

NEW CONCEPTS OF BONDING IN NONPERIODIC METALLIC SYSTEMS*

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Using the generalized valence bond method, we have examined numerous Li atom clusters (up to 13 atoms). Our conclusion is that the optimum metallic bonding involves *singly-occupied* orbitals localized interstitially, e.g., in bond midpoints, triangular hollows, and tetrahedra. For Li_7^+ , the low energy isomers have local five-fold symmetry axes (as in an icosahedron) but lead to low overall symmetry. The guiding principle is that the optimum structures (denoted OPTET) optimize the number of tetrahedral hollows while keeping the sharing of vertices below a threshold. These OPTET structures are significantly more stable than the high-symmetry icosahedral, hcp-like and fcc-like clusters. Speculations are given on the relevance of these results for amorphous metallic systems.

1. INTRODUCTION

The valence bond principles of structural chemistry¹, based on spin pairing of hybridized atomic orbitals localized on various atoms, lead to excellent rationalization of the geometries and bonding for nonmetallic molecules and solids; e.g., Si and Ge are tetrahedral in both crystalline and amorphous phases, Se and Te lead to helical chains for both crystalline and amorphous solids, As_4 is tetrahedral, etc. These simple valence bond ideas of nonmetallic systems have been confirmed by *ab initio* generalized valence bond (GVB) calculations^{2,3} that lead directly to localized spin-paired atomic orbitals corresponding to various bond pairs. Valence bond principles have also proven valuable in understanding defects and surface reconstruction in nonmetallic solids such as the Si vacancy⁴ and the GaAs surface⁵.

This paper presents the qualitative principles of our new model of metallic bonding. These principles have led to the prediction of several low-energy (OPTET) isomers that (coincidentally?) have local five-fold symmetry axes and cannot lead to bulk solids with long range (periodic) order. GVB calculations confirm that these OPTET clusters are lower in energy than high symmetry icosahedral, fcc-like and hcp-like clusters. These principles may lead to new rationalizations and predictions concerning the geometric and electronic structures of defects and interfaces for metallic systems. In particular, these

*This work was partially supported by a grant from the National Science Foundation (No. DMR82-15650).

[†]Contribution No. 7221

principles may lead to new insights regarding how local structure and alloying may control formation of amorphous metallic systems.

2. RESULTS

In order to lay the foundation for developing these chemical concepts, we have used GVB approaches to examine the bonding in various one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) clusters of Li atoms⁶. In all cases, we discuss the many-electron states in which the electrons are all spin-paired (singlet). The electronic structures of the various clusters are given in terms of the singly-occupied GVB orbitals.

2.1 One-Dimensional Systems

The optimum GVB wavefunction of $\text{Li}_{(1D)}$ has a *singly-occupied orbital localized at each bond midpoint*. Typical bond orbitals are shown in Figure 1 for the Li_8 chain at an internuclear separation of $R=3.1 \text{ \AA}$ [near the

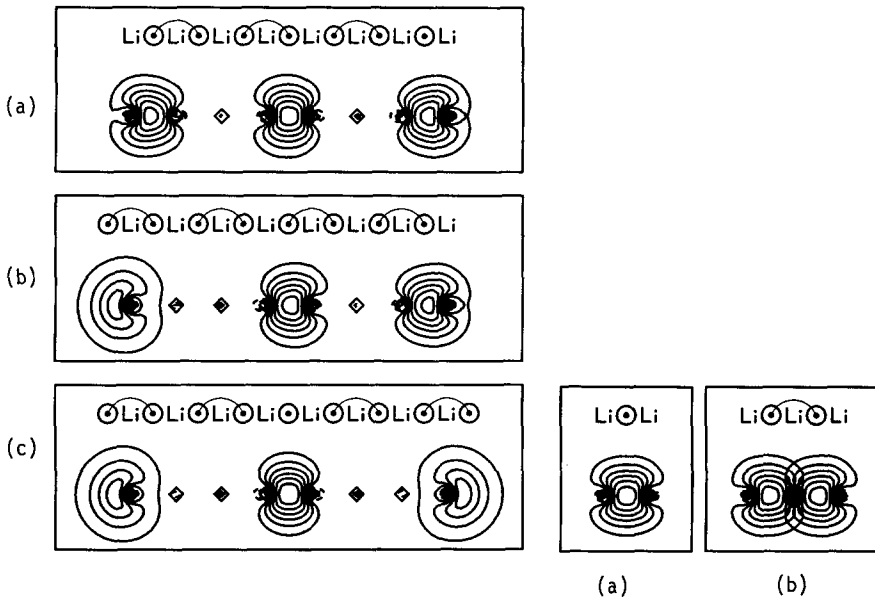


FIGURE 1
The GVB description of the (a) Li_8^+ , (b) Li_8 and (c) Li_8 chain clusters. The schematic diagrams show all of the singly-occupied GVB orbitals with the spin coupling for the principal resonance structure represented by connected dots. In each case orbitals at the middle and both ends are shown in contour plots. Contour spacings are at 0.015 a.u.

FIGURE 2
Contour orbital plots for the GVB orbitals of (a) Li_2^+ and (b) linear Li_3^+ . Contour spacings are at 0.015 a.u. $R = 3.1 \text{ \AA}$.

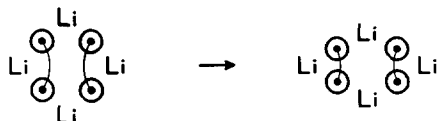
equilibrium bond distance of $\text{Li}_{(1D)}$, $R_e = 3.14 \text{ \AA}^6$]. For Li_8^+ , Li_8 and Li_8^- , there are seven bond-localized orbitals (each very similar to the bond orbitals of Li_2^+ and linear Li_3^+ as shown in Figure 2) and zero, one or two "surface" orbitals. In the ground state, adjacent (singly-occupied) bond orbitals are spin-paired [leading to two equivalent resonance structures]; however, the overlap between paired bond orbitals is small (≈ 0.34 ; normal two-electron bonds have large overlaps, 0.7 to 0.8), so that even the higher spin states involve similar orbitals and strong bonding. Even the maximum spin state (e.g., triplet ($S=1$) for Li_3^+ or $S=3.5$ for Li_8^+) is bound strongly with respect to the separated atoms limit! Indeed the calculations lead to a vanishing singlet-triplet gap for $\text{Li}_{(1D)}^6$.

2.2 Two-Dimensional Systems

Starting with the H_4 and Li_4 symmetric ring clusters (and considering just one of the two equivalent resonance structures), the optimum geometric distortion is expected to increase overlap of adjacent spin-paired orbitals while decreasing overlap of adjacent *nonpaired* orbitals. In square H_4 , the orbitals are atom-centered, leading to an unstable rectangular distortion



with no chemical bonding between the two H_2 fragments. For square Li_4 , the orbitals are bond-centered, leading to a rhombic distortion



which is stable due to the one-electron bonding. Such distortions lower the energy of one resonance structure (and raise the energy of the other resonance structure) reducing the resonance energy substantially. Nevertheless, square Li_4 ($\theta = 90^\circ$) distorts to a rhombus ($\theta_{\text{opt}} = 57.3^\circ$)⁷. Similarly, hexagonal Li_6 ($\theta = 120^\circ$) distorts to a trigonal hexagon ($\theta_{\text{opt}} = 69.3^\circ$)⁷. Potential energy curves for these distortions are shown in Figure 3. Allowing similar distortions for $\text{Li}_{(1D)}$ results in a zig-zag chain (alternating 70° and 180° angles). The optimum planar structures for Li_4 and Li_6 both resemble planar close-packed clusters. As shown in Figure 4, the optimum orbitals for Li_6 are quite similar to those in $\text{Li}_{(1D)}$.

Examining larger two-dimensional close-packed arrays of Li atoms, we find the general result that interior regions tend to have orbitals localized at

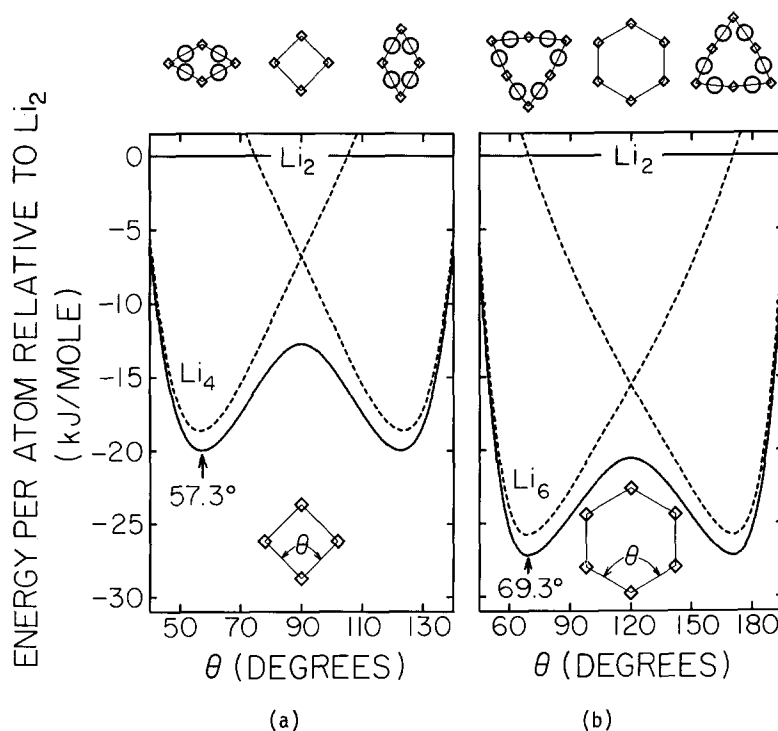


FIGURE 3.

Potential Energy curves for geometric distortions of the (a) Li_4 and (b) Li_6 clusters. Dashed curves represent the separate resonance structures, while solid lines show the energy including all possible resonance structures. The energy per atom is given relative to Li_2 (at equilibrium). Diagrams above the plots show the cluster geometries at various angles (θ) where squares mark the atomic positions and circles mark the positions of the orbitals.

the centers of equilateral triangles while surface (edge) regions have orbitals localized at bond midpoints. Extrapolating to the infinite two-dimensional (close-packed) system $[\text{Li}_{(2D)}]$ leads to the description in Figure 5a, where alternate pairs of triangular hollows have spin-paired singly-occupied orbitals and adjacent such pairs are empty⁹.

This GVB wavefunction for $\text{Li}_{(2D)}$ would lead to metallic character. Half of the triangular hollows are empty, providing means for conduction. The structure shown in Figure 5a is only one of an infinite number of low-lying resonance structures, another of which is illustrated in Figure 5b.

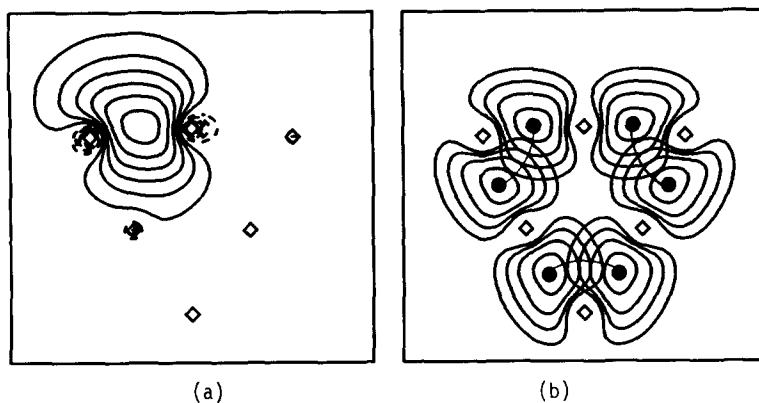


FIGURE 4

GVB orbitals for the planar Li_6 cluster. Solid and dashed lines show positive and negative orbital amplitudes, respectively. (a) Shows one of the six equivalent singly-occupied orbitals (0.015 contour spacings). (b) Shows contours ≥ 0.045 a.u. for all six orbitals. The atomic positions are marked by squares. The connected dots represent the dominant spin pairing.

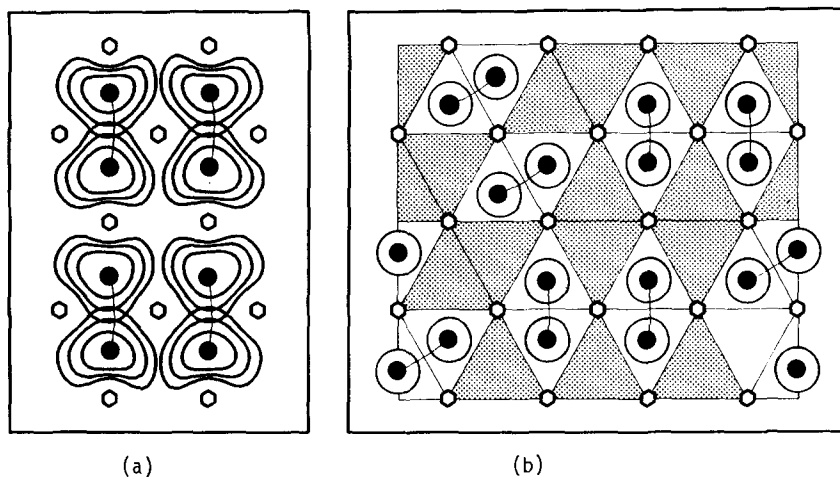


FIGURE 5

The GVB description of $\text{Li}_{(2D)}$. (a) Shows contours ≥ 0.060 a.u. for the planar Li_{12}^{4+} cluster. (b) shows an alternate resonance structure for $\text{Li}_{(2D)}$ where connected circles represent the singly-occupied orbitals and shaded rhombi represent empty hollows.

2.3 Three-Dimensional Systems

First we consider several high symmetry clusters consisting of one central (bulk) atom and 12 surface atoms: the icosahedral (I_h), face-centered cubic (fcc) and hexagonal close-packed (hcp) Li_{13}^+ clusters. In each case we find that the orbitals prefer to be singly-occupied and centered at tetrahedral interstices.

Of these three clusters, I_h is lowest in energy. The I_h ground state involves orbitals localized at the centers of 12 of the 20 triangular faces and spin-paired in rhombi (0.63 overlap) just as for the bulk atoms of $Li_{(2D)}$.

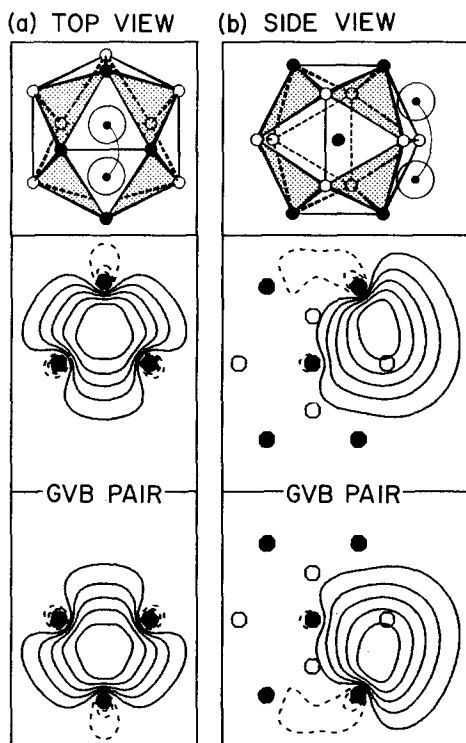


FIGURE 6

GVB orbitals for one of the five equivalent primary resonance structures of icosahedral Li_{13}^+ . The atoms in the plane are marked by solid circles while atoms above and below the plane are marked by open circles. Connected dots represent the spin-paired electrons. Only one of the six equivalent bond pairs is shown (0.015 a.u. contour increments). Solid and dashed lines show positive and negative orbital amplitudes, respectively. Shaded triangular faces do not contain orbitals.

The four triangular faces adjacent to a spin-paired rhombus are empty (to avoid repulsive interactions between unpaired orbitals), as indicated in Figure 6.

The fcc and hcp clusters lie 0.26 and 0.57 eV higher than I_h , respectively. Both fcc and hcp have only eight tetrahedra, thus, some of the tetrahedra have two spin-paired orbitals (on opposite faces). For fcc, the tetrahedra are edge-sharing, and all twelve electrons are accommodated by the tetrahedra. For hcp, six of the tetrahedra share one face with an adjacent tetrahedron, and ten of the twelve electrons are accommodated by tetrahedra, leaving two remaining electrons that end up along surface sites (bond midpoints) that do *not* border a tetrahedron.

In order to compare the energies of planar and 3D clusters, we solved for the ground state electronic structures of several close-packed planar Li_{13}^+ clusters. The lowest energy planar structure (Figure 7) is 0.18 eV *lower* than I_h ! Apparently, with such small clusters, surface effects are quite large so that planar clusters (which lead to an increased number of internal sites) are quite competitive.

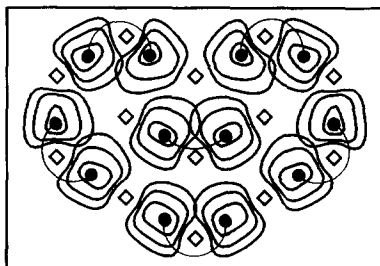


FIGURE 7

GVB orbitals for planar close-packed Li_{13}^+ . Only contours ≥ 0.060 a.u. are shown (0.015 a.u. spacings). Squares mark the atomic positions. The dominant spin pairing is shown by the connected dots.

The above results suggest that the *optimum structures* of small clusters should *maximize* the number of *tetrahedra* and the number of *internal sites*. The icosahedron has the maximum number of tetrahedra (20), however, these 20 tetrahedra all share the *same* central bulk atom. Guided by a set of rules (See Section 3) based on the I_h , fcc and hcp results, we considered alternative arrangements of 13 atoms that maximize the number of tetrahedra while minimizing the number of tetrahedra shared by any given atom. This led us to predict

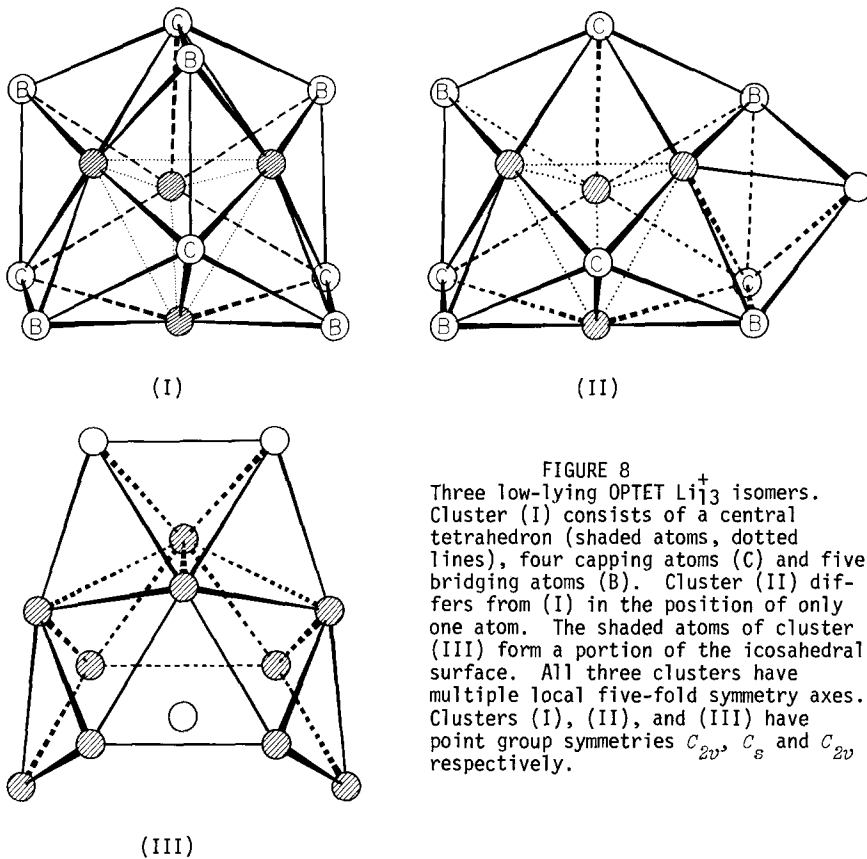


FIGURE 8
Three low-lying OPTET Li_{13}^+ isomers. Cluster (I) consists of a central tetrahedron (shaded atoms, dotted lines), four capping atoms (C) and five bridging atoms (B). Cluster (II) differs from (I) in the position of only one atom. The shaded atoms of cluster (III) form a portion of the icosahedral surface. All three clusters have multiple local five-fold symmetry axes. Clusters (I), (II), and (III) have point group symmetries C_{2v} , C_s and C_{2v} respectively.

several new Li_{13}^+ clusters [(I), (II) and (III) as shown in Figure 8], each lower in energy than I_h . The best, the tetra-capped penta-bridged tetrahedron (I), has an energy 0.58 lower than the icosahedron! The Li_{13}^+ isomers in Figure 8 all contain 15 tetrahedra. Structures (I) and (II) differ in the location of the thirteenth atom. In (I), the thirteenth atom bridges the central tetrahedron and in (II) the thirteenth atom occupies an exterior position. Cluster (III) was obtained by removing two adjacent atoms from the surface of the icosahedron and capping surface sites on the opposite side of the cluster (allowing all of the atoms to relax). Clusters (II) and (III) are only 0.08 and 0.19 eV higher than (I) respectively.

In summary, the relative energies of the various Li_{13}^+ clusters are: (I), 0.00 eV; (II), 0.08 eV; (III), 0.19 eV; planar, 0.40 eV; I_h , 0.58 eV; fcc, 0.84 eV; hcp, 1.15 eV.

3. DISCUSSION

Based on these results for the high symmetry Li_{13}^+ clusters we derived the following rules for 3D structures⁶.

- α) Orbitals (each with one electron) are localized in different tetrahedral hollows where possible.
- β) If necessary, two orbitals may be placed in one tetrahedron (localized on opposite faces or edges) but they must be spin-paired.
- γ) However, no more than three electrons may be distributed between a pair of *edge-shared* tetrahedra.
- δ) No more than two electrons may be distributed between a pair of *face-shared* tetrahedra, and these must be spin-paired (singlet).
- ε) Additional electrons must be in surface orbitals at edge or face sites that do not share edges with occupied tetrahedra.
- ζ) It is unfavorable to occupy more than four tetrahedra (or pairs of tetrahedra) sharing one central atom.

Rule ζ is related to the fact that the low-lying valence orbitals of Li are $2s$ and $2p$, so that hybridization can lead to only four (linearly independent) orbitals associated with one atom. This also reduces the (Pauli principle) repulsion between orbitals that are *not* spin-paired (this becomes increasingly repulsive when the orbitals are close). The above principles are consistent with the relative calculated energies since I_h is lowest, with fcc and hcp 0.26 and 0.57 eV higher, respectively.

We have used these rules to predict the OPTET (optimum tetrahedral) clusters presented in Figure 8. It is interesting to note that the OPTET clusters generally possess local fivefold symmetry axes (as does I_h). Exact five-fold axes are not consistent with three-dimensional space groups and hence these OPTET arrangements which optimize the bonding in clusters are inconsistent with crystalline symmetry (long range order). It is interesting to speculate whether this OPTET type of local bonding with its penchant for local five-fold symmetry axes may be the driving force for forming amorphous structures in metallic systems¹⁰.

These considerations suggest that there may be several regimes of structure for metal clusters. The smallest clusters either form planar structures (as in Li_4 and Li_6) or have very low energy planar configurations. For intermediate size, the OPTET structures are stable [e.g., Li_8^6 , Li_{13}^+ , and probably extending well into the 20's], while for very large clusters, structures approaching bulk character (hcp, fcc, bcc) may be stable.

The larger OPTET clusters are derived from adding atoms to the surface of the smaller OPTET clusters. This involves adding atoms to concave sites,

forming at least two new tetrahedra for each atom added. For larger clusters, the number of tetrahedra shared by a given atom will tend to increase as the ratio of empty to occupied tetrahedra increases. We expect there may be many $Li_{(n)}$ OPTET isomers lying within 0.1 eV of the optimum structure for larger values of n (where n is the number of atoms), and hence a greatly increasing number of different clusters will be in thermal equilibrium for larger n . Some of these clusters may be suitable nuclei for forming crystalline systems while others may prefer growth into amorphous solids. The relative energies and numbers of the different types of clusters may thus play an important role in controlling the kinetics for forming crystalline vs. amorphous systems.

3.1 Force Fields

Ab initio quantum chemical calculations of the quality described above are limited to a relatively small number of atoms (less than 100). In order to simulate the properties of a small portion of a metal we need to examine structures and kinetics for far larger systems (at least 1000 atoms). Thus we believe that it is essential to develop force fields that accurately reflect the local bonding effects of metallic systems. The above studies suggest that these force fields cannot be described merely in terms of nuclear positions but must also involve the positions of the localized (correlated) electrons. Consequently we have been using our cluster results to develop force fields involving both nuclear and electronic coordinates⁶. These force fields involve such terms as atom - electron - atom bend and atom - electron - atom asymmetric stretch, etc. Such force fields (involving many-body terms) may well provide a means for simulating amorphous metallic systems.

4. CONCLUSIONS

We believe that these ideas involving interstitially localized singly-occupied orbitals will form a useful starting point in developing valence bond ideas for predicting geometries, electronic structures, and properties of metallic clusters, and for describing localized phenomena in solids, such as defects or interfaces. They may provide useful conceptual ideas for predicting the chemistry and catalytic properties of such systems and for predicting the factors controlling stabilization of amorphous systems.

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