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A new internally contracted direct multiconfiguration–reference configuration interaction (MRCI) method is described which allows the use of much larger reference spaces than any previous MRCI method. The configurations with two electrons in the external orbital space are generated by applying pair excitation operators to the reference wave function as a whole, while the singly external and internal configurations are standard uncontracted spin eigenfunctions. A new efficient and simple method for the calculation of the coupling coefficients is used, which is well suited for vector machines, and allows the recalculation of all coupling coefficients each time they are needed. The vector $\mathbf{H} \cdot \mathbf{c}$ is computed partly in a nonorthogonal configuration basis. In order to test the accuracy of the internally contracted wave functions, benchmark calculations have been performed for F^-, H_2O, NH_2, CH_2, CH_3, OH, NO, N_2, and O_2 at various geometries. The deviations of the energies obtained with internally contracted and uncontracted MRCI wave functions are mostly smaller than 1 mH and typically 3–5 times smaller than the deviations between the uncontracted MRCI and the full CI. Dipole moments, electric dipole polarizabilities, and electronic dipole transition moments calculated with uncontracted and contracted MRCI wave functions also are found to be in close agreement. The efficiency of the method is demonstrated in large scale calculations for the CN, NH_3, CO_2, and Cr_2 molecules. In these calculations up to 3088 reference configurations and up to 154 orbitals were employed. The biggest calculation is equivalent to an uncontracted MRCI with more than 78 million configurations.

I. INTRODUCTION

Multiconfiguration–reference configuration interaction methods (MRCI) are most powerful tools for calculating accurate potential energy functions (PEFs) and molecular properties. In comparison to many other methods used in quantum chemistry, which are based on single configuration reference states, MRCI wave functions yield a more balanced global description of PEFs. In recent full CI (FCI) benchmark calculations,[1-10] it has been demonstrated for a number of small molecules that MRCI wave functions, which include all single and double excitations relative to complete active space self-consistent field (CASSCF) reference functions, yield PEFs which closely parallel the FCI results. Many previous applications of the MRCI method have shown that highly accurate results are obtained when large atomic basis sets are used. Another advantage of the MRCI method is that wave functions for electronically excited states can be calculated. There are also many cases known in which ground electronic state wave functions cannot be well represented by a single configuration, and in which a balanced description of electron correlation effects requires MRCI wave functions.

The main bottleneck of the conventional MRCI method is the fact that the size of the configuration expansion and the computational effort rapidly increases with the number of reference configurations. This makes it necessary either to apply configuration selection schemes using perturbation theory,[11-14] or to select quite a small number of dominant reference configurations. However, it is often difficult to make a selection of a small number of configurations which is balanced for all parts of the PEFs or for various electronic states. Moreover, the effect of configuration selection on nonenergetic properties like dipole or transition moments is difficult to predict and sometimes large. It is, therefore, generally desirable (i) to include *all* single and double excitations relative to the reference configurations into the wave functions, and (ii) to be able to use much larger reference spaces than has been possible so far.

The inclusion of all single and double excitations relative to a small number of reference configurations has been made possible by the development of direct CI procedures.[15-32] In these methods the required eigenvectors are calculated iteratively without explicitly constructing and storing the Hamiltonian matrix. In each iteration the product $\mathbf{H} \cdot \mathbf{c}$, where $\mathbf{c}$ is a trial vector, is calculated directly from the molecular integrals and the coupling coefficients. The coupling coefficients, which depend only on the structure of the configurations, are usually stored on a formula file. Various techniques for their evaluation have been described, most of which employ group theoretical methods.[24,29,31,33-37] It is now well known that the nontrivial coupling coefficients for a singles and doubles CI depend only on the reference space and hence involve the labels of just the internal orbitals.[17,24,30]

Despite all this progress, the applicability of the

MRCI(SD) method has been limited so far by the fact that the length of the configuration expansion and of the formula file quite rapidly increases with the number of reference configurations. In general, an MRCI(SD) wave function can be written in the form

$$\Psi = \sum_I c^I \Psi_I + \sum_S \sum_a c_a^S \Psi_S^a + \sum_P \sum_{ab} C_{ab}^P \Psi_P^{ab}, \qquad (1)$$

where a,b denote external orbitals (not occupied in the reference configurations) and S and P denote internal $N - 1$ and $N - 2$ electron hole states. Ψ_I, Ψ_S^a, and Ψ_P^{ab} are internal, singly external, and doubly external configurations, respectively. Here and in the following, superscripts denote different matrices or vectors, and subscripts their elements. The reference space is a subset of the internal configurations Ψ_I. Table I shows for several applications how the number of internal states I, S, and P depends on the number of reference configurations. The effort for any MRCI(SD) calculation in-

creases at least with $n_P \cdot N^4 + n_P^x \cdot N^3$, where N is the number of external orbitals, n_P the number of $N - 2$ electron states P, and $1 < x \leqslant 2$. It is obvious from Table I that such calculations with large basis sets and more than about 100 reference configurations are very expensive.

In order to reduce the number of variational parameters in MRCI wave functions two different contraction schemes have been proposed and used. In the "externally" contracted CI of Siegbahn[38,39] the singly and doubly external configurations are contracted as

$$\Psi_S = \sum_a \alpha_a^S \Psi_S^a, \qquad (2)$$

$$\Psi_P = \sum_{ab} \alpha_{ab}^P \Psi_P^{ab}. \qquad (3)$$

The contraction coefficients α are obtained by first order perturbation theory. The number of variational parameters

TABLE I. Number of reference configurations and internal functions for the test calculations discussed in this paper.

Molecule	State	Ref. Conf.[a]	N el. I	$N - 1$ el. S	$N - 2$ el. P(uncontracted)	$N - 2$ el. Dp(contracted)
NH_2	$^2B_1$	49	49	364	414	35
NH_2	$^2A_1$	59	59	364	504	36
H_2O	$^1A_1$	55	142	736	694	49
F^-	^1S [b]	276	276	2352	2368	64
F^-	^1S [c]	492	492	2352	2688	64
CH_2	$^1A_1$	56	56	210	210	36
CH_2	$^1B_1$	51	51	294	295	35
CH_3	$^2A_2''$	188	188	1078	1044	48
N_2	$^1A_1$ [b]	32	32	210	210	36
NO	$^2\Pi$ [c]	54	54	364	496	36
OH [d]	2Π [c]	252	1512	5444	2866	81
OH [d]	$^2\Sigma^+$ [c]	258	1536	5467	2887	81
O_2	$^3\Sigma_g^-$ [b]	14	14	294	510	36
CN [e]	$^2\Sigma^+$ [c]	616	616	4116	6048	64
CN [f]	$^2\Sigma^+$ [c]	987	6281	25014	14235	100
NH_3 [g]	$^1A''$ [c]	1308	1308	6048	5873	81
CO_2 [h]	$^1\Sigma_g^+$ [b]	41	2406	14785	5745	143
CO_2 [h]	$^1\Pi_u$ [b]	74	2700	21924	11236	144
Cr_2 [i]	$^1\Sigma_g^+$ [b]	3088	22144	182216	108192	144

[a] The definition of the reference space for NH_2, H_2O, CH_2, CH_3, N_2, F^-, and NO is the same as in the MR-CI(BIG) calculations of Bauschlicher et al. (Refs. 1–10). The number of N electron functions corresponds to the number of internal configurations in the MR-CI wave functions and does not include functions of symmetries other than the specified ones.
[b] Calculated using D_{2h} symmetry.
[c] Calculated using C_{2v} symmetry.
[d] Space (3221) of Ref. 7.
[e] Active space: $3\sigma - 6\sigma$, $1\pi - 2\pi$, CASSCF reference.
[f] Active space: $3\sigma - 6\sigma$, $1\pi - 2\pi$, 1δ; all configurations which in the CASSCF wave functions had coefficients larger than 0.002 at any of 10 distances between 1.6 and 4.0 bohr were included in the reference.
[g] Active space: $2a_1 - 5a_1$, $1b_2 - 2b_2$, $1b_1 - 2b_1$, CASSCF reference.
[h] Active space: $3\sigma_u$, $4\sigma_u$, $5\sigma_g$, $1\pi_u$, $1\pi_g$, $2\pi_u$; all configurations which in the CASSCF wave functions have coefficients larger than 0.02 at any of the $D_{\infty h}$ CO distances 2.0, 2.2, 2.4 bohr were included in the reference wave functions. The orbitals $2\sigma_u$, $3\sigma_g$, and $4\sigma_g$ are doubly occupied in all reference configurations but correlated at the CI level. For further details see Ref. 55.
[i] All orbitals resulting from $4s$ and $3d$ atomic orbitals correlated. The reference configurations were generated from the CASSCF by applying the following restrictions: four electrons allowed in the four orbitals resulting from $4s$, $3d_{z^2}$, two electrons allowed in the two orbitals resulting from $3d_{x^2-y^2}$, two electrons allowed in the two orbitals resulting from $3d_{zx}$, two electrons allowed in the two orbitals resulting from $3d_{zy}$, two electrons allowed in the two orbitals resulting from $3d_{xy}$.

is then equal to the number of internal states shown in Table I. The effort for an externally contracted CI should be somewhat smaller than the effort for one iteration with the uncontracted wave function. Therefore, the scaling of the computational expense with the number of reference configurations is the same as in an uncontracted CI. Most importantly, the leading term for large basis sets is still $n_P \cdot N^4$. A further disadvantage of this method is that some contraction coefficients α_a^S may be zero due to Brillouin's theorem, which might lead to considerable errors for one-electron properties.

Another contraction scheme was first discussed by Meyer[40] and Siegbahn[41] and was first worked out in detail and implemented by Werner and Reinsch.[30] In this method the configurations are generated by applying pair excitation operators to the reference wave function as a whole. This effectively generates linear combinations of the configurations Ψ_P^{ab} with different internal states P and is therefore called "internally contracted CI." There are two major advantages of this scheme: (i) *the contracted configurations span exactly the first order interacting space of the reference function*, and (ii) *the number of contracted internal states is essentially independent of the number of reference configurations*. It depends only on the number of correlated orbitals. For m correlated orbitals at most m^3 contracted internal $N - 1$ electron states can be obtained by two annihilations and one creation, and m^2 contracted $N - 2$ electron states by two annihilations.[30,40–42] Hence, the main bottleneck of the MRCI method, namely the strong dependence of the number of internal $N - 2$ electron states on the number of reference configurations, is eliminated. It has been demonstrated by Werner and Reinsch[42] that the error caused by the contraction is negligible, both for the energy and for one-electron properties. The method has been applied successfully to a large number of small molecules,[43] and highly accurate results have been obtained. Further evidence for the accuracy of internally contracted wave functions will be given in this paper.

There are two problems, however, connected with the internal contraction. First, the contracted configurations are, in general, not orthogonal. The orthogonalization is not difficult for the small number of internal $N - 2$ electron functions, but can be a bottleneck for the large number of internal $N - 1$ electron or N electron states. Second, the structure for the contracted configurations is extremely complex. Each contracted configuration may be a linear combination of hundreds of uncontracted CSFs. Therefore, the calculation of the coupling coefficients is much more difficult than for an uncontracted wave function, and it has not been clear how group theoretical methods could be employed. In the first implementation of Werner and Reinsch,[30] Slater determinants were used to represent the contracted internal parts of the functions. This method was quite efficient for small reference spaces and scalar computers. However, because of the lack of vectorization, the evaluation of the coupling coefficients was often the rate determining step on modern vector machines. Moreover, the size of the formula file rapidly increased with the number of reference configurations. For these reasons the general advan-

tage of the internal contraction was only partly exploited in this implementation.

In the present paper a new internally contracted CI method is described which eliminates the above bottlenecks. In order to avoid the problem of orthogonalizing the internal and singly external configurations, standard uncontracted orthogonal spin eigenfunctions are used for these spaces. This also much facilitates the evaluation of the coupling coefficients. The doubly external configurations, which obviously represent the dominant part of the configuration expansion, are internally contracted, and hence the main advantage of the contraction is preserved. In contrast to our previous method,[30] some parts of the vector **H·c** are calculated in the basis of nonorthogonal contracted functions, which also facilitates the computation of the coupling coefficients. Orthogonalization is performed only at an intermediate stage in order to update the CI vector in each iteration. A new method to compute the coupling coefficients has been developed,[44] which employs group theoretical techniques and which is vectorizable. This method is efficient enough to recompute all coupling coefficients each time they are required, thereby eliminating the large formula file. These new techniques have enabled us to perform MRCI calculations with more than 3000 reference configurations using very large basis sets.

In Sec. II we define the configuration space used. In Sec. III the formulas for the residual vector $\mathbf{g} = (\mathbf{H} - E\,\mathbf{S})\cdot\mathbf{c}$ are summarized. Section IV deals with the structure and the computation of the coupling coefficients. In Sec. V we briefly outline the organization of our program and the direct CI procedure. In Sec. VI the calculation of density matrices is discussed. Finally, in Sec. VII we present a number of calculations in order to demonstrate the efficiency of the method and the accuracy of internally contracted wave functions.

II. DEFINITION OF THE CONFIGURATION SPACE

In the following we will distinguish three different orbital subspaces: (i) *Core* orbitals, which are doubly occupied in all configurations and, hence, not correlated. (ii) *Valence* orbitals (labeled $i,j,k,l,...$), which are occupied in the reference configurations and correlated in the CI wave function. (iii) *External* orbitals (labeled $a,b,c,d,...$), which are unoccupied in the reference wave function. The labels $r,s,t,u,...$ will be used to denote any orbital. We also use the term *internal* orbital to describe those orbitals which are occupied in the reference, i.e., (i) and (ii) above. The core orbitals can be removed from the whole formalism by replacing the one-electron Hamiltonian **h** by a core Fock matrix **F**

$$\mathbf{F} = \mathbf{h} + \sum_{r}^{\text{core}} (2\mathbf{J}^{rr} - \mathbf{K}^{rr}) \tag{4}$$

and by adding the core energy

$$E_c = \sum_{r}^{\text{core}} (h_{rr} + F_{rr}) \tag{5}$$

to the total energy. In the remainder of this paper all summations involving internal orbitals will run over valence orbitals only.

For the following discussion it is useful to define sets of

standard spin adapted configuration state functions (CSFs) with zero, one and two electrons in the external orbital space. If necessary, we will distinguish *orbital configurations*, which are defined by the number of electrons in each orbital irrespective of the spin coupling, and the *spin coupling*. We will use genealogical spin eigenfunctions[45,46] with the external electrons coupled last. The spin couplings will be labeled μ, ν, etc., and the internal parts of the orbital configurations with zero, one, and two electrons in the external orbital space by $\{I,J,...\}$, $\{S,T,...\}$, and $\{P,Q,...\}$, respectively. Hence, the internal, singly external, and doubly external configuration spaces are spanned by the CSFs $\Psi_{I\mu}$, $\Psi_{S\mu}^{a}$, and $\Psi_{P\mu}^{ab}$. The reference orbital configurations will be denoted by R. All spin couplings for a given orbital configuration are always included. The set of $N-2$ electron states P is obtained from all possible two electron annihilations (or some predefined subset) acting on each reference configuration. The $N-1$ electron states S are generated from the $N-2$ electron states P by adding one electron to the valence space, and the internal configurations I from the $N-1$ electron states S by adding another electron. For simplicity, the spin labels μ, ν will be omitted whenever they are not explicitly needed. In that case it is assumed that the indices I,S,P denote individual spin eigenfunctions.

In order to define our internally contracted configuration space we will employ the usual one-electron creation and annihilation operators $\eta_i^{\rho\dagger}$, η_j^{σ}, where ρ and σ denote the electron spin ($\rho,\sigma = \{\alpha, \beta\}$). These operators obey the usual anticommutation rules, and can be used to define n-particle excitation operators

$$\widehat{E}_{ij} = \sum_{\rho} \eta_i^{\rho\dagger} \eta_j^{\rho}, \tag{6}$$

$$\widehat{E}_{ij,kl} = \sum_{\rho} \eta_k^{\rho\dagger}\widehat{E}_{ij} \eta_l^{\rho} = \widehat{E}_{ij}\widehat{E}_{kl} - \delta_{jk}\widehat{E}_{il}, \tag{7}$$

$$\widehat{E}_{ij,kl,mn} = \sum_{\rho} \eta_m^{\rho\dagger}\widehat{E}_{ij,kl} \eta_n^{\rho} = \widehat{E}_{ij,kl}\widehat{E}_{mn}$$
$$- \delta_{lm}\widehat{E}_{ij,kn} - \delta_{jm}\widehat{E}_{in,kl}, \tag{8}$$

etc. The internally contracted doubly external configurations are defined as

$$\Psi_{ijp}^{ab} = \frac{1}{2} (\widehat{E}_{ai,bj} + p\widehat{E}_{bi,aj})\Psi_0, \tag{9}$$

where $p = 1$ for external singlet pairs and $p = -1$ for triplet pairs. Ψ_0 is the reference wave function, which may be composed of many configurations Ψ_R

$$\Psi_0 = \sum_{R\mu} a^{R\mu}\Psi_{R\mu}. \tag{10}$$

It has been shown before[40,47] that the configurations Ψ_{ijp}^{ab} are spin eigenfunctions which span exactly the first order interacting space of Ψ_0, provided Ψ_0 is a spin eigenfunction. The contracted configurations Ψ_{ijp}^{ab} can be expanded in terms of the set of standard uncontracted doubly external CSFs Ψ_{Pv}^{ab} according to

$$\Psi_{ijp}^{ab} = \sum_{Pv} \langle \Psi_{ijp}^{ab} | \Psi_{Pv}^{ab} \rangle \Psi_{Pv}^{ab}, \tag{11}$$

where the contraction coefficients are given in terms of the

reference coefficients $a^{R\mu}$ by

$$\langle \Psi_{ijp}^{ab} | \Psi_{Pv}^{ab} \rangle = \frac{1}{2} \sum_{R\mu} a^{R\mu} \langle \Psi_{R\mu} | \widehat{E}_{ia,jb} + p\widehat{E}_{ja,ib} | \Psi_{Pv}^{ab} \rangle. \tag{12}$$

This shows that these configurations are obtained by contracting different *internal* states.

The internally contracted configurations Ψ_{ijp}^{ab} defined in Eq. (9) are, in general, not orthonormal. The overlap matrix is given by

$$\langle \Psi_{ijp}^{ab} | \Psi_{klq}^{cd} \rangle = \frac{1}{2} \delta_{pq} (\delta_{ac}\delta_{bd} + p\delta_{ad}\delta_{bc}) S_{ij,kl}^{(p)}, \tag{13}$$

where the matrix $S_{ij,kl}^{(p)}$ is determined by the second order density matrix of the reference wave function $|0\rangle = \Psi_0$

$$S_{ij,kl}^{(p)} = \langle 0|\widehat{E}_{ik,jl} + p\widehat{E}_{il,jk}|0\rangle. \tag{14}$$

The configurations can be orthogonalized by the symmetric orthogonalization

$$\Psi_{Dp}^{ab} = \sum_{i\geqslant j} T_{D,ij}^{(p)}\Psi_{ijp}^{ab}, \tag{15}$$

$$\mathbf{T}^{(p)} = (\mathbf{S}^{(p)})^{-1/2}, \tag{16}$$

which implies the normalization

$$\langle \Psi_{Dp}^{ab} | \Psi_{Dp}^{ab} \rangle = (2 - \delta_{ab})^{-1}. \tag{17}$$

The different normalization of the diagonal configurations Ψ_{Dp}^{aa} and the off-diagonal configurations Ψ_{Dp}^{ab} is essential for the matrix formulation of the residual vector and the removal of all coupling coefficients depending on external orbital labels.[17,30]

The great advantage of the internal contraction is that the number of configurations in the CI wave function is essentially independent of the number of reference configurations. The number of internal $N-2$ electron states is at most m^2, where m is the number of correlated orbitals. It is possible to define contracted singly external and internal configurations in a way similar to Eq. (9). However, as has been discussed in detail in Ref. 47, this is not as advantageous as for the doubly external configurations. One of the major problems is that rather large sets of nonorthogonal configurations are generated, which are difficult to orthonormalize. Moreover, the evaluation of the Hamiltonian matrix elements between contracted singly and doubly external configurations becomes quite difficult and time consuming. Therefore, we propose not to contract the internal and singly external configurations but to use the standard CSFs $\Psi_{I\mu}$ and $\Psi_{S\mu}^{a}$ as bases for these spaces. Note that this definition of the singly external configuration space is difficult to that of Ref. 47.

Using the configuration basis defined above, the total wave function may be written as

$$\Psi = \sum_I c^I\Psi_I + \sum_S \sum_a c_a^S\Psi_S^a + \sum_D \sum_p \sum_{ab} C_{ab}^{Dp}\Psi_{Dp}^{ab},$$

$$\mathbf{C}^{Dp} = p(\mathbf{C}^{Dp})^+$$

$$= \sum_I c^I\Psi_I + \sum_S \sum_a c_a^S\Psi_S^a + \sum_{i\geqslant j} \sum_p \sum_{ab} C_{ab}^{ijp}\Psi_{ijp}^{ab},$$

$$\mathbf{C}^{ijp} = p(\mathbf{C}^{ijp})^+. \tag{18}$$

From Eqs. (15) and (18), we obtain the relation

$$\mathbf{C}^{ijp} = \sum_D T^{(p)}_{ijp,D} \mathbf{C}^{Dp}. \tag{19}$$

This can be used to transform the coefficient matrices C^{Dp} from the orthogonal to the nonorthogonal basis after they have been updated in a direct CI iteration. The coefficients C^{ijp} are then used to evaluate part of the residual vector in the nonorthogonal basis (cf. Sec. III). This part can be transformed back to the orthogonal basis in a similar manner.

III. THE FORM OF THE RESIDUAL VECTOR

In the orthogonal configuration basis, the residual vector can be expressed as

$$\langle \Psi^{ab}_{Dp} | \hat{H} - E | \Psi \rangle = \left[\frac{1}{2} [\mathbf{G}^{Dp} + p(\mathbf{G}^{Dp})^\dagger] - E\mathbf{C}^{Dp} \right]_{ab}, \tag{20}$$

$$\langle \Psi^a_S | \hat{H} - E | \Psi \rangle = [\, \mathbf{g}^S - E\mathbf{c}^S \,]_a, \tag{21}$$

$$\langle \Psi_I | \hat{H} - E | \Psi \rangle = g^I - Ec^I. \tag{22}$$

For simplicity, in this section we will often omit the labels of the spin functions and assume that the indices I, S, and P denote particular internal states including the spin coupling. The index D denotes orthogonalized internally contracted $N - 2$ electron states [cf. Eq. (15)]. In order to obtain the above quantities in a compact form, we define integral matrices

$$(\mathbf{J}^{mn})_{ab} = (ab\,|mn), \tag{23}$$

$$(\mathbf{K}^{mn})_{ab} = (am|nb), \tag{24}$$

and vectors

$$(\mathbf{F}^k)_a = F_{ak}, \tag{25}$$

$$(\mathbf{I}^{kmn})_a = (ak\,|mn). \tag{26}$$

We further define "external" exchange matrices

$$[\mathbf{K}(\mathbf{C})]_{rs} = \sum_{tu} C_{tu}\,(rt\,|us) \tag{27}$$

with column vectors

$$[\mathbf{K}^k(\mathbf{C})]_a = [\mathbf{K}(\mathbf{C})]_{ak}. \tag{28}$$

These matrices can be evaluated directly from the two electron integrals in the AO basis, and then transformed into the MO basis (cf. Ref. 30). As described below, in our implementation two such operators are evaluated for each pair function in each iteration, and then all contributions of two electron integrals with three or four external orbitals are accounted for. Hence, a full integral transformation is not needed. In principle, one of these two exchange operators per pair can be eliminated as discussed in Ref. 30. This is useful for calculations with only few reference configurations, but becomes difficult if large reference spaces are used, since many coupling coefficients have to be modified. In this case, ideally one should perform an integral transformation for the integrals with up to three external orbitals, and then there is only one exchange operator per pair and iteration to be calculated. However, as will be demonstrated in Sec. VII,

for such cases the evaluation of the exchange operators $K(C)$ takes only a small fraction of the total computation time, and the disadvantage of calculating a larger number of operators is relatively small. We note that it is a particular feature of the internally contracted MRCI method that one can advantageously avoid a full integral transformation. For the uncontracted MRCI basis, there are many more pair functions, and in this case the cost of the calculation of the exchange operators is much more significant, and often might be more efficiently performed in the MO basis, as discussed, e.g., in Ref. 32.

Next we have to define the coupling coefficients, which depend on the structure of the configurations and the contraction coefficients. Contributions of integrals which involve only internal orbitals are included into the coefficients γ. Indices in parentheses denote the interaction, and subscripts indicate that these coefficients may be regarded as elements of vectors. We also use the abbreviation $|S^a\rangle = |\Psi^a_S\rangle$ and $|P^{ab}\rangle = |\Psi^{ab}_P\rangle$ $(a \neq b)$. The external dummy labels a,b are arbitrary and enter here only formally. They never occur in the actual implementation, since they always match with the external indices in the one and two particle excitation operators. Ordered according to the various interactions the coupling coefficients are given by

pair–internal:

$$\sigma_{mn}(ijp,I) = \tfrac{1}{2}\langle 0|\hat{E}_{im,jn} + p\hat{E}_{in,jm}|I\rangle, \tag{29}$$

pair–pair:

$$\alpha_{mn}(ijp,klq) = \delta_{pq}\langle 0|\hat{E}_{ik,jl,mn} + p\hat{E}_{il,jk,mn}|0\rangle, \tag{30}$$

$$\beta_{mn}(ijp,klq) = \langle 0|\hat{E}_{im,jl,nk} + p\hat{E}_{il,jm,nk} + q\hat{E}_{im,jk,nl}$$
$$+ pq\hat{E}_{ik,jm,nl}|0\rangle, \tag{31}$$

$$\gamma(ijp,klq) = \delta_{pq}\sum_{mn} F_{mn}\langle 0|\hat{E}_{ik,jl,mn} + p\hat{E}_{il,jk,mn}|0\rangle$$
$$+ \frac{1}{2}\sum_{mn}\sum_{op}(mn|op)\langle 0|\hat{E}_{ik,jl,mn,op}$$
$$+ p\hat{E}_{il,jk,mn,op}|0\rangle, \tag{32}$$

single–internal:

$$\sigma_k(S,I) = \langle S^a|\hat{E}_{ak}|I\rangle, \tag{33}$$

$$\alpha_{kmn}(S,I) = \langle S^a|\hat{E}_{ak,mn}|I\rangle, \tag{34}$$

pair–single:

$$\sigma_k(ijp,S) = \langle \Psi^{ab}_{ijp}|\hat{E}_{bk}|S^a\rangle$$
$$= \frac{1}{2}\sum_P \langle 0|\hat{E}_{ia,jb} + p\hat{E}_{ib,ja}|P^{ab}\rangle$$
$$\times \langle P^{ab}|\hat{E}_{bk}|S^a\rangle, \tag{35}$$

$$\sigma_k(Dp,S) = \sum_{i \geq j} T^{(p)}_{D,ij}\sigma_k(ijp,S), \tag{36}$$

$$\alpha_{kmn}(ijp,S) = \langle \Psi^{ab}_{ijp}|\hat{E}_{bk,mn}|S^a\rangle$$
$$= \frac{1}{2}\sum_P \langle 0|\hat{E}_{ia,jb} + p\hat{E}_{ibja}|P^{ab}\rangle$$
$$\times \langle P^{ab}|\hat{E}_{bk,mn}|S^a\rangle, \tag{37}$$

single–single:

$$\alpha_{mn}(S,T) = \langle S^a | \hat{E}_{mn} | T^a \rangle, \tag{38}$$

$$\beta_{mn}(S,T) = \langle S^a | \hat{E}_{am}\hat{E}_{nb} - \delta_{mn}\delta_{ab} | T^b \rangle, \tag{39}$$

$$\gamma(S,T) = \sum_{mn} F_{mn} \langle S^a | \hat{E}_{mn} | T^a \rangle$$
$$+ \frac{1}{2} \sum_{mn} \sum_{op} (mn|op) \langle S^a | \hat{E}_{mn,op} | T^a \rangle. \tag{40}$$

A method to evaluate all these coefficients very efficiently will be discussed in Sec. IV. It is noted that the first part of Eqs. (35) and (37) is a transformation from the contracted basis to the standard CSFs $|P^{ab}\rangle$, while Eq. (36) corresponds to a transformation from the nonorthogonal to the orthogonal basis. Note also that in Eqs. (35) and (37) the sum P extends only over the spin couplings of a single orbital configuration. In order to evaluate the coefficients $\sigma_k(Dp,S)$ directly, the two transformation matrices may be multiplied before the product with $\langle P^{ab} | \hat{E}_{bk} | S^a \rangle$ is formed (cf. Sec. IV).

We are now ready to give the explicit formulas for the quantities $\mathbf{G}^{Dp}$, $\mathbf{g}^S$, and g^I which represent the residual vector and which must be calculated in each iteration of the direct CI procedure. As mentioned before, it is advantageous to evaluate part of the matrices $\mathbf{G}^{Dp}$ in the nonorthogonal basis,

because then the internal $N - 2$ states are connected to individual orbital pairs (ij) and the coupling coefficients are simple density matrix elements

$$\mathbf{G}^{Dp} = \mathbf{K}(\tilde{\mathbf{C}}^{Dp}) + 2\mathbf{F}\cdot\mathbf{C}^{Dp} + \sum_{i \geqslant j} T^{(p)}_{D,ij} \mathbf{G}^{ijp}, \tag{41}$$

where the matrices $\tilde{\mathbf{C}}^{Dp}$ are given by

$$(\tilde{\mathbf{C}}^{Dp})_{ak} = p(\tilde{\mathbf{C}}^{Dp})_{ka} = \sum_S (\mathbf{c}^S)_a \sigma_k (Dp,S),$$

$$(\tilde{\mathbf{C}}^{Dp})_{ab} = (\mathbf{C}^{Dp})_{ab}. \tag{42}$$

The part calculated in the nonorthogonal basis is

$$\mathbf{G}^{ijp} = \sum_{mn} \mathbf{K}^{mn} \sum_I \sigma_{mn}(ijp,I)c^I + 2p \sum_S \Bigg[\sum_k \mathbf{F}^k \sigma_k(ijp,S)$$
$$+ \sum_{kmn} \mathbf{I}^{kmn}\alpha_{kmn}(ijp,S) \Bigg] \cdot (\mathbf{c}^S)^\dagger$$
$$+ \sum_{k \geqslant l} \sum_q \Bigg\{ \sum_{mn} [2\mathbf{J}^{mn}\alpha_{mn}(ijp,klq)$$
$$+ \mathbf{K}^{mn}\beta_{mn}(ijp,klq)] + \mathbf{1}\gamma(ijp,klq) \Bigg\} \cdot \mathbf{C}^{klq}. \tag{43}$$

The residual for the singly external configurations is represented by the vectors

$$\mathbf{g}^S = \sum_k \mathbf{F}^k \sum_I \sigma_k(S,I)c^I + \sum_{kmn} \mathbf{I}^{kmn} \sum_I \alpha_{kmn}(S,I)c^I + \sum_T \Bigg\{ \delta_{ST}\mathbf{F} + \sum_{mn} [\mathbf{J}^{mn}\alpha_{mn}(S,T)$$
$$+ \mathbf{K}^{mn}\beta_{mn}(S,T)] + \mathbf{1}\gamma(S,T) \Bigg\} \cdot \mathbf{c}^T + 2 \sum_{i \geqslant j} \sum_p \Bigg\{ \sum_k [\mathbf{C}^{ijp}\mathbf{F}^k + \mathbf{K}^k(\mathbf{C}^{ijp})]\sigma_k(ijp,S) + \sum_{kmn} \mathbf{C}^{ijp}\cdot\mathbf{I}^{kmn}\alpha_{kmn}(ijp,S) \Bigg\}. \tag{44}$$

For the internal configurations one obtains

$$g^I = \sigma^I + \sum_S \Bigg[\sum_k (\mathbf{F}^k)^\dagger \cdot \mathbf{c}^S \sigma_k(S,I)$$
$$+ \sum_{kmn} (\mathbf{I}^{kmn})^\dagger \cdot \mathbf{c}^S \alpha_{kmn}(S,I) \Bigg]$$
$$\times \sum_{i \geqslant j} \sum_p \sum_{mn} tr\{\mathbf{C}^{ijp\dagger}\cdot\mathbf{K}^{mn}\}\sigma_{mn}(ijp,I). \tag{45}$$

In Eq. (45) σ^I represents the contributions of all internal configurations to g^I. This term is evaluated in a similar way as in modern full CI[48,49] and MCSCF[50] methods

$$\sigma^I = \sum_{mn} \Bigg[F_{mn} - \frac{1}{2} \sum_k (mk|kn) \Bigg] \sum_J \langle I | \hat{E}_{mn} | J \rangle c^J$$
$$+ \frac{1}{2} \sum_{kl} \sum_K \langle I | \hat{E}_{kl} | K \rangle \sum_{mn} (kl|mn) \sum_J \langle K | \hat{E}_{mn} | J \rangle c^J. \tag{46}$$

A new technique[44] to calculate the one-particle coupling coefficients $\langle I | \hat{E}_{mn} | J \rangle$ efficiently for arbitrary internal configuration spaces will be outlined in Sec. IV. Using the quantities $\mathbf{G}^{Dp}$, $\mathbf{g}^S$, and g^I the energy expectation value can easily be obtained

$$E = N^{-1} \Bigg[\sum_{Dp} tr[\mathbf{C}^{Dp\dagger}\cdot\mathbf{G}^{Dp}] + \sum_S \mathbf{c}^{S\dagger}\cdot\mathbf{g}^S + \sum_I c^I g^I \Bigg], \tag{47}$$

where the norm N is given by

$$N = \sum_{Dp} tr[\mathbf{C}^{Dp\dagger}\cdot\mathbf{C}^{Dp}] + \sum_S \mathbf{c}^{S\dagger}\cdot\mathbf{c}^S + \sum_I c^I c^I. \tag{48}$$

IV. EVALUATION OF THE COUPLING COEFFICIENTS

The bottleneck in our previous implementation of the internally contracted MCSCF-CI method[30] was the calculation and storage of the coupling coefficients given in Eqs. (29)–(40). In order to perform the direct CI efficiently, it is important that these coefficients are obtained in a particular order. For instance, the coefficients $\alpha_{mn}(ijp,klq)$ and $\beta_{mn}(ijp,klq)$ necessary for the evaluation of $\mathbf{G}^{ijp}$ are needed for a given orbital pair (ij), and all values for different (mn) are needed for given (ij) and (kl). In the following we describe a new simple method to obtain the coefficients in the desired order. This procedure is efficient enough to recalculate all coupling coefficients each time they are needed, even for calculations with a very large number of reference configurations. This entirely eliminates the formula file.

As has already been discussed in Ref. 47, the third and fourth order density matrices $\langle 0 | \hat{E}_{ik,jl,mn} | 0 \rangle$ and

$\langle 0|\hat{E}_{ik,jl,mn,op}|0\rangle$ can be factorized into lower order transition density matrices[47]

$$\langle 0|\hat{E}_{ik,jl,mn}|0\rangle$$
$$= \sum_K \langle 0|\hat{E}_{ik,jl}|K\rangle\langle K|\hat{E}_{mn}|0\rangle - \delta_{ml}\langle 0|\hat{E}_{ik,jn}|0\rangle$$
$$- \delta_{km}\langle 0|\hat{E}_{in,jl}|0\rangle, \qquad (49)$$

$$\gamma(ijp,klp) = H_{ij,kl} + pH_{ij,lk}, \qquad (50)$$

$$H_{ij,kl} = \sum_K \langle 0|\hat{E}_{ik,jl}|K\rangle\sigma_{\text{ref}}^K + \sum_{mn}\langle 0|\hat{E}_{im,jn}|0\rangle(km|ln)$$
$$- \sum_m [\langle 0|\hat{E}_{ik,jm}|0\rangle\tilde{F}_{lm} + \langle 0|\hat{E}_{im,jl}|0\rangle\tilde{F}_{km}]$$
$$- \sum_m \sum_K [\langle 0|\hat{E}_{ik,jm}|K\rangle B_{lm,K}$$
$$+ \langle 0|\hat{E}_{im,jl}|K\rangle B_{km,K}], \qquad (51)$$

where σ_{ref}^K is given by Eq. (46) but evaluated with the reference configurations and coefficients instead of the internal configurations, and

$$\tilde{F}_{mn} = F_{mn} - \sum_k (mk|kn), \qquad (52)$$

$$B_{ij,K} = \sum_{kl} (ij|kl)\langle 0|\hat{E}_{kl}|K\rangle. \qquad (53)$$

The above expressions can be evaluated as matrix products if the second order transition density matrices $\langle 0|\hat{E}_{ik,jl}|K\rangle$ for a given (ij) and the first order transition density matrices $\langle K|\hat{E}_{mn}|0\rangle$ are kept in high speed memory. The crucial point is to obtain the second order transition density efficiently for a given orbital pair (ij). This can be achieved as follows: First, we realize that for the case that the one and two particle excitation operators $\hat{E}_{ij}$ and $\hat{E}_{ij,kl}$ act only on states in which all external orbitals are unoccupied they can be factorized[44]

$$\hat{E}_{ij} = \hat{E}_{ia}\hat{E}_{aj}, \qquad (54)$$

$$\hat{E}_{ik,jl} = \hat{E}_{ia}\hat{E}_{jb}\hat{E}_{bl}\hat{E}_{ak} \quad (a<b). \qquad (55)$$

The external dummy labels a and b are arbitrary and fixed. Hence, we can obtain the one-particle and two-particle coupling coefficients as

$$\langle I_\mu|\hat{E}_{ij}|J_\nu\rangle = \sum_\rho \langle I_\mu|\hat{E}_{ia}|S_\rho^a\rangle\langle S_\rho^a|\hat{E}_{aj}|J_\nu\rangle, \qquad (56)$$

where I, J, and S again denote orbital configurations and μ, ν, ρ the spin couplings. The summation in Eq. (56) extends only over the spin couplings of one orbital configuration S, which is uniquely determined by annihilating from I one electron in the orbital i. Similarly, the orbital configuration J is obtained from S by putting one additional electron into orbital j. Defining basic coupling coefficient matrices

$$X_{\mu\nu}^{Ii,S} = \langle I_\mu|\hat{E}_{ia}|S_\nu^a\rangle, \qquad (57)$$

the dimension of which is given by the number of possible spin couplings for the orbital configuration I and S, Eq. (56) can be written in matrix form as

$$\langle I_\mu|\hat{E}_{ij}|J_\nu\rangle = (\mathbf{X}^{Ii,S}\cdot\mathbf{X}^{Jj,S\dagger})_{\mu\nu}. \qquad (58)$$

Similarly, the second order transition density matrix elements are obtained as

$$\langle 0|\hat{E}_{ik,jl}|I_\sigma\rangle = \sum_R \sum_\lambda \sum_\mu \sum_\nu \sum_\rho a^{R\lambda}X_{\lambda\mu}^{Ri,S}X_{\mu\nu}^{Sj,P}X_{\nu\rho}^{Tl,P}X_{\sigma\rho}^{Ik,T}. \qquad (59)$$

Here R runs over the reference orbital configurations and $a^{R\lambda}$ are the coefficients of the reference configurations. Equation (59) represents a sequence of matrix · vector multiplications. As required, the transition matrix elements can easily be obtained for a fixed orbital pair (ij) provided the matrices $\mathbf{X}$ are available. Using symmetric group techniques it can be shown[44] that most of the matrices $\mathbf{X}$ are identical. The small set of unique matrices can be kept in high speed memory. The addresses of these matrices depend on the number and the position of the singly occupied orbitals in the corresponding orbital configurations and can be stored in a table. For more details about this technique we refer to a separate publication.[44]

The advantage of the above method is that all coupling coefficients can be efficiently obtained from a relatively small number of quantities which can be held in high speed memory. The lists of orbital configurations and the address lists are usually not exceedingly large, since the number of orbital configurations is much smaller than the number of CSFs. The amount of logic needed during the actual calculation of the transition densities is small, and the computation time is dominated by matrix multiplications. On vector computers, the evaluation of matrix elements between configurations with many spin couplings, which form a significant fraction of the computational effort, is therefore particularly efficient.

The coupling coefficients involving the internal and singly external configurations can be calculated by a similar technique. For instance, the coefficients $\alpha_{mn}(S,T)$ and $\beta_{mn}(S,T)$ are given by

$$\alpha_{mn}(S_\mu,T_\nu) = (\mathbf{X}^{Sm,P}\cdot\mathbf{X}^{Tn,P\dagger})_{\mu\nu}, \qquad (60)$$

$$\beta_{mn}(S_\mu,T_\nu) = (\mathbf{X}^{Im,S\dagger}\cdot\mathbf{X}^{In,T} - \delta_{mn}\mathbf{1})_{\mu\nu}. \qquad (61)$$

The optimal order of the multiplications in the calculation of the vector $\mathbf{g}^S$ depends on the number of spin couplings involved and is decided automatically by the program. This has been discussed in detail by Saunders and van Lenthe.[32] The crucial part in the single–single interaction is the term involving the all-internal two-electron integrals. Explicitly, this takes the form

$$\sum_{T\nu}\sum_{ij}\sum_{kl}(ij|kl)\langle S_\mu|\hat{E}_{ij}\hat{E}_{kl}|T_\nu\rangle\mathbf{c}^{T\nu}. \qquad (62)$$

We found it advantageous to factorize this as

$$\sum_{ij}\sum_\rho\langle S_\mu|\hat{E}_{ij}|U_\rho\rangle\sum_{kl}(ij|kl)\sum_{T\nu}\langle U_\rho|\hat{E}_{kl}|T_\nu\rangle\mathbf{c}^{T\nu}. \qquad (63)$$

The lower order term $-\delta_{jk}\hat{E}_{il}$ can be absorbed into the one-electron part by modifying the one-electron integrals in the same way as in Eq. (46).

The most time consuming part in a calculation with many reference configurations is usually the pair–single interaction involving the singly external integrals I_a^{kmn} [Eqs. (43) and (44)], for which we adopt the following algo-

rithm. First, we set up the transformation from contracted pair functions Ψ_{ijp}^{ab} to the orthonormal basis of doubly external spin eigenfunctions P^{ab}, of which the matrix elements

$$\frac{1}{2} \sum_P \langle 0 | \widehat{E}_{ia,jb} + p\widehat{E}_{ib,ja} | P^{ab} \rangle$$

are needed in Eq. (35). Ideally, this matrix is constructed and held in memory for all ijp of a given symmetry, together with the coefficient and residual matrices $\mathbf{C}^{ijp}$, $\mathbf{G}^{ijp}$ associated with each pair ijp, but if there is not enough memory, smaller batches of ijp may be treated separately with little loss of efficiency. Next, the list of singly external configurations $|S^a\rangle$ is scanned. For each $|S\rangle$,

(i) the coupling coefficients between CSFs $\langle P^{ab} | \widehat{E}_{bk,mn} | S^a \rangle$ are constructed using the factorization techniques described above;

(ii) these are transformed to the contracted pair function basis according to Eq. (35);

(iii) the coupling coefficients are contracted with the integrals as $\Sigma_{kmn} \alpha_{kmn} (ijp,S) I_b^{kmn}$;

(iv) the residual vectors and matrices are updated as

$$g_a^S = 2 \sum_b \sum_{ijp} C_{ab}^{ijp} \left[\sum_{kmn} \alpha_{kmn} (ijp,S) I_b^{kmn} \right], \qquad (64)$$

$$G_{ab}^{ijp} = 2 \sum_S c_a^S \left[\sum_{kmn} \alpha_{kmn} (ijp,S) I_b^{kmn} \right]. \qquad (65)$$

It is instructive to compare this procedure with the effort required in an uncontracted MRCI calculation. In an uncontracted calculation, stage (i) is performed in exactly the same way, but of course there is no transformation (ii) to be done. (iii) and (iv) are the same except that $|\Psi_{ijp}^{ab}\rangle$ is replaced by $|\Psi_P^{ab}\rangle$. Thus the effort for the uncontracted calculation is less for the coupling coefficients (no transformation is needed), but is greater by a factor equal to the ratio of the numbers of uncontracted and contracted pair functions, for stages (iii) and (iv). We find that for contracted calculations on a CRAY-XMP, (i), (ii) and (iii)–(iv) take approximately 40%, 30%, and 30%, respectively, of the CPU time for a typical case, although these ratios do vary widely for different calculations; typically the number of uncontracted functions is greater than the number of contracted functions by a factor or 10–100 for a large MRCI problem (cf. Table I). The conclusion is that we expect the contracted calculation to be considerably cheaper. The contracted case also has the great advantage that there are many fewer $\mathbf{C}^{ijp}, \mathbf{G}^{ijp}$ to be held in memory. Similar considerations for the pair–pair interactions show an even greater advantage for the internally contracted method. This has enabled us to perform contracted calculations for which the equivalent uncontracted calculation would be impossible with current hardware.

V. THE DIRECT CI PROCEDURE

Given the Hamiltonian residual vectors as described in the previous section, the eigenvectors and eigenvalues of the Hamiltonian are calculated iteratively using a modified Davidson[51] procedure. This consists of *macroiterations*, in which new matrices $\mathbf{G}^{Dp}$ and $\mathbf{g}^S$ are evaluated and the $\mathbf{C}^{Dp}$ and $\mathbf{c}^S$ are updated, and *microiterations*, in which we simul-

taneously optimize the coefficients c^I of the internal configurations and the coefficients α_n of sets of external expansion vectors $(\mathbf{C}^{Dp})^{(n)}, (\mathbf{c}^S)^{(n)}$ for which residual vectors $(\mathbf{G}^{Dp})^{(n)}, (\mathbf{g}^S)^{(n)}$ are available from previous macroiterations. This approach allows for optimum convergence of the expensive macroiterations at the cost of some additional inexpensive microiterations and is particularly useful if there is a strong coupling of the internal and external configuration spaces. In each macroiteration, first the quantities $(\mathbf{G}^{Dp})^{(n)}$, $(\mathbf{g}^S)^{(n)}$, and $(g^I)^{(n)}$ without the contributions of the internal configurations [i.e., the first terms in Eqs. (43)–(45)] are calculated. From these quantities the matrix elements $\langle \Psi_{\text{ext}}^m | \widehat{H} | \Psi_{\text{ext}}^n \rangle$, $\langle \Psi_I | \widehat{H} | \Psi_{\text{ext}}^n \rangle$, and $\langle \Psi_{\text{ext}}^m | \Psi_{\text{ext}}^n \rangle$ are easily evaluated, where

$$\Psi_{\text{ext}}^n = \sum_S \sum_a (\mathbf{c}^S)_a^n \Psi_S^a + \sum_{Dp} \sum_{ab} (\mathbf{C}^{Dp})_{ab}^n \Psi_{Dp}^{ab} \qquad (66)$$

are external expansion functions, and the superscript n denotes different expansion vectors. The above matrix elements are used to optimize variationally the expansion

$$\Psi = \sum_I c^I \Psi_I + \sum_n \alpha_n \Psi_{\text{ext}}^n. \qquad (67)$$

The corresponding eigenvalue problem is solved iteratively (microiterations). In order to facilitate convergence in cases with near degeneracies or for excited states, the Hamiltonian matrix is calculated explicitly for a predefined subset of the internal configurations. This subset can be selected, for instance, according to the magnitude of the diagonal matrix elements $\langle \Psi_I | \widehat{H} | \Psi_I \rangle$. It is noted that both in the macroiterations and in the microiterations nonorthogonal expansion functions are used. This not only eliminates I/O intensive Schmidt orthogonalization steps, but also makes it possible to limit the number of expansion vectors to a predefined number (typically 3–5). The first expansion vector is always the present optimized vector, and the other expansion vectors are the updates of the previous iterations. We note that in each macroiteration only the last row (or column) of the matrices $\langle \Psi_{\text{ext}}^m | \widehat{H} | \Psi_{\text{ext}}^n \rangle$, $\langle \Psi_{\text{ext}}^m | \Psi_{\text{ext}}^n \rangle$, and $\langle \Psi_I | \widehat{H} | \Psi_{\text{ext}}^n \rangle$ must be evaluated. The change of the first expansion vector is accounted for by simple transformations of the above matrices.

The optimization of the wave function in Eq. (67) yields the optimized coefficients $\{c^I\}$ for the internal configurations, the coefficients α_n for the external expansion vectors, and the variational energy for the present iteration. The coefficients α_n are used to obtain improved external coefficients $\mathbf{C}^{Dp}, \mathbf{c}^S$, and the corresponding parts of $\mathbf{G}^{Dp}, \mathbf{g}^S$. Finally, the contributions of the internal configurations are added to $\mathbf{G}^{Dp}, \mathbf{g}^S$ using the new coefficients $\{c^I\}$. A new expansion vector is then obtained as

$$\Delta(\mathbf{C}^{Dp})_{ab} = -\langle \Psi_{ab}^{Dp} | \widehat{H} - E | \Psi \rangle / \langle \Psi_{ab}^{Dp} | \widehat{H} - E | \Psi_{ab}^{Dp} \rangle, \qquad (68)$$

$$\Delta(\mathbf{c}^S)_a = -\langle \Psi_a^S | \widehat{H} - E | \Psi \rangle / \langle \Psi_a^S | \widehat{H} - E | \Psi_a^S \rangle. \qquad (69)$$

The energy denominators in Eq. (68) are approximated as in Refs. 17 and 30.

This method is easily extended to a multistate treatment. The evaluation of excited state wave functions with

the internally contracted MRCI method will be discussed in a separate publication.[52]

VI. DENSITY AND TRANSITION DENSITY MATRICES

For the evaluation of expectation values of one electron properties like dipole or quadrupole moments the first order density matrix is needed, and the calculation of electronic transition moments requires the first order transition density matrix. The second-order density matrix is necessary, e.g., for the calculation of energy gradients with respect to nuclear displacements. We will briefly discuss the evaluation of the density matrix, since some advantage may be taken by factorizing the coupling coefficients and by performing summations in a different order than in the direct CI. We will consider only the first order density matrices; the algorithm is straightforwardly extended to transition densities[53] and second order density matrices.[54]

The first-order density matrix is given by

$$D_{ab}^{(1)} = \left[\sum_S \mathbf{c}^S \cdot \mathbf{c}^{S\dagger} + 2 \sum_{Dp} \mathbf{C}^{Dp} \cdot \mathbf{C}^{Dp\dagger} \right]_{ab}, \qquad (70)$$

$$D_{an}^{(1)} = \left[\sum_S \mathbf{c}^S \sum_I c^I \sigma_n (S,I) \right.$$

$$\left. + 2 \sum_{i \geqslant j} \sum_p \mathbf{C}^{ijp\dagger} \cdot \sum_S \mathbf{c}^S \sigma_n (ijp,S) \right]_a, \qquad (71)$$

$$D_{mn}^{(1)} = \sum_{IJ} c^I c^J \langle I | \widehat{E}_{mn} | J \rangle + \sum_{ST} \mathbf{c}^{S\dagger} \cdot \mathbf{c}^T \langle S | \widehat{E}_{mn} | T \rangle$$

$$+ \sum_{i \geqslant j} \sum_{k \geqslant l} \sum_p \text{tr}\{\mathbf{C}^{ijp\dagger} \cdot \mathbf{C}^{klp}\} \alpha_{mn} (ijp,klp). \qquad (72)$$

Defining

$$A_{ij,kl}^P = \text{tr}\{\mathbf{C}^{ijp\dagger} \cdot \mathbf{C}^{klp}\}, \qquad (73)$$

we can write the last term of Eq. (72) as

$$\sum_{i \geqslant j} \sum_{k \geqslant l} A_{ij,kl}^P \left[\sum_I \langle 0 | \widehat{E}_{ik,jl} + p\widehat{E}_{il,jk} | I \rangle \langle I | \widehat{E}_{mn} | 0 \rangle \right.$$

$$\left. - \delta_{lm} \langle 0 | \widehat{E}_{ik,jn} | 0 \rangle - \delta_{km} \langle 0 | \widehat{E}_{in,jl} | 0 \rangle \right]. \qquad (74)$$

Hence, we can reverse the summations and first evaluate

$$v^I = \sum_{i \geqslant j} \sum_{k \geqslant l} A_{ij,kl}^P \langle 0 | \widehat{E}_{ik,jl} + p\widehat{E}_{il,jk} | I \rangle, \qquad (75)$$

$$D_{mn} = \sum_{i \geqslant j} \sum_{k \geqslant l} A_{ij,kl}^P [\delta_{lm} \langle 0 | \widehat{E}_{ik,jn} | 0 \rangle - \delta_{km} \langle 0 | \widehat{E}_{in,jl} | 0 \rangle] \qquad (74)$$

and, finally,

$$D_{mn}^{(1)} = D_{mn} + \sum_I v^I \langle I | \widehat{E}_{mn} | 0 \rangle. \qquad (75)$$

This saves the intermediate calculation of the third order density matrix. All other interactions are processed with similar algorithms to those applicable to the one electron parts of the Hamiltonian as described in Secs. III and IV.

VII. APPLICATIONS

In this section, we will first demonstrate that internally contracted MRCI wave functions yield results which are in close agreement with corresponding uncontracted calcula-

tions. Second, in order to demonstrate the efficiency of our method, we will present some large MRCI calculations, most of which were previously impossible. These applications will be presented and discussed in detail in separate publications.[55-58]

In order to test the accuracy of the internally contracted wave functions, we have performed a number of benchmark calculations for which recently full CI (FCI) and uncontracted MRCI calculations have been published.[1-10] The calculated energies are presented in Table II. In most cases we have considered only the largest basis sets and reference spaces used by Bauschlicher et al. The SCF and CASSCF energies are also given, since in some cases slightly different results than in Refs. 1-10 were obtained. These discrepancies are probably due to differences in the basis set input data.[59] Table II demonstrates that for all molecules and geometries the deviations between uncontracted and internally contracted MRCI calculations are very small. The energy differences are typically between 0.5 and 1 mH and about 3-4 times smaller than the differences between uncontracted MRCI and full CI. In particular, no significant change of the error with geometry is found, even though the importance of different reference configurations and the magnitude of the contraction coefficients varies strongly. Hence, there is virtually no loss of accuracy in calculated potential energy functions when the internal contraction is applied. In the majority of applications the differences between contracted and uncontracted calculations will be much smaller than errors introduced by the truncation of the basis set and the reference space.

In Table III some calculated properties are compared for FCI, internally contracted, and uncontracted MRCI. Again it is found that the differences between contracted and uncontracted CI are very small, even in cases where the correlation contribution is large. For the OH molecule, a comparison with the externally contracted MRCI method of Siegbahn[38] has also been made.[7,9] As expected, the internally contracted MRCI wave functions lead to more accurate results, in particular for the dipole moment. It is noted that some of the CASSCF results in Tables II and III slightly differ from those given in Refs. 7 and 9, in particular for the OH calculations with the space (322) at $r = 4.0$ bohr and with space (3221) at 1.8 bohr. In these cases local minima have been found in the previous MCSCF calculations.[59]

Table IV shows a timing analysis for some rather large MRCI calculations. A calculation for the electronic ground state of the CN molecule with 616 reference configurations and a large basis set takes only 4.5 minutes CPU time on a CRAY-XMP48. Accurate calculations of the CN $A^2\Pi$ and $B^2\Sigma^+$ state radiative lifetimes are presented in a separate publication.[56] Even larger calculations have been performed for excited states of NH_3[58] and CO_2,[55] and for the ground state of Cr_2.[57] In the latter case 3088 reference configurations were employed, which for a basis set of 136 orbitals lead to more than 78 million uncontracted configurations. Obviously such calculations are not cheap even with the internally contracted CI method. However, they can routinely be performed, while up to now a reasonable MRCI calculation for Cr_2 was believed to be impossible.[60] It is noted that

TABLE II. Comparison total energies for internally contracted and uncontracted MRCI wave functions and full CI results using DZP basis sets.[a]

Molecule	State	Geom.	SCF	CASSCF	Contracted MRCI	ΔE (contr. — uncontr.)[b]	ΔE (uncontr. — full CI)[c]
NH_2	$^2B_1$	r_e	— 55.573 009	— 55.620 752	— 55.738 542	0.000 876	0.003 202
		$1.5r_e$	— 55.387 411	— 55.498 124	— 55.602 324	0.000 945	0.001 940
		$2.0r_e$	— 55.188 708	— 55.411 062	— 55.503 655	0.000 531	0.001 338
		$N\cdots H_2$	— 55.388 944	— 55.430 552	— 55.541 081	0.000 555	0.002 924
NH_2	$^2A_1$	r_e	— 55.523 192	— 55.561 066	— 55.684 428	0.001 106	0.003 228
		$1.5r_e$	— 55.321 446	— 55.399 564	— 55.513 331	0.001 447	0.002 836
		$2.0r_e$	— 55.157 035	— 55.312 772	— 55.412 366	0.000 964	0.001 803
		$N\cdots H_2$	— 55.370 423	— 55.421 460	— 55.532 757	0.000 539	0.002 785
H_2O	$^1A_1$	r_e	— 76.040 551	— 76.129 886	— 76.253 490	0.000 618	0.002 516
		$1.5r_e$	— 75.800 505	— 75.953 151	— 76.068 544	0.000 819	0.002 042
		$2.0r_e$	— 75.582 297	— 75.839 926	— 75.949 724	0.000 793	0.001 752
F^-	^1S		— 99.444 462	— 99.582 645	— 99.658 453	0.000 131	0.000 909
OH	$^2\Pi$	$r = 1.8$	— 75.410 343	— 75.465 983[d]	— 75.587 581	0.000 666	0.002 535
	$^2\Pi$	$r = 1.8$	— 75.410 343	— 75.470 908[e]	— 75.588 175	0.000 846	0.001 761
	$^2\Pi$	$r = 1.8$	— 75.410 343	— 75.479 334[f]	— 75.588 544	0.000 473	0.001 765
	$^2\Sigma^+$	$r = 1.8$	— 75.250 690	— 75.304 826[d]	— 75.432 297	0.000 849	0.002 796
	$^2\Sigma^+$	$r = 1.8$	— 75.250 690	— 75.307 172[e]	— 75.432 860	0.000 914	0.002 168
	$^2\Sigma^+$	$r = 1.8$	— 75.250 690	— 75.325 616[f]	— 75.433 556	0.000 498	0.001 888
CH_2	$^1A_1$	r_e	— 39.886 297	— 39.945 529	— 39.025 362	0.000 441	0.001 379
	$^1B_1$	r_e	— 39.927 947	— 39.965 954	— 39.044 360	0.000 511	0.001 388
CH_3	$^2A_2''$	r_e	— 39.566 509	— 39.624 789	— 39.718 436	0.000 688	0.002 088
		$1.5r_e$	— 39.283 945	— 39.409 115	— 39.480 863	0.000 828	0.001 162
		$2.0r_e$	— 39.013 010	— 39.238 005	— 39.301 817	0.000 639	0.000 676
N_2	$^1\Sigma_g^+$	$r = 2.1$	— 108.955 790	— 109.094 744	— 109.149 884	0.000 042	0.000 716
		$r = 2.5$	— 108.835 280	— 109.030 241	— 109.086 495	0.000 060	0.000 763
		$r = 3.0$	— 108.619 497	— 109.900 408	— 109.956 613	0.000 130	0.000 783
NO	$^2\Pi$	$r = 2.2$	— 129.265 969	— 129.373 576	— 129.476 638	0.000 503	0.002 184
		$r = 3.3$	— 129.032 385	— 129.226 858	— 129.318 463	0.000 667	0.002 113
		$r = 4.4$	— 128.939 885	— 129.194 791	— 129.270 886	0.000 176	0.001 668
O_2	$^2\Sigma_g^-$	$r = 2.25$	— 149.635 316	— 149.731 897	— 149.869 925	0.001 149	0.004 073
		$r = 2.30$	— 149.631 270	— 149.733 778	— 149.871 676	0.001 166	0.004 105
		$r = 2.35$	— 149.625 115	— 149.733 689	— 149.871 381	0.001 181	0.004 132

[a] Uncontracted MRCI and FCI results from Refs. 1–10. In all cases except for OH the largest basis sets and reference wave functions described in Refs. 1–10 have been used.

[b] Energy difference between internally contracted and uncontracted MRCI.

[c] Energy difference between uncontracted MR-CI and full CI.

[d] Space (222) of Ref. 7; in the CASSCF calculations, the energy average of the $^2\Pi_x$, $^2\Pi_y$, and $^2\Sigma^+$ states was optimized with weights 0.25, 0.25, and 0.5, respectively.

[e] Space (322) of Ref. 9. The energy average of the $^2\Pi_x$ and $^2\Pi_y$ states was optimized. The orbital $5a_1$ is a σ orbital.

[f] Space (3221) of Ref. 7. In this case we were not able to reproduce the CASSCF results in Ref. 7. The orbitals $5a_1$ and $1a_2$ are the two δ orbital components.

the binding energy of Cr_2 obtained from the variational MRCI energies at the experimental r_e and at infinity is still slightly negative (— 0.03 eV). However, as will be discussed in more detail in Ref. 57, if unlinked clustered and relativistic effects are taken into account, a positive binding energy is obtained. The CO_2 calculations performed for the lowest $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^1\Delta_u$, and $^1\Pi_u$ states[55] made possible for the first time a definite assignment of the bands in the absorption spectrum. The timings shown in Table IV demonstrate that for very large internally contracted MRCI calculations most CPU time is spent in the single–pair interactions. Most of this time is needed for calculating the coupling coefficients. In the Cr_2 calculation the number of these coefficients is of the order of 10^9; it would therefore not be possible to store them on disk. Even if it were possible, reading the coeffi-cients would take longer than their calculation, since about 10^6 coupling coefficients are obtained per second! In these very large MRCI calculations we see that processing the integrals with three and four external integrals, which dominates a single reference CI calculation, needs only a small fraction of the total CPU time. It is noted that all matrix operations are performed with a small set of optimized subroutines. In particular, large dimension matrix multiplications, which often dominate the whole calculation, can efficiently use the multitasking facilities now available on many computers. This is an important consideration for calculations requiring large amounts of memory in order to efficiently use a multiprocessor machine. All calculations shown in Table IV ran with an average speed of 60–80 Mflop on a CRAY-XMP48.

TABLE III. Comparison calculated properties for internally contracted and uncontracted MRCI wave functions and full CI results using DZP basis sets.[a]

Molecule	State	CASSCF	MRCI Intern. contr.		Extern contr.	Uncontracted		FCI
Dipole moments[b]								
CH$_2$	$^1A_1$	0.6915	0.7151	(0.7132)		0.715	(0.713)	(0.716)
	$^1B_1$	0.2340	0.2617	(0.2618)		0.263	(0.262)	(0.264)
OH $X\,^2\Pi$	$r = 1.8^c$	0.6447	0.6561		0.6421	0.6558		(0.6561)
	$r = 2.4$	0.6664	0.6821		0.6774	0.6818		(0.6822)
	$r = 4.0$	0.1927^d	0.2329		0.2237	0.2343		(0.2391)
Electronic transition moments for OH $X\,^2\Pi$–$A\,^2\Sigma^+$:								
OH	$r = 1.8^e$	0.1618	0.1237		0.1227	0.1230		0.1195
	$r = 1.8^f$	0.1647	0.1198			0.1225		0.1195
	$r = 1.8^g$	0.1356	0.1210		0.1199	0.1198		0.1195
Dipole polarizabilities:[b]								
F$^-$	^1S	13.92	15.66	(15.97)		15.75	(16.03)	(16.30)

[a] Uncontracted MR-CI and Full CI values from Refs. 7, 9, and 10. The reference wave functions for CH$_2$ and F$^-$ are the same as in the MRCI (CH$_2$) and MRCIBIG(8) (F$^-$) calculations in Ref. 10.
[b] Values in parentheses calculated as energy derivatives with respect to a finite electric field of 0.005 a.u.; other values calculated as expectation values (dipole moments) or dipole moment derivatives (polarizabilities).
[c] Space (322) of Ref. 9.
[d] This CASSCF dipole moment differs from the one in Ref. 9.
[e] Space (222) of Ref. 7.
[f] Space (322) of Ref. 7.
[g] Space (3221) of Ref. 7. In this case our CASSCF energies and transition moment are not in agreement with those in Ref. 7.

VIII. CONCLUSIONS

A new efficient MRCI method has been developed which made possible to perform considerably larger calculations than with any other MRCI method before. This has been achieved through three principle advances: (i) the direct CI procedure is performed in an internally contracted configuration basis; (ii) a nonorthogonal basis is used where this leads to simplifications[47]; (iii) a new efficient method to recalculate all coupling coefficients each time they are needed has been developed.[44] It has been demonstrated that the internal contraction of the doubly external configurations does not lead to a significant loss of correlation energy nor

TABLE IV. Timing analysis for internally contracted MR-CI calculations.[a]

Molecule	CN ($X\,^2\Sigma^+$)	NH$_3$($A\,^1A''$)	CO$_2$($X\,^1\Sigma_g^+$)	CO$_2$(1 $^1\Pi_u$)	Cr$_2$($X\,^1\Sigma_g^+$)
No. of orbitals	90	95	153	153	136
No. of corr. orbitals	8	9	12	12	12
No. of ref. config.	616	1308	41	74	3 088
No. of uncontr. CSFs	4 925 432	5 422 877	7 745 785	15 337 242	78 874 576
No. of var. parameters	138 808	209 772	469 207	596 316	2 467 852
Initialization[b]	12.6	30.9	41.5	47.9	785.4
Time per iteration[c]	37.0	76.8	157.0	237.6	2724
Analysis of times per iteration (in percent):					
Single–single	14.4	13.0	28.3	29.8	24.6
Single–pair	42.8	39.4	38.3	47.7	61.8
Pair–pair	30.7	31.6	22.3	14.4	7.2
1 external integrals	41.2	38.9	39.9	48.6	63.4
0,2 external integrals	43.4	47.7	49.6	43.7	34.7
3,4 external integrals	12.2	10.2	10.4	7.4	1.9

[a] All times are single processor CPU times for CRAY-XMP48 in seconds.
[b] This includes partial integral transformation, calculation of basic coupling coefficients, (approximate) diagonal Hamiltonian matrix elements, initial CI in reference space, transformation matrix for pair orthogonalization, starting approximation (by first order perturbation theory).
[c] In order to converge the energy to 10^{-6} hartree, seven iterations for CN and CO$_2$, eight iterations for NH$_3$, and eleven iterations for Cr$_2$ were needed.

deteriorates the accuracy of calculated properties like dipole moments, polarizabilities, or electronic transition moments.

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