PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Empirical chemical pseudopotential theory of molecular and metallic bonding

G. C. Abell
Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio 45342

(Received 19 March 1984)

A unified analysis of molecular and metallic bonding is presented, with chemical pseudopotential theory providing a fundamental context. Unperturbed atomic orbitals are used as the local orbital basis in the determination of the secular equation matrix elements. The two-center approximation gives an expression for the binding energy in terms of bond densities and pair interactions, the latter of which, for a given atomic species, depend only on the pair separation and not on the overall chemical environment. The repulsive and attractive pair interactions are parametrized as simple exponentials and all but nearest-neighbor interactions are ignored. More distant interactions are shown to play a relatively insignificant role insofar as binding energy is concerned. Under a certain scaling, an expression for binding energy is obtained and shown to be nearly universal, in agreement with recent observations. The scaled binding energy depends on a single parameter S, which is essentially the ratio of the steepness of the repulsive pair interaction to that of the attractive pair interaction. Whereas the scaled binding energy shows a very weak dependence on the parameter S in the relevant domain, the preference for molecular versus metallic bonding is shown to be exponentially dependent upon it. The criterion for bonding preference is just the optimization of binding energy with respect to nearest-neighbor coordination Z, which is the dominant topological variable in the determination of binding energy. The molecular regime is characterized by $S \simeq 2$, and the binding energy is shown to be nearly independent of the nearest-neighbor coordination Z in this case. The energetics of bonding in the molecular regime is thus dominated by *nonlocal* features of the topology, such as the nature and size of interaction loops. A correspondence is established between the contribution of nonlocal topological features to the binding energy, and chemical stability and reaction paths of molecular systems. As a quantitative test of the empirical-chemical-pseudopotential-binding energy expression, known potential-energy curves for H_2 and symmetric linear H_3 were used as inputs to determine the repulsive and attractive pair interactions for hydrogen pairs. These were then used to successfully predict binding energies for various other hydrogen species, including H_3, H_4, and H_{14}, for which accurate first-principles calculations exist. A similar procedure was used for Lithium species.

I. INTRODUCTION

This paper presents a unified analysis of the disparate problems of molecular and metallic binding. The basic approach is a linear combination of atomic orbitals (LCAO) parametrization whose fundamental context is chemical pseudopotential (CP) theory.[1] The primary goal is to develop a very general description of bonding which isolates key features that determine whether a given species prefers molecular versus metallic bonding and which explains outstanding differences, as well as similarities, between molecular and metallic bonding. That there is a similarity of bonding in molecules and simple metals, and in intermediate bonding situations as well, has been persuasively demonstrated by recent observations of an apparently universal relation between binding energy and interatomic spacing.[2] The existence of such a relation is surprising considering that the bonding energetics of simple metals are well described by plane-wave pseudopotential theory[3], which is essentially a perturbed free-electron theory, while bonding in molecules is usually described by LCAO theory. In the former case the atoms represent a small perturbation, while in the latter case they represent the zeroth-order description. This unexpected bonding similarity contrasts sharply with the otherwise profound differences between the energetics of metals and molecules. Thus, the existence of close-packed metals is strongly at odds with the nearly complete avoidance of small loop topologies in molecular structures and reactions.[4] Molecular bonding is characterized by strong interactions between a few atoms, with binary coupling (i.e., the simple covalent bond) as the predominant bonding mode. As a result, the molecular unit usually consists of a relatively small number of atoms, whereas metallic bonding is almost always macroscopic. Universality notwithstanding, any theory that attempts to describe molecules and metals on a common footing must explain these fundamental differences.

Certain key aspects of CP theory that have been incorporated into the overall scheme are (i) implicit use of free-atom valence orbitals as the zeroth-order representation, (ii) solution of a secular equation appropriate to an *orthogonal* basis, and (iii) the two-center approximation. As a parametrized scheme, our approach is akin to the complete neglect of differential overlap (CNDO) method[5] and less so to the extended Hückel method;[6] these are undoubtedly the most successful of the semiempirical *molecular* theories. An important difference is that we parametrize the two-center matrix elements by a common functional form rather than in terms of interatomic matrix elements of a specified effective environment potential. The advantage of this approach is that it allows a general analysis of binding in very simple terms. A disadvantage is that without specifying the perturbing potential due to the environment of a given atom, one cannot expect to obtain truly quantitative results for particular systems. Thus a secondary goal of the paper is to develop a method for quantitative determination of the potential hypersurface of a given species. To that end we present a somewhat indirect method for obtaining the effective one-electron potential and demonstrate its predictive power for some hydrogen (H_n) and lithium (Li_n) species.

The organization of the paper is as follows: In Sec. II we use CP theory to develop a general expression for binding energy. In Sec. III we introduce an exponential parametrization of the two-center matrix elements appearing in the binding-energy expression and show that the resulting functional form is consistent both with the observation of binding-energy universality *and* with bonding diversity. In Sec. IV we present a brief discussion of the role of orbital topology in molecular behavior. In Sec. V we describe a method for obtaining a quantitative representation of the two-center matrix elements and demonstrate the predictive power of the scheme for some H_n and Li_n species. In Sec. VI we present our concluding remarks.

II. BINDING ENERGY

In this section we use a localized-orbital (LO) approach, based on CP theory, to develop a model Hamiltonian for monovalent atoms which, when suitably parametrized, provides the foundation for a very general analysis of binding energy. The total self-consistent-field (SCF) Hamiltonian is written as[1]

$$H=T+\sum_a V_a \ , \tag{1}$$

where T is the kinetic-energy operator and V_a is the effective potential from atom a and is summed over all atoms. The crucial assumption for our purposes is that the V_a's are short ranged and strongly localized about the corresponding atoms. This is really a generalization of the Wigner-Seitz effective potential[1(a)] and simplifies the general LO equation [1(b)] to Anderson's LO pseudopotential equation:

$$\left[T+V_a+\sum_{b\,(\neq a)}(V_b-|\phi_b\rangle\langle\phi_b\,|\,V_b)\right]|\,\phi_a\rangle=\epsilon_a\,|\,\phi_a\rangle . \tag{2}$$

The ϕ_a are atomiclike LO's that span the band molecular-orbital subspace determined by

$$H\,|\,\psi_i\rangle=\epsilon_i\,|\,\psi_i\rangle \ . \tag{3}$$

In Eq. (2), V_a is the SCF one-electron atomic potential, including exchange and correlation, appropriate to the isolated atom, while $V_{b\,(\neq a)}$ is the difference from the atomic potential V_a due to the presence of atom b.[1(a)] We do *not* identify $V_{b\,(\neq a)}$ with the "Wigner-approximation" potential used by Anderson[1] and Bullett[7]—instead, we define it formally as some as yet unspecified local approximation to the unique ground-state potential implicit in density-functional theory.[8] For widely separated atoms, $V_{b\,(\neq a)}$ can probably be identified with the "Wigner-approximation" potential, but, in general, this will not be the case. Thus the one-electron-like Schrödinger equation (3) is that appropriate to density-functional theory rather than to, say, Hartree-Fock theory. Using Eq. (1) we may rewrite Eq. (2) as

$$H\,|\,\phi_a\rangle=\epsilon_a\,|\,\phi_a\rangle+\sum_{b\,(\neq a)}|\,\phi_b\rangle\langle\phi_b\,|\,V_b\,|\,\phi_a\rangle \ ,$$

or

$$H\,|\,\phi_a\rangle=\sum_b |\,\phi_b\rangle D_{ba} \ ,$$

where [1(b)]

$$D_{aa}=\epsilon_0+\sum_{b\,(\neq a)}(\langle\phi_a\,|\,V_b\,|\,\phi_a\rangle-S_{ab}\langle\phi_b\,|\,V_b\,|\,\phi_a\rangle) \tag{4a}$$

and

$$D_{ba}=\langle\phi_b\,|\,V_b\,|\,\phi_a\rangle \ . \tag{4b}$$

In these expressions, $S_{ab}=\langle\phi_a\,|\,\phi_b\rangle$ is the overlap and $\epsilon_0=\langle\phi_a\,|\,(T+V_a)\,|\,\phi_a\rangle$ is the energy of the atomic subsystem. It can be shown that, in the LO basis, $\hat{D}=\hat{S}^{-1}\hat{H}$ and is generally nonhermitian.[1(b)] However, for a regular structure (a structure in which every atom "sees" the same environment) $\hat{S}$ and $\hat{H}$ commute so that $\hat{D}$ is Hermitian; moreover, it follows that $\hat{D}=\hat{S}^{-1/2}\hat{H}\hat{S}^{-1/2}$, i.e., that

$$\langle\phi_a\,|\,D\,|\,\phi_b\rangle=\langle\phi_a^w\,|\,H\,|\,\phi_b^w\rangle \ ,$$

where $\hat{\phi}^w=\hat{\phi}\hat{S}^{-1/2}$ is an orthogonal (Wannier) basis. This allows us to write, for regular structures,

$$H=\sum_{m,n}D_{mn}\,|\,\phi_m^w\rangle\langle\phi_n^w\,| \ ,$$

or, using Eqs. (4a) and (4b),

$$H=\sum_m\left[\epsilon_0+\sum_{k\,(\neq m)}V_R(r_{km})\right]|\,\phi_m^w\rangle\langle\phi_m^w\,| +\sum_m\sum_{k\,(\neq m)}V_A(r_{km})\,|\,\phi_m^w\rangle\langle\phi_k^w\,| \ . \tag{5}$$

In this last equation we have introduced the additional approximation of replacing the LO basis with the unperturbed atomic orbital basis ϕ_a^0, so that ϵ_0 here is the energy of the isolated atom, while

$$V_R(r_{km})=\langle\phi_m^0\,|\,V_k\,|\,\phi_m^0\rangle-S_{km}^0\langle\phi_k^0\,|\,V_k\,|\,\phi_m^0\rangle$$

and

$$V_A(r_{km})=\langle\phi_k^0\,|\,V_k\,|\,\phi_m^0\rangle$$

are, respectively, repulsive and attractive two-center interactions which, for a given species, depend only on the pair separation $r_{km}\equiv|\,\mathbf{r}_k-\mathbf{r}_m\,|$. This atomic-orbital approximation, which is crucial to the ensuing analysis, requires further comment. First, within this approximation, D is Hermitian for any structure so that Eq. (5) is not limited to regular structures. Second, it is implicit in Eq. (2) that, because of the pseudopotential perturbation,

$$V_{\text{ps}} \equiv \sum_{b\,(\neq a)} (V_b - |\phi_b\rangle\langle\phi_b|V_b) ,$$

the ϕ_a are necessarily different from the unperturbed atomic orbitals in a way that depends on the overall environment.[1] Thus, depending on the importance of V_{ps}, the two-center form of Eq. (5) may actually be a relatively crude approximation and hardly seems justified as a foundation for a general discussion of binding energy. Before attempting to resolve this problem, we now compound the difficulty by introducing an apparently unrelated approximation for the binding energy, namely that

$$E_B \equiv E_T - N\epsilon_0 = \sum_i n_i(\epsilon_i - \epsilon_0) + U_{es} , \tag{6}$$

where E_B is the binding energy, N is the total number of atoms, $n_i = 0$ or 1 is the occupancy of ψ_i, and the ϵ_i are the one-electron eigenvalues given by Eq. (3). The quantity U_{es} is a short-range repulsive term due to the ion-ion interaction minus the *interatomic* part of the electron-electron interaction given by the superposition of *free-atom* electron densities.[9] The intra-atomic part of this latter interaction has been absorbed into ϵ_0. Thus, U_{es} may be represented as a sum of pair interactions (e.g., Born-Mayer repulsions) which themselves depend on the pair separation, but *not* on the molecular environment. This interatomic repulsion may therefore be effectively combined with the diagonal renormalization term V_R in Eq. (5). The use of Eq. (6) relies on certain cancellations that are fairly well understood in the context of local-density-functional theory using either[10] the virial equation or[11] the Hellman-Feynman theorem. This requires, however, that, in the calculation of the change in $\sum_i n_i\epsilon_i$ corresponding to some displacement of atoms, one must ignore changes in the one-electron potential that arise due to relaxation in the self-consistent field induced by the displacement.[11,12] The Hamiltonian (5) is based on unperturbed atomic orbitals; strictly speaking, its matrix elements should be iterated to self-consistency according to Eq. (2); but given that we are interested in E_B, we assume that the effect on $\sum_i n_i\epsilon_i$ of "renormalization" of ϕ_a^0 due to the molecular environment is offset by changes in the double-counting terms.[13] Thus, expression (6) for the binding energy ignores renormalization of the atomic basis and uses the unperturbed atomic orbitals as the LO basis. In this view, the two-center approximation in Eq. (5) and the use of Eq. (6) for E_B are complementary assumptions whose justification is to be found within density-functional theory. Clearly, the above arguments for the validity of Eqs. (5) and (6) need to be sharpened and formalized. In the absence of a compelling formal demonstration, we will be content to show in a later section that these equations provide a simple means for accurately predicting H_n and Li_n potential hypersurfaces. In any event, Eqs. (5) and (6) constitute a useful zeroth-order framework for a general discussion of chemical binding, and in the following section we develop a general analysis of E_B based on an exponential parametrization of V_A and V_R.

III. EXPONENTIAL PARAMETRIZATION AND UNIVERSALITY

The expansion of ψ_i in terms of the ϕ_m^w is

$$\psi_i = \sum_m C_{mi}\,|\phi_m^w\rangle , \tag{7}$$

where the C_{mi} are determined by the secular equation appropriate to the Wannier basis. Equation (3) gives

$$\sum_i n_i\epsilon_i = \sum_i n_i\langle\psi_i|H|\psi_i\rangle ,$$

from which it follows that by substituting Eq. (7) for ψ_i and Eq. (5) for H and then using the definition of E_B given by Eq. (6), we obtain

$$E_B = \sum_m \left[q_m \sum_{k\,(\neq m)} V_R(r_{km}) + \sum_{k\,(\neq m)} p_{km} V_A(r_{km}) \right] . \tag{8}$$

In this expression, V_R has been redefined to include U_{es}, while

$$q_m \equiv \sum_i n_i\,|C_{mi}|^2 \tag{9a}$$

is the net electron density on ϕ_m^w (q_m is thus mostly on site m) and

$$p_{km} \equiv \sum_i n_i C_{ki}^* C_{mi} \tag{9b}$$

is the bond order[14] associated primarily with sites k and m. Expressions (9a) and (9b) assume that the spectrum of H is discrete; generalization to the case of a continuous spectrum is straightforward using the appropriate Green's-function formalism[15] and will not be described here. The distinction between the mth site and mth Wannier orbital, made immediately below Eqs. (9a) and (9b), is important because of possible confusion concerning the question of charge self-consistency. Since we do not specify the ϕ_m^w in detail, an accurate description of charge distribution is not possible in the present scheme; however, the consequences of self-consistency for E_B are implicitly included, as is discussed below Eq. (6).

We particularize Eq. (8) to the case of a regular structure and obtain

$$\mathscr{E}_B \equiv E_B/N = \sum_k Z_k(qV_{Rk} + p_k V_{Ak}) , \tag{10a}$$

where $\mathscr{E}_B$ is the binding energy per atom, Z_k is the number of atoms in the kth-neighbor (coordination) shell, p_k is the bond order between the reference atom and an atom in the kth shell relative to the reference atom, and q is the number of valence electrons per atom. Although the present scheme is limited to species with overall charge neutrality (i.e., there are no long-range electrostatic forces), we retain q as a variable in order to approximate multivalent atoms by a degenerate s orbital. For a given structure the p_k will, in general, depend on the relative sizes of the V_{Aj} and on q; i.e.,

$$p_k = p_k(v_2, \ldots, v_j, \ldots; q) ,$$

where $v_j \equiv V_{Aj}/V_{A1}$. If one is interested in the variation of $\mathscr{E}_B$ with interatomic separation r (i.e., uniform expan-

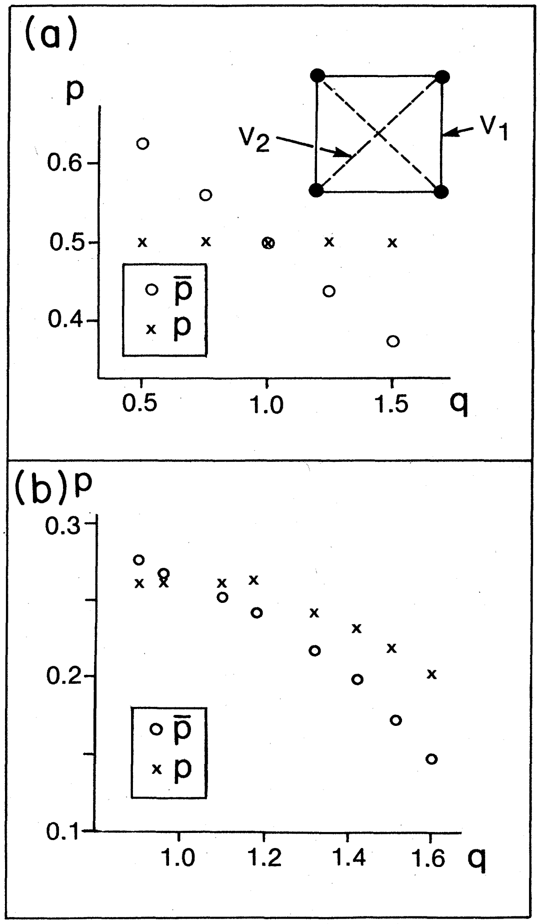

FIG. 1. Plot of $p=p_1(0,0,\ldots;q)$ and $\bar{p}=Z^{-1}(\sum_k Z_k v_k p_k)$ vs the number of valence electrons per atom q. (a) Four-atom square with $v_2=0.5$. (b) bcc lattice with $v_2=0.5$, $v_3=0.06$, and $v_k=0$ for $k>3$.

sion), it must be recognized that the v_j (and *a fortiori* the p_k) will, in general, depend on r. Thus, strictly speaking, Eq. (10a) does not allow straightforward analysis of the potential hypersurface with respect to even the simplest coordinate (uniform expansion). However, if $V_A(r)$ is sufficiently short ranged, then one may reasonably ignore all but V_{A1} in the secular equation. This case requires only the nearest-neighbor bond order, p_1, which is now independent of r, thus greatly simplifying Eq. (10a):

$$\mathscr{E}_B \cong Z_1(qV_{R1}+p_1V_{A1}) \;. \tag{10b}$$

The repulsive pair interaction has been cut off at the first shell because V_R, which is the Pauli force overlap repulsion plus interatomic electrostatic repulsion, always falls off much faster than V_A. Because this latter approximation affects only the diagonal matrix elements of the secular equation, which are all alike in a regular homopolar structure, it cannot change the molecular-orbital coefficients of Eq. (7) and thus has no effect on q and p. One might well object that the nearest-neighbor approximation is, for the most part, limited to transition metals in a close-packed structure (for a bcc lattice, $r_2/r_1=2/\sqrt{3}\cong 1.15$), and that Eq. (10b) cannot have general significance. Thus, it is known that the band structure of bcc transition metals is very poorly represented by this approximation.[16] For the simple metals, where the interatomic matrix elements extend well beyond the first shell, the nearest-neighbor approximation fails utterly in a band-structure determination. But the binding energy is given by an integration over the band structure, so that its detailed shape may well be unimportant.[17] We have some numerical evidence that, to a very good approximation,

$$\sum_k Z_k v_k p_k \cong Zp \;, \tag{11}$$

where $Z=Z_1$ is the number of nearest-neighbor atoms and we use p to represent the first-shell bond order in a nearest-neighbor approximation [thus, we distinguish $p=p_1(0,0,\ldots;q)$ from $p_1=p_1(v_2,\ldots,v_j,\ldots;q)$]. The evidence is shown in Fig. 1, which is a plot of p and $\bar{p}\equiv Z^{-1}(\sum_k Z_k v_k p_k)$ versus q for a four-atom square structure with $v_2=0.5$ and for a bcc lattice with $v_2=0.5$ and $v_3=0.06$. In the latter case the p_k were determined by the recursion method.[18] The approximation given by Eq. (11) is seen to be nearly exact at $q=1$ (half-filled band) and to become progressively worse as q departs from this value. Thus, Eq. (11) is our primary justification for using the nearest-neighbor approximation in the determination of $\mathscr{E}_B$ for arbitrary regular structures. We assume that the effect of more distant interactions on $\mathscr{E}_B$ is minor and can be treated as a small perturbation, even when the V_{Ak} decay slowly. Thus, we write

$$\mathscr{E}_b(G,q;r)\cong Z(G)[qV_R(r)+p(G,q)V_A(r)] \;, \tag{12}$$

where the shell subscript has been suppressed with the understanding that all quantities (apart from q) refer to the first shell, and where the symbol G represents the primary interaction topology—it is the map of nearest-neighbor interactions or "bonds." We use this terminology because, in general, there is not a one-to-one correspondence between interaction topology and structure—it is only in the nearest-neighbor approximation that such a correspondence exists. Equation (12) provides the basis for a very general study of the dependence of $\mathscr{E}_B$ on structure and atomistic properties. To this end, we choose the following functional representation for the pair interactions:

$$V_R=A\exp(-\theta r) \;, \tag{13a}$$

$$V_A=-B\exp(-\lambda r) \;, \tag{13b}$$

where A, B, θ, and λ are positive definite quantities characteristic of a given atomic species. This choice is based in part on analytical convenience, but also on the physical grounds that atomic orbitals decay exponentially with r. Moreover, diatomic potentials have frequently been represented in this manner[19] [thus, the Morse potential is a special case of Eqs. (13) having $\theta=2\lambda$]; so too have pair interactions in transition metals[20] and semiconductors.[21] Finally, the pair potentials derived in Sec. V from *ab initio* configuration-interaction calculations of hydrogen and lithium species show a nearly exponential decay. One can generalize Eqs. (13) somewhat by allowing A and B to vary with r. So long as this variation satisfies the criteria $|d\ln A/dr| \ll \theta$ and $|d\ln B/dr| \ll \lambda$ in the relatively small range of interest $[r(\text{diatomic}) \le r \le r(\text{metallic})]$, the ensuing analysis based on the use of Eqs. (13) goes through essentially unchanged. The binding energy for a given structure is simply

$$\mathscr{E}_B(r) = Z[Aq\exp(-\theta r) - Bp\exp(-\lambda r)] \ . \tag{14}$$

This expression has the appearance of a central pair potential, but it is important to recognize that while p is unaffected by a uniform expansion, it is quite sensitive to structural variations at constant volume. Hence, except for diatomic species, Eq. (14) is a *noncentral* potential. This aspect will not be of concern in the present article; our interest is primarily in the variation of $\mathscr{E}_B$ with respect to r at constant G (i.e., fixed topology). The equilibrium interatomic separation r_e is determined from $(d\mathscr{E}_B/dr)=0$, which gives

$$\theta Aq\exp(-\theta r_e) = \lambda Bp\exp(-\lambda r_e) \ , \tag{15}$$

from which

$$r_e = (\theta-\lambda)^{-1}\ln(ASq/Bp) \tag{16}$$

and

$$D_e = ZAq(S-1)\exp(-\theta r_e) \ , \tag{17a}$$

or, equivalently [using Eq. (15)],

$$D_e = ZBpS^{-1}(S-1)\exp(-\lambda r_e) \ , \tag{17b}$$

where

$$S = \theta/\lambda \ , \tag{17c}$$

and $D_e \equiv -\mathscr{E}_B(r_e)$ is the cohesive energy. Note that Eq. (16) is identical in form to Pauling's empirical expression relating bond length to bond order;[22] this latter expression has been widely used in discussions of bond lengths in both metallic[23] and covalent solids.[24] In order to scale $\mathscr{E}_B$ according to the prescription of Ferrante *et al.* (Ref. 2, hereafter referred to as FSR), we also need the second derivative of $\mathscr{E}_B$, which is

$$(d^2\mathscr{E}_B/dr^2)_{r=r_e} = Z[\theta^2 Aq\exp(-\theta r_e) - \lambda^2 Bp\exp(-\lambda r_e)] \ . \tag{18}$$

The scaling procedure is

$$\mathscr{E}_B^*(x) = \mathscr{E}_B(r)/D_e \ , \tag{19a}$$

with

$$x \equiv (r-r_e)/l \tag{19b}$$

and

$$l^2 \equiv D_e/(d^2\mathscr{E}_B/dr^2)_{r=r_e} \ . \tag{19c}$$

Dividing the first term on the right-hand side of Eq. (14) by Eq. (17a) and the second term by Eq. (17b) gives the result

$$\mathscr{E}_B^* = \{\exp[-\theta(r-r_e)] - S\exp[-\lambda(r-r_e)]\}/(S-1) \ . \tag{20}$$

Following the same procedure for Eq. (18) gives, via Eq. (19c), $l^{-2} = (\theta^2 - \lambda^2 S)/(S-1)$, or since $S=\theta/\lambda$,

$$l = (\theta\lambda)^{-1/2} \ . \tag{21}$$

Combining Eqs. (19b) and (21) gives $r - r_e = x/(\theta\lambda)^{1/2}$, which, when substituted into Eq. (20), gives

$$\mathscr{E}_B^*(x;S) = [\exp(-S^{1/2}x) - S\exp(-S^{-1/2}x)]/(S-1) \ . \tag{22}$$

While the scaling has eliminated most of the variables, Eq. (22) is not a universal function unless the ratio S is itself universal, which is almost certainly not true. Nonetheless, we will show that Eq. (22) is consistent with the observation[2] of an apparent universality in that on the one hand, it is sensibly independent of S for $|x| < 1$, while, on the other hand, the structural preference of a given atomic species depends *exponentially* on S. The criterion used for structural preference is simply the optimization of D_e (the role of entropy is ignored here). The universality aspect of Eq. (22) is illustrated by Fig. 2, which may be compared with Fig. 1 of FSR (Ref. 2) by noting that the H_2^+ results shown there are very well fitted[25] by a Morse potential, which has $S=2$.

But is the range of S values shown in Fig. 2 consistent with the structural diversity emphasized by FSR?[2] To address this question we will analyze the structure dependence of D_e. For this purpose we introduce a new scaling procedure that retains the structural variables:

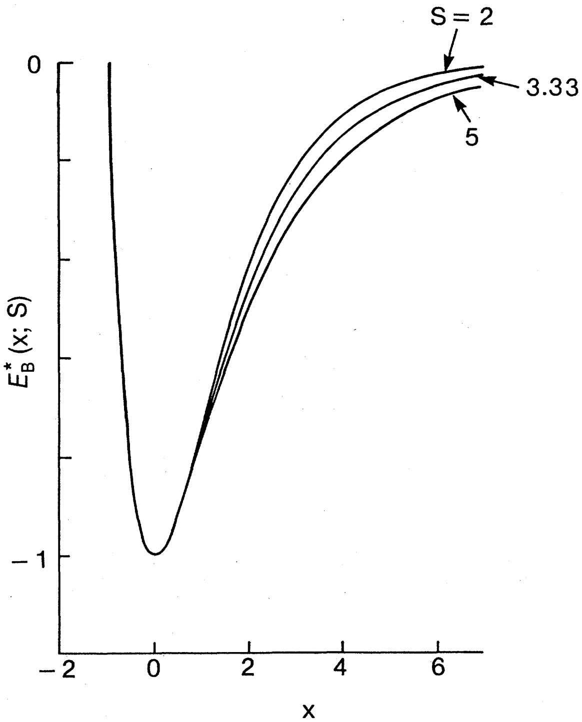

FIG. 2. Plot of the scaled binding energy [Eq. (22)] vs $x = (r-r_e)/l$ for different values of $S=\theta/\lambda$. The $S=2$ curve is the Morse potential. Note that the curves are nearly indistinguishable for $x \lesssim 1$.

$$\mathscr{E}^*_B(x)=\mathscr{E}_B(r)/qD_{e2}\ , \qquad (23a)$$

$$x=(r-r_{e2})/l\ , \qquad (23b)$$

where

$$D_{e2}=A(S-1)\exp(-\theta r_{e2})=BS^{-1}(S-1)\exp(-\lambda r_{e2}) \qquad (24)$$

is the cohesive energy of the diatomic species ($Z=q=p=1$),

$$r_{e2}=(\theta-\lambda)^{-1}\ln(AS/B) \qquad (25)$$

is the diatomic equilibrium separation, and l is given by Eq. (21). This scaling gives

$$\mathscr{E}^*_B(x)=Z[\exp(-S^{1/2}x) -(p/q)S\exp(-S^{-1/2}x)]/(S-1)\ , \qquad (26)$$

with

$$x_e=S^{1/2}(1-S)^{-1}\ln(p/q) \qquad (27)$$

given by $(d\mathscr{E}^*_B/dx)=0$, and

$$D^*_e=Z(p/q)^{v}\ , \qquad (28)$$

where

$$v\equiv S/(S-1)\ . \qquad (29)$$

The exponential role of S in the determination of cohesive energy is apparent from Eqs. (28) and (29). A critical value of S may be defined as that value at which, with $q=1$, the cohesive energies of the fcc lattice and the diatomic species as given by Eq. (28) are the same. For an fcc lattice (coordination number $Z=12$), the recursion method[18] gives $p(\text{fcc})=0.206$ when $q=1$. Using Eq. (28), the definition of the critical value can be expressed as

$$12(0.206)^{v_c}=1\ ,$$

which gives, by Eq. (29), $S_c\cong 2.7$. This value must not be taken too seriously, as it excludes the role of intermolecular repulsions for the diatomic species, which will depend on the density; however, it indicates a region where metallic and molecular bonding should be of comparable importance. This result demonstrates that the range of S values shown in Fig. 2 is consistent with structural diversity.

A more detailed analysis of cohesive energy requires a determination of the bond order p. Because p depends only on G (primary interaction topology) and q, it may be obtained from the secular equation by assigning a value of zero to all diagonal matrix elements and a value of negative unity to all matrix elements between nearest neighbors—this is simply Hückel molecular-orbital (HMO) theory.[14,26] From Eq. (12), with $V_R=0$ and $V_A=-1$, one obtains $p(G,q)=-Z^{-1}\mathscr{E}^{\text{HMO}}_B$, or using Eqs. (6) and (10a), ignoring the term U_{es},

$$p(G,q)=-(NZ)^{-1}\sum_i n_i\epsilon_i^{\text{HMO}}\ , \qquad (30a)$$

where $\epsilon_i^{\text{HMO}}\equiv\epsilon_i-\epsilon_0$ in the HMO limit of the secular equation, described above. The q dependence of p enters through the Fermi level, below which $n_i=1$ and above which $n_i=0$. Going beyond Eq. (30a) requires a general analysis of bond order as a function of G. A good starting point is to isolate the important components of a regular structure or topology, which include the following: (i) number of nearest neighbors, Z; (ii) size of primitive loops; (iii) total number of atoms, N. Anticipating the coordination number Z as the dominant topological variable, we propose to find a reference system such that

$$p(G,q)=p_{\text{ref}}(Z,q)+\Delta p\ , \qquad (30b)$$

where the bond order of the reference depends only on Z and q, and where $\Delta p \ll p$. To eliminate the role of loops and of N, which has to do with finiteness, we seek an infinite reference system having no loops. Bethe lattices[27] are regular infinite structures completely characterized by Z, so we take them as reference structures. The bond order of a Bethe lattice is

$$p_\beta(Z,q)=-Z^{-1}\int_{-\infty}^{\epsilon_F}\epsilon n_\beta(Z,\epsilon)d\epsilon\ , \qquad (31)$$

which is the generalization of Eq. (30a) to a continuum. The Fermi level ϵ_F is determined by

$$q=\int_{-\infty}^{\epsilon_F} n_\beta(Z,\epsilon)d\epsilon\ , \qquad (32)$$

where

$$\pi n_\beta(Z,\epsilon)=\Theta(4(Z-1)-\epsilon^2)Z[4(Z-1)-\epsilon^2]^{1/2}/(Z^2-\epsilon^2) \qquad (33)$$

is the density of states per site (both spins included) for a Bethe lattice[27] (Θ is the unit step function). Equations (32) and (33) do not lead to an analytical solution of Eq. (31) for arbitrary Z and q, but a large-Z expansion of Eq. (33) gives

$$\lim_{Z\to\infty} n_\beta(Z,\epsilon)\cong\Theta(4Z-\epsilon^2)(4Z-\epsilon^2)^{1/2}/\pi Z\ . \qquad (34)$$

Equations (31) and (32) are analytic in this limit and, to leading order in the coordination number Z, we obtain the result

$$p_\beta(Z,q)\cong\alpha(q)Z^{-1/2}\ , \qquad (35)$$

where

$$3\pi\alpha(q)=8[1-u^2-u^4/3+O(u^6)]^{3/2}\ ,$$

with $u\equiv\pi(q-1)/4$. Figure 3 compares exact solutions of Eq. (31) with Eq. (35) at corresponding values of Z and q. It is seen that the large-Z approximation is within a few percent of the exact Bethe-lattice result over the entire range of coordination number Z at $q=1$ [Fig. 3(a)] and over much of the range of q at $Z=2$ [Fig. 3(b)]. Thus, we take Eq. (35) for the Z dependence of the bond order of an arbitrary regular topology G and write

$$p(G,q)=\alpha(q)Z^{-1/2}+\Delta p\ . \qquad (36)$$

In almost every case where p is known exactly (or nearly so),[14,28] we find that $|\Delta p|/p\lesssim 0.15$, so that the Z-dependent reference term is indeed dominant. This is true even when $Z=1$ (diatomic species), for which the Bethe

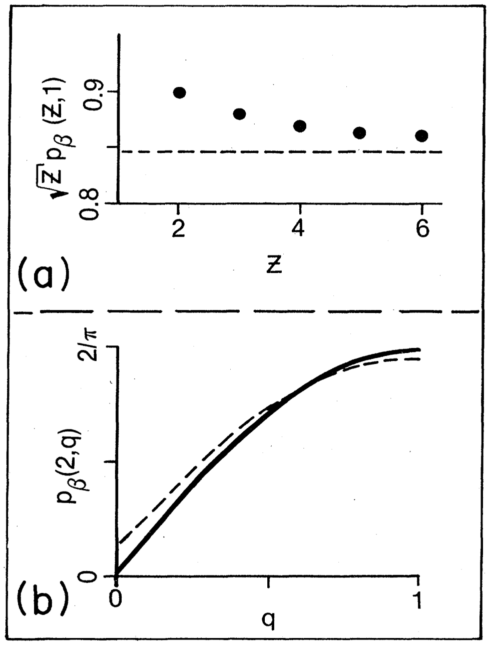

FIG. 3. Comparison of the Bethe-lattice bond order given by Eq. (31) with the approximate result, Eq. (35), represented by the dashed curve. (a) $\sqrt{Z}p_\beta$ vs coordination number Z with $q=1$. (b) p_β vs q with $Z=2$.

lattice is undefined. Certain pathological regular topologies, with $N \geq 3$ atoms and $N-1$ bonds per atom (e.g., triangle, tetrahedron), have large negative values of Δp, but such topologies are rarely of interest. Substituting Eq. (36) into Eq. (28) gives

$$q^{v}D_e^{*}=\alpha^{v}Z^{(2-v)/2}+v\alpha^{v-1}Z^{(3-v)/2}\Delta p+O((\Delta p/p_\beta)^2) , \tag{37}$$

where v is defined in Eq. (29). The role of coordination number Z in the optimization of the cohesive energy for a given species is now clear: (i) when $S \gg 2$ ($v \cong 1$), which is the hard-core limit, Eq. (37) gives, in leading order,

$$D_e^{*} \propto Z^{1/2} , \tag{38}$$

and close packing is strongly preferred; (ii) when $S<2$ ($v>2$), Eq. (37) gives

$$D_e^{*} \propto Z^{-\delta}, \quad \delta > 0 \tag{39}$$

which favors the diatomic species ($Z=1$) when $q=1$, and otherwise is highly unfavorable for close packing. As we showed earlier, an approximate value separating these two regimes is $S_c \cong 2.7$.

The exponential parametrization described in this section has for some time now been used to study transition metals. The first such application appears to have been that of Ducastelle[20] in a study of elastic constants. More recently, this approach has been used in studies of transition adatoms on transition metals,[29] small transition-metal clusters,[30] atomic relaxation near transition-metal surfaces,[31] elastic properties of metallic glasses,[32] and effects of chemisorbed oxygen on nickel surface vibrations.[33] In all these studies, the d-orbital anisotropy is averaged out and the d band is effectively represented by a degenerate s band. As a further approximation, the continued-fraction expansion of the site-diagonal Green's function is terminated at the second moment. The local density of states obtained from this latter approximation is,[34] with energy in units of the nearest-neighbor hopping energy, the same as Eq. (34). Thus, the second-moment approximation, which has been reasonably successful in the study of transition-metal energetics, is seen to be identical with the large-Z approximation for the Bethe lattice. From this, together with Eq. (37), we may conclude that the second-moment approximation is most useful when $S \gg 2$ and that the importance of higher moments increases rapidly as S approaches the value 2. (Thus, when $S=3$, $D_e^{*} \propto Z^{1/4}$, and when $S=2.5$, $D_e^{*} \propto Z^{1/6}$ to leading order.) Empirically determined values of S for transition metals[29] fall in the range $3 \leq S \leq 5$, which is consistent with the use of the second-moment approximation and with the observed preference for close packing [see Eq. (38)]. Lannoo[21] has applied the exponential parametrization in a study of force constants in covalent systems, assuming degenerate sp^3 hybrid orbitals, and has obtained the empirical values $S(\mathrm{C})=1.4$, $S(\mathrm{Si})=1.9$, and $S(\mathrm{Ge})=2.0$. These values are consistent both with the observed preference for covalent bonding in the diamond lattice (note that the hybrid orbitals are paired off so that $Z=1$ as far as orbital interactions are concerned) and with the increasing tendency toward metallization in going (down column IV) from C to Sn. We would argue that in these systems the preference for directed bonds, as opposed to a nearly isotropic close-packed arrangement of atoms, follows from the optimization of D_e^{*} in Eq. (37). The covalent-bond topology corresponds to the minimum value of Z (and to a very favorable value of Δp), consistent with Eq. (39).

In addition to these previous determinations of the parameter S for transition metals and covalent systems, we have obtained values for neutral ($q=1$) simple and noble metals using Eqs. (16), (21), and (25). These equations may be combined to give

$$S^{1/2}-S^{-1/2}=-[l/(r_e-r_{e2})]\ln p , \tag{40}$$

where l, r_e, and p refer to a known metallic structure. Thus, if r_{e2} is known, S may be readily determined. An independent determination is provided by the following relation:[35]

$$\left[\frac{\partial B}{\partial P}\right]_T=1-(r_{\mathrm{WS}e}/3l)\mathscr{E}^{*'''}(0)/\mathscr{E}^{*''}(0) , \tag{41}$$

where the left-hand side is the zero-temperature derivative of the bulk modulus with respect to pressure, $r_{\mathrm{WS}e}$ is the equilibrium Wigner-Seitz radius, and $\mathscr{E}^{*''}$ and $\mathscr{E}^{*'''}$ are the second and third derivatives of the "universal" binding-energy function with respect to x. In the present theory, the latter function is given by Eq. (22), from which $\mathscr{E}^{*''}(0)=1$ and $\mathscr{E}^{*'''}(0)=-(S+1)/\sqrt{S}$, so that Eq. (41) gives

$$S^{1/2}+S^{-1/2}=3l\left[\left[\frac{\partial B}{\partial P}\right]_T-1\right]r_{\mathrm{WS}e} \ . \tag{42}$$

A difficulty with using Eq. (40) is that the exponential parametrization is applied over a very wide range of interatomic separations, so that the corresponding value of S is an average over that range. Moreover, S depends on bond order, which is a calculated quantity. By contrast, Eq. (42) refers to a much smaller range and S is given exclusively in terms of measurable quantities; a problem here, however, is the very strong dependence of S on $(\partial B/\partial P)_T$, a quantity that is difficult to measure accurately.[36] (A 5% uncertainty in this quantity gives a 30% uncertainty in S.) Table I shows values of S obtained from Eqs. (40) and (42) for some alkali and noble metals and for Al. The present theory implicitly treats the noble-metal d shell as part of the atomic core, which is probably inadequate;[37] thus, the significance of the corresponding values of S shown in Table I is somewhat uncertain. Apart from Cs and Li, the agreement between the two determinations of S is reasonable; moreover, taking $S_c \cong 2.7$, the values shown are generally consistent with the metallic state. In Sec. V we obtain $V_R(r)$ and $V_A(r)$ directly from first-principles binding-energy calculations for hydrogen and lithium species. These have been fitted, over the range $r(\text{diatomic}) \le r \le r(\text{metallic})$, with simple exponentials as in Eq. (13) with the result that $S(\mathrm{H}) \cong 1.6$ and $S(\mathrm{Li}) \cong 8.0$. The value for H is consistent with its strong preference for covalent bonding, while the value for Li agrees well with that obtained from Eq. (40) and shown in Table I.

The preceding discussion has shown that for simple metals, transition metals, and some covalent species, empirically determined values of the parameter S—which measures the steepness of the repulsive pair interaction to that of the attractive pair interaction—fall approximately in the range $2 \lesssim S \lesssim 5$. This range is sufficiently small to give an apparent binding-energy universality, as shown in Fig. 2. Moreover, the value of S for a given species is generally consistent with the observed bonding preference (metallic or covalent); this becomes apparent when the cohesive energy given by Eq. (37) is optimized with respect to the coordination number Z.

IV. MOLECULAR REGIME

It is interesting that when $S \cong 2$ $(v \cong 2)$ the leading term in Eq. (37) is nearly a constant, independent of Z. Structural preference is thus determined in this intermediate regime by the quantity Δp, which depends on nonlocal features of the topology such as total number of atoms N and size of elementary loops. We have previously found[28] a striking correlation between this quantity and ground-state properties, including reaction paths, of a great variety of molecular species in both regular and nonregular topologies. In the latter case, we generalized Eq. (30b) to

$$\mathscr{E}_B^{\mathrm{HMO}}(G,q)=\mathscr{E}_{\mathrm{ref}}(Z,q)+\Delta \ , \tag{43}$$

where

$$N\mathscr{E}_{\mathrm{ref}}=-\sum_m Z_m p_\beta(Z_m,q) \tag{44}$$

summed over all sites m, with $p_\beta(Z_m,q)$ calculated for the mth site as if it belonged to a Bethe lattice characterized by Z_m (this is very similar to the second-moment method with nearest-neighbor bonds assumed to be identical), and where

$$\Delta \equiv N^{-1}\sum_i n_i \epsilon_i^{\mathrm{HMO}}-\mathscr{E}_{\mathrm{ref}} \tag{45}$$

is the HMO generalization of $Z\,\Delta p$ [see Eqs. (30)]. Use of approximation (35) in Eq. (44) does not change Δ noticeably. The correlation referred to above is simply that

TABLE I. Values of the parameter $S=\theta/\lambda$ for some noble and simple metals, from Eqs. (40) and (42).

M	$l/r_{\mathrm{WS}e}$ [a]	$(\partial B/\partial P)_T$ [a]	$l/\Delta r_e$ [b]	p_m [e]	S [f]	S [g]
Cu	0.192	5.23	0.79[c]	0.206	3.68	3.13
Ag	0.168	5.86	0.69[c]	0.206	3.76	2.73
Au	0.148	5.90	0.59[c]	0.206	2.31	2.35
Al	0.212	4.72			3.29	
Li	0.323	3.5	1.62[d]	0.26	3.59	6.3
Na	0.270	3.90	0.97[d]	0.26	3.22	3.27
K	0.254	4.07	1.05[d]	0.26	3.15	3.63
Rb	0.239	4.07		0.26	2.46	
Cs	0.240	4.0	0.96	0.26	2.2	3.27

[a] From compilation of Ref. 35.

[b] $\Delta r_e \equiv r_e - r_{e2}$, where r_e is taken from Ref. 51.

[c] r_{e2} taken from R. C. Baetzold [J. Chem. Phys. 55, 4355 (1971)].

[d] r_{e2} taken from Ref. 53.

[e] Calculated by the recursion method of Ref. 18.

[f] From Eq. (42).

[g] From Eq. (40).

$\Delta < 0$ is associated with a stable species or with thermally allowed reaction paths, while $\Delta > 0$ corresponds to unstable or highly reactive species or to thermally forbidden reaction paths. Consider, for example, the n-atom string and ring topologies, referred to as S_n and R_n, respectively, and Möbius rings M_n (a ring in which one of the off-diagonal matrix elements has its sign reversed). Figure 4 shows Δ versus n for certain $q=1$ and $q \neq 1$ species of S_n, R_n, and M_n. (Thus, S_5^+ has $q=0.8$.) The most striking feature in Fig. 4 is the appearance of distinct families. Within each family, the magnitude of Δ falls off approximately as n^{-2}. The cyclic topologies (M_n, R_n) have magnitudes of Δ appreciably larger than their acyclic counterparts (S_n). Consider now the correspondence of Δ to the ground-state character of sp^2-hybridized systems [in these systems, the sp^2-orbitals are relegated to a "molecular core," while the π electrons (one per atom) are treated as valence electrons]: (i) For $-\Delta > 0$ the family headed by S_2 corresponds to stable polyene molecules and molecule ions. The R_n members of the family headed by M_3^-, R_3^+ correspond to annulenes satisfying the Hückel $4n+2$ rule relating electron number to aromatic stabilization.[4(b)] (ii) For $-\Delta < 0$ the family headed by $S_2^\pm$ corresponds to highly reactive polyene radicals and radical ions. Finally, the family of cyclics headed by M_3^+, R_3^- corresponds to species, called antiaromatic diradicals, satisfying the Hückel $4n$ rule. No such species has ever been isolated in a form that retains the indicated topology. The correspondence of Δ to chemical behavior is not limited to sp^2-hybridized systems. Thus, apart from M_3^-, the leading members of the families with $-\Delta > 0$ have achieved special status: S_2 corresponds to the almost universal two-center—two-electron $(2c\text{-}2e)$ bond, while S_3^+ and R_3^+ correspond to the $(3c\text{-}2e)$ bond types so important in boron chemistry.[38] The theory of pericyclic reactions[4(b)] also demonstrates the correspondence of Δ to chemical behavior: Cyclic species with $-\Delta > 0$ correspond to saddle points of low-energy (thermally allowed) chemical reactions, while cyclics with $-\Delta < 0$ correspond to high-energy intermediates in ground-state forbidden reactions. The observable consequences of these topological "selection rules" are well documented.[4]

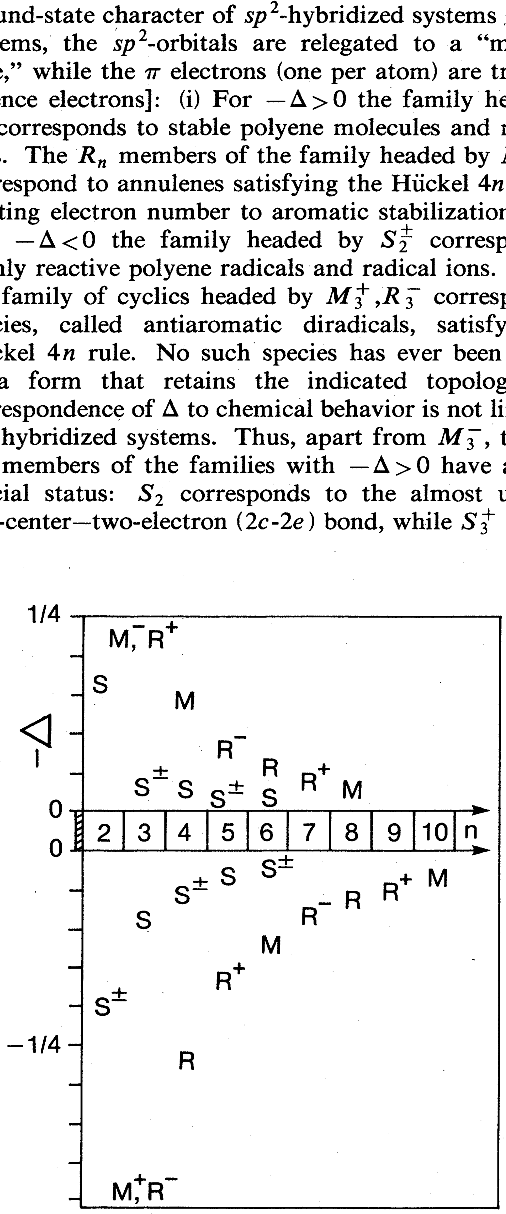

FIG. 4. Plot of Δ, the contribution of nonlocal topological features to the HMO energy, vs number of strongly coupled atoms n for string (S_n), ring (R_n), and Möbius-ring (M_n) primary interaction topologies.

Generally speaking, when $q=1$, the quantity Δ (or for regular structures, Δp) militates against interaction topologies with small (three- and four-atom) loops and favors the covalent bond (S_2) and six-atom loops (e.g., benzene). However, Δ—considered either as a function of N for fixed G and q, as a function of q for fixed N and G, or as a function of G for fixed N and q— is a highly oscillatory quantity. For example, when q changes from $q=1$ to $q=\frac{2}{3}$, $\Delta(R_3)$ changes from a relatively large positive value to a relatively large negative value. Or when $q=1$ and G is a string topology, $\Delta < 0$ for N even and $\Delta > 0$ for N odd. As a final example, when $q=1$ and $N=4$, Δ has a very large positive value for a tetrahedron, a small negative value for a string, and a relatively large negative value for a Möbius ring. The fact that the quantity Δ correlates so strongly with observed ground-state properties of molecular species implies that the leading term in Eq. (37) is nearly constant, and therefore relatively unimportant. Thus, in the present theory, molecular behavior is characterized by $S \cong 2$. Strictly speaking, the quantity Δ is a measure of relative stability rather than absolute stability. Statements about absolute stability require an analysis of the dynamical matrix of the species in question. Thus, it is not at all obvious that the quantity Δ should correlate with chemical stability. Apparently, $\Delta > 0$ implies that the dynamical matrix has at least one negative eigenvalue. Harmonic analysis of Eq. (7) is possible,[39] but is beyond the scope of the present study.

Chemical theory has recognized for some time that the topology of valence-orbital interactions is a fundamental determinant of structural stability and reaction pathways,[40] so we place no claim to originality in that regard. However, the present theory has demonstrated the role of interaction topology in a total-energy context and has accounted for both metallic and covalent bonding extremes in terms of a single parameter S. This parameter is essentially a measure of the steepness of $V_R(r)$ relative to that of $V_A(r)$.

V. QUANTITATIVE DETERMINATION OF V_A AND V_R

In Sec. II it was argued that Eqs. (5) and (6), when used together in the determination of binding energy, had fundamental justification within chemical pseudopotential theory and, more generally, within local-density-functional theory. In this section we present empirical evidence in support of these arguments.

The great virtue of Eqs. (5) and (6), when combined in the form of Eq. (8), lies in the fact that knowledge of V_A and V_R for a pair of monovalent atoms M allows a straightforward determination of any point on the E_B hypersurface of an arbitrary M_n species. The hypersurface analysis of Sec. III is based on a parametrized version of V_A and V_R which allows for a very general application, but which is no more than an approximate representation of V_A and V_R for any particular system. In this section we give a quantitative application in which known potential-energy curves for H_2 and symmetric linear H_3 are used as inputs to determine V_A and V_R. These are then used, through Eq. (8), to predict hypersurface points for various H_3, H_4, and H_{14} species, that are already known to a high degree of accuracy from total-energy calculations based on the configuration-interaction (CI) technique. We also present results for some Li species. Toward this end note that Eq. (8) gives, with p_{km} and q_m obtained by direct solution of the secular equation in the Hückel limit,

$$E_B(M_2;r)=2[V_R(M;r)+V_A(M;r)] , \tag{46a}$$

$$E_B(\text{sl-}M_3;r)\cong 4[V_R(M;r)+V_A(M;r)/\sqrt{2}] , \tag{46b}$$

$$E_B(e\text{-}M_3;r)=6[V_R(M;r)+V_A(M;r)/2] , \tag{46c}$$

where r is the nearest-neighbor separation and M_2, sl-M_3, and e-M_3 are, respectively, the diatomic, symmetric linear triatomic, and equilateral triatomic species. [Expression (46b) is an approximate solution, but where we have used it the corrections are less than a percent of E_B and will be ignored.] Knowledge of $E_B(r)$ for any two of these species determines $V_R(r)$ and $V_A(r)$. To obtain V_A and V_R for hydrogen pairs, we used Truhlar and Horowitz's functional representation[41] of Siegbahn and Liu's CI calculations[42] for sl-H_3, together with Liu's functional representation of the H_2 potential[43] calculated by Kolos and Wolniewicz.[44] These calculations (and their functional representations) are claimed to be within 1 kcal/mol of the true adiabatic potentials.[42] Values of V_A and V_R for hydrogen pairs, derived from Eqs. (46a) and (46b) using the above CI calculations, are presented in Table II. Their functional representations are

$$(8-\sqrt{32})V_A=E_B(H_2;r)-{}^3E(r)-2\,{}^3E(2r)$$

and

$$2V_R=E_B(H_2)-2V_A ,$$

where $E_B(H_2)+2\epsilon_0(H)$ is given by Eq. (1) and Table III of Ref. 43, and ${}^3E(r)$ is given by Eq. (10) and Table I of Ref. 41. It is encouraging that V_R and V_A are indeed repulsive and attractive, with magnitudes that decrease monotonically (and almost exponentially—see Sec. III) toward the zero of energy (separated atoms), but the real test of the basic assumptions contained in Eq. (8) is whether or not V_A and V_R can be used to predict E_B for other configurations. Total-energy calculations exist for a variety of additional hydrogenic species, including nonlinear H_3 structures,[42] symmetric linear H_4 (sl-H_4),[45] rectangular H_4 (r-H_4),[46] square H_4 (s-H_4),[46(b),47] and symmetrical cyclic monatomic H_{14} (c-H_{14}).[48] These calculations are based on truncated CI expansions and are thus upper-bound approximations to the true ground-state potentials, with an accuracy that generally decreases with increasing electron number.

Using the pair interactions of Table II, Eq. (8) gives predicted values of E_B for nonlinear H_3 which, when compared with the corresponding CI calculations[42] at 56 distinct points, show a root-mean-square deviation of 0.27 eV, which is about 6% of the maximum value of $-E_B(H_3)$. The individual deviations are nearly constant for a given bond angle and increase as the system changes from sl-H_3 toward e-H_3. Generally speaking, the predicted hypersurface for nonlinear H_3 lies below and is parallel with the CI hypersurface.[42] Table III gives a representative sampling of the comparison for both linear and nonlinear H_3. Figure 5 compares predicted values of $E_B(\text{sl-}H_4;r)$ with the CI values of Bender and Schaefer,[45] who estimate that their calculated values are about 0.54 eV above the true surface. The predicted values are from exact solution of the secular equation, but are very well approximated by $E_B(\text{sl-}H_4)\cong 6V_R(H)+4.47V_A(H)$. Table IV compares predicted interaction energies of r-H_4 with various CI results. Interaction energy is defined as $E_I\equiv E_T(r\text{-}H_4)-2E_T(H_2;r_e)$, where the calculations of $E_T(H_2)$ and $E_T(r\text{-}H_4)$ use the same atomic basis so that correlation errors tend to cancel. (Clearly, E_I is *not* a variational quantity.) The predicted values in this case are given by

$$E_I=4[V_R(r_1)+V_R(r_2)+V_R(d)+V_A(r_1)]-2D_e(H_2) ,$$

TABLE II. Hydrogen pair interactions obtained from CI calculations of $E_B(H_2)$ (Ref. 44) and $E_B(\text{sl-}H_3)$ (Ref. 42) using $(4-\sqrt{8})V_A(H)=2E_B(H_2)-E_B(\text{sl-}H_3)$ and $2V_R(H)=E_B(H_2)-2V_A(H)$.

r (Å)[a]	V_A (eV)[a]	V_R (eV)[a]	r (Å)	V_A (eV)	V_R (eV)
0.741	−5.093	2.730	1.799	−0.587	0.104
0.846	−4.234	1.952	1.904	−0.448	0.074
0.952	−3.506	1.407	2.010	−0.339	0.053
1.058	−2.889	1.020	2.116	−0.254	0.037
1.164	−2.366	0.742	2.222	−0.189	0.026
1.270	−1.922	0.539	2.328	−0.140	0.019
1.375	−1.548	0.391	2.433	−0.103	0.013
1.481	−1.235	0.283	2.539	−0.075	0.009
1.587	−0.974	0.203	2.645	−0.055	0.006
1.693	−0.760	0.146	2.751	−0.040	0.005

[a] The conversion from a.u. used 1 hartree = 27.2 eV and 1 bohr = 0.529 Å. The increment in r is 0.2 bohr = 0.1058 Å.

TABLE III. Comparison of predicted values with CI calculations (Ref. 42) of $E_B(H_3)$.

ϕ (deg)[a]	r_1 (Å)[a]	r_2 (Å)[a]	E_B (eV)[b]	ΔE (eV)[c]
180	1.22	1.22	−3.524	−0.025[d]
180	2.05	0.76	−4.640	0.036
150	0.94	0.94	−4.279	−0.056
150	1.41	1.41	−2.709	−0.085
120	1.49	0.86	−4.333	−0.052
120	1.80	1.59	−1.662	−0.041
90	1.32	1.32	−2.961	−0.333
90	1.31	0.77	−4.410	−0.392
60	1.32	1.32	−2.425	−0.834

[a] ϕ is the angle between the two sides of length r_1 and r_2.

[b] Predicted value based on Eqs. (1) and (2).

[c] $\Delta E \equiv E_B(\text{predicted}) - E_B(\text{CI})$.

[d] Nonzero because Eq. (3b) is approximate.

TABLE IV. Comparison of predicted values with CI calculations of $E_I = E_T(H_4) - 2E_T(H_2;r_e)$ for rectangular and square H_4.

r_1 (Å)	r_2 (Å)	E_I (eV)[a]	E_I (eV)
0.741	1.587	1.36	1.12[b]
0.794	1.164	4.54	4.08[c]
1.164	1.375	4.98	5.44[c]
1.164	1.587	4.06	4.46[c]
1.270	1.270	6.50[d]	
1.307	1.307		6.17[d]

[a] This work.

[b] Reference 46(a).

[c] Reference 46(b).

[d] Optimized value. CI result is from Ref. 47.

where $D_e(H_2) = 4.733$ eV, while r_1 and r_2 are the short and long sides of the rectangle and d is the diagonal distance. Table IV also compares optimized values of E_I for s-H_4 for which

$$E_B(s\text{-}H_4;r) = 8V_R(r) + 4V_R(\sqrt{2}r) + 4V_A(r) .$$

The final comparison is for optimized c-H_{14}, where we predict $-E_B = 22.3$ eV at $r_e = 1.03$ Å compared to the CI results: (i) $-E_B = 19.6$ eV corrected to 25.3 eV at $r_e = 0.98$ Å[48(a)] and (ii) $-E_B = 18.5$ eV corrected to (24.2±3) eV at $r_e = 1.00$ Å.[48(b)]

The above results for hydrogenic species strongly support the basic assumptions; in particular, the degree of transferrability of V_A and V_R is remarkable. Additional support is provided by comparison with existing calculations for Li_2, Li_3, and Li_4. $V_R(\text{Li})$ and $V_A(\text{Li})$ were isolated using Eqs. (46a) and (46c) in conjunction with Gerber and Schumacher's[49] functional representation of their CI calculations for Li_2 and Li_3. It must be emphasized that these Li calculations are considerably less accurate than the H_2 and H_3 calculations. Moreover, even though there are no calculations for e-Li_3, most of the calculated points are in the neighborhood of e-Li_3, while only three points lie in the neighborhood of sl-Li_3. The resulting values of V_R and V_A derived from Eqs. (46a) and (46c) are thus based on an extrapolation of existing CI calculations of limited accuracy, and hence will probably be noticeably altered when more accurate CI results for e-Li_3 or sl-Li_3 become available. These values are functionally represented by

$$3V_A(\text{Li};r) = -[1 - \tanh G(Q_a,0,0)]F(Q_a,0,0)$$

and

$$V_R(\text{Li}) = 0.5E_B(Li_2) - V_A(\text{Li}) ,$$

where $Q_a = (r - r_0)/\sqrt{3}$, with $r_0 = 2.978$ Å, while G, F, and $E_B(Li_2)$ are specified by Eqs. (4)–(9) of Ref. 49. The Li_3 hypersurface based on these pair interactions is considerably flatter than the CI hypersurface, but shows the same general trends. The maximum deviation occurs for sl-Li_3 and is about 15% of the corresponding value of $E_B(\text{sl-}Li_3)$. We predict the following optimized values for square (s-) Li_4 and tetrahedral (t-) Li_4: $-E_B(s\text{-}Li_4) = 1.88$ eV at $r_e = 2.91$ Å and $-E_B(t\text{-}Li_4) = 1.77$ eV at $r_e = 3.02$ Å. These may be compared with the CI results of Beckman *et al.*:[50] $-E_B(s\text{-}Li_4) = 1.85$ eV at $r_e = 2.95$ Å and $-E_B(t\text{-}Li_4) = 1.71$ eV at $r_e = 2.98$ Å. Using the recursion method[18] with a nearest-neighbor approximation for V_A and V_R, the predicted optimized values of E_B and r_e for bcc Li are $-E_B(r_e) = 0.89$ eV/atom and $r_e = 3.11$ Å. The corresponding experimental values for bcc Li are[51] 1.66 eV/atom and 3.023 Å. The agreement here is poor, but the bcc prediction is very sensitive to errors in V_A and V_R.

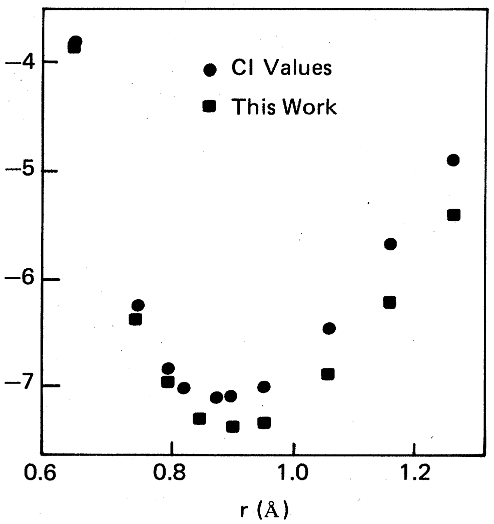

FIG. 5. Comparison of predicted values of E_B with CI calculations of Bender and Schaefer (Ref. 45) for symmetric linear H_4.

It would be interesting to determine V_R and V_A from a simpler total-energy scheme, such as the local-spin-density (LSD) approximation.[52] In fact, we have obtained preliminary results based on the LSD calculations of Martins *et al.*[53] for Li_3, K_3, and Na_3. Reasonably well-behaved pair interactions are obtained only if the LSD binding energies are shifted by small constant terms; presumably, the effect of this is to correct for small correlation errors in the LSD calculations. The LSD pair interactions obtained for Li are similar to those given by the CI calculations,[49] and give $S(\mathrm{Li}) \cong 8.5$ over the relevant range of interatomic separations, which is very close to the value obtained from fitting the CI pair interactions. The LSD pair interactions for K, when fitted by simple exponentials over the relevant range, give $S(\mathrm{K}) \cong 3$, which compares well with the values obtained from Eqs. (40) and (42) (see Table I). Finally, the LSD calculations for Na give $S(\mathrm{Na}) \cong 2.5$, but in contrast with what was found for Li and K, $S(\mathrm{Na})$ decreases significantly with increasing interatomic separation.

The results of this section strongly support the notion contained in Eq. (8) that two-center atomic pair interactions determine the overall shape of the potential hypersurface, at least for H_n and Li_n species. The deviation shown in Table III for e-H_3 indicates that three-center terms cannot always be ignored, but the overall success of the two-center approximation is quite good. With the LSD method it should be possible to obtain useful approximations of V_A and V_R for larger, more complex atoms than those considered in this section.

VI. CONCLUDING REMARKS

A key assumption underlying the major results of this article is that use of unperturbed atomic orbitals as the LO basis in CP theory gives accurate binding energies. Without this assumption, the two-center matrix elements depend not only on the pair separation for a given atomic species but also on the total molecular environment through the self-consistent adjustment of the LO basis, according to the pseudopotential equation (2). To that extent, any conclusions based on the assumption of transferrable pair interactions are likely to be misleading. But the success of that assumption in the determination of binding energies for Li_n and especially for H_n species, described in Sec. V, implies that the net contribution associated with the self-consistent adjustment of the LO basis is quite small. It was suggested in Sec. II that this is due to cancellations which can be understood in the context of local-density-functional theory. However, that assertion remains to be demonstrated.

Perhaps the major accomplishment of our work is the development of a relatively simple general model of bonding energetics. The model successfully mimics both metallic and molecular bonding behavior; in the latter case it provides a method for predicting stability and reaction pathways. For homopolar species, the key atomistic pair parameter is the ratio (S) of the steepness of the repulsive pair interaction relative to that of the attractive interaction. It was shown in Sec. III that this parameter determines structural preference. The scaled binding energy given by Eq. (26) suggests that S may also determine variations in the dynamical matrix for different species in a given structure. Harmonic analysis of the scaled binding energy, using the approach of Finnis *et al.*,[54] would be a useful extension of the present study. The model should also be extended to include heteropolar species.

ACKNOWLEDGMENTS

The author is grateful to the Chemical Science Division, Office of Energy Research, U. S. Department of Energy, for supporting this work. The Mound Facility is operated by Monsanto Research Corporation for the U. S. Department of Energy under Contract No. DE-AC04-76DP00053.

---

[1] (a) P. W. Anderson, Phys. Rev. Lett. **21**, 13 (1968); Phys. Rev. **181**, 25 (1969); (b) J. D. Weeks, P. W. Anderson, and A. G. H. Davidson, J. Chem. Phys. **58**, 1388 (1973).

[2] J. Ferrante, J. R. Smith, and J. H. Rose, Phys. Rev. Lett. **50**, 1385 (1983); J. H. Rose, J. R. Smith, and J. Ferrante, Phys. Rev. B **28**, 1835 (1983).

[3] V. Heine and D. Weaire, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 250.

[4] (a) R. Hoffman and R. B. Woodward, Science **167**, 825 (1970); (b) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry* (Harper and Row, New York, 1976).

[5] J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys. **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.* **44**, 3289 (1966); D. P. Santry and G. A. Segal, *ibid.* **47**, 158 (1967).

[6] R. Hoffman, J. Chem. Phys. **39**, 1397 (1963).

[7] D. W. Bullett, J. Phys. C **8**, 2695 (1975).

[8] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[9] V. Heine, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 1; L. M. Mattheiss, Phys. Rev. **133**, A1399 (1964).

[10] D. G. Pettifor, J. Chem. Phys. **69**, 2930 (1978).

[11] K.-M. Ho, C.-L. Fu, and B. N. Harmon, Phys. Rev. B **28**, 6687 (1983).

[12] e.g., see V. Heine, in *Solid State Physics*, Ref. 9, pp. 114ff.

[13] J. van der Rest, F. Gautier, and F. Brouers, J. Phys. F **5**, 2283 (1975).

[14] A. Streitwieser, Jr., *Molecular Orbital Theory* (Wiley, New York, 1961).

[15] E. N. Economou, *Green's Functions in Quantum Physics* (Springer, Berlin, 1979).

[16] W. A. Harrison, *The Physics of the Chemical Bond* (Freeman, San Francisco, 1980), p. 485.

[17] M. Derenne, F. Brouers, and J. van der Rest, Phys. Rev. B **26**, 1048 (1982).

[18] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972).

[19] Y. P. Varshni, Rev. Mod. Phys. **29**, 664 (1957).

[20] F. Ducastelle, J. Phys. (Paris) **31**, 1055 (1970).

[21] M. Lannoo, J. Phys. (Paris) **40**, 461 (1979).

[22] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960).

[23] A. Simon, Angew. Chem. Int. Ed. Eng. **22**, 95 (1983).

[24] W. H. Zachariasen, J. Less-Common Met. **62**, 1 (1978).

[25] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.

[26] E. Hückel, Z. Phys. **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

[27] E. N. Economou, *Green's Functions in Quantum Physics*, Ref. 15, p. 89.

[28] G. C. Abell, Chem. Phys. Lett. **101**, 452 (1983); bond order may be obtained for regular topologies by using Eq. (30) of the present article.

[29] M. C. Desjonquères and D. Spanjaard, J. Phys. C **15**, 4007 (1982); C. M. Sayers, *ibid.* **12**, 4333 (1979).

[30] D. Tománek, S. Mukherjee, and K. H. Bennemann, Phys. Rev. B **28**, 665 (1983); M. B. Gordon, F. Cyrot-Lackmann, and M. C. Desjonquères, Surf. Sci. **80**, 159 (1979).

[31] G. Allan, Surf. Sci. **89**, 142 (1979); K. Masuda, Phys. Rev. B **26**, 5968 (1982).

[32] F. Cyrot-Lackmann, Phys. Rev. B **22**, 2744 (1980).

[33] J. W. M. Frenkon, J. F. van der Veen, and G. Allen, Phys. Rev. Lett. **51**, 1876 (1983); G. Allan and J. Lopez, Surf. Sci. **95**, 214 (1980).

[34] C. M. Sayers, J. Phys. F **9**, 123 (1979).

[35] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).

[36] S. N. Biswas, P. Van't Klooster, and N. J. Trappeniers, Physica (Utrecht) **103B**, 235 (1981).

[37] J. A. Moriarty, Phys. Rev. B **26**, 1754 (1982).

[38] W. N. Lipscomb, *Boron Hydrides* (Benjamin, New York, 1963).

[39] T. Kakitani, Prog. Theor. Phys. **51**, 656 (1974).

[40] R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc. **87**, 395 (1965); **87**, 2046 (1965); **87**, 2511 (1965).

[41] D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **68**, 2466 (1978); **71**, 1514(E) (1979).

[42] P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978).

[43] B. Liu, J. Chem. Phys. **58**, 1925 (1973).

[44] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

[45] C. F. Bender and H. F. Schaefer III, J. Chem. Phys. **57**, 217 (1972).

[46] (a) F. H. Ree and C. F. Bender, Phys. Rev. Lett. **32**, 85 (1974); (b) J. D. Goddard and I. G. Csizmadia, Chem. Phys. Lett. **64**, 219 (1979).

[47] M. Rubinstein and I. Shavitt, J. Chem. Phys. **51**, 2014 (1969).

[48] (a) M. Seel, P. S. Bagus, and J. Ladik, J. Chem. Phys. **77**, 3123 (1982); (b) D. H. Kislow, J. M. McKelvey, C. F. Bender, and H. F. Schaeffer III, Phys. Rev. Lett. **32**, 933 (1974).

[49] W. H. Gerber and E. Schumacher, J. Chem. Phys. **69**, 1692 (1978). The functional representation of $E_B(\mathrm{Li}_3)$ includes a correction to give agreement with the experimental dissociation energy of Li_2; the corresponding hypersurface is therefore *not* a variational upper bound.

[50] H.-O. Beckmann, J. Koutecký, and V. Bonacić-Koutecký, J. Chem. Phys. **73**, 5182 (1980).

[51] C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971).

[52] O. Gunnarsson, J. Harris, and R. O. Jones, J. Chem. Phys. **67**, 3970 (1977).

[53] J. L. Martins, R. Car, and J. Buttet, J. Chem. Phys. **78**, 5646 (1983).

[54] M. W. Finnis, K. L. Lear, and D. G. Pettifor, Phys. Rev. Lett. **52**, 291 (1984).