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Generalized Brillouin Theorem Multiconfiguration Method for Excited States

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The Generalized Brillouin Theorem Multiconfiguration Method (GBT-MC) of Grein and Chang is extended and applied to the calculation of excited states. Orthogonality constraints to lower states as well as second-order interaction effects of states lying close together have been taken into account. In this way quadratic convergence can be guaranteed. Difficulties with coupling coefficients and Lagrangian multipliers of SCF methods can be circumvented. Test calculations have been performed on valence electron excited states of C, H_2O, and CH_2O, and on core excited states of Li.

Key words: MC method – Excited states – core hole states – Carbon – Lithium – Water – Formaldehyde

1. Introduction

Multiconfiguration (MC) wave functions allow for a large portion of the electron correlation via a very compact configuration expansion and have proven very successful in the investigation of molecular ground states. Applications to excited states have appeared only in recent years.

In general, the different techniques for the determination of MC functions [1] can be divided into the following three steps:

1) Choice of a one-electron basis set; construction of a set of orthonormal starting MO's χ_i; selection of a set of n configurations ϕ_ν built from the χ_i.
2) Optimization of the linear coefficients C_ν in the n-MC function

$$\Psi = \sum_{\nu=1}^{n} C_\nu \cdot \phi_\nu(\chi_i) \tag{1}$$

and calculation of an upper bound to the energy E of the state in question.
3) Improvement of the occupied MO's χ_i within the given one-electron basis and repetition of steps 2 and 3, until no further lowering of E is achievable.

Many of the methods developed so far for the optimization of Ψ often encounter difficulties when applied to the treatment of excited states. For the case of the SCF approach, Das [2] and Hinze [3] have explained the origin of these difficulties and have proposed methods on how to overcome them. Another approach is the so-called Generalized Brillouin Theorem (GBT) Method which, so far, has mainly been used in ground state calculations (Grein and Change [3]).

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It is the aim of this work to extend the GBT-MC method to excited state calculations (Sect. 2). Special attention is drawn to the problem how to guarantee the (quadratic) convergence of the energy. The proposed method is also able to yield single configuration (1-MC) wave functions for open and excited shell systems without the usual difficulties associated with coupling coefficients, Lagrangian multipliers and orthogonality constraints. Simple test calculations are presented in Sect. 3 for ^3P states of the carbon atom. In Sect. 4 the $^1A_1$ states of the H_2O and H_2CO molecules are discussed. Some of the excited states exhibit the special difficulties connected with a pseudo-crossing. Finally it will be shown in Sect. 5 that the GBT-MC method is specially useful for core excited states.

2. Quadratically Convergent GBT-MC Method for Excited States

The GBT-MC method for ground states has been described in detail by Grein and Chang [4]. Applying a unitary transformation to the MO's χ_i:

$$\chi_i' = \chi_i + \sum_j d_{ij}\chi_j \tag{2}$$

the MC function (1) is transformed, up to first order in d_{ij}, into

$$\Psi' = \Psi + \sum_{i<j} d_{ij}\Psi_{ij} \tag{3}$$

where the Ψ_{ij} denote singly substituted MC functions:

$$\Psi_{ij} = \sum_{n=1}^{n} C_\nu \cdot [\phi_\nu(\chi_i \to \chi_j) - \phi_\nu(\chi_j \to \chi_i)] \tag{4}$$

The optimum orbital transformation coefficients may now be obtained from the so-called Super-CI (SCI) problem, which is the linear variation problem based on Ψ and all the Ψ_{ij}. Because of the Generalized Brillouin Theorem [5], which states that the fully optimized MC function Ψ^{opt} is non-interacting with all its singly substituted wave functions:

$$\langle \Psi^{\mathrm{opt}} | H - E | \Psi_{ij}^{\mathrm{opt}} \rangle = 0 \tag{5}$$

the d_{ij}, which appear in the eigenvector of the SCI problem, will tend to zero as Ψ approaches Ψ^{opt}. Several additional considerations are necessary in the case of excited states.

Let us be interested in the mth state of its symmetry. In order to obtain an upper bound to its energy in *step 2*, the MC expansion (1) should at least contain representative configurations of the $m - 1$ lower states ($n \geqslant m$). According to the Hylleraas-Undheim theorem [6], an upper bound to the mth energy is then given by the mth root of the $n \times n$ eigenvalue problem corresponding to Eq. (1), the so-called *MCI problem*. Some further comments concerning the selection of configurations and of the molecular orbitals in *step 1*, which are of significance to excited state problems, will be given in the subsequent sections.

The main difficulty in excited state MC calculations is how to prevent the MO's in *step 3* from being "improved" in such a manner that the energy expectation value decreases, indeed, but that the MC function becomes a (bad) representation of a lower state (root flipping problem). In the case of the GBT approach, one may again appeal to the Hylleraas-Undheim theorem. To keep the eigenvector of the *SCI problem* non-interacting with the $m-1$ lower states, it suggests itself to include also the $m-1$ lower MCI wave functions in the SCI basis. In this way one takes account of the fact that the MCI coefficients C_ν are not constant but vary linearly with an MO improvement. Keeping the C_ν fixed in each SCI step can only slightly reduce the rate of convergence in the case of the ground state, but may fully destroy the convergence in the case of excited states. This situation is sketched in Fig. 1.

We will now mathematically formulate this idea. Let Ψ^m be the mth root of the MCI problem. After orbital transformation (1), the non-normalized mth root of the new MCI problem is given by

$$\Psi^{m'} = \left(1 - \tfrac{1}{2} \sum_{ij} d_{ij}^2\right) \Psi^m + \sum_{ij} d_{ij} \Psi_{ij}^m + \sum_{ij,kl} d_{ij} d_{kl} \Psi_{ij,kl}^m + \sum_{\mu} \eta_\mu \cdot \Psi^\mu + \sum_{\mu,ij} \eta_\mu \cdot d_{ij} \Psi_{ij}^\mu + O(d^3). \tag{6}$$

The $\Psi_{ij,kl}^m$ are doubly substituted MC functions, the Ψ^μ are the other roots of the original MCI problem. The energy expectation value corresponding to wave function (6) is, up to second order in d,

$$\begin{aligned}\langle E\rangle = \frac{1}{S}\Big\{&(1 - \sum_{ij} d_{ij}^2)E^m + 2 \sum_{ij} d_{ij} \langle \Psi_{ij}^m | H | \Psi^m \rangle \\ &+ 2 \sum_{ij,kl} d_{ij} d_{kl} (\langle \Psi_{ij}^m | H | \Psi_{kl}^m \rangle + \langle \Psi^m | H | \Psi_{ij,kl}^m \rangle) \\ &+ 2 \sum_{\mu,ij} \eta_\mu d_{ij} (\langle \Psi_{ij}^m | H | \Psi^\mu \rangle + \langle \Psi^m | H | \Psi_{ij}^\mu \rangle) + \sum \eta_\mu^2 \cdot E^\mu \Big\}.\end{aligned} \tag{7}$$

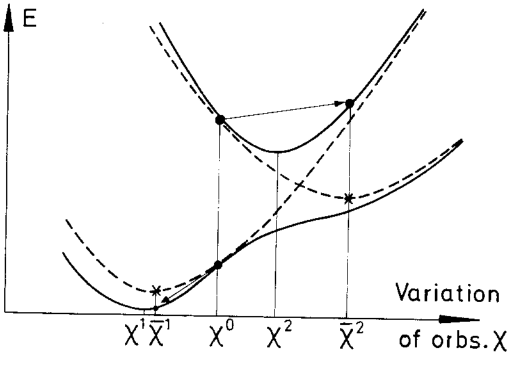

Fig. 1. Orbital and energy improvement in the GBT procedure. — Energy eigenvalues of the MCI problem, --- energy expectation values of MC functions with constant CI coefficients C_ν. χ^0 are the starting MO's, χ^m ($m = 1, 2$) the optimal MO's for the mth state, and $\bar{\chi}^m$ are the MO's determined by the GBT method under the restriction of constant C_ν. The arrows denote that the ground state energy will be improved in any case but that for excited states the contrary may happen. Grein and Banerjee [7] have proposed to suppress these oscillations by strong damping via a root shifting method of Saunders and Hillier [8]

S is the normalization constant and the E^{μ} are the energy eigenvalues of the original MCI problem. Optimizing $\langle E\rangle$ results in the following SCI eigenvalue problem:

$$\begin{pmatrix} E^{m}-\langle E\rangle & \langle\Psi^{m}|H-\langle E\rangle|\Psi^{m}_{ij}\rangle & 0 \\ \langle\Psi^{m}_{kl}|H-\langle E\rangle|\Psi^{m}\rangle & \begin{array}{l}\langle\Psi^{m}_{kl}|H-\langle E\rangle|\Psi^{m}_{ij}\rangle \\ \quad +\langle\Psi^{m}_{ij,kl}|H-\langle E\rangle|\Psi^{m}\rangle\end{array} & \begin{array}{l}\langle\Psi^{m}_{kl}|H-\langle E\rangle|\Psi^{\lambda}\rangle \\ \quad +\langle\Psi^{m}|H-\langle E\rangle|\Psi^{\lambda}_{kl}\rangle\end{array} \\ 0 & \begin{array}{l}\langle\Psi^{\mu}_{ij}|H-\langle E\rangle|\Psi^{m}_{ij}\rangle \\ \quad +\langle\Psi^{\mu}_{ij}|H-\langle E\rangle|\Psi^{m}\rangle\end{array} & (E^{\mu}-\langle E\rangle)\,\delta_{\mu\lambda} \end{pmatrix} \begin{pmatrix} 1 \\ d_{ij} \\ \eta_{\mu} \end{pmatrix} = \vec{0} \tag{8}$$

This equation may very efficiently be solved by single-vector diagonalization techniques, using the starting vector (1, 0, 0, . . .). Equation (8) differs in two respects from the SCI equation of the conventional GBT procedure. Firstly, as anticipated, the other MC functions occur as basis functions. Omitting them as e.g. in Ref. [7] means, that one works with an "improved" MC function which is not correct in the first order, and with an energy expression which is not correct in the second order. Secondly, there occur extra matrix elements which are formally obtained by exchanging a single substitution between a bra and a ket. It is interesting to note that some of these additional matrix elements also occur in the MC-SCF formalism of Das *et al.* [2b]. Usually they are omitted either because only the linear terms are retained in Eq. (6) as in Ref. [4] or because it is argued that they are usually orders of magnitude smaller than the non-exchanged terms [1]. However, firstly this statement will not hold in every case; and secondly, concerning the diagonal elements, it is not the ratio

$$\langle\Psi^{m}_{ij,ij}|H|\Psi^{m}\rangle/\langle\Psi^{m}_{ij}|H|\Psi^{m}_{ij}\rangle$$

but

$$\langle\Psi^{m}_{ij,ij}|H|\Psi^{m}\rangle/\,\{\langle\Psi^{m}_{ij}|H|\Psi^{m}_{ij}\rangle-E^{m}\}$$

which determines the influence of the extra matrix elements. This latter ratio may be quite large in the case of two nearly degenerate, strongly mixed states. In such a case, the convergence behavior of the method may be fully destroyed, if the extra matrix elements are neglected. However, as long as the mth state is well separated from the other ones, the procedure remains "nearly" quadratically convergent. Therefore, it seems justified to omit these extra matrix elements in most cases, since it results in a considerable simplification of the computational procedure. Furthermore it is usually sufficient to retain only the $m-1$ lower Ψ^{μ}'s in the SCI problem.

Another computational simplification may and should be carried out in those cases where one of the Ψ^{m}_{ij} is nearly equivalent to a lower MC function Ψ^{μ}. In order to avoid the nearly linear dependency, this Ψ^{μ} may be omitted from the SCI basis. In many cases such a Ψ^{μ} corresponds to a configuration which has only been included in the MC expansion to represent one of the lower states and to make the Hylleraas-Undheim theorem applicable, but which does not significantly contribute to electron correlation. Then it is even simpler to omit this configuration also in the MC expansion. In this case the $(m-1)$st MC root is still an upper bound to the energy of the mth state, since upon convergence it becomes identical with the mth root of the SCI problem.

Usually less than 10 iterations are sufficient to reach the limit of the MC root within 1 meV. Single configuration calculations converge even faster. If the starting orbitals are not too bad, the SCI energy converges from below and considerably faster than the MC energy, which decreases. The orbitals and the other roots of the MCI and SCI problems, which may be taken as approximations to other states, of course converge more slowly.

Hinze [9] has proposed an MC-SCF procedure where the MO's are optimized in the mean field of several states. This idea has several advantages. Firstly MC functions of several states are obtained from a single iteration process; secondly, because of a unique orthogonal MO basis for several states, the evaluation of transition integrals is drastically facilitated; finally the root-flipping problem is circumvented. A corresponding technique is simply incorporated into the GBT method by optimizing a weighted mean of several MC roots in the SCI step. By changing the weights, one or another of the states can be optimized to a larger extent. This technique is not recommendable in cases where two states differ by a significant orbital reorganization, as e.g. a valence and a core excited state.

3. Test Calculations on ^3P States of the Carbon Atom

We have tested the proposed method on some $^3P^e$ states of the carbon atom. The ground state is $1s^2 2s^2 2p^2\ ^3P$. The valence excited state $1s^2 2p^4\ ^3P$ has so far not been detected experimentally, but since its term value is needed in semiempirical molecular calculations, its energy has been determined by several empirical and semiempirical methods which, however, did not agree. Jordan and Longuet-Higgins [10] obtained 18.86 eV by vertical analysis of experimental energies. Verhaegen and Moser [11] obtained 19.23 eV from isoelectronic extrapolation of correlation energies and Pittel and Schwarz [12] predicted 19.39 eV from vertical analysis of correlation energies. Furthermore, different SCF energies have also been reported: −36.9448 a.u. by Verhaegen and Moser [11] and −37.1464 a.u. somewhat later by Offenhartz [13]. For comparison three types of calculations are carried out, the results of which are collected in Table 1.

Table 1. Energy values for the carbon atom

Type of Function	Ground State ^3P	$1s^2 2p^4\ ^3P$	Excitation Energy
Single configuration	−37.6886 a.u.	−36.9448 a.u.	20.24 eV
Two configurations	−37.7060 a.u.	−36.9276 a.u.	21.18 eV
(Internal correlation)	(−0.47 eV)	(+0.47 eV)	
MC	−37.743 a.u.	−36.979 a.u.	20.8 eV
(Semi-internal correlation)	(−1.0 eV)	(−1.4 eV)	
Total energy	−37.845 a.u.	−37.137 a.u.[a]	19.3 eV
(External correlation)	(−2.8 eV)	(−4.3 eV)	

[a] MC energy + semiempirical all-external correlation correction.

1) Our single configuration calculations are comparable to ordinary SCF calculations. However, our method avoids the difficulty in connection with Lagrangian multipliers and does not start from an energy expression with coupling coefficients. The symmetry-fixed coefficients of a multideterminantal configuration can automatically be determined by the GBT procedure. However, it turned out that the numerical accuracy is increased and the computational time is decreased when some phase relations of the determinants are accounted for in the MC basis. Therefore we usually couple two singly occupied shells to a singlet or a triplet. Our excited state energy agrees with the value of Verhaegen and Moser, the corresponding SCF term value is 20.24 eV (see Table 1).

2) The two $^3P^e$ valence configurations are of course interacting with each other. The corresponding internal correlation energy of the ground state is –0.47 eV. Verhaegen and Moser [11] did not perform a two-configuration calculation for the upper state but proposed to approximate the internal correlation energy of the excited state by the negative value of that of the ground state. Since the optimized orbitals for the ground and the excited state differ considerably, this identity is not exact. However, our calculation shows that the internal correlation energy of the upper state is only about 0.005 eV smaller in magnitude than that of the lower one.

3) According to Sinanoğlu [14], specific non-transferable correlation effects of considerable magnitude are caused by interaction of the valence configurations with the lowest Rydberg type configurations. The most significant semi-internal correlation configurations of the two valence states under consideration are $1s^2 2s2p^2 3s'\ ^3P$ (two different spin couplings), and $1s^2 2s2p^2 3d'\ ^3P$ (three different spin couplings), which lower the ground state by 1 eV. In the case of the $1s^2 2p^4\ ^3P$ state we have furthermore to take into account that it is not the lowest one of its symmetry. The following states are lower in energy: $1s^2 2s^2 2pnp\ ^3P$, $1s^2\ (2s2p^2\ ^4P)ns\ ^3P$, $1s^2\ (2s2p^2\ ^4P)nd\ ^3P$ and $1s^2(2s2p^2\ ^2D)3d\ ^3P$. Among these the $n > 3$ configurations may be neglected in the MC expansion since the different spatial extent results in negligible interaction. On the other hand the $1s^2 2s2p^2 3d'$ correlation configurations and the $1s^2 2s2p^2 3d$ Rydberg state configurations must not be identified, since their $3d$ and $3d'$ orbitals differ considerably in spatial extent. Performing the corresponding MC calculation for the $1s^2 2p^4\ ^3P$ state resulted in an energy lowering of 1.4 eV. An estimate of the total energy is finally obtained by adding the semiempirical all-external correlation energy increments given by Sinanoğlu [19]. It shows that the estimate of Moser [11] is the most reliable one, whereas the prediction of Longuet-Higgins [10] is low by nearly half an electron-volt.

4. Valence and Rydberg Excited States of Molecules

In order to gain more insight into the method, especially in the case of two states with small energy separation, we have performed calculations on the ground and lower excited $^1A_1$ states of water and formaldehyde.

4.1. $^1A_1$ *States of Water*

The ground state configuration is $\phi_0 = 1a_1{}^2\ 2a_1{}^2\ b_2(\sigma)^2\ 3a_1(n)^2\ b_1(\pi)^2\ {}^1A_1$. The two lowest excited states of the same symmetry are obtained by excitation of oxygen lone pair electrons ($3a_1$, b_1) into the lowest empty MO's. The experimental vertical excitation energies are 9.7 eV for $\tilde{B}$ ($3a_1 \rightarrow 3sa_1$) and 10.2 eV for $\tilde{D}$ ($b_1 \rightarrow 3pb_1$) [13]. These configurations are expected to interact strongly.

The calculations are performed for the ground state equilibrium geometry (R(O-H) = $1.8a_0$; $\alpha = 105°$). The AO basis is the same as that used by Buenker and Peyerimhoff [16]. It consists of a contracted Gaussian lobe set of double-zeta quality augmented by polarization functions and one *sp* set of Rydberg functions on oxygen, giving a total of $11a_1$, $2a_2$, $6b_2$, and $7b_1$ symmetry orbitals. The ground state SCF energy of 76.0311 a.u. is 1.0 eV above the Hartree-Fock limit [17].

4.1.1. Ground State

Results for the ground state are collected in Table 2. Double excitation of each of the three highest occupied orbitals into an empty orbital of the same symmetry results in an energy lowering of about 1/3 eV. The correlation orbitals b_2^*, a_1^*, b_1^* are of valence character with only a slight admixture of diffuse functions, as may be seen from Table 3.

Concerning the MC functions *II* and *III* it should be remembered that the wave function

$$\Psi = \phi_0 + C_1 \cdot (b_1 \rightarrow b_1^*) + C_2 \cdot (b_1^2 \rightarrow b_1^{*2}) \tag{9a}$$

can be transformed by a unitary MO transformation into

$$\Psi = \phi_0' + C_1' \cdot (b_1' \rightarrow b_1^{*\prime}) \tag{9b}$$

or into

$$\Psi = \phi_0'' + C_2'' \cdot (b_1''^2 \rightarrow b_1^{*''2}) \tag{9c}$$

Table 2. MC energies of the ground state of water

Case	Number of Configs.	Wave Function*	Energy (a.u.)
I	1	ϕ_0	−76.0311
II	2/3	$\phi_0 + (b_1^2 \rightarrow b_1^{*2})$ and/or $(b_1 \rightarrow b_1^*)$	−76.0424
III	2/3	$\phi_0 + (3a_1 \rightarrow a_1^{*2})$ and/or $(3a_1 \rightarrow a_1^*)$	−76.0435
IV	3	$\phi_0 + (3a_1^2 \rightarrow a_1^{*2}) + (b_1^2 \rightarrow b_1^{*2})$	−76.0552
V	3	$\phi_0 + (3a_1 \rightarrow a_1^*) + (b_1 \rightarrow b_1^*)$	−76.0638
VI	5	$\phi_0 + (3a_1 \rightarrow a_1^*) + (b_1 \rightarrow b_1^*) + 2(3a_1b_1 \rightarrow a_1^*b_1^*)$	−76.0663
VII	4	$\phi_0 + (3a_1^2 \rightarrow a_1^{*2}) + (b_1^2 \rightarrow b_1^{*2}) + (b_2^2 \rightarrow b_2^{*2})$	−76.0684
VIII	4	$\phi_0 + (3a_1 \rightarrow a_1^*) + (b_1 \rightarrow b_1^*) + (b_2 \rightarrow b_2^*)$	−76.0880
IX	7	Case *VII* + *VIII*	−76.0910[a]

* $\phi_0 = 1a_1^2\ 2a_1^2\ b_2^2\ 3a_1^2\ b_1^2$.

[a] A straightforward CI, including single and double excitations from all valence orbitals, yields −76.1886 a.u. [16].

Table 3. Orbital expectation values $\langle 1/r_0 \rangle$ and $\langle (r - \langle r \rangle)^2 \rangle$ for the three lowest $^1A_1$ states of water calculated from the case *VIII* wave functions[a]

		Occupied Valence Orbitals					Correlation Orbitals			Rydberg Orbitals	
	State	$1a_1$	$2a_1$	b_2	$3a_1$	b_1	b_2^*	a_1^*	b_1^*	$3sa_1$	$3pb_1$
r^2	X	0.053	1.63	2.1	1.9	1.6	4.6	5.2	6.6	–	–
	$\tilde{B}$	0.053	1.63	2.4	1.9	1.6	3.2	9.6	3.1	23[b]	40
	$\tilde{D}$	0.053	1.62	2.3	2.0	1.8	3.7	5.9	6.2	26	44
$1/r$	X	7.64	1.22	1.0	1.1	1.2	0.9	0.8	0.8	–	–
	$\tilde{B}$	7.64	1.21	0.9	1.1	1.1	1.0	0.9	1.0	0.29	0.22
	$\tilde{D}$	7.64	1.19	1.0	1.1	1.1	1.0	0.9	1.0	0.27	0.17

[a] It should be noted that the MC wave function is invariant against a unitary transformation of those orbitals which have the same occupancy in all configurations. Therefore the inner shell orbitals are not fully determined.

[b] The three components of r^2 (6.6; 8.5; 7.7a_0^2) indicate that the 3*s* orbitals of $\tilde{B}$ has some admixture of $3pa_1$ and a_1^*.

with the approximate relation $C_1'^2 \approx C_2''$. Therefore wave functions of type (9b), which describe the correlation by a single excitation, have quite large configuration mixing coefficients C'. In the wave functions II and III, C' is about 0.25-0.3, corresponding to C'' values of 0.07-0.08. Although wave functions (9a), (9b), (9c) are equivalent, the convergence of the GBT procedure is faster in the case of (9a).

When we correlate two or more electron pairs, single and double excitations are no longer equivalent. In the case of double excitations, the individual energy lowerings are nearly additive (compare wave functions *I-IV*). This does not hold for several singly substituted configurations, since these are strongly interacting (compare wave functions *IV* with *V* and *VII* with *VIII*). In the underlying case, several single excitations are considerably more effective than several double excitations in describing electron correlation. Whereas the optimum orbitals in doubly substituted MC expansions are approximately natural orbitals, this is not the case for orbitals of singly substituted MC expansions. We arrive at the conclusion that natural orbitals are not necessarily most suitable, when correlation shall be effectively described by a short CI expansion.

4.1.2. Excited States

In Tables 4 and 5 we present MC energies for the first two excited $^1A_1$ states. Whereas it is very difficult to handle single configuration wave functions with two open shells of the same symmetry with singlet spin coupling by the SCF technique [18] there occur no problems with the GBT method. Of course the 1-MC functions (cases *I*) interact with the lower lying configurations. The interaction of ϕ_0 with ($3a_1 \rightarrow 3s$) is considerably weaker (energy shift = +0.17 eV, Table 4) than with ($b_1 \rightarrow 3p$) (ΔE = +0.51 eV, Table 5).

Table 4. MC energies of the first excited $^1A_1$ state of water ($\tilde{B}$)

Case	Number of Configs.	Wave function	Energy (a.u.)
I	1	$(3a_1 \to 3s)$	−75.7153
II	2	$(3a_1 \to 3s) + \phi_0$	−75.7089
III	3	$(3a_1 \to 3s) + \phi_0 + (b_1 \to 3p)$	−75.7149
IV	4	Case *III* + $(b_2 \to b_2^*)$	−75.7150
V	5	Case *III* + $(3a_1b_1 \to 3s3p)$	−75.7151
VI	4	Case *III* + $(3a_1^2 \to 3sa^*)$	−75.7153
VII	8	Case *VI* + $(3a_1b_1 \to 3sb_1^*) + (3a_1b_2 \to 3sb_2^*)$	−75.7167
VIII	6	Case *VI* + $(3a_1b_1^2 \to 3sb_1^{*2}) + (3a_1b_2^2 \to 3sb_2^{*2})$	−75.7302

Table 5. MC energies of the second excited $^1A_1$ state of water ($\tilde{D}$)

Case	Number of Configs.	Wave Function	Energy (a.u.)
I	1	$(b_1 \to 3p)$	−75.7119
II	2	$(b_1 \to 3p) + \phi_0$	−75.6931
III	3	$(b_1 \to 3p) + \phi_0 + (3a_1 \to 3s)$	−75.6910
IV	4	Case *III* + $(b_2 \to b_2^*)$	−75.6953
V	6	Case *IV* + $(3a_1b_1 \to 3s3p)$	−75.6953
VI	9	Case *V* + $(b_2b_1 \to b_2^*3p) + (b_1^2 \to \pi^*3p)$	−75.6963
VII	10	Case *IV* + $(b_1^2 \to 3pb_1^*) + (3a_1^2b_1 \to 3pa_1^{*2})$ + + $(b_1b_2^2 \to 3pb_2^{*2}) + (3a_1b_1^2 \to 3sb_1^{*2})$ + $(3a_1^2 \to 3sa_1^*) + (3a_1b_2^2 \to 3sb_2^{*2})$	−75.7090
VIII	7	Case *IV* + $(b_1^2 \to 3pb_1^*) + (b_1b_2^2 \to 3pb_2^{*2})$ + $(3a_1b_1^2 \to 3sb_1^{*2}) + (3a_1b_2^2 \to 3sb_2^{*2})$	−75.7090

The two Rydberg states are both strongly mixed. The 3-MC functions of the three states are

$$(X\,^1A_1) \approx 0.90\phi_0 - 0.32\,(3a_1 \to a_1^*) - 0.27\,(b_1 \to b_1^*)$$

$$(\tilde{B}\,^1A_1) \approx 0.03\phi_0 + 0.92\,(3a_1 \to 3s) - 0.40\,(b_1 \to 3p)$$

$$(\tilde{D}\,^1A_1) \approx 0.13\phi_0 + 0.42\,(3a_1 \to 3s) + 0.90\,(b_1 \to 3p)$$

Furthermore the 3*s* orbitals possess different amounts of 3*p* admixture. However, the Rydberg mixing has no large influence on the energy. Therefore the energies are raised by only ~0.1 eV if the average of both states is optimized, thereby avoiding any possible convergence difficulties with the third root. At the single-configuration level the excitation energies are too small by about 1 eV (see Table 6). One can approximately take account of the missing correlation contribution on the 3-MC level. Including the valence shell correlation in all three states in the same manner by including Rydberg and correlation orbitals of the same symmetry in the MO basis (cases *VIII*), the calculated excitation energies agree well with the CI results and with the experimental values (see Table 6). It is interesting to note that in the

Table 6. Excitation energies of water

		First Excited State		Second Excited State	
	Ground State	Wave Fct.	E (eV)	Wave Fct.	E (eV)
SCF-like level	Case *I*	Case *II*	8.77	Case *III*	9.25
3-MC level	Case *V*	Case *III*	9.49	Case *III*	10.14
4-MC level	Case *VIII*	Case *IV*	10.15	Case *IV*	10.69
"Balanced" MC level	Case *VIII*	Case *VIII*	9.73	Case *VIII*	10.31
CI value [16]			9.80		10.32
Experimental [15]	$X\,^1A_1$	$\tilde{B}\,^1A_1$	9.7	$\tilde{D}\,^1A_1$	10.2

ground state the addition of double excitations to the single excitations is rather inefficient, whereas in the excited states the situation is just reversed.

4.2. $^1A_1$ *States of Formaldehyde*

The ground state configuration of CH_2O is $1a_1^2\,2a_1^2\,3a_1^2\,4a_1^2\,1b_2^2\,5a_1(\sigma)^2\,1b_1(\pi)^2\,2b_2(n)^2\,{}^1A_1$. The excited $^1A_1$ states have been the subject of much controversy [20]. From the more recent experimental [21] and theoretical [22] investigations we know that the lowest excited $^1A_1$ states are obtained by excitation of an oxygen lone pair electron $2b_2(n)$ into $np(b_2)$ and $nd(b_2)$ Rydberg orbitals. The energy of the lowest of these states, $\tilde{C}(n \to 3p)$, is 7.97 eV. Directly above the first ionization limit ($^2B_2$) at 10.87 eV the absorption spectrum shows no special features, but the photoionization mass spectrum indicates a metastable species near 12 eV. Above this energy the absorption and photoionization coefficients show pronounced structures with maximum near 13 eV. The second vertical ionization limit ($^2B_1(\pi)$) is 14.5 eV.

The main problem has been the location of the $\pi \to \pi^*\ {}^1A_1$ state. Even the most recent *ab initio* calculations [22, 23] predict the state with large $\pi \to \pi^*$ character in a wide range from 9.7 to 12.2 eV, most probably slightly above 11 eV. Furthermore the mixing of $\pi \to \pi^*$ with $\pi \to 3p$ and $n \to np,nd$ is calculated very differently.

We have performed MC calculations on several $^1A_1$ states. The following geometric parameters were used: $R(CO) = 2.29a_0$, $R(CH) = 2.12a_0$, $\alpha(CH_2) = 118°$. A contracted Gaussian lobe set of double-zeta quality was augmented by one *sp* Rydberg set [24] but with no *d* functions.

4.2.1. Ground State (Table 7)

Ground state energies are given in Table 7. The single configuration result lies less than 0.1 a.u. above the Hartree-Fock limit [23]. As in the case of H_2O the energy lowerings of double excitations are nearly additive, whereas the interaction of single excitations contribute an additional amount of correlation energy.

Table 7. MC energies of the $X\ ^1A_1$ ground state of formaldehyde

Case	Number of Configs.	Wave Function	Energy (a.u.)
I	1	ϕ_0	113.811
II	2/3	$\phi_0 + (n \rightarrow b_2^*)$ and/or $(n^2 \rightarrow b_2^{*2})$	113.820
III	2/3	$\phi_0 + (\pi \rightarrow \pi^*)$ and/or $(\pi^2 \rightarrow \pi^{*2})$	113.852
IV	2/3	$\phi_0 + (\sigma \rightarrow a_1^*)$ and/or $(\sigma^2 \rightarrow a_1^{*2})$	113.821
V	4	$\phi_0 + (n^2 \rightarrow b_2^{*2}) + (\pi^2 \rightarrow \pi^{*2}) + (\sigma^2 \rightarrow a_1^{*2})$	113.870
VI	4	$\phi_0 + (n \rightarrow b_2^*) + (\pi \rightarrow \pi^*) + (\sigma \rightarrow a_1^*)$	113.885

4.2.2. Lowest $^1A_1$ Rydberg State (Table 8)

The SCF excitation energy is too small again. However, we obtain a quite good result when we correlate the three highest valence shells in both the ground and the excited state. The interaction of the $(n \rightarrow 3p)$ configuration with ϕ_0 and $(\pi \rightarrow \pi^*)$ is negligibly small.

4.2.3. $\pi \rightarrow \pi^*$ Singlet State (Table 9)

The interaction of the excited valence configuration with ϕ_0 is very strong, so that it collapses if the orthogonality to the ground state is not taken into account. Again the interaction with the lowest $(n \rightarrow 3pb_2)$ Rydberg configuration is quite weak. However, the π^* orbital has considerable diffuse orbital $(3pb_1)$ admixture, and $(\pi \rightarrow \pi^*)$ and $(\pi \rightarrow 3p)$ have nearly equal weights in the 10-MC function. The complement of this function, another state with $\pi \rightarrow \pi^*$ character was found ~1.5 eV higher in energy. This is in rough agreement with most *ab initio* calculations [22] which find the $\pi \rightarrow \pi^*$ configuration mixing with several higher Rydberg configurations[1].

5. Core Excited States of the Lithium Atom

The GBT method has also been tested to see how good highly excited core hole states can be handled. As an example[2] the lithium atom has been chosen, since accurate experimental data are available [25].

We used a Gaussian lobe basis (8/3/2). Calculations with a larger basis showed that the valence states are too high by about 0.1 eV, and the core excited states by about 0.2 eV. Different MC results are presented in Table 10. For each term we have calculated a wave function which includes internal and the main part of the semi-internal correlation. To this energy we have added the semiempirical external

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[1] Contrary to this, Langhoff *et al.* [23] very definitely stated that the $\pi \rightarrow \pi^*$ state is pure and has no diffuse components. However, it should be noted that they have not taken account of the orthogonality constraints to any of the lower $^1A_1$ Rydberg states, except in one case, in which they found an appreciable admixture of diffuse character!

[2] Further examples are discussed by the present authors in: Intern. J. Quantum Chem. Symp. 10, 91 (1976).

Table 8. MC energies of the $\tilde{C}(n \to 3pb_2)$ state of CH_2O

Case	Number of Configs.	Wave Functions	Energy (a.u.)	Reference G.S. Wave F.	Excitation Energy (eV)
I	1	$(n \to 3p)$	113.533	*I*	7.0
II	2	$\phi_0 + (n \to 3p)$	113.533		
III	3	$\phi_0 + (n \to 3p) + (\pi \to \pi^*)$	113.533		
IV	3	$\phi_0 + (n \to 3p) + (\pi^2 n \to \pi^{*2} 3p)$	113.580		
V	3	$\phi_0 + (n \to 3p) + (\sigma^2 n \to \sigma^{*2} 3p)$	113.581		
VI	5	$\phi_0 + (n \to 3p) + (\pi^2 n \to \pi^{*2} 3p) + (\sigma^2 n \to \sigma^{*2} 3p) + (n^2 \to b_2^* 3p)$	113.597	*VI*	7.85

Table 9. MC energies of a $(\pi \to \pi^*)$ $^1A_1$ state of CH_2O

Case	Number of Configs.	Wave Function	Energy (a.u.)	Reference G.S. Wave F.	Excitation Energy (eV)
I	1	$(\pi \to \pi^*)$	113.650	*I*	4.4
II	2	$\phi_0 + (\pi \to \pi^*)$	113.434	*I*	10.3
III	3	$\phi_0 + (n \to 3p) + (\pi \to \pi^*)$	113.432		
IV	10	$\phi_0 + (n \to 3p) + (\pi \to \pi^*) +$ $+ (\pi \to 3p) + (\pi \to \pi^*$, $n\sigma\pi$-excit.) $+ (\pi \to 3p$, $n\pi\sigma$-excit.)	113.450	*VI*	11.8

correlation energy increments of Sinanoğlu [19]. The results agree within about 0.1 eV with the experimental excitation energies. According to our basis defect the calculated values tend to be slightly too large. A few comments on some results are in order:

$1s^2 3s$ ^2S: The GBT method guarantees that the $1s^2 ns$ configuration is automatically noninteracting with all lower $1s^2 ms$ configurations, as they differ only by a single excitation. Therefore the second root of the 2-MC ansatz $1s^2 2s + 1s^2 3s$ yields the same energy as the single $1s^2 3s$ configuration.

$1s2s^2$ ^2S: This configuration is automatically noninteracting with $1s^2 2s$. Taking both configurations, the 2-MC function is invariant under unitary transformations of $1s$ and $2s$. Therefore the 2-MC function converges faster. When other configurations are included, e.g. $1s2p^2$ for internal correlation, $1s^2 2s$ is no longer noninteracting rigorously. Nevertheless, since the configurations are still nearly orthogonal, the energy will not increase but decrease (by 0.15 eV in our case) if we add $1s^2 2s$. The reason is that then the $1s$ orbital of the correlation configuration $1s2p^2$ can be freely optimized in the $1s2s$ subspace and is not forced to be the same as in the $1s2s^2$ configuration. The internal correlation energy is 1.30 eV, which agrees with the value of the "core analog" Be $1s^2 2s^2$ (1.29 eV). The question whether there is a noticeable interaction with the lower lying $1s^2 ns$ configurations has a negative answer.

Table 10. MC calculations on lithium

Term	MC Function	Energy (a.u.)	Excitation Energy (eV)	+ External Correlation (eV)	Exp. (eV)
$1s^22s\ {}^2S$	1-MC	−7.4295	0	0	0
	3-MC: + $(1s2s^2)$ + $(1s2p^2)$	−7.4299			
$1s^22p\ {}^2P^0$	1-MC	−7.3593	1.91	1.9	1.85
	3-MC: + $(1s2p2p)$	−7.3682	1.67		
	5-MC: + $(1s2p3d)$	−7.3725	1.55		
$1s^23s\ {}^2S$	1-MC (=2-MC)	−7.3070	3.33	3.4	3.32
$1s^2\ {}^1S^+$	1-MC	−7.2333	5.34	5.45	5.39
$1s2s^2\ {}^2S$	1-MC (=2-MC)	−5.3415	56.82		
	3-MC: + $(1s^22s)$ + $(1s^23s)$	−5.3413	56.82		
	2-MC: 1-MC + $(1s2p^2)$	−5.3836	55.67		
	3-MC: + $(1s^22s)$	−5.3890	55.52	56.7	56.35
$1s2s2p\ {}^4P^0$	1-MC	−5.3518	56.54	57.45	57.44
$1s2s2p\ {}^2_aP^0$	2-MC	−5.3396	56.87		
	3-MC: + $(1s^22p)$	−5.2896	58.23		
	5-MC: + $(1s2p3d)$	−5.2947	58.09	59.0	58.91
$1s2s2p\ {}^2_bP^0$	2-MC	−5.2051	60.53		
	3-MC: + $(1s^22p)$	−5.1995	60.68		
	5-MC: + $(1s2p3d)$	−5.2321	59.79	60.45	60.40
$1s2s\ {}^3S^+$	1-MC	−5.1067	63.21	64.45	64.41
$1s2s\ {}^1S^+$	1-MC	−5.0784	63.98		
	2-MC: + $(1s^2)$	−5.0333	65.20	66.25	66.15

This also justifies the omission of the continuum. The estimated excitation energy, including a basis defect in the SCF energy of about 0.2 eV, is then 56.5 eV. The experimental value has been determined only very recently and is 56.35 ± 0.01 eV [25].

$1s2s2p\ {}^2P^0$: There exist two linear independent terms, differing in the spin coupling. They may be approximated by $1s(2s2p\ {}^3P)^2P$ and $1s(2s2p\ {}^1P)^2P$. The neglect of the $1s^22p\ {}^2P$ ground state results in much too low energies, especially for the lower term ($\Delta E({}^2_aP^0) = 1.36$ eV; $\Delta E({}^2_bP^0) = 0.15$ eV). Also the semi-internal correlation by $1s2p3d$ is very different in both terms ($\epsilon({}^2_aP^0) = 0.14$ eV; $\epsilon({}^2_bP^0) = 0.89$ eV).

6. Summary and Conclusion

We have developed an MC method which is based on the generalized Brillouin theorem and leads to upper bounds of excited state energies. The upper bound property is guaranteed by including the lower configurations in both the MCI and SCI steps. The off-diagonal matrix elements in the SCI matrix lead to the very good convergence property. The convergence behavior is often drastically made worse, if not all interaction matrix elements are explicitly taken into account (e.g. in perturbative schemes or when not all single substitutions are considered in order to reduce the dimension of the SCI problem).

In several cases not all lower configurations have to be included in the MC ansatz. In some cases we may obtain single configuration wave functions with the upper bound property, which cannot be obtained by the ordinary RHF technique. To this class belong many of the higher excited Rydberg states, and, in practice at least, also several types of core excited and ionized species. For example, the different singly ionized species of a molecule are automatically non-interacting in our method. Furthermore the method can quite efficiently overcome the convergence problems often met in ordinary SCF hole state calculations. Since we have not to introduce Lagrangian multipliers we can handle states with several open shells of the same symmetry equally well. In the case where the symmetry adapted configurations are a complicated sum of determinants (as e.g. $1s2p3d\ ^2P$ of Li), we can do without specifying the coupling coefficients whereby the computational effort is often even reduced.

When we go beyond the SCF approximation the main problem with the MC method is the selection of correlation configurations. Examples given for water show how critical this is. Krauss, Schaefer, Sinanoğlu, Wahl, and others [21] have given advice which, however, leads to unwieldy long MC expansions in the case of excited states of polyatomic molecules.

The second unsolved problem with the GBT-MC method is a computational one. Before the method can compete with ordinary CI methods, special techniques have to be developed in order to calculate the SCI matrix from the AO integrals more quickly by exploiting that the SCI basis consists mainly of single excitations and that all off-diagonal matrix elements vanish when the iteration has converged.

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