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Valence-only model potential calculations on copper hydride molecule

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Different sets of one-electron functions obtained according to the strong-orthogonal geminal theory (GEM) [1], the Generalized Molecular Orbital (GMO) method [2] and the exchange maximization between virtual and occupied orbitals (EVO) [3], are tested as basis for CI calculations. The efficiency of the three procedures is discussed investigating the electronic structure of the CuH molecule using an effective-core potential. The values computed for the bond length, the dissociation energy and the vibrational frequency of the ground electronic state are compared with the experimental ones. The charge distribution is examined to estimate the contribution of the *d* electrons to the Cu-H bond. Comparisons are made with the results obtained by other theoretical works in which the copper atom is treated as a one valence electron atom.

Key words: SCF-Geminal-CI calculations—copper hydride—model potentials

1. Introduction

The design of accurate and simple models for calculations on transition metal compounds requires both the use of a pseudopotential method and the inclusion of the correlation energy by a CI expansion. Indeed, the aim of using core-effective potentials is to save a substantial part of the computing time. This same criterion must be fulfilled also in the CI calculations.

The length of the CI expansion obviously depends on the dimension of the active space but the rate of convergence of the CI energy is strictly related with the nature of the one-electron functions used in building the Slater determinants. As is well known, the canonical HF orbitals are not well-suited, in general, to describe correlation effects of strongly localized electron pairs.

The present investigation will show that acceptable results may be obtained using a simple pseudopotential operator like the one proposed by Durand and Barthelat [4], together with CI calculations performed using a basis of Slater determinants expanded in an "optimum" basis of one electron functions. These functions are computed according to three different approaches, which seem able to fulfill the criterion of simplicity and of saving time.

As a first test for our method we have considered the CuH molecule. On this molecule, theoretical studies [5, 6, 7] have been performed with the aim of testing the reliability of different model potential methods and the possibility of considering the copper atom as a one-valence electron atom, merging the $3d^{10}$ filled shell into the core. This further simplification was successful [6, 7] only introducing correction terms which take into account the core polarization and the core-valence correlation. In the present work no core-valence corrections are introduced but the $3d$ electrons are considered as valence electrons.

All the previous works have shown that simple HF SCF calculations are unable to predict values for the bond length (R_e), the dissociations energy (D_e) and the vibrational frequency (ω) within acceptable errors compared to the experimental data. Considering that the most important source of these errors is the lack of the valence correlation in the HF SCF method, we faced the problem of finding a suitable and inexpensive way to carry out the CI calculations.

2. Theoretical method and computational details

The potential energy curve of the ground state $^1\Sigma^+$ of the CuH molecule has been obtained according to the following computational scheme: SCF valence-only calculation, transformation (or modification) of the canonical HF orbitals and limited CI calculation.

The model potential we adopted is that proposed by Durand and Barthelat [4], and the corresponding parameters for the copper atom are taken from the work of Pelissier [8]. The atomic basis set is obtained from pseudopotential calculation on Cu(^{2}S, $3d^{10}4s^1$) which gives an energy slightly better than that quoted in Ref. [8] (see Table 1). In the molecular calculations two basis sets for the copper atom have been used. The first (Basis I) is obtained according to the contraction $(5s, 3p, 6d) \rightarrow (2s, 1p, 2d)$. Due to the presence of the "s-like" $3d$ functions $x^2 + y^2 + z^2$, the actual dimension of the Basis I is 17. A contraction scheme of the type $(5s, 3p, 6d) \rightarrow (3s, 2p, 3d)$, without inclusion of the s-like $3d$ functions, is used for Basis II. The basis set for the hydrogen atom is of $(6s, 3p)$ type contracted to $(4s, 1p)$. The first four s components are optimized for H(^{2}S), while the last two are optimized for H$^-$(^{1}S). The three p Gaussians are obtained by expanding a Slater orbital with an exponent equal to 1 [9]. As shown in Table 1, such a basis is flexible enough to describe both the neutral atoms and the corresponding ions.

Table 1. Basis sets for Cu and H atoms[a]

	Cu ($^2S, 3d^{10}4s^1$) Exponents/contraction coefficients		
s	5.16230/−0.02052	p^b	0.1916/0.37990
	2.64053/0.09713		0.0600/0.50851
	1.00415/−0.23031		0.0200/0.22190
	0.10860/0.58754		
	0.03861/1.		
d	62.89440/0.02018		
	17.23230/0.11427		
	6.01642/0.30139		
	2.17198/0.41095		
	0.74839/0.36227		
	0.24018/0.18036		
	$\varepsilon_{4s} = -0.24345\ (-0.23795)^c$		
	$\varepsilon_{3d} = -0.48258\ (-0.49074)$		
	$E_T = -50.13355\ (-50.11658)^d$		
Cu$^+$ ($^1S, 3d^{10}$)			
$E_T = -49.89224$	IP^e = 6.57 eV (6.40)		
	H (^2S) Exponents/contraction coefficients		
s	13.06180/0.01962		
	1.96892/0.13678		
	0.44555/0.48124		
	0.12211/1.		
	0.03716/1.		
	0.01910/1.		
	E_T: $H = -0.49933$		$H^- = -0.48739\ (-0.4878)^f$
	virial ratio = −2.003		= −2.003 (−2.002)

[a] Energies in atomic units. In parenthesis are the values taken from other works.

[b] From Ref. [8].

[c] Orbital energies. All electron (AE) values from Ref. [13].

[d] Pseudopotential value from Ref. [8].

[e] Ionization potential. *AE* value from Ref. [13].

[f] STO large basis calculation of Ref. [14]

Also the transition energy ^{2}S $(d^{10}s^1) \rightarrow {}^2D(d^9s^2)$ of the copper atom has been computed with the GEM-CI procedure described below, using for both states the one-electron functions obtained from the ground state calculations. The value of 2.18 eV so obtained compares fairly well with the experimental one of 1.49 eV. The slightly high estimate is due to the fact that the employed orbitals are not the optimal ones for the ^2D state.

In the following, the three methods adopted for the Basis I to modify the canonical HF orbitals in the molecular calculations on CuH are briefly described, while more details are reported in the Appendix.

The Basis II has been used, for comparison, to perform standard SCF-CI calculations, employing the MRD-CI program of Buenker et al. [10]. Only single and double (SD) excitations with respect to the reference determinant built with the canonical HF orbitals are included in the CI treatment. The energy is obtained from a secular determinant of dimension about 2200.

3. Strong-orthogonal geminals of rank two (GEM)

This approach to determine partially correlated wavefunctions [1b] is a simplification of the more general geminal theory [1a]. The basic difficulty met in the computation of rank two geminals is represented by the ambiguity in the choice of the different pairs of occupied and virtual orbitals entering in the definition of the geminals. The GEM method is briefly summarized in the Appendix, together with a simple procedure which allows the selection of the couples of the initial orbitals in a well defined and efficient way. The procedure is based on the transformation of both the occupied and virtual orbitals by means of two orthogonal transformations producing a set of occupied (I) and virtual (V) orbitals for which the exchange integral $\langle IV|IV\rangle$ is maximum. This new basis is used in the geminal calculation whose total density matrix supplies the natural orbitals to be transferred to the CI calculation. In this case, we choose a very limited CI space, spanned by only 12 orbitals, the 6 strongly and the 6 weakly occupied natural orbitals. It's worth noticing that the GEM wavefunction is far from fulfilling the Brillouin theorem so that the single-excited configurations directly interact (and in an important way) with the reference determinant built from the six strongly occupied orbitals. A small CI calculation is carried out including only the reference determinant and the four single and the four double excitation of the type $1\sigma(2\sigma) \rightarrow 3\sigma(4\sigma)$. The 9-term wavefunction is used as reference wavefunction to generate the single and double excitations included in the final CI secular problem.

4. Generalized molecular orbital (GMO) method

Along the original proposal by Hall [2], the SCF standard calculation may be followed by a simple MC-type calculation in which the wavefunction is built as a linear combination of a reference determinant and some selected pair-excited configurations, all having an equal weight. As shown in the Appendix, the GMO method, reformulated in terms of density matrix formalism, is in all equivalent to the method for the determination of the wavefunction of a many-shell system. The computational advantages of the GMO method are self-evident, while its major limitation lies in the fact that all the pair-excited configurations are considered as equally important in determining the final one-electron functions for the CI expansion. These latter functions are obtained as natural orbitals of the total MC density matrix. The SD-CI calculation includes, in this case, excitations with respect to a reference 9-term wavefunction built with all the pair-excitations of the type $2\sigma \rightarrow n\sigma$ ($n = 3, 4, \ldots, 10$). Indeed, the 2σ MO is the most significant in the description of the CuH bond, being mainly composed of s and d_σ orbitals on Cu and s orbitals on H atom, with small but not negligible contributions of p_σ orbitals on both centers.

5. Exchange maximization between virtual and occupied orbitals

This method [3], outlined in the Appendix, can be considered as a means of "localization" of the virtual orbitals in the space spanned by the occupied ones. As a consequence, the one-electron functions set as the basis of the CI calculation, in this case, are the six HF canonical orbitals and the 12 most "localized" virtual orbitals, the degree of localization being determined by the magnitude of the eigenvalues of the matrix $\boldsymbol{W}$ defined in the Appendix. Like in the previous case, the reference CI wavefunction used in the configuration selection is composed by 9 terms representing pair excitations in the σ space.

As a final remark, we wish to stress that our CI calculation is performed in a limited space, spanned, however, by well-selected active orbitals, and including up to quadruple excitations. The final dimension of the secular determinant is about 1200 for GMO-CI and EVO-CI calculations and 300 for GEM-CI calculations. The selection of the configurations has been done according to the usual second-order energy criterion, with a threshold of 10^{-7} Hartree.

6. Results and discussion

The results relative to the ground state properties of the CuH molecule, obtained with the computational methods described above, are reported in Table 2.

At SCF level, both Basis I and Basis II produce too large an equilibrium bond distance and too low a vibrational energy. The Basis II (of dimension 31) predicts a dissociation energy nearly identical to that of the Basis I (of dimension 24). This is an indication of the fact that the small Basis I is not affected by any important basis set superposition error. Both basis sets account for less than the 50% of the experimental binding energy. Very important corrections of the SCF results are obtained at CI level. However, in the case of the SD-CI method (which makes use of the canonical HF orbitals as one-electron functions) the calculation is unable to give good results of the dissociation energy, the theoretical value being less than 80 per cent of the experimental one. The same holds for Basis I, in the case of the EVO-CI procedure. On the contrary, the GEM and GMO

Table 2. Ground state properties of the CuH molecule

	R_e/Å	D_e/eV	ω/cm^{-1} [a]
Basis I			
SCF	1.554	1.40	1641.8
GEM-CI	1.520	2.71	1845.0
GMO-CI	1.492	2.35	1659.0
EVO-CI	1.508	2.06	1713.3
Basis II			
SCF	1.560	1.39	1633.7
SD-CI	1.470	2.01	1759.5
Experimental values [b]			
	1.463	2.85	1866.4

[a] The vibrational frequency is computed using harmonic and anharmonic terms.
[b] From Ref. [15]

methods, which modify the HF orbitals according to a MC criterion, reproduce fairly well the experimental D_e quantity. In this respect, the GEM-CI procedure seems highly reliable, since, with a very small CI expansion, it accounts for a large part of the correlation energy associated with the two electron pairs, mainly involved in the Cu-H bond.

As for the equilibrium bond length, the best results are obtained from the CI calculation of the Basis II, while the Basis I predicts R_e values which are in error of 0.03-0.06 Å, compared to the experimental one. It must be noted that the description of the $3d$ intrashell and $3d$-$4s$ intershell correlation of the Basis II is much more effective than that of Basis I. This kind of correlation seems important in determining a correct value for the R_e quantity.

The vibrational energies, computed according to Cremaschi's procedure [11], are reported in Table 2. The smallest error with respect to the experimental value is that associated with the result of the GEM-CI procedure (about 21 cm^{-1}). This may confirm the ability of this method to describe in a good manner the electron potential in the bond region.

The Mulliken population analysis, performed on the GEM-CI wavefunction at the experimental equilibrium distance, gives the following occupation numbers: 0.9527, 0.1235, 9.6227 for s, p and d orbitals of the Cu atom, respectively. The corresponding values for the hydrogen atom are 1.2817 and 0.0194 for s and p orbitals respectively. These results, qualitatively confirmed by the analysis performed on the EVO-CI and GMO-CI wavefunctions, clearly show that the $3d$ shell of the copper atom undergoes a very important perturbation, the actual electron distribution being far from the atomic ground state $3d^{10}4s^1$ configuration. This confirms that the copper atom cannot be considered as a one valence electron atom, due to the high polarizing effect of the hydrogen atom. As a consequence, the theoretical results are expected to be strongly dependent also on the particular basis set adopted for the $3d$ orbitals: this basis should be flexible enough to describe all the low lying configurations $3d^{10}4s^1$, $3d^94s^2$ and $3d^{10}4p^1$, which are important in a strongly polar bond like the CuH one. The charge transfer from the $3d$ shell cannot be described by simple perturbation treatments [6, 7].

Let us now compare our GEM-CI results with those of other pseudopotential investigations on the CuH molecule [5, 6, 7]. The theoretical approach of Das [5] is the most similar to the present one, being composed of SCF calculation on a 12 electron molecule, followed by a limited MC and CI calculation: in spite of the large STO basis employed, the agreement with our results is surprisingly good. Other pseudopotential investigations [6, 7] consider the copper atom as a single valence electron, the contribution of the d electrons being taken into account by means of additional corrections such as the core polarization and the core-valence correlation. The results quoted in Ref. [6] and [7] are as accurate as the GEM-CI ones as for the value of R_e but the dissociation energy and the vibrational frequency are underestimated.

7. Conclusions

The main goal of the present investigation was not to produce theoretical values of absolute accuracy, due to the limitations both of the basis set used and of our pseudopotential approach which neglects all core-valence corrections; instead we aimed to show that simple computational procedure to modify the canonical HF orbitals are suitable to produce some important improvements in the results of the standard SCF-CI method. The procedures we tested present some advantages, especially in their ability to generate compact wavefunctions and to spare computation time. Indeed, the EVO method requires a computer time comparable to that of one cycle of SCF procedure. The GMO and GEM methods which seem in many respects more effective than the EVO method, require a computer time which is only twice or three times larger than that of the standard SCF energy minimization. As stressed in the Appendix, the GEM and GMO methods in the formulation of the one-particle density matrix use the same algorithms and can be incorporated in a unique, general SCF program.

8. Appendix

In this Appendix, we briefly describe the three approaches we have tested to obtain orbitals suited to give a more compact CI expansion.

1. In the geminal method (GEM) the electrons are partitioned in core electrons, electron pairs to be described by rank-two geminals and electrons belonging to open shells.

The MO set is partitioned in occupied and virtual orbitals: $\boldsymbol{T} = [\boldsymbol{T}^0 | \boldsymbol{T}^v]$, and the corresponding density matrices are $\boldsymbol{R}^0 = \boldsymbol{T}^0 \tilde{\boldsymbol{T}}^0$ and $\boldsymbol{R}^v = \boldsymbol{T}^v \tilde{\boldsymbol{T}}^v$.

The partner orbitals needed to form the rank-two geminals are worked out finding the singular vectors of the rectangular $m_0 \times m_v$ $(m_0 \leqslant m_v)$ matrix of elements

$\langle \Psi_0 | \mathscr{H} | \Psi_{IV} \rangle = \mathrm{Tr}\,[\boldsymbol{R}^I \boldsymbol{K}(\boldsymbol{R}^V)]$ where Ψ_0 is a basic determinant of doubly-occupied m_0 orbitals I and Ψ_{IV} are the similar single determinants obtained by exciting a pair of electrons from an occupied orbital I to a virtual orbital V.

$\boldsymbol{K}(\boldsymbol{R}^V)$ is the exchange part of the two-electron matrix, of argument $\boldsymbol{R}^V$. Then, corresponding to of the m_0 non-zero singular eigenvalues, we have a couple of orbitals, strongly occupied $\phi_{\mu 1}$ and weakly occupied $\phi_{\mu 2}$, by which the geminals $g_\mu\ (1, 2)$ are written as linear combinations

$$g_\mu\ (1,2) = c_{\mu 1}\phi_{\mu 1}(1)\phi_{\mu 1}(2) - c_{\mu 2}\phi_{\mu 2}(1)\phi_{\mu 2}(2) \qquad (1)$$

The energy takes the form

$$E = \Sigma_k \nu_k \operatorname{Tr}(\boldsymbol{f}\boldsymbol{R}^k) + \Sigma_{k,l} \operatorname{Tr}[\boldsymbol{R}^k \boldsymbol{G}_{k1}(\boldsymbol{R}^l)] \qquad (2)$$

where the occupation numbers ν_k and the parameters a_{kl} and b_{kl} appearing in the two-electron integral matrix $\boldsymbol{G}_{kl}$ depend on the $c_{\mu i}$ $(i = 1, 2)$ expansion coefficients of the geminals. The details are reported in Ref. [1b].

2. In the Generalized Molecular Orbital (GMO) approach the electrons are partitioned in core and valence electrons (open shell will be included in a further extension not considered in the present version). In the pair-excited MC-SCF theory, assuming an equal expansion coefficient for all the excited pairs IV, the trial wavefunction may be written as

$$\Psi = a\Psi_0 + b\Sigma_I \Sigma_V \Psi_{IV}.$$

The energy assumes a form of the type (2), similar to that of a three shell system, formed by core (c), strongly occupied (o, m_0 in number) and weakly occupied (v, m_v in number) orbitals. The parameters ν_k, a_{k1} and b_{k2} are then expressed in terms of the a and b expansion coefficients as follows:

$$\nu_c = 2, \qquad \nu_o = -2b^2 m_v, \qquad \nu_v = 2b^2 m_o$$

$$a_{cc} = 2, \qquad a_{co} = -4b^2 m_v, \qquad a_{cv} = 4b^2 m_o, \qquad a_{ov} = -4b^2$$

$$b_{cc} = -1, \qquad b_{co} = 2b^2 m_v, \qquad b_{cv} = -2b^2 m_o,$$

$$b_{oo} = b^2 m_v, \qquad b_{ov} = 2b(a+b), \qquad b_{vv} = b^2 m_o.$$

In both the GEM and GMO method the optimization of the orbitals and the expansion coefficients is performed in a similar way. The orbitals are optimized by a sequence of orthogonal transformations $\boldsymbol{U}$ of the atomic basis, acting directly on the one-particle density matrices $\boldsymbol{R}^k \rightarrow \boldsymbol{U}\boldsymbol{R}^k\tilde{\boldsymbol{U}}$. The optimization of the expansion coefficients is performed simultaneously since they are expressed directly in terms of the varied orbitals, thanks to the simple 2×2 secular problem. Some details are reported in Ref. [12].

3. The exchange maximization between virtual and occupied orbitals (EVO) is obtained by diagonalizing the matrix $\boldsymbol{W}$ of elements $\Sigma_I \langle VI|V'I\rangle$, i.e. $\boldsymbol{W} = \tilde{\boldsymbol{T}}^v \boldsymbol{K}(\boldsymbol{R}^o)\boldsymbol{T}^v$.

The "localized" virtual orbitals are then obtained as $\boldsymbol{T}^{v\prime} = \boldsymbol{T}^v \boldsymbol{V}$, where $\boldsymbol{V}$ is just the eigenvector matrix of $\boldsymbol{W}$.

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