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Effective Algorithms of the RI Approximation for the CIS Method: an Example of Application of the High-Memory Strategy in the *Ab Initio* Calculations

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Two variants of the CIS methods with the RI approximation have been implemented. Both methods employ the high-memory strategy: the first, RI-CIS(1), is based on the full storage of the decomposed electronic repulsion integrals (ERI) tensor and CIS Hamiltonian, while the second, RI-CIS(2), stores only the decomposed ERI tensor. Both variants of the RI-CIS were tested for parallelism, performance, and precision. The results are compared with the default CIS method and RIJCOSX approximation. The considered methods demonstrate higher performance compared to their analogs and higher precision compared to the RIJCOSX approximation. Even the worse scaling of the RI methods did not lead to the lower performance in the conducted test calculations. The reported algorithms show that the performance of the quantum chemistry calculations is limited not only by the CPU power but also by the availability of RAM. The large volume of available memory can significantly increase the speed of the calculation by employing more effective but memory-consuming algorithms.

Keywords: Configuration interaction, resolution of identity, ab initio, electronic repulsion integrals, Davidson diagonalization.

Introduction

Configuration interaction (CI) methods [1] are key approaches for the electronic structure calculations, especially in the cases of strong electronic correlation. These methods are used for calculation of the excited states in the modeling of photochemical reactions and calculations of the electronic spectra. However, the computational costs of these methods rapidly grow with the increase of the excitation number and active space size. This fact limits the applicability of the CI methods for the large molecular systems without any additional approximations.

Configuration interaction with single excitations (CIS) is the simplest method within the framework of CI theory. It can be considered as the extension of the Hartree—Fock methods for the description of the excited states by taking the single electronic transition into consideration.

The CIS method does not take into account double and higher excitations and, thus, gives lower precision for systems with a strong electronic correlation and a high contribution of biradical configurations. However, it is a helpful tool to achieve the preliminary information for the calculations with more complicated methods, especially in case of large molecules. The TD-DFT method [2] uses similar basics and has the same limitations but can achieve higher precision if the proper exchange-correlation functional is chosen. Both of these methods are useful for the simulations of large systems due to their numerical efficiency (calculation time grows only $O(N^4)$). However, the performance of these methods can be further increased if approximations such as Cholesky Decomposition (CD) [3] and Resolution of Identity (RI) [4] are used. Currently, the attention of quantum chemical software developers is focused on the more complicated advanced methods, while the simpler ones are undeservedly forgotten because their optimization seems unnecessary. For instance, the implementation of the restricted Hartree—Fock (RHF) method with the RI approximation was not optimal in the frequently used quantum chemical packages until recently [5], despite the theoretical background being well-known [6]. The realization of CIS in

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the ORCA package [7, 8] contains the RI only for the Coulomb contribution (RIJ), while the exchange term can be simplified only with the chain of spheres (COSX) [9] approximation. The previous successful realization of the RI-RHF method encouraged us to perform a similar job for other basic quantum chemical methods, such as CIS.

The most time-consuming part of the CIS calculations, like that of most other quantum chemical methods, is the calculation of electronic repulsion integrals (ERI). The obvious way is to calculate them, store in memory and use in the iterative calculation cycles. However, the total amount of ERIs is N_{AO}^4 (where N_{AO} is the number of atomic orbitals), which is too high to be stored for any practically valuable calculation. The use of the symmetry of the ERI tensor and different techniques that avoid storing negligibly small ERIs do not solve this problem. Thus, the direct method, which is based on the recalculation of ERI at each iteration, was proposed [10]. However, this approach leads to a significant increase in calculation time due to the multiple recalculations of ERIs.

The approximations based on the ERI tensor decomposition, such as CD [3] and RI [4], can reduce both computational cost and memory requirement of the calculation. They are successfully applied to boost methods such as RHF [5], MP2 [11], CASPT2 [12], CCSD [13], and many others. The possibility to store the decomposed ERI tensor helps to avoid multiple recalculations of the most time-consuming parts of the calculation. It should be noted that memory required for storing the CIS Hamiltonian is comparable to that required for the decomposed ERI tensor. Thus, the use of modern computers makes the application of high-memory algorithms possible, and no direct method with multiple recalculations of data is really needed in the present time.

Two variants of the CIS method with the RI approximation are presented in the article:

- the first one with storing both RI-ERI tensor and CIS Hamiltonian in RAM;
- the second one with storing RI-ERI tensor and without storing CIS Hamiltonian in RAM.

The paper is organized as follows: first, the basic CIS theory and the modifications needed for the RI approximation are discussed; then, the testing objects are presented, and the details of the calculations are provided; finally, the results of the benchmark calculations and the comparison of different algorithms are shown.

1. Theory

1.1. CIS Method

The CIS wavefunction is constructed as a linear combination of the configuration state functions (CSF) formed as all the possible single excitations of the ground state RHF wavefunction:

$$|\Psi_{\mathrm{CIS}}\rangle = \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{virt}} C_i^a |\Phi_i^a\rangle = \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{virt}} C_i^a \cdot \frac{1}{\sqrt{2}} (a_{a\alpha}^{\dagger} a_{i\alpha} + a_{a\beta}^{\dagger} a_{i\beta}) |\Phi_0\rangle, \tag{1}$$

where $a_{a\alpha}^{\dagger}$ and $a_{i\alpha}$ are the creation and annihilation operators corresponding to the addition of the electron with α spin to the a-th virtual orbital and the removal of the electron with α spin from the i-th core orbital. Hereinafter, indices i, j, k, and l are used for the core subspace; a and b for the virtual; and p, q, etc. for any of them.

The coefficients C_i^a of the decomposition of the CI wavefunction $|\Psi_{\mathrm{CIS}}\rangle$ by the CSFs $|\Phi_i^a\rangle$ can be found by solving the linear variational problem – CI Hamiltonian diagonalization. The

Hamiltonian matrix elements can be found as:

$$H_{ijab} = \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = \begin{cases} 2(ai|bj) - (ab|ij), & a \neq b, i \neq j \\ F_{ab} + 2(ai|bi) - (ab|ii), & a \neq b, i = j \\ -F_{ij} + 2(ai|aj) - (aa|ij), & a = b, i \neq j \\ F_{aa} - F_{ii} + 2(ai|ai) - (aa|ii) + E_{core}, & a = b, i = j \end{cases}, \quad (2)$$

where $(ai|bj)$ is the electronic repulsion integral (3), F_{pq} is the element of the Fockian matrix (4), E_{core} is the core energy containing the internuclear repulsion V_{nn}, the diagonal elements of the one electron Hamiltonian ($\hat{h}$) in the core subspace, Coulomb and exchange integrals (5):

$$(ai|bj) = \iint \frac{\varphi_i(r_1)\varphi_a(r_1) \cdot \varphi_j(r_2)\varphi_b(r_2)}{|r_1 - r_2|} dr_1 dr_2 \; ; \quad (3)$$

$$F_{pq} = h_{pq} + \sum_{k \in \text{core}} \Big[2(pq|kk) - (pk|qk) \Big] \; ; \quad (4)$$

$$E_{core} = V_{nn} \; + 2 \sum_{k \in \text{core}} h_{kk} \; + \sum_{k,l \in \text{core}} \Big[2(kk|ll) - (kl|kl) \Big]. \quad (5)$$

The full diagonalization of the Hamiltonian matrix is a very time-consuming task. However, only a small number of the lowest eigenvalues is needed because most of the higher eigenvalues do not have any physical meaning. Lowest eigenvalues can be found using the Davidson algorithm [14, 15], which does not require the full storage of the Hamiltonian matrix H. Only the procedure of multiplication of the trial vector by the matrix is needed:

$$H|\Psi_n\rangle = \sum_J d_{nJ} |\Phi_J\rangle = \sum_J \left[\sum_I C_{nI} H_{IJ} \right] |\Phi_J\rangle = \sum_{I,J} C_{nI} H_{IJ} |\Phi_J\rangle, \quad (6)$$

where matrix elements H_{IJ} can be calculated "on the fly". At first, the ERIs in the atomic orbital basis $(\alpha\beta|\gamma\delta)$ are calculated. Then they are used to calculate ERIs for the molecular orbitals $(pq|rs)$. Finally, the matrix elements H_{IJ} are calculated (2) and used for the multiplication (6). The Hamiltonian matrix can be stored in case of small molecules or large amount of available RAM. It requires storage of $n_\text{c}^2 \cdot n_\text{v}^2$ elements (n_c and n_v are the numbers of core and virtual orbitals). However, in any case, the calculation of $(\alpha\beta|\gamma\delta)$ is needed. The ERI tensor containing N_AO^4 elements can not be stored in RAM for any valuable calculation. The recalculation of $(\alpha\beta|\gamma\delta)$ on each iteration significantly increases the computational time, which is an inevitable cost of avoiding storage of the integrals.

1.2. Resolution of Identity (RI) Approximation

The resolution of identity approximation [6], which is also called Density Fitting (DF), is widely used to speed up the ERI calculation. This approach gives two significant advantages. First, it reduces the scaling of the calculations from $O(N^4)$ to $O(N^3)$ due to the change of the four-center integrals to the three-center ones. Second, it reduces the memory requirements and makes the recalculation of the ERIs at each iteration unnecessary [5].

The key idea of RI is to use the approximation of the product of two basis functions (pair density) as a linear combination of functions from the auxiliary basis set $\{\rho_\mu(r)\}$:

$$\rho_{ij} = \chi_i(r)\chi_j(r) \approx \widetilde{\rho}_{ij} = \sum_\mu C_\mu^{ij}\rho_\mu(r), \tag{7}$$

where $\{\rho_\mu(r)\}$ is a special set of auxiliary basis functions that has the dimension higher than the dimension of atomic orbital basis but significantly lower than the number of pair products $\chi_i(r)\chi_j(r)$ ($N_{\text{aux}} \approx 3N_{\text{AO}} \div 5N_{\text{AO}}$). C_μ^{ij} coefficients are determined by the minimization of the approximation error. The most suitable for ERI is RI-V or Coulomb fitting, which is based on the minimization of the Coulomb self-repulsion of the density difference:

$$\Delta_{ij} = \iint \frac{\left[\rho_{ij}(r_1) - \widetilde{\rho}_{ij}(r_1)\right]\left[\rho_{ij}(r_2) - \widetilde{\rho}_{ij}(r_2)\right]}{|r_1 - r_2|} dr_1 dr_2 = \\ = (\rho_{ij} - \widetilde{\rho}_{ij}|\rho_{ij} - \widetilde{\rho}_{ij}) = \|\rho_{ij} - \widetilde{\rho}_{ij}\|^2 \ \to \min; \tag{8}$$

$$\left\| \chi_i \cdot \chi_j \ - \ \sum_\mu C_\mu^{ij}\rho_\mu(r) \right\| \ \to \min . \tag{9}$$

This is a standard problem of linear algebra that leads to a system of equations:

$$\sum_\mu C_\mu^{ij}(\rho_k|\rho_\mu) = (\rho_k|\chi_i\chi_j) \quad \Leftrightarrow \quad \sum_\mu V_{k\mu}C_\mu^{ij} = (ij|k), \tag{10}$$

where $(ij|k)$ is the three-center integral (11) containing one auxiliary and two orbital basis functions; $V_{k\mu}$ is the two-center coulomb integral (12) of two auxiliary functions:

$$(ij|k) = \iint \frac{\chi_i(r_1)\chi_j(r_1)\cdot\rho_k(r_2)}{|r_1 - r_2|} dr_1 dr_2 \ ; \tag{11}$$

$$V_{k\mu} = \iint \frac{\rho_k(r_1)\cdot\rho_\mu(r_2)}{|r_1 - r_2|} dr_1 dr_2. \tag{12}$$

The solution of eq. (10) is the following:

$$C_\mu^{ij} = \sum_k (V^{-1})_{\mu k}(ij|k). \tag{13}$$

The substitution of (7) into the $(\alpha\beta|\gamma\delta)$ gives:

$$(\alpha\beta|\gamma\delta) = (\chi_\alpha\chi_\beta|\chi_\gamma\chi_\delta) \approx \left(\sum_\mu C_\mu^{\alpha\beta}\rho_\mu \middle| \sum_\nu C_\nu^{\gamma\delta}\rho_\nu\right) = \sum_{\mu,\nu} C_\mu^{\alpha\beta}C_\nu^{\gamma\delta}(\rho_\mu|\rho_\nu) = \sum_{\mu,\nu} C_\mu^{\alpha\beta}C_\nu^{\gamma\delta}V_{\mu\nu} \ . \tag{14}$$

The further substitution of coefficients C_μ^{ij} (13) in (14) leads to:

$$(\alpha\beta|\gamma\delta) \approx \sum_{\mu,\nu}\left[\sum_k (V^{-1})_{\mu k}(\alpha\beta|k)\right] V_{\mu\nu}\left[\sum_l (V^{-1})_{\nu l}(\gamma\delta|l)\right] = \\ = \sum_k\sum_l\left[(\alpha\beta|k)(\gamma\delta|l)\sum_{\mu,\nu}(V^{-1})_{\mu k}V_{\mu\nu}(V^{-1})_{\nu l}\right]. \tag{15}$$

V is a symmetric, positive definite matrix, so the same is true for V^{-1}, and:

$$\sum_{\mu,\nu}(V^{-1})_{\mu k}V_{\mu\nu}(V^{-1})_{\nu l} = (V^{-1})_{kl} \ . \tag{16}$$

Thus, the four-center ERIs can be expressed through two- and three-center integrals as follows:

$$(\alpha\beta|\gamma\delta) \approx \sum_{k,l}(\alpha\beta|k)(V^{-1})_{kl}(l|\gamma\delta). \tag{17}$$

The precision of the resulting RI approximation depends on the quality of the auxiliary basis set $\{\rho_\mu\}$. These sets are specially optimized for the exact representation of the pair densities $\rho_{ij}(r)$ and their Coulomb interactions. There are standard auxiliary basis sets specially designed for the calculations with the particular orbital basis sets (e.g., cc-pVXZ-RI [6], def2/JKFIT, def2/RIFIT [16]). The calculation error is negligible if the appropriate auxiliary basis set is used, but it can also be reduced by taking a larger auxiliary basis set.

1.3. RI-CIS Variants

A series of testing calculations using the CIS method with the RI approximation was conducted. The Davidson diagonalization [14, 15] was used to solve the variational CI problem. Two different implementations of the RI-CIS method based on the mentioned above formulae were realized. These two methods employ different strategies for the calculation and storage of the H_{CIS} matrix:

1) The first one rejects the recalculation of the Hamiltonian on the fly and employs storage of the full Hamiltonian matrix. Let us call it RI-CIS(1). Despite the fact that this method can be inapplicable for the large systems where the Hamiltonian storage is impossible, it must have higher performance for the smaller systems.
2) The second variant is a direct RI-CIS where the Hamiltonian matrix is recalculated on the fly during each Davidson iteration. However, it is not a commonly used direct CI because the three-center ERI tensor is stored but not recalculated. Let us call it RI-CIS(2). This approach must be less effective than RI-CIS(1) for the small molecules, but it would be the only choice if the H_{CIS} can not be stored in memory.

Each of the considered algorithms leads to the reduction of the number of operations and calculation time, that can be different for different size of molecule and used basis set. Thus, the more efficient algorithm can be determined only by the testing calculations.

2. Computational Details

Both reported algorithms RI-CIS(1) and RI-CIS(2) were implemented in the **NOPT** – the author's software written in C++ for the calculation of the **N**on-**O**rhogonal CI [17] and its extension by the **P**erturbation **T**heory [18, 19] (available upon request from the authors). It was compiled with the Libint [20] library version 2.9.0 for the atomic integrals and BLAS for the matrix multiplications. Both algorithms were then tested for accuracy, performance, parallelism, and scaling.

The benchmark calculations were done using the ORCA 5.0.3 [7, 8] package. The approximation error was estimated by the comparison with the default variant of CIS, and the performance was compared with the CIS in the RIJCOSX approximation. The comparison was performed for the calculation of the same molecule using the same basis set.

The testing calculations were performed for the polyene molecules C_2H_4, C_4H_6, C_6H_8, C_8H_{10}, $C_{10}H_{12}$ with the correlation consistent basis sets cc-pVnZ (n = D, T, Q) and their analogs aug-

mented by diffuse functions aug-cc-pVnZ. The corresponding auxiliary basis sets (cc-pVnZ-RI and aug-cc-pVnZ-RI) were taken for the RI approximation. All the basis sets were downloaded from the Basis Set Exchange database (BSE) [21–23]. The structures of all the molecules were taken to be planar, all double C=C bonds were in the trans configuration, and all single C–C bonds were in the s-trans-conformation. All the angles were 120°, and the bond lengths of C–H and two types of C–C were taken from the butadiene microwave geometry [24]. The structure of $C_{10}H_{12}$ is shown in Fig. 1.

All the testing calculations were carried out on the computer with two central processors Intel Xeon E5-2697 v3 with 2.60 GHz frequency and 14 cores per CPU. The computer had 196 GB of RAM, which was sufficient for all the calculations.

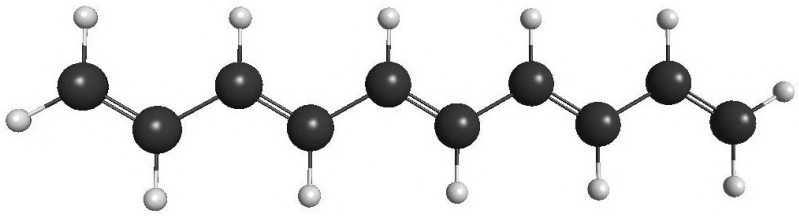


Figure 1. Structure of $C_{10}H_{12}$. Image was made using wxmacmolplt software [25]. Carbon atoms are black, hydrogen atoms are gray. Two different types of C–C bonds are drawn as single and double

3. Results and Discussion

3.1. Accuracy Tests

The tests of the accuracy of the excitation energies calculated by RI-CIS and RIJCOSX-CIS were conducted by comparing of the 10 lowest values calculated for the polyene molecules with the values calculated by default CIS. The excitation energies calculated by both variants of RI-CIS are equal; the deviation of $\sim 10^{-8}$ Hartree is caused by the numerical error and can be considered negligible. The maximum deviations for the excitation energies calculated for C_2H_4 and $C_{10}H_{12}$ with different basis sets by different approximate CIS methods are given in Tab. 1. The RIJCOSX-CIS was used with two variants of the grid: DefGrid2 and DefGrid3.

These deviations in the excitation energies show that the error of the RI approximation decreases with the increase of the basis set, especially with the augmentation. At the same time, the RIJCOSX error is higher than the RI error for small molecules. The use of the DefGrid3 does not significantly increase precision. The increase of the basis set in the cc-pVnZ series does not affect the RIJCOSX error, while the augmentation leads to larger errors. Both approximations show a decrease in error with the increase in molecule size. In the case of large molecule and compact basis set, the errors are similar for RI and RIJCOSX.

The decrease of the RIJCOSX error with the increase in the molecule size is probably caused by the method of grid construction. The grid points are generated around the atoms. The electronic density for the large polyenes is delocalized along the chain of the conjugated carbon bonds, while the density for the small polyenes is more delocalized in the orthogonal direction. Thus, the

Table 1. Errors of the excitation energies of different molecules calculated by different methods with different basis sets

Molecule	Basis set	Δ, cm^{-1}		
		RI-CIS	RIJCOSX-CIS	
			DefGrid2	DefGrid3
C_2H_4	cc-pVDZ	104.0	173.7	155.8
	aug-cc-pVDZ	18.8	278.3	255.6
	cc-pVTZ	30.1	155.5	186.9
	aug-cc-pVTZ	24.6	242.4	252.6
	cc-pVQZ	15.1	162.4	189.6
	aug-cc-pVQZ	21.6	236.9	244.6
$C_{10}H_{12}$	cc-pVDZ	60.9	75.6	70.2
	aug-cc-pVDZ	13.1	113.5	93.2

localization of the grid points better fits electronic density for the larger polyenes, and the energy errors become lower.

The deviations of the excitation energies of C_2H_4 and $C_{10}H_{12}$ calculated by RI-CIS and RIJCOSX-CIS with DefGrid2 and DefGrid3, as a function of the state number, are presented in Fig. 2. The figure shows that the RIJCOSX error depends significantly on the electronic state, and the picture is the same with any basis set. Contrarily, the RI error is significantly smaller if a larger and more diffuse basis is used.

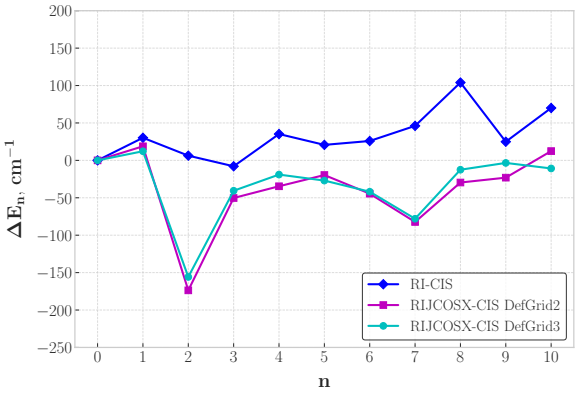
3.2. Performance Tests

A series of calculations with the standard and approximate variants of the CIS method was carried out. The analysis of the total computational time and the time of one Davidson iteration as a function of molecule size (the number of carbon atoms) and basis set dimension was performed. The use of different convergers and initial CIS guesses in ORCA and NOPT resulted in a different number of iterations. However, the number of iterations also depends on the convergence criteria, which can vary in different situations. So, the most representative parameter is the time per iteration, and all the following comparisons are based on this value.

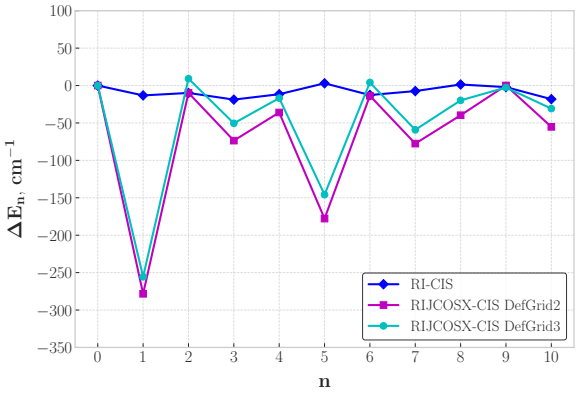
3.2.1. Parallelism test

The parallelism tests were performed for all the considered CIS methods by the calculations of the $C_{10}H_{12}$ molecule with the cc-pVDZ and aug-cc-pVDZ basis sets using different numbers of threads. The results are presented in Fig. 3.

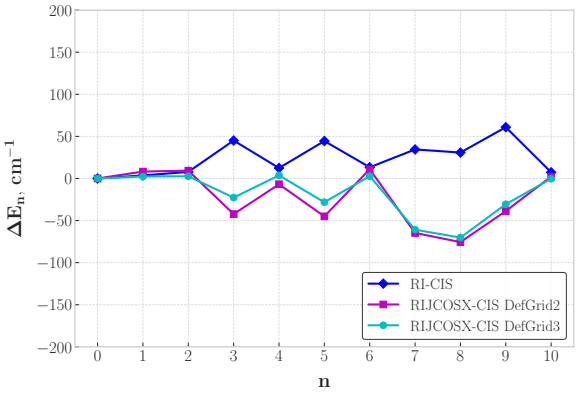
Similar slopes of the curves indicate that all the considered methods have a similar parallelism efficiency. This is true for both compact and augmented basis sets. The efficiency decreases with the increase in the number of threads for all methods. However, this decrease is lower for the CIS(2), and it becomes faster than CIS-RIJCOSX with DefGrid3.



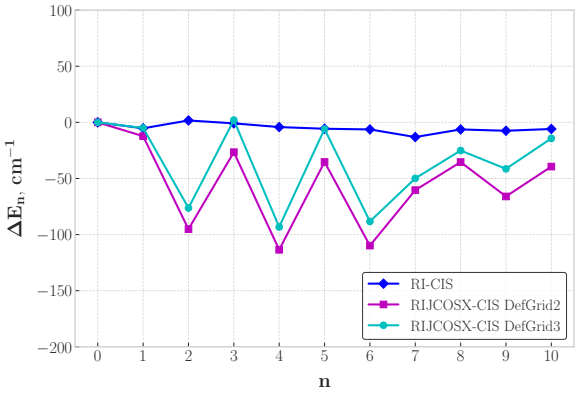
(a) Error for C_2H_4 with cc-pVDZ basis



(b) Error for C_2H_4 with aug-cc-pVDZ basis

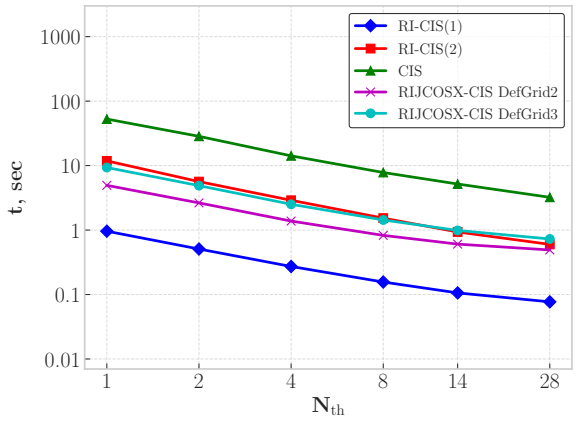


(c) Error for $C_{10}H_{12}$ with cc-pVDZ basis

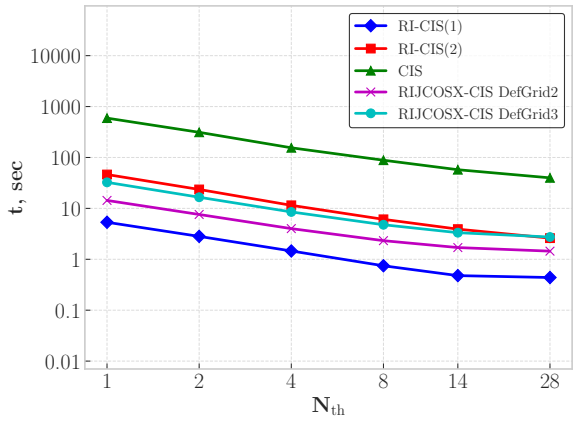


(d) Error for $C_{10}H_{12}$ with aug-cc-pVDZ basis

Figure 2. Error of the excitation energy calculated by the approximate CIS methods as a function of the number of state ($\Delta E_n = E_n^{\text{appr.CIS}} - E_n^{\text{CIS}}$)



(a) cc-pVDZ basis set



(b) aug-cc-pVDZ basis set

Figure 3. Dependence of the time per iteration t on the number of threads N_{th} with different CIS variants. Axes are in the logarithmic scale

The quantitative characteristic of parallelism efficiency can be obtained by fitting the shown curves by the equation:

$$t \sim N_{\text{th}}^{-\alpha} \ . \tag{18}$$

α and R^2 of the fitted curves are given in Tab. 2. The fitting is done for two intervals $N_{\text{th}} \in [1; 14]$, where only one CPU can be engaged in the calculation, and $N_{\text{th}} \in [1; 28]$, where both CPUs are engaged at the last point.

Table 2. The fitted α and R^2 of the equation (18) for the calculations of the $C_{10}H_{12}$ with cc-pVDZ and aug-cc-pVDZ basis sets

Basis set	cc-pVDZ				aug-cc-pVDZ			
Method	$N_{\text{th}} \in [1; 14]$		$N_{\text{th}} \in [1; 28]$		$N_{\text{th}} \in [1; 14]$		$N_{\text{th}} \in [1; 28]$	
	α	R^2	α	R^2	α	R^2	α	R^2
RI-CIS(1)	0.840	0.997	0.772	0.988	0.925	0.999	0.799	0.967
RI-CIS(2)	0.959	0.999	0.904	0.994	0.946	0.998	0.881	0.991
CIS	0.892	0.998	0.850	0.995	0.891	0.997	0.827	0.990
RIJCOSX-CIS DefGrid2	0.807	0.992	0.712	0.971	0.820	0.993	0.714	0.966
RIJCOSX-CIS DefGrid3	0.861	0.996	0.783	0.984	0.873	0.995	0.768	0.972

3.2.2. Scaling test (basis set)

A series of test calculations was carried out for the C_2H_4 molecule with cc-pVnZ and aug-cc-pVnZ (n = D, T, Q) basis sets using different variants of the CIS method. The dependence of the time per iteration on the number of basis functions was analyzed. The results are shown in Fig. 4.

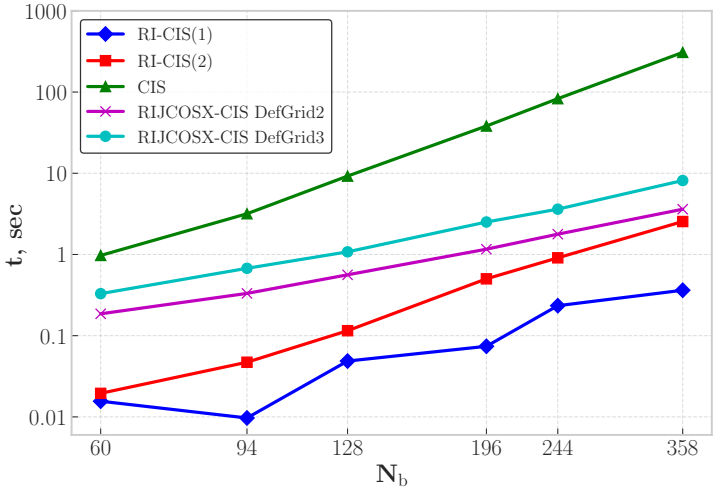


Figure 4. Dependence of the time per iteration t on the basis set dimension N_{b} for C_2H_4 calculated with $N_{\text{th}} = 1$. Axes are in the logarithmic scale

The figure shows that both RI-CIS methods demonstrate higher performance for any of the considered basis sets, with RI-CIS(1) having the highest one. The RIJCOSX methods are slower

than RI for the considered molecule, and the use of the denser grid (DefGrid3) leads to a decrease in performance compared to that with DefGrid2. The default CIS method is slower than any approximate variant.

The dependence of the calculation time per iteration on the dimension of the basis set was fitted with the function:

$$t \sim N_{\mathrm{b}}^{\beta} \ . \tag{19}$$

The fitted β and R^2 parameters of equation (19), presented in Tab. 3, demonstrate that, despite the higher performance, RI-CIS methods have worse scaling compared to RIJCOSX. The better scaling of the RIJCOSX methods can be explained by the slower increase in the number of integrals per point and the constant number of grid points. However, the scaling of RI-CIS is better than that of the default CIS.

Table 3. The fitted β and R^2 of the equation (19) for calculations of the C_2H_4 in different basis sets

Method	Parameter	
	β	R^2
RI-CIS(1)	2.050	0.876
RI-CIS(2)	2.833	0.993
CIS	3.264	0.998
RIJCOSX-CIS DefGrid2	1.678	0.995
RIJCOSX-CIS DefGrid3	1.791	0.997

Table 4. The fitted γ and R^2 of the equation (20) for the calculations of $C_{2n}H_{2n+2}$, $n = 1, 2, 3, 4, 5$ polyenes with cc-pVDZ and aug-cc-pVDZ basis sets

Basis set	cc-pVDZ		aug-cc-pVDZ	
Method	γ	R^2	γ	R^2
RI-CIS(1)	2.639	0.957	4.136	0.978
RI-CIS(2)	4.030	0.989	4.260	1.000
CIS	2.591	0.996	3.294	0.996
RIJCOSX-CIS DefGrid2	2.057	0.999	2.370	0.999
RIJCOSX-CIS DefGrid3	2.119	0.999	2.416	1.000

3.2.3. Scaling test (molecule size)

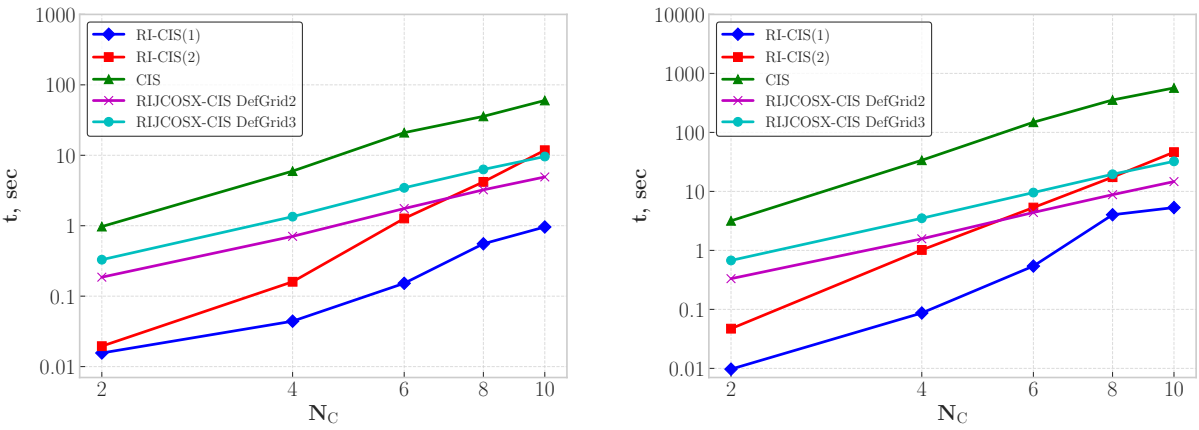
A series of test calculations was carried out for the $C_{2n}H_{2n+2}$ with n = 1, 2, 3, 4, 5 molecules with cc-pVDZ and aug-cc-pVDZ basis sets using different variants of CIS method. The results are shown in Fig. 5.

The figure shows that RI-CIS(1) has the highest performance for any considered molecule size. Both RI-CIS methods have smaller computation times compared to the default CIS methods. RI-CIS(2) is faster than RIJCOSX with any grid for small molecules but becomes slower for the larger ones.

The dependence of the calculation time per iteration on the number of carbon atoms N_{C} was fitted with the function:

$$t \sim N_{\mathrm{C}}^{\gamma} \ . \tag{20}$$

The fitted γ and R^2 parameters of equation (20), presented in Tab. 4, demonstrate that both RI-CIS methods have worse scaling compared to RIJCOSX. Default CIS has intermediate γ. Two variants of RI-CIS have different behaviors: the scaling of RI-CIS(2) is worse but more stable with the basis augmentation. RI-CIS(1) has γ values close to those of the RIJCOSX variants



(a) cc-pVDZ basis set

(b) aug-cc-pVDZ basis set

Figure 5. Dependence of the time per iteration t on the number of carbon atoms N_C for the calculations by the different CIS variants. Axes are in the logarithmic scale

with the compact basis but much higher with the augmented one. However, despite having worse scaling, RI-CIS(1) demonstrates higher performance for all the considered molecules. Moreover, the better precision of the RI-CIS methods makes them preferable, even in those cases where they may become slower due to the worse scaling.

Conclusion

The testing of the accuracy and performance of the considered CIS methods can be summarized as follows:

- RI approximation can introduce a relatively small error to the CIS results. This error is caused by the approximate calculation of the ERIs and is less than 150 cm^{-1}. The precision can be improved by employing a larger auxiliary basis set.
- RI approximation demonstrates a higher precision compared to RIJCOSX, especially for smaller molecules and augmented basis sets.
- Implementation of the considered algorithm has parallelism similar to that of the variants implemented in ORCA.
- RI-CIS methods have higher performance compared to RIJCOSX method for small and moderate-sized molecules. The worse scaling may make RI methods slower for the case of large molecules and basis sets. However, the better precision makes RI approximation preferable.
- RI-CIS(1) is the best choice as long as the available memory is sufficient.

The considered realization of the RI-CIS demonstrates the efficiency of the high-memory strategy in quantum chemical calculations. The employment of algorithms for the decomposition of the ERI tensor decreases the memory requirements, making it possible to store them in the RAM of modern computers. This situation is typical for the quantum chemical calculations, where a huge amount of intermediate data is calculated but cannot be stored and must be recalculated at each step. The use of the high memory strategy helps to avoid multiple recalculations and significantly increases performance.

The availability of a high volume of RAM makes this strategy applicable. However, the efficient technologies of large tensor decomposition, such as resolution of identity, Cholesky decomposition, etc., are even more important than the physical volume of memory.

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