ELSEVIER

20 December 1996

Chemical Physics Letters 263 (1996) 687–690

CHEMICAL PHYSICS LETTERS

Ab initio molecular orbital calculations by the resonating Hartree–Fock approach: superposition of non-orthogonal Slater determinants

Norikazu Tomita [1], Seiichiro Ten-no, Yoshitaka Tanimura

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Received 22 August 1996; in final form 9 October 1996

Abstract

The resonating Hartree–Fock (ResHF) method is applied to ab initio MO calculations of CO. This method approximates correlated wavefunctions by superposition of non-orthogonal Slater determinants, where both the CI coefficients and the orbitals in the determinants are variationally determined. The ResHF, with two or three generating determinants, explains the correlation energy to the same extent as the full-valence CASSCF wavefunction with 328 CSFs. Furthermore, the method reproduces the dipole moment more accurately, reflecting a better long-range behavior of the wavefunction. This implies the ResHF method provides more suitable reference functions in multireference methods.

1. Introduction

The multireference (MR) descriptions for many-electron wavefunctions, such as MR configuration interaction (MRCI) or MR perturbation theory (MRPT) [1], have been common bases in the ab initio methods to treat correlation effects with chemical accuracy. The multiconfiguration self-consistent field (MCSCF) method [2] is the most popular and powerful tool to explain the non-dynamic correlation effects, focusing certain chemical bonds. Important effects of orbital relaxation among configuration state functions (CSFs) are, however, neglected due to the strong constraints of orbital partitioning. When characters of main configurations are very different from each other, it is not adequate to describe these configurations with a single set of orbitals since the relaxation from the mean orbitals becomes important. We call these effects the orbital relaxation effects (ORE). The ORE includes important many-electron (at least more than two) excitations especially for strongly correlated systems. This means the usual MR recipe based on the MCSCF wavefunction with a limited number of excitations is not necessarily an optimal way to treat the dynamic correlation effects.

In this Letter, we apply the resonating Hartree–Fock (ResHF) method to the ab initio molecular orbital calculations. The ResHF method was proposed by Fukutome [3] to treat strongly correlated systems and was applied to the one-dimensional half-filled Hubbard model [4], whose exact solutions were known. They showed that the ResHF method

[1] Present address: National Research Institute for High Energy Physics, Oho 1-1, Tsukuba 305, Japan.

0009-2614/96/$12.00 Copyright © 1996 Elsevier Science B.V. All rights reserved
PII S0009-2614(96)01266-3

was capable of giving very good results in the correlation energy, the spin-correlation function of the ground state, and the k-dispersions of the lowest singlet and triplet collective excitations. It should be noted that the method was also successfully applied to the semi-empirical molecular orbital (MO) calculations [5]. We shall briefly introduce the method in the next section. In Section 3 we show the result of the CO molecule which is one of the simplest π electron systems. Conclusions are given in Section 4.

2. Theory

2.1. The resonating HF wavefunction

The ResHF method approximates a correlated wavefunction by superposition of unrestricted Hartree–Fock (UHF) wavefunctions which are non-orthogonal to each other such that the different-orbitals-for-different-spins (DODS) are allowed. Using the Thouless transformation [6], the ResHF wavefunction can be written as

$$\Psi = \sum_{f=1}^{N_S} C_f \Phi_f = \sum_{f=1}^{N_S} C_f \exp\left(\hat{R}_f\right)\Phi_0, \qquad (1)$$

where N_S represents the number of Slater determinants (S-dets) we shall take into account in the model, C_f are the CI coefficients and Φ_0 is the reference determinant. The anti-Hermite (skew-symmetric for real wavefunctions) operators $\hat{R}_f$ consist of single-electron excitation operators

$$\hat{R}_f = \sum_{a\, i \in f} r_{ai}^{(f)}\left(\hat{a}_a^+ \hat{a}_i - \hat{a}_i^+ \hat{a}_a\right), \qquad (2)$$

where a and i refer to the virtual and the occupied spin orbitals in Φ_0, respectively. Φ_0 is arbitrary as long as the excitation operators are not truncated. The way to evaluate matrix elements over non-orthogonal S-dets has been well known especially in the traditional valence bond (VB) methods [7] as well as in the molecular orbital methods [8]. Based on such background, both sets of the coefficients C_f and $r_{ai}^{(f)}$ are variationally determined using a similar algorithm to the direct optimization procedure [4]. Therefore it is necessary to prepare N_S sets of spin orbitals whereas the MCSCF method requires only one set of spatial orbitals. In this Letter, we employ a half-projection of each MO set in order to exclude the triplet-type spin contamination. We should notice that Igawa has recently proposed a method to calculate the matrix elements over fully spin-projected states of non-orthogonal S-dets [9], which we do not implement here. The effect of the projection scheme to $\langle \hat{S}^2 \rangle$ is also examined in the following sections.

2.2. The orbital relaxation and the breathing orbital effects (ORE and BOE)

The most prominent feature of the ResHF method is that it allows us to treat the ORE consisting from many-electron excitations (up to all-electron excitations) as we will explain below. Although the usual MCSCF method can represent states at all geometries qualitatively correctly, the obtained wavefunctions are not flexible enough. This is because the spatial orbitals are partitioned as active or inactive (dormant) levels and the orbitals are optimized in a mean-field environment. When the total wavefunction consists from a few main CSFs whose characters are different from each other, the included orbitals do not follow the resonation among metastable states. To recover the relaxation in the resonation, many-electron excitations from the MCSCF wavefunction can be required if the size of active space is not large enough. In this context, the MCSCF method apparently breaks down since the required number of active orbitals increases as the size of the molecule increases. Since the ORE cannot be explained by the CASSCF method, they may be classified as dynamic correlation effects. However, the effects are long-range on the contrary to the usually called dynamic correlation effects based on the localized fluctuation potential [10] in the pair electron theory.

Recently, similar effects were discussed in three-electron bond dissociation based on the breathing orbital VB (BOVB) method [11]. The method optimizes orbitals and CI coefficients keeping different orbitals for different Lewis structures such that the orbital relaxation in each VB structure is allowed. They call the relaxation effects the breathing orbital effects (BOE), the physical nature of which is closely related with the ORE. The difference between the BOVB and the ResHF is the unit to represent main components of the wavefunction: the BOVB chooses Lewis structures and the ResHF does S-dets. The

ResHF method is free from such VB structures. Therefore the ResHF is more flexible than the BOVB method and the ORE is more general than the BOE.

3. Results and discussions

We apply the ResHF method to the calculation of the carbon monoxide molecule, which has been a typical prototype molecule in the ab initio methods. The double-zeta plus polarization [3s2p1d] set [12], which is sufficient to check the ability of the present method, is used throughout this Letter. The polarization functions are used as six-component Gaussian-type functions. In optimizing orbitals, we choose the HF determinant as an initial function. Similar to the generalized VB (GVB) case, the spin-projection makes the HF solution unstable and we obtain a new DODS-type solution of a generating S-det. Similarly, for solutions with one more generating S-dets, the HF determinant is added to the DODS solution and reoptimized.

We compare the correlation energies at the CASSCF and the ResHF levels in Table 1. The ResHF wavefunctions with only two and three generating S-dets can remarkably reproduce almost 40 and 50% of the correlation energy calculated at the internally contracted MRSDCI level [13]. These amounts are comparable with the full-valence CASSCF calculation that includes 328 CSFs in the C_{2v} symmetry. For two-electron systems, the half-projected ResHF wavefunction of one generating S-det is equivalent to the GVB wavefunction. The present method, however, can treat the extra ORE among configurations for many-electron systems as well. This kind of correlation energy, which may include many (more than two) electron excitations from reference wavefunctions, is difficult to treat in the standard ab initio methods.

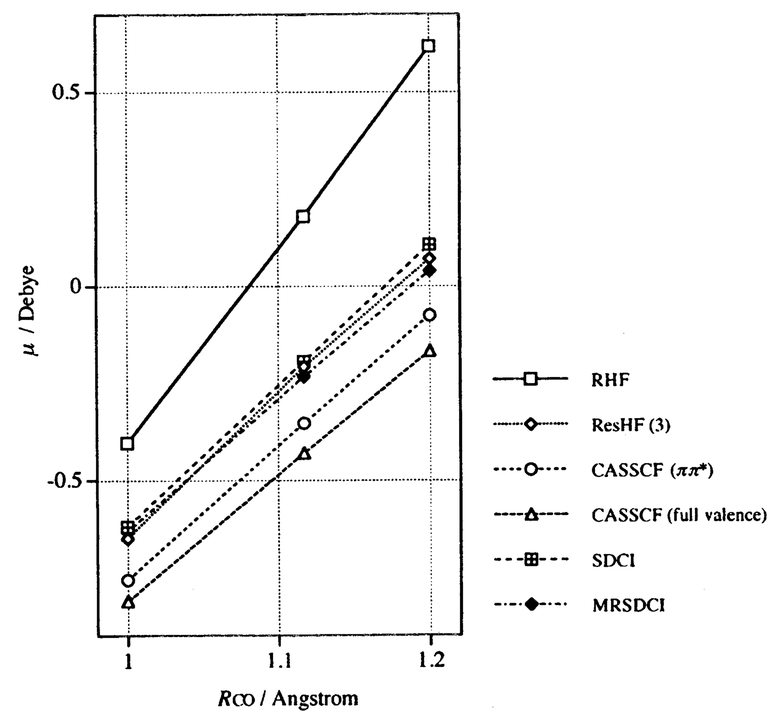

Fig. 1. Dipole moment of the CO molecule around the equilibrium nuclear distance. The ResHF wavefunctions are constructed with three generating S-dets.

In treating dynamic correlation effects, a rapid convergence of CI expansions can be achieved, if and only if the residual perturbation term is localized. In other words, the reference function should be correct at least in its long-range behavior. The simplest way to check this point is to examine the multipole moment which reflects the quality of the induced electrostatic field. It is well known that the HF wavefunction cannot reproduce even the sign of the dipole moment of the CO molecule around the equilibrium distance. This is another reason why we

Table 1
Comparison of the correlation energies [a] based on the ResHF method with those obtained based on other ab initio methods [b]

Method	$E_{corr.}/E_h$	(%)	Number of CSFs [c]
ResHF(2)	−0.1137	(40)	2
ResHF(3)	−0.1476	(51)	3
CASSCF (π, π^*)	−0.0745	(26)	12
CASSCF (full valence)	−0.1284	(45)	328
MRSDCI [d]	−0.2876	(100)	218576

[a] In the Hartree atomic unit. All of the results are calculated at the bond length of R_{CO} = 1.117 Å. The RHF energy E_{HF} = −112.75932 E_h is used.
[b] The C_{2v} symmetry is used.
[c] Number of the half-projected states in the ResHF method.
[d] The internally contracted MRSDCI method is used; see Ref. [12]. Two core orbitals are treated as frozen.

Table 2
Expectation values of $\hat{S}^2$ of the total wavefunction, the generating S-dets and their half-projected functions [a] in case of $N_s = 2$

S-det	$\langle \phi_f \mid \hat{S}^2 \mid \phi_f \rangle / \langle \phi_f \mid \phi_f \rangle$	$\langle \tilde{\phi}_f \mid \hat{S}^2 \mid \tilde{\phi}_f \rangle / \langle \tilde{\phi}_f \mid \tilde{\phi}_f \rangle$
1	0.605	0.128
2	0.621	0.134
total	–	0.029

[a] Half-projected functions are denoted by $\tilde{\phi}_f$.

choose the molecule in this preliminary work. Fig. 1 shows the dipole moment calculated at various level of approximations. Squares and circles represent the dipole moment calculated at the RHF and the CASSCF in which the four (π, π^*) orbitals are treated as active, respectively. One can see that the 12 CSFs CASSCF method overestimates the experimental value. Furthermore, the extension of the active space to the full valence does not improve the result. The ResHF wavefunction with three generating S-dets reproduces the quantity very well on the contrary. This implies that mainly the (σ, π) separation due to the orbital partitioning makes the mean field worse and the ORE is essential for this quantity of CO. Therefore, we can expect that the ResHF approach is more suitable to generate reference wavefunctions for MR treatments than the usual MCSCF method.

Finally, we mention the spin projection of our wavefunction. We have used the half-projection. In Table 2, the expectation values of $\hat{S}^2$ of the S-dets, half-projected S-dets and the ResHF wavefunction of two generating determinants are given. One can see that the resonance component of different S-dets is definitely important to reproduce the singlet state though each S-det is considerably projected. In case of $N_s = 3$, similar quality of the projection is also achieved.

4. Conclusion

We have applied the ResHF method to the molecular orbital calculation of the CO molecule. We showed that the ResHF wavefunction with two or three generating S-dets can reproduce correlation energies comparable with that obtained in the full-valence CASSCF method which includes 328 CSFs. In addition, it was also shown that the present method can reproduce the dipole moment, which reflect the quality of the electrostatic field, much better than the usual MCSCF method. This implies the importance of the ORE among the main CSFs. The spin adapted version of the ResHF and the way to treat dynamic correlation effects based on the wavefunction are discussed in separate papers [14].

Acknowledgement

One of the authors (NT) would like to thank the post-doctoral fellowship in the Institute for Molecular Science. The conventional ab initio calculations were carried out using the MOLPRO 94 program package on HP 735 and IBM AIX6000 computers.

References

[1] K. Andersson and B.O. Roos, in: Modern electronic structure theory, Part I, ed. D.R. Yarkony (World Scientific, Singapore, 1995), and references therein.
[2] R. Shepard, Theor. Chim. Acta 84 (1992) 55, and references therein.
[3] H. Fukutome, Prog. Theor. Phys. 80 (1988) 417.
[4] A. Ikawa, S. Yamamoto and H. Fukutome, J. Phys. Soc. Jpn. 62 (1993) 1653.
[5] A. Igawa and H. Fukutome, Prog. Theor. Phys. 80 (1988) 611.
[6] D.J. Thouless, Nucl. Phys. 21 (1960) 225.
[7] G.A. Gallup, R.L. Vance, J.R. Collins and J.M. Norbeck, Adv. Quantum Chem. 16 (1982) 229.
[8] H.F. King, R.E. Stanton, H. Kim, R.E. Wyatt and R.G. Parr, J. Chem. Phys. 47 (1967) 1936.
[9] A. Igawa, Int. J. Quantum Chem. 54 (1995) 235.
[10] O. Sinanoğlu, Proc. Natl. Acad. Sci. 47 (1961) 1217.
[11] P.C. Hiberty, J.P. Flament and E. Noizet, Chem. Phys. Lett. 189 (1992) 259;
P.C. Hiberty, S. Humbel and P. Archirel, J. Phys. Chem. 98 (1994) 11697.
[12] T.H. Dunning Jr. and P.J. Hay, in: Methods of electronic structure theory, ed. H.F. Schaefer III (Plenum Press, New York).
[13] H.-J. Werner and P.J. Knowles, J. Chem. Phys. 89 (1988) 5803.
[14] S. Ten-no, in preparation.