

**AB INITIO COMPUTATIONS ON SMALL COPPER COMPOUNDS — CuO**

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Ab initio computations on CuO were performed with the Hartree–Fock method and a proper dissociation MC SCF procedure. In particular the influence of the GTO basis set for Cu in molecular computations has been studied. A potential energy curve and a Mulliken population analysis are presented. The equilibrium bond length is predicted reasonably well but the dissociation energy is only a fraction of the observed value. The bond appears to be a slightly ionic  $\sigma$ -type bond, in which metal 3d orbitals participate only to a small extent.

**1. Introduction**

Knowledge about the nature of the bond between a solid state surface and an adsorbate is a first step in understanding the mechanism of heterogeneous catalysis. In the course of a study of the role of copper in oxygenation it became apparent that information about the bond between copper and oxygen is not known experimentally. The objective of our study is to provide information from ab initio computations on CuO<sub>2</sub>. Since ab initio calculations on molecules as large as CuO<sub>2</sub> are not yet routine affairs, we now present a pilot study on CuO in order to investigate the reliability of calculations involving Cu and O. The choice of a basis set for Cu is a first objective in the present study. Four basis sets of different size are tried for Cu. The ability of these sets to describe the copper atom is examined in section 2. The performance of the basis sets for Cu in molecular computations on CuO is described in section 3. Molecular computations were performed with the single determinant HF method as well as with a MC SCF procedure. With the latter method dissociation of the molecule could be described properly. These computations were aimed at a potential energy curve and a Mulliken population analysis of the MO's.

**2. Basis sets for Cu**

For Cu only a few GTO basis sets are available in the

literature [1–3]. In this paper we study two of them in more detail, viz. Roos' (12,6,4) set and Wachters' (14,9,5) set. The third set is of the same size and quality as Wachters' set and not considered here.

(i) Roos et al. [1] optimized their (12,6,4) set for the electronic configuration ( $\dots 3d^9 4s^2$ ), i.e. the  $^2D$  state of Cu. However, the ground state of Cu is  $^2S$  ( $\dots 3d^{10} 4s^1$ ) and the  $^2D$  state lies 0.0548 au higher [4]. Using the exponents of Roos'  $^2D$  optimized basis set for a calculation of the  $^2S$  ground state leads to an energy value 0.0765 au *higher* than that for the  $^2D$  state. Contraction of the basis set as is customary in molecular calculations may make this difference even larger.

The authors of ref. [1] indicate that their set has too compact 3d exponents and too diffuse 4s exponents. Therefore the maximum of the d charge density will be too close to the nucleus and the s charge density too far away for effective participation in a bond. They suggest to replace their 4s exponents (0.131029 and 0.047955) by larger exponents (e.g. 0.32 and 0.08) and to add a fifth d function with a small exponent (e.g. 0.2). This modification reverses the order of both states (cf. table 1). Many authors who use Roos' basis sets for third-row atoms have followed the recommendations and insert less diffuse 4s functions and add an extra d function to the sets [5].

To allow for hybridization or polarization of the s functions one often adds two sets of 4p functions with about the same exponents as the 4s functions [2,5–7] to the basis.

(ii) Wachters has optimized (14,9,5) GTO basis sets for the  $^2S$  as well as for the  $^2D$  state of Cu [2]. The author claims these sets to be of double  $\zeta$  quality and the energy to be converged with respect to exponent variation up to 0.002 au. The latter is confirmed by Huzinaga [8] who reoptimized Wachters' set for Cu in the  $^2D$  state and found an energy lowering of 0.0014 au. For both Wachters' sets a gap nearly as large as found in Roos' basis exists between the 3s and 4s exponents. From table 1 it is clear that neither of Wachters' sets leads to a correct ordering of both states. As may be expected, the set optimized for the  $^2S$  state gives the best result with respect to the energy difference  $\Delta E(^2S - ^2D)$ . Wachters obtained a double set of 4p functions, required for the description of polarization effects, from an exponent optimization in the excited configurations  $^2P(\dots 3d^{10}4p^1)$  and  $^4F(\dots 3d^9 4s^1 4p^1)$  of Cu. In the present study a polarization function is obtained via a molecular energy optimization on CuO.

Table 1 summarizes the atomic energy results of the Cu basis sets mentioned above, as well as the effect of addition of the 4p polarization function to Wachters'  $^2S$  set. Moreover, two "hybrid" sets are constructed, one (set a) consisting of the s and p functions of the  $^2S$  set and the d functions of the  $^2D$  set, and one (set

b) consisting of the d functions of the  $^2S$  set and s and p functions of the  $^2D$  set. Table 1 shows that set (a) gives a poor result for the  $^2S$  energy and a good result for the  $^2D$  energy compared to the optimized sets. With set (b) only slightly higher energies are obtained for both states than with the optimized sets. From these calculations we conclude that the energy of the  $^2S$  state is very sensitive to changes in the d functions but not to changes in the s or p functions while the energy of the  $^2D$  state is rather insensitive both to changes of the d and of the s functions. It might seem that very large basis sets are required to describe the order of the Cu( $^2S$ ) and Cu( $^2D$ ) energy levels correctly. However, Clementi [9] employing an (11,6,5) STO basis set, optimized separately for both states correctly, still finds only 25% of the observed energy difference. This suggests that a major source of error is not the limited number of basis functions but the neglect of correlation effects.

### 3. Molecular calculations

#### 3.1. Basis sets

In order to test the sensitivity of molecular calcula-

Table 1  
Atomic energies of the  $^2S$  and  $^2D$  states of Cu, calculated with different basis sets <sup>a)</sup>

		$E(^2S)$	$E(^2D)$	$\Delta E(^2D - ^2S)$
Roos et al [1]	(12,6,4) (= basis I)	-1638.3356	-1638.4121	-0.0765
	(12,6,5)	-1638.4544	-1638.4480	-0.0064
	(12,7,5) (= basis II)	-1638.4707	-1638.4596	0.0111
Wachters [2]	(14,9,5) $^2S$ opt (basis III)	-1638.8735	-1638.8740	-0.0005
	(14,9,5) $^2D$ opt	-1638.8425	-1638.8745	-0.0320
	(14,10,5) $^2S$ opt (basis IV)	-1638.8740	-1638.8743	-0.0003
	(14,9,5) <sup>b)</sup>	-1638.8443	-1638.8747	-0.0304
	(14,9,5) <sup>c)</sup>	-1638.8719	-1638.8740	-0.0021
Clementi and Roetti [9]		-1638.9628	-1638.9496	0.0132
experimental [4]		-	-	0.0548

<sup>a)</sup> Energies are given in au and are calculated in a SCF computation with the same exponent sets for the  $^2S$  and the  $^2D$  states, except in Clementi's calculation

<sup>b)</sup> s and p exponents taken from the  $^2S$  opt set, d exponents from the  $^2D$  set.

<sup>c)</sup> d exponents taken from the  $^2S$  opt set, s and p exponents from the  $^2D$  set.

tions on CuO to the basis set for Cu we have used four different basis sets for Cu (table 1):

(I) Roos' original (12,6,4) set [1]

(II) Basis I modified according to the author's recommendation [1] and extended with a 4p function (exponent 0.12) to allow for polarization of the  $s$  orbital (cf. basis IV).

(III) Wachters' (14,9,5) basis set optimized for the  $2S$  state of Cu [2].

(IV) Basis III extended with a 4p function (exponent 0.12) to allow for polarization of the  $4s$  orbital (cf. basis II).

For computational reasons only one 4p function could be incorporated in the molecular calculations. Since there is little advantage in the use of two 4p sets contracted to one in describing polarization effects [10], we preferred one uncontracted 4p function. The exponent of the 4p function in sets II and IV has been obtained via an energy optimization on CuO ( $r_{\text{Cu-O}} = 3.3$  au) using a proper dissociation MC SCF function (cf. section 3.2) and basis IV for Cu. The energy was not very sensitive to variation of the exponent of this polarization function (table 2), but the total energy was lowered by approximately 0.02 au upon addition of the function. In all calculations we used a (6,3) GTO basis set for oxygen [11], which is supposedly of the same accuracy (compared to the HF limit) as the sets we use for Cu. The Cu basis sets were contracted to [5,3,2]. In the molecular computations we refer to bases I to IV when the [5,3,2] contracted bases I to IV for Cu and the [3,2] basis for O are used. For the contractions we followed a scheme of the "general" type suggested by Raffennetti [12], since this avoids large molecular

energy losses caused by a bad description of the atomic orbitals. In the contracted bases all inner shells are described by the atomic orbitals optimized in an atomic SCF calculation, while the outer shell in each symmetry (s,p,d) is described by two functions as recommended by Raffennetti [12]: the atomic SCF orbital and the gaussian with the most diffuse exponent in that symmetry. Thus we obtained a split valence contraction, which is capable of describing the atom adequately, while retaining the flexibility in the valence region. The molecular integral computations were done with the aid of the integral program BIGMOLI [13] which takes advantage of the molecular symmetry.

In the calculations on CuO the starting MO's were obtained from a closed shell determinant computation in basis I on  $\text{CuO}^-$ . The seven innermost MO's were virtually identical to the 1s, 2s, 3s and 2p AO's on Cu and the 1s AO on O. These seven MO's were kept fixed to this result in all other SCF calculations. Irrespective of the set (I, II, etc.) chosen, the MO coefficients are identical, since they refer to the AO's 1s, 2s, etc. in the general contraction scheme we adopt. Test calculations with basis I in which all MO's were varied, indicate that this approximation causes an error in the total energy of about 0.0001 au.

### 3.2. Proper dissociation MC SCF function

Multiconfiguration calculations were performed with a proper dissociation MC SCF function ("PD MC SCF function") for CuO. At large internuclear distance this wavefunction represents the antisymmetrized product of the HF ground state functions for Cu [4] and O [4]. The ground state of the molecule CuO is  $^2\Pi$  [14]. Presently the proper dissociation function for CuO ( $^2\Pi$ ) is derived. The spin function for a doublet obtained by combining the Cu doublet function and the O triplet function may be shown to be:

$$\left(\frac{2}{3}\right)^{1/2} \beta\alpha\alpha - 6^{-1/2} \alpha\alpha\beta - 6^{-1/2} \alpha\beta\alpha. \quad (1)$$

For the  $\Pi_+$  and  $\Pi_-$  components we write the proper dissociation function in terms of AO's, using the spin functions (1) and taking the  $z$  axis as the internuclear axis:

Table 2

Optimization of a 4p polarization function in CuO ( $r_{\text{Cu-O}} = 3.37$  au) with the PD MC SCF method and Wachters' basis set for Cu( $2S$ ) [2] a)

$\alpha(4p)$	$E$
0 1	-1713 537278
0 12	-1713 537812
0 14	-1713 537562
0 17	-1713 536202
-	-1713.518765

a) Values are given in au.

$$\begin{aligned} \Psi(2\Pi_+) &= \left(\frac{2}{3}\right)^{1/2} |(\text{core})\bar{s}p_{+1}\bar{p}_{+1}p_0p_{-1}| \\ &\quad -6^{-1/2} |(\text{core})sp_{+1}\bar{p}_{+1}p_0\bar{p}_{-1}| \\ &\quad -6^{-1/2} |(\text{core})sp_{+1}\bar{p}_{+1}\bar{p}_0p_{-1}|, \end{aligned} \quad (2a)$$

$$\begin{aligned} \Psi(2\Pi_-) &= \left(\frac{2}{3}\right)^{1/2} |(\text{core})\bar{s}p_1\bar{p}_1p_0p_{+1}| \\ &\quad -6^{-1/2} |(\text{core})sp_1\bar{p}_1p_0\bar{p}_{+1}| \\ &\quad -6^{-1/2} |(\text{core})sp_{-1}\bar{p}_{-1}\bar{p}_0p_{-1}|. \end{aligned} \quad (2b)$$

In (2a) and (2b)  $s$  is the 4s orbital of Cu,  $p_{+1}$ ,  $p_0$  and  $p_{-1}$  are the 2p orbitals on O; (core) denotes the core, defined by the doubly occupied inner orbitals of Cu and O.

From (2a) and (2b) a real wavefunction  $\Psi_{\Pi}$  may be constructed in terms of the orbitals  $p_x$ ,  $p_y$  and  $p_z$ .

$$\begin{aligned} \Psi(\Pi) &= \left(\frac{2}{3}\right)^{1/2} |s\bar{p}_x p_y \bar{p}_y p_z| - 6^{-1/2} |s\bar{p}_x p_y \bar{p}_y \bar{p}_z| \\ &\quad - 6^{-1/2} |s\bar{p}_x p_y \bar{p}_y p_z|. \end{aligned} \quad (3)$$

For brevity the (core) is deleted from the formula. In CuO the bond is formed between 4s on Cu and 2p<sub>z</sub> on O in the MO  $\psi_{\sigma} = 2^{-1/2}(s + p_z)$ . The associated anti-bonding MO is  $\psi_{\sigma}^* = 2^{-1/2}(s - p_z)$ . In the molecule  $p_x$  and  $p_y$  become the non-bonding orbitals  $\pi_x$  and  $\pi_y$ .

Substituting these MO's in formula (3) one obtains the proper dissociation (PD) function (4) at  $r = \infty$  in terms of MO's:

$$\begin{aligned} \Psi(2\Pi) &= \frac{3}{2} (6^{-1/2} |\psi_{\sigma} \bar{\psi}_{\sigma} \pi_x \pi_y \bar{\pi}_y| - 6^{-1/2} |\psi_{\sigma}^* \bar{\psi}_{\sigma}^* \pi_x \pi_y \bar{\pi}_y|) \\ &\quad - \frac{1}{2} (2(6^{-1/2}) |\psi_{\sigma} \psi_{\sigma}^* \pi_x \pi_y \bar{\pi}_y| - 6^{-1/2} |\bar{\psi}_{\sigma} \bar{\psi}_{\sigma}^* \pi_x \pi_y \bar{\pi}_y|) \\ &\quad + 6^{-1/2} |\psi_{\sigma} \bar{\psi}_{\sigma}^* \pi_x \pi_y \bar{\pi}_y|. \end{aligned} \quad (4)$$

In order to ensure that throughout the SCF process a  $\Pi$  state is described an equivalence restriction is imposed on  $\pi_x$  and  $\pi_y$ . In (4),  $|\psi_{\sigma} \bar{\psi}_{\sigma} \pi_x \pi_y \bar{\pi}_y|$  is identical to the HF determinant. We note that (4) is derived for a dissociation of CuO( $2\Pi$ ) in Cu( $2S$ ) and O( $3P$ ) but the function may describe dissociation in Cu( $2D$ ) and O( $3P$ ) as well. In this case the MO's  $\psi_{\sigma}$  and  $\psi_{\sigma}^*$  will be constructed from 3d<sub>z<sup>2</sup></sub> on Cu and 2p<sub>z</sub> on O.

All SCF calculations were performed with a MC SCF program [15]. In computations with the HF method the use of this program allows the necessary symmetry restrictions on  $\pi_x$  and  $\pi_y$ .

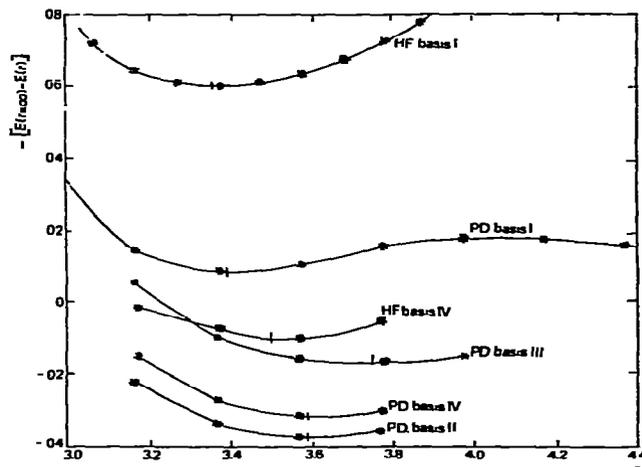


Fig 1 Potential energy curves obtained in the different molecular computations on CuO.  $-[E(r = \infty) - E(r)]$  is plotted against  $r$  for all calculations. All values are in au. Calculations are indicated by \*, the minima in the curves by †

### 3.3 Results

The potential energy curves for CuO using the basis sets I to IV are presented in fig. 1. In all bases PD MC SCF calculations were performed; in bases I and IV HF calculations as well. The calculated internuclear distances  $r_e$  and dissociation energies  $D_e$  are shown in table 3. Using basis I the CuO molecule is not stable relative to the ground state atoms, neither in the HF nor in the PD

Table 3

Summary of the results of molecular computations on CuO with different basis sets for Cu (see text) a)

Basis for Cu	$r_e$	$D_e$ b)
basis I, HF method	3.36	-0.060
PD MC SCF	3.38	-0.008
basis II, PD MC SCF	3.59	0.037
basis III, PD MC SCF	3.75	0.016
basis IV, HF method	3.50	0.009
PD MC SCF	3.59	0.031
experimental	3.356 c)	≈ 0.10-0.13 d)

a) All values are in au.

b)  $D_e$  is defined as  $E_{r=\infty} - E_{r=r_e}$ .

c) Refs [16,17].

d) Refs [14,18].

MC SCF computations. With the latter method a maximum occurs in the potential curve at  $r = 4.1$  au as shown in fig. 1b. It is well known that a HF function does not always predict stability correctly (viz. on  $F_2$  in ref. [19]) but if a PD MC SCF function does not predict a stable molecule a basis set deficiency of some kind may be present. With basis II a stable CuO is predicted with the PD MC SCF method. The use of bases III or IV leads to a prediction of stable CuO with the HF function (IV) as well as with the PD MC SCF function (III and IV). Addition of a 4p polarization function to basis III ( $\equiv$  basis IV) shortens the bond length  $r_e$  and increases the bond energy. In these computations with basis I and more pronounced with IV a larger internuclear distance is obtained than with the HF method. Apparently the observed  $D_e$  is not known with great accuracy, since different values are tabulated ( $D_e \approx 0.10$ – $0.13$  au) [14,18], but  $D_e$  calculated with the PD MC SCF

method and basis II or IV is rather poor (viz. 25–30% of the observed value). A HF computation with basis IV yields only 9%, though in studies of other metal oxides [16,17] dissociation energies calculated in this way have been reported around 25% of the observed result. The internuclear distances calculated with basis I are close to the observed bond length in the gas phase [20], with all other bases for Cu worse results are obtained in this respect.

A Mulliken population analysis of the MO's was performed for all computations at distances near the calculated equilibrium distance. The results for the highest  $\sigma$  MO's are the most interesting. These are given in table 4. From this table it is apparent that in the HF and PD MC SCF computations with basis I the bond is largely formed in the MO's  $8\sigma$  and  $9\sigma$ . In both MO's much participation of the metal 3d is observed. In the computations with all other bases the bond is largely

Table 4

Mulliken population analysis of the highest  $\sigma$  MO's of Cu in the different bases. All values are given in au and the populations are normalized to the occupation of the MO's

	Basis I, HF, $r = 3.37$		Basis I, PD MC SCF, $r = 3.37$		Basis II, PD MC SCF, $r = 3.57$		Basis III, PD MC SCF, $r = 3.77$		Basis IV, HF, $r = 3.57$		Basis IV, PD MC SCF, $r = 3.57$		
	Cu	O	Cu	O	Cu	O	Cu	O	Cu	O	Cu	O	
$8\sigma$ population	(s)	0.09	0.00	0.85	0.00	0.09	0.02	0.11	0.02	0.10	0.02	0.09	0.02
	(p)	0.00	0.46	0.00	1.15	0.00	0.00	0.00	0.01	0.02	0.00	0.01	0.00
	(d)	1.45		0.00		1.88		1.86		1.86		1.88	
	sum	1.54	0.46	0.85	1.15	1.97	0.02	1.97	0.03	1.98	0.02	1.98	0.02
$9\sigma$ population	(s)	0.69	0.00	0.38	0.00	0.33	0.01	0.54	0.00	0.30	0.05	0.43	0.01
	(p)	0.00	1.16	0.00	0.30	0.06	1.45	0.00	1.36	0.08	1.53	0.06	1.45
	(d)	0.15		1.06		0.11		0.00		0.04		0.01	
	sum	0.84	1.16	1.44	0.30	0.50	1.46	0.54	1.36	0.42	1.58	0.50	1.46
$10\sigma$ population <sup>a)</sup>	(s)			0.11	0.00	0.02	0.00	0.06	0.00			0.03	0.00
	(p)			0.00	0.05	0.00	0.02	0.00	0.03			0.00	0.02
	(d)			0.10		0.01		0.00				0.00	
	sum			0.21	0.05	0.03	0.02	0.06	0.03			0.03	0.02
total population	28.39	8.61	28.48	8.52	28.65	8.35	28.61	8.39	28.51	8.49	28.61	8.39	

<sup>a)</sup>  $10\sigma$  is the antibonding MO used in the PD MC SCF function.

formed in the MO  $9\sigma$  and participation in the bond by  $3d$  is much less. We also note a striking difference in the character of the MO's  $8\sigma$  and  $9\sigma$  between the HF and PD MC SCF computations with basis I. In the computations with basis IV this large difference does not show up. The net charge transfer found in PD MC SCF computations with bases II, III and IV is about 0.4 from Cu to O. In the HF computation with basis IV 0.5 is transferred.

#### 4. Conclusions

(i) The only basis set in this study with which a correct order of the  $^2S$  and  $^2D$  state is predicted is the set of Roos et al. [1] modified according to the authors' recommendations. It is concluded that the energy of the  $^2S$  state is much more sensitive to changes in the  $d$  functions than the  $^2D$  state energy, but both states are rather insensitive to changes in the  $s$  or  $p$  functions.

(ii) Molecular computations show that with basis I (cf. section 3.1) CuO is predicted to be unstable both via the HF method and via the PD MC SCF method. Moreover, a maximum occurs in the potential curve obtained via the PD MC SCF method. This maximum may be related to the prediction of a ground state Cu( $^2D$ ) by this set. Since  $^2D$  is a repulsive state for a bond between Cu and O( $^3P$ ), the minimum must be obtained from the interaction between Cu( $^2S$ ) and O( $^3P$ ). We therefore tentatively ascribe the form of the potential curve to an avoided crossing of the atomic Cu levels  $^2S$  and  $^2D$ .

(iii) With bases II, III or IV a stable CuO molecule is predicted both with the HF method and the MC SCF method. Addition of a  $4p$  polarization function improves the stability and shortens the bond length. With the PD MC SCF method 25–30% of the observed dissociation energy is obtained in bases II and IV. The bond length in bases II and IV obtained via the PD MC SCF method is about 7% (0.23 au) too long compared to the observed value. From the large energy lowering upon addition of the  $4p$  function, viz. 0.02 au in basis IV, we conclude that polarization of the metal  $4s$  AO is an important factor in the bond formation. Our data for the internuclear distance and dissociation energy indicate that correlation may play a large role in the CuO bond. This suggests that a CI computation of the potential curve might improve the result. Bagus, in a

SCF CI study on FeO [17] obtained an important improvement of  $D_e$ , viz. from 25% of the observed value in the SCF computation to about 50% in a limited CI computation. The corresponding improvement of the bond length was 2% (0.07 au). A limited CI computation on CuO is presently being carried out in our laboratory.

(iv) From the Mulliken population analysis of the MO's it becomes clear that the bond is mainly formed by the interaction between the  $4s$  orbital of Cu and a  $2p$  orbital on O with a minor participation of the  $3d$  orbital. The CuO bond is shown to be only slightly ionic. If we might extrapolate the latter result to the situation of absorbed O atoms on a Cu crystal surface, we might conclude that the metal–metal bonds are hardly influenced by the absorbed oxygen, at least for low surface coverages.

(v) Comparing bases II and IV we conclude that both behave very similar in the molecular computations and lead to the same conclusions for CuO. Basis III has the advantage of a smaller number of basis functions and thus requires less integral computation time than basis IV. However, we consider Roos' modifications as rather arbitrary which is in our opinion a disadvantage. Moreover, the integral computation time is only a fraction of the total calculation time. For these reasons we prefer basis IV for future computations on molecules involving Cu, e.g. CuO<sub>2</sub>.

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