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A proposal for the proper use of pseudopotentials in molecular orbital cluster model studies of chemisorption

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The interaction of CO with Cu₅, Ni₅, and Al₄ are treated as model systems for molecular adsorption on metal surfaces. The effect of the use of pseudopotentials for the metal atoms is studied by considering three types of clusters. In the first case, all of the metal electrons are explicitly included in the wave function; an all electron (AE) treatment. In the second case, the metal atom which directly interacts with the CO is described by as AE but the remaining metal atoms include a pseudopotential for their core electrons. Finally, in the third case, all of the metal atoms in the cluster have a pseudopotential treatment for the core electrons. The AE cluster results are taken as reference values for the two pseudopotential treatments. The mixed cluster results are in excellent agreement with those of the all AE clusters; however, the results for the all pseudopotential cluster of Ni₅CO or of Cu₅CO are qualitatively different. The pseudopotential treatment for all of the metal atoms often leads to results that contain serious errors and it is not a reliable approach.

I. INTRODUCTION

One approach used to investigate the chemical interaction of an adsorbate, atom, or molecule, with a surface is the *ab initio* molecular orbital (MO) cluster model (see, for example, Refs. 1 and 2). This approach can be used to accurately treat the local changes in charge density which occur when the adsorbate-substrate chemical bond is formed. *Ab initio* calculations have been used with great success for gas phase molecular systems (see, for example, Ref. 3). A significant problem in the cluster modeling of a solid surface involves the size of the cluster; it normally contains only the substrate atoms directly involved in the local chemical bonding with the adsorbate and a small number of nearby substrate atoms. Clearly a much larger number of substrate atoms must be included to model all the properties of the solid surface. For H/Be(0001), for example, it has been shown⁴ that the substrate-adsorbate equilibrium separation, R_e (Be-H), and the adsorbate vibrational frequency converge reasonably rapidly with respect to cluster size. However, the value of the adsorbate binding energy, D_e , even for rather large clusters is limited by effects due to the finite size of the cluster; i.e., to cluster edge effects. An important successful use of the MO cluster model case, therefore, has been to obtain a qualitative description of the interaction and the nature of the chemical bonding between the adsorbate and the substrate. However, for some cases, it is necessary to use reasonably large clusters containing ~ 10 – 20 substrate atoms to obtain even a qualitative description of the interaction. Consider, for example: (1)

the adsorption and subsequent reaction of halogen atoms, F and Cl, with a Si(111) surface⁵ where 23 substrate atom clusters were used, and (2) the coverage dependent changes for the adsorption of O on Ni(100)⁶ where 25 substrate atoms were used.

Clearly, such large clusters lead to very large, immense, calculations if all the electrons of the substrate and adsorbate atoms are explicitly included in the calculation of the cluster wave function. The problem can be greatly reduced in size and computational difficulty if the core electrons of the atoms are treated with a pseudopotential. In this way the effect of these core electrons may be included in the one electron operator and only the valence electrons are explicitly included in the wave function. Pseudopotentials suitable for use in *ab initio* MO calculations have been developed^{7–17} and have generally come to be referred to as “effective core potentials”, ECP’s; we shall retain this notation for them.

For the first row transition metal (TM) atoms it would seem reasonable to include the Ar, $1s^2 - 3p^6$, core electrons in the ECP and explicitly treat only the $3d$ and $4s$ electrons of the TM. However, this still leads to rather large calculations even for clusters of modest size. To further reduce the size of the problem, ECP’s which include the $3d$ electrons have also been developed. For Ni, for example, an ECP which includes the Ar core and nine $3d$ electrons makes it possible to treat Ni as a one electron atom.¹⁸ Such an ECP has been used to study the interaction of Ni with H,¹⁸ O,^{6,19} and CO.²⁰ This one electron ECP greatly reduces the size of the cluster calculations and makes the study of large clusters feasible.²¹

An ECP can lead to serious errors for TM systems even if the $3d$ electrons of the TM are included. For example, Basch and Osman²² carried out a calculation on the CuO

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diatomic molecule including the Ar core of Cu and the He core of O in ECP's. For the separation of the ground, $X^2\Pi$, and the lowest $^2\Sigma^+$ excited state, the value they obtained, 1.9 eV, is twice as large as either experiment²³ or all electron (AE) calculations.²⁴ The inclusion of the $3d$ electrons in the ECP may lead to more serious errors. Even if the $3d$ electrons are not directly involved in the bonding, the $3d$ orbital has a significant spatial extent and will overlap the orbitals arising from the other atoms at normal interatomic separations.^{2,6} In the case of O/Ni(100),⁶ it was found that the O atom approaches sufficiently near to Ni that it penetrates, to a nontrivial extent, the Ni $3d$ orbital; the one electron ECP cannot account for this. In this case,⁶ an empirical correction for the change in the effective charge²⁵ of the Ni atom to reflect this penetration was successful, although it was necessary to calibrate it against AE calculations. For the interaction of TM's with π accepting ligands like CO or PF₃, there is considerable evidence²⁶⁻²⁸ to show that the TM d electrons are directly involved in the chemical bond. The $d\pi$ to ligand π^* donation makes a rather large contribution to the metal-ligand binding energy. Obviously, when the d electrons are included in the ECP, this $d\pi$ donation is not accounted for.

The interaction of the lone pair ligands, CO for example, with one metal atom leads, very often, to a repulsive potential curve²⁷⁻³⁰; it has been shown that this is largely due to the repulsion between the metal valence s electron(s) and the ligand lone pair. If, however, the cluster contains four or five metal atoms chosen to represent the first two layers of a single crystal surface, the interaction energy is in reasonable agreement with the chemisorption energy of the ligand on a metal surface.^{26,28,29} While this agreement may be due to a fortuitous cancellation, it is clear that, at least, modestly large clusters must be used to obtain reasonable binding energies of the adsorption of lone pair molecular ligands. Thus one is faced with conflicting problems, large clusters require substantial computational effort; for TM's, the effort involved for a five atom system is already very substantial. An ECP dramatically reduces the effort but its use may lead to poor or incorrect results. A possible solution to this dilemma is to use an AE treatment of the atom(s) directly involved in the chemical interaction with the adsorbate and to approximate the remaining, "environmental," metal atoms with an ECP. This ECP is chosen to include as many electrons as possible in the pseudopotential; for example, to explicitly treat only one, the $4sp$, electron for Cu or Ni. This solution will drastically reduce the level of computational effort for adsorption at on-top or bridge sites where only one and two AE metal atoms, respectively, are required. However, since the metal atoms directly involved in the interaction with the adsorbate are AE, the use of the ECP for the environmental atoms may not lead to serious errors.

In order to test this solution, we consider the interaction of CO with Cu₅ and Ni₅ clusters chosen to represent the (100) surface of these fcc crystals and with an Al₄ cluster representing Al(111). We consider the interaction at an on-top site with the CO internuclear axis normal to the surface and with the C atom closest to the metal. Thus, only one metal atom directly interacts with the ligand. We chose these clusters

because Cu₅CO provides a reasonable value for the adsorption energy^{26,28} of CO/Cu(100) and, as we show, Ni₅CO also does for CO/Ni(100). We present results for three different types of clusters. The first, the reference calculation, is one in which all of the metal electrons are explicitly included in the wave function, it is an all AE treatment. The second is a mixed treatment, where the metal atom which directly interacts with the CO is AE, but the other metal atoms are described with ECP's. The third treatment is one where the ECP is used for all of the metal atoms; this is called all ECP. The ECP's for Ni and Cu include all but the $4sp$ electron in the pseudopotential; the Al ECP involves the explicit treatment of the three electrons that arise from Al $3s^23p^1$. Self-consistent-field (SCF) wave functions are calculated for the clusters. Although the SCF treatment does not represent the full extent of the metal to CO $2\pi^*$ donation,²⁷ it does provide a reasonable and qualitatively correct description of the chemical bonding.²⁶⁻³⁰ The distance of the CO from the metal surface is varied and the equilibrium metal-C distance, R_e (M-C), and the dissociation energy D_e are determined.

The mixed cluster results are virtually identical to the all AE results for R_e and D_e . The all ECP results are rather different from the all AE; in particular the all ECP D_e differs from the all AE value by a factor of ~ 2 . However, the overall energetics do not give a full description of the interaction. A knowledge of the contributions of various charge rearrangements to D_e can give a basic understanding of the nature of the interaction. We have recently developed the constrained space orbital variation technique (CSOV).³⁰ The CSOV is a technique which provides an analysis of the ligand-metal interaction in terms of a decomposition of the energetics and charge motion into intra- and interunit contributions. Here, we compare the CSOV analyses for the mixed and all ECP Cu₅CO and Ni₅CO clusters. The CSOV decompositions for the all ECP clusters correspond to a qualitatively different bonding situation than that found for the mixed clusters. All our results indicate that the all ECP treatment for Cu₅ and for Ni₅ leads to results which are qualitatively, as well as quantitatively, incorrect. Much more importantly, our results show that the mixed cluster treatment leads to results for R_e and D_e which are essentially identical to the all AE treatment. Hence, the mixed cluster approach can be used with confidence to simulate the environment of the adsorption site. The all ECP cannot and must be carefully checked for every case.

The geometry of the clusters and the electronic configurations used are described and the CSOV technique for the analysis of the bonding is reviewed in Sec. II. The basis sets and ECP parameters are briefly described in this section; details are given in the Appendix. The results and comparisons among the all AE, mixed, and all ECP treatments are given in Sec. III and the conclusions are summarized in Sec. IV.

II. COMPUTATIONAL CONSIDERATIONS

The Cu₅ and Ni₅ clusters are square pyramids, C_{4v} point group symmetry; Al₄ is a trigonal pyramid, T_d symmetry. The metal-metal distances are those of the bulk fcc crystals.³¹ For Cu₅ and Ni₅, the top atom represents the adsorp-

tion site metal atom on the (100) crystal face. The four lower atoms represent the nearest neighbors in the second layer of the (100) surface to the first layer adsorption site. For Al_4 , the top atom represents the adsorption site on the (111) face and the three lower atoms are its second layer nearest neighbors. The CO internuclear axis is coincident with the four-fold axis of Cu_5 and Ni_5 and with one of the threefold axes of Al_4 . The point group symmetry of Cu_5CO and Ni_5CO is C_{4v} , the same as the bare metal cluster; for Al_4CO , the symmetry is C_{3v} . The clusters are shown in Fig. 1. The CO σ orbitals belong to the a_1 irreducible representation of C_{3v} or C_{4v} ; the CO π orbitals belong to the e representation. In order to be consistent with the standard nomenclature for σ and π charge donations in the metal carbonyl interaction, we shall use the notations σ and a_1 and π and e interchangeably.

For all three types of clusters, the all AE, the mixed, and the all ECP, we report symmetry and equivalence restricted³² SCF results. Previous work^{27,33} has shown that if electron correlation is included through a multiconfigurational SCF, MCSCF, treatment, the metal to CO $2\pi^*$ donation is larger than for the SCF. While the qualitative features of the metal-ligand interaction given by the SCF and MCSCF wave functions are very similar, the D_e is larger in the MCSCF case. Our main concern here is to compare the results obtained for the clusters with differing numbers of metal atoms described with ECP's. We expect the differences and similarities found for the SCF wave functions will also be found for correlated wave functions.

The ground states of Cu_5 , Cu_5CO , Al_4 , and Al_4CO have been discussed in detail^{26,29}; the results are summarized here. The ground state of CO is $X^1\Sigma^+$ with the orbital occupation $\dots 5\sigma^2 1\pi^4$. The ground state of Cu_5 is derived from atomic occupations that are $\text{Cu}(2S) \dots 3d^{10} 4s^1$. The five 4s electrons form the Cu_5 valence sp shells with the occupation $va_1^2 ve^3$; the ground state of Cu_5 is 2E . The orbitals of Cu_5CO are perturbed orbitals of the component Cu_5 and CO units and can be clearly identified with one of these components; the Cu_5CO ground state is also 2E . The T_d ground state of Al_4 is 3T_2 ; this state reduces to 3E and 3A_2 in the C_{3v} symmetry of Al_4CO . The 3A_2 component leads to the ground state of Al_4CO ; the valence orbital occupation is

$$\text{Al}_4(^3A_2): 1a_1^2 2a_1^2 1e^4 3a_1^2 2e^2. \quad (1)$$

The $1a_1$, $2a_1$, and $1e$ orbitals of Al_4 are composed largely of the Al atom 3s orbitals; the $3a_1$ and $2e$ orbitals have largely Al 3p atomic character. As for Cu_5CO , and Al_4CO orbitals can be clearly identified as arising from either the Al_4 or CO units and the ground state is 3A_2 . When ECP's are used to describe either the second layer metal atoms or all the metal atoms, some of the closed shell metal core electrons are not included explicitly in the cluster wave function. The valence orbitals discussed above are, however, explicitly included in all three types of clusters.

For Ni_5 , the SCF state considered arises from Ni atoms which have a $3d^9 4s^1$ occupation. The five atomic 4s electrons lead to valence $4sp$ orbitals $va_1^2 ve^3$ coupled to 2E just as they did for Cu_5 . The choice of occupation for the cluster orbitals which are largely derived for the atomic d electrons is rather complicated.

The d electrons are reasonably localized about the atomic nuclei, much more so than the valence $4sp$ electrons. This localization is clearly shown by the different spatial extents of the Hartree-Fock 3d and 4s orbitals of the Ni $3d^9 4s^1 (^3D)$ state given in Fig. 2. It is this contracted character of the 3d orbitals which leads to the difficulties for the choice of the d shell occupation. Since the internuclear Ni-Ni separation is large relative to the spatial extent of the 3d orbitals, the overlap of 3d orbitals on adjacent Ni's is small. If one forces all, or many, of the d orbitals to be fully occupied, corresponding to $3d-3d$ bonds between the Ni's, one mixes large amounts of ionic character into the wave function. This is easily seen by considering H_2 at large internuclear separations, the low overlap region. It is well known that at these longer bond lengths, the localized $1\sigma_g^1 1\sigma_u^1$ occupation is a much better description than $1\sigma_g^2$ which describes the system near r_e . In a similar way, one must consider a description of Ni_5 which has five open d orbitals, one on each Ni, in order to obtain a reasonable energy relative to the separated, $3d^9 4s^1$, atoms. The 25 atomic 3d orbitals of the five Ni's are in the a_1 , b_2 , e , b_1 , and a_2 representations of the C_{4v} symmetry of the cluster. For the AE cluster an open shell occupation of $b_2^1 e^2 b_1^1 a_2^1$ coupled high spin to 6A_2 has the

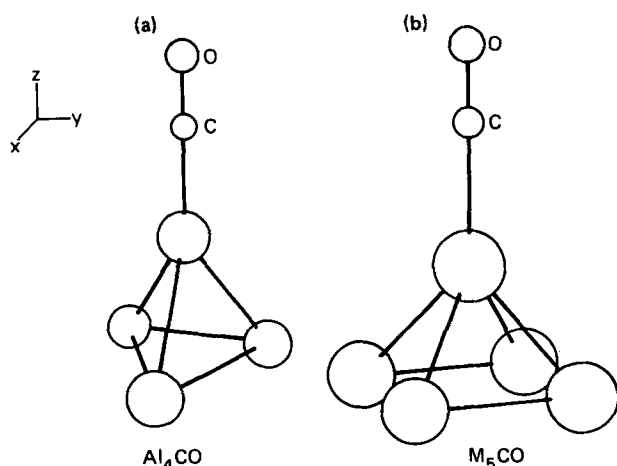


FIG. 1. Representations of the $M_n\text{CO}$ clusters; (a) Al_4CO and (b) M_5CO ; $M = \text{Cu}$ or Ni .

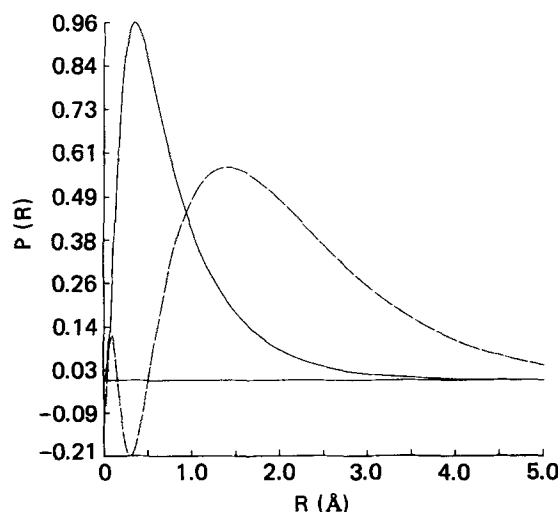


FIG. 2. The radial density of the 3d and 4s orbital of Ni 3D .

desired property of a $3d^9$ description of each Ni.

We have used this d configuration, high spin coupled to the 2E open valence sp shell, ve^3 , to give a state with a total symmetry of 7E . In this state, the open b_2 shell orbital has almost entirely $d(x^2 - y^2)$ character on the first layer Ni atom. The $d\pi$ occupation of the first layer atoms for this state is essentially 4; a population analysis for $Ni_5(^7E)$ gives 3.98 $d\pi$ electrons. This is desirable since the metal $d\pi$ to CO $2\pi^*$ donation makes a large contribution to the bonding.^{27,28} This choice of open shell has nearly the maximum possible adsorption site $d\pi$ electrons available for donation to the CO $2\pi^*$. There are other possible states with these two properties, dissociation to d^9 and nearly $d\pi^4$ adsorption site character. For example, the adsorption site Ni atom d hole could be a localized a_1 with $d(2z^2 - x^2 - y^2)$ character or a b_1 with $d(xy)$ character and the $d(x^2 - y^2)$ b_2 orbital could be doubly occupied. Because of the model nature of the calculations and the limitations of the SCF model to represent d electron interactions, we have not examined these other high spin configurations. We have examined lower spin configurations which involve fewer d electrons in open shells and found that they have considerably higher energies. A 7E state is also used for the all AE Ni_5CO cluster; this is consistent with the results for Cu and Al where the bare metal and metal-CO clusters had the same ground state symmetries.

For the mixed Ni_5 and Ni_5CO clusters, the configuration of the electrons arising from the Ni $3d$ and $4s$ shells is

$$da_1^2 db_1^2 de^4 db_1^2 va_1^2 ve^3(^3E); \quad (2)$$

where the db_2 orbital is also $d(x^2 - y^2)$ localized on the adsorption site atom. These are the appropriate analogs to the 7E state of the all AE clusters. For the all ECP clusters, all the metal d electrons are represented by the ECP and only the $va_1^2 ve^3$ metal electrons are explicitly included in the wave function leading to 2E states.

For all the clusters, the CO bond length was fixed at 2.173 bohr during the optimization of the R (M-C) distance and it is for this CO bond length that the D_e is computed. This is the equilibrium CO separation in $Ni(CO)_4$ ³⁴ and is used to take, in part, account of the CO bond stretching due to metal to $2\pi^*$ donation or charge transfer. For the Cu_5CO mixed cluster, we have also performed MCSCF calculations,²⁷ and optimized the C-O bond length as well as the R (M-C).

In addition to the overall description of the bonding such as R_e (M-C) and D_e , it is of interest to decompose it into its components and to compare their contributions to the bonding for the different clusters. The partitioning of the components of bonding is performed using the CSOV technique. In the CSOV analysis, the orbitals arising from one of the units, M_n or CO, are held fixed and those arising from the other unit, denoted X, are allowed to vary. The variational space for these orbitals, denoted Y, may be constrained so that only a subset of the full basis set is used. Thus, a particular CSOV calculation is described as $V(X;Y)$; the CSOV procedure is described in detail in Ref. 30. The analysis starts from the interaction of the fixed or frozen orbitals (FO) of the separated units. This is followed by a series of six CSOV calculations. (1) $V(M_n;M_n)$. Here, the CO orbitals are fixed

as the free molecule orbitals. Polarization of the M_n orbitals within the metal atom centered basis sets is allowed. (2) $V(M_n; \text{full } \sigma \text{ basis})$. The CO virtual, unoccupied, orbitals of σ symmetry are included and metal to CO σ donation is possible. (3) $V(M_n; \text{full basis})$. With the CO orbitals still frozen, the full basis set space is used for the variation of the M_n orbitals and metal to CO π donation is now possible. (4) $V(CO;CO)$. The metal orbitals from step (3) are frozen and intraunit polarization of the CO is allowed. (5) $V(CO; \text{full } \sigma \text{ basis})$. CO to metal σ donation is possible. (6) $V(CO; \text{full basis})$. This CSOV step allows the possibility of CO to metal π donation. A comparison between step (6) and the full, unconstrained, SCF results shows if the CSOV has accounted for all of the important contributions to the bonding. This procedure has been shown to be appropriate for the analysis of the dative bonds which are formed between certain metals and CO.^{28,30}

The energy at each of the CSOV steps, measured relative to the separated systems, is denoted E_{INT} :

$$E_{INT} = E(M_n) + E(CO) - E(M_nCO). \quad (3)$$

Here $E(M_n)$ and $E(CO)$ are the full, unconstrained SCF energies for the bare metal cluster and free CO, respectively; $E(M_nCO)$ is the energy at one of the six CSOV steps. Positive values of E_{INT} indicate bonding and negative values repulsion between the metal cluster M_n and CO.

The basis sets for the AE and ECP atoms are reasonably large; they are of double zeta quality or better for the regions of space where the valence orbitals are large. The basis sets for Ni and Cu include p basis functions to represent the $4p$ character of the valence electrons. This can be extremely important³⁵ for obtaining even correct qualitative behavior; calculations which do not include such functions should be viewed with considerable caution. The basis sets in the valence region are slightly different for the AE and ECP cases; however, the small differences between these basis sets are not expected to be important. The parameters used for the basis sets and the ECP's are described in the Appendix.

III. RESULTS AND DISCUSSION

For a fixed C-O bond distance of 2.173 bohr, we have computed the equilibrium metal-C separation, R_e (M-C), and the binding energy, see Eq. (3), at this separation, D_e . For all three types of clusters, these results are given in Table I. The all AE cluster results for Al_4CO and Cu_5CO are taken from Refs. 29 and 26(b), respectively. The mixed and all AE clusters give very similar results for all of the metals. The differences are greatest for Ni_5CO ; R_e differs by 0.04 bohr or 1% and D_e by 0.05 eV or < 10%. This close agreement is taken as evidence that the mixed clusters give essentially the same results as the all AE clusters. The mixed cluster results are obtained at a considerable savings in computational effort over that for the all AE cluster. We may take the basis set size as a measure of this effort. The AE basis sets, given in the Appendix, lead to 221 and 251 basis functions for the all AE calculations for Cu_5CO and Ni_5CO , respectively. These are rather large calculations. For the mixed cluster, the basis set sizes are 96 and 91 for Cu_5CO and Ni_5CO . These are modest numbers of basis functions. The savings of 125 and 160 func-

TABLE I. SCF values of $R_e(M-C)$, in bohr, and D_e , in eV, for the three types of M_nCO clusters, all ECP, mixed, and all AE. For comparison the SCF interaction energy, E_{INT} in eV, is given for the one metal atom-CO clusters, M_1CO , at the $R_e(M-C)$ for the all AE M_nCO clusters. In all cases, $R(C-O) = 2.173$ bohr.

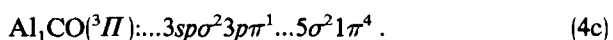
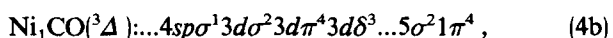
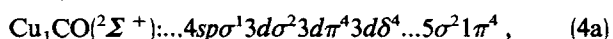
Cluster	All ECP $R_e(M-C)D_e$		Mixed $R_e(M-C)D_e$		All AE $R_e(M-C)D_e$		M_1CO^b E_{INT}
Cu_5CO	3.90	0.77	3.90	0.48	3.88	0.45	-0.45
Ni_5CO	3.70	1.32	3.86	0.51	3.82 ^a	0.56	-0.45
Al_4CO	3.82	0.08	3.77	0.23	3.74	0.24	-0.21

^a The quadratic interpolation for R_e is for a grid of 0.25 bohr steps; a smaller grid could lead to changes in the equilibrium value.

^b Interpolated SCF interaction energies for the $R_e(M-C)$ obtained for the all AE M_nCO cluster. See the text and Eq. (4) for the M_1CO configurations.

tions, respectively, results in a large reduction of computational effort at a very small loss of accuracy in the wave function. The differences between the all ECP and the all AE results vary for the different metals. The largest disagreement for R_e is 0.12 bohr or 3%; although this is larger than the error for the mixed cluster R_e 's, it is not a very large difference. For the D_e , the differences for Cu_5CO and Ni_5CO are 0.28 and 0.86 eV, respectively. These are very substantial differences. For Al_4CO , the all AE and the all ECP cluster D_e are rather small. We shall consider first the significance and consequences of the D_e errors for Ni_5CO and Cu_5CO and return to Al_4CO .

Before continuing with our analysis of the bonding for the M_nCO clusters, we comment briefly on the importance of using neighboring metal atoms to the adsorption site atom to represent its environment. In previous work, we have considered the interaction of one metal atom, Cu and Ni²⁷ and Al,²⁹ with CO. In Table I, we compare the E_{INT} of these clusters at the all AE $R_e(M-C)$ with the M_nCO values. The M_1CO values are for AE SCF calculations. The configurations used^{27,29} are



These are appropriate M_1CO configurations which are as nearly as possible, with a single metal atom, analogous to the M_5CO configurations discussed in Sec. II. For these metals, the M_1CO metal-CO interaction is repulsive. For $CuCO$, for example, the repulsion is 0.45 eV at $R_e(Cu-C)$ while for Cu_5CO the interaction is attractive by 0.45 eV. The difference of ~ 1 eV in E_{INT} clearly shows that it is important to include environmental metal metal atoms. For comparison, the experimental binding of CO on Cu(100) is 0.6 to 0.7 eV³⁶ depending on the coverage. The Cu_5CO SCF D_e is in good agreement with experiment and indicates that these relatively small clusters may be useful for a qualitative study of the energetics of the metal-CO interaction.

The results in Table I for R_e and D_e suggest that, even though there are substantial errors for the D_e ; the all ECP clusters could be satisfactory for a qualitative analysis of the metal-CO interaction. Our previous analyses²⁶⁻³⁰ have shown that the metal to CO $2\pi^*$ donation is of significant

importance for the bonding. For the Cu-CO interaction, we found^{27,28} that the $d\pi$ donation was more important than the valence, $4p\pi$, donation; we estimated that, for SCF wave functions, the $d\pi$ donation accounted for 2/3 of the energetics associated with the Cu to CO π donation. Since the Cu and Ni $3d$ electrons are not explicitly treated with the ECP which we used, this $d\pi$ to CO $2\pi^*$ donation cannot be present in the all ECP wave functions for Ni_5CO and Cu_5CO . An estimate of the metal to CO $2\pi^*$ donation is given by the CO $2\pi^*$ Mulliken population. The $2\pi^*$ population is taken to be the total CO π population minus four, assuming that this represents the occupation of the CO 1π ; the results are in Table II. The mixed and all AE $2\pi^*$ populations for Cu_5CO and Ni_5CO are almost identical; they are ~ 3 times larger than the all ECP cluster $2\pi^*$ populations. This is consistent with our observation^{27,28} that the $d\pi$, not present in the ECP wave function, makes an important contribution to the metal π donation and to the metal-CO bond. The very small CO $2\pi^*$ populations for the all ECP wave functions are not consistent with their large D_e . This suggests that the metal-CO binding energy in the all ECP Cu_5CO and Ni_5CO clusters may have a different origin than in the all AE and mixed clusters. If this is true, then it is due to an artifact of the ECP and not to a real physical effect. The SCF treatment does not fully describe the metal to CO π donation; correlation effects lead to a significant increase over SCF for this donation.^{27,33} However, one must require that a satisfactory ECP gives correct representations for both uncorrelated SCF as well as for correlated treatments.

The difference between the CO $2\pi^*$ populations for the all ECP and for the mixed and all AE clusters led us to make a more detailed CSOV analysis of the bonding for Cu_5CO and Ni_5CO . We apply this analysis to the all ECP and the mixed clusters. The agreement between the mixed and the all AE results for $R_e(M-C)$, D_e , and the CO $2\pi^*$ population are strong evidence that the CSOV results for these clusters would be very similar. The bond distances used for the CSOV analysis are near the preliminary values for the equilibrium obtained in MCSCF calculations which include correlation in the π space. For Cu_5CO , they are $R(Cu-C) = 3.70$ and $R(C-O) = 2.15$ bohr; for Ni_5CO , $R(Ni-C) = 3.75$ and $R(C-O) = 2.173$. These metal-C distances are somewhat shorter than the SCF R_e because the MCSCF leads to an increase in the metal to CO π donation and hence a stronger bond. They are sufficiently close to the SCF equilibrium distances shown in Table I that they will certainly also describe the bonding at these distances. They are also very close to each other, so that values for Cu and Ni can be compared. In

TABLE II. CO $2\pi^*$ populations for the three types of M_nCO clusters. The populations are for $R(C-O) = 2.173$ bohr and for $R(M-C)$ near the all AE $R_e(M-C)$ given in Table I.

	CO $2\pi^*$ population		
	All ECP	Mixed	All AE
Cu_5CO	0.04	0.10	0.11
Ni_5CO	0.04	0.11	0.12
Al_4CO	0.30	0.34	0.44

TABLE III. CSOV analysis of the interaction energies for Cu_5CO and Ni_5CO at bond distances near the equilibrium, see the text, for the all ECP and mixed clusters. For the FO results, total values of E_{INT} , Eq. (3), are given. For intermediate steps, the change in E_{INT} from the previous step in the table, ΔE_{INT} , is given to show the change in the interaction associated with the new variation permitted in the CSOV step. For the full SCF, E_{INT} and ΔE_{INT} are given. E_{INT} and ΔE_{INT} are in eV.

	Cu_5CO		Ni_5CO	
	Mixed	All ECP	Mixed	All ECP
$E_{\text{INT}}(\text{FO})$	-0.52	-0.22	-0.54	+0.21
$V(\text{M}_5; \text{M}_5)$	0.24	0.05	0.27	0.07
$V(\text{M}_5; \text{full } \sigma \text{ basis})$	0.03	0.04	0.05	0.08
$V(\text{M}_5; \text{full basis})$	0.32	0.12	0.34	0.08
$V(\text{CO}; \text{CO})$	0.21	0.13	0.20	0.15
$V(\text{CO}; \text{full } \sigma \text{ basis})$	0.12	0.65	0.13	0.72
$V(\text{CO}; \text{full basis})$	0.02	0.00	0.02	0.00
$\Delta E_{\text{INT}}(\text{full SCF})$	0.03	0.01	0.03	0.00
$E_{\text{INT}}(\text{full SCF})$	+0.45	+0.97	+0.50	+1.31

Table III we report the results for E_{INT} , see Eq. (3), for the six CSOV steps, $V(X; Y)$, described in Sec. II. Also included in the table are the frozen orbital E_{INT} obtained by superimposing and freezing the free M_n and CO component orbitals as well as the full, unconstrained SCF results for M_nCO . In Table III, we give the value of $E_{\text{INT}}(\text{FO})$ and the differences, increase, of the interaction energies over that for the previous CSOV step. This difference, ΔE_{INT} , directly shows the contribution of the CSOV variation to the interaction energy.

The first significant difference between the all ECP and the mixed clusters is for $E_{\text{INT}}(\text{FO})$. The mixed clusters are repulsive by ~ 0.5 eV when the M_5 and free CO orbitals are placed together. This has been shown to arise largely from the repulsion between the CO 5σ lone pair and the adsorption site valence σ electrons.²⁷⁻³⁰ When the core electrons of the adsorption site atom are represented by an ECP, this repulsion is considerably reduced; the all ECP Cu_5CO is less repulsive by 0.3 eV and the Ni_5CO by 0.7 eV. The effect for Ni_5CO is so large that simply superimposing the Ni_5 and CO charge distributions leads to an 0.2 eV attraction between them. This is blatant nonsense; no chemical bond has been allowed to form and there is no basis for an attractive interaction given the large repulsion between the electrons of the metal and CO. We speculate that this artifact of the ECP arises because there is an attractive long range behavior for the ECP which is larger than the repulsion arising from the metal valence, $4sp$, σ electrons. The metal charge polarization allowed in the $V(\text{M}_5; \text{M}_5)$ CSOV step reduces the mixed cluster repulsion by ~ 0.25 eV. This is because the metal σ charge polarizes away from CO to reduce the metal-CO 5σ overlap. This energetic effect is much smaller for the all ECP clusters. The metal to CO σ donation allowed at the $V(\text{M}_5; \text{full } \sigma \text{ basis})$ step does not, as expected, make a significant contribution to E_{INT} for either the all ECP or mixed clusters. The metal to CO $2\pi^*$ donation contribution as given by ΔE_{INT} at the $V(\text{M}_5; \text{full basis})$ step for the all ECP clusters is $\sim 1/3$ as large as for the mixed clusters. This is consistent

with estimates²⁸ that two-thirds of the SCF energy lowering from the Cu to CO π donation is due to the $d\pi$ donation. This cannot occur for the all ECP clusters.

The energy lowering due to the internal polarization of the CO in the field of the frozen metal cluster, $V(\text{CO}; \text{CO})$ is similar for both the all ECP and mixed clusters although somewhat smaller in the all ECP case. There is a dramatic difference between the importance of the CO to metal σ donation as given by ΔE_{INT} for $V(\text{CO}; \text{full } \sigma \text{ basis})$. For the mixed cluster, there is a modest energy lowering ~ 0.1 eV. This is in contrast to the much larger $\Delta E_{\text{INT}} \sim 0.7$ eV for the all ECP clusters. As for the all ECP errors for $E_{\text{INT}}(\text{FO})$, we speculate that this large ECP error at the $V(\text{CO}; \text{full } \sigma \text{ basis})$ CSOV step is due to an attractive tail in the ECP. The CO to metal π donation is small for all clusters. The interaction energy at the $V(\text{CO}; \text{full basis})$ CSOV step is very close, within 0.03 eV, to the SCF for both all ECP and mixed clusters. This is a clear indication that the CSOV analysis has accounted for all important bonding effects for these M_5CO clusters, either all ECP or mixed.

The conclusions as to the nature of the bonding based upon this CSOV analysis are dramatically different between the mixed and all ECP clusters. The mixed clusters show that the metal to CO π donation is more important than the CO to metal σ donation and that the intraunit polarization, of both the CO and metal units, is important. The intraunit polarization can be viewed as being due to the motion of charge which leads to an enhancement of the electrostatic interaction between the units.^{28,30} For the all ECP clusters, the CO to metal σ donation is very large; it accounts for more than half of the total interaction, E_{INT} (full SCF). Further, the all ECP treatment seriously underestimates the FO repulsion for Cu_5CO and shows, incorrectly, an FO attraction for Ni_5CO . These all ECP treatment errors shown by the CSOV analysis are much more serious than the ECP errors in R_e and D_e , see Table I. The all ECP R_e and D_e arise from entirely different bonding effects than do the mixed or all AE values. This analysis raises serious questions about the physical significance of the results of CO/Ni interaction studies which use this ECP.²⁰

For the Al_4CO cluster, the three treatments give reasonably similar results for $R_e(\text{M-C})$, D_e , and the CO $2\pi^*$ population, see Tables I and II. They all have a large Al to CO $2\pi^*$ donation and are all weakly bound. The Al $1s^2 2s^2 2p^6$ core is rather contracted compared to the valences $3s$ and $3p$. The $\langle r \rangle$ for the atomic Hartree-Fock orbitals clearly show this; $\langle r \rangle_{2s} = 0.63$ and $\langle r \rangle_{2p} = 0.60$ bohr compared to $\langle r \rangle_{3s} = 2.60$ and $\langle r \rangle_{3p} = 3.43$ bohr. This is in contrast to the spatial extent of the Ni $3d$ compared to the $4s$ orbital; $\langle r \rangle_{3d} = 1.05$ and $\langle r \rangle_{4s} = 3.38$ bohr for the $3d^9 4s^1 (^3D)$ state. This extent of the $3d$ orbital is also shown in Fig. 2. Since the Ne core in Al has this contracted form, and since the core does not include an orbital involved in the bonding, it is not surprising to find reasonable agreement among the three treatments. If a larger ECP valence basis set and an improved ECP were used for the Al_4CO all ECP cluster, the agreement between the all ECP and all AE results would probably be better. Given these considerations, we have not pursued the comparison of the ECP and AE treatments further.

IV. CONCLUSIONS

In order to study the interaction of an atom or molecule with a metal surface using the molecular orbital cluster model, it is useful and may, for many purposes, be necessary to use a large cluster to represent the surface. A pseudopotential, or ECP, treatment of the core electrons of these atoms leads to a great simplification and reduces the computational effort of the molecular orbital calculations. Alternatively, an ECP treatment permits the study of clusters of heavier metal atoms. This is especially true for an ECP for the transition metals which includes the d electrons in the core and where only one valence, sp , electron per atom is explicitly treated.

We have examined a mixed cluster approach to the use of ECP's. In this approach, the substrate atoms which interact directly with the adsorbate have all their electrons included in the wave function; the core electrons of the environmental substrate atoms are treated with an ECP. We have tested the mixed cluster approach for the on-top site chemisorption of CO on Cu and Ni; here only one metal atom is directly involved in the interaction with CO. For five metal atom clusters, one adsorption site atom and four second layer environmental atoms, we have compared the properties of SCF wave functions for an all AE, a mixed, and an all ECP treatment of the metal atoms. For this case, the mixed and the all AE treatments give very similar results for the equilibrium distance, the binding energy, and the metal to CO π donation as measured by the CO $2\pi^*$ population. However, the basis set for the mixed cluster is $\sim 1/3$ the size of the all AE cluster basis set. The computational requirements depend on the basis set size n between $\sim n^3$ to n^6 , depending upon the nature of the calculation. Thus, the mixed cluster offers great advantages over the AE cluster at a very small cost in the accuracy of the computed properties of the interaction.

The all ECP treatment leads to even greater computational savings over the all AE or mixed cluster. However, it leads to significant errors in the computed properties and to a qualitatively different description of the bonding than that given by the mixed clusters. The metal $3d\pi$ electrons make an important contribution to the donation to CO $2\pi^*$ and this cannot be taken into account if the adsorption site atom is represented by an ECP where the $3d$ electrons are included in the core. If the ECP did not affect the valence $4sp$ electron contribution to the bonding, the all ECP cluster would have a smaller D_e than the mixed and all AE clusters. This is not the case; the all ECP D_e is much larger. This is a clear indication of substantial ECP artifacts. The CSOV analysis of the bonding for the all ECP cluster is different in almost every way from that for the mixed cluster. The all ECP cluster has a large contribution to E_{INT} from the CO to metal σ donation, almost six times larger than for the mixed cluster. The mixed treatment also shows that there are large intraunit polarization contributions to E_{INT} . The all ECP clusters have CO intraunit polarization contributions that are somewhat smaller than the mixed clusters and have very small metal intraunit contributions. Thus, the all ECP clusters give a seriously incorrect description of the transition metal-CO bonding.

The mixed cluster approach which has been described

here has also been used for the study of the repulsive portion of the interaction of He with a Cu(110) surface.³⁷ Here mixed clusters of Cu₉ (1 AE and 8 one electron ECP atoms) for the on-top site and Cu₁₂ (2 AE and 10 ECP atoms) for the bridge site led to very reasonable results for several features of the interaction. On the other hand, the equivalent all ECP clusters gave physically unreasonable results.

In the case of Al where the Ne core is included in the ECP, the results of the all ECP treatment of Al₄CO are reasonably close to those for the mixed and all AE treatments. We believe that this is because the Ne core is quite contracted relative to the valence $3s$ and $3p$ shells; this is not the case for the TM's where the $3d$ orbital has considerable spatial extent relative to the valence $4s$, see Fig. 2. One might imagine that an ECP treatment for the first row TM atoms which included only the Ar core in the pseudopotential and explicitly treated the $3d$ electrons would give results comparable to those for the mixed or AE clusters. While this extended ECP appears attractive and may be an improvement over the one electron ECP, we must caution that it may have serious problems. For example, Basch and Osman have used such a pseudopotential for the Cu atom (explicit treatment of $3d^{10}4s^1$) in their study of the $X^2\Pi$ and the lowest $^2\Sigma^+$ states of the CuO diatomic molecule. The $^2\Pi-^2\Sigma^+$ energy separation which they obtain is twice as large as the value from AE calculations²⁴ or from experiment.²³ Gropen *et al.*³⁸ have made detailed studies of the use of Ar core ECP's for several molecules containing TM atoms. They have examined diatomic oxides and hydroxides of Sc, Ti, Cr, Ni, and Zn and the rotational barrier of NiH₄⁺; in several cases, they found serious problems associated with the use of an Ar core ECP. The ScO molecule gave dramatic evidence for these problems; several different ECP's for Sc all led to very short equilibrium Sc-O internuclear distances. Gropen *et al.*³⁸ conclude that the difficulty of Ar core ECP's for TM's is related to the fact that the $3s$ and $3p$ orbitals, which are included in the ECP, occupy almost the same region of space as the $3d$ orbital.

Thus, an ECP core for first row TM's which is most likely to consistently give equally good results as our ECP treatment for Al would also include only the Ne core.³⁹ Pettersson *et al.*³⁹ have shown that it is possible to considerably simplify the treatment of the $3s$, $3p$, and $3d$ shells, through the use of frozen orbitals, and retain reasonable accuracy for molecules. However, Ne core ECP's for these TM atoms even with the simplified M shell treatment can easily lead to very large computations for clusters with modest numbers of metal atoms. The much reduced, one electron, treatment for the atoms which form the environment of the atoms involved in the chemisorption interaction is, for many adsorption sites, a tractable alternative. It may be combined with the simplified M shell and Ne core ECP treatment of Pettersson *et al.*³⁹ for the TM atoms which have a direct interaction with the adsorbate. In this way, very high coordination sites can be treated. For the adsorption of CO at an on-top site, we have shown that this very simple treatment of the environmental substrate atoms gives results which are essentially identical to an all AE treatment. We expect that this result is true for other adsorption sites as well.

APPENDIX: BASIS SETS AND ECP PARAMETERS

The basis sets and ECP parameters used in this work are described separately for each atom.

1. Carbon and oxygen atoms

All the electrons of these atoms were included in the cluster calculations; an ECP was not used for them. The basis set is due to van Duijneveldt⁴⁰; it is the 9s5p set of primitive Gaussians with a segmented contraction of 5211 for the *s* and 311 for the *p* functions. This leads to 4s and 3p contracted Gaussian type orbitals (CGTO's) denoted (9s5p/4s3p).

2. Al atom

The basis set for the all electron Al atom is taken from the 10s6p elementary set of Roos and Siegbahn.⁴¹ An unsegmented, overlapping, contraction of 6421 for the *s* and 521 for the *p* functions due to Broer *et al.*⁴¹ is used. The final basis set is (10s6p/4s3p). The ECP for ten, Ne core, electrons is an *l* dependent potential developed by Kahn⁴² following the approach described by Kahn, Baybutt, and Truhlar⁷; it includes up to *d* components. The ECP is fit to Gaussian type functions and is of the general form:

$$V^{\text{ECP}} = V_L^{\text{ECP}}(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^{+l} |lm\rangle \times [V_l^{\text{ECP}}(r) - V_L^{\text{ECP}}(r)] \langle lm|, \quad (\text{A1})$$

$$V_L^{\text{ECP}}(r) = \sum_k d_{kl} r^{n_{kl}} \exp(-\zeta_{kl} r^2), \quad (\text{A2})$$

and

$$V_l^{\text{ECP}}(r) - V_L^{\text{ECP}}(r) = \sum_k d_{kl} r^{n_{kl}} \exp(-\zeta_{kl} r^2). \quad (\text{A3})$$

The total one electron Hamiltonian includes; the kinetic energy terms, the Coulomb attraction term Z_{eff}/r , where Z_{eff} is

TABLE A.I. The parameters of Eqs. (A2) and (A3) for the ECP for Al.

n_k	ζ_k	d_k
V_2^{ECP}		
2	1.102 342 2	-0.412 379 27
2	3.064 174 0	-4.702 049 9
2	8.570 197 3	-14.438 678
2	28.428 745	-32.301 771
2	115.137 88	-86.242 324
2	606.749 16	-250.960 51
1	1489.231 3	-3.00
$V_0^{\text{ECP}} - V_2^{\text{ECP}}$		
2	0.871 240 15	2.231 690 5
2	2.821 456 1	14.308 960
2	8.332 897 2	38.357 070
2	28.030 296	67.528 484
2	106.298 47	310.244 17
2	377.318 86	1203.619 3
0	748.438 95	3.00
$V_1^{\text{ECP}} - V_2^{\text{ECP}}$		
2	0.954 140 01	2.463 302 2
2	3.569 604 9	14.152 698
2	11.836 259	50.512 262
2	35.535 393	165.818 08
2	104.472 48	518.742 89
2	297.721 55	1359.456 0
0	485.889 18	5.00

the nuclear charge minus the number of electrons represented by the ECP ($Z_{\text{eff}} = 3$ for this Al ECP), and V^{ECP} . For the atoms where this ECP is used, the basis set for the valence electrons is 4s and 3p elementary functions contracted 31 and 3, to 2s and 1p CGTO's.⁴² This ECP and the associated valence basis set have been extensively tested and compared to all electron calculations by Cox and Bauschlicher.⁴³ The ECP basis set and the ECP parameters of Eqs. (A2) and (A3) have not been published elsewhere; they are given in Tables A.I and A.III.

3. Ni atom

The all electron basis sets used for the Ni₅ and Ni₅CO cluster calculations is taken partly from the work of Roos, Veillard, and Vinot,⁴⁴ partly from Wachters,⁴⁵ and partly from Hay.⁴⁶ The *s* basis set functions are the 12 primitive functions of Roos *et al.* with an unsegmented 632111 contraction to 6 CGTO's. The nine elementary *p* functions of Wachters for the ³F state are contracted 612 to 3 CGTO's. To represent the valence 4p character of the Ni, the two functions optimized by Wachters for the excited 3d⁸4s¹4p¹ (⁵G) state are used without contraction. The exponents were multiplied by 1.3. The five primitive *d* functions of Wachters are contracted 311 to 3 CGTO's and the diffuse *d* function of Hay is added. The basis set is (12s11p6d/6s5p4d). This basis set was used for the all electron atoms in the all AE and mixed clusters; it was also used for the one Ni atom, Ni₁CO, cluster described in Sec. III. The ECP which includes the 27

TABLE A.II. The parameters of Eqs. (A2) and (A3) for the ECP for Cu.

n_k	ζ_k	d_k
V_3^{ECP}		
2	0.267 585 40	-0.107 039 93
2	0.714 863 74	-1.630 216 40
2	1.889 211 70	-9.265 726 90
2	4.938 223 00	-25.154 441 0
2	15.187 933 0	-51.876 167 0
1	43.099 087 0	-17.895 116 0
0	131.214 940	-0.159 127 77
$V_0^{\text{ECP}} - V_3^{\text{ECP}}$		
2	0.086 091 78	-0.012 939 718
2	1.024 884 90	-9.303 371 10
2	1.267 646 10	25.247 156 0
2	5.405 950 40	50.194 659 0
2	16.714 828 0	88.649 017 0
1	29.952 061 0	22.325 913 0
0	49.795 317 0	3.011 573 80
$V_1^{\text{ECP}} - V_3^{\text{ECP}}$		
2	0.615 135 89	-8.186 452 8
2	0.728 451 13	7.826 987 3
2	0.723 346 24	6.598 095 8
2	4.871 561 10	61.159 663
2	17.657 185 0	71.384 436
1	16.881 804 0	20.175 263
0	37.133 786 0	4.983 529 1
$V_2^{\text{ECP}} - V_3^{\text{ECP}}$		
2	0.371 651 31	-8.446 513 8
2	0.423 736 20	13.610 627
2	1.902 845 90	24.682 646
2	5.548 807 30	63.411 102
2	15.273 489 0	53.970 043
1	12.265 607 0	22.084 596
0	25.755 990 0	7.019 026 3

TABLE A.III. Basis function exponents and contraction coefficients for the $2s1p$ CGTO basis sets used with the ECP's for Al and Cu.

Cu		s	Al	
Exponents	Coefficients		Exponents	Coefficients
1.147 25	− 0.0314	s	22.294 02	0.002 087
0.820 079	0.2283		1.380 277	0.153 981
0.119 652	− 0.5427		0.156 081	− 0.706 066
0.041 080	1.0		0.056 100	1.0
1.670 00	− 0.0121	p	5.339 69	− 0.008 290
0.122 00	0.2479		0.226 62	0.454 545
0.053 00	0.4164		0.060 59	0.658 827
0.021 00	0.4580			

$1s^2-3d^9$ electrons was the modified effective potential developed by Melius *et al.*⁴⁷ The parameters of Eq. (A2) and (A3) are taken from Table VI of Ref. 47 with the d_{30} term corrected from − 0.085 to − 0.85. The basis set for this ECP has 4s and 3p elementary functions, contracted 31 and 3 to $2s1p$ CGTO's. It is also taken from Ref. 47, the s function exponent of 0.1982 given in Table VI has been corrected to 0.9182.

4. Cu atom

The Cu basis set used for the all AE Cu_5 and Cu_5CO clusters is constructed in a very similar way to the Ni basis set described above. The six s CGTO's are the 12 elementary functions of Roos *et al.*⁴⁴ with a 63211 unsegmented contraction. The nine elementary p functions of Wachters⁴⁵ for the $3d^{10}4s^1$ (2S) state have a 621 segmented contraction. Wachters' two diffuse p functions for the $d^9 4s^1 4p^1$ (4F) state are added and not contracted; the exponents for these functions have been multiplied by 1.3. The d CGTO's are a 311 contraction of Wachters' five primitive functions for the 2S state. The basis set is $(12s11p5d/6s5p3d)$. This is the basis set used in all AE study of Cu_5CO by Bagus and Seel.^{26(b)} A somewhat different basis set was used for the all electron Cu atom in the mixed cluster and in the Cu_1CO cluster described in Sec. III. In this set the $14s9p5d$ elementary functions are taken from Wachters,⁴⁵ optimized for the 2S state. The s and p spaces are contracted to $8s4p$ using his scheme 1. The diffuse p functions for the $3d^{10}4p^1$ (2P) state were added without contraction and with the exponents multiplied by 1.5. In addition to the three $3d$ CGTO, contracted as in the previous set, the diffuse d function recommended by Hay⁴⁶ was used. This basis set is $(14s11p6d/8s6p4d)$.

Following the procedure given by Christansen, Lee, and Pitzer¹³ and Kahn, Hay, and Cowan,¹⁴ one of us (BCL) obtained a relativistic ECP for the 28 electron $1s^2-3d^{10}$ core of Cu. This ECP contains angular momentum components up to f . The basis set for use with this ECP was obtained by fitting the relativistic numerical $4s$ and $4p$ pseudo-orbitals for atomic Cu with four s and four p elementary GTO's; these functions were contracted 31 and 4 to form the $(4s4p/2s1p)$ basis. The basis set exponents and contraction coefficients and the ECP parameters of Eqs. (A2) and (A3) are given in Tables A.II and A.III.

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