of the Federal Republic of Germany, and in part by the National Science Foundation under Grant No. DMR 77-21384. The author is indebted to Professor O. K. Andersen and the Max-Planck-Institut für Festkörperforschung in Stuttgart for their hospitality while this work was being carried out, and to Professor H. G. von Schnering for valuable discussions.

APPENDIX

Since we have introduced energy-level shifts due to nonorthogonality which were not in the earlier treatments[16] (these were absorbed in the repulsive term), it is desirable to see whether the method still gives reasonable one-electron energies. This will provide a more complete accomodation between extended Hückel theory and universal-parameter theory and will allow us to discuss absolute predictions of bond length. By treating the molecule N_2, isoelectronic with C_2H_2, we shall also be able to see whether the parameters remain relevant when we change the average column number for the bond, as well as when we change the column-number difference (variation of polarity). We will also be able to test the approximate procedure we used to obtain σ bonds in this paper.

In extended Hückel theory,[26]

$$V_{ij}=K(\epsilon_i+\epsilon_j)S_{ij}/2\ , \tag{A1}$$

where S_{ij} is the nonorthogonality of the coupled levels i and j and K is a numerical constant. Then using the universal form for V_{ij}, we obtain

$$\begin{aligned} S_{ss\sigma}&=-1.32\hbar^2/(md^2\epsilon_s K)\ ,\\ S_{sp\sigma}&=1.42\hbar^2/[md^2(\epsilon_s+\epsilon_p)K/2]\ ,\\ S_{pp\sigma}&=2.22\hbar^2/(md^2\epsilon_p K)\ ,\\ S_{pp\pi}&=-0.63\hbar^2/(md^2\epsilon_p K)\ . \end{aligned} \tag{A2}$$

In order to obtain an explicit expression for the nonorthogonality of two sp^3 hybrids, and thus to discuss the diamond-structure semiconductors, it is convenient to note from a tabulation of the atomic terms values[16,17,21] that $\epsilon_s=2\epsilon_p$ to a very good approximation. Then we can obtain

$$S_2=3.31\hbar^2/Kmd^2\epsilon_h\ . \tag{A3}$$

We may then immediately minimize the d-

dependent term in the bond energy $2(V_2-S_2V_2)$ to obtain $S_2=\frac{1}{2}$ or

$$d^2=6.62\hbar^2(Km\epsilon_h) . \tag{A4}$$

If we use the usual $K=1.75$ this leads to a prediction of 1.48 Å for diamond, in comparison to the observed 1.54 Å, and an increase only to 1.86 Å, compared with 2.80 Å for tin. (Inclusion of metallization as in Sec. IV C only increases this to 2.03 Å). However, the 1.75 was adjusted empirically to fit carbon compounds[26] so it may be more to the point to deduce K values which give correct spacings, 1.63, 0.97, 0.91, and 0.77 for C, Si, Ge, and Sn, respectively, if the metallization term is neglected. These values could be used to give a repulsion,

$$V_0(d)=\frac{21.3}{K}\left[\frac{\hbar^2}{m}\right]^2\frac{1}{|\epsilon_h|}\frac{1}{d^4} , \tag{A5}$$

almost identical to Eq. (5), where $\epsilon_h=(\epsilon_s+3\epsilon_p)/4$. However, rather than use any such adjustable parameter in the body of the paper we have chosen to make direct calculations of ratios of quantities (e.g., the ratio of double-bond spacing to single-bond spacing). Similarly, we shall estimate the ratio of the N_2 internuclear distance to the diamond spacing after treating the electronic structure of N_2.

As a first step in the calculation of molecular levels in nitrogen we evaluate the four nonorthogonality values from Eq. (A2). They are 0.20, −0.28, −0.64, and 0.18, respectively, based upon the internuclear distance of 1.09 Å for N_2 and the value $K=1.62$ which gives the correct spacing [Eq. (A4)] for carbon. For a pair of coupled levels the shift of the average, which can be taken as a shift of each term value, is $-V_{ij}S_{ij}$. We generalize this to the coupled pairs of σ levels as a shift $-S_{pp\sigma}V_{pp\sigma}-S_{sp\sigma}V_{sp\sigma}=11.66$ eV in ϵ_p, a form which should be valid at least to first order in the $S_{ij}V_{ij}$ shifts. There was also a shift in ϵ_p for σ orientation due to the peripheral s state, which we neglected in the treatment of bonding, but which should be included here. It is $-0.40\hbar^2/md^2=-2.57$ eV. Thus the p-state term value entering the σ-state calculation is $\epsilon_{p\sigma}=-13.84+11.66-2.57=-4.75$ eV with the starting term value ϵ_p from Ref. 21. The s state is shifted by $-V_{ss\sigma}S_{ss\sigma}-V_{sp\sigma}S_{sp\sigma}$, but not by the peripheral state,[17] to $\epsilon_{s\sigma}=-21.98$ eV. The π-oriented states are shifted only $-S_{pp\pi}V_{pp\pi}=0.73$ eV.

The bonding and antibonding π states are obtained immediately as $\epsilon_p+0.73\pm4.04$ eV $=(17.15, -9.07)$ eV, listed also in Table V. Similarly, we construct even combinations of $p\sigma$ states and even combinations of $s\sigma$ states, which are coupled to each other by $V_{sp\sigma}$, to obtain energies

TABLE V. Molecular levels for N_2 obtained with universal parameters (including nonorthogonality and s^* shifts), compared with Ransil (Ref. 32).

	Universal	Ransil
$p\sigma^*$	+12.67	
π^*	−9.07	−8.2
π	−17.15	−14.8
$p\sigma$	−13.95	−15.1
$s\sigma^*$	−16.68	−19.4
$s\sigma$	−35.48	−38.6

$$E=\frac{\epsilon_{s\sigma}+V_{ss\sigma}+\epsilon_{p\sigma}-V_{pp\sigma}}{2}\pm\left[\left[\frac{\epsilon_{p\sigma}-V_{pp\sigma}-\epsilon_{s\sigma}-V_{ss\sigma}}{2}\right]^2+V_{sp\sigma}^2\right]^{1/2} , \tag{A6}$$

and the same formula, with the sign in front of $V_{ss\sigma}$ and $V_{pp\sigma}$ changed, for the odd combinations. These are listed in Table V, along with molecular-orbital self-consistent-field calculations. The agreement is gratifying, and comparble with the agreement from the earlier parametrization.[16] These results follow immediately from the use of the parameters which we have used in the treatment of bonding.

It is also interesting to note that the results are quite close to what is obtained using the bond-orbital approximation which was utilized here in the treatment of carbon-row systems. We make sp^2 hybrids on the nitrogen with energy −10.49 eV, including nonorthogonality and peripheral state shifts, and a coupling of $-3.26\hbar^2/md^2$, and obtain energies of −31.40 eV for $s\sigma$ and +10.42 eV for $p\sigma^*$. The two nonbonding states, $s\sigma^*$ and $p\sigma$, then both take the energy of the s^2p hybrids orthogonal to the sp^2 hybrids, −16.23 eV. The π-state energies are the same as before and as in Table V.

We conclude that the molecular levels are reasonably well given by the universal-parameter theory and that the corrections which we regarded as small in treating the bonding are also rather small in the treatment of molecular levels. We may, however, have more confidence in the treatment of bonding which is less sensitive to the approximation made here; we needed only the form of the repulsion, d^{-4}, not the coefficient.

Finally, we may estimate the ratio of the bond length in N_2 to that in diamond or ethane. The ratio of the bond tensions is $2\times(3.26+2\times0.63)$ for the nitrogen triple bond to 2×3.22 for the carbon single bond and now the ratio of the repulsive terms is the reciprocal of the ratio of the sp^3-hybrid energies, according to Eq. (A5), $-13.15/(-16.94)$. Generalizing Eq. (7) to include both effects leads to a predicted bond length of 1.15 Å, in comparison to the observed 1.09 Å. Again we have underestimated the difference, but much less so than had we assumed that the repulsion remained fixed in the series rather than that K remains fixed. The same treatment of the other first-row diatomic molecules gives similar accuracy except at the end of the series, O_2, and F_2, suggesting that perhaps smaller values of K are appropriate for these systems (d is underestimated).

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