

KPACK: Relativistic Two-component *Ab Initio* Electronic Structure Program Package

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We describe newly developed software named KPACK for relativistic electronic structure computation of molecules containing heavy elements that enables the two-component *ab initio* calculations in Kramers restricted and unrestricted formalisms in the framework of the relativistic effective core potential (RECP). The spin-orbit coupling as relativistic effect enters into the calculation at the Hartree-Fock (HF) stage and hence, is treated in a variational manner to generate two-component molecular spinors as one-electron wavefunctions for use in the correlated methods. As correlated methods, KPACK currently provides the two-component second-order Møller-Plesset perturbation theory (MP2), configuration interaction (CI) and complete-active-space self-consistent field (CASSCF) methods. Test calculations were performed for the ground states of group-14 elements, for which the spin-orbit coupling greatly influences the determination of term symbols. A categorization of three procedures is suggested for the two-component methods on the basis of spin-orbit coupling manifested in the HF level.

Key Words : Electronic structure program, Relativistic quantum chemistry, Two-component method, Relativistic effective core potential, Group-14 elements

Introduction

There has been growing interest in the variational treatment of spin-orbit (SO)-coupling in *ab initio* calculations, especially at the self-consistent field (SCF) level.¹⁻⁵ The SO-coupling is a purely relativistic effect and is an important mechanism that couples the spin of the electron orbiting a nucleus to its orbital motion. This effect increases approximately as Z^4 and consequently, becomes significant and even comparable to the size of electron correlation for heavy atoms.³ Unfortunately, the SO-coupling cannot be treated in the framework of the nonrelativistic Schrödinger equation or the one-component scalar relativistic approach since the spin originated from the relativity is only introduced in *ad hoc* fashion. To fully incorporate the relativistic effects, the Dirac equation must be solved in the all-electron four-component framework, which is exact, but limited in the range of applicability (at most a few heavy atoms) due to too high computational cost by huge basis sets required.⁴ Instead, quasi-relativistic two-component approaches are often employed, and among a few available, the two-component SO relativistic effective core potential (SOREP) in particular has been demonstrated as an efficient alternative, for which only the valence (and semi-core) electrons are explicitly considered and the one-electron effective SO operators are provided.⁶⁻⁸

During the last two decades, our group had developed several relativistic quantum chemistry computer codes in the framework of the two-component SOREP, ranging from a simple SCF program to highly correlated methods.⁹⁻¹⁶ The development began with a focus on the self-consistent treatment of SO-coupling, and initially delivered a computer code for Kramers restricted Hartree-Fock (KRHF) method,⁹

in which time-reversal (or Kramers) symmetry was imposed on the one-electron functions, working in conjunction with the atomic orbital (AO) integral program ARGOS¹⁷ for the evaluation of SOREP integrals. The Kramers restricted versions of second-order Møller-Plesset perturbation theory (KRMP2)¹⁰ and configuration interaction (KRCI)^{11,12} codes were written in due succession for the incorporation of electron correlation upon the KRHF wavefunction. Also, a code for the evaluation of derivative integrals was devised in order for the geometry optimization at the KRHF level of theory.¹³ The two-component HF and MP2 methods without imposing time-reversal symmetry, which are called Kramers unrestricted HF (KUHF) and MP2 (KUMP2) respectively, were also proposed and programmed.¹⁴ Furthermore, the two-component Kramers restricted coupled-cluster (KRCC)¹⁵ calculation was made feasible by interfacing ARGOS into the all-electron four-component MOLFDIR suite of programs,¹⁸ which was then further modified and combined with a spinor rotation code to allow Kramers restricted complete-active-space SCF (KRCASSCF) calculation.¹⁶ Lee¹⁹ provided an extensive review on our former implementations and test results of a number of two-component methods, showing that it is possible to obtain reasonable spectroscopic and thermodynamic data for molecules containing heavy elements by using SOREP.

Although above implementations were successful in the technical realization of a series of two-component methods, the codes suffered from a major drawback, *uncorrealation*. The codes were developed independently of one another and therefore, were separately compiled into executable programs that often lack in cooperation or else are sequentially executed with the intercommunication of data occurred through

the storage devices, *e.g.*, hard-disk drives, which are usually slow. In addition, the codes were written in programming languages that have become obsolescent, and were serial-programmed and hence, it is impossible to exploit the potential of modern parallel processors. Moreover, not only the programs required individual inputs in various formats sometimes containing duplicate information, but also third-party programs noted above had to be run prior to or during the execution of our codes to fetch necessary integrals or coefficients, creating difficulties in the usage and leading to an error-prone program structure especially in the region of data transfer. The computational limits (*e.g.* maximum number of basis functions, highest angular momentum, *etc.*) were often forced by the third-party programs, restricting the capability of our programs. Besides, these third-party programs are now either ceased to develop or evolved to the next generation that are no longer compatible with our codes. For these reasons, a continual development of our two-component codes was hampered.

In 2009, recognition of above drawbacks led us to begin building a new relativistic electronic structure program package named KPACK, which is completely written from scratch and conforms to the recent Fortran standard. In developing KPACK, we placed major emphases on the efficiency through parallel processing and the integration of existing two-component methods into a single executable program, thereby surpassing the predecessors. Compared to the predecessors, the efficiency has been greatly improved by employing faster algorithms and parallelizing the computationally intensive sections for multi-core CPU and even many-core GPU processors. Also, the underlying theories were carefully revised and modified to ensure the numerical robustness near the region of convergence, where the predecessors were shown to experience some difficulties in converging. The missing features such as AO integral routines in the previous codes are now programmed and compounded, allowing KPACK to be an independent electronic structure program package. The KPACK is intended for relativistic calculations in the framework of the two-component SOREP that can be employed for larger molecules where

Table 1. List of two-component methods currently available in KPACK (marked ✓). The mark ✗ denotes the method either under development or included in the roadmap

	Kramers restricted	Kramers unrestricted	Spin-orbit ^a
Hartree-Fock	✓	✓	n/a
Møller-Plesset second-order perturbation theory	✓	✓	n/a
Configuration interaction	✓	✓	✓
Complete-active-space self-consistent field	✓	n/a	✗
Coupled-cluster theory	✗	✗	✗
Density functional theory	✗	✗	n/a

^aOne-component scalar relativistic one-electron orbitals are employed for the two-component treatment of spin-orbit coupling and electron correlation.

all-electron approaches are rather restricted, and also for the small to moderate sized molecules where highly correlated level of theories can be performed. The two-component methods that are currently available in the development version of KPACK are listed in Table 1.

The rest of the paper is organized as follows. First, a brief overview of the basic two-component theories and a summary of the implementation are given. Next, the ground state calculations for group-14 elements were performed as a test bed, through which the ability of various levels of two-component methods were assessed in terms of SO-coupling strength. Later, we suggest a new categorization of two-component procedures on the basis of the SO-coupling scheme present in the SCF stage, and finally the conclusions will be stated.

Theory and Implementation

SOREP and AO Integrals. The relativistic effects can be roughly divided into two sorts: the scalar relativistic (spin-free) effects, mostly from mass-velocity and Darwin terms, and the SO-coupling effects.²⁰ Both effects are conveniently treated in the framework of the two-component SOREP that consists of an (SO-)averaged RECP (AREP), which replaces the core electrons and also incorporates the scalar relativistic effects, and an effective one-electron SO operator⁸

$$U^{\text{SOREP}} = U^{\text{AREP}} + U^{\text{SO}}. \quad (1)$$

The theory and application of SOREP has been recently summarized in a review article by Dolg and Cao,⁵ which also provides a complete list of published SOREPs to date.

For a molecule with n valence electrons, the electronic two-component Hamiltonian operator with SOREP is expressed (in a.u.) as⁸

$$H = \sum_I^n h_I + \sum_{I>J}^n \frac{1}{r_{IJ}} + h_{\text{nuc}} \quad (2)$$

$$h_I = -\frac{1}{2}\nabla_I^2 + \sum_A^N \left(-\frac{Z_A^{\text{eff}}}{r_I} + U_A^{\text{SOREP}} \right) \quad (3)$$

where I, J denote the valence electrons, A denotes the nucleus, Z_A^{eff} and U_A^{SOREP} are the effective charge and the SOREP of the core A , and h_{nuc} is the nuclear repulsion energy. Although the form of the two-component Hamiltonian, Eq. (2), does not differ essentially from the nonrelativistic case, the SO contribution through the U^{SO} term introduces nonzero spin off-diagonal matrix elements, inducing the effective one-electron wavefunctions to be composed by mixture of two functions corresponding to α and β spins (hence the name two-component).²¹ Note that, in the one-component scalar relativistic scheme, the U^{AREP} term is merely adopted in the Hamiltonian and as a result, the effective one-electron wavefunctions can be described by a set of the functions of a single spin, so-called spin orbitals.

Like most other quantum chemistry packages, the KPACK also employs the real-valued atom-centered Gaussian basis

functions to calculate AO integrals *i.e.* the integrals over basis functions. The algorithms of McMurchie and Davidson²² and Pitzer and Winter²³ are employed to compute the one-electron AREP and SO integrals respectively, and other one-electron integrals such as overlap, kinetic, nuclear attraction integrals are evaluated using Obara-Saika recurrence relations²⁴ and Gauss-Hermite quadrature scheme.²⁵ The two-electron repulsion integrals are calculated through the recursive algorithm through Rys polynomials.²⁶⁻²⁸

KR/KU HF. In the relativistic regime, spin symmetry of nonrelativistic quantum chemistry is replaced by time reversal symmetry, for which corresponding operator for an electron can be written in an anti-unitary form²⁹

$$T = -i\sigma_y K_0 \quad (4)$$

where σ_y is the Pauli y -matrix applied on the spin and K_0 is the complex conjugation operator acting on the orbital. Solving the HF solution of the two-component Hamiltonian, Eq. (2), under time-reversal symmetry results in the KRHF method^{9,21,30,31} and the corresponding one-electron pseudo-eigenvectors are called spinors, which are generally complex-valued and form the doubly degenerate pairs called Kramers pairs³⁰ *i.e.* $(\varphi, T\varphi)$. It is also possible to perform the same HF procedure without imposing time-reversal symmetry, and that corresponds to the KUHF method.¹⁴

In the two-component HF theory, the underlying Fock equation is expressed identical to the nonrelativistic HF (see *e.g.* Ref. 32)

$$\mathbf{FC} = \mathbf{SCE}, \quad (5)$$

which can also be expressed in the form of spin blocked matrix equation²¹

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}_i^\alpha \\ \mathbf{C}_i^\beta \end{pmatrix} = \varepsilon_i \begin{pmatrix} \mathbf{S}^{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}_i^\alpha \\ \mathbf{C}_i^\beta \end{pmatrix} \quad (6)$$

where \mathbf{F} and \mathbf{S} are Fock and overlap matrices, and ε_i and \mathbf{C}_i are the energy and the coefficients for the spinor i . The nonzero spin off-diagonal blocks of Fock matrix are due to direct results of the SO integrals and additional two-electron exchange integrals.²¹ In the case of KRHF, time-reversal symmetry must be conserved during the diagonalization of Fock matrix and for this, we have implemented the diagonalization algorithms of Rösch³¹ and Dongarra *et al.*,³³ which are based on quaternion algebra. Moreover, Pulay's direct inversion in the iterative subspace (DIIS) procedure³⁴ has been modified for a two-component wavefunction and hired as an accelerator for SCF iteration.

MS Integrals. The molecular spinor (MS), an eigenfunctions of a two-component Fock matrix at the SCF convergence is given by

$$\varphi_i = \sum_\mu \sum_\sigma C_{\mu i}^\sigma \mu^\sigma \quad (7)$$

where φ_i denotes the i -th spinor, μ denotes the AO basis, σ denotes the associated spin functions, and $C_{\mu i}^\sigma$ is the

corresponding HF coefficients. The integral transformation from the AO to MS basis is performed prior to a post-HF stage in order to generate the one- and two-electron MS integrals defined by

$$[i|j] = \sum_{\mu\nu} \sum_{\sigma_1\sigma_2} C_{\mu i}^{\sigma_1*} C_{\nu j}^{\sigma_2} \int d\mathbf{r}_1 \mu^{\sigma_1*}(\mathbf{r}_1) h(\mathbf{r}_1) \nu^{\sigma_2}(\mathbf{r}_1) \quad (8)$$

$$[ij|kl] = \sum_{\mu\nu\rho\lambda} \sum_{\sigma_1\sigma_2} C_{\mu i}^{\sigma_1*} C_{\nu j}^{\sigma_1} C_{\rho k}^{\sigma_2*} C_{\lambda l}^{\sigma_2} \int d\mathbf{r}_1 d\mathbf{r}_2 \mu^{\sigma_1*}(\mathbf{r}_1) \nu^{\sigma_1}(\mathbf{r}_1) \frac{1}{r_{12}} \rho^{\sigma_2*}(\mathbf{r}_2) \lambda^{\sigma_2}(\mathbf{r}_2). \quad (9)$$

The nonrelativistic eight-fold permutational symmetry of electron repulsion integrals is no longer valid due to the complex coefficients, yet the Hermitian symmetry is retained and can be exploited to reduce the number of integrals to be evaluated. In our implementation of the MS transformation, the scheme devised by Esser *et al.*³⁵ is employed, in which, for the KRHF spinor sets, time-reversal symmetry is inserted into Eqs. (8) and (9) to produce two and eight distinct integral subsets of one- and two-electron integrals, respectively, reducing the required storage and operation count significantly. For the KUHF spinor sets, Eqs. (8) and (9) with the Hermitian symmetry are directly employed to implement the corresponding routines. The two-electron MS integrals are stored under Yoshimine sorting procedure³⁶ for one-dimensional indexing purpose and also random access.

KR/KU MP2. A simplest electron correlation can be reached by the MP2 theory,³⁷ which estimates electron correlation on top of HF energy by means of perturbation theory. The expression of the conventional MP2 energy is retained for a relativistic case

$$E^{(2)} = \sum_{i>j} \sum_{a>b} \frac{[ia|jb] - [ib|ja]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (10)$$

where i, j denote the occupied spinors, and a, b denote the virtual spinors. The major difference to a nonrelativistic MP2 is that the spinor energies and MS integrals are employed in the place of orbital energies and molecular orbital integrals. The Eq. (10) is directly coded for the KUMP2 routines and, for the KRMP2, the time-reversal symmetry applied expression²⁰ of Eq. (10) is employed to reduce the operation count by a factor of roughly 2.5. The earlier implementation of the KUHF and KUMP2 by Kim *et al.*¹⁴ was limited to configurations of even number of electrons owing to convergence problem. This issue has been resolved in KPACK and therefore, the calculations of open-shell states even with an odd number of electrons can readily be performed.

KR/KU CI. The eigenfunctions of approximate many-body Hamiltonian can be obtained *via* the CI method, in which the wavefunction is expressed as a linear combination of n -electron functions

$$\Psi^{\text{CI}} = \sum_p C_p \Phi_p \quad (11)$$

where Φ_p is a determinant based on the two-component HF

reference and C_p is the complex CI coefficient. Since the spinors are orthonormal, the two-component CI eigenvalue equation is

$$\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E} \quad (12)$$

where \mathbf{H} is the CI matrix, \mathbf{C} is the CI coefficients matrix, and \mathbf{E} is the diagonal matrix constituting the ground and excited states CI energies. The matrix element of the \mathbf{H} , *i.e.* $H_{pq} = \langle \Phi_p | H | \Phi_q \rangle$, can be evaluated using the Slater's rules³² and MS integrals similarly to the nonrelativistic case. The nonzero matrix elements occur between the determinants that differ by at most two spinors.

Due to the very large dimension of \mathbf{H} in Eq. (12), a computation of all eigenvalues or a full diagonalization is practically impossible and usually not required. The lowest few eigenvalues, which correspond to the energies of the ground and first few excited states, are necessary and can be obtained *via* Davidson diagonalization.³⁸ The original algorithm is intended for real-valued molecular orbitals and hence, applicable to a real symmetric CI matrix, however, the algorithm can be easily extended for a Hermitian matrix of the determinants from the two-component spinors. The CI routines of KPACK can work in conjunction with both KRHF and KUHF for the KRCI and KUCI procedures, respectively. It can be also used to perform SOCI calculations by simply omitting U^{SO} of Eq. (1) only for the HF stage.

KRCASSCF. The CASSCF method³⁹⁻⁴¹ as a multi-configurational SCF is usually applied to the systems of large static correlation, which differs from dynamical correlation by arising from the (nearly-)degenerate states. Jensen *et al.*^{42,43} devised a generalized MCSCF scheme in the four-component framework by employing the Kramers basis operators.⁴⁴ Kim and Lee¹⁶ took an alternative approach by employing the elementary spin excitation operator to extend the nonrelativistic CASSCF into the two-component framework, and following their approach, the theory of KRCASSCF was carefully revised and implemented to KPACK with many improvements.⁴⁵

The spinor space is divided into three categories as the nonrelativistic CASSCF: inactive, active and external. The inactive and external spaces have the occupation number of unity and zero, whereas the active space can have a varying occupation number. Although the KRCASSCF wavefunction can be expressed as a linear combination of determinants composed of optimized molecular spinors similar to the CI wavefunction [*cf.* Eq. (11)], the principal difference is in the simultaneous optimization of spinor and configuration. The optimized spinor set can be obtained by applying unitary transformation⁴⁶

$$\Psi' = \Psi\mathbf{U} \quad (13)$$

where the unitary matrix \mathbf{U} is composed of the anti-Hermitian spinor and configuration transformation matrices.

In our implementation of KRCASSCF, the two-step approach^{47,48} is employed; the configurations are first optimized with fixed spinor space followed by the rotation of the

spinor space with the pre-optimized configurations, and the same procedure is iterated until the convergence. For the optimization of configurations, the KRCI routines described above is employed to generate the CI coefficients, which, in turn, are used to compute the first- and second-order reduced density matrices. The spinor rotation parameters for the unitary transformation, Eq. (13), are then calculated through the second-order Newton-Raphson method where the gradients and Hessians are evaluated in terms of the reduced density matrix elements and MS integrals in a similar manner to the work by Fleig *et al.*,⁴⁹ however, differed by the type of excitation operators employed in the derivation.

Implementation. As shown in Figure 1, the KPACK is currently composed of six modules with each module being associated with a specific theory discussed above and is written entirely in fully standard-compliant Fortran 95. The computationally intensive sections of the code (*e.g.* construction of Fock matrix, Davidson algorithm, *etc.*) are parallel-programmed in order to fully exploit the resources provided by the multi-core CPU and many-core GPU processors. The OpenMP APIs⁵⁰ for CPUs and CUDA programming model^{51,52} for GPUs are employed for the parallel processing. To maximize the efficiency in the computation of linear algebra, the processor-optimized BLAS and LAPACK libraries (*e.g.* Intel MKL) have also been employed wherever necessary.

In order to fully utilize the parallelization feature of KPACK, we recommend a system with multi-core CPU and CUDA-enabled GPU card under Linux OS; for instance, the program has been developed and tested on the PC featuring Intel Core i7-3960x six-core CPU, NVIDIA Tesla C2050 GPU card. The physical limit is usually imposed by the size of core-memory (RAM) since KPACK stores the integrals in the RAM for a rapid access. As the maximum size of RAM increases through process generations, a modern high-end

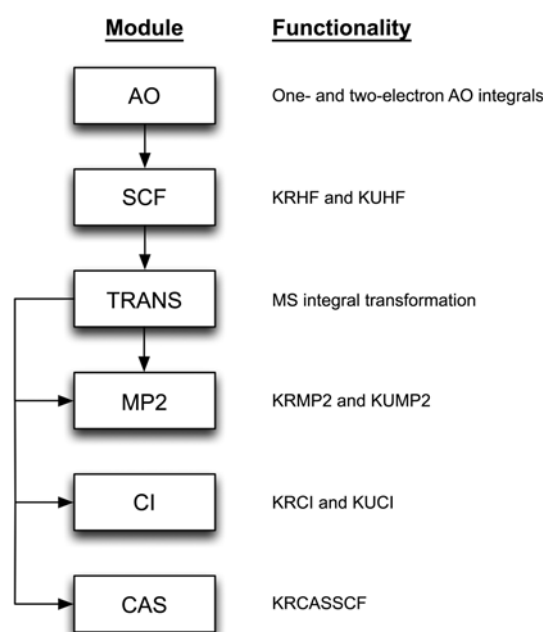


Figure 1. Modules and their functionalities of KPACK. The arrows indicate the flow of program.

CPU architecture such as Sandy Bridge-E processor can support up to 64GB of memory, large enough to store the MS integrals of active space of approximately 250 Kramers pairs in C_1 symmetry. The integrals can also be chosen to be stored in the hard disk drive if the required storage exceeds the size of RAM, but are then accessed with much higher latency.

Test Calculation

Group-14 Elements. The ground term symbol of group-14 elements is a well-known example that is strongly affected by the change of SO-coupling scheme from LS - to jj -coupling, going down the group.⁵³ The two limiting coupling schemes for the electronic configuration of p^2 for neutral atoms lead to following ground terms:

LS -coupling: open-shell 3P_0 term,
 jj -coupling: closed-shell $(1/2, 1/2)_0$ term.

As can be seen from Figure 2, the shell structure of ground state changes gradually from a triplet (3P_0) to a singlet $(1/2, 1/2)_0$ as the SO-coupling increases. The light atoms, C and Si, can be assigned to a purely LS -coupling, whereas the large SO splitting shown in the heaviest homologue Fl (also known as element-114) is attributed to the jj -coupling, exhibiting some sort of a chemical inertness by the filled $7p_{1/2}$ spinor shell⁵⁴. The intervening atoms in the group, Ge, Sn and Pb, have the SO-coupling *intermediate* between the two limiting cases, thus, their ground state is neither triplet nor singlet, but rather having a multi-configurational character.

Computational Details. We report the test calculations performed using the KPACK package developed in this work, for the *intermediate*-coupling metals of group-14, Ge, Sn and Pb, in order to assess how well such coupling can be dealt with various two-component methods. The analysis

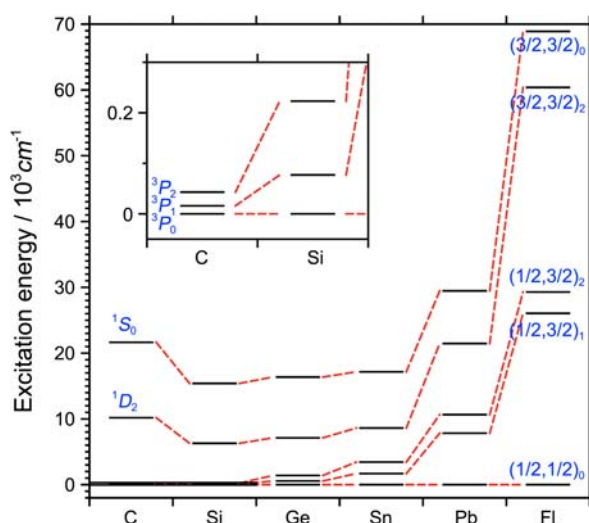


Figure 2. Energy levels of the terms arising from p^2 configuration for group-14 elements. The inset shows the splitting in 3P term of C and Si in greater details. Experimental values⁶⁵ for C-Pb, and theoretical results^{66,67} for Fl are used.

Table 2. Energy deviations (δE , in mh) relative to *full*-CI and number of unpaired electrons^a (N_s) for one- and two-component HF calculations of ground states of Ge, Sn and Pb

	Ge	Sn	Pb
AREP-UHF ^b	28.87 (2.0)	32.36 (2.0)	103.90 (2.0)
KRHF	54.22 (0.0)	43.74 (0.0)	66.25 (0.0)
KUHF	26.60 (1.99)	25.68 (1.94)	65.00 (1.12)

^aValues are given in parentheses. ^bOne-component scalar relativistic level.

was carried out by examining the energy deviation (δE) of each method from the *full*-CI result. Throughout this section, the energy is given in the unit of *mhartree* (mh). The large-core energy-adjusted SOREPs (ECPNMDF type) of Stuttgart-Cologne group^{55,56} were employed for the metals. With this SOREP, a neutral atom has 4 valence electrons in the outermost shell with ns^2np^2 electronic configuration and the core electrons are replaced by the potential. The accompanying basis sets in an uncontracted form were used: (6s6p) for Ge and Sn, (6s6p2d) for Pb. It is a common practice to decontract the basis set for the two-component calculation since the basis functions have often been contracted for the one-component scalar relativistic calculations, which could be insufficient for describing the orbital polarization by SO-coupling.

KR/KU HF Results. The δE 's of the one-component scalar relativistic AREP-UHF and the two-component KRHF and KUHF levels of theory for Ge, Sn and Pb are listed in Table 2. For all cases, the lowest energies are obtained by KUHF method and the reason is straightforward; the SO-coupling, in general, lowers the energy of ground state from the non-relativistic case, and the unrestricted of time-reversal symmetry adds an extra flexibility to the wavefunction further lowering the energy. To illustrate the behavior of KUHF at varying SO-coupling strengths exhibited by the metals, the energy difference (ΔE) of the UHF and KRHF energies with respect to the KUHF energy (denoted as ΔE_{KUHF}^{UHF} and ΔE_{KUHF}^{KRHF}) were measured (Figure 3), where the point reach-

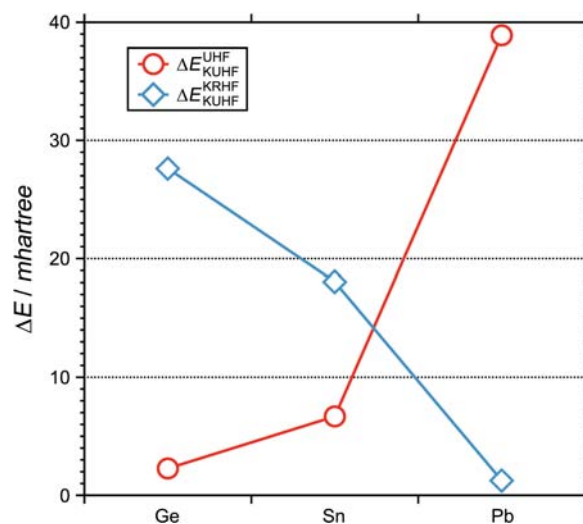


Figure 3. Plot of ΔE_{KUHF}^{UHF} and ΔE_{KUHF}^{KRHF} for Ge, Sn, and Pb.

ing the horizontal axis implies, at least, the energy convergence of the two compared methods.

The small value of $\Delta E_{\text{KUHF}}^{\text{UHF}}$ of Ge suggests that KUHF behaves as the scalar relativistic (*LS*-coupling) AREP-UHF rather than KRHF as also evidenced by a much higher $\Delta E_{\text{KUHF}}^{\text{KRHF}}$ value, proving that the *jj*-coupling is an ill-suited scheme for Ge. The UHF-like behavior of KUHF for a weak SO-coupling is indicative of that the open-shell triplet structure by Hund's rule of maximum multiplicity is dominant over the SO splitting for a given orbital angular momentum in the KUHF wavefunction. It will be shown later in this section that the KUHF wavefunction of Ge is, indeed, a triplet through the calculation of the number of unpaired electrons.

As expected for heavier homologue, an opposite trend from Ge was seen for Pb, in which large $\Delta E_{\text{KUHF}}^{\text{UHF}}$ and small $\Delta E_{\text{KUHF}}^{\text{KRHF}}$ values are observed, indicating that the energy level of $p_{1/2}$ spinor is considerably lowered by the strong SO-coupling and hence, the $J=0$ ground state is preferred with a leading *jj*-coupling $(1/2, 1/2)_0$ configuration. Of course, the neglect of SO-coupling for Pb in the AREP-UHF calculation produced an incorrect result as shown by the large δE value, which is approximately 40 *mh* larger than those of the KRHF and KUHF energies.

For Sn atom, which possesses a stronger SO-coupling than Ge yet weaker than Pb, the coupling scheme was found to be *intermediate*, as both E points in the plot lay above the axis, but the lower value of $\Delta E_{\text{KUHF}}^{\text{UHF}}$ than $\Delta E_{\text{KUHF}}^{\text{KRHF}}$ suggest that, to some extent, the coupling is closer to *LS*- than *jj*-scheme. Although not reported in the table, the KUHF result of Fl, which exhibits an enormous SO-coupling compared to the lighter homologues, were shown to converge to the KRHF energy, demonstrating that the *jj*-coupling is automatically imposed during the SCF iterations. To summarize, the KUHF is able to capture the transition of SO-coupling schemes in descending group-14, from the *LS*- to the *jj*-coupling through the *intermediate*-coupling region.

Even though the spin is no longer a good quantum number in the relativistic case, the number of unpaired electrons N_S (Table 2) may provide insight into the characteristic of KUHF wavefunction, which can be calculated by⁵⁷

$$N_S = 2\sqrt{\langle S_x \rangle^2 + \langle S_y \rangle^2 + \langle S_z \rangle^2}. \quad (14)$$

Note that the filled closed-shell $p_{1/2}$ spinor in the KRHF results in $N_S=0$, while the open-shell triplet UHF wavefunction leads to $N_S=2$. The calculated N_S for Ge and Sn are noninteger number, yet quite close to the N_S of UHF *i.e.* a triplet. Therefore, the SO-coupling schemes for Ge and Sn are likely to be the *LS*-coupling, as confirmed above by the smaller value of $\Delta E_{\text{KUHF}}^{\text{UHF}}$. The low value of N_S for Pb, approximately 1.1, suggests a large deviation from the *LS*-coupling, but is still far from zero, even though the previous calculations implied the *jj*-coupling. It is possible that the N_S might be overestimated due to a mixing of higher energy states, which is inherent in the unrestricted formalism (*cf.* spin-contamination in nonrelativistic UHF) and thereby,

Table 3. Energy deviations (δE , in *mh*) relative to *full*-CI for two-component MP2 and CI calculations of ground states of Ge, Sn and Pb

	Ge		Sn		Pb	
	KR	KU	KR	KU	KR	KU
MP2	27.58	10.14	21.11	11.83	19.68	21.45
CISD	7.17	1.92	4.60	3.51	3.43	5.19
CISDT	1.92	1.34	3.81	2.30	2.22	2.57
CISDTQ ^a	0	0	0	0	0	0

^a*Full*-CI level.

resulting N_S value being shifted to but not crossing the *LS*-coupling limit. Therefore, the N_S values may not be a good measure to estimate the position of the coupling scheme between the two extremes, but still provide valuable information in determining the character of KUHF wavefunction. We believe that this mixing is the driving force for KUHF to describe the *intermediate*-coupling properly at the HF level of theory.

KR/KU MP2 and CI Results. Table 3 summarizes the δE 's of the two-component Kramers restricted and unrestricted calculations in MP2 and CI levels of theory. At the *full*-CI level both KRCI and KUCI converges to the same energy, proving the correctness of our implementation. For Ge and Sn, the inadequacy of the KRHF result by a convergence to the $(1/2, 1/2)_0$ state leads to a pronounced effect on the quality of KRMP2 where $\delta E(\text{KRMP2})$ is 2-3 times larger in energy than $\delta E(\text{KUMP2})$. The KRMP2 errors could be as much as 17 *mh* larger than the KUMP2 one. This effect appeared less severe for KRCI, in which the variational treatment of electron correlation partly recovered the open-shell character as implied by the high contributions from excited determinants in the final CI vector. In the case of Ge, although $\delta E(\text{KRCISD})$ was found roughly 4 times larger than $\delta E(\text{KUCISD})$ the difference only amounted to about 5 *mh*. The difference between KR and KU formalisms became almost negligible when the triple excitations were included. For weak SO-coupling cases, the KUCI shows a better performance at the same CI excitation level compared to KRCI, mainly due to the appropriate open-shell configuration obtained in the KUHF reference.

Again, the heavier Pb atom shows a preference towards the *jj*-coupling by slightly lower δE 's in both KRMP2 and KRCI calculations than the corresponding unrestricted calculations and this is in contrast to the two-component HF results where KUHF predicted a lower energy by about 1 *mh*. This is probably due to the contamination in the KUHF solution as mentioned earlier, in which the excited states mix into the single configuration, lowering the energy. Nevertheless, for Pb, the energy difference between any KR and KU methods signifies little (< 2 *mh*).

KRCASSCF Results. The KRCASSCF calculations were performed with the valence p -orbital as active space, and the δE 's and the populations of $p_{1/2}$ and $p_{3/2}$ spinors are given in Table 4. The δE 's of Ge and Sn were in the range of 20-25 *mh*, while that of Pb was 54 *mh* roughly twice larger due to

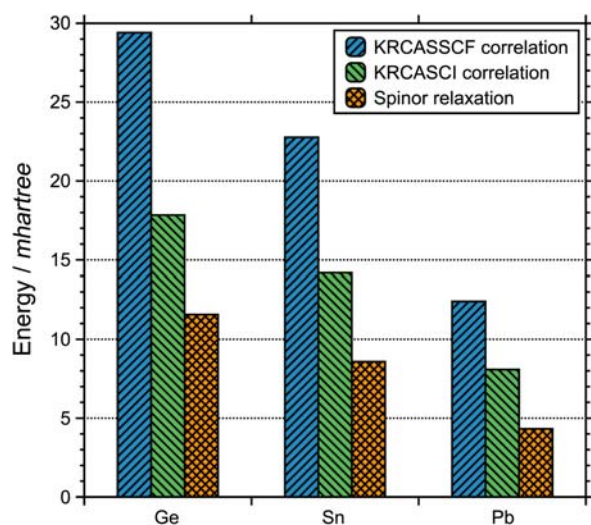
Table 4. Energy deviations (δE , in *mh*) relative to *full*-CI for two-component KRCASSCF calculations and the populations of $p_{1/2}$ and $p_{3/2}$ spinors for Ge, Sn and Pb

	Ge	Sn	Pb
δE			
KRCASSCF	24.81	20.97	53.85 (20.25) ^a
Population			
$p_{1/2}$	1.43	1.56	1.84
$p_{3/2}$	0.57	0.44	0.16

^aResult without *d*-basis functions (see text for details).

the presence of *d*-basis functions for Pb, that were absent for Ge and Sn. The *d*-functions brought an additional lowering in the *full*-CI energy by the correlation with *d*-orbitals, and hence the *full*-CI energy was re-calculated without *d*-functions, showing that δE of Pb was to be in similar magnitude with the others. This implies that KRCASSCF can produce energies in similar quality regardless of the SO-coupling strengths, and a certain degree of open-shell characteristic of group-14 atoms may be recovered through the rotation of the spinor space *via* the multi-configurational approach, making a fruitful use of KRHF reference, which has been previously shown to be improper for weak SO-coupling cases. The examination of KRCASSCF populations of Ge and Sn shows that about one half electron resides in the $p_{3/2}$, spinor, at which a considerable excitation has been made in order to restore the *LS*-coupling. Although Pb appeared quite *jj*-coupling, there is a non-negligible population in $p_{3/2}$ amounting approximately 8%, in agreement with the result of Liu *et al.*⁵⁸

In Figure 4, the electron correlation energies of the KRCASSCF and KRCASCI ($\Delta E_{\text{KRCASSCF}}^{\text{KRHF}}$ and $\Delta E_{\text{KRCASCI}}^{\text{KRHF}}$), and the spinor relaxation energy are shown. The reason for the decrease in the KRCASSCF correlation energy down the group, *e.g.* the correlation energy for Pb was almost halved compared to Ge, is as follows; the SO-coupling becomes

**Figure 4.** Correlation energies of two-component KRCASSCF and KRCASCI levels of theory, and spinor relaxation energy (see text for details) for Ge, Sn and Pb.

stronger and the electronic structure is better described by the single configuration (*jj*-coupling) KRHF, hence less correlation energy. The KRCASCI denotes a *full*-CI among the valence *p*-electrons sharing some similarities with KRCASSCF, but lacks the optimization of spinor space that is strongly related to the static correlation such that the energy difference between KRCASSCF and KRCASCI ($\Delta E_{\text{KRCASSCF}}^{\text{KRCASCI}}$), can be regarded as spinor relaxation energy. The spinor relaxation energy may be interpreted as the quantity that the KRHF fails to address. It is apparent that the quality of KRCASCI degrades quickly as the SO-coupling becomes weaker. The results indicate that the mere treatment of dynamical correlation through the CI procedure is simply insufficient and the static correlation with at least minimal active space seem crucial to revert the SO-coupling scheme from the *jj*- to the *LS*-coupling for weak SO-coupling cases.

Discussion

Conventionally, the two-component approaches were classified into two major procedures, the *jj*-coupling and the *intermediate*-coupling, according to the stage at which SO-coupling enters into the computation.³ The *jj*-coupling procedure indicated that the SO-coupling was treated self-consistently in the HF level of theory to generate the molecular spinors for subsequent correlated methods, whereas the *intermediate*-coupling procedure described both SO and electron correlation effects to be taken into consideration only in the post-HF stage. Such categorization assumed that one could only commence the correlation calculation with either extreme of the SO-coupling scheme, namely *LS*- or *jj*-coupling schemes.

After having demonstrated that the KUHF exhibits somewhat *mixed*-coupling procedure in the HF level, we would like to suggest the following categorization of two-component correlated methods into three procedures based on the SO-coupling scheme manifested in the SCF rather than the stage of introduction:

(1) *LS*-coupling procedure: One-component scalar relativistic (*LS*-coupling) molecular orbitals are utilized as the one-electron basis and the SO-coupling and the electron correlation effect are treated on the same footing in the post-HF stage. As noted, this corresponds to the conventional *intermediate*-coupling procedure and is often referred to as the SO methods. So-called SOCI^{17,59-62} and SOCC,⁶³ in which the SO operator is treated through the CI and CC methods, respectively, upon the AREP-HF solution, will belong to the *LS*-coupling procedure.

(2) *jj*-coupling procedure: The two-component correlated methods such as KRMP2, KRHF, KRCASSCF and KRCC belong to this procedure, which employ the two-component KRHF spinors. In the KRHF, time-reversal symmetry and the self-consistent treatment of the SO operator always lead the one-electron wavefunctions to conform the *jj*-coupling scheme where the electrons will occupy $l-1/2$ spinor shell before filling $l+1/2$.

(3) *mixed*-coupling procedure: In KUHF, the SO operator

is treated in the HF level, and time-reversal symmetry is lifted to allow an additional flexibility in the wavefunction. Such process generates the broken-symmetry solutions with a mixture of *LS*- and *jj*-coupling schemes whose dominances are determined by the strength of SO-coupling. Any correlated method based on KUHf reference falls into this procedure type (e.g. KUMP2, KUCI).

All above procedures do converge to the same limit at the *full*-CI level as far as the same basis functions are concerned, however, the *full* electron correlation can hardly ever be applied in practice due to an unaffordable computational cost. Therefore, at an affordable level of electron correlation (usually up to doubles) the accuracy of these procedures largely depend on the adequacy of the SO-coupling described in the employed one-electron basis, since a high level of excitation is then not required to properly describe the SO-coupling in the post-HF step. Note that for certain *LS*-coupling procedures, despite large spatial difference between the *LS*-orbitals and the *jj*-spinors, the orbital relaxation by strong SO-coupling can be described satisfactorily in the correlated step through the exploited methodology, e.g. SOCCSD performs significantly better over the SOCI counterpart in the *jj*-coupling regime, producing results comparable to the KRCCSD.⁶⁴ Although the present categorization is derived from the use of SOREP, which provides a convenient separation of scalar relativistic and SO effects, this may be extended to other relativistic Hamiltonians if modified appropriately.

Conclusions

The development of a relativistic two-component electronic structure program KPACK has been reported, which succeeds our group's previous code developments by the augmentation and improvement of functionalities, and is fully rewritten for modern parallel processors. The program offers efficient relativistic quantum chemistry calculations for molecules containing one or more heavy elements in the framework of a two-component SOREP and is mainly designed to perform the two-component HF, MP2, CI and CASSCF calculations in Kramers restricted and unrestricted formalisms, in which the SO-coupling is treated self-consistently. The future extension will include relativistic coupled-cluster theory and density functional theory as well as geometry optimization, and some progress is being made. The public beta release of KPACK will be available shortly.

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