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The Role of *p* Orbitals in Determining the Interatomic Distance and the Electronic Band Structure in Alkali Metal Crystals

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Extended Hückel tight binding (EH–TB) calculations are shown to give a satisfactory description of alkali crystals. It is found that maximization of the valence *p* orbital overlap is a significant factor in determining the large interatomic separation. © 1986 Academic Press, Inc.

Introduction

As one progresses along the periodic table from the alkali metals through the transition metals it is usually considered that the metallic valence electrons are formed from a mixing of the *s* orbitals/band with the *d* orbitals/band (for example, the 3*d* orbitals with the 4*s* ones). Once the *s* and *d* levels are filled, the *p* orbitals are assumed to fill, causing the large changes observed in physical and chemical properties. Chemists, however, often consider the importance of the valence *p* orbitals for coordination chemistry, even when they are "formally" unoccupied. For instance, the number of ligands of a metal complex is determined by the 18-electron rule. (The number 18 comes from double occupation of the nine-valence orbitals, where the three *p* orbitals are included along with five *d* orbitals and the *s* orbital of the metal atom.)

In this communication, we first show results of EH–TB calculations for alkali metal crystals. The occupied density of states include extensive *p*–character. Then, we discuss the unusually large interatomic spacings of alkali metal crystals. Aided by simple symmetry and phase relation arguments, our calculations demonstrate the (usually neglected) importance of *p* orbitals, and the utility of a "chemist's interpretation" of solid state properties. In the third part we show how a determination of the energy relation (in semiempirical calculations) between *s* and *p* levels can be aided by an examination of the calculated band structure diagrams.

Results and Discussion

1. Band Structure and Density of States

In Fig. 1a and b are presented the band structure and the density of states for the rubidium bcc crystal. These results were obtained using an extended Hückel tight binding calculation with the parameters given in Table I. The diagrams compare rather well with the calculation by Mor-

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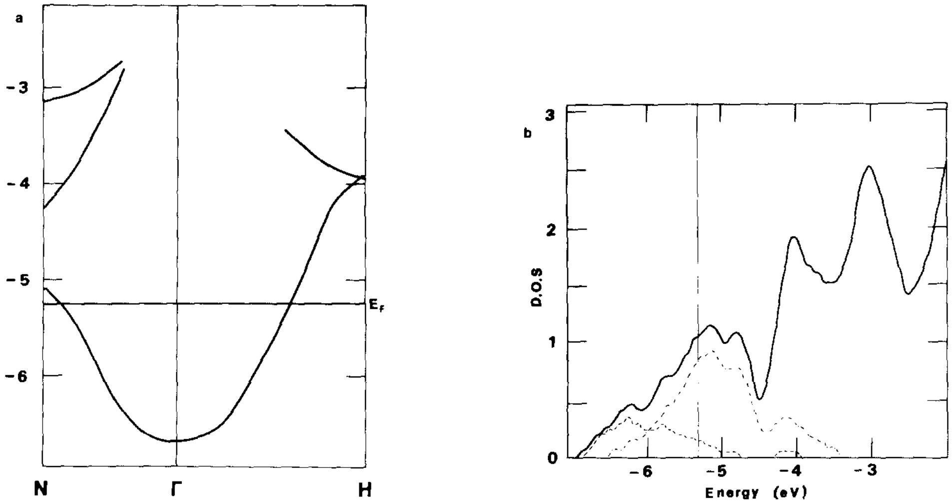

FIG. 1. Band structure (a) and density of states (b) of bcc rubidium. Dotted lines correspond to the *s* and *p* contribution.

TABLE I

PARAMETERS USED IN THE EXTENDED HÜCKEL TIGHT BINDING CALCULATIONS

	H_{ii} (eV)	Exp	Distance, Å
Na	Core		
2*s*	−76.1	3.286	
2*p*	−41.3	3.4	
Na	Valence	(Set 1)	
3*s*	−8.5	0.77	3.67
3*p*	−7.5	0.77	
Na	Valence	(Set 2)	
3*s*	−8.5	0.815	3.64
3*p*	−6.25	0.815	
Li			
2*s*	−9.0	0.703	3.03
2*p*	−8.0	0.703	
K			
4*s*	−6.25	0.8	4.53
4*p*	−5.0	0.8	
Rb			
5*s*	−4.0	0.865	4.84
5*p*	−3.4	0.865	
5*d*	−2.9	3.92(0.677) 0.85(0.677)	

ruzzi *et al.* (*3*). The occupied states are made of *s* and *p* orbitals, with the *d* orbitals contributing mostly to vacant states. The orbital population analysis gives more 5*p* electron density (0.533) than 5*s* (0.435), with the 4*d* being negligible (0.032). Figures 2a and b show similar results for the sodium bcc crystal. The 3*p* orbital population (0.608) also exceeds the 3*s* (0.392).

The *p* contribution appreciably increases the cohesive energies in all alkali crystals. Three terms (*s*–*s*, *s*–*p*, and *p*–*p*) are involved in the bond. In the simple diatomic description, *s* and *p* orbitals mix, forming one (occupied) molecular orbital. In the tight binding model of the crystal, the hybridization varies across the Brillouin zone. The lowest band, for instance, is pure *s* at the zone center Γ and pure *p* at the zone edges *N* and *H*. Thus *s*–*s* overlap dominates near the center of the Brillouin zone, *p*–*p* near the edges, and various *s*–*p* hybrids in between. Our results show that despite the very diffuse character of the valence shell and the known limitations of semiempirical LCAO methods, the EH–TB method can give a reasonable approximation to bulk alkali metals, at least from the

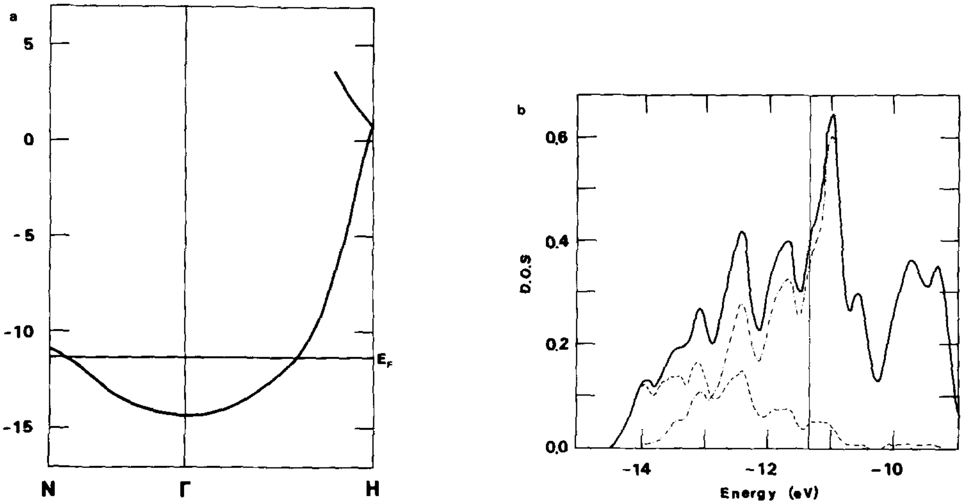

FIG. 2. Band structure (a) and density of states (b) of bcc sodium.

point of view of band structure and density of states.

2. Atomic Distances

The extended Hückel method is inadequate at representing bond lengths. The worse situation is for the dihydrogen molecule, where an optimization leads to a collapse of the two atoms. This results because the one-electron energy is proportional to overlap which is maximized when the two atoms are superposed. The dialkali metals, with one valence electron coming from each atom, are similar. To overcome this inherent weakness in the extended Hückel method, a core–core repulsive potential is often added to the calculation (*9*). The repulsive formula $\exp(a-br)$ can be computed by fitting the parameters a and b to EH results involving the filled $(n-1)$ shell instead of the valence shell. The repulsive energy between two alkali ions has elsewhere been shown to be proportional to overlap, and can be fitted with an exponential expression (*13*). Long range Z^2/r terms do not represent the steepness of the repulsion found from more sophisticated calculations. Part of these terms are implicitly incorporated through the choice of the parameters (the diffuseness of the Slater orbital includes an effective field which results in a compromise between attraction and repulsion). Another part would be screened by the core electrons.

In our calculations, distances were obtained for the bulk crystals *without* introducing repulsive corrections. This was not observed for diatomic molecules. A quick calculation suffices to show that the inner shell repulsion drops quickly with distance and becomes insignificant in determining the structure and total energy at distances larger than 2 Å (see Fig. 3). For the sodium atom, the $2s$ and $2p$ orbital exponents can be estimated from the Slater rules. We have employed values similar to those found in the literature (*1*). Figure 3 is a calculation of the fully occupied inner shell $2s$ and $2p$ orbitals of a disodium molecule. In bulk sodium, the interatomic distance is 3.66 Å, hence, the minimum is not likely to result from neutral core–core repulsion alone.

So where does the observed distance come from? In Fig. 3b we present the $3p$–$3p$ and $3s$–$3p$ overlap between two sodium atoms as they approach one another in a diatomic molecule or a bulk crystal. The Slater type orbital coefficients are listed in

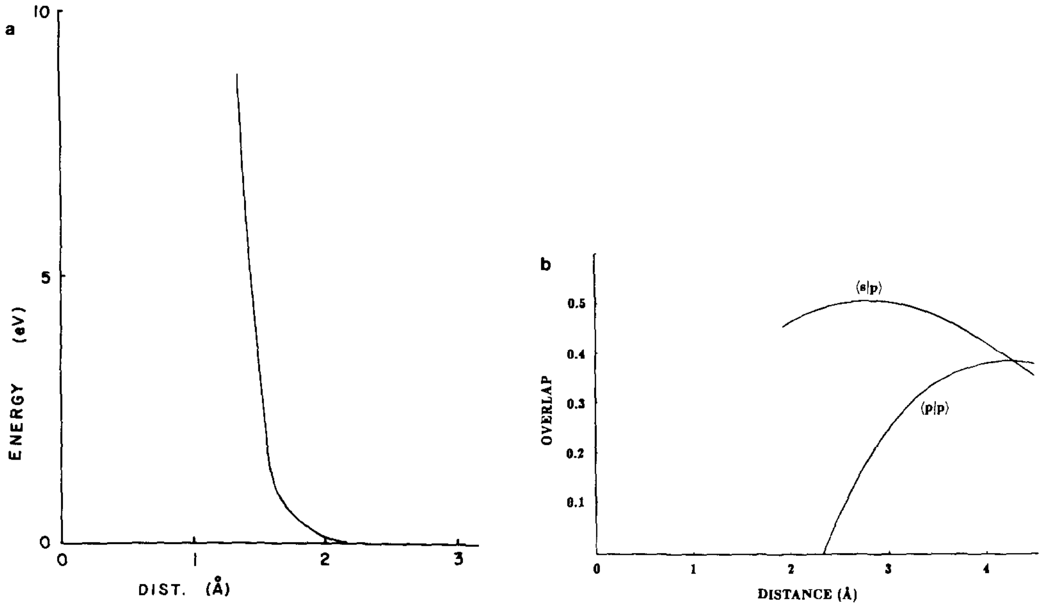

FIG. 3. (a) Core–core repulsion for Na. (b) The *p*–*p* and *s*–*p* overlap.

Table I. The $3p$–$3p$ overlap shows a maximum at ca. 4.1 Å. The reason for maximum overlap at large interatomic distance can be readily visualized in Fig. 4. It can be seen that *the node in the 3p wavefunctions at the nuclei prevent the atoms from approaching beyond a well-defined value.* The $3s$–$3p$ overlap term exhibits a maximum at 2.8 Å which is shorter than that of the $3p$–$3p$ term, but it also does not lead to a collapse.

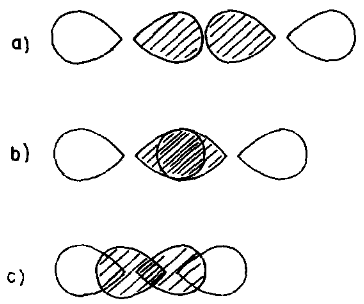

FIG. 4. Schematic diagram of *p* orbital overlap showing: (a) approaching atoms, (b) bonding (in-phase) overlap, and (c) antibonding (out-of-phase) overlap.

In the abscence of core–core repulsion, simple maximization of the $3s$–$3s$ overlap would lead the diatomic species to collapse. This is the result obtained by EHT on diatomic molecules or small clusters. The atomic *p* population increases with the cluster size for the atoms with a large coordination number. For instance, in a planar triangular Li_6 cluster, the tetracoordinated atoms are 42.4% $2p$-like and 57.6% $2s$-like. In the bcc crystal, the number of nearest neighbors is eight and the $2p$ population exceeds the $2s$ value. Therefore, it is not surprising that the *p*–*p* and *p*–*s* overlap is a large factor in determining the distance. As the *p* population increases, the bond length increases. For Li_2, the experimental distance is 2.67 Å (see Note). For Li_5 and Li_7 aggregates (*10*), it reaches 3.05 and 3.14 Å, respectively.

We note that this rather simple analysis of interatomic spacing is not obvious from basic solid state band theory models. The description of sodium as a lattice of positive cores surrounded by a sea of electrons completely hides the antisymmetric, nodal character of the p orbitals.

3. The Energies of the s and p Levels

3.1. The importance of the p orbitals is also seen in the sensitivity of the band shape to the p parameters. At the center and edges of the Brillouin zone where the s and p orbitals do not mix (the lowest valence band is pure s at Γ and pure p at N), the orbital energies E are related to the overlap of the tight binding Bloch sums, S and to the atomic levels, H, by Eq. (1) which can be derived from the Wolfsberg–Helmholtz equation.

$$E = H \cdot (1.75 - 0.75/S). \qquad (1)$$

Such an expression remains valid when the weighted formula is used. The variations of E (the derivative) are thus inversely proportional to the square of the overlap. At Γ all the atoms are contributing in-phase and the overlap is extremely large, 9.48 (remember that this is the overlap between one s orbital with all others in the crystal). Therefore, the energy of the bottom of the band near Γ (-14.2 eV) is rather insensitive to small changes in the s–s overlap. On the other hand, at the N zone edge, the p–p overlap is smaller, 2.8, partly because the p orbitals have nodes and directionality. It decreases as one moves away from N where the predominant in-phase p character is lost. The energy of the band near N (which is close to the Fermi level at -9.6 eV), is very sensitive to p–p overlap. As one moves across k-space, the response of the band energies to changes in p orbital parameterization is therefore more sensitive than their response to the s orbitals.

3.2. The H_{pp}–H_{ss} gap. Input for extended Hückel calculations are the atomic levels, H_{ii}, and the Slater exponents. Considering H_{pp} as a parameter, how should we choose its energy? In our first set of parameters (Table I), it is 1 eV above the s level. The energy difference between the atomic ground state ^{2}S and the first excited state ^{2}P of the sodium atom (2) leads one to estimate the energy difference between the levels as 2.25 eV. We used this as a second set of parameters (set 2 in Table I) and it led to a reasonable (but short) Na–Na distance (3.64 Å) and to a large p orbital population (0.444).

The more sophisticated models of electronic structure always show free-electron-like parabolic patterns at the bottom of the valence band (3). We found that in order to get a parabolic shape in EH–TB calculations, we must use an initial state p orbital energy, H_{ii}, which is only slightly above the s orbital energy, as in parameter set 1. The second set does not give the correct band structure whereas the first one does (see Fig. 5). Indeed, taking the free electron (FE) theory as a useful starting point, the occupied band must be parabolic in shape, hence our choice of the first set.

At Γ, as noted above, the energy bands are composed of pure s, p, and d orbitals. As one departs from Γ, the p orbitals begin to mix with s orbitals. This mixing increases as we approach the band edge, where the p orbitals become in-phase and pass below the s orbitals. The p orbital mixing imposes a widening of the FE-like parabola, lowering the energy at the edge of

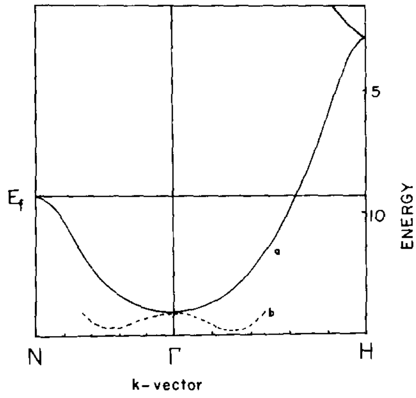

FIG. 5. Electronic band structure of Na showing (a) correct, and (b) "counterintuitive" behavior.

the Brillouin zone. If the s-p mixing is excessive at values close to Γ, it lowers the band leading to the unsatisfactory result that Γ is a local maxima instead of a local minima (Fig. 5, curve b).

3.3. Why does decreasing the s–p energy separation decrease the s–p mixing? According to perturbation theory, it seems necessary to increase the energy gap between the $3s$ and $3p$ atomic levels. If we do this, the result is just the opposite as desired—the mixing is increased. Conversely, if we reduce the energy gap, the mixing appears to be reduced (Fig. 5, curve a). Thus, we arrive at the situation that excessive $3s$–$3p$ mixing is reduced when we close the energy gap between them (as noted above).

From perturbation theory, the orbital mixing is expressed by $(H_{ij}-ES_{ij})/(E_i-E_j)$ (*12*). In general, the H_{ij} term is negative and much larger than the $-ES_{ij}$ term. Hence, the numerator is constant and the perturbation decreases when the p level is raised because the denominator is increased. In the present case, however, the numerator is dominated by the $-ES_{ij}$ term (positive). This is known as the counterintuitive effect (*4, 11*). Indeed, near Γ, the E value is quite large because of the many bonding interactions with all of the nearest neighbor atoms in the crystal. Also, the valence orbitals for alkali and alkaline earth metals are very diffuse, leading to large S_{ij} terms. If the $3p$ level is lowered, the H_{ij} term is increased and the numerator $(H_{ij}-Es_{ij})$ from the perturbation formula is reduced according to the Wolfsberg–Helmholz formula: $H_{ij} = k \times S_{ij}\,(H_{ij} + H_{jj})/2$.

Our use of the weighted H_{ij} formula (Ref. (*4*)) instead of the Wolfsberg–Helmholtz formula minimized the "counterintuitive effect" (*4, 11*). In addition, lowering the atomic p level energy in a systematic way (across the periodic table) enabled an even better correspondence with known band structures (*3, 8*). Forcing the H_{pp}–H_{ss} gap to equal the experimental gas phase atomic energy gap is not an appropriate approximation for the metal. Indeed, on forming a metal from a free atom, the s electrons are pushed away from the nucleus, decreasing the screening of the nucleus for the other electrons. This contributes to reduce the H_{pp}– H_{ss} gap. Semiempirical LCAO parameters calculated to reproduce the band dispersion are known to inverse the atomic order; for example, the $4s$ level of nickel is found 0.76 eV below the $3d$ level (*5*). Renormalized atoms lead to the same conclusion for the titanium atom (Fig. 3 in (*6*)). Although this form of parameterization renders exact quantification of distances impossible, it does not distract from the basic argument of the importance of p orbitals in crystal structure determination.

Conclusion

Our calculations and discussion emphasize that alkali metal clusters and crystals have large interatomic distances because of the dominance of p–p and s–p overlap. The core–core and partially screened ionic repulsions seem to be more important for the smaller alkali metals and for diatomic molecules where the p character is less significant. The incorporation of "vacant peripheral states" with the occupied band has been recently proposed by Harrison and Louie (*7*) in other, more rigorous, solid state band structure calculations. Their addition "very considerably improved the accuracy of the conduction bands." This is analogous to the role of the p orbitals in our model of alkali crystals. In Table I are presented EH–TB parameters for lithium, sodium, potassium, and rubidium atoms with the calculated metal–metal bond distances. Preliminary results (*8*) also show that the EH–TB method using the valence orbitals of the second row of transition metals (from rubidium to cadmium) can give band dispersions similar to those of Ref. (*3*) and reasonably accurate bond lengths.

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Note added in proof. The Li_2 experimental distance, 2.67 Å, is small with respect to the bulk experimental value, 3.02 Å, as well as to the values computed (*10*) for large clusters (3.05–3.26 Å). However, it is still larger than the value where the inner 1*s* shell repulsion is significant. For the diatomic molecule, one electron calculations such as EHT are clearly unsatisfactory. It is even worse with parameters obtained for the bulk crystal. STO3G calculations lead to a small Mulliken *p* orbital population (0.073) and to a small 2*s*–2*p* overlap population of 0.05, compred with the 2*s*–2*s* value of 0.29. Large basis sets and CI would increase the *p* population but the partition into one electron terms from such calculations is not obvious. Assuming the same set of parameters for the bulk calculation, a repulsive A/r formula with $A = 7.129$ Å · eV would correct the standard EHT Li_2 calculation and provide the 2.67-Å distance. It would correspond to the repulsion of two central charges of 0.703*e*. For Li, at this short distance the nuclear charge is not screened and not incorporated into the H_{ij} terms, and a repulsive formula has to be introduced.

References

1. W. C. Ermler, R. S. Mulliken, and E. Clementi, *J. Amer. Chem. Soc.*, **98,** 388 (1976); M. Karplus and R. N. Porter, "Atoms and Molecules," Benjamin, Menlo Park, Calif. (1970); *IBM J. Res. Dev.* **9,** 2 (1965).
2. C. E. Moore, Atomic Energy Levels, NSRDS-NBS Vol. 35, Part I, p. 89 (1971).
3. V. L. Morruzzi, J. F. Janak, and A. R. Williams, "Calculated Electronic Properties of Metals," Pergamon, New York (1978).
4. J. H. Ammeter, H.-B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.* **100,** 3686 (1978); M.-H. Whangbo and R. Hoffmann, *J. Chem. Phys.* **68,** 5498 (1978).
5. L. Salem and C. Leforestier, *Surf. Sci.* **82,** 1979, 412.
6. C. D. Gelatt, Jr., H. Ehrenreich, and R. E. Watson, *Phys. Rev. B: Condens. Matter* **115,** 1613 (1977).
7. W. A. Harrison, *Phys. Rev. B:* **24,** 5835 (1981); S. G. Louie, *Phys. Rev. B: Condens. Matter* **22,** 1933 (1980).
8. M. Criado-Sancho and C. Minot, *J. Solid State Chem.* **63,** 76 (1986).
9. Z. Engelke and C. L. Beckel, *Int. J. Quantum Chem.* **58,** 209 (1974); C. R. Guerillot, R. Lissilour, and R. Le Beuze, *Theor. Chim. Acta* **52,** 1 (1979); A. Gavezzotti and M. Simonetta, *Acta Crystallogr. Sect. A* **31,** 645 (1975); **32,** 997 (1976); A. Gavezzotti, M. Simonetta, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.* **122,** 292 (1982); A. B. Anderson, *J. Chem. Phys.* **60,** 2477 (1974); A. B. Anderson, *J. Chem. Phys.* **62,** 1187 (1975); A. B. Anderson and R. Hoffmann, *J. Chem. Phys.* **60,** 4271 (1974); B. Bigot and C. Minot, *J. Amer. Chem. Soc.* **106,** 6601 (1984).
10. S. Fraga and B. J. Ransil, *J. Chem. Phys.* **36,** 1127 (1962); P. Fantucci, J. Koutecky, and G. Pacchioni, *J. Chem. Phys.* **80,** 325 (1984); G. Pacchioni and J. Koutecky, *J. Chem. Phys.* **81,** 325 (1984); A. Julg, I. Laszlo, A. Pellegatti, *J. Mol. Struct. Theor. Chem.* **105,** 393 (1983).
11. C. A. Coulson, *Proc. Cambridge Philos. Soc.* **33,** 111 (1937).
12. For an analogous argument on the carbon atoms, see L. Salem, *J. Amer. Chem. Soc.* **90,** 546 (1968).
13. D. W. Hafemeister and W. H. Flygone, *J. Chem. Phys.* **43,** 795 (1965).