INCREASING THE STABILITY OF LINEAR r_{12}-CALCULATIONS ON THE MULTI-REFERENCE LEVEL OF THEORY*

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Abstract: We investigate the performance of two approaches to remedy the notorious instability problems on explicitly correlated multi-reference averaged coupled-pair functional (r_{12}-MR-ACPF) level of theory for the cases of HF molecule and Ne dimer. These two approaches are: i) the restriction of the unitary orbital invariance while retaining a chemically meaningful ansatz; ii) the contraction of associated r_{12}-terms to geminals using amplitudes from the first-order perturbation theory wavefunction. We observe that our modifications outperform the extremal pair approach, which is commonly used on explicitly correlated coupled-cluster (CC-R12) level of theory and conclude that using geminals, which are e.g. taken from the first-order Møller-Plesset perturbation theory wavefunction instead, might be a better choice.

1. INTRODUCTION

The r_{12}-method of Kutzelnigg and co-workers [1, 2] provides a unique way to include terms that are linear in the interelectronic distances, $r_{12} := |\mathbf{r_1} - \mathbf{r_2}|$, into the ansatz for the wavefunction without having to deal with integrals over the coordinates of more than two electrons. In our recent multi-reference (MR) formulation [3-5], these linear r_{12}-terms have the form

$$\widetilde{\phi}_{i'j'}^{ij} := \sum_{\kappa < \lambda} \overline{r}_{\kappa\lambda}^{ij} \phi_{i'j'}^{\kappa\lambda} - \sum_{p<q} \overline{r}_{pq}^{ij} \phi_{i'j'}^{pq} \qquad (1)$$

$\overline{r}_{\kappa\lambda}^{ij}$ and $\overline{r}_{pq}^{ij}$ are antisymmetrized 2-electron integrals over r_{12}, and $\phi_{i'j'}^{\kappa\lambda}$ and $\phi_{i'j'}^{pq}$ denote Slater determinants, usually taken from the smallest meaningful subset of the references. In these two types of Slater determinants, the internal orbitals φ_i, and φ_j are substituted by arbitrary orbitals taken from the given set (indices p and q) or from a (hypothetical) complete set (indices $\varkappa$ and λ). Off diagonal terms, i.e. where $\{i, j\} \neq \{i', j'\}$, insure that the wavefunction is invariant with respect to unitary transformations among the internal orbitals [6], These linear r_{12}-tenns, Eq. (1), take care of the cusps [7, 8] in the wavefunction at regions, where pairs of

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*Dedicated to the memory of Professor Jacek Rychlewski

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electrons with opposite spin (i.e. singlets) come close to each other. Together with a moderate configuration interaction (CI) expansion, these r_{12}-terms indeed allow to solve the electronic Schrödinger equation close to the basis set limit, which, *in praxi,* would not be possible with Slater determinants alone. Please note that by their definition, the linear r_{12}-terms, Eq. (1), are orthogonal to the Slater determinants, $\phi_{i',j'}^{pq}$ of the CI expansion. The Hamiltonian and overlap matrix elements are evaluated by means of the so-called standard approximation [2], which is essentially the resolution of the (one-electron) identity (RI),

$$\sum_p \left| \varphi_p(1) \right\rangle \left\langle \varphi_p(1) \right| \approx 1 \tag{2}$$

that is approximated in the given basis set.

Meanwhile, the r_{12}-method has been combined with the most common approximations to full-CI (see [5, 9-12] for details). On closed-shell level of theory, these methods include Møller-Plesset perturbation theory (MPPT) [13] in second (MP2) [14, 15] and higher orders, and coupled-cluster singles and doubles (CCSD) with various estimations of the triples contribution, e.g. the most common CCSD(T) approximation [9, 16, 17]. Moreover, the r_{12}-method has been extended [3, 4, 18] to general open-shell and multiple-reference CI with singles and doubles [MR-CI(SD)] and the *a priori* size extensivity corrected MR averaged coupled-pair functional (MR-ACPF) [19, 20]. Very recently, an open-shell CC theory with linear r_{12}-terms has become available as well [21, 22].

Unfortunately, when the wavefunction has to be determined iteratively, inaccuracies in the computed matrix elements often give rise to serious instabilities [9]. On the r_{12}-MR-CI and -ACPF levels of theory, these instabilities may lead to spurious solutions which, in extreme cases, can lie well below the lowest eigenvalue of the Schrödinger equation. In our software [23], the Hessian matrix $\partial^2 F/\partial c_i \partial c_j$, of the energy functional, F, (i.e. of CI or ACPF type) that is to be stationarized, is computed in the subset of the trial vectors, which have been iterated in the spirit of Davidson's [19, 24] method. The n-th excited state (with $n = 0$ being the ground state) should give rise to at most n non-positive eigenvalues of the Hessian. When this condition is not fulfilled, the accuracy of the Hamiltonian matrix elements is questionable and the resulting instabilities can make it difficult or even impossible to obtain a converged solution.

Beside the approximate resolution of the identity, Eq. (2), as an obvious source for inaccuracies leading to instabilities, there are two other main sources. First, there is the 4-index transformation of the 2-electron integrals from the atomic orbital (AO) to the molecular orbital (MO) basis. The maximum number of cancelled figures in the floating point result in these transformations can be roughly estimated as $2 \log_{10} C$ with $C := \max|\{\lambda_i\}|/\min|\{\lambda_i\}|$ being the condition number as computed from the set of eigenvalues, $\{\lambda_i\}$, of the overlap matrix of the AO basis functions. Thus, the computations become inaccurate in IEEE double precision (8-byte) format as the above number approaches $\log_{10} 2^{52} \cong 15.7$, the number of significant

digits in this format. The most difficult MOs to transform are those with a large number of nodes. In traditional CI calculations, these MOs are usually of lesser importance because of their rather high orbital energies. However, this argument does not apply to the r_{12}-method. Secondly, as the basis set approaches completeness, the metric between the r_{12}-terms, which, as we recall, is block-diagonal [3, 4], becomes near-singular. The associated condition number of the latter metric, however, usually does not become large enough to fully explain the occurring instabilities. This is especially true when the r_{12}-terms are normalized to one, as it is the case in our software [23]. We conclude this discussion by noting that very recently, Noga *et al.* [22, 25, 26] showed that with basis sets that are carefully optimized for the r_{12}-method, such instabilities can be significantly reduced or even avoided.

In order to handle the instabilities discussed above, Kutzelnigg and coworkers [9, 27-29] recently proposed reducing the (in leading order) $\frac{1}{8}N^4$ r_{12}-terms in the orbital invariant ansatz [6], $\widetilde{\phi}_{i'j'}^{ij}$, to a more physical number of $\frac{1}{2}N^2$ terms, $\widetilde{\phi}_{\mu}^{\mu}$, by using so-called extremal (orbital) pairs,

$$\psi_{\mu}(1,2) := \sum_{i<j} b_{ij}^{\mu}\left[\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)\right] \tag{3}$$

These extremal pairs, $\psi_{\mu}(1, 2)$, are computed by requiring that they make the expectation value of a certain totally symmetric Hermitean 2-electron operator, $\hat{\Omega}(1, 2)$, extremal (i.e. either minimal or maximal), which leads to the eigenvalue equation $\hat{\Omega}\psi_{\mu} = \lambda_{\mu}\psi_{\mu}$. The authors of Ref. [9] recommend obtaining the extremal pairs by diagonalizing the matrix whose trace gives the r_{12}-contribution of MP2-R12 in approximation A. We then have

$$\widetilde{\phi}_{\mu}^{\mu} := \sum_{\substack{i<j \\ i'<j'}} b_{\mu}^{i'j'} b_{ij}^{\mu} \widetilde{\phi}_{i'j'}^{ij} \tag{4}$$

as linear r_{12}-terms in the ansatz of the wavefunction.

2. MODIFIED r_{12}-ANSÄTZE

2.1. Restricted unitary invariance

The extremal pair approach, as mentioned in the previous section, is applicable to the MR case as well, although this leads to a rather complicated formalism. A simpler way to reduce the number of independent r_{12}-terms is to restrict the invariance of the ansatz with respect to unitary transformations of the orbitals to disjunct subsets ("shells") [5, 18],

$$A_i := \left\{\varphi_{i_1}, \varphi_{i_2}, \dots \varphi_{i_m}\right\} \tag{5}$$

such that the union gives the original set of n_{int} internal orbitals.

$$\left\{ \varphi_1, \varphi_2, \ldots \varphi_{n_{int}} \right\} = A_1 \cup A_2 \cup \ldots \tag{6}$$

These subsets are conveniently chosen in a way that the respective orbitals do not mix when the geometry of the chemical system under investigation is changed. E.g., in the case of a diatomic, one may have one subset of core and another subset of valence orbitals. Moreover, it is possible to further divide these sets. The finest division possible seems to be putting a bonding and the corresponding antibonding orbital into one subset, and each non-bonding orbital into a separate subset as well. This method (which in our software [23] is activated by the keyword r12shell) is implemented in the following way: let the two internal orbitals $\varphi_{i'} \in A_k$ and $\varphi_{j'} \in A_l$ give rise to r_{12}-terms, $\widetilde{\phi}_{i'j'}^{ij}$, Eq. (1), then only those terms will be kept for which $\left\{ \varphi_i, \varphi_j \right\} = A_k \cup A_l$ holds.

2.2. Geminals

For a diatomic, it will not pose any specific problem to restrict the unitary invariance such that the quality of the wavefunction is sufficiently independent from the geometry. However, in a polyatomic molecule, in general, the atomic orbitals mix in a more complicated way when forming molecular orbitals. Thus, it may become difficult to find invariant subsets that are small enough to sufficiently reduce the number of linear r_{12}-terms, but that are still large enough so that the different subsets essentially do not mix. In such cases, it may be advantageous to do an internal contraction of the r_{12}-terms to geminals, [5, 30],

$$\widetilde{\phi}_{i'j'} := \sum_{i<j} c_{ij}^{i'j'} \widetilde{\phi}_{i'j'}^{ij} \tag{7}$$

E.g. in the single reference case, this reduces the number of r_{12}-terms from $\frac{1}{8}N^4$ to $\frac{1}{2}N^2$ The contraction coefficients, $c_{ij}^{i'j'}$, are taken from the first-order Epstein-Nesbet [31, 32] perturbation theory (ENPT) wavefunction,

$$\Psi_c^{(1)} = \frac{\hat{Q}}{E_0 - \hat{H}_0} \left(\hat{H} - E_0 \right) \Psi_0, \quad \hat{Q} := 1 - \left| \Psi_0 \right\rangle\left\langle \Psi_0 \right| \tag{8}$$

which, in our program code [23], is used as start wavefunction. Ψ_0 is the zeroth-order wavefunction consisting of the references, and E_0 is the corresponding expectation value of the Hamiltonian, $\hat{H}$. It is even possible (and meaningful) to contract all r_{12}-terms together,

$$\widetilde{\phi} := \sum_{i'<j'} \widetilde{\phi}_{i'j'} = \sum_{\substack{i<j \\ i'<j'}} c_{ij}^{i'j'} \widetilde{\phi}_{i'j'}^{ij} \tag{9}$$

In our software [23], the geminal, Eq. (7), and the contracted geminal options, Eq. (9), are invoked by setting the variable r12fix in the Fortran namelist input (file ciudgin) of program ciudg to 1 or 2, respectively.

3. DETAILS OF CALCULATIONS

3.1. General

Although these two different approaches, i.e. restricted unitary invariance and the usage of geminals, Eq. (7) and (9), have already been described in the literature [5, 18, 30], their performance has not yet been investigated in detail. To this end, we study these two approaches on two systems that cover the extreme cases of chemical interactions, i.e. HF with its strong polar covalent bond and Ne_2, which is bound by the weak dispersion forces only. All calculations were performed with the AMICA suite of programs [23], which is based on the COLUMBUS [33] package.

We compare these modifications to the original unitary invariant r_{12}-ansatz using different basis sets, reference spaces, and functional (i.e. ACPF [19] and ACPF-2 [20]). The orbitals are optimized in MCSCF calculations and the redundancies with respect to the orbital rotations are resolved by diagonalizing the Q matrix [34], In the r_{12}-MR-ACPF and -ACPF-2 calculations, all electrons are correlated and the energies are sharply converged to 10^{-10} E_h. Since the r_{12}-MR-AGPF methods are, in general, only approximately size extensive, we compute the interaction energy, $V(R)$, of a dimer AB (consisting of atoms A and B) with an interatomic distance R with the supermolecule approach and include the usual counterpoise corrections for the basis set superposition error (BSSE) of the Boys-Bernardi [35] type,

$$V(R) = E_{AB}(R) - E_{AB}(\infty) + [E_A - E_{AQ}(R)] + [E_B - E_{QB}(R)].$$ (10)

The indices AQ and QB denote atoms A and B with a "ghost basis set" Q. "Infinite" separation is in fact realized by an interatomic distance of 100 a_0. Too large interatomic separations are not practical because they may give rise to a cancellation of valid digits when handling, e.g., the 2-electron integrals over r_{12}. The molecular constants R_e and D_e are obtained by interpolating the energies at three interatomic distances using a polynomial that is quadratic in $1/R$,

$$V(R) = \sum_{i=0}^{2} \frac{a_i}{R^i}.$$ (11)

For HF, we choose the interatomic distances 1.7228, 1.7328, and 1.7428 a_0. For the single reference treatment of Ne_2, we take the values 3.1, 3.125 and 3.15 Å. And finally for the MR calculations of Ne_2, we use $R = 3.075$, 3.1, and 3.125 Å.

3.2. Basis sets

For fluorine, we take Partridge's [36] 18s13p set and augment it by one diffuse s and p using logarithmical extrapolation [5], i.e. $\eta_{n+1} = \eta_n^2/\eta_{n-1}$. Then we add the dfgh-part of the aug-cc-pV5Z basis of Dunning and co-workers [37]. Finally, we augment two tight d and one

tight f that have been logarithmically extrapolated. The resulting basis set is of $[19s14p7d5f3g2h]$ quality. For hydrogen, we take the s-functions of the uncontracted aug-cc-pV6Z set [38] and combine them with the pdfg-functions of aug-cc-pV5Z [38], We finally add one logarithmically extrapolated tight p-function. This basis set is of $[11s6p4d3f2g]$ quality. For neon, we take the [set from Ref. [39].

For the treatment of the HF molecule, we also truncate the *spdfgh/spdfg* set by successively omitting the functions with the respectively highest *l*-quantum numbers, resulting in *spdfg/spdf* and *spdf/spd* sets with 268, 228, and 180 basis functions. We recall that for the ground states of first-row elements, the basis set formally has to be saturated up to $L = 3$, i.e. including f-functions [40]. Moreover, in the case of Ne_2 it turns out that g-functions are mandatory to obtain physically meaningful interaction energies since with the basis set truncated to *spdf* e.g. with r_{12}-ACPF, we obtain a D_e value of 160 μE_h. This is 38% larger than the basis set limit [39] and therefore, we confine our studies on Ne_2 to basis sets of *spdfgh* and *spdfg* quality with 376 and 332 functions, respectively.

3.3. Restricted unitary invariant ansatze

The Hartree-Fock wavefunction of the F-atom consists of five orbitals, i.e. 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ and the one of the H-atom, only of the 1s orbital. In the HF molecule, these atomic orbitals give rise to six molecular orbitals, i.e. $1\sigma(1s_F)$, $2\sigma(2s_F)$, 3σ(H-F bond), $1\pi_x$ and $1\pi_y$ (non-bonded electron pairs), and 4σ (anti-bonding electron pair). We choose four different

Table 1. Orbital subsets used in the restricted unitary invariant r_{12}-ansatze for the F, Ne, HF, and Ne_2 calculations

Ansatz	F/Ne	HF[a]	Ne_2
A	$\{1s\}, \{2s, 2p_x, 2p_y, 2p_z\}$	$\{1\sigma\}, \{2\sigma, 3\sigma, 1\pi_x, 1\pi_y, 4\sigma\}$	$\{1\sigma_g, 1\sigma_u\}, \{2\sigma_g, 2\sigma_u, 3\sigma_g, 1\pi_u^x, 1\pi_u^y, 1\pi_g^x, 1\pi_g^y, 3\sigma_u\}$
B	$\{1s, 2s\}, \{2p_x, 2p_y, 2p_z\}$	$\{1\sigma, 2\sigma\}, \{3\sigma, 1\pi_x, 1\pi_y, 4\sigma\}$	$\{1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u\}, \{3\sigma_g, 1\pi_u^x, 1\pi_u^y, 1\pi_g^x, 1\pi_g^y, 3\sigma_u\}$
C	$\{1s\}, \{2s\}, \{2p_x, 2p_y, 2p_z\}$	$\{1\sigma\}, \{2\sigma\} \{3\sigma, 1\pi_x, 1\pi_y, 4\sigma\}$	$\{1\sigma_g, 1\sigma_u\}, \{2\sigma_g, 2\sigma_u\}, \{3\sigma_g, 1\pi_u^x, 1\pi_u^y, 1\pi_g^x, 1\pi_g^y, 3\sigma_u\}$
D	$\{1s\}, \{2s\}, \{2p_x\}, \{2p_y\}, \{2p_z\}$	$\{1\sigma\}, \{2\sigma\}, \{1\pi_x\}, \{1\pi_y\}, \{3\sigma, 4\sigma\}$	$\{1\sigma_g, 1\sigma_u\}, \{2\sigma_g, 2\sigma_u\}, \{1\pi_u^x, 1\pi_g^x\}, \{1\pi_u^y, 1\pi_g^y\}, \{3\sigma_g, 3\sigma_u\}$

[a] Shown are orbital subsets for the multi-reference calculations; in the single-reference case, the 4σ orbital is omitted.

orbital subspaces for the restricted invariant ansatz (see Table 1). We note in passing that it is important that the orbital space partitioning of the dimer corresponds to an equivalent partitioning of the (single) heavy atoms (F and Ne). To this end, for HF, we separate the inner core orbitals ($1s$, respectively 1σ) from the remaining orbitals in ansatz A. In ansatz B, we also put the $2s$, respectively 2σ orbital into the core. In ansatz C we have two different sets of core orbitals and finally in ansatz D, all orbitals with the exception of the bonding/anti-bonding $\{3\sigma, 4\sigma\}$ pair, are individual. We follow a similar strategy for Ne_2 (see Table 1).

3.4. Reference spaces

For the HF molecule, our smallest MR space is a complete active space (CAS) consisting of only the bonding (3σ) and the corresponding antibonding orbital (4σ). In C_{2v} symmetry, this space gives rise to 3 references and we therefore denote it CAS-3. A larger reference space (CAS-5) is obtained by also including the nonbonding electron pairs in the form of the two nonbonding ($1\pi_x$ and $1\pi_y$) orbitals. Finally, we construct a restricted active space (RAS-70) from the CAS-5 by allowing for all single and double excitations from valence orbitals into orbitals arising from the fluorine $3p$.

For Ne_2, we use a single-reference ansatz and the RAS-109 of Ref. [39], which is constructed by allowing for all single and double excitations from $2p$ to $3p$ orbitals.

4. RESULTS AND DISCUSSION

Table 2 shows the number of variational parameters within the respective r_{12}-ansatz. While reducing this number has no significant (if any) influence on the computational costs of a single iteration, it can be expected that the instabilities attenuate or even vanish with a decreasing number of r_{12}-terms. Tables 3 to 7 show the change of the total energy at R_e, as well as of the spectroscopic constants D_e and R_e on r_{12}-MR-ACPF-2 level of theory for the different r_{12}-ansätze and reference spaces. The notation of the modified ansätze is as described in Table 1 and Section 2.2, respectively. Using r_{12}-MR-ACPF instead of ACPF-2 leads to about 1 mE_h and 0.1 mE_h lower total energies for HF and Ne_2 (see Tables 3 to 7), but the errors due to the various modified ansätze are virtually unchanged.

Table 2. The number of variational parameters associated with the r_{12}-terms

Ansatz	HF				Ne	Ne_2
	F	Single reference	CAS-3	CAS-5/RAS-70		
Invariant	196	141	1194	1980	141	2194
r12inv, A	98	129	599	986	129	1098
r12inv, B	96	117	486	820	117	978
r12inv, C	56	71	302	496	71	590
r12inv, D	52	65	260	482	65	530
r12fix=1	36	45	145	226	45	190
r12fix=2	1	1	1	1	1	1

For the HF molecule (see Tables 3 to 5) the changes in the spectroscopic constants due to the various modifications of the r_{12}-ansatz, in all combinations of basis sets and reference spaces, are insignificant when compared to the errors of our calculations in the *spdfgh/spdfg* basis and RAS-70. Compared to the experimental values [41, 42], the errors of this latter calculation (see Table 5) are -0.02 ± 0.02 kcal/mol for D_e (when corrected by -0.58 kcal/mol for spin-orbit coupling and scalar relativistic effects [43]) and -0.0002 Å for R_e.

Table 3. The total energy, D_e, and R_e of the HF molecule obtained with r_{12}-MR-ACPF-2 in the CAS-3 reference space and the *spdf/spd* basis[a,b]

	$E(R_e)/E_h$	D_e/kcal mol^{-1}	R_e /Å
Invariant	−100.452048	140.9384	0.916209
Invariant (ACPF)	−0.000886	0.2906	0.000617
r12inv, A	0.000030	0.0011	−0.000013
r12inv, B	0.000048	−0.0098	−0.000010
r12inv, C	0.000061	−0.0085	−0.000021
r12inv, D	0.000081	−0.0087	−0.000023
r12fix=1	0.000025	−0.0100	−0.000016
r12fix=2	0.000050	−0.0116	−0.000029

[a] Given are the differences *w/r/t* the invariant ACPF-2 values.

[b] The corresponding values for ACPF differ by at most 3 units in the last digit.

In the case of Ne_2 (see Tables 6 and 7), however, the changes in D_e and R_e for the restricted invariant ansätze B to D are of similar size as the estimated errors of our recent treatment [39], i.e. ± 1 μE_h for D_e and ± 0.002 Å for R_e. The changes in the restricted unitary ansatz A and the geminal approach are somewhat smaller, especially in the largest *spdfgh* basis set, but they are still too large to allow for an accurate treatment.

Next we investigate the size extensivity error,

$$\Delta E_{\text{ext}} = E_{Ne_2}(\infty) - 2E_{Ne} \tag{12}$$

of our modified r_{12}-ACPF ansatze. We recall that ACPF [19] and r_{12}-ACPF [3] are accurately size extensive for equivalent closed-shell subsystems and thus also for non-interacting Ne atoms. ACPF-2 [20] exhibits slight deviations from size extensivity because of the dampening of the singles contribution. To this end, we compute the dissociation energy using the regular formula that is valid for size extensive methods,

$$D_e := 2E_{NeQ}(R_e) - E_{Ne_2}(R_e) \tag{13}$$

and use the supermolecule approach [c.f. Eq. (10)] as well,

$$D_e^! := D_e + \Delta E_{\text{ext}} = E_{Ne_2}(\infty) - E_{Ne_2}(R_e) + 2[E_{NeQ}(R_e) - E_{Ne}] \tag{14}$$

Both formulas contain counterpoise corrections for the BSSE (see Sect. 3.1). We observe a negligible size extensivity error of r_{12}-ACPF of 0.02 μE_h (see Table 8), which can be attributed to the numerical problems that have already been discussed in Sect. 3.1. We find all restricted unitary invariant ansätze (see Sect. 2.1) to be accurately size extensive as well. The geminal approaches, Eq. (7) and especially Eq. (9), however, give rise to substantial size extensivity errors, which apparently can only to some extent be corrected by the supermolecular approach, Eq. (14). Indeed, the ENPT-1 wavefunction [c.f. Eq. (8)] is not separable [44] and the size extensivity error [c.f. Eq. (12)] of, e.g., the ENPT-1 energy,

Table 4. The total energy, D_e, and R_e of the HF molecule obtained with r_{12}-MR-ACPF-2 and the *spdfg/spdfbasis*[a,b]

Ansatz	CAS-3			CAS-5			RAS-70		
	$E(R_e)/E_h$	D_e /kcal mol^{-1}	R_e /Å	$E(R_e)/E_h$	D_e /kcal mol^{-1}	R_e /Å	$E(R_e)/E_h$	D_e /kcal mol^{-1}	R_e /Å
Invariant	100.453423	141.1728	0.916147	−100.453591	141.1429	0.916259	−100.457425	141.6737	0.916637
Invariant (ACPF)	−0.000887	0.2915	0.000618	−0.000875	0.2782	0.000609	−0.000748	0.0675	0.000139
r12inv, A	0.000022	−0.0009	−0.000003	0.000022	−0.0010	−0.000003	0.000023	−0.0018	−0.000006
r12inv, B	0.000027	−0.0069	−0.000004	0.000028	−0.0074	−0.000004	0.000034	−0.0104	−0.000030
r12inv, C	0.000035	−0.0063	−0.000005	0.000036	−0.0068	−0.000005	0.000041	−0.0096	−0.000031
r12inv, D	0.000041	−0.0075	−0.000005	0.000040	−0.0085	−0.000003	0.000046	−0.0116	−0.000032
r12fix=1	0.000013	−0.0056	−0.000005	0.000014	−0.0051	−0.000005	0.000009	−0.0027	−0.000001
r12fix=2	0.000051	−0.0067	−0.000012	0.000051	−0.0064	−0.000013	0.000033	−0.0012	−0.000003

[a] Given are the differences *w/r/t* the invariant ACPF-2 values.

[b] The corresponding values for ACPF differ by at most 1 unit in the last digit.

Table 5. The total energy, D_e, and R_e of the HF molecule obtained with r_{12}-MR-ACPF-2 and the *spdfgh/spdfg* basis [a,b]

Ansatz	CAS-5			RAS-70		
	$E(R_e)/E_h$	D_e /kcal mol^{-1}	R_e /Å	$E(R_e)/E_h$	D_e /kcal mol^{-1}	R_e /Å
Invariant	−100.453853	141.1925	0.916238	−100.457737	141.7304	0.916620
Invariant (ACPF)	−0.000875	0.2784	0.000608	−0.000750	0.0677	0.000139
r12inv, A	0.000023	−0.0011	−0.000002	0.000024	−0.0015	−0.000006
r12inv, B	0.000028	−0.0067	−0.000001	0.000033	−0.0090	−0.000021
r12inv, C	0.000035	−0.0060	−0.000002	0.000040	−0.0082	−0.000023
r12inv, D	0.000038	−0.0073	−0.000001	0.000043	−0.0097	−0.000022
r12fix=1	0.000011	−0.0042	−0.000003	0.000007	−0.0023	0.000001
r12fix=2	0.000052	−0.0057	−0.000009	0.000035	−0.0013	−0.000002

[a] Given are the differences *w/r/t* the invariant ACPF-2 values.

[b] The corresponding values for ACPF differ by at most 2 units in the last digit.

Table 6. The total energy, D_e, and R_e. of Ne_2 obtained with r_{12}-MR-ACPF-2 and the *spdfg* basis[a,b]

Ansatz	Single reference			RAS-109		
	$E(R_e)/E_h$	$D_e/\mu E_h$	$R_e/Å$	$E(R_e)/E_h$	$D_e/\mu E_h$	$R_e/Å$
Invariant	−257.862245	117.41	3.1152	−257.869415	127.10	3.1002
Invariant (ACPF)	−0.000085	1.02	−0.0015	−0.000817	1.40	−0.0031
r12inv, A	0.000052	0.27	−0.0003	0.000052	0.28	−0.0003
r12inv, B	0.000041	−1.20	0.0032	0.000046	−1.47	0.0041
r12inv, C	0.000071	−1.19	0.0033	0.000074	−1.37	0.0039
r12inv, D	0.000098	−1.20	0.0034	0.000099	−1.28	0.0036
r12fix=1	0.000015	−0.78	0.0018	0.000013	−0.69	0.0014
r12fix=2	0.000051	−3.79	0.0029	0.000033	−2.64	0.0020

[a] Given are the differences *w/r/t* the invariant ACPF-2 values.

[b] The corresponding values for ACPF differ by at most 1 unit in the last digit.

Table 7. The total energy, D_e, and R_e of Ne_2 obtained with (single reference) r_{12}-ACPF-2 and the *spdfgh* basis[a,b]

Ansatz	$E(R_e)/E_h$	$D_e/\mu E_h$	$R_e/Å$
Invariant	−257.862779	116.04	3.1205
Invariant (ACPF)	−0.000084	1.02	−0.0015
r12inv, A	0.000041	0.24	−0.0003
r12inv, B	0.000033	−0.71	0.0008
r12inv, C	0.000059	−0.70	0.0009
r12inv, D	0.000081	−0.71	0.0009
r12fix=1	0.000011	−0.25	0.0003
r12fix=2	0.000046	−2.60	0.0011

[a] Given are the differences *w/r/t* the invariant ACPF-2 values.

[b] The corresponding values for ACPF differ by at most 1 unit in the last digit.

Table 8. The dissociation energy[a] of Ne_2 computed with r_{12}-ACPF using the regular (D_e), and the supermolecular approach (D_e') and the associated size extensivity error (ΔE_{ext})[a]

Ansatz	D_e^b	$D_e'^b$	ΔE_{ext}
Invariant	118.31	118.34	0.02
r12inv, A	0.28	0.28	0.02
r12inv, B	−1.26	−1.26	0.02
r12inv, C	−1.25	−1.25	0.02
r12inv, D	−1.26	−1.26	0.02
r12fix=1	−1.97	−0.81	1.19
r12fix=2	7.85	−3.85	−11.67

[a] $R = 3.1$ Å; *spdfg* basis set; all energies in μE_h; see Eq. (12) to (14) in text.

[b] Given are the differences *w/r/t* the invariant r_{12}-ACPF values.

$$E_c^{(1)} := \left\langle \Psi_0 \left| \hat{H} \right| \Psi_c^{(1)} \right\rangle \tag{15}$$

is as large as 81 mE_h. This, in fact, explains the poor performance of the geminal ansätze in the case of Ne_2, as was discussed before (c.f. Table 6). However, in the case of a stronger interaction, as is e.g. the case for HF, a size extensivity error of a few μE_h is negligible and the geminal approaches, Eq. (7) and Eq. (9) can be expected to give reliable results.

Table 9. The errors of the total energies of HF molecule and of Ne atom (in μE_h) calculated with r_{12}-ACPF-2[a] using the modified ansätze and with CCSD-R12 using extremal pairs with respect to the corresponding invariant ansatz

Ansatz	HF[b]	Ne			
		spdf[c]	*spdfg*[e]	*spdfgh*[e]	*spdfghi*[e]
r12inv, A[d]	58	40	17	13	13
r12inv, B[d]	57	38	16	12	12
r12inv, C[d]	107	62	27	21	19
r12inv, D[d]	125	91	34	23	20
r12fix=1[d]	14	13	6	3	2
r12fix=2[d]	46	33	40	43	41
CCSD–R12[e]	203	104	47	38	36

[a] The corresponding r_{12}-ACPF values differ by not more than $1 \mu E_h$.

[b] $[15s9p6d5f]/[6s3p2d]$ set of Ref. [28].

[c] Subsets of $[17s11p8d7f6g5h4i]$ set of Ref. [28].

[d] r_{12}-ACPF-2 with restricted unitary invariant (r12inv, A through D) and geminal ansatz (r12fix=1 and r12fix=2), this work.

[e] From Tables 3 and 6 of Ref. [28].

In Table 9 we finally compare the performance of our modified r_{12}-ACPF-2 ansätze with the performance of CCSD-R12 using the extremal pair approach [28], This comparison is valid because (single reference) ACPF-2 [19, 20] can be regarded as an approximation to CCSD. We note that for the cases of Table 9, the errors of CCSD(T) due to the extremal pair approach are virtually the same as for CCSD (i.e. the deviations are not larger than 3 μE_h [28]). The errors of the restricted unitary invariance approach (see Sect. 2.1) are consistently smaller than are the errors of the extremal pair approach. Somewhat surprising, this is also the case for the choice of r12inv, D, which is rather close to the original non-invariant ansatz [2]. In the single reference case, the geminal approach, Eq. (7), gives rise to the same number of terms as the extremal pairs approach, which are equal to the number of electron pairs. Despite this fact, our geminal approach dramatically outperforms the extremal pair method by a factor of 8 to 18, i.e. by about an order of magnitude. Indeed, the $\frac{1}{2}N^2$ terms of the extremal pair approach are constructed from $\frac{1}{8}N^4$ r_{12}-terms using only $\frac{1}{2}N^2$ coefficients, b_{ij}^μ see Eq. (4). The same number of terms in the geminal method, Eq. (7), however, is generated by as much as $\frac{1}{8}N^4$ coefficients, $c_{ij}^{i'j'}$. Even when all r_{12}-terms are contracted together to one

term (keyword r12fix = 2), in small basis sets, this method betters the extremal pair approach by a factor of 3 and in large basis sets, the error is virtually the same. Thus, we conclude that the extremal pair approach of Kutzelnigg and co-workers [9, 27-29] is not an optimal choice. Our results suggest that for CC-R12 theory, it might be better to take geminals, Eq. (7), from, e.g., the first-order MPPT wavefunction.

We summarize by noting that in the case of a (strong) covalent interaction, surprisingly inflexible r_{12}-ansätze, where the unitary invariance is restricted to pairs of the bonding and the corresponding antibonding orbital, or where all r_{12}-terms are contracted together to form geminals, do not influence the accuracy of the calculation. In the case of a (weak) dispersion interaction, however, even rather subtle approximations as removing the invariance of the ansatz with respect to mixing of core and valence electrons or using geminals significantly deteriorates the accuracy. Thus one may take the strength of the treated chemical interaction as guidance to decide how to modify the r_{12}-MR ansatz in order to reduce the number of r_{12}-terms to cope with existing numerical instabilities.

Acknowledgements

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