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REGULAR ARTICLE

A relativistic 4-component general-order multi-reference coupled cluster method: initial implementation and application to HBr

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Abstract We present the initial implementation of a determinant-based general-order coupled cluster method which fully accounts for relativistic effects within the four-component framework. The method opens the way for the treatment of multi-reference problems through a state-selective expansion of the model space. The evaluation of the coupled cluster vector function is carried out via relativistic configuration interaction expansions. The implementation is based on a large-scale configuration interaction technique, which may efficiently treat long determinant expansions of more than 10^8 terms. We demonstrate the capabilities of the new method in calculations of complete potential energy curves of the HBr molecule. The inclusion of spin–orbit interaction and higher excitations than coupled cluster double excitations, either by multi-reference model spaces or the inclusion of full iterative triple excitations, lead to highly accurate results for spectral constants of HBr.

Keywords Relativistic 4-component · Multi-reference · Coupled cluster · Spectroscopic properties

1 Introduction

The most efficient many-body theory to approach the exact energy in atomic and molecular electronic structure calculations is today provided by the coupled cluster (CC) model. In the treatment of molecules containing light atoms—i.e., up to the third row of the periodic table—the use of extensive one-particle basis sets and excitation levels beyond quadruples in non-relativistic CC calculations [13,31] allows for the determination of spectroscopic properties with an accuracy where relativistic contributions beyond scalar terms become important. In heavy-element systems, on the other hand, relativistic effects may be as important or even more important than electron correlation. Accurate electronic structure calculations of molecules with elements from the sixth row and beyond require a consistent treatment of relativistic effects, and here the inclusion of the spin–orbit interaction in quantum chemical methodology on the same footing as electron correlation comprises the greatest challenge.

Relativistic CC calculations for small molecules containing heavy elements can presently not attain the same precision as non-relativistic CC calculations for small molecules containing light elements. The limiting factors are the number of electrons which need to be correlated, the size of the required one-particle basis sets, the more complicated electronic structure of many heavy-element compounds, and the less-developed technology for relativistic CC calculations.

The CC model currently witnesses rapid progress, with modern developments concerning iterative excitation levels higher than CC doubles [5,16,21,22,29] and various multi-reference (MR) approaches [1,20,23,29]. However, none of these methods have been generalized

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to a relativistic formalism, which we understand as also including spin–orbit interaction terms. The 4-component implementations by Visscher et al., Kramers-restricted [36] and unrestricted [37], respectively, are not generally applicable to open-shell/multi-reference states. The only relativistic multi-reference approaches reported to the date are the Fock-Space CC implementations by Landau et al. [25] and Visscher et al. [39]. These methods, as the Fock-space approach in general, suffer from the use of a common orbital basis for all of the occurring ionized systems. When the Fock space sector is increased to higher than ±2, the calculations become difficult to converge. Calculations with 4 or 5 open shells are therefore not possible in general with current FSCC implementations. The treatment of a large variety of heavy-element systems, especially many compounds from the *d*- and *f*-block elements, is therefore out of reach with the available FSCC methodology.

In this paper, we present the first relativistic general-order coupled cluster method which moreover is capable of treating multi-reference problems and molecules with an arbitrary number of unpaired electrons. The essential idea is to generalize a non-relativistic variant of state-specific MRCC to the relativistic formalism, which retains the advantages of the single-reference approach and which allows for a flexible definition and robust treatment of MR expansions.

In the following section (2) we review this state-selective multi-reference approach and the underlying relativistic theory of our implementation. Section 3 gives a detailed account on the implementation of the method, and in Sect. 4 we present an initial application. We unfold some of the capabilities of the new method in this application. Some aspects, however, like the treatment of a large number of unpaired electrons in the reference state, have been demonstrated successfully with the non-relativistic precursor method [24] and for the relativistic case will be left for future work.

2 Theoretical background

2.1 Multi-reference coupled cluster approach

There is to the date no general consensus on how a multi-reference coupled cluster theory should be formulated. The original idea for our type of multi-reference CC approach is ascribed to Oliphant and Adamowicz [27,28]. In the present approach which is based on the generalized implementation of these ideas by Olsen [24,29] the projection manifold is extended to simulate excitations from additional reference functions beside those from the Fermi vacuum state. The reference state is formally re-interpreted as a multi-configuration state including the additional reference functions which is generated via a zero-order expansion. The parameters of the reference functions which are kept fixed in the implementations by Oliphant et al. are reoptimized in the present approach.

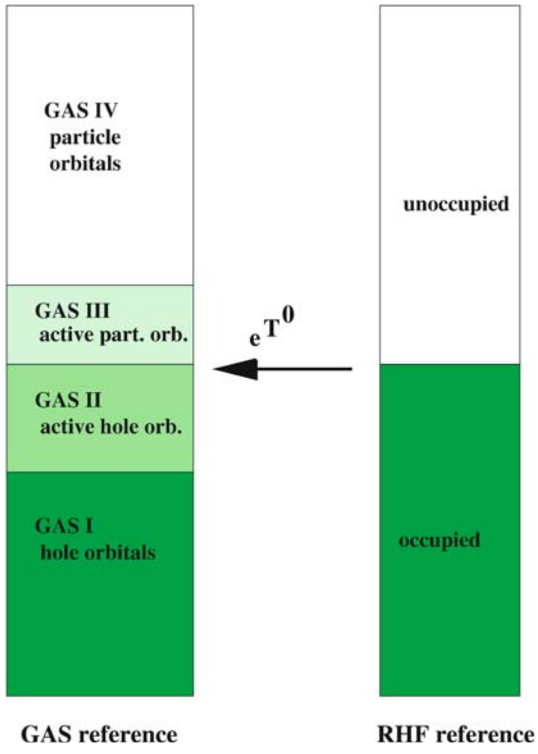

Fig. 1 A generalized active space CC reference space generated by a zero-order expansion $e^{\hat{T}^0}$ acting on a closed-shell (or simple high-spin open-shell) reference state. Although some active hole orbitals are now unoccupied and some active particle orbitals occupied, the original occupation of the orbitals is “memorized” in the CC expansion (state-selectivity)

In Fig. 1 we illustrate the expanded reference state. The number of active spaces is here arbitrary, as are the occupation constraints of the active spaces with respect to electrons (generalized active spaces, GAS). By these means, a very flexible definition of reference states is possible which allows for the efficient description also of complicated electronic structures, as often encountered in heavy-element molecules. More details on GAS expansions can be found in the literature [8,10].

The procedure retains the advantages of the single-reference formalism, especially commutative cluster operators, although higher excitations than those arising from a standard single-reference ansatz are included in the amplitude equations. The drawback of this formalism—in contrast to FSCC or the state-universal ansatz [19,20] or a new multi-reference exponential ansatz by Hanrath [12]—is the variance with respect to the choice of the Fermi vacuum, because despite the multi-determinantal nature of the reference state a "memory" of the occupied and unoccupied orbitals in the original reference state is retained in the cluster expansion. This also explains the term "state-selective". In other words, the various reference functions are not strictly treated on the same footing. The remedy, a separate cluster expansion for every reference function, leads to the state-universal Hilbert-space CC theory which is far less efficient [19]. The loss of Fermi vacuum invariance, however, does not appear to be of crucial importance in application and problems can be avoided by proper choices of reference spaces.

2.2 Relativistic approach

The environment of our implementation is a local version of the relativistic quantum chemistry program package `DIRAC` [11]. Various available Hamiltonians within the package can be used directly by our CC program, such as the 4-component operators Dirac–Coulomb, spin-free [4], and Levy Leblond [26], and 2-component operators such as the Infinite-Order Two-Component (IOTC) form of the Barysz–Sadlej–Snijders (BSS) Hamiltonian [3,18]. There are two essential features that allow the use of identical codes for 2- and 4-component methods. When a 4-component operator is used, the negative-energy states are discarded after the spinor optimization step and the following integral transformation, which can be viewed as an a posteriori no-pair approximation. The set of transformed integrals therefore is structurally identical to that from a two-component operator where the no-pair approximation has been invoked a priori, albeit numerically different. Second, the one-particle functions defined by a spinor optimization are by construction pairwise related through time-reversal symmetry, thus Kramers-paired spinors, irrespective of the Hamiltonian in use.

The inclusion of spin–orbit interaction in a rigorous manner eliminates the non-relativistic S and M_S as good quantum numbers already in the one-particle functions, which are in this case (2- or 4-component) spinors. We generally refer to Kramers-paired spinors defined by the action of the time-reversal operator $\hat{K}$ as

$$\begin{aligned}\hat{K}\Phi_i &= \Phi_{\bar{i}}\\ \hat{K}\Phi_{\bar{i}} &= -\Phi_i.\end{aligned} \tag{1}$$

Similar to spin projection, we denote the Kramers projection M_K of the spinor as

$$\begin{aligned}M_K &= \frac{1}{2} \quad \text{for } \Phi_i \quad \text{and}\\ M_K &= -\frac{1}{2} \quad \text{for } \Phi_{\bar{i}}.\end{aligned}$$

Likewise for a many-particle state which we represent by strings of creation operators for the Kramers-paired spinors, the auxiliary quantum number M_K becomes

$$\begin{aligned}M_K &= 0 \quad \text{for the string } a_i^\dagger a_{\bar{j}}^\dagger\\ M_K &= \frac{1}{2} \quad \text{for the string } a_i^\dagger a_{\bar{j}}^\dagger a_k^\dagger\\ &\text{etc.}\end{aligned}$$

Beside a partitioning of the Hamiltonian operator, the primary use of the auxiliary quantum number is to classify many-particle states. It may therefore be used to define restricted excitation manifolds and cluster operators in the context of relativistic CC theory, similar to the way restricted Configuration Interaction (CI) and Multi-Configuration (MC) SCF expansions have been defined in the relativistic framework earlier [9,10].

One- and many-particle functions are consistently classified according to irreducible representations of double point groups which are limited to the binary groups (D_{2h} and its subgroups). In a formulation using quaternion algebra and based on the Frobenius–Schur lemma [32,35] these double groups decompose into real-valued (D_{2h}^*, D_2^*, and C_{2v}^*) and complex-valued groups (C_{2h}^*, C_2^*, C_s^*, C_i^*, and C_1^*). For the former, real algebra can be used throughout whereas for the latter the imaginary parts of all occurring quantities need to be considered as well. The treatment of spin–orbit interaction is therefore possible for a large fraction of small molecules without the necessity to account for complex algebra, but merely by an extended set of integrals compared to the non-relativistic framework.

Our current implementation treats the real-valued and some of the complex-valued double groups (C_{2h}^*, C_2^*, and C_s^*). The remaining groups, the so-called quaternion-matrix groups (C_i^* and C_1^*), require modifications in our configuration interaction program [9] and are not implemented yet.

3 Implementation

3.1 Coupled cluster vector function

The essential quantity to be evaluated in the course of a coupled cluster optimization is the coupled cluster vector function Ω_μ for a given element μ of the excitation manifold:

$$\Omega_\mu = \left\langle \mu \left| \mathrm{e}^{-\hat{T}} \hat{H} \mathrm{e}^{\hat{T}} \right| \mathrm{Ref} \right\rangle \tag{2}$$

The cluster operators $\hat{T} = \sum_m \hat{T}_m$ are now generalized to the relativistic framework, which entails the possibility of flipping the Kramers projection along with the excitation:

$$\begin{aligned} \hat{T}_1 &= \sum_{ia} \left\{ t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \right\} \\ \hat{T}_2 &= \sum_{i<j,a<b} \left\{ t_{ij}^{ab} \hat{\tau}_{ij}^{ab} + t_{\bar{i}j}^{ab} \hat{\tau}_{\bar{i}j}^{ab} + t_{i\bar{j}}^{ab} \hat{\tau}_{i\bar{j}}^{ab} + t_{ij}^{\bar{a}b} \hat{\tau}_{ij}^{\bar{a}b} \right. \\ &\qquad + t_{ij}^{a\bar{b}} \hat{\tau}_{ij}^{a\bar{b}} + t_{\overline{ij}}^{ab} \hat{\tau}_{\overline{ij}}^{ab} + t_{\bar{i}j}^{\bar{a}b} \hat{\tau}_{\bar{i}j}^{\bar{a}b} + t_{\bar{i}j}^{a\bar{b}} \hat{\tau}_{\bar{i}j}^{a\bar{b}} \\ &\qquad + t_{i\bar{j}}^{\bar{a}b} \hat{\tau}_{i\bar{j}}^{\bar{a}b} + t_{i\bar{j}}^{a\bar{b}} \hat{\tau}_{i\bar{j}}^{a\bar{b}} + t_{ij}^{\overline{ab}} \hat{\tau}_{ij}^{\overline{ab}} + t_{\overline{ij}}^{\bar{a}b} \hat{\tau}_{\overline{ij}}^{\bar{a}b} \\ &\qquad \left. + t_{\overline{ij}}^{a\bar{b}} \hat{\tau}_{\overline{ij}}^{a\bar{b}} + t_{\bar{i}j}^{\overline{ab}} \hat{\tau}_{\bar{i}j}^{\overline{ab}} + t_{i\bar{j}}^{\overline{ab}} \hat{\tau}_{i\bar{j}}^{\overline{ab}} + t_{\overline{ij}}^{\overline{ab}} \hat{\tau}_{\overline{ij}}^{\overline{ab}} \right\} \\ &\text{etc.} \end{aligned} \tag{3}$$

In the trivial case of spin orbitals, the Kramers flipping would correspond to the introduction of terms accounting for spin–orbit interaction. In our implementation, this special case is generalized to be applicable with any kind of one-particle space of Kramers-paired functions, e.g., 2- or 4-component spinors. As we here introduce no time-reversal symmetry restrictions on the amplitudes, we call this approach *Kramers-unrestricted* relativistic CC, referring to the many-particle but not the one-particle space. The excitations are categorized according to the change in the auxiliary quantum number M_K, e.g., $\hat{\tau}_i^{\bar{a}}$ corresponds to $\Delta M_K = -1$, $\hat{\tau}_{\bar{i}j}^{ab}$ to $\Delta M_K = +1$, $\hat{\tau}_{\bar{i}j}^{\bar{a}b}$ to $\Delta M_K = 0$, etc.

The evaluation of the CC vector function proceeds in an analogous fashion as described in reference [29], where the CC vector function is obtained in four steps which are based on CI expansions and string manipulations. Although this formalism is rather inefficient, it allows the generation of a general relativistic CC code by reusing much of the code which we previously have developed for relativistic CI [9,10]. Furthermore, the developed code may be used in calculations where only a small number of electrons is correlated, and will provide a test code for the more advanced and efficient relativistic CC codes currently under development.

In the following, we first consider the general features of this CI-based vector function implementation as also mentioned in reference [29] and then review the four required steps in the evaluation.

As $\mathrm{e}^{-\hat{T}}$ does not decrease the excitation rank of the state it is acting on, the configuration space spanned by $\hat{H}\mathrm{e}^{\hat{T}}\,|\mathrm{Ref}\rangle$ can be restricted to the space of the excitation manifold $\langle\mu|$. Since the Hamiltonian is an operator with a maximum de-excitation (down) rank of 2, this implies that the evaluation of $\hat{H}\mathrm{e}^{\hat{T}}\,|\mathrm{Ref}\rangle$ has to be carried out in a space with a maximum excitation level increased by 2 relative to the excitation manifold. For example, in a CCSD calculation the expression $\mathrm{e}^{\hat{T}}\,|\mathrm{Ref}\rangle$ can be restricted to atmost quadruple excitations. We illustrate the linear transformation step $\hat{H}\mathrm{e}^{\hat{T}}\,|\mathrm{Ref}\rangle$ in Fig. 2. The computational scaling of this procedure is given as $O^{n+2}V^{n+2}$ where O is the number of occupied spinors, V the number of virtual spinors and n is the highest CC excitation level in the calculation. Compared to a CC implementation with an optimal scaling as $O^n V^{n+2}$ (such as the string-based non-relativistic implementation of Kállay et al. [23]) this reduced efficiency therefore limits the number of electrons which may be correlated (roughly up to 10 or 12) and the size of the employed one-particle basis sets (roughly up to triple-zeta quality). Due to the use of the highly efficient direct CI technique based on Generalized Active Space expansions [9,10] fairly large calculations with more than 1×10^8 Slater determinants in the extended space are nevertheless possible.

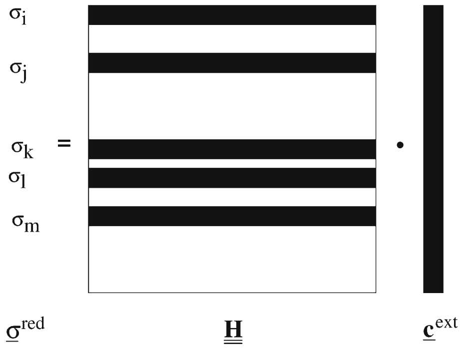

Fig. 2 Reduced linear transformation step for the CI-based evaluation of the CC vector function. $\underline{\mathbf{c}}^{\mathrm{ext}}$ is a reference vector from the extended space which is projected onto a reduced space $\underline{\sigma}^{\mathrm{red}}$ defined by the CC excitation manifold

In the following, we describe the relativistic implementation focussing on the individual steps required for the CC vector function.

Step 1:

$|a\rangle = \mathrm{e}^{\hat{T}}\,|\mathrm{Ref}\rangle$, expansion of the reference vector.

$$\begin{aligned} |a\rangle &= \left(\sum_{n=0} \frac{1}{n!} \hat{T}^n \right) |\mathrm{Ref}\rangle \\ &= |\mathrm{Ref}\rangle + \hat{T}\,|\mathrm{Ref}\rangle + \frac{1}{2}\hat{T}\left\{\hat{T}\,|\mathrm{Ref}\rangle\right\} + \frac{1}{6}\cdots \end{aligned} \tag{4}$$

The expansion is carried out by invoking the routines for calculating a CI sigma vector repeatedly, i.e., once for each term $\hat{T}\,|\mathrm{Ref}\rangle$, as described in detail in the context

Table 1 Excitation-class ordered operators in second quantization, corresponding integrals, and associated change in Kramers projection

Operator	Integral class	Kramers projection
$a^\dagger_i a_j$	h_{ij}	$\Delta M_K = 0$
$a^\dagger_{\bar{i}} a_{\bar{j}}$	$h_{\overline{ij}}$	$\Delta M_K = 0$
$a^\dagger_i a^\dagger_k a_l a_j$	$(ij\|kl)$	$\Delta M_K = 0$
$a^\dagger_{\bar{i}} a^\dagger_{\bar{k}} a_{\bar{l}} a_{\bar{j}}$	$(\bar{i}\bar{j}\|\overline{kl})$	$\Delta M_K = 0$
$a^\dagger_i a^\dagger_{\bar{k}} a_l a_{\bar{j}}$	$(i\bar{j}\|\bar{k}l)$	$\Delta M_K = 0$
$a^\dagger_i a_{\bar{j}}$	$h_{i\bar{j}}$	$\Delta M_K = +1$
$a^\dagger_{\bar{i}} a_j$	$h_{\bar{i}j}$	$\Delta M_K = -1$
$a^\dagger_i a^\dagger_k a_l a_{\bar{j}}$	$(i\bar{j}\|kl)$	$\Delta M_K = +1$
$a^\dagger_{\bar{i}} a^\dagger_{\bar{k}} a_{\bar{l}} a_j$	$(\bar{i}j\|\overline{kl})$	$\Delta M_K = -1$
$a^\dagger_i a^\dagger_k a_{\bar{l}} a_{\bar{j}}$	$(i\bar{j}\|k\bar{l})$	$\Delta M_K = +2$
$a^\dagger_{\bar{i}} a^\dagger_{\bar{k}} a_l a_j$	$(\bar{i}j\|\bar{k}l)$	$\Delta M_K = -2$

of relativistic CI theory [9] and relativistic MCSCF theory [10]. In this step, the contraction is not performed with integrals, however, but with the CC amplitudes of the current iteration.

A restricted set of excitations may be defined by reducing the range of allowed M_K values for the construction of excitations on input. This leads to approximate CC calculations within a reduced coupling scheme. The expansion in step 1 is otherwise truncated when the highest excitation level has been reached which may couple to the excitation manifold, in line with the arguments in the above discussion (Sect. 3.1).

Step 2:

$|b\rangle = \hat{H}\,|a\rangle$: linear transformation of the expanded reference vector.

This step again corresponds to the calculation of a linear transformation (CI sigma vector) of the expanded reference vector $|a\rangle$. The contraction is now carried out with integrals over Kramers-paired spinors which are classified according to excitation classes and the associated change of the auxiliary quantum number M_K. This is displayed in Table 1. This excitation class formalism does not only define the structure of the Hamiltonian operator (with a ΔM_K range of $\{+2, \ldots, -2\}$) but is also used in the definition of the cluster excitation operators in Eq. (3).

A relativistic sigma vector therefore consists of a sum of five contributions according to

$$\boldsymbol{\sigma} = \sum_{\Delta M_K=-2}^{\Delta M_K=+2} \boldsymbol{\sigma}^{\Delta M_K} \tag{5}$$

with a sample contribution corresponding to the partition $\Delta M_K = +1$ decomposed into 1- and 2-electrons parts

$$\begin{aligned}\boldsymbol{\sigma}^{+1}(\mathcal{T}^\dagger, \overline{\mathcal{T}^\dagger}) = {} & \sum_{ij}\sum_{\mathcal{S}} \left\langle \mathcal{T}^\dagger | a^\dagger_i | \mathcal{S}^\dagger \right\rangle \sum_{\overline{\mathcal{S}}} \left\langle \overline{\mathcal{T}}^\dagger | a_{\bar{j}} | \overline{\mathcal{S}}^\dagger \right\rangle \\ & \cdot h_{i\bar{j}} \cdot C_{\mathcal{S},\overline{\mathcal{S}}} \\ & + \sum_{\substack{i\geq k\\ lj}} \sum_{\mathcal{S}} \left\langle \mathcal{T}^\dagger | a^\dagger_i a^\dagger_k a_l | \mathcal{S}^\dagger \right\rangle \sum_{\overline{\mathcal{S}}} \left\langle \overline{\mathcal{T}}^\dagger | a_{\bar{j}} | \overline{\mathcal{S}}^\dagger \right\rangle \\ & \cdot \left[\left(i\bar{j}|kl \right) - \left(k\bar{j}|il \right) \right] \cdot C_{\mathcal{S},\overline{\mathcal{S}}} \\ & + \sum_{\substack{ik\\ l\geq j}} \sum_{\mathcal{S}} \left\langle \mathcal{T}^\dagger | a^\dagger_i | \mathcal{S}^\dagger \right\rangle \sum_{\overline{\mathcal{S}}} \left\langle \overline{\mathcal{T}}^\dagger | a^\dagger_{\bar{k}} a_{\bar{l}} a_{\bar{j}} | \overline{\mathcal{S}}^\dagger \right\rangle \\ & \cdot \left[\left(l\bar{i}|jk \right) - \left(j\bar{i}|lk \right) \right] \cdot C_{\mathcal{S},\overline{\mathcal{S}}},\end{aligned} \tag{6}$$

where $\mathcal{S}^\dagger$ denotes a string of unbarred creation operators. A full account of the sigma vector partitions is given in reference [8].

As discussed above, the vector $\hat{H}e^{\hat{T}}\,|Ref\rangle$ should be in the space of atmost n-fold excitations whereas $e^{\hat{T}}\,|Ref\rangle$ may be in the space of $n+2$-fold excitations. The operation count of this step thus scales as $O^{n+2}V^{n+2}$.

The efficiency of the direct CI steps in terms of required computer memory benefits from the batching of coefficients in the linear transformation steps. In terms of speed, the string-based CI algorithm [10,30] allows for the treatment of large expansions as no explicit comparison of configurations/occupations is carried out and higher than double excitations are treated on the same footing as double excitations.

Step 3:

$|c\rangle = e^{-\hat{T}}\,|b\rangle$, expansion of the transformed reference vector.

$$\begin{aligned}|c\rangle &= \left(\sum_{n=0} \frac{-1}{n!}\hat{T}^n \right) |b\rangle \\ &= |b\rangle - \hat{T}\,|b\rangle + \frac{1}{2}\hat{T}\left\{ \hat{T}\,|b\rangle \right\} - \frac{1}{6}\cdots\end{aligned} \tag{7}$$

The expansion is carried out in complete analogy with step 1. It is assured that the expansion is restricted to the excitation manifold $\langle\mu|$.

Step 4:

$\Omega_\mu = \langle\mu|c\rangle$, evaluation of transition density matrix elements.

$$\Omega_\mu = \left\langle \mathrm{Ref} \middle| \hat{\tau}^\dagger_\mu \middle| c \right\rangle$$

The projection of the excitation manifold $\langle\mu|$ against the expanded transformed reference vector $|c\rangle$ corresponds to the calculation of transition density matrix elements and yields the CC vector function. Employing the concise implementation described in references [9,10] the evaluation becomes equivalent to the calculation of CI sigma vectors, where instead of a contraction with integrals a contraction with expansion coefficients is performed. For the present case, the left-hand vector of expansion coefficients is a unit vector. As this step is carried out in the space of atmost n-fold excitations, it scales as O^nV^{n+2} and is therefore significantly faster than step 2.

3.2 Optimization algorithm

In the current implementation, we employ the following straightforward iterative algorithm: Given the CC amplitudes $\boldsymbol{t}$ of iteration n and the CC vector function $\boldsymbol{\Omega}(\boldsymbol{t})$ computed from these (as discussed in Sect. 3.1) the equations

$$\boldsymbol{\Delta t}_n = \boldsymbol{J}_n^{-1} \cdot \boldsymbol{\Omega}_n(\boldsymbol{t}) \tag{8}$$

$$\boldsymbol{t}_{n+1} = \boldsymbol{t}_n + \boldsymbol{\Delta t}_n \tag{9}$$

are solved selfconsistently, until the change of the CC energy calculated from the current iteration's amplitudes is smaller than a predefined threshold value. $\boldsymbol{J}$ denotes the CC Jacobian, the inverse of which may be approximated in different fashions. We have tested the simplest option with an inverse Jacobian where only the diagonal elements are considered. Whereas molecular calculations close to the equilibrium bond distance on bound potential energy curves converge in a satisfactory manner, the diagonal approximation gives divergent properties when the bond is stretched. We therefore implemented an algorithm where the Jacobian is approximated by a set of subspace vectors. Within this scheme, we obtain fast convergence for complete potential curves in both single-reference and multi-reference CC models. All calculations reported in the following section have therefore been carried out with the subspace Jacobian optimization.

4 Application to the HBr molecule

To demonstrate that our newly implemented method is operational and to outline its potential we discuss an initial application to a diatomic molecule and calculate full potential energy curves of the ground state at various levels of theory and computational demand. This investigation therefore does not aim at highest precision for the obtained quantities.

4.1 Objective and setup

The spectroscopic properties of the HBr molecule are significantly influenced by relativistic effects and electron correlation. Furthermore, this molecule is heavy enough to elucidate these effects and small enough to keep the computational demand of this pilot study limited. In particular, we investigate the importance of spin–orbit interaction by comparing with the 4-component spin–orbit free formalism of Dyall [4]. In work to be published [6,33] we have interfaced the original non-relativistic CC program to this 4-component spin–orbit free formalism. Here, the transformed molecular integrals are structurally equivalent to a set of integrals in a scalar relativistic (one-component) framework such as the Douglas–Kroll–Hess formulation [14,15,40], but the Hamiltonian for obtaining the integrals remains 4-component. The corresponding CC calculations are thus based on non-relativistic point-group symmetry. Moreover, a proper description of the dissociation of the molecule requires the inclusion of higher excitations, which are studied also by exploiting multi-reference approaches. We finally compare our results to MRCI calculations carried out with the spin–orbit free program `LUCITA` [7] and the fully relativistic program `LUCIAREL` [9,10] where the same basis sets and active orbital spaces are used as in the corresponding CC calculations.

We use two different uncontracted basis sets, in the following denoted as DZ and TZ. The smaller set DZ consists of the sp-pvdz set from the MOLFDIR suite in the DIRAC program package [11] for Br ($15s12p6d$) and H ($4s1p$). The larger set TZ is the relativistic finite nucleus optimized triple zeta basis set including valence-correlating functions for Br ($23s16p10d1f$) and the cc-pVTZ of the `MOLCAS5` package [2] for H ($5s2p1d$). Virtual orbitals beyond an energy of 10 a.u. are discarded which does not comprise a mentionable approximation here. All calculations are performed with the Dirac–Coulomb Hamiltonian, i.e., without two-electron contributions of spin-other-orbit type (Gaunt term). As Visscher et al. [38] have shown for HBr, the influence of these lacking terms on the properties studied here is at least one order of magnitude smaller than the errors we will discuss.

We correlate 6 and 8 electrons occupying $\sigma_{1/2}$, a $\pi_{1/2}$, and a $\pi_{3/2}$ orbital formed from the atomic valence orbitals of Br ($4p$) and H ($1s$), and in addition Br ($4s$) in the case of 8 electrons, respectively, in the reference state. A spin–orbit free benchmark calculation including the Br d electrons (18 electrons in total) and full triple excitations is also carried out to elucidate the effect of core–electron correlation. A fully relativistic CCSDT with 18 correlated electrons is feasible in principle with our current implementation, but has not been carried out due to extensive memory and computing time requirements. We perform single-reference (SR) and multi-reference calculations, where the latter are defined by a Complete Active Space (CAS) expansion with 6 (8) electrons in 4 (5) orbitals. The correlating orbital is the antibonding $\sigma^*_{1/2}$ with bromine and hydrogen contributions. All calculations are performed in the (double) point group $C_{2v}^{(*)}$.

4.2 Results and discussion

The results for the equilibrium bond length, the harmonic vibrational frequency, and the dissociation energy for various CC models and Hamiltonians are compiled in Table 2. The molecular bond is well described at all computational levels with very small deviations from experiment. For both basis sets the multi-reference treatment stretches the bond as does the inclusion of higher excitations in the calculation including full iterative triples (CCSDT) and MR models (MRCCSD). The same stretching is observed when spin–orbit interaction is included which is due to a weakening of the bond by a reduced σ-bonding character of the bonding valence p orbital on bromine. Increasing the basis set from DZ to TZ reduces the bond length and brings it closer to the experimental value. Correlating the $4s$ electrons results in a slight stretching of the bond which is compensated when the Br d electrons are included (CCSDT (18)). The bond contraction is caused by allowing for excitations out of the diffuse Br d orbitals. Spin–orbit coupling will lead to a bond elongation which almost exactly compensates for the final minute deviation of -0.0002 Å from the experimental value. However, we expect that the error from basis set incompleteness or the basis set superposition error (BSSE) with the TZ set are in the same order of magnitude.

For most of the calculations, an elongation of the bond is accompanied by a reduction of the harmonic frequency. The multi-reference methods produce in general somewhat lower harmonic frequencies than the corresponding single-reference method. Spin–orbit coupling reduces the harmonic frequency by 7 cm^{-1} in the TZ basis and by 6 cm^{-1} in the DZ basis. In the strive for harmonic frequencies with an accuracy of a few cm^{-1}, spin–orbit coupling is thus required even for a closed-shell molecule like HBr.

Table 2 Spectral constants of HBr using various CC models and the corresponding CI models with (SO) and without (SOF) spin–orbit interaction, single-reference and multi-reference (MR), and correlating (n) electrons

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
DZ SO CCSDT (6)	1.4159	2690.8	3.74
DZ SO MRCISD (6)	1.4173	2678.7	3.72
DZ SO MRCCSD (6)	1.4173	2685.2	3.73
TZ SOF MRCISD (6)	1.4145	2675.1	4.04
TZ SOF MRCCSD (6)	1.4148	2675.1	4.05
TZ SO MRCISD (6)	1.4151	2668.4	3.90
TZ SO MRCCSD (6)	1.4154	2668.0	3.90
TZ SOF MRCISD (8)	1.4180	2641.4	3.90
TZ SOF MRCCSD (8)	1.4192	2637.1	3.90
TZ SOF CCSDT (8)	1.4178	2647.3	3.96
TZ SO MRCISD (8)	1.4187	2634.9	3.77
TZ SO MRCCSD (8)	1.4193	2630.6	3.76
TZ SOF CCSDT (18)	1.4142	2663.9	4.01
TZ SOF CCSDT (18) +Δ_{SO}	1.4143	2657.4	3.77
Exp. [17]	1.41444	2648.975	3.92
apVTZ SO CCSD(T) (26) [34]	1.408	2706	3.92

Whereas the difference between MRCI and MRCC calculations is negligible for the small number of 6 correlated electrons, it becomes more pronounced when 8 electrons are correlated, and here the harmonic frequency is the property which is most affected (-4 cm^{-1}). The error of 15 cm^{-1} observed for the SOF CCSDT (18) calculation is explained to a large part by the neglect of spin–orbit interaction, and finally also by basis set incompleteness or the BSSE which increases the harmonic frequency.

The largest differences between the various calculations are observed for the dissociation energy. Clearly, single-reference CCSD treatments do not yield satisfactory results as they give too high energies for the separated atoms. The multi-reference calculations decrease the dissociation energy significantly. We illustrate the effect of the multi-reference treatment on full potential curves in Fig. 3 where the difference between the single- and multi-reference methods becomes obvious. The inclusion of higher excitations can of course also be achieved by increasing the general excitation level to full triples, as shown in Table 2. This calculation is more expensive computationally, though, than the MRCCSD run and does not give a higher accuracy. Addressing spin–orbit interaction, the decrease in dissociation energy has two sources: First, as already mentioned, there is a bond weakening due to the increased π character of the bonding spinor, and second, the spin–orbit splitting lowers the energy of the bromine ground

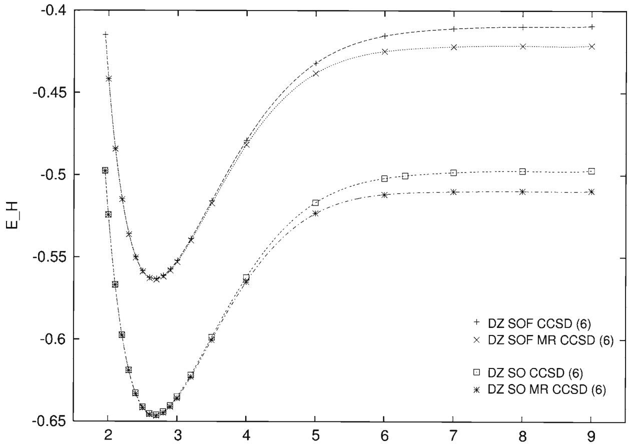

Fig. 3 Potential curves of the ground state of HBr neglecting (SOF) and including (SO) spin–orbit interaction. The energy offset is $-2,605\ E_H$

state in the atomic limit. The latter effect is the dominating.

The dissociation energy varies strongly with the extent of the basis set and the number of correlated electrons. Clearly, for obtaining the right answer for the right reason, a large basis set has to be used and at least 18 electrons have to be correlated. The dissociation energy resulting from the TZ SOF CCSDT (18) calculation is too high by roughly 0.1 eV. The increase of the dissociation energy through core–electron correlation is also found by Styszyński [35] at the CCSD(T) level (see also Table 2 for one reference calculation). However, spin–orbit interaction (as reported here) and a counterpoise correction [39] decrease the dissociation energy in this order of magnitude.

For a final comparison with experiment, we add a spin–orbit shift ($+\Delta_{\mathrm{SO}}$) to the properties obtained with the TZ SOF CCSDT (18) model which is the difference between the values with and without spin–orbit interaction at TZ MRCCSD(8) level. The bond length and vibrational frequency are now in excellent agreement with experiment, but the dissociation energy is slightly too low most likely due to remaining correlation (number of electrons) and basis set errors.

All of the calculations have been performed in serial on a Linux cluster equipped with Pentium IV Xeon 2.4 GHz processors, except for TZ SO MRCCSD(8) for which we required a machine with more core memory (IBM Regatta Power 4+). A single-point calculation at TZ SO MRCCSD(6) level which included about 36×10^6 terms in the extended CI space finished in one to two days with an allocation of roughly 3 GB of core memory. The spin–orbit free calculations TZ SOF CCSDT(18) were slightly less demanding, computationally. When correlating eight electrons including spin–orbit interaction (TZ SO MRCCSD(8), 224×10^6 terms in the extended space) the demand increased to 1 week runtime and roughly 12 GB of allocated core memory.

5 Conclusions and outlook

We present the initial implementation of a fully relativistic CC method which allows for multi-reference expansions and higher than CC double excitations. The current version is very general with respect to the definition of multi-reference spaces by means of the GAS technique, but it lacks optimal efficiency due to the CI-driven CC vector function evaluation. In a showcase application we demonstrate its applicability in the dissociation problem of the HBr molecule. Here, we show the effect of including spin–orbit interaction and higher excitations in calculations of full potential energy curves of the electronic ground state. When using multi-reference expansions and a basis set of triple-zeta quality, the final results for spectral properties of the molecule are in close agreement with experiment. The method is prepared for the application to heavy-element systems with a large number of open shells such as small actinide molecules.

For the treatment of systems where a large number of electrons needs to be correlated, i.e., exceeding about 10 to 12, the efficiency bottleneck forces us to alter the algorithm for evaluating the CC vector function. In current work, we are generalizing a commutator-driven evaluation of the CC vector function as implemented for the non-relativistic case by J. Olsen (unpublished) to the relativistic framework. This method will exhibit the optimal scaling of $O^n\ V^{n+2}$ as do conventional CC implementations and will open for the more accurate treatment of heavy-element compounds with a large number of correlated electrons and extensive basis sets.

The Kramers-unrestricted approach pursued here does not account for the time-reversal symmetry relations between CC amplitudes. We are currently exploring the implementation of various schemes for accounting for time-reversal symmetry at the many-particle level in general open-shell CC theory. A fully Kramers-symmetry adapted formulation entails a non-commuting CC formalism and will be implemented for a newly-developed suite of general contraction methods (J. Olsen, unpublished) including CC models.

We are furthermore exploring the calculation of excited states of different double group symmetry representation than the ground state, where a re-definition of the Fermi vacuum via relativistic MCSCF calculations yields the desired reference state. For the calculation of excited states of the same symmetry as the ground state, we are considering an initial implementation of linear response theory as it is utilized in the `DIRAC` program package for Hartree–Fock and MCSCF wave functions.

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