Theor Chim Acta (1988) 74: 151-155

Theoretica Chimica Acta

Numerical Hartree–Fock and MCSCF calculations on diatomic copper: calibration of basis sets

Harry Partridge[1], **Kent W. Richman**[2], **and E. A. McCullough, Jr.**[2]

[1] NASA Ames Research Center, Moffet Field, CA 94035, USA
[2] Department of Chemistry and Biochemistry, Utah State University 0300, Logan, UT 84322, USA

(Received September 23/Accepted September 29, 1987)

NHF and NMCSCF results for Cu_2 are compared with calculations employing basis set expansions. We find that nearly all previous SCF calculations using Gaussian basis sets have underestimated the bond length by about the same amount (0.03 Å) as that attributed to the unlinked cluster and relativistic corrections. The error is shown to be due to deficiencies in the 3d primitive set which yield sizable basis set superposition errors.

Key words: Numerical Hartree-Fock — Basis set — MCSCF

The Cu dimer has become a benchmark system for theoreticians since the ground state of Cu_2 is well characterized experimentally [1] and its electronic structure is somewhat simpler than the other transition metal dimers [2]. The bonding in Cu_2 is essentially a 4s-4s bond, yet to obtain quantitative results, it is crucial to correlate the 3d shell [3]. The importance of basis set effects [4], unlinked cluster corrections [4-6] and relativistic effects [4, 6-7] have all been previously discussed. However, the accuracy of the resulting spectroscopic parameters (r_e, w_e and D_e) is still not as high as that found for the first- and second-row atoms where the spectroscopic constants can be computed to chemical accuracy; e.g. D_e to 1 kcal/mole and r_e to 0.005 Å [8]. Furthermore, recent STO results [9] for r_e differ from the published GTO results [4, 6]. In order to improve the GTO results, it is important to determine the origin of this difference and to understand the deficiencies of such calculations. In this work we report numerical restricted Hartree-Fock (NRHF) and numerical multiconfiguration self-consistent-field (NMCSCF) calculations for Cu_2 to calibrate, at these levels, the 1-particle basis sets commonly employed in molecular calculations and determine how best to correct the deficiencies. While NHF and NMCSCF calculations will not yield quantitative results for Cu_2, they provide an "exact" result with which to calibrate the 1-particle basis set. Our main finding is that nearly all previous SCF calculations using Gaussian basis sets have underestimated the bond length by about the same amount (0.03 Å) as that attributed to the unlinked cluster and relativistic corrections. The principal source of error is shown to be deficiencies in the 3d primitive set which results in a sizable basis set superposition error (BSSE). It is important to minimize the BSSE errors for quantitative results on Cu_2 as well as other transition metal compounds. This will be particularly true for weakly bound systems such as the transition metal–water complexes [10].

The NRHF and NMCSCF calculations were carried out using the partial-wave procedure of McCullough [11] and the final results are shown in Table 1. The NMCSCF calculations are valence 2-electron treatments which correlate the 4s-like orbitals. The NMCSCF(4) calculation is a 4 configuration expansion formed from the $7\sigma_g$, $8\sigma_g$, $7\sigma_u$, and the $4\pi_u$ orbitals which correspond to the bonding and antibonding 4s-like orbitals and configurations to describe the 4s–4p near degeneracy. These configurations are the important configurations from a CASSCF wavefunction in which the 4s and 4p orbitals are active and this calculation should correspond closely with the CASSCF results reported by Bauschlicher [12]. The 3d, 4s, and 4p orbitals were optimized in the MCSCF but the remaining orbitals were frozen in their RHF form. The NMCSCF(13) adds

Table 1. Restricted Hartree-Fock and MCSCF properties of Cu_2

Basis	D_e (eV)	r_e (Å)		
A	0.55	2.423	(14s11p6d3f)/[8s6p4d2f]	Scharf et al. [6]
B	0.56	2.423	(16s11p6d3f)/[10s7p4d3f]	Scharf et al. [6]
C	0.51	2.44	(15s11p6d2f)/[9s6p4d2f]	Werner and Martin [5]
D	0.52	2.400	(14s11p6d2f)/[8s7p3d2f]	Raghavachari et al. [14]
E	0.58	2.423	(15s11p6d4f1g)/ [9s7p4d3f1g]	Langhoff and Bauschlicher [4]
F	0.58	2.424	Basis E-g orbital	
F(−BSSE)	0.53	2.442		
G	0.58	2.426	Basis F employing a general contraction	
H	0.52	2.418	(15s11p6d) uncontracted	
ANO [6s4p3d]		2.418	(15s11p6d) primitive set	
ANO [6s5p4d]	0.49	2.444	(17s13p9d) primitive set	
ANO [7s6p5d]	0.49	2.444	(17s13p9d) primitive set	
I		2.446	(9s7p5d3f2g) STO	McLean [19]
J	0.52	2.44	(12s10p7d3f1g)	Tatewaki and Sekiya [9]
NRHF[a]	0.52	2.447		
MCSCF	1.25	2.44		Bauschlicher [12]
NMCSCF(4)[a]	1.24	2.461		
NMCSCF (13)[a]	1.25	2.461		

[a] Energies at $r = 4.6$, E(NRHF) = −3277.94661, E(MCSCF(4)) = −3277.97289, E(MCSCF(13)) = −3277.97357

four σ, three π, and two δ orbitals and is expected to be near the 2-electron valence limit for Cu_2.

The spectroscopic properties were computed by quadratic interpolation in r using the energies at 4.5, 4.6, and 4.7 bohr; interpolation in $1/r$ or using more points changes r_e by at most a few units in the third decimal. The absolute error in the molecular energy should not exceed about 2×10^{-5} Hartree. This was determined by comparing the energy of Cu computed as a diatomic molecule with the energy obtained from Fischer's numerical atomic code [13]. The spectroscopic properties are very well converged.

Since most molecular calculations employ an STO or GTO basis set, we compare the NHF results with a representative sample of recent results in Table 1. Most previous calculations on Cu_2 have employed contracted gaussian basis sets. Sets A and B are the (14s11p6d3f)/[8s6p4d2f] and (16s11p6d3f)/[10s7p4d3f] bases of Scharf et al. [6]. Set C is the (15s11p6d2f)/[9s6p4d2f] basis of Werner and Martin [5], and set D is the (14s11p6d2f)/[8s7p3d2f] basis of Raghavachari et al. [14]. Basis E is the (15s11p6d4f1g)/[9s7p4d3f1g] set of Langhoff and Bauschlicher [4] and basis F is the same as basis E with the g functions deleted. Basis G uses the same primitive set as basis F but employs a general contraction for the inner functions. The inner (8s6p3d) functions are contracted to [2s2p1d] using the atomic SCF orbitals with the other functions uncontracted. Basis H is the uncontracted (15s11p6d) primitive set of basis F with the f functions deleted. All of these basis sets, except C, are constructed starting from Wachters [15] (14s9p5d) basis which was optimized for the Cu ^2S state. (Basis C takes the d exponents optimized for the Cu(^2D) state.) They differ mainly in the polarization and diffuse functions which were added. In particular, all the basis sets, except D include tight f functions and basis sets D through G also include diffuse f functions. All of the sets, except C, add the Hay diffuse d functions, and all add diffuse s and p functions. Set C replaces the outer two s functions with three s functions and the outer d function with two d functions and adds 2 diffuse p functions.

Also included in Table 1 are results using the atomic natural orbital (ANO) general contraction scheme of Almlöf and Taylor [16]. The contractions are taken from the ANOs and, for first- and second-row systems, Almlöf and Taylor have shown that there is little contraction error at either the SCF or correlated level. A [6s4p3d] ANO set was derived from basis H which is based on the 11 electron SDCI natural orbitals of the Cu ^2S state. In addition, [6s5p4d] and [7s6p5d] ANO sets were derived from the (16s11p8d) basis set of Faegri and Speis [17] supplemented with a diffuse s (0.019463), two diffuse p (0.093943, 0.037577) and a diffuse d (0.0929420) function.

For set F we have estimated the basis set superposition error (BSSE) using the counterpoise technique [18]. The results obtained after correcting for the estimated BSSE are listed in the table as set F(−BSSE).

Also shown in Table 1 are results from two Slater basis calculations. Set I is the (9s7p5d3f2g) basis of McLean [19], and set J is the (12s10p7d3f1g) Slater basis of Tatewaki and Sekiya [9]. The total energy obtained with the latter basis is very near the RHF limit. At $r = 4.6$ bohr it gives $E = -3277.9464\ E_H$ compared to $-3277.9466\ E_H$ obtained with the partial-wave code. Thus, the basis set error is only $2 \times 10^{-4}\ E_H$, not $1 \times 10^{-3}\ E_H$ as estimated by Tatewaki and Sekiya. Their overestimation of the error appears to arise from comparing the atomic energy in their basis with an erroneously low numerical atomic energy. Actually, their atomic energy of −1638.9637 Hartree is the exact RHF energy of Cu to four decimals.

For the results summarized in Table 1, one observes immediately the chronic underestimation of r_e (by up to 0.03 Å) which afflicts all of the Gaussian bases, except C, that are derived from Wachters primitive set. The estimated BSSE in set F is of the order of 0.024 eV. r_e is considerably improved by correcting for the error, but it is still 0.01 bohr shorter than the NRHF result. Basis G, which is much more flexibly contracted than basis F, gets 0.140 E_H lower in energy but yields nearly identical results. Furthermore, the uncontracted results with basis H demonstrate that the error in the calculations are not due to errors introduced by contracting the basis.

The results using basis C are considerably better than for the other GTO basis sets. At first this might appear to be inconsistent with the other results since the primitive sets employed are quite similar. To explain the discrepancy we used the valence primitive set of basis C and the contraction scheme of basis F (the four tightest 3d functions are the same as basis F). With this contraction we reproduced the spectroscopic properties reported for basis C and computed a BSSE of 0.011 eV or slightly less than half that with basis F. In analyzing the results we found that nearly all of the effect comes from the 3d orbitals. For example, using the s, p and f sets from basis F and the d space from basis C, we obtain $r_e = 2.45$ Å and $D_e = 0.51$ eV. We should note, however, that the energy obtained using the primitive d set of basis C is 0.15 eV higher than that obtained with the Hay diffuse d. Thus, the basis set with the lowest total energy does not have the lowest BSSE and this is not due to differences in the core functions but to differences in the valence region. It is thus apparent that the primitive GTO basis sets commonly employed for Cu have deficiencies in the 3d space, which result in significant BSSE.

The results using the Faegri and Speis primitive set are in substantially better agreement with the NRHF results. Using the [7s6p5d] ANO set the energy is only 0.01 E_H above the NRHF result. The inclusion of f functions would lengthen the bond and increase D_e slightly. Thus, the new basis sets developed by Faegri and Speis overcome the errors in the Wachters primitive 3d set.

Comparing the NMCSCF results with the calculations of Bauschlicher, we observe that the underestimation in r_e is not confined to the SCF level description even though the MCSCF well depth is much deeper. The problem is less severe at the correlated level (22 electron) [4] where the effect on the spectroscopic constants is smaller since the potential is significantly steeper. However, there are still significant basis set deficiencies and BSSE at the correlated level. Current work is aimed at obtaining near Hartree-Fock quality GTO primitive sets for the first row transition metal atoms [20] and ANO contraction schemes [21] which are a least triple-zeta in the valence region and substantially reduce the BSSE [10]. For example, the (20s12p9d) primitive sets [20] are within 0.001 E_H and the (23s15p11d) sets are within 0.0001 E_H of the NHF atomic limits.

In conclusion, our results show that some caution must be used in the choice of the 3d basis sets since there are deficiencies in the GTO 3d primitive sets commonly employed. This is particularly true for weakly interacting systems where it is important to minimize the BSSE. Employing more accurate primitive sets, such as those optimized by Faegri and Speis [17] and Partridge [20], and ANO contractions [16], yields significantly improved spectroscopic constants.

Acknowledgments. This work was supported in part by the National Aeronautics and Space Administration and by the National Science Foundation. The authors acknowledge helpful discussions with C. W. Bauschlicher, Jr.

References and notes

1. Morse MD (1986) Chem Rev 86:1049
2. For a general discussion of the bonding in transition metal diatomics see, for example, Walch SP, Bauschlicher CW Jr (1985) In: Bartlett RJ (ed) Comparison of ab initio quantum chemistry with experiment for small molecules. Reidel, Dordrecht
3. Bauschlicher CW Jr, Walch SP, Siegbahn PEM (1982) J Chem Phys 76:6015
4. Langhoff SR, Bauschlicher CW Jr (1986) J Chem Phys 84:4485
5. Werner HJ, Martin RL (1985) Chem Phys Lett 113:451
6. Scharf P, Brode S, Ahlrichs R (1985) Chem Phys Lett 113:447
7. Martin RL (1983) J Chem Phys 78:5840
8. See for example Bauschlicher CW Jr, Langhoff SR, Taylor PR (1987) J Chem Phys 86:5595; Bauschlicher CW Jr, Partridge H, Langhoff SR, Walch SP, Taylor PR (1987) J Chem Phys 86:7007
9. Tatewaki H, Sekiya M (1986) J Chem Phys 85:5895
10. Bauschlicher CW Jr: Chem Phys Lett, submitted
11. McCullough EA Jr (1986) Computer Phys Reports 4:265
12. Bauschlicher CW Jr (1983) Chem Phys Lett 97:204
13. Fischer CF (1977) The Hartree-Fock method for atoms. Wiley, New York
14. Raghavachari K, Sunil KK, Jordan KD (1985) J Chem Phys 83:4633
15. Wachters AJH (1981) J Chem Phys 75:4539
16. Almlöf J, Taylor PR (1987) J Chem Phys 86:4070
17. Faegri K, Speis HJ (1987) J Chem Phys 86:7035
18. Boys SF, Bernardi F (1970) Mol Phys 19:553
19. McLean AD: private communication
20. Partridge H: unpublished
21. Bauschlicher CW Jr, Partridge H, Taylor PR: unpublished