A formulation of multiple-reference CI
with terms linear in the interelectronic distances

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A formulation of the extension of the method of Kutzelnigg and Klopper, to include terms that are linear in the interelectronic distances in the Ansatz for the wavefunction, to general multiple-reference CI (r_{12}-MR-CI) with the same basis set requirements as in the closed-shell single reference case, is presented. The implementation into existing direct CI programs is straightforward. The additional CPU time needed by the r_{12} part should be negligible. r_{12}-MR-CI is readily extended to r_{12}-MR-ACPF, which allows for accurate approximations of full-CI energies. This implies the possibility of accurately solving the electronic Schrödinger equation for medium-sized atoms and molecules.

1. Introduction

The most common technique used to solve the Schrödinger equation approximately for medium-sized atoms and molecules is to expand the wavefunction in antisymmetrized products of orbitals (i.e. Slater determinants), which themselves are expanded in a finite (one-electron) basis set. It is, however, well known that such an approach suffers from slow convergence with respect to increasing basis set. This slow convergence is due to the inability of the simple product Ansatz to describe accurately the behaviour of the wavefunction at regions where two electrons approach each other and where the wavefunction does not tend to zero [1], since it is well known that at these regions the wavefunction is linear in the interelectronic distance r_{12} [2].

Convergence is dramatically improved if one includes terms which are linear in r_{12} in the Ansatz for the wavefunction [1]. Such a naive approach, however, leads to many (up to 4) electron integrals which require expensive numerical integrations, and whose number ($\propto n^8$, where n is the number of one-electron basis functions, as compared to $\propto n^4$ with simple orbital products) is (with the exception of very small systems) too large for them to be handled efficiently.

Recently, Kutzelnigg and Klopper [3,4] have shown that when using one-electron completeness insertions which are approximated in the given basis set, and which are required to be saturated up to a given value of l, it is possible to avoid three- and four-electron integrals. The resulting types of integrals (see below) are efficiently computed using standard methods [5,6]. Their so-called "r_{12}" method has so far been formulated for and implemented in Møller–Plesset perturbation theory up to second-order (MP2) [3,4,5,7], MP3 [4,8], CI(D) [4,8] (including reformulation in CEPA and CPF), CC(SD) and CC(SD)[T] [9]. These r_{12} methods are, however, presently limited to a single-reference closed-shell Ansatz, and therefore (perhaps with the exception of CC(SD)[T]) are not capable of accurately approximating a full-CI expansion.

Recently, it was shown how to account for higher substitutions in a general multiple-reference (MR)-CI(SD) Ansatz [10]. With this method (ACPF), which requires no changes to the part of the CI code where the action of the Hamiltonian on a trial function is computed, it is in fact possible to accurately approximate full-CI [10]. A MR formulation would also be particularly useful for studying general chemical systems.

Based on the ideas of Kutzelnigg and Klopper [4] in the present work a formulation of r_{12}-MR-CI is given, which is readily implemented in any existing

MR-CI code. The integrals required (in terms of the basis functions), are the same as in single-reference CI. Except for calculating and transforming the integrals not needed in a traditional CI, the additional computational effort needed for including the r_{12} terms is expected to be negligible.

2. Notations

Throughout this work, we will mainly use the syntax of ref. [4]. a_κ^μ and $a_{\kappa\lambda}^{\mu\nu}$ are the usual excitation operators which, when acting on a Slater determinant ϕ, replace the orbitals κ by μ and λ by ν. We then define

$$\phi_\kappa^\mu := a_\kappa^\mu \phi , \quad \phi_{\kappa\lambda}^{\mu\nu} := a_{\kappa\lambda}^{\mu\nu} \phi . \tag{1}$$

A Slater determinant will be labeled with μ, ν if it belongs to the reference space and with κ, λ if it is an arbitrary determinant.

In the case of the orbital indices, i_μ, j_μ, k_μ, ... denote occupied orbitals, a_μ, b_μ, c_μ, ... denote virtual orbitals expressible in the given basis set and α_μ, β_μ, γ_μ, ... denote virtual orbitals belonging to a complete set, all with respect to the μth reference. If orbitals are occupied in, or virtual with respect to all references, the indices denoting the reference will be dropped; i.e. i, j, k, ... denote internal orbitals, a, b, c, ... denote external orbitals expressible in the given basis set and α, β, γ, ... denote external orbitals, belonging to a complete basis set. p, q, r, ... are arbitrary orbitals expressed in the given basis set, and finally κ, λ, μ, ... are arbitrary orbitals belonging to a complete set. All orbitals of each set are assumed to be normalized and pairwise orthogonal. Spatial orbitals are labelled with capital letters. We use the Einstein summation convention.

One- and two-electron integrals are denoted in tensor syntax,

$$W_\kappa^\mu := \langle \kappa | \hat{W}_1 | \mu \rangle , \quad X_{\kappa\lambda}^{\mu\nu} := \langle \kappa\lambda | \hat{X}_{12} | \mu\nu \rangle . \tag{2}$$

Antisymmetrized two-electron integrals are denoted by a bar

$$\bar{X}_{\kappa\lambda}^{\mu\nu} := X_{\kappa\lambda}^{\mu\nu} - X_{\kappa\lambda}^{\nu\mu} . \tag{3}$$

We further define

$$[Y_{\kappa\lambda}]_{\kappa\lambda} := Y_{\kappa\lambda} - Y_{\lambda\kappa} ,$$

$$[Z_{\kappa\lambda}^{\mu\nu}]_{\kappa\lambda}^{\mu\nu} := Z_{\kappa\lambda}^{\mu\nu} - Z_{\lambda\kappa}^{\mu\nu} - Z_{\kappa\lambda}^{\nu\mu} + Z_{\lambda\kappa}^{\nu\mu} ,$$

$$\{Z_{\kappa\lambda}^{\mu\nu}\}_{\kappa\lambda}^{\mu\nu} := Z_{\kappa\lambda}^{\mu\nu} + Z_{\mu\nu}^{\kappa\lambda} , \tag{4}$$

for integrals over two or more electrons. We also use the commutators and anticommutators

$$[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A} , \quad \{\hat{A}, \hat{B}\} := \hat{A}\hat{B} + \hat{B}\hat{A} . \tag{5}$$

3. Theory

The Ansatz for the wavefunction Ψ is

$$\Psi = c^\kappa \phi_\kappa , \tag{6}$$

with the coefficients c^κ being determined variationally or otherwise. ϕ_κ denotes a Slater determinant which is given by an antisymmetrized Hartree-product ξ_κ of normalized and pairwise orthogonal spin-orbitals χ_p,

$$\phi_\kappa := \hat{\mathcal{A}}\xi_\kappa , \quad \xi_\kappa := \prod_{p=1}^{N} \chi_{\kappa_p}(\boldsymbol{r}_p) , \tag{7}$$

where $\hat{\mathcal{A}}$ is the usual antisymmetrizer and N is the number of electrons. In eq. (6) it is assumed that the expansion consists of some reference determinants ϕ_μ and of at least all determinants that can be created from ϕ_μ by single or double substitutions of orbitals occupied in ϕ_μ by virtual orbitals contained in the given basis set, i.e. we have at least CI(SD). We then define additional trial functions which are linear in the interelectronic distances,

$$_\mu\tilde{\phi}_{i_\mu j_\mu} := \hat{Q}_\mu \hat{\mathcal{A}} r_{i_\mu j_\mu} \xi_\mu ,$$

$$\hat{Q}_\mu := (|_\mu\phi_{k_\mu}^{\alpha_\mu}\rangle\langle{}^\mu\phi_{\alpha_\mu}^{k_\mu}| - |_\mu\phi_{k_\mu}^{a_\mu}\rangle\langle{}^\mu\phi_{a_\mu}^{k_\mu}|)$$

$$+ \tfrac{1}{4}(|_\mu\phi_{k_\mu l_\mu}^{\alpha_\mu\beta_\mu}\rangle\langle{}^\mu\phi_{\alpha_\mu\beta_\mu}^{k_\mu l_\mu}| - |_\mu\phi_{k_\mu l_\mu}^{a_\mu b_\mu}\rangle\langle{}^\mu\phi_{a_\mu b_\mu}^{k_\mu l_\mu}|) . \tag{8}$$

The effect of $\hat{Q}_\mu$ is to remove those components of $\hat{\mathcal{A}} r_{i_\mu j_\mu} \xi_\mu$ which are already contained in the CI expansion in eq. (6). We then get

$$\tilde{\phi}_{i_\mu j_\mu} = (\langle \,^\mu \phi_{\alpha_\mu}^{k_\mu} | \hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu \rangle_\mu \phi_{k_\mu}^{\alpha_\mu}$$

$$- \langle \,^\mu \phi_{a_\mu}^{k_\mu} | \hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu \rangle_\mu \phi_{k_\mu}^{a_\mu})$$

$$+ \tfrac{1}{4} (\langle \,^\mu \phi_{\alpha_\mu \beta_\mu}^{k_\mu l_\mu} | \hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu \rangle_\mu \phi_{k_\mu l_\mu}^{\alpha_\mu \beta_\mu}$$

$$- \langle \,^\mu \phi_{a_\mu b_\mu}^{k_\mu l_\mu} | \hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu \rangle_\mu \phi_{k_\mu l_\mu}^{a_\mu b_\mu})$$

$$= (\bar{r}_{\alpha_\mu j_\mu}^{i_\mu j_\mu} a_{i_\mu}^{\alpha_\mu} - \bar{r}_{a_\mu j_\mu}^{i_\mu j_\mu} a_{i_\mu}^{a_\mu}) \phi_\mu$$

$$+ (\bar{r}_{i_\mu \beta_\mu}^{i_\mu j_\mu} a_{j_\mu}^{\beta_\mu} - \bar{r}_{i_\mu b_\mu}^{i_\mu j_\mu} a_{j_\mu}^{b_\mu}) \phi_\mu$$

$$+ \tfrac{1}{2} (\bar{r}_{\alpha_\mu \beta_\mu}^{i_\mu j_\mu} a_{i_\mu j_\mu}^{\alpha_\mu \beta_\mu} - \bar{r}_{a_\mu b_\mu}^{i_\mu j_\mu} a_{i_\mu j_\mu}^{a_\mu b_\mu}) \phi_\mu . \tag{9}$$

Since the first two terms on the rhs of eq. (9) give rise to matrix elements which involve a partial wave expansion which, in the atomic case, terminates at a given value of l (i.e. $l_{i_\mu} + 2 l_{j_\mu}$, respectively, $2 l_{i_\mu} + l_{j_\mu}$), the influence of these terms vanishes in the standard approximation [4] (see section 4.2).

At this point it is important to notice that it is not necessary to define a_μ, b_μ and α_μ, β_μ as being virtual with respect to ϕ_μ only, since all all-internal single $_\mu \phi_{i_\mu}^k$ and double $_\mu \phi_{i_\mu j_\mu}^{kl}$ replacements of orbitals occupied in ϕ_μ are already contained in the CI (eq. (6)), the influence of semi-internal substitutions with one orbital belonging to the complete basis set $_\mu \phi_{i_\mu j_\mu}^{\alpha_\mu k}$ vanishes in the standard approximation, and determinants resulting from triple and higher substitutions of orbitals in ϕ_μ do not overlap with $\hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu$.

We finally define additional correlation functions, equivalent to $\hat{\mathscr{A}} r_{i_\mu j_\mu} \xi_\mu$ and which are orthogonal to the Slater determinants expressible in the given basis set, by

$$_\mu \tilde{\phi}_{i'_\mu j'_\mu}^{ij} := \bar{R}_{\alpha\beta}^{ij} a_{i'_\mu j'_\mu}^{\alpha\beta} \phi_\mu$$

$$= (\bar{r}_{\alpha\beta}^{ij} a_{i'_\mu j'_\mu}^{\alpha\beta} - \bar{r}_{ab}^{ij} a_{i'_\mu j'_\mu}^{ab}) \phi_\mu , \tag{10}$$

where $\bar{R}_{\alpha\beta}^{ij} := \bar{r}_{\alpha\beta}^{ij}$, if χ_α or χ_β are not contained in the given basis set, otherwise $\bar{R}_{\alpha\beta}^{ij} := 0$. This Ansatz contains additional terms [9,11] in which $i \neq i'_\mu$ and $j \neq j'_\mu$ to ensure the same unitary transformation properties among orbitals as in the corresponding CI functional. The Ansatz for the wavefunction (compare eq. (6)) containing terms that are linear in the interelectronic distances is then given by

$$\Psi = \,^\mu \tilde{C}_{ij}^{i'_\mu j'_\mu} \,_\mu \tilde{\phi}_{i'_\mu j'_\mu}^{ij} + c^\kappa \phi_\kappa . \tag{11}$$

4. Matrix elements

4.1. Preliminary considerations

This section contains the derivation of explicit and easily evaluable expressions for all matrix elements which occur in the r_{12} part of r_{12}-MR-CI. Since computational efficiency is not critical for the r_{12} part (see below), there is no need for repartitioning the Hamiltonian or using spin-free formalisms. We therefore decided to formulate the additional matrix elements needed for the r_{12} part using Slater determinants of spin-orbitals and the usual Hamiltonian,

$$\hat{H} := \hat{H}^{(1)} + \hat{H}^{(2)} ,$$

$$\hat{H}^{(1)} := a_\kappa^\mu h_\mu^\kappa , \quad \hat{H}^{(2)} := \tfrac{1}{4} a_{\kappa\lambda}^{\mu\nu} \bar{g}_{\mu\nu}^{\kappa\lambda} , \tag{12}$$

with $g_{12} := 1/r_{12}$. Please note that with the Ansatz according to eq. (11), it is in general not possible to formulate a generalized Brillouin theorem [12] which could be used to aid the derivations. The following matrix elements occur in the r_{12} part of r_{12}-MR-CI:

$$\langle \,^\mu \tilde{\phi}_{ij}^{i_\mu j_\mu} | \hat{O} | \phi_\kappa \rangle = \bar{R}_{ij}^{\alpha\beta} \langle \phi^\mu | a_{\alpha\beta}^{i_\mu j_\mu} \hat{O} | \phi_\kappa \rangle , \tag{13}$$

$$\langle \,^\mu \tilde{\phi}_{ij}^{i_\mu j_\mu} | \hat{O} |_\nu \tilde{\phi}_{k_\nu l_\nu}^{kl} \rangle$$

$$= \bar{R}_{ij}^{\alpha\beta} \langle \phi^\mu | a_{\alpha\beta}^{i_\mu j_\mu} \hat{O} a_{k_\nu l_\nu}^{\gamma\delta} | \phi_\nu \rangle \bar{R}_{\gamma\delta}^{kl} . \tag{14}$$

$\hat{O}$ is either 1 (i.e. overlap), $\hat{H}^{(1)}$, or $\hat{H}^{(2)}$. It is impractical in the general MR-CI case to give explicit formulas for the matrix elements of $\hat{O}$ because of the large number of cases to be distinguished. However, all matrix elements are readily computed using a straightforward application of standard formalisms, e.g. the Slater–Condon rules [13]. The expressions which result from the symbolic evaluation of the matrix elements of $\hat{O}$ are compiled in table 1. Table 2 contains the integrals resulting from the expressions of table 1.

In the formulas for the matrix elements, the expressions of table 1 actually occur again with α and β being interchanged and the sign changed. If one uses the Slater–Condon rules, it is therefore not necessary to repeat the procedure with α and β interchanged, since it is sufficient to simply multiply the resulting integrals (see table 2) by two.

Table 1

Expressions resulting from the symbolic evaluation of the matrix elements occurring in the r_{12} part of r_{12}-MR-CI

Matrix element	$\hat{O}=1$	$\hat{O}=\hat{H}^{(1)}$	$\hat{O}=\hat{H}^{(2)}$
$\langle {}^{\mu}\phi^{i_k j_k}_{\alpha\beta}|\hat{O}|\phi_{\kappa}\rangle$		$h^p_{\alpha}\delta^d_{\beta},\, h^{k^-}_{i^-}\delta^c_{\alpha}\delta^d_{\beta}$	$\bar{g}^{pq}_{\alpha\beta},\, \bar{g}^{pk^-}_{\alpha i^-}\delta^d_{\beta},\, \bar{g}^{k^-l^-}_{i^-j^-}\delta^c_{\alpha}\delta^d_{\beta}$
$\langle {}^{\mu}\phi^{i_k j_k}_{\alpha\beta}|\hat{O}|{}_{\nu}\phi^{\gamma\delta}_{k_l l_l}\rangle$	$\delta^{\gamma}_{\alpha}\delta^{\delta}_{\beta}$	$h^{\gamma}_{\alpha}\delta^{\delta}_{\beta},\, h^{k^-}_{i^-}\delta^{\gamma}_{\alpha}\delta^{\delta}_{\beta}$	$\bar{g}^{\gamma\delta}_{\alpha\beta},\, \bar{g}^{\gamma k^-}_{\alpha i^-}\delta^{\delta}_{\beta},\, \bar{g}^{k^-l^-}_{i^-j^-}\delta^{\gamma}_{\alpha}\delta^{\delta}_{\beta}$

Table 2

Integrals resulting from the matrix elements occurring in the r_{12} part of r_{12}-MR-CI

Matrix element	$\hat{O}=1$	$\hat{O}=\hat{H}^{(1)}$	$\hat{O}=\hat{H}^{(2)}$
$\langle {}^{\mu}\tilde{\phi}^{i_k j_k}_{ij}|\hat{O}|\phi_{\kappa}\rangle$		$\bar{R}^{\alpha d}_{ij}h^p_{\alpha},\, \{\bar{R}^{cd}_{ij}h^{k^-}_{i^-}\}$ [a]	$\bar{R}^{\alpha\beta}_{ij}\bar{g}^{pq}_{\alpha\beta},\, \bar{R}^{\alpha d}_{ij}\bar{g}^{pk^-}_{\alpha i^-},\, \{\bar{R}^{cd}_{ij}\bar{g}^{k^-l^-}_{i^-j^-}\}$
$\langle {}^{\mu}\tilde{\phi}^{i_k j_k}_{ij}|\hat{O}|{}_{\nu}\tilde{\phi}^{kl}_{k_l l_l}\rangle$	$\bar{R}^{\alpha\beta}_{ij}\bar{R}^{kl}_{\alpha\beta}$	$\bar{R}^{\alpha\beta}_{ij}h^{\gamma}_{\alpha}\bar{R}^{kl}_{\gamma\beta},\, \bar{R}^{\alpha\beta}_{ij}h^{k^-}_{i^-}\bar{R}^{kl}_{\alpha\beta}$	$\bar{R}^{\alpha\beta}_{ij}\bar{g}^{\gamma\delta}_{\alpha\beta}\bar{R}^{kl}_{\gamma\delta},\, \bar{R}^{\alpha\beta}_{ij}\bar{g}^{\gamma k^-}_{\alpha i^-}\bar{R}^{kl}_{\gamma\beta},\, \bar{R}^{\alpha\beta}_{ij}\bar{g}^{k^-l^-}_{i^-j^-}\bar{R}^{kl}_{\alpha\beta}$

[a] Integrals that vanish exactly are enclosed by braces.

4.2. Approximation of integrals

We now give easily evaluable expressions for the integrals in table 2 using the "standard approximation" of ref. [4],

$$A^{\kappa}B_{\kappa}\rightarrow A^p B_p\,, \tag{15}$$

which is certainly justified, if the partial wave expansion of the integral on the lhs of eq. (15) terminates at some finite l and the basis set is saturated up to that l value. Since all integrals arising from the symbolic evaluation of the matrix elements occurring in the r_{12} part are over at least two internal orbitals (see eqs. (13) and (14) of section 4.1), this is clearly the case for many types of integrals (see below) if atoms are considered. As in the single-reference case [4], the basis set is required to be saturated up to $3l_{occ}$, where l_{occ} is the largest azimuthal quantum number of all internal orbitals. If Brillouin theorems [12] hold, various expressions can be simplified or vanish entirely (see below). Additionally, there occur expressions which are difficult to evaluate and which can not be approximated in a simple way. These expressions will be neglected, since fortunately they converge fast enough to zero to ensure that the truncation error is still smaller than in traditional CI (i.e. smaller than $\propto l^{-3}$ [1]).

In the molecular case, the partial wave expansions, in general, do not terminate. However, experience shows that if the molecular orbitals are expanded in basis functions centered at the locations of the nu-

clei, the partial wave expansions of those types of integrals whose expansions terminate in the atomic case, converge rapidly. For example in the case of F_2, the internal orbitals are accurately described using 1- and 2d orbitals; at most 2f polarisation functions, in addition to the usual sp-basis set, for the SCF- and MCSCF-energies are necessary for convergence to about 1 mhartree [14].

It should be noted that the approximations needed for closed-shell single-reference CI(SD) with SCF orbitals have already been derived in ref. [4]. Those needed for internally contracted MR-CI have been derived by Kutzelnigg [15]. In the following, the application of the standard approximation will be denoted by "$\overset{sa}{=}$".

The approximation of the following three integrals is straightforward [4,15]

$$\bar{R}^{\alpha\beta}_{ij}(\delta^{\gamma}_{\alpha}\delta^{\delta}_{\beta})\bar{R}^{kl}_{\gamma\delta}=\bar{R}^{\alpha\beta}_{ij}\bar{R}^{kl}_{\alpha\beta}\overset{sa}{=}[r^{\kappa\lambda}_{ij}r^{kl}_{\kappa\lambda}-r^{pq}_{ij}r^{kl}_{pq}]^{kl}_{ij}$$

$$=[(r^2_{12})^{kl}_{ij}-r^{pq}_{ij}r^{kl}_{pq}]^{kl}_{ij}=:\check{S}^{kl}_{ij}\,, \tag{16}$$

$$\bar{R}^{\alpha\beta}_{ij}(\bar{g}^{pq}_{\alpha\beta})\overset{sa}{=}\bar{r}^{\kappa\lambda}_{ij}\bar{g}^{pq}_{\kappa\lambda}-\bar{r}^{rs}_{ij}\bar{g}^{pq}_{rs}$$

$$=[\delta^p_i\delta^q_j-r^{rs}_{ij}g^{pq}_{rs}]^{pq}_{ij}\,, \tag{17}$$

$$\bar{R}^{\alpha\beta}_{ij}(\bar{g}^{\gamma\delta}_{\alpha\beta})\bar{R}^{kl}_{\gamma\delta}\overset{sa}{=}\bar{r}^{pq}_{ij}\bar{g}^{rs}_{pq}\bar{r}^{kl}_{rs}-\bar{r}^{\kappa\lambda}_{ij}\bar{g}^{rs}_{\kappa\lambda}\bar{r}^{kl}_{rs}-\bar{r}^{pq}_{ij}\bar{g}^{\mu\nu}_{pq}\bar{r}^{kl}_{\mu\nu}$$

$$+\bar{r}^{\kappa\lambda}_{ij}\bar{g}^{\mu\nu}_{\kappa\lambda}\bar{r}^{kl}_{\mu\nu}=\bar{r}^{pq}_{ij}\bar{g}^{rs}_{pq}\bar{r}^{kl}_{rs}-4\bar{r}^{kl}_{ij}\,. \tag{18}$$

The next two integrals [4,15] involve products containing the overlap integral, eq. (16),

$$\bar{R}_{ij}^{\alpha\beta}(h_{i''}^{k''}\delta_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}=h_{i''}^{k''}\bar{R}_{ij}^{\alpha\beta}\bar{R}_{\alpha\beta}^{kl}\stackrel{\text{sa}}{=}h_{i''}^{k''}\check{S}_{ij}^{kl}, \qquad (19)$$

$$\bar{R}_{ij}^{\alpha\beta}(\bar{g}_{i''j''}^{k''l''}\delta_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}$$

$$=\bar{g}_{i''j''}^{k''l''}\bar{R}_{ij}^{\alpha\beta}\bar{R}_{\alpha\beta}^{kl}\stackrel{\text{sa}}{=}\bar{g}_{i''j''}^{k''l''}\check{S}_{ij}^{kl}. \qquad (20)$$

The remaining four types need special treatment,

$$\bar{R}_{ij}^{\alpha\beta}(h_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}=\bar{R}_{ij}^{\alpha\beta}h_{\alpha}^{\gamma}\bar{R}_{\gamma\beta}^{kl}$$

$$=\bar{r}_{ij}^{\alpha\beta}h_{\alpha}^{\gamma}\bar{r}_{\gamma\beta}^{kl}-\{\bar{r}_{ij}^{ab}h_{a}^{\gamma}\bar{r}_{\gamma b}^{kl}\}_{ij}^{kl}+\bar{r}_{ij}^{ab}h_{a}^{c}\bar{r}_{cb}^{kl}$$

$$=\bar{r}_{ij}^{\alpha\beta}h_{\alpha}^{\gamma}\bar{r}_{\gamma\beta}^{kl}-\{\bar{r}_{ij}^{ab}h_{a}^{\gamma}\bar{R}_{\gamma b}^{kl}\}_{ij}^{kl}-\bar{r}_{ij}^{ab}h_{a}^{c}\bar{r}_{cb}^{kl}, \qquad (21)$$

where we have used

$$\bar{r}_{ij}^{ab}h_{a}^{\gamma}\bar{R}_{\gamma b}^{kl}=\bar{r}_{ij}^{ab}h_{a}^{\gamma}\bar{r}_{\gamma b}^{kl}-\bar{r}_{ij}^{ab}h_{a}^{c}\bar{r}_{cb}^{kl}. \qquad (22)$$

The expression in eq. (22) may either cancel with the corresponding g integrals (see below) due to a Brillouin condition [4,12], or if the basis set used is saturated in every occurring l quantum number. We then get

$$\bar{R}_{ij}^{\alpha\beta}(h_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}\stackrel{\text{sa}}{=}\bar{r}_{ij}^{\alpha\beta}h_{\alpha}^{\gamma}\bar{r}_{\gamma\beta}^{kl}-\bar{r}_{ij}^{ab}h_{a}^{c}\bar{r}_{cb}^{kl}$$

$$\stackrel{\text{sa}}{=}[r_{ij}^{\kappa\lambda}h_{\kappa}^{\mu}r_{\mu\lambda}^{kl}-r_{ij}^{pq}h_{p}^{r}r_{rq}^{kl}]_{ij}^{kl}. \qquad (23)$$

To proceed further, we have to find an evaluable expression for the first term on the extreme rhs of eq. (23) (please note that $[\hat{h}_1, r_{12}]=[\hat{T}_1, r_{12}]$ since $\hat{V}_1$ and r_{12} commute)

$$r_{ij}^{\kappa\lambda}h_{\kappa}^{\mu}r_{\mu\lambda}^{kl}\equiv\langle ij|r_{12}\hat{h}_1 r_{12}|kl\rangle=\tfrac{1}{2}\langle ij|r_{12}[\hat{T}_1, r_{12}]$$

$$+[r_{12}, \hat{T}_1]r_{12}+r_{12}^2\hat{h}_1+\hat{h}_1 r_{12}^2|kl\rangle$$

$$=\tfrac{1}{2}\langle ij|[r_{12}, [\hat{T}_1, r_{12}]]+\{r_{12}^2, \hat{h}_1\}|kl\rangle$$

$$\stackrel{\text{sa}}{=}\tfrac{1}{2}(\delta_i^k\delta_j^l+\{(r_{12}^2)_{ij}^{pl}h_p^k\}_{ij}^{kl}), \qquad (24)$$

where we have used $[r_{12}, [\hat{T}_1, r_{12}]]=1$. We finally get

$$\bar{R}_{ij}^{\alpha\beta}(h_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}$$

$$\stackrel{\text{sa}}{=}[\tfrac{1}{2}(\delta_i^k\delta_j^l+\{(r_{12}^2)_{ij}^{pl}h_p^k\}_{ij}^{kl})-r_{ij}^{pq}h_p^r r_{rq}^{kl}]_{ij}^{kl}. \qquad (25)$$

It is, however, not necessary to neglect the expression in eq. (22) since it can be rewritten as

$$r_{ij}^{ab}h_a^{\gamma}R_{\gamma b}^{kl}=r_{ij}^{ab}(h_a^{\kappa}r_{\kappa b}^{kl}-h_a^p r_{pb}^{kl})$$

$$=r_{ij}^{ab}([\hat{T}_1, r_{12}]_{ab}^{kl}+(r_{12}\hat{h}_1)_{ab}^{kl}-h_a^p r_{pb}^{kl}). \qquad (26)$$

The integrals of $[\hat{T}_1, r_{12}]$ are of non-standard type, but efficient programs to evaluate them in terms of Cartesian Gaussians already exist [5,6]. The final result then is [4,15]

$$\bar{R}_{ij}^{\alpha\beta}(h_{\alpha}^{\gamma}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}\stackrel{\text{sa}}{=}\text{Expr. on the rhs of eq. (25)}$$

$$+[\{r_{ij}^{ab}([\hat{T}_1, r_{12}]_{ab}^{kl}+r_{ab}^{pl}h_p^k-h_a^p r_{pb}^{kl})\}_{ij}^{kl}]_{ij}^{kl}. \qquad (27)$$

The next g integral has a similar structure as the previously treated $\hat{h}$ integral,

$$\bar{R}_{ij}^{\alpha\beta}(\bar{g}_{\alpha i''}^{\gamma k''}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}=\bar{R}_{ij}^{\alpha\beta}\bar{g}_{\alpha i''}^{\gamma k''}\bar{R}_{\gamma\beta}^{kl}$$

$$=\bar{r}_{ij}^{\alpha\beta}\bar{g}_{\alpha i''}^{\gamma k''}\bar{r}_{\gamma\beta}^{kl}-\{\bar{r}_{ij}^{ab}\bar{g}_{ai''}^{\gamma k''}\bar{r}_{\gamma b}^{kl}\}_{ij}^{kl}+\bar{r}_{ij}^{ab}\bar{g}_{ai''}^{ck''}\bar{r}_{cb}^{kl}$$

$$\stackrel{\text{sa}}{=}\bar{r}_{ij}^{\kappa\lambda}\bar{g}_{\kappa i''}^{\mu k''}\bar{r}_{\mu\lambda}^{kl}-\{\bar{r}_{ij}^{pq}\bar{g}_{pi''}^{\kappa k''}\bar{r}_{\kappa q}^{kl}\}_{ij}^{kl}+\bar{r}_{ij}^{pq}\bar{g}_{pi''}^{rk''}\bar{r}_{rq}^{kl}. \qquad (28)$$

We neglect contributions arising from $g_{\alpha i''}^{k''\gamma}$, since the truncation error (in the atomic case) of $r_{ij}^{\kappa\lambda}g_{\kappa i''}^{k''\mu}r_{\mu\lambda}^{kl}$ is $\propto l^{-7}$ [4] and the truncation error of $r_{ij}^{\kappa q}g_{\kappa i''}^{k''r}$, if it does not cancel due to a Brillouin condition [4,12] together with the corresponding h integrals anyway (see above), is at most $\propto l^{-5}$ (see below). Since r_{12} and g_{12} commute, we then get

$$r_{ij}^{\kappa\lambda}g_{\kappa i''}^{\mu k''}r_{\mu\lambda}^{kl}=g_{ii''}^{\kappa k''}(r_{12}^2)_{\kappa j}^{kl}\stackrel{\text{sa}}{=}\tfrac{1}{2}\{g_{ii''}^{pk''}(r_{12}^2)_{pj}^{kl}\}_{ij}^{kl},$$

$$g_{pi''}^{\kappa k''}r_{\kappa q}^{kl}=r_{pq}^{\kappa l}g_{\kappa i''}^{kk''}\stackrel{\text{sa}}{=}r_{pq}^{rl}g_{ri''}^{kk''}, \qquad (29)$$

and the final result is [15]

$$\bar{R}_{ij}^{\alpha\beta}(\bar{g}_{\alpha i''}^{\gamma k''}\delta_{\beta}^{\delta})\bar{R}_{\gamma\delta}^{kl}\stackrel{\text{sa}}{=}[\{\tfrac{1}{2}g_{ii''}^{pk''}(r_{12}^2)_{pj}^{kl}-r_{ij}^{pq}r_{pq}^{rl}g_{ri''}^{kk''}\}_{ij}^{kl}$$

$$+r_{ij}^{pq}g_{pi''}^{rk''}r_{rq}^{kl}]_{ij}^{kl}. \qquad (30)$$

The last $\hat{h}$ and g integrals (see eqs. (32) and (33) below) cancel each other if the extended Brillouin theorem [4,12] holds. The h integral vanishes within the standard approximation if the basis set used is saturated in every occurring l quantum number. Its evaluation is nevertheless straightforward (compare the derivation of eq. (27))

$$\bar{R}_{ij}^{\alpha\beta}(h_{\alpha}^p\delta_{\beta}^d)=\bar{R}_{ij}^{\alpha d}h_{\alpha}^p=\bar{r}_{ij}^{\kappa d}h_{\kappa}^p-\bar{r}_{ij}^{qd}h_q^p$$

$$\stackrel{\text{sa}}{=}[[r_{12}, \hat{T}_1]_{ij}^{pd}+h_i^q r_{qj}^{pd}-r_{ij}^{qd}h_q^p]_{ij}. \qquad (31)$$

The last g integral, which may cancel with the corresponding $\hat{h}$ integral (see above),

$$\bar{R}_{ij}^{\alpha\beta}(\bar{g}_{\alpha i''}^{pk''}\delta_{\beta}^d)=\bar{R}_{ij}^{\alpha d}\bar{g}_{\alpha i''}^{pk''}=\bar{r}_{ij}^{\kappa d}\bar{g}_{\kappa i''}^{pk''}-\bar{r}_{ij}^{rd}\bar{g}_{ri''}^{pk''}, \qquad (32)$$

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does not automatically vanish in a more general case since (in the atomic case) the partial wave expansion of the first term on the rhs of eq. (32) may involve orbitals with l quantum numbers that are not contained in the given basis set, e.g. $l_\kappa = l_i + l_j + l_d = l_{i''} + l_{k''} + l_p > l_{max}$. However, using the procedure described in the appendix of ref. [4], it can be shown that $|r_{ii}^{aa}| \propto l_a^{-3}$ and $|g_{ii}^{aa}| \propto l_a^{-2}$, where ϕ_i is a 1s Slater-type orbital (STO) and ϕ_a is a STO with azimuthal quantum number l_a. This means that neglecting $\bar{R}_{ij}^{\alpha d} g_{\alpha i}^{k''p}$ introduces an error of at most $\propto l^{-5}$ (in the atomic case). Using the fact that r_{12} and g_{12} commute we finally get

$$\bar{R}_{ij}^{\alpha\beta}(\bar{g}_{\alpha i}^{pk''}\delta_\beta^d) \overset{sa}{=} \bar{r}_{ij}^{\kappa d}g_{ki}^{pk''} - \bar{r}_{ij}^{rd}g_{ri}^{pk''}$$

$$= [g_{ii''}^{\kappa k''}r_{kj}^{pd} - r_{ij}^{rd}g_{ri''}^{pk''}]_{ij}$$

$$\overset{sa}{=} [g_{ii''}^{rk''}r_{rj}^{pd} - r_{ij}^{rd}g_{ri''}^{pk''}]_{ii}. \tag{33}$$

4.3. Handling of integrals

To evaluate the formulas derived in section 4.2 efficiently, it is recommended that one computes the following matrices:

$$\tilde{A}_{IJ}^{PL} := (r_{12}^2)_{IJ}^{PL} = (r^2)_I^P\delta_J^L - 2r_I^P \cdot r_J^L + \delta_I^P(r^2)_J^L,$$

$$\tilde{B}_{IJ}^{PL} := r_{IJ}^{QR}r_{QR}^{PL}, \quad \tilde{C}_{IJ}^{KL} := \{\tilde{A}_{IJ}^{PL}h_P^K\}_{IJ}^{KL},$$

$$\tilde{D}_{IJ}^{PQ} := r_{IJ}^{RQ}h_R^P, \quad \tilde{E}_{IJ}^{KL} := \tilde{D}_{IJ}^{PQ}r_{PQ}^{KL},$$

$$\tilde{F}_{IJ}^{KL} := \{r_{IJ}^{AB}[\tilde{T}_1, r_{12}]_{AB}^{KL}\}_{IJ}^{KL}, \quad \tilde{G}_{IJ}^{PD} := h_I^R r_{RJ}^{PD},$$

$$\tilde{H}_{IJ}^{KL} := \{\tilde{G}_{IJ}^{AB}r_{AB}^{KL}\}_{IJ}^{KL}, \quad \tilde{I}_{IJ}^{KL} := \{\tilde{D}_{IJ}^{AB}r_{AB}^{KL}\}_{IJ}^{KL},$$

$$\tilde{J}_{IJ}^{PQ} := r_{IJ}^{RS}g_{RS}^{PQ}, \quad \tilde{K}_{IJ}^{KL} := \tilde{J}_{IJ}^{PQ}r_{PQ}^{KL},$$

$$\tilde{L}_{IJI'}^{KLK''} := \{\tilde{A}_{IJ}^{PL}g_{PI'}^{KK''}\}_{IJ}^{KL}, \quad \tilde{M}_{IJI'}^{KLK''} := \{\tilde{B}_{IJ}^{PL}g_{PI'}^{KK''}\}_{IJ}^{KL},$$

$$\tilde{N}_{IJI'}^{PQK''} := r_{IJ}^{RQ}g_{RI'}^{PK''}, \quad \tilde{O}_{IJI'}^{KLK''} := \tilde{N}_{IJI'}^{PQK''}r_{PQ}^{KL},$$

$$\tilde{P}_{IJI'}^{PDK''} := g_{II'}^{RK''}r_{RJ}^{PD}. \tag{34}$$

$\tilde{C}_{IJ}^{KL}$, $\tilde{E}_{IJ}^{KL}$, $\tilde{F}_{IJ}^{KL}$, $\tilde{H}_{IJ}^{AB}$, $\tilde{I}_{IJ}^{KL}$, $\tilde{K}_{IJ}^{KL}$, $\tilde{L}_{IJI'}^{KLK''}$, $\tilde{M}_{IJI'}^{KLK''}$ and $\tilde{O}_{IJI'}^{KLK''}$ are invariant with respect to a simultaneous interchange of (IJ) with (KL). $\tilde{J}_{IJ}^{PQ}$ and $\tilde{K}_{IJ}^{KL}$ are invariant with respect to a simultaneous interchange of the two lower indices with one another and, at the same time, of the two upper indices with one another. $\tilde{L}_{IJI'}^{KLK''}$, $\tilde{M}_{IJI'}^{KLK''}$, $\tilde{N}_{IJI'}^{PQK''}$, $\tilde{O}_{IJI'}^{KLK''}$ and $\tilde{P}_{IJI'}^{PDK''}$ are

symmetric with respect to an interchange of I'' and K''.

The computation of $\tilde{A}_{IJ}^{PL}$, $\tilde{C}_{IJ}^{KL}$, $\tilde{D}_{IJ}^{PQ}$, $\tilde{E}_{IJ}^{KL}$, $\tilde{F}_{IJ}^{KL}$, $\tilde{H}_{IJ}^{AB}$, $\tilde{I}_{IJ}^{KL}$, $\tilde{K}_{IJ}^{KL}$, $\tilde{L}_{IJI'}^{KLK''}$ and $\tilde{M}_{IJI'}^{KLK''}$ is simple because all intermediate matrices can be held in memory. In the cases of $\tilde{B}_{IJ}^{PL}$, $\tilde{G}_{IJ}^{KL}$ and $\tilde{J}_{IJ}^{PQ}$ it is recommended that one matrix is kept in memory during the transformation and the file containing r_{PQ}^{RS} and g_{PQ}^{RS} is read once. In the cases of $\tilde{N}_{IJI'}^{PQK''}$, $\tilde{O}_{IJI'}^{KLK''}$ and $\tilde{P}_{IJI'}^{PDK''}$, a matrix might become too large to be held in memory completely. It is then recommended that the matrices be computed only for a given pair $(I''K'')$ at a time.

Table 3 contains the final expressions for all integrals occurring in the r_{12} part in terms of the matrices of eq. (33). Their counterparts over spin-orbitals are easily obtained by noting that all matrices vanish unless the labels which are exactly one upon another, belong to orbitals with the same spin.

5. Conclusions

It has been shown that even without the possibility of using Brillouin theorems [12] (see ref. [4]) it is possible to formulate easily evaluable expressions for r_{12}-MR-CI, which have the same basis set requirements as in the single-reference r_{12}-CI [4]. The basis set truncation error of the present formulation (in the atomic case) is $\propto l^{-5}$ in the worst case which is still better than $\propto l^{-3}$ [1] of traditional CI. The maximum performance to be expected, is the same as in the single-reference case, i.e. $\propto l^{-7}$. Apart from the types of integrals common to large scale quantum chemistry (h_Q^P and g_{PQ}^{RS}), the only additional types necessary are $(r^2)_I^P$, $r_I^P r_{RJ}^{PQ}$ and $[\hat{T}_1, r_{12}]_I^{PQ}$, which are readily computed; e.g., in terms of Cartesian Gaussians. The integrals $[\hat{T}_1, r_{12}]_{IJ}^{PQ}$ may be avoided at the expense of a basis set of higher quality (see section 4.2).

The largest memory requirements during the CI iterations are $\approx N^2n^2$ (at most) for the matrix elements of eqs. (17), (31) and (33) and $\approx \frac{1}{8}N^4$ for the remaining matrix elements (see table 3) if only the parts needed for one pair $(I''K'')$ are kept in memory. N is the number of internal (spatial) orbitals and n the number of basis functions. The CPU time used for one CI iteration is $\propto N^8$ for the inter-

Table 3
Non-vanishing values of the symbolic expressions resulting from the matrix element evaluations of the Hamiltonian occurring in the r_{12} part of r_{12}-MR-CI

Matrix element	Expression	Value in the standard approximation [a]	Eq. [b]
$\langle {}^\mu\tilde{\phi}^{i_\mu j_\mu}_{\alpha\beta} \vert {}_\nu\tilde{\phi}^{\gamma\delta}_{k_\nu l_\nu} \rangle$	$\delta^\gamma_\alpha \delta^\delta_\beta$	$\tilde{S}^{kl}_{ij} := [\tilde{A}^{kl}_{ij} - \tilde{B}^{kl}_{ij}]^{kl}_{ij}$	(16)
$\langle {}^\mu\tilde{\phi}^{i_\mu j_\mu}_{\alpha\beta} \vert \hat{H}^{(1)} \vert {}_\nu\tilde{\phi}^{\gamma\delta}_{k_\nu l_\nu} \rangle$	$h^\gamma_\alpha \delta^\delta_\beta$	$[\frac{1}{2}(\delta^k_l \delta^l_j + \tilde{C}^{kl}_{ij}) - \tilde{E}^{kl}_{ij}]^{kl}_{ij} +$ [c] $[\tilde{F}^{kl}_{ij} + \tilde{H}^{kl}_{ij} - \tilde{I}^{kl}_{ij}]^{kl}_{ij}$	(25), (27)
	$h^{k''}_{l''} \delta^\gamma_\alpha \delta^\delta_\beta$	$h^{k''}_{l''} \tilde{S}^{kl}_{ij}$	(19)
$\langle {}^\mu\tilde{\phi}^{i_\mu j_\mu}_{\alpha\beta} \vert \hat{H}^{(2)} \vert {}_\nu\tilde{\phi}^{\gamma\delta}_{k_\nu l_\nu} \rangle$	$\bar{g}^{\gamma\delta}_{\alpha\beta}$	$2[\tilde{K}^{kl}_{ij} - r^{kl}_{ij}]^{kl}_{ij}$	(18)
	$\bar{g}^{\gamma k''}_{\alpha i''} \delta^\delta_\beta$	$[\frac{1}{2}\tilde{L}^{klk''}_{iji''} - \tilde{M}^{klk''}_{iji''} + \tilde{O}^{klk''}_{iji''}]^{kl}_{ij}$ [d]	(30)
	$\bar{g}^{k''l''}_{i''j''} \delta^\gamma_\alpha \delta^\delta_\beta$	$\bar{g}^{k''l''}_{i''j''} \tilde{S}^{kl}_{ij}$	(20)
$\langle {}^\mu\tilde{\phi}^{i_\mu j_\mu}_{\alpha\beta} \vert \hat{H}^{(1)} \vert \phi_\kappa \rangle$	$h^p_\alpha \delta^d_\beta$	$[\tilde{G}^{pd}_{ij} - \tilde{D}^{pd}_{ij} - [\hat{T}_1, r_{12}]^{pd}_{ij}]_{ij}$	(31)
$\langle {}^\mu\tilde{\phi}^{i_\mu j_\mu}_{\alpha\beta} \vert \hat{H}^{(2)} \vert \phi_\kappa \rangle$	$\bar{g}^{pq}_{\alpha\beta}$	$[\delta^p_i \delta^q_j - \tilde{J}^{pq}_{ij}]^{pq}_{ij}$	(17)
	$\bar{g}^{pk''}_{\alpha i''} \delta^d_\beta$	$[\tilde{P}^{pdk''}_{iji''} - \tilde{N}^{pdk''}_{iji''}]_{ij}$ [d]	(33)

[a] See section 4.2; for the definitions of the matrices, see section 4.3.

[b] Number of the equation in which the formula has been derived.

[c] Correction to previous expression.

[d] A term with truncation error of at most $\propto l^{-5}$ in the atomic case which has been neglected.

actions of the r_{12} determinants among themselves (eq. (14) in section 4.1), $\propto N^2 n^2$ for the interaction of the r_{12} determinants with the determinants of the traditional CI(SD) (eq. (13) in section 4.1), and $\propto N^2 n^4$ for the traditional CI(SD) part, which clearly dominates for $n \gg N$.

Since the ${}_\mu\tilde{\phi}^{ij}_{l_\mu j_\mu}$, eq. (10), are in general not pairwise orthogonal, one has to compute the metrical tensor using $\tilde{S}^{kl}_{ij}$ according to eq. (16). This non-orthogonality, however, does not complicate the calculation. In some MR cases, the Ansatz according to eq. (11) contains redundant terms which are easily deleted.

The method is presently being implemented in the Columbus-MR-CI(SD) program [16] which is a direct CI program based on the "graphical unitary group approach" (GUGA). In our implementation, the part where the CI matrix elements are computed is not changed. To compute the interaction between the r_{12} part of the Ansatz and the CSFs, the latter are decomposed into Slater determinants and the formulas needed are computed for each occurring walk.

The implementation of the present method into ACPF [10] is also straightforward: the ${}_\mu\tilde{\phi}^{ij}_{l_\mu j_\mu}$ are simply added to the correlation function Ψ_c. With r_{12}-MR-ACPF one has a powerful tool to solve the electronic Schrödinger equation approximately for medium sized chemical systems simultaneously at both the full-CI expansion limit and the basis set limit.

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