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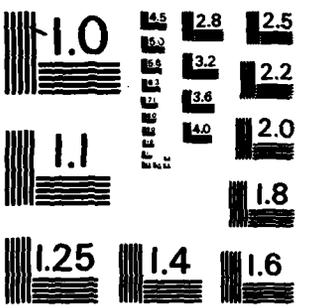

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The results of different theoretical methods are compared in the analysis of three illustrative problems. The methods involved are: local density functional (LDF), Xα, Hartree-Fock, generalized valence bond (GVB) and configuration interaction (CI). The three problems considered are: (1) the bonding of Mo_2 and Cr_2, (2) the photoelectron spectra of Cu clusters and (3) the chemisorption of N_2 on Ni. THe comparisons provide new insights both into these problems and into the physical content of the methods per se. In the case of the comparison of studies on Cu clusters, one is led to

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Theoretical Studies of Metal Clusters and of Chemisorption on Metals

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(Alpha)

Abstract

The results of different theoretical methods are compared in the analysis of three illustrative problems. The methods involved are: local density functional (LDF), Xα, Hartree-Fock, generalized valence bond (GVB) and configuration interaction (CI). The three problems considered are: (1) the bonding of Mo_2 and Cr_2, (2) the photoelectron spectra of Cu clusters and (3) the chemisorption of N_2 on Ni. The comparisons provide new insights both into these problems and into the physical content of the methods per se. In the case of the comparison of studies on Cu clusters, one is led to reinterpret the nature of photoemission from narrow d-bands and its relationship to conventional band theory.

I. Introduction

In theoretical studies of a quantitative or semi-quantitative nature which address the chemisorption of atoms or molecules on a metal surface, two common basic approaches are presently employed. In the first approach, one represents the metal surface by a slab of finite thickness and exploits the periodicity of the metal in the two directions parallel to the surface to simplify the calculations. This approach invariably utilizes the local density functional (LDF) method in which various approximate treatments of exchange and correlation are implemented in order to achieve local potentials. With such local potentials, tractable one-electron Schrodinger equations are obtained which can be solved easily by standard procedures.

In the second approach one represents the metal surface by a cluster of atoms. In this approach LDF and Xα methods as well as the Hartree-Fock method have been applied to describe the electronic structure of the cluster. When employing a finite cluster, traditional ab initio methods of incorporating electronic correlation effects in finite systems can be used, e.g., configuration interaction (CI) methods. However, relatively little work has been done along this line for metal clusters per se.

Both of these approaches are rather gross simplifications of the actual physical problem. However, each has some desirable characteristics which would be advantageous to retain in a more general approach. For example, the slab approach to chemisorption does not suffer from the undesirable "edge effects" which can cause problems in cluster calculations. On the other hand, in the cluster approach one can treat the chemisorption of a single atom or molecule rather than a periodic array of adsorbates. This is advantageous in dealing with local ionizations such as occur in the treatment of core level

photoelectron spectra. Also when using ab initio methods in the cluster approach, important correlation effects in the adsorbate molecule can be treated explicitly.[1,2] Such a strategy cannot be utilized in the slab approach or in cluster calculations which use LDF methods, as there is no known systematic procedure for improved treatment of correlation effects within the LDF framework. Thus there remains considerable opportunity for new, more flexible and more general theoretical approaches to the problem of chemisorption on metals.

Nevertheless, considerable insight to a number of specific problems can be afforded by judicious application of the slab and cluster approaches, in spite of their inherent shortcomings. In the following, the discussion will be restricted to finite systems and hence cluster methods. Within this context, we wish to discuss three specific systems in which two or more theoretical methods are utilized to investigate the system. As we shall see, the objective of using several methods to study a particular problem is that it allows one to separate those effects which are strictly artifacts of a given method from those effects which constitute the underlying physics of the problem. Thus, as a result, we also gain significant new insights into the efficacy of the methods themselves.

The examples we have chosen to discuss are: (1) bonding in the Mo_2 and Cr_2 diatomic molecules; (2) the ground state and ion states (photoelectron spectrum) of Cu clusters, and (3) bonding and photoelectron spectra of N_2 chemisorbed on Ni. In the first case, results of Hartree-Fock LCAO, generalized valence bond (GVB)-CI, Xα-LCAO and LDF-LCAO calculations are discussed which demonstrate the importance of specific intra-atomic correlation effects in describing the bonding in Cr_2. For the Cu cluster example, Xα- scattered wave and Hartree-Fock calculations are compared, which leads to new insight

regarding photoemission from the Cu d-bands. In the third case, a comparison of Hartree-Fock (HF), GVB and GVB-CI calculations shows the importance of including certain N_2 correlation effects and of using a representation of the metal which allows for the electronic polarizability of the substrate. These examples are discussed in turn in the next three sections. In the final section, we draw some general conclusions and speculate about future directions.

II. Bonding in Mo_2 and Cr_2

There has been a recent surge of interest both experimentally[3-6] and theoretically[7-11] regarding the bonding in Mo_2 and Cr_2. This interest does not derive from entirely academic issues. Rather, these molecules constitute a "testing ground" for theoretical techniques which would pretend to a general validity for larger metal clusters. Such test systems are particularly important, because our understanding of metal-metal bonding is quite primitive in comparison to that regarding bonding in non-metal systems.

In Table I, a comparison of various theoretical results for the equilibrium bond length and dissociation energies of Mo_2 and Cr_2 is presented together with the experimental values. Focusing on Mo_2 for the present, we note from Table I that all of the calculations give bond lengths within 0.2 A of the experimental value, with most results giving much closer agreement. The GVB results also predict a second minimum at ~ 3.1 A. None of the other calculations produce a secondary energy minimum in their potential curves. The agreement among the results for the dissociation energy is not very impressive. There is a group of results between 4.2 to 5.3 eV, all from LDF calculations. The results from the Xa and GVB calculations give much smaller bond energies. We will return to this point shortly.

Four of the seven results for Mo_2 shown in Table I were obtained from LDF calculations. However, they employ different basis sets, different density functionals, etc. which makes comparisons among different methods (e.g., GVB, Xα and LDF) very difficult and not very informative. In order to make a more meaningful comparison between methods, we have carried out a series of LDF and Xα calculations[12,13] using the same basis sets employed in the GVB calculations. Thus the differences in these results may be attributed directly to the methods as they are not confused by various approximations made in the implementation of the methods. The results of these calculations are designated as LDF-1, LDF-2 and Xα in Table I. Both sets of LDF calculations are based on the electron gas data of Ceperley and Alder[14], but different published fits to the exchange-correlation potential are used. LDF-1 uses the fit of Perdew and Zunger[15] and LDF-2 uses the fit of Vosko, Wilk and Nusair[16]. Thus, the only difference among the LDF-1, LDF-2 and Xα calculations is the functional form of the exchange-correlation potential used; all other aspects of the calculations are identical. Note the significant difference between the LDF(1 and 2) results and the Xα results.

We will focus now on the Cr_2 results presented in the lower half of Table I. Note that here the GVB and Xα results are not only quantitatively different (i.e., in the value of the bond energy) from the LDF results, they are qualitatively different (i.e., large discrepancies in bond length and bond energy) and in severe disagreement with experiment. As the GVB method includes interatomic correlation effects in an accurate and well-defined manner, the large discrepancy between GVB and experiment suggests that atomic correlation effects may not be treated properly. Having noted that the GVB and Xα results are similar we may hypothesize that the GVB and Xα results may differ from the LDF results because of different treatment of atomic

correlation effects.[12,13,18] To test this hypothesis for the LDF to Xα differences a number of atomic calculations were performed for the LDF-1 and Xα methods.[12] Only those results which are necessary to make our present point are summarized in Table II. However, in order to make the key point, it is necessary to back up slightly.

The ground electronic configuration and state of the Cr and Mo atoms is $(d^5s^1)\ ^7S$, i.e., all the spins are aligned. In order to form a strong covalent bond, the intra-atomic exchange interactions must be smaller than the interatomic energy lowering afforded by the overlap of orbitals on different sites. If the atomic exchange interaction is over-estimated by the theory (in comparison to experiment), it will reduce the tendency for a strong bond to form. In the formation of a covalent bond there are two components which contribute to the binding energy, a covalent component and an ionic component.[13] The ionic component naturally includes terms which are intra-atomic in nature. Again, if these terms are over-estimated by the theory strong bond formation will be jeopardized. We will refer to these two atomic effects as the exchange *effect* and the ionic effect, respectively.

Returning to Table II and keeping in mind that it is the d-electrons which are important in forming a strong bond, we see that the importance of the exchange effect can be estimated by the energy needed to go from the ground state to the $s^{\uparrow}d^{4\uparrow}d^{\downarrow}$ configuration. Likewise, the importance of the ionic effect can be estimated from the energy required to excite an electron from the ground state to the $d^{5\uparrow}d^{\downarrow}$ configuration.[22] For the case of Mo_2, both LDF-1 and Xα underestimate the ionic effect when compared to experiment. For the exchange effect, both methods slightly overestimate the energy. There is nothing dramatic here to interfere with bonding and both methods predict a strong multiple bond with the LDF giving a considerably higher bond energy.

The situation is quite different however, in the case of Cr_2. Here we see from Table II that the Xα method significantly overestimates both the exchange and ionic effects with the result that it does not yield a strong multiple bond, unlike the LDF method. Thus we have traced the failure of the Xα method in qualitatively describing the Cr_2 bond to the overestimation of some atomic electronic interaction energies, i.e., to atomic correlation effects. Fig. 1 shows the binding curves determined from the GVB, LDF and Xα methods; all calculations used the same basis set.

The problem in the GVB calculation has been identified as the overestimation of the ionic effect.[13,18] In fact, the energy of the $d^{5\uparrow}d^{\downarrow}$ configuration is 1.25 eV higher than the Xα result, giving a result which is nearly 3 eV higher than experiment. This is responsible for the lack of a strong multiple bond in the GVB calculations for Cr_2. If this problem is corrected, a binding curve is obtained which is qualitatively similar at small R to the LDF results, i.e., a strong multiple bond is formed with $R_e \sim 1.7$ A.[13,18] However, the previous minimum at around 3.1 A remains and becomes a second (local) minimum. Recall, that a second minimum was also found in the case of Mo_2.[7] Thus at large R there is a discrepancy between the GVB and LDF results. If these second minima at large R are verified experimentally, the problem of spin-coupling in LDF methods will have to be addressed. It is clear in the context of the GVB method that the two minima arise because of changes in spin-coupling as a function of R.[7] However, these effects are <u>not</u> included in the LDF method, and it is not obvious at present how the method could be modified to include them.

Thus from a systematic comparison of results from several methods, one can learn not only something about bonding in Mo_2 and Cr_2, but also something about the methods themselves. We have seen that the Xα and GVB methods

overestimate atomic coulomb interactions (ionic effect) leading (in the case of Cr_2) to the failure to form a strong multiple bond. The LDF methods, on the other hand, are apparently able to properly account for this interaction; however, it is far from transparent how this is accomplished. The GVB method can take account of changes in spin-coupling properly, whereas the LDF cannot. One advantage that the ab initio methods have over the LDF methods is that they are susceptible to systematic improvements.

III. Ionization from Cu Clusters: Implications Regarding Band Theory

One of the principal experimental probes of the electronic structure of metal surfaces and chemisorbed species on metals is photoelectron spectroscopy. As the metal is frequently represented by a cluster of atoms in theoretical work, it is therefore of interest to study the ground state and ion states of metal clusters in order to see if we can learn how ionization from such clusters is related to ionization (photoemission) from the metal surface.

Although everyone recognizes that the energy of a photoelectron, $KE_k = h\nu - \Delta E_k$, measures the difference in the ground state and the (k^{th}) ion state <u>total energies</u> (ΔE_k) for a given photon energy, this is often too readily forgotten. The problem is the ease with which one can lapse into thinking in terms of one-electron theory. Here one often imagines, on the basis of some molecular orbital or band structure calculation for the ground state, that one is measuring the binding energy, assumed equal to an orbital energy $|\epsilon_k|$, of an electron in some one-electron orbital ϕ_k. Even when "relaxation effects" are taken into account, the mental picture may be one in which one assumes that the binding energy will be decreased from its value $|\epsilon_k|$, due to final

(ion) state electronic relaxation, but that the general picture is otherwise correct. Indeed, one frequently finds that this is a very useful and even fairly accurate way to think about the photoemission process. However, it should be apparent that this approach cannot be expected to be generally valid. In fact, there are an increasing number of instances where the idea of electronic relaxation (which seems to connote a modest change in electronic structure between the ground state and ion state) may be more appropriately replaced by the idea of <u>electronic reorganization</u> (by which we wish to connote a major change between the ground state and ion state.)[23]

Certainly for delocalized electrons in extended systems, especially in the case of the valence electrons of metals (delocalization is explicitly assumed in band theory), the relaxation effects will be negligible. Thus, in band structure calculations for metals, we might expect that the computed eigenvalues (orbital energies) would accurately represent the relative ionization energies of the metal to the extent that one-electron band theory is adequate. In fact, such comparisons between photoemission results and band structure calculations for Cu[24,25] (as well as many other metals) have been made and the agreement is rather good, although discrepancies have been noted and the possible importance of relaxation effects has been raised.[25]

There is a fundamental problem, however. Band structure calculations invariably use LDF (or Xα) methods and there is no theoretical justification in these methods for identifying the absolute values of the one-electron energies (orbital energies) with experimental ionization energies.[26] Although the practice is common and seems to be justified <u>de facto</u> by its success, the question remains: why does it work?

In order to gain some insight about the problem, we will investigate the differences between Xα-scattered wave (SW) results[27,28] and Hartree-Fock (HF)

results[29,30] for Cu clusters. In Fig. 2 the orbital energies from the two methods are presented for Cu_{13}, which consists of a central atom surrounded by its 12 nearest neighbors (i.e., the local environment of the fcc lattice). In these molecular orbital calculations the orbitals are symmetry functions, just as are the Bloch functions of band theory. Therefore, those orbitals which involve the 12 nearest neighbor atoms are forced to be delocalized over this set of equivalent sites. For each case in Fig. 2, the t_{2g} and e_g levels are largely localized on the central Cu atom. The solid boxed-in regions represent the energy range in which the combinations of d-orbitals on the 12 nearest neighbors are found (analogous to the d-bands of the metal). The two dashed lines in each case represent the extremities of the occupied s-like orbital combinations. In the HF results the s- and d-like levels are virtually disjoint, whereas in the Xα-SW results the s-like levels totally overlap the d-like levels. The latter situation is much like that obtained from band structure calculations. Furthermore, if one assumes that relaxation effects are small and that one can use the orbital energies to compare with photoelectron spectra, the Xα results reflect the Cu metal experimental distribution of levels, whereas the HF results do not. This is rather a curious situation because, as we have pointed out above, the assumption regarding the interpretation of the $|\varepsilon_k|$ as ionization potentials in the Xα theory cannot be justified, whereas in the HF theory this interpretation is perfectly valid (Koopmans' theorem) as long as the relaxation effects are small. For the d-levels in the boxes in each case, the relaxation effects are very small because of the delocalization of the electrons over the 12 equivalent sites. Thus for the case where we can legitimately compare the levels with photoemission data (HF case), the cluster results do not resemble the metal, yet for the Xα case where we cannot validly make this comparison the results very much resemble

the situation in the metal.

A convenient way to obtain corrected one-electron energies for the Xα and LDF methods, which are interpretable in terms of ionization energies is the Slater transition state procedure.[31] When this is done, there is an overall shift of the one-electron levels, but the relative positions of the s- and d-like levels remains essentially the same. Thus there remains a fundamental difference between the HF and Xα results.

The resolution of this difference for the Cu clusters came when it was realized[28] that ionization from localized d-like orbitals (atomic like) would significantly change the relative d and s ionization energies of the HF calculations. Similar conclusions for Ni clusters were simultaneously reached.[32] Let us focus on the HF results for d-like orbitals (the box in Fig. 2) involving the twelve equivalent Cu atoms. If we do not force the orbitals to be symmetry adapted (i.e., delocalized over this set of atoms) but rather "break" the symmetry so as to allow ion states to have localized d-holes if it is energetically favorable, then we find that the d-holes (unlike the s-like holes) become strongly localized. There are concomitant large relaxation effects, amounting to 4-5 eV in energy, which reduce the Koopmans' theorem d-like ionization energies. However, one no longer has a one-electron energy which can be related to the ionization energy, rather one must consider the difference in total energies between the ground state and ion states, ΔE_k, to obtain the ionization energies. If one were to plot a diagram similar to Fig. 2 for the symmetry unrestricted HF results, except that the ΔE_k are used rather than the orbital energies, an ionization spectrum would result in which the d-like ionization energies are completely overlapped by the s-like ionization energies.[28-31] In this regard the calculated spectrum looks very similar to that of the Xα-SW results shown in Fig. 2.

In spite of having achieved this agreement between the ionization spectra of the two methods and the similarity of both results with the photoemission results of the metal, there is still a difference in the physical picture provided by the two methods with regard to the ionization process. In this ab initio approach (symmetry unrestricted HF) one must view the ionization of d-electrons as an essentially localized process, largely confined to a single atom. On the other hand, the Xα or LDF molecular orbital cluster approach or band theory approach traditionally view the ionization as delocalized in which an electron is removed from an extended region in space (a symmetry or Bloch orbital).

It turns out that in the Xα (or LDF) method, the orbital energies give apparent agreement with the experimental ionization spectrum because two energy contributions are ignored.[28] The first is an electron self-energy contribution and the second is the relaxation energy. If symmetry is broken in the Xα calculations and these two energy contributions are taken into account explicitly, one finds that the two contributions are of opposite sign, but of roughly the same magnitude, producing a near cancellation of the two energies.[28] The physical effects associated with these energy contributions however cannot be ignored.

The implications of these cluster results are clear: ionization of d-electrons from Cu is localized and the resulting electronic relaxation effects are large (4-5 eV). We believe this is directly relevant to the physical picture in the metal and that it challenges the traditional view regarding band theory and the interpretation of photoemission. In fact, the discrepancies already noted[25] between band theory results and photoemission experiments may have their origin in the effects we have just discussed.

IV. N_2 Chemisorbed on Ni: Bonding and Valence Photoemission

The nitrogen molecule chemisorbs weakly on Ni, having an adsorption energy of 0.36 eV for Ni (110)[33] and ~ 0.5 eV for the Ni (100)[34] surface. It is known to be oriented with its internuclear axis perpendicular to the surface.[35,36] Understanding the nature of the N_2 to Ni substrate bond involves three issues which are usually raised: (1) whether Ni *d*-electrons are involved in the bonding, (2) the extent of σ-bonding between a nitrogen lone pair and the metal, and (3) the extent of π-bonding between the metal and the N_2 2π orbital (which is unoccupied in the gas phase).

Through an extensive series of ab initio calculations for N_2 on a variety of clusters we have attempted to address these questions as well as the nature of the final states in core and valence level photoemission and the vibrational frequencies and intensities of N_2 on Ni in a consistent framework.[2] In the present discussion we shall focus on results for two linear clusters, Ni-N_2 and Ni_3-N_2, because a number of the essential physical points can be illustrated without getting into too many details. Likewise, we shall restrict our remarks here to the nature of bonding in the ground state and a discussion of the valence photoelectron spectrum.

At the outset it should be noted that if one wishes to discuss the valence ionization spectrum, the Hartree-Fock method is inadequate as it gives the incorrect order for the 1π and 5σ ionization energies in the gas phase.[37] In order to correct this problem the π-electrons of N_2 must be correlated. The simplest wave function which accomplishes this is obtained from a GVB-perfect pairing[38] calculation for the two π pairs. Alternatively, one might use the $X\alpha$ or LDF methods which give the correct ordering.

Regarding the bonding of N_2 to Ni, the first point to be addressed is

that of the participation of the Ni d-electrons in the bonding. This point can be examined by treating the Ni atom at two levels of approximation using effective potentials. The first effective potential is the modified effective potential (MEP)[39,40] in which the ten valence electrons are explicitly considered. The *second* potential is the d^9-averaged MEP[41] in which the localized 3d electrons are incorporated into the potential, leaving only the 4s electron to be considered explicitly. For a double zeta basis set and treating correlation in the three N_2 bonding pairs at the GVB-PP level for the Ni-N_2 cluster, both calculations give a binding energy of approximately 0.03 eV. This shows that the dπ-bonding interaction is negligible. However, this small binding energy leads to the next question: why is the σ-bonding interaction for Ni-N_2 so small?

Consider the Ni-N_2 bond being formed from a lone pair on the closest N atom overlapping with the Ni 4s orbital. Clearly, this is not a very favorable situation for forming a two-electron bond. In order to form a dative bond between the Ni and N_2 it is necessary for the Ni 4s electron to be able to move out of the way so that the lone pair can experience a nuclear attraction from a less screened Ni atom. It is very difficult for a single Ni atom to exhibit sufficient polarization to accomplish this effectively. However, in a larger cluster or on the metal surface this polarization can be accomplished more readily. A simple case which exhibits the effect is the linear Ni_3-N_2 cluster.

For the linear Ni_3-N_2 calculations the d^9-averaged MEP was used for the Ni atoms. Thus in these calculations we isolate the σ-bonding component exclusively. That is, no dπ-bonding is possible (although, in fact, it is negligible) because of the effective potential used and no other π-interactions are possible (because the 4p orbitals are unoccupied in the Ni

atom) as could possibly occur with larger clusters containing several surface atoms. The calculated binding energy is 0.5 eV and the polarization of the "surface" Ni atom is observed. In order to assess the importance of π-bonding between the metal and the N_2 2π orbital, larger clusters must be studied.[2] The results of these calculations show that such π-interactions are negligible. Thus, the conclusion is that the bonding in nickel-N_2 chemisorption is dominated by σ-bonding. A similar conclusion was reached for the case of CO/Cu(100) using Xα-SW calculations.[42]

Results for the valence ion states are presented in Table III, again based on the Ni_3-N_2 cluster calculations. In the ground state the 2π level of N_2 is unoccupied. When a valence electron is ionized (i.e., ionization from 5σ, 1π or 4σ) two possible final states are important in each case. Consider, for example, ionization from the 5σ orbital. In this case the two final states are: (1) an electron is ionized from the 5σ and an electron is transferred from the metal to the 2π orbital of N_2 - this final state is designated as $(5\sigma)_s^{-1}$ where the subscript denotes that the ion is screened, and (2) an electron is ionized from the 5σ and no charge transfer takes place - this final state is designated as $(5\sigma)_u^{-1}$. The agreement between the calculated values and the experimental ionization energies for the N_2/Ni(110) system is quite good.

Although previous <u>ab initio</u> calculations have been carried out for the N_2/Ni system,[43] they have employed an Ni-N_2 cluster and the Hartree-Fock method. The deficiencies of this approach are apparent from the discussion above. Thus it is not surprising that the conclusions of this previous work are at odds with the present study.[2]

V. Summary

The three problems we have discussed demonstrate, in one way or another, the importance of electronic localization and correlation effects. It would appear that there are a wide variety of problems in surface science and in electronic structure theory in general for which these effects cannot be ignored. Thus, more sophisticated approaches to electronic structure beyond the traditional molecular orbital and band structure methods will be necessary in the future. For finite systems such approaches are already available and are significantly contributing to our understanding.

A crucial aspect of methods which incorporate correlation effects, all too often neglected, is their ability to provide simple physical pictures which can be used to think about related problems where detailed calculations have not been performed. It is this author's opinion that it will be those methods which address this critical issue which will become the standard approaches in the next generation of electronic structure theory.

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TABLE I. Comparison of Results for Mo_2 and Cr_2.

Molecule	Method	Bond Length (A)	Bond Energy (eV)
Mo_2	GVB[a]	1.97	1.40
		(3.09)[*]	(0.49)[*]
	HF[a]	...	>9 eV unbound
	LDF[b]	2.1	4.2
	LDF[c]	1.95	4.35
	LDF-1[d]	1.96	5.33
	LDF-2[d]	1.96	4.97
	Xα[d,e]	2.11	3.34
	Expt.	1.93[f]	4.20[g]
Cr_2	GVB[a,h]	3.06	0.35
	HF[h]	...	>20 eV unbound
	Xα-D[e,i]	2.75	1.0
	LDF[b]	1.7	2.8
	LDF[c]	1.7	1.8
	LDF-1[d]	1.65	2.88
	LDF-2[d]	1.68	2.58
	Xα[d,e]	2.53	0.49
	Expt.	1.68[j]	1.56[k]

[*] Second minimum in binding curve.

[a]Ref. 7.
[b]Ref. 10.
[c]Ref. 9.
[d]Ref. 12.
[e]With α=0.70.
[f]Ref. 5.
[g]Ref. 17.
[h]Ref. 8.
[i]Ref. 11,20.
[j]Ref. 3.
[k]Ref. 19.

TABLE II. Calculated Energies of Various Mo and Cr Atomic Configurations Compared to the Ground State (in eV).

Atom	Configuration	LDF-1	Xα	Expt[a]
Mo	$s^{\uparrow}d^{5\uparrow}$	0.0	0.0	0.0
	$s^{\uparrow}d^{4\uparrow}d^{\downarrow}$	2.36	2.51	2.2
	$d^{5\uparrow}d^{\downarrow}$	1.16	2.48	3.2
Cr	$s^{\uparrow}d^{5\uparrow}$	0.0	0.0	0.0
	$s^{\uparrow}d^{4\uparrow}d^{\downarrow}$	2.96	4.11	2.7
	$d^{5\uparrow}d^{\downarrow}$	4.56	5.84	4.4

[a]Ref. 21.

Table III. Ionization Energies (eV) for N_2 Chemisorbed on Ni.

Experiment[a]	Theory[b]	
Ionization Energy	Ionization Energy	Assignment
12.8	12.6	$(1\pi)_s^{-1}$
13.1	13.6	$(5\sigma)_s^{-1}$
16.8	18.1	$(4\sigma)_s^{-1}$
15.8	16.3	$(5\sigma)_u^{-1}$
17.5	17.2	$(1\pi)_u^{-1}$
	20.1	$(4\sigma)_u^{-1}$

[a]Experimental data are from Horn *et al.*[36] for N_2/Ni(110) and are relative to the vacuum with a work function of 5.0 eV.

[b]Calculated at the GVB-CI level with the restriction that excitations into different symmetries and between Ni_3 and N_2 are not allowed.[2] R(Ni-N)=1.99A, R(N-N)=1.14A, and R(Ni-Ni)=2.49A. Basis sets are double-zeta plus polarization for N_2 and d^9-averaged MEP-2s2p for Ni. In the charge transfer states (labels with subscript s) one of the 2π orbitals is singly occupied (by excitation from Ni_3). Ionization energies are referenced to the calculated ground state of Ni_3N_2 (Ni $4p\pi$ orbitals are not occupied).

Figure Captions

Fig. 1

Theoretical results for the Cr_2 molecule. Binding curves for the LDF-1 method (triangles),[12,13] the LDF-2 method (X's),[12] the Xα method (squares)[12,13] and the GVB method (circles).[8] All calculations used the same gaussian basis sets.

Fig. 2

Comparison of orbital energies for Cu_{13} as determined by the Hartree-Fock method[29] and the Xα-SW method[27]. The energy extent of the d-like orbitals in each case is shown by the solid box. Likewise the extent of the s-like orbitals is denoted by the dashed lines. For the HF results there is virtually no overlap between the s-like and d-like states. For the Xα-SW results, the d-like states are completely overlapped by the s-like states.

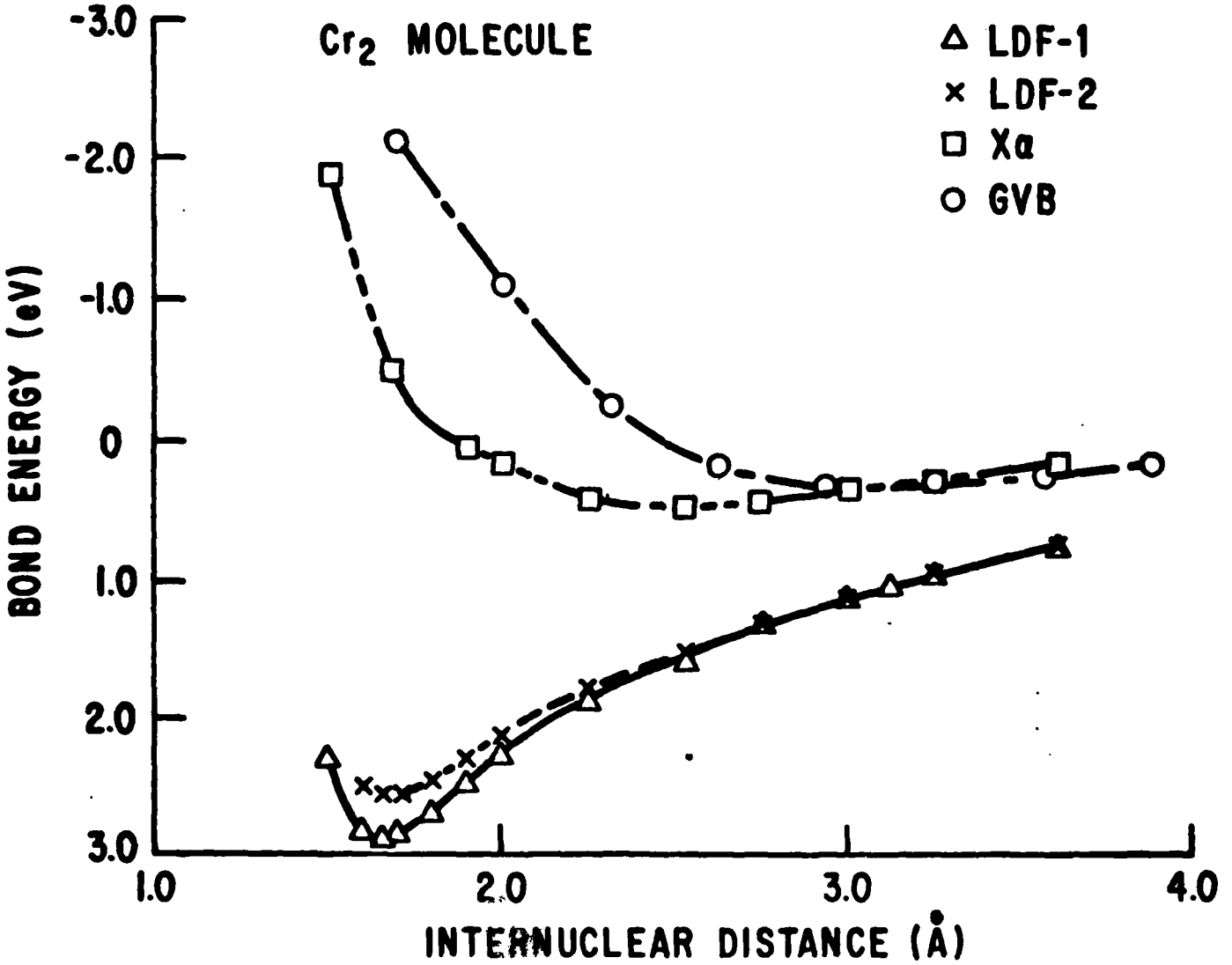

Cr_2 MOLECULE
LDF-1
LDF-2
Xα
GVB
BOND ENERGY (eV)
-3.0
-2.0
-1.0
0
1.0
2.0
3.0
1.0
2.0
3.0
4.0
INTERNUCLEAR DISTANCE (Å)

Fig. 1

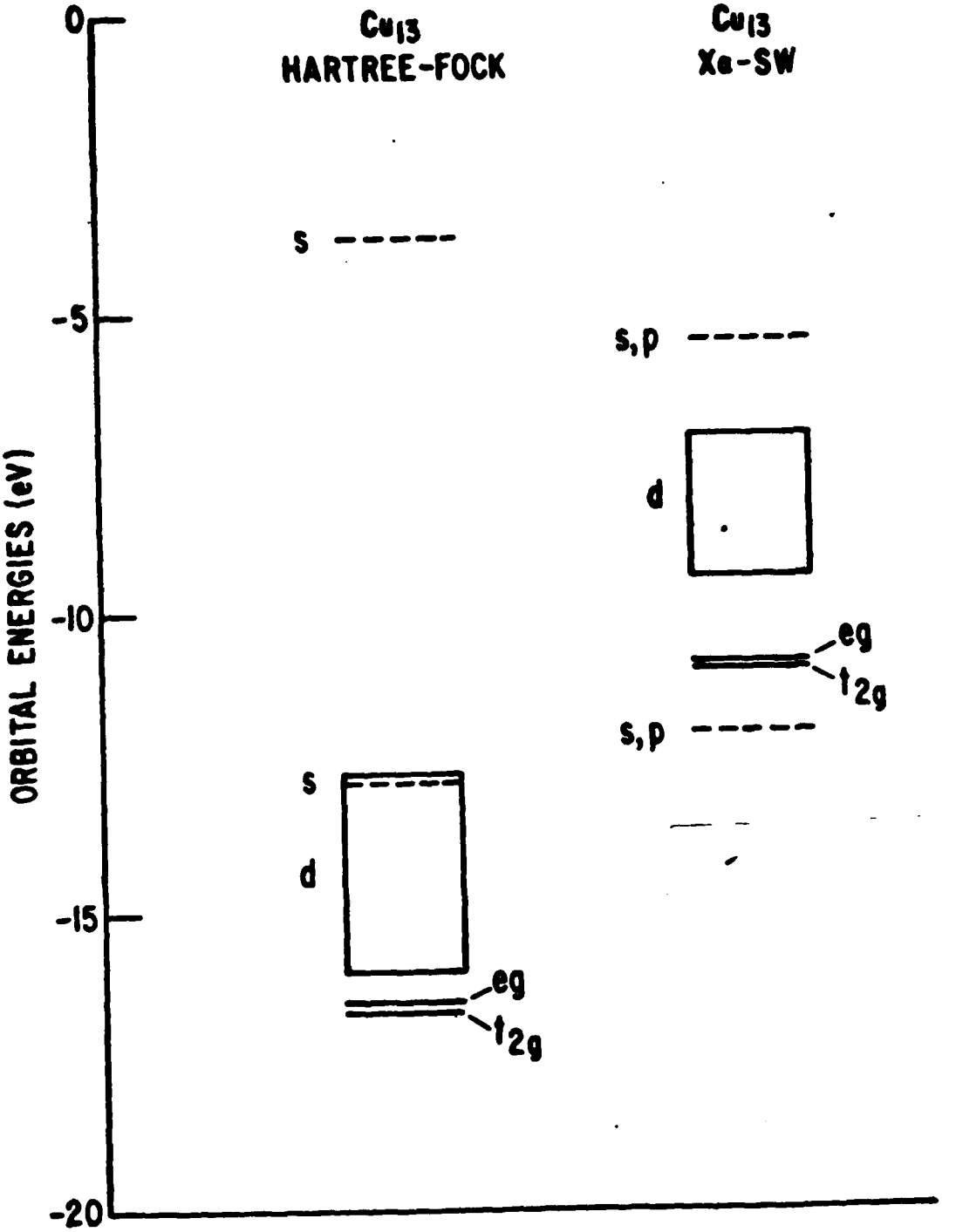
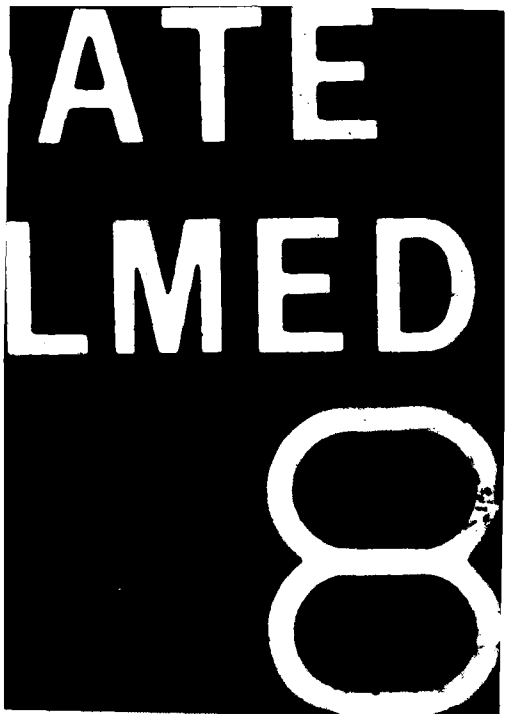

0
-5
-10
-15
-20
ORBITAL ENERGIES (eV)
Cu13
HARTREE-FOCK
s
s
d
eg
t2g
Cu13
Xα-SW
s,p
d
eg
t2g
s,p

Fig. 2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