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Treating large intermediate spaces in the CIPSI method through a direct selected CI algorithm

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Summary. A general direct selected configuration interaction algorithm has been implemented and coupled to the second-order multireference many-body perturbation theory CIPSI algorithm. The new direct selected CI code is highly vectorizable and able to handle any list of determinants selected to describe a given electronic state of any spin multiplicity. In the present work selection of determinants has been carried out through the CIPSI algorithm but this is not a constraint of the direct selected CI code. The largest case treated so far involves a CI expansion containing 215 260 determinants selected from single and double excitations from 371 references. In this case there were 8 active electrons in 28 molecular orbitals for NH_3 in a DZP basis set. The direct selected CI calculation needs only 14 Mb of central storage (for the 215 260 determinants case) and takes 406 seconds per iteration on an IBM 3090/600J with vector facility.

Key words: CIPSI algorithm – Direct selected CI – Large intermediate spaces

1 Introduction

Multireference Configuration Interaction methods (MRCI) nowadays belong to the most reliable quantum-chemical methods used to study ground and excited electronic states of molecular systems [1]. Although MRCI methods have been used for about twenty years [2, 3], it has not been possible to include all single and double excitations relative to the reference space except for rather small cases. To overcome the difficulty posed by the very large dimensions of the MRCI expansion, very efficient algorithms have been designed and implemented very recently [see Ref. [4] and references therein]. These algorithms are generally based on direct CI procedures [5–22] and also on the use of either externally and internally contracted CI techniques [23–25]. In the contracted CI techniques the number of variational parameters is largely reduced and the contraction coefficients are obtained by first-order perturbation theory.

An alternative approach would come from the fact that of the generated single and double excitations only a few have a noticeable contribution to the wavefunction. It will be enough to treat variationally the important generated configurations (or determinants) and use perturbation theory to have an estimate of the energy contribution of those generated terms not included into the variational MRCI. This is precisely the philosophy of CIPSI algorithm [26] in its three-class version [27]. In fact, a very recent study [28] has revealed that inclusion of about 1% of the total MRCI expansion in the variational (intermediate) class is enough to have meaningful results. Moreover, it has been proven that the second-order energy estimate of the contribution of those determinants of the MRCI expansion not included into the variational space is, for a series of test calculations, smaller than the error with respect to the exact FCI solution. A similar conclusion can be extracted from the results obtained through the internally contracted MRCI method [4].

For a large variety of chemical applications [29–41] it is usually enough to include 5000–10 000 determinants in the variational MRCI, i.e. in the intermediate class if using the CIPSI algorithm, to have results which will differ less than 1 mh from the full variational MRCI result. However, for transition-metal dimers or oxides a large increase of the intermediate space dimension is necessary to have results near the variational MRCI one [42]. Following the above ideas it is expected that inclusion of around 200 000 determinants in the intermediate space of a CIPSI calculation has to provide results with almost negligible errors with respect to the full variational MRCI. The bottle-neck of a three-class CIPSI calculation lies on the evaluation and storage of the CI matrix $\boldsymbol{H}$ in the basis set of the determinants belonging to this intermediate space. For this reason the dimension of the intermediate space cannot exceed 50 000 if the standard version of the CIPSI package is used [43], and a direct CI approach is needed.

Here we will present a general direct selected CI code that can handle any kind of MRCI expansion. This code has then been coupled to the CIPSI package which is the algorithm used to select both, the reference and the intermediate spaces, and also to compute the second-order energy contribution of those terms of the MRCI expansion not included in the variational space. The performance of such a code will be shown by comparison to selected FCI calculations. An analysis of the computer time spent at each step of the calculation will also be presented.

2 The direct-CI algorithm

The goal of a direct-CI procedure is to solve the matrix equation:

$$\boldsymbol{H}\boldsymbol{c}_i = E_i\boldsymbol{c}_i \tag{1}$$

without explicitly computing and storing the $\boldsymbol{H}$ matrix (the matrix representation for the non-relativistic electronic hamiltonian in the basis set of the Slater determinants).

As is well known, the solution of Eq. (1) may be obtained iteratively by the procedure suggested by Davidson [44]. Starting from a normalized trial vector $\boldsymbol{c}^{(n)}$, the residual vector $\sigma^{(n)}$ is computed as:

$$\sigma_I^{(n)} = \sum_J \boldsymbol{H}_{IJ}\boldsymbol{c}_I^{(n)} \tag{2}$$

and the energy for the n iteration is simply:

$$E^{(n)} = \sigma^{(n)}\boldsymbol{c}^{(n)} \tag{3}$$

In the above procedure the most time-consuming step is the evaluation of the residual vector $\sigma^{(n)}$ and many efficient ways of computing it have been proposed in the last years, especially for certain kinds of CI spaces having a very compact structure as CAS (Complete Active Space), RAS (Restricted Active Space), and FCI (Full Configuration Interaction) spaces [see [1, 45–48] and references therein].

Following the ideas already reported in those previous works, we have developed a new direct selected CI code having the following main features:

(i) Use of Slater determinants as a basis of n-electron functions. These determinants are written as products of α- and β-strings.

(ii) Neither the reference space nor the MRSDCI space have a defined structure.

(iii) The electronic hamiltonian has been written, as usual, using modified bielectronic integrals.

(iv) The product of generators of the unitary group has been decomposed into their α and β components leading to an expansion for the residual vector containing three different contributions: $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$ biexcitations (vide infra).

(v) The number of intermediate states appearing in the $\alpha\alpha$ and $\beta\beta$ contributions to the residual vector has been reduced by using the anticommutation properties of the quasi-particle creation and annihilation operators.

(vi) The list of determinants entering on the summation of Eq. (2) has been ordered and addressed in order to allow some vectorization in this disordered space.

Because of the incompleteness of the selected CI spaces we are interested in, our code is not fully vectorizable. However, the ordering and addressing carried out enables a maximization of the possible vectorization.

The residual vector takes the form:

$$\sigma(I_\alpha, I_\beta) = \sigma_1(I_\alpha, I_\beta) + \sigma_2(I_\alpha, I_\beta) + \sigma_3(I_\alpha, I_\beta) \tag{4}$$

where I_α and I_β are the corresponding α- and β-strings. If $\{CI\}$ is the subset of Slater determinants contained in the selected CI expansion, $\{I_\alpha\}$ is the set of the α-strings appearing in $\{CI\}$ and $\{I_\beta\}$ the analogous of $\{I_\alpha\}$ for the β-strings. The explicit formulae for the three contributions to σ are:

$$\begin{aligned}\sigma_1(I_\alpha, I_\beta) = \sum_{J_\alpha \in \{I_\alpha\}} c(J_\alpha, I_\beta) \Bigg[& \sum_{il} \langle J_\alpha | i_\alpha^+ l_\alpha | I_\alpha \rangle \sum_j (ij \mid jl)'' \\ & - 2 \sum_{i<k} \sum_{j<l} \langle J_\alpha | i_\alpha^+ k_\alpha^+ j_\alpha l_\alpha | I_\alpha \rangle [(ij \mid kl)'' - (il \mid kj)''] \Bigg] \\ & \forall I_\beta \in \{I_\beta\} / |J_\alpha I_\beta\rangle \in \{CI\} \quad \text{and} \quad |I_\alpha I_\beta\rangle \in \{CI\}\end{aligned} \tag{5}$$

$$\begin{aligned}\sigma_2(I_\alpha, I_\beta) = \sum_{J_\beta \in \{I_\beta\}} c(I_\alpha, J_\beta) \Bigg[& \sum_{il} \langle J_\beta | i_\beta^+ l_\beta | I_\beta \rangle \sum_j (ij \mid jl)'' \\ & - 2 \sum_{i<k} \sum_{j<l} \langle J_\beta | i_\beta^+ k_\beta^+ j_\beta l_\beta | I_\beta \rangle [(ij \mid kl)'' - (il \mid kj)''] \Bigg] \\ & \forall I_\alpha \in \{I_\alpha\} / |I_\alpha J_\beta\rangle \in \{CI\} \quad \text{and} \quad |I_\alpha I_\beta\rangle \in \{CI\}\end{aligned} \tag{6}$$

$$\sigma_3(I_\alpha, I_\beta) = \sum_{ij} \sum_{J_\alpha \in \{I_\alpha\}} \langle J_\alpha | i_\alpha^+ j_\alpha | I_\alpha \rangle \times \sum_{\substack{J_\beta \in \{I_\beta\} \\ J_\beta / | J_\alpha J_\beta \rangle \in \{CI\}}} c(J_\alpha, J_\beta) \sum_{kl} \langle J_\beta | k_\beta^+ l_\beta | I_\beta \rangle (ij \mid kl)'' \quad | J_\alpha J_\beta \rangle \in \{CI\} \quad \text{and} \quad | I_\alpha I_\beta \rangle \in \{CI\} \tag{7}$$

where the $(ij \mid kl)''$ symbol stands for the modified bielectronic integrals.

The constraints on the summation also produce a decrease on the vectorization capability of the algorithm. Fortunately, some of the queries needed to assure that the above restrictions hold have been avoided by the use of the addressing lists. Of course, this addressing scheme is not necessary when the CI space has a defined structure; this is because in an FCI space, for instance, each α-string appears with each β-string and vice versa. Moreover, the address of each of those strings is quite obvious. In a selected CI space without any defined structure it is necessary to use some auxiliary vectors containing information about the position of the α- or β-strings appearing with a given β- or α-string in the $\{CI\}$. The detailed description of these vectors is given in the next section.

There is a particular case which merits an additional comment. For an even number of electrons and regardless the spin multiplicity of the electronic state considered there is always a component having a zero value for the z component of the spin angular momentum operator (i.e. $S_z = 0$). In this case it has been shown [45] that:

$$\sigma_2(I_\alpha, I_\beta) = (-1)^S \sigma_1(I_\beta, I_\alpha) \tag{8}$$

with S being related to the spin multiplicity given by $2S + 1$. Then, σ_2 is directly obtained from σ_1. On the other hand, there is a relationship between some elements of σ_3, namely:

$$\sigma_3^{ijkl}(I_\alpha, I_\beta) = (-1)^S \sigma_3^{klij}(I_\beta, I_\alpha) \tag{9}$$

In this particular case, the use of Eqs. (8) and (9) allows a considerable time saving of the computation of the residual vector σ.

3 Description of the string and auxiliary lists

Once the list of determinants included in the $\{CI\}$ space has been obtained from a selection procedure, a translation to α- and β-strings is carried out and these strings are sequentially stored in two integer vectors *LISTA* and *LISTB* of dimension the number of determinants included in the $\{CI\}$ subset. Optionally, if the address of any string cannot be stored in an integer, these two vectors must be declared as *REAL**8. Two different versions of the code have been written accordingly. Next step is the ordering of α-strings in increasing order and, for a given α-string, we order the corresponding β-strings in the same way.

Three auxiliary vectors are now constructed from the ordered *LISTA* and *LISTB*. These vectors (*IALFA*, *IALBE*, and *IALDIR*) have the dimension of the maximum of $\{I_\alpha\}$ and $\{I_\beta\}$. The *IALFA* vector contains the list of α-strings contained in $\{I_\alpha\}$ and *IALBE* the number of β-strings appearing with each α-string. Finally, *IALDIR* contains the entry of each α-string in *LISTA*. Since equations giving the σ_1 and σ_2 components are formally identical except by a transposition of the c array appearing in Eqs. (5) and (6), an analogous ordering of *LISTA* and *LISTB* starting by the β-strings is needed to efficiently compute σ_2. Likewise, a new set of *IALFA*, *IALBE*, and *IALDIR* is constructed and stored on the previous ones provided σ_1 has already been computed.

It is very useful to introduce another auxiliary integer vector, *LAUX*, of dimension the number of determinants included in the $\{CI\}$ space. This vector contains the position of a given β-string of *LISTB*, when *LISTB* has been firstly ordered by $\{I_\alpha\}$, in the *IALFA* vector, when it has been constructed from *LISTB* vector firstly ordered following $\{I_\beta\}$.

In the special case of $S_z = 0$, it is convenient to introduce another list, *LTRA*, that for a given determinant written as $|I_\alpha I_\beta\rangle$ contains the position of the $|I_\beta I_\alpha\rangle$ determinant. This is because, in this case, the *LISTA* and *LISTB* are identical except for the ordering of their elements. It is clear that, in this case, it is only necessary to explicitly store *LAUX* and *LTRA* and not *LISTA* and *LISTB*.

It should be noted that the ordering and addressing described in this section is what permits a substantial vectorization of the algorithm that otherwise will not be possible in a general CI space without a defined structure. In other words, the strategy here presented allows to mimic as much as possible the vectorization scheme already present in the FCI or RAS algorithms of Olsen et al. [45]. As it has been already pointed out in Ref. [46], non-degenerate point group symmetries are easily incorporated into this address scheme by the use of index vectors for string addresses.

4 The selection procedure

In the present work we have used the CIPSI algorithm [26] to select both the reference and the subset of the MRCI space to be variationally treated. Technically, this is done using the three-class version of the CIPSI algorithm [27].

Starting from the Hartree–Fock determinant (or the adequate combination for the desired electronic state) all the single and double excitations are generated. Those having a contribution to the first-order wavefunction greater than a certain first threshold η are included into the reference space $\{G\}$ which is iteratively improved. When the reference space is large enough (or the computer small enough) a second selection is carried out on the space of generated determinants (i.e., the MRSDCI space, $\{GD\}$). This second selection is also carried out according to a predefined threshold, τ, as when selecting the reference space. For a recent review see Ref. [28].

The use of CIPSI has an additional advantage, namely the second-order energy contribution of those determinants of the MRCI expansion not included into the variational space $\{M\}$ is directly obtained and may be a useful guide to know whether the variational space is or is not large enough; it provides a measure of how far a truncated variational space is from the full MRCI one. Hence, for a given electronic state m, the total energy may be written as:

$$E_m = E_m^V + E_m^{(2)} \tag{10}$$

where E_m^V is the variational energy obtained by diagonalization of the CI matrix in the $\{G\} + \{M\} = \{CI\}$ space and $E_m^{(2)}$ is the perturbational second-order contribution of those determinants belonging to $\{GD\}$ but not included in $\{M\}$.

5 Test calculations

In order to test the performance of the present selected direct-CI algorithm, three different numerical tests have been carried out. The first one is for the HF molecule using a Van Duijnevelt basis set consisting of 4*s*3*p*1*d* contracted functions for F and 2*s*1*p* for H. This first example will allow us to compare full variational MR(SD)CI with the FCI value reported in [28]. This point is important because it will show the efficiency of the selection procedure and the convergence of the selected MRCI as a function of the reference space. The FCI is in this case about 13 million determinants in C_{2v} symmetry.

The second example is the one reported by Knowles and Handy [49] for NH_3 using a 3*s*2*p*1*d* ANO (Atomic Natural Orbital) contraction of the 13*s*8*p*1*d* primitive set for N and a 2*s*1*p* ANO contraction of 8*s*1*p* primitive set for H. Atomic coordinates, gaussian exponents, and contraction coefficients have been taken from [49]. We will use this second example to perform an analysis of timing and vectorization efficiency as well as to analyze the convergence of CIPSI energies towards the FCI value reported in [49]. It is worth recalling that FCI for NH_3 in this basis set involves about 209 million determinants in C_s symmetry. In these two examples the 1*s* electrons of F and N, respectively, were not correlated and have been frozen at the SCF level. The SCF orbitals have been always used to construct the Slater determinants used as the *n*-electron basis in the present MRCI calculations.

Finally, we will present results for N_2 as a real albeit small case. Calculations for N_2 have been carried out at 2.1 a.u. for the internuclear distance and use nonempirical pseudopotentials to describe the 1*s* cores. The primitive basis set contains 7*s*7*p*2*d*1*f* functions contracted to 3*s*3*p*2*d*1*f* functions. The MRCI expansion has to handle 10 active electrons in 58 orbitals. An FCI for this molecule will involve about 10^{10} determinants. Starting orbitals for this calculation are also the SCF ones. Further details about this calculation are reported in Refs. [50, 51].

6 Results and discussion

In Table 1 we report results for HF using four different selected reference spaces including up to 388 determinants. In this case we have been able to treat variationally the full MRCI expansion. Hence, the selection criterion only applies

Table 1. Summary of results for HF including the dimension of the $\{G\}$, $\{M\}$ and $\{GD\}$ subspaces, the variational MRCI energy, E_{MRCI}, and the error with respect to the FCI energy, ΔE. Energies are in atomic units

dim $\{G\}$	dim $\{GD\}$	E_{MRCI}	ΔE
113	81868	-100.272466	0.001641
194	125016	-100.272912	0.001195
278	159009	-100.273067	0.001040
388	191984	-100.273068	0.001039
FCI [28]	1.3×10^7	-100.274107	—

to the choice of the reference space. It is remarkable that by using only a small number of selected references the MRCI energy only differs 1 mh from the FCI value. Of course, the basis set used for this molecule is quite limited and from this result alone it cannot be deduced that for the largest cases the behavior will be similar, too. The important point is, however, the ability of the selected MRCI procedure to converge rather well to the exact FCI result.

The same situation is observed for the NH_3 test. In Table 2 we report results for five different reference spaces and, for each of these spaces, the result obtained by truncating the MRCI according to the second threshold τ. In some cases, the number of generated determinants to be included in the full variational space is fairly large and it is interesting to explore the convergence of the energy obtained by applying Eq. (10). This will give an idea of how good the second-order energy contribution of those generated determinants not included in the variational space is. From the test calculations reported in Table 2 it is clear that, once the most important ($\approx 5 \times 10^4$) determinants have been included in the variational space, the resulting energy is quite stable and it can only be lowered by increasing the reference space. As in the cases reported in [28] the second-order energy contribution is one order of magnitude smaller than the error in respect to the FCI. This would suggest that it is more important to have a large enough reference space than a full variational MRCI result on a smaller reference space, even if in the latter part of the correlation energy has to be

Table 2. Summary of results for NH_3 as a function of the number of reference determinants (dim$\{G\}$), and for a given reference space as a function of the dimension of the variational space (dim$\{G + M\}$). The number of generated determinants are given by dim$\{GD\}$. The E_m^V, $E_m^{(2)}$ and E_m refer to the energies variational of $\{G + M\}$, pertubational of $\{GD - M\}$ and total computed as the sum of both, respectively. ΔE stands for the error of E_m with respect to the FCI value reported in [49]

dim $\{G\}$	dim $\{GD\}$	dim $\{G+M\}$	E_m^V	$E_m^{(2)}$	E_m	ΔE
1	6444	6445	−56.411048	0.000000	−56.411048	0.0126
41	170378	19224	−56.417406	0.000488	−56.417894	0.0057
		79222	−56.419222	0.000024	−56.419246	0.0044
		97111	−56.419349	0.000007	−56.419356	0.0043
		116697	−56.419461	0.000001	−56.419462	0.0041
		170419	−56.419600	0.000000	−56.419600	0.0040
135	459522	24767	−56.418279	0.000907	−56.419186	0.0044
		57017	−56.419881	0.000415	−56.420296	0.0033
		79002	−56.420433	0.000276	−56.420709	0.0029
		95856	−56.420724	0.000207	−56.420931	0.0027
		203671	−56.421643	0.000034	−56.421677	0.0019
257	715273	31705	−56.418896	0.001134	−56.420030	0.0036
		69066	−56.420413	0.000550	−56.420963	0.0026
		79942	−56.420696	0.000469	−56.421165	0.0024
		94752	−56.421003	0.000385	−56.421388	0.0022
371	897411	36797	−56.419299	0.001318	−56.420617	0.0030
		51470	−56.419907	0.000976	−56.420883	0.0027
		80539	−56.420796	0.000619	−56.421415	0.0022
		91789	−56.421032	0.000535	−56.421567	0.0020
		107548	−56.421307	0.000444	−56.421775	0.0018
		215260	−56.422267	0.000161	−56.422428	0.0012

recovered by perturbation theory. This result is in agreement with previous studies using smaller selected MRCI expansion [28, 52] and will not be further commented on.

We will now turn our attention to the analysis of vectorization efficiency and computer time required to perform these selected direct CI calculations. With respect to the vectorization it has to be recalled that the larger the number of α-strings appearing with more than (let us say) 20 β-strings, the larger the efficiency of the vectorial process is. These figures are reported in Table 3 where it is shown that for a given reference space, the number of both, vectorizable and not vectorizable α-string operations, increase when increasing the dimension of the selected MRCI expansion. An important feature appearing from results in Table 3 is that the ratio between vectorizable and not vectorizable α-string operations increases when increasing the dimension of the reference space. However, when enlarging the reference space from 135 to 371 references this increment does not occur and it seems as if the new determinants in the selected MRCI expansion are generated from the same set of α- and β-strings.

With respect to the computer time requirements, results in Table 3 clearly indicate that the most consuming step is σ_3. In any case the present version of the code is able to compute an eigenvector of the $\boldsymbol{H}$ matrix for a selected MRCI expansion of up to 215 260 determinants by using about 400 seconds per iteration on an IBM 3090/600 with vector facility but using only 14 Mb of central storage.

We will now comment some results obtained for N_2 using a contracted $3s3p2d1f$ basis set in each N atom and pseudopotentials for the inner shell $1s$ cores. If the reference space is iteratively constructed so as to include the most important 231 reference determinants starting from the SCF molecular orbitals, 1 731 861 determinants are generated. If a value of 0.00005 is set up for the τ selection threshold the resulting selected MRCI expansion contains 136 339 determinants. The number of α-strings appearing in this set is 10 452 and the time per iteration is 367 and 692 seconds for σ_1 and σ_3, respectively. Note that σ_2 is not explicitly computed provided $S_z = 0$. The final energy is -19.833135 a.u.

Table 3. Timing and vectorization analysis for some selected MRCI calculations carried out for NH_3. The first two columns contain the dimension of the reference and selected MRCI spaces (dim$\{G\}$ and dim$\{G+M\}$, respectively). The third column gives the number of α-strings ($N_{\{I_\alpha\}}$) appearing in each case and the 4th and 5th columns the number of α-strings which appear with less than or more than 20 different β-strings ($N_{\{I_\alpha\}} \leqslant 20$; $N_{\{I_\alpha\}} > 20$). Finally time (in seconds) per iteration spent in the evaluation of the σ_1, σ_3 contributions to σ and of the σ itself is reported in the last three columns

dim $\{G\}$	dim $\{G+M\}$	$N_{\{I_\alpha\}}$	$N_{\{I_\alpha\}} \leqslant 20$	$N_{\{I_\alpha\}} > 20$	t_{σ_1}	t_{σ_3}	t_σ
41	19224	1276	1031	245	17	26	43
	79222	2478	1818	660	41	91	132
	97111	2796	2035	761	50	115	165
	116697	3098	2255	843	57	145	202
	134469	3376	2526	850	66	174	240
	170419	4259	3399	860	93	248	341
135	203671	5251	3752	1499	105	301	406
371	215260	5193	3741	1452	103	315	418

with second-order energy contribution of -0.002527 a.u. The dissociation energy computed (with $r = 2.1$ a.u.) is 8.9 eV which is close to the value reported in [51] for a basis set of the same quality. Improvement of the starting orbitals through CASSCF or approximate Natural Orbital procedure will account for the small difference (5%) with respect to the value reported by Almlöf et al. [53].

Finally, using 64 Mb of central storage, we have been able to handle a selected MRCI expansion containing up to 600 000 determinants from a test calculation involving 16 electrons in 32 orbitals. The present version is still under development and a series of modifications to further decrease the computer time are currently being carried out [54].

7 Conclusions

A new selected direct-CI scheme has been presented and implemented. The resulting code is general and can handle any spin multiplicity and, also, any MRCI space regardless of the selection procedure employed. Using only 14 Mb of central storage it is possible to carry out the diagonalization of a MRCI containing 215 000 selected determinants. The algorithm exhibits a rather good vectorization capability and its performance with respect to computer time is reasonable. The present approach towards a selected direct-CI is by no means the only possible. In fact, recent work by Caballol and Malrieu using the hole-particle formalism permits to handle selected direct-CI calculations in a very efficient way [55]. Further test calculations are needed in order to assess which strategy is more convenient and to combine the different approaches in a general direct CI algorithm.

The test calculations carried out up to now show that in principle it is possible to handle quite large selected MRCI expansions with a reasonable cost. A point to be stressed is that for a given MRSDCI space obtained from a reference set it seems sufficient to select around 10% of the total expansion to have meaningful results. This is specially true if perturbation theory is used to account for the contribution of those generated determinants in the MRSDCI expansion not included in the selected MRCI one. The whole procedure is specially well suited for calculations following the philosophy of the CIPSI algorithm.

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