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COMMENTS ON THE ELECTRONIC STRUCTURE
OF DIMERIC COPPER, AS CALCULATED WITH
THE HARTREE-FOCK-SLATER METHOD

by

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1. INTRODUCTION

The interest in transition metal dimers has increased rapidly in the last years. Although only a few of these species were actually detected as molecules in the gaseous state, academic interest was revived by the technique known as matrix isolation, which allowed the formation of a great number of these dimers trapped in non-interacting solid noble-gas matrixes⁽¹⁾. These could then be studied by different spectroscopies, which may be helpful in elucidating some aspects of the metal-metal bond.

The investigation of properties of transition metal dimers has also important practical motivations; one of them is related to heterogeneous catalysis and chemisorption⁽²⁾. It is believed that a better knowledge of the bond between two transition metal atoms may be the first step in understanding larger metal clusters or surfaces⁽³⁾.

One useful tool to be employed in the study of the electronic structure of transition metal dimers, among other molecular orbital procedures, is the first principles LCAO numerical discrete variational (DVM) method⁽⁴⁾, which is self-consistent (SCF) and makes use of the local $x\alpha$ approximation for the exchange interaction⁽⁵⁾. The DVM method has been recently employed in a study of the electronic structure and hyperfine interactions of iron dimers⁽⁶⁾. It would be useful to compare the performance of the DVM method with standard "ab initio" procedures, which have been employed to investigate a limited number of homonuclear first-row transition metal dimers. In this letter are reported and discussed some aspects of the electronic structure of Cu_2 as obtained by the DVM method.

The choice of Cu_2 was based on the fact that, unlike other dimeric molecules of transition elements which have ground state high-spin configurations as yet undetermined, Cu_2 has a ground state which can be unambiguously assigned to a closed-shell $1\Sigma_g^+$. Moreover, the equilibrium interatomic distance is known in the gas state.

2. SUMMARY OF THE CALCULATION PROCEDURE

The DVM method was employed in its standard form⁽⁴⁾, with the inclusion of all electrons. The one-electron equations to be solved are of the form

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{coul}} + V_{\chi\alpha} \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (1)$$

(in Hartrees) where $\psi_i(\vec{r})$ are molecular orbitals expressed as linear combinations of symmetry functions obtained from numerical Hartree-Fock- $\chi\alpha$ ⁽⁵⁾ atomic orbitals. The interelectronic component of the Coulomb potential V_{coul} was approximated expanding the molecular electronic charge density as a sum over spherical densities around each nucleus, weighed by the Mulliken population P_i of the orbitals in each atom

$$\rho(\vec{r}) \cong \sum_i P_i \delta_i(r) \quad (2)$$

where the sum is over all occupied atomic orbitals of both atoms⁽⁷⁾

The populations P_i are iterated to self-consistency.

The exchange term $V_{\chi\alpha}$ in equation (1) is the standard local term proposed by Slater⁽⁵⁾

$$V_{\chi\alpha}(\vec{r}) = -3\alpha \left[(3/8\pi) \rho(\vec{r}) \right]^{1/3} \quad (3)$$

where $\alpha = 2/3$ has been used⁽⁸⁾ for both atom and molecule.

An expanded numerical Hartree-Fock-Slater atomic basis was used for copper, with the inclusion of the vacant 4p, 4d, 5s and 5p orbitals. The configuration considered was $3d^{10}4s$. For the obtention of the wave functions of such diffuse orbitals, the use of a spherical attractive potential well in the atomic calculations was necessary.

3. ELECTRONIC STRUCTURE OF DIATOMIC COPPER

Bonding in Cu_2 results from the combination of 4s orbitals which form σ orbitals and of 3d orbitals which form e_g , t_2g and π . The 3d orbitals need shorter distances to interact, since they are considerably more contracted. In Fig. 1 are shown the valence eigenvalues ϵ_i obtained for Cu_2 with the DVM method, for $D_{\infty h}$ symmetry at several interatomic distances and configuration $(6e_g^2 3t_2g^4 1t_2g^4 7\sigma_g^2 1t_2g^4 3\pi_g^4 6\sigma_u^2)$. The experimental equilibrium distance is 2.22\AA ⁽⁹⁾. Also shown in Fig. 1 are the 3d and 4s level energies for atomic copper in configuration $3d^{10}4s^1$, obtained from a Hartree-Fock-Slater spin-restricted calculation. It may be seen that at large distances the energies of the orbitals $7\sigma_g$ and $7\sigma_u^*$ converge to the 4s level and the remaining molecular orbitals to the 3d. At shorter distances and in the vicinity of the equilibrium distance, there is considerable splitting of all levels indicating strong interaction between both 4s and 3d orbitals.

In Table 1 are given the populations of the atomic orbitals at 2.22\AA and 4.76\AA , after self-consistency was achieved. It may be seen that the populations are very similar to that of atomic copper in configuration $3d^{10}4s^1$. At 2.22\AA another calculation

was performed with basis functions corresponding to $\text{Cu } 3d^9 4s^2$, but still the final configuration of copper in the dimer was very much near $3d^{10} 4s^1$. The diffuse orbitals 4d, 5s and 5p have very small populations; however, their inclusion in the basis was found to have an important effect in the eigenvalues ϵ_i .

In Table 2 is shown the population analysis of the valence levels, for the equilibrium distance and for 4.76Å. Observing this table and Fig. 1, it is clear that 4s electrons form a bond through the $7\sigma_g$ orbital, which at short distances also has some 3d character. The antibonding counterpart of $7\sigma_g$ is the first empty $7\sigma_u^*$ orbital which at 2.22Å has some 4p character. At large distances, $7\sigma_g$ and $7\sigma_u^*$ become pure 4s as their eigenvalues approach, and the other orbitals merge to form the 3d level.

It is known that homonuclear diatomic molecules, as treated by an LCAO molecular orbital model, may present different self-consistent solutions depending on whether or not the full point symmetry $D_{\infty h}$ is imposed for the orbitals⁽¹⁰⁾. Lowering the symmetry to $C_{\infty v}$, that is, removing the mirror plane between the atoms, may lead to another self-consistent solution which in principle will have a lower total energy since the variational freedom is larger. It would be interesting to investigate this effect on the one-electron eigenvalues of the present case. In Table 3 are shown for Cu_2 at 2.22Å the valence eigenvalues for symmetries $D_{\infty h}$ and $C_{\infty v}$. It is seen that the values are slightly lower ($\sim 0.2\text{eV}$) for $C_{\infty v}$. Calculations at other distances showed this effect to be more pronounced at shorter distances. At very large distances, levels for $C_{\infty v}$ also converge to the atomic values. The difference for the two symmetries is less pronounced for the more

diffuse orbitals $7\sigma_g$ ($\equiv 12\sigma$) and $7\sigma_u^*$ ($\equiv 14\sigma^*$). In Table 1 are compared the self-consistent populations for both symmetries. At shorter distances, the general trend is a slight increase in the $4s$ population and decrease in $3d$, when lowering the symmetry to $C_{\infty v}$; This may be understood considering that the more stable solution will represent a stronger bond, which is achieved mainly via $4s$ electrons.

In Table 3 are displayed eigenvalues for Cu_2 , reported by other authors, for the purpose of comparison. One may observe that the $\chi\alpha$ -multiple scattering (MS- $\chi\alpha$) method produces energies⁽¹¹⁾ that are quite similar to the DVM values. However, the LCAO-Hartree Fock ("ab initio")⁽¹²⁾ one electron levels are very different, in two respects. First, they are much lower than the $\chi\alpha$ values; second, the last occupied level is the $7\sigma_g$ of almost pure $4s$ character⁽¹²⁾⁽¹³⁾, whereas in the $\chi\alpha$ calculations the last occupied level is $6\sigma_u$ (13σ in $C_{\infty v}$) which is part of the $3d$ "band". In the DVM and MS- $\chi\alpha$ calculations, the $7\sigma_g$ level (12σ in $C_{\infty v}$) is found at lower energies, among the $3d$ levels, and shows considerable $3d$ - $4s$ mixing.

This apparent discrepancy may be understood if one takes into account the different meanings of the Fock operator eigenvalues and the eigenvalues of the DVM and MS models with the $\chi\alpha$ exchange approximation. The former eigenvalues, according to Koopmans' theorem, represent approximately the ionization potentials of the electrons in the molecule; the latter have no such physical meaning. However, ionizations potentials may be obtained through the use of the transition state concept⁽⁵⁾ a SCF calculation is performed (spin-polarized) for a "transition state" in which $1/2$ electron has been removed from the orbital in question. The eigenvalue of this

orbital will then represent, to a good approximation, the ionization potential with reversed sign.

In Table 3 are given the ionization potentials relative to the four outer orbitals of Cu_2 , calculated with the DVM method in the manner described above. It is seen that there is indeed a large difference with respect to the orbital eigenvalues. The transition state procedure produces ionization potentials which are much higher, and also reverses the result indicated by mere observation of the eigenvalues in that the first ionized electron is in the orbital $7\sigma_g$ with mainly 4s character. These results are now qualitatively consistent with the "ab initio" calculation. The DVM ionization potentials are somewhat lower; in theory, the χ_a transition state values should be more accurate in the sense that it takes into account relaxation effects. The author is not aware of reliable experimental values with which to compare.

The lower symmetry calculations of transition state ionization potentials show an increase of as much as -0.8eV for the 3d electrons, but a much smaller effect for the σ electrons of 4s character.

A similar discrepancy between one-electron energies and transition state ionization potentials is obtained for atomic copper with the Hartree-Fock-Slater method. As seen in Table 3, the spin polarized calculation of $\text{Cu}(3d^{10}4s^1)$ gives a level ordering $4s_{\uparrow} < 3d_{\uparrow} < 3d_{\downarrow}$, but the first ionization is from the 4s level. The calculated value 7.56eV compares well with the experimental value 7.73eV ⁽¹⁴⁾.

In summary, this calculation for dimeric copper shows that the χ_a approximation has to be used with caution, when one is considering such molecules with valence levels of very different natu-

res as to spacial delocalization. The ordering of the orbital energies obtained may be misleading, as well as orbital composition. In the present case, the $6\sigma_g$ and $7\sigma_g$ orbitals present considerable $4s$ $3d$ mixing; however, as seen in Table 1, SCF calculations for Cu_2^{+1} indicate that an electron removed from $6\sigma_u$ is almost purely $3d$, and from $7\sigma_g$ is almost purely $4s$.

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TABLE CAPTIONS

Table 1:

Atomic populations for Cu_2 and Cu_2^{+1}

Table 2:

Main contributions of atomic orbitals in population analysis of the valence levels of Cu_2 in $D_{\infty h}$ symmetry; at interatomic distances 2.22\AA and 4.76\AA .

Table 3:

One-electron levels of atomic and dimeric copper. Energies in eV.

a) From reference (11). α value used for Cu: 0.707, $r_e = 2.22\text{\AA}$.

b) Values obtained approximately from Figure 3 in reference (12), for $r_e = 2.22\text{\AA}$.

TABLE 3

Cu(3d ¹⁰ 4s ¹)			Cu ₂ -D _{∞h} (DVM)		Cu ₂ -C _{∞v} (DVM)			Cu ₂ -D _{∞h} (MS-Xα) (a)		Cu ₂ -D _{∞h} ("ab initio") (b)	
spin restricted one-electron eigenvalues	spin polarized one-electron eigenvalues		one-electron eigenvalues ε _i	ionization potentials	one-electron eigenvalues ε _i	ionization potentials	one-electron eigenvalues	ionization potentials	one-electron eigenvalues	ionization potentials	
3d	-4.29	3d _{z²} ^S -4.20	10.34	6σ _g -6.85	-	11σ	-7.05	-	6σ _g -6.47	6σ _g -13.4	
4s	-3.77	3d _{xy} ^S -4.11	10.08	3π _u -6.01	-	5π	-6.25	-	3π _u -5.42	3π _u -13.1	
		4s _{z²} ^S -4.32	7.56	1δ _g -5.45	-	1δ	-5.69	-	1δ _g -5.00	1δ _g -12.6	
				7σ _g (4s) -5.31	9.33	2δ(3d)	-5.46	14.66	1δ _u (3d) -4.77	1δ _u (3d) -12.4	
				1δ _u (3d) -5.21	13.93	12σ(4s)	-5.45	9.49	7σ _g (3d,4s) -4.74	3π _g (3d) -12.1	
				3π _g (3d) -4.96	13.79	6π(3d)	-5.21	14.52	3π _g (3d) -4.43	6σ _u (3d) -11.7	
				6σ _u (3d) -4.92	13.58	13σ(3d)	-5.16	14.24	6σ _u (3d) -4.38	7σ _g (4s) -6.3	
				7σ _u [*] -2.64	-	14σ [*]	-2.71	-	7σ _u [*] -1.99	-	

	$\text{Cu}_2 - D_{\infty h}$		$\text{Cu}_2 - C_{\infty v}$	
	2.22\AA	4.76\AA	2.22\AA	4.76\AA
3d	9.961	9.997	9.953	9.996
4s	0.981	0.999	0.988	0.999
4p	0.013	0.002	0.008	0.002
4d	0.007	0.	0.013	0.001
5s	0.009	0.001	0.013	0.001
5p	0.029	0.	0.029	0.001

$\text{Cu}_2^{+1} - D_{\infty h}$				
	$6\sigma_{u\uparrow}^0$		$7\sigma_{g\uparrow}^0$	
	$6\sigma_{u\uparrow}^1$	$6\sigma_{u\uparrow}^1$	$7\sigma_{g\uparrow}^1$	$7\sigma_{g\uparrow}^1$
	spint	spint	spint	spint
3d	4.46	4.96	4.94	4.97
4s	0.43	0.42	0.03	0.44
4p	-0.	-0.	-0.	-0.

TABLE I

	2.22\AA	4.76\AA
	$6\sigma_g$	33%(4s), 64%(3d)
$3\pi_u$	-100%(3d)	-100%(3d)
$1\delta_g$	-100%(3d)	-100%(3d)
$7\sigma_g$	62%(4s), 37%(3d)	97%(4s)
$1\delta_u$	-100%(3d)	-100%(3d)
$3\pi_g$	-100%(3d)	-100%(3d)
$6\sigma_u$	98%(3d)	99%(3d)
$7\sigma_u^*$	76%(4s), 20%(4p)	99%(4s)

TABLE II

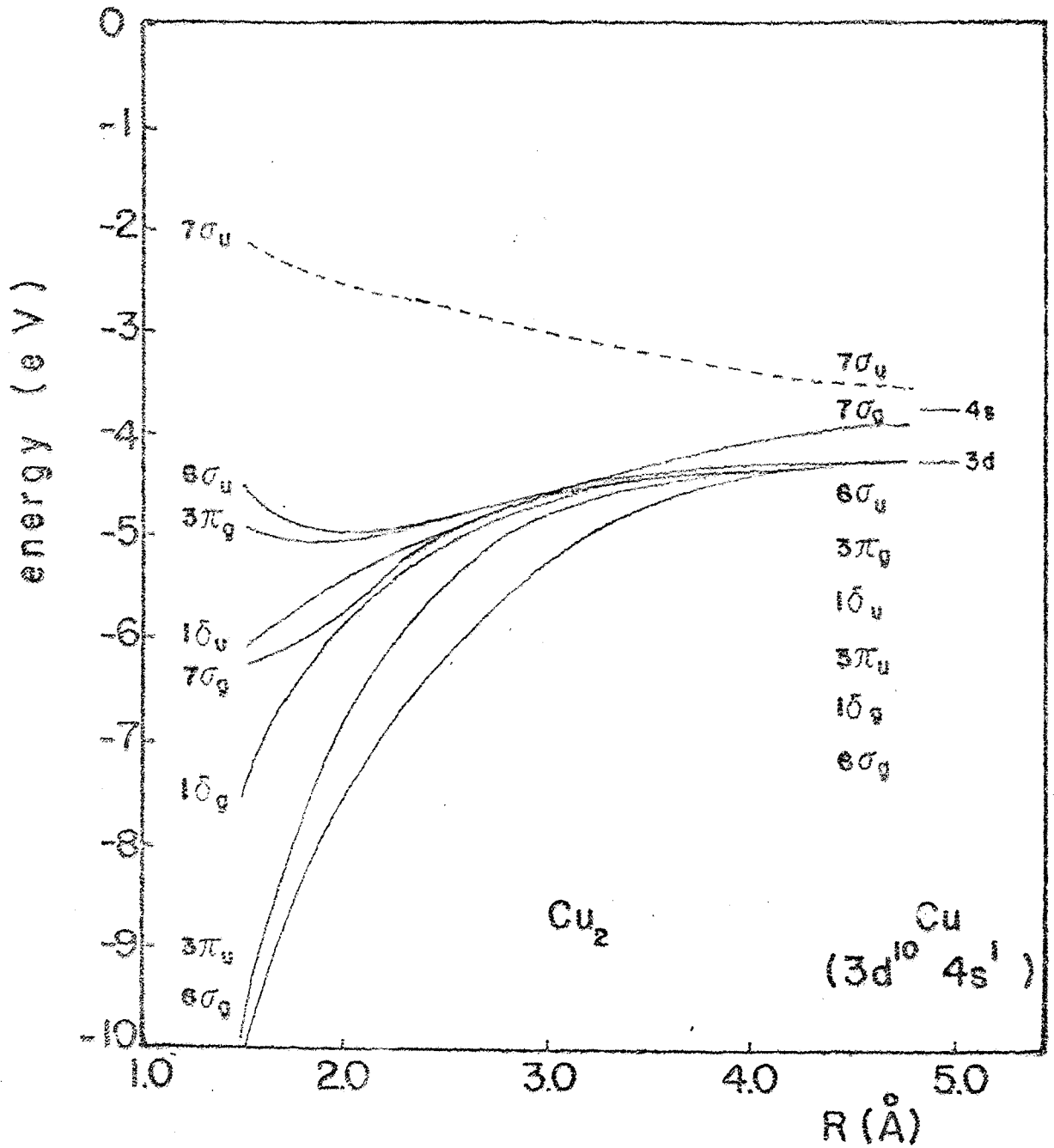


FIGURE I

Valence eigenvalues of dimeric copper (D_{oh}) and atomic copper.