Theoret. Chim. Acta (Berl.) 61, 379–385 (1982)

THEORETICA CHIMICA ACTA

A Short CI Expansion for a Symmetry-Adapted Description of Localized Hole States: Application to the $3d\sigma_u$ Hole State of the Cu_2^+ Ion

Marc Benard

E.R. 139 du C.N.R.S., Laboratoire de Chimie Quantique, Institut Le Bel, Université Louis Pasteur, 4 rue Bl. Pascal, F-67000 Strasbourg, France

A simple formalism is developed to describe by means of a symmetry-adapted wavefunction the localized hole states which may arise in symmetric systems. A short CI expansion is generated in a systematic way from the delocalized molecular orbitals of the SCF ground state. For the $3d\sigma_u$ hole state of the Cu_2^+ ion, the symmetry adapted and the broken symmetry solutions approximately correspond to the same energy at that level of CI.

Key words: Configuration interaction – Localized hole states – Cu_2^+ ion.

1. Introduction

During the last ten years, molecular orbital calculations on ionization or excitation of an electron from inner shells have raised the problem of hole localization and symmetry-breaking in computed wavefunctions [1]. It has been shown that the removal of space symmetry conditions in this type of calculations changed drastically the nature of the stationary point obtained at convergence of the SCF iterations. The total energy associated with this type of "broken-symmetry solution" is substantially lower than the energy corresponding to the symmetry-adapted solution, in some cases by more than 10 eV. [1–2]. In a consistent way, the occurrence of the broken-symmetry solutions has considerably improved the agreement between theory and experiment for a large scope of spectroscopic properties related to the core hole states [3]. It is known that the occurrence of symmetry-breaking gives an indication for strong correlation effects in a system which is not allowed to dissociate correctly [11]. Relaxation of space symmetry

0040-5744/82/0061/0379/$01.40

constraints allows such a correct dissociation and the energy difference between the symmetry-adapted and the broken-symmetry solutions can be considered as part of the correlation energy (since the correlation energy is usually defined with respect to the energy of the RHF symmetry adapted configuration). However, broken symmetry solutions display some disadvantages, since

- this part of the correlation energy is difficult both to estimate and to improve
- it strongly depends upon the geometry of the system, which makes broken symmetry solutions unadapted to compute potential energy curves.

This situation is very similar to the one encountered with Unrestricted Hartree–Fock solutions, which occur from the relaxation of *spin* symmetry constraints.

Because of these reasons, the search for a symmetry adapted wavefunction as accurate as the broken symmetry solution is still active. Several approaches have been considered up to now:

- a full CI calculation performed on the broken symmetry solution will yield a wavefunction displaying the full molecular symmetry. However, when the wavefunction is distorted too much, the CI expansion constructed from single and double excitations will remain far from full symmetry [4];
- still starting from the broken symmetry solution, an alternative way to recover the proper symmetry consists in applying the appropriate group theoretical projection operator. However, this method is not of current use because of difficult optimization and orthogonality problems [5];
- one may rather start from the symmetry-adapted SCF wavefunction and perform either a CI expansion on the basis of single- and double-excitations, or a MCSCF treatment on a limited set of configurations. The first approach was chosen by Butscher et al. to describe several core ionized and core-valence excited states of N_2 [6]. These authors obtained very accurate results, but after a brute force treatment involving 200 000 to 300 000 configurations. On the other hand, Ågren et al. [1] obtained a correct description of the 1s core level states of O_2^+ after a MCSCF treatment involving a limited number of configurations (2 to 5).

This short review shows that the latter approach seems up to now the most promising one. However, the authors did not propose any systematic way to select the active space from which the MCSCF configurations are generated. The fact that this active space can be restricted to 4 orbitals only* might be far from general and, at worst, specific to the case of O_2^+.

The aim of this article is to describe the systematic generation of a restricted CI expansion performed from the symmetry-adapted SCF wavefunction. For diatomic systems, the size of this expansion will be usually less than 100 configurations. The corresponding correlation energy is of the same order of magnitude as the energy gain brought by symmetry breaking, but discontinuities on the potential curves are obviously avoided [11]. An application is given for a 3d level hole state of the Cu_2^+ ion, a system for which the occurrence of a broken symmetry solution has been pointed out recently [7, 8].

---

* The $1\sigma_g$ and $1\sigma_u$ 1s core orbitals and the $1\pi_u$ and $1\pi_g$ valence orbitals of O_2^+

2. Theoretical Considerations

Let us consider a system with n equivalent centers. The symmetry adapted inner-shell orbitals related to these centers can be divided into subsets of near degenerate MO's corresponding to the same atomic shell. For instance, all MO's corresponding to a given s shell will be collected into a unique subset of size n. However, the MO's corresponding to a given p shell can be further separated if p_x, p_y and p_z are not allowed to transform into each other. Therefore, the $3n$ MO's of a given p shell will be split into three subsets of size n if x, y and z belong to different irreducible representations. Otherwise, one can get either two subsets of size $2n$ and n or one unique subset of size $3n$. The subsets involving d-type orbitals can be defined from similar considerations.

Let us assume that one electron is ionized, or excited, from an orbital belonging to a given subset i, of size n. The symmetry-adapted SCF ground state configuration for this hole state will correspond to:

$$\cdots (i_1^2, i_2^2, \ldots, i_{n-1}^2, i_n^1) \cdots (\text{valence orbitals})^v \, (\text{virtual orbitals})^t \tag{1}$$

Assuming that v is the total occupancy of valence orbitals, and t that of virtual orbitals (t being 0 for an ionization and 1 for an excitation). According to the definition of subsets, each orbital of subset i, including i_n is delocalized over the n centers. The problem consists in localizing i_n on a given center through a CI treatment. This process will be done through a mixing of i_n with the $n-1$ other orbitals of subset i. One may think of an expansion involving all excitations generated inside subset i. However, if the active space* is restricted to subset i alone, the CI expansion will be limited to $n-1$ single excitations. Such an expansion will obviously not perturb the ground state because of Brillouin's theorem. Therefore, the active space must be extended over the whole set of MO's, but the generation of configurations must be constrained in order to retain only those contributing to the localization of i_n. If we restrict our expansion to the first order interacting space, those configurations must satisfy two conditions:

- they must correspond to mono- or biexcitations with respect to the ground state (1);
- they must correspond to a one-electron excitation *inside* subset i, in order to be effective in the localization process.

Such a set of configurations is generated by the *monoexcitations* arising from $n-1$ reference states:

$$\begin{array}{l} \cdots (i_1^1, i_2^2, \ldots, i_{n-1}^2, i_n^2) \cdots \\ \cdots (i_1^2, i_2^1, \ldots, i_{n-1}^2, i_n^2) \cdots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \cdots (i_1^2, i_2^2, \ldots, i_{n-1}^1, i_n^2) \cdots . \end{array} \tag{2}$$

These reference states correspond to all possible one-electron replacements inside subset i.

---

* The active space in a CI treatment is defined as the orbital set from which configurations are generated.

The case of a diatomic molecule is especially simple. In the SCF ground state of the ionized or excited molecule, subset i is reduced to (i_1^2, i_2^1), and the CI expansion will be performed over the whole set of configurations which are monoexcited with respect to the unique reference state

$$\cdots (i_1^1, i_2^2) \cdots .$$

In practice, the systematic generation of this set of configurations is extremely easy, even in the most general case. The molecular orbitals of the system are divided into three groups which appear sequentially:

- the set of virtual orbitals, of total population t ($t = 0$ or 1) in the SCF ground state;
- the n orbitals of subset i;
- the other orbitals, all occupied in the SCF ground state.

If p_1 and p_2 are the populations of groups 1 and 2 respectively, the configurations to be kept must satisfy the conditions:

$$\begin{aligned} &t \le p_1 \le t+1 \\ &2n-1+t \le p_1+p_2 \le 2n+t. \end{aligned} \tag{4}$$

If the CI expansion is performed through the unitary group approach [10], conditions (4) can be easily satisfied at the level of configuration generation. Configurations which are singly excited with respect to the ground state may be discarded in a further step.

3. Application to the $3d\sigma_u$ Hole State of Cu_2^+

3.1. Survey of Recent Results

Cox et al. [7] have performed ab initio MO SCF calculations for the localized and delocalized $3d\sigma_u$ hole state of the Cu_2^+ ion, at a Cu–Cu distance of 2.40 Å. When the molecular symmetry is broken, this $3d$ ionized state shows virtually complete localization with an energy gap of about 2.8 eV with respect to the symmetry-adapted solution. Similar results have been achieved by Post and Baerends using the LCAO Hartree–Fock Slater (HFS) method [8].

Configuration interaction was also performed by Cox et al. for both the localized and the delocalized solutions (Table 1). In these CI calculations, the expansion was performed as usual over all singly and doubly excited configurations arising from a given set of active orbitals. In a first calculation (Expansion 1), the active space for the delocalized system was restricted to the set of 4 orbitals $d\sigma_g$, $d\sigma_u$, $s\sigma_g$ and $s\sigma_u$. A similar expansion was used for the localized solution with the equivalent set of orbitals. The corresponding energy lowering for the symmetry-adapted solution was found much larger than for the broken-symmetry solution (1.16 eV instead of 0.09 eV) but the difference was just about one third of the energy gap at the SCF level. In a second CI calculation (Expansion 2), the size of the active set was increased from 4 to 8 orbitals and the difference in correlation energy between the symmetry-adapted and the broken-symmetry solution was

Table 1. SCF and CI energies for the $D_{\infty h}$ (symmetry-adapted) and $C_{\infty v}$ (broken-symmetry) solutions of Cu_2^+ (at 2.40 Å)

	Number of active orbitals	Number of configurations		Energy (a.u.)		$E_{D_{\infty h}} - E_{C_{\infty v}}$
		$D_{\infty h}$	$C_{\infty v}$	$D_{\infty h}$	$C_{\infty v}$	
SCF				−3270.7042	−3270.8066	0.1024
CI Exp. 1 (From Ref. [7])[a]	4	10	18	−3270.7467	−3270.8101	0.0634
CI Exp. 2 (From Ref. [7])[a]	8	104	208	−3270.7808	−3270.8243	0.0435
CI Exp. 3 (This work)[b]	30	37	71	−3270.8232	−3270.8102	−0.0130

[a] All single and double excitations generated from the active space

[b] Single excitations with respect to the $d\sigma_g^1\, d\sigma_u^2\, s\sigma_g^2$ configuration (configurations which are singly excited with respect to the SCF ground state $d\sigma_g^2\, d\sigma_u^1\, s\sigma_g^2$ have been discarded)

then slightly more than half of the SCF gap. Therefore, the "classical" CI expansion for the symmetry-adapted solution of Cu_2^+ seems to be a slowly convergent process.

3.2. Computational Details [12]

SCF calculations for the delocalized $3d\sigma_u$ hole state of the Cu_2^+ ion and for the equivalent localized state were performed with a Gaussian basis set [12, 7, 5] contracted to [5, 3, 2]. This basis set had been used by Demuynck et al. [9] and by Cox et al. [7] in the calculations reported in section 3.1. The Cu–Cu distance was set equal to 2.40 Å, namely the distance used in Ref. [9] and [7]. The energy difference at the SCF level between the symmetry-adapted ($D_{\infty h}$) and the broken-symmetry ($C_{\infty v}$) solutions is 0.1024 a.u.

In order to localize the $3d\sigma_u$ hole state while retaining the $D_{\infty h}$ symmetry, a new CI expansion (Expansion 3) was performed on the symmetry-adapted MO's. The configurations were selected according to the criterions defined in Sect. 2. The active set included the ten occupied $3d$ orbitals (including the half-filled $3d\sigma_u$), the occupied $s\sigma_g$ and the whole set of unoccupied orbitals, that is 30 orbitals on the whole. The inner shell orbitals were kept frozen. We retained all configurations which are doubly excited with respect to the SCF ground state $d\sigma_g^2\, d\sigma_u^1\, s\sigma_g^2$ and singly excited with respect to the $d\sigma_g^1\, d\sigma_u^2\, s\sigma_g^2$ configuration*. A set of 37 configurations was generated including the SCF ground state. The energy lowering with respect to the SCF ground state is now 0.1190 a.u. A similar expansion performed on the broken-symmetry MO's generated 71 configurations, but yielded an energy decrease of 0.0036 a.u. only. Therefore, at this level of CI, the $D_{\infty h}$ solution becomes slightly lower in energy than the $C_{\infty v}$ one (Table 1).

4. Conclusion

In the present work, we have developed a computationally inexpensive method to calculate a symmetry adapted wavefunction for a localized hole state. The CI expansion performed over the symmetry-adapted SCF molecular orbitals involves a very limited set of configurations. In the case of a diatomic molecule, these configurations are monoexcited with respect to a unique configuration which is near-degenerate with the SCF ground state. The application to the $3d\sigma_u$ hole state of the Cu_2^+ ion, which is almost completely localized, shows that the symmetry-adapted and the broken-symmetry solutions approximately correspond to the same energy at that level of CI. However, at the SCF level, and at several levels of classical "single and double" CI, the broken-symmetry solution was significantly lower in energy. The method presented here can be applied

---

* In point group $D_{\infty h}$, the subset of $d\sigma$ molecular orbitals active in the localization process is of size $n = 2$: $d\sigma_g$ and $d\sigma_u$. However, xy and yz belong to a twofold degenerate representation and therefore, the subset size for a $d\pi$ state would be $2n = 4$

without any loss of efficiency to localized hole states which may arise in systems displaying a number of equivalent sites larger than two.

References

1. Ågren, H., Bagus, P. S., Roos, B. O.: Chem. Phys. Letters **82**, 505 (1981) and references therein
2. Bagus, P. S., Schaefer III, H. F.: J. Chem. Phys. **56**, 224 (1972).
3. Dill, D., Wallace, S., Siegel, J., Dehmer, J. L.: Phys. Rev. Letters **41**, 1230 (1978); Müller, J., Ågren, H., Goscinski, O.: Chem Phys. **38**, 349 (1979); Ågren, H., Nordgren, J.: Theoret. Chim. Acta **58**, 111 (1981); Rescigno, T. R., Orel, A. E.: J. Chem. Phys. **70**, 3390 (1979)
4. Jackels, C. F., Davidson, E. R.: J. Chem. Phys. **64**, 2908 (1976)
5. Broer-Braam, H. B.: Ph.D. Thesis, University of Gröningen (1981) and references therein
6. Butscher, W., Buenker, R. J., Peyerimhoff, S. D.: Chem. Phys. Letters **52**, 449 (1977)
7. Cox, P. A., Bénard, M., Veillard, A.: Chem. Phys. Letters **87**, 159 (1982)
8. Post, D., Baerends, E. J.: Chem. Phys. Letters **86**, 176 (1982)
9. Demuynck, J., Rohmer, M.-M., Strich, A., Veillard, A.: J. Chem. Phys. **75**, 3443 (1981)
10. See for instance: The unitary group for the evaluation of electronic energy matrix elements edited by J. Hinze; Heidelberg: Springer 1981
11. See for instance Bénard, M., Paldus, J.: J. Chem Phys. **72**, 6546 (1980); Bénard, M.: J. Chem. Phys. **71**, 2546 (1979). Concerning the hole states of Cu_2^+, the aspects more specifically related to the stability problem will be investigated in a forthcoming paper
12. SCF and CI calculations were carried out with the ASTERIX system of programs [13]. The CI program has been developed using the Unitary Group Approach (UGA) [10]
13. Bénard, M., Dedieu, A., Demuynck, J., Rohmer, M.-M., Strich, A., Veillard, A.: ASTERIX: a system of programs for the Univac 1110, unpublished. Bénard, M., Barry, M.: Comp. Chem. **3**, 121 (1979)

Received February 17, 1982