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Two-component Kramers restricted complete active space self-consistent field method with relativistic effective core potential revisited: Theory, implementation, and applications to spin-orbit splitting of lower p -block atoms

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The relativistic two-component complete active space self-consistent field theory in Kramers restricted formalism (KRCASSCF) through the framework of the spin-orbit relativistic effective core potential is implemented into the KPACK package. This paper continues the development previously reported [Y. S. Kim and Y. S. Lee, *J. Chem. Phys.* **119**, 12169 (2003)] and extends the theory by means of adding time-reversal symmetry into the relevant expressions so as to complete the course of theoretical development. We retained the usage of elementary spinor excitation operator for defining the spinor rotation operator and derived the gradient and Hessian in simpler forms than previously found. To eliminate redundant computation resulting from repeating sums in the derivatives, a suitable decomposition method is proposed, which also facilitates the implementation. The two-step near second-order approach is employed for convergence. The present implementation is applicable for both closed- and open-shell systems and is used to calculate the atoms of lower p -block. The results for $5p$ and $6p$ are in good agreement with the experiments, and those for $7p$ are comparable to multi-reference configuration interaction results, showing that KRCASSCF is a versatile tool for the relativistic electronic structure calculation of molecules containing moderate-weight through superheavy elements. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822426>]

I. INTRODUCTION

The inseparable interplay between spin-orbit coupling and electron correlation effects for molecules containing one or more heavy elements requires that the spin-orbit coupling is treated variationally at the self-consistent field (SCF) level of theory in order for a proper description of the correlation.¹ This is especially important in the calculation of static correlation, which arises from near-degeneracy, as the energetic separation between the valence orbitals are not only small, the spin-orbit coupling also splits a degenerate orbital ($l > 0$) in an atom into the energetically close $l + \frac{1}{2}$ and $l - \frac{1}{2}$ spinors. Therefore, a multi-configurational approach in the multi-component relativistic framework based on Dirac equation is desirable, since the framework of the nonrelativistic Schrödinger equation or the one-component scalar relativistic approach does not directly treat the spin-orbit coupling but only in *ad hoc* fashion.

The fully relativistic all-electron four-component theory is exact but rather limited in the range of applicability to, at most, a few heavy atoms owing to the unaffordable computational cost.² Instead, the quasi-relativistic two-component approaches are often employed as an efficient alternative and, in particular, the relativistic effective core potential (RECP)³⁻⁵ as an approximate two-component method has gained popu-

larity for the efficiency by considering the valence (and semi-core) electrons explicitly and also by a high degree of reliability comparable to the all-electron calculations. The recent two-component RECP is referred to as spin-orbit RECP (SOREP) and provides one-electron effective spin-orbit operators, which can be utilized in the SCF stage with time-reversal symmetry to manifest *jj*-coupling in one-electron functions.⁶

As an approach to treat static correlation in the nonrelativistic theory, multi-configurational (MC)SCF theory has been devised, in which orbital space and configurations are simultaneously optimized. The MCSCF methods are usually classified by the manner of specifying the spaces, and the most widely used one is the complete active space (CAS)SCF of Roos and co-workers,⁷⁻⁹ for which the wavefunction is conveniently defined by choosing the active orbitals.¹⁰ The theory of nonrelativistic MCSCF has been extended to four-component framework by Jensen *et al.*,¹¹ later to two-component by Fleig *et al.*,¹² and both employed Kramers basis operators,¹³ the excitation operators that conform time-reversal symmetry, in placement of spin summed excitation operators appearing in the orbital rotation operator. Kim and Lee¹⁴ took an alternative approach by employing elementary spinor excitation operators instead of the Kramers bases, which tend to generate rather complicated expressions, in search of simpler equations for Kramers restricted (KR)CASSCF; however, the formulated gradients and

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Hessians were deficient in time-reversal symmetry, even though the method relied on the inherent time-reversal symmetry in one-electron functions. Thyssen *et al.*¹⁵ reported an implementation of KRMCSF formulated in Ref. 11, and recently, Ganyushin and Neese¹⁶ presented a derivation and implementation of the CASSCF approach, in which spin-orbit coupling is variationally treated while retaining the one-component framework. Furthermore, the inclusion of dynamical correlation onto the multi-configurational wavefunction through the configuration interaction (CI), KRMCSF/CI,¹⁷ and the second-order perturbation theory, DC-CASPT2,¹⁸ has also been reported.

In present work, the formulation of two-component KRCASSCF theory with the SOREP begun in Ref. 14 are continued and a full implementation is reported. We retained the use of elementary excitation operators in the expansion of spinor rotation operator, which composites the unitary transformation in the spinor space, but time-reversal symmetry is now applied to the resulting expression of the derivatives. Moreover, the spinor gradient and Hessian are decomposed into small number of sums that renders the expressions to even simpler forms, and the redundant work in the evaluation can be reduced. Test calculations are performed on atomic properties such as excitation energy and ionization potential for the lower p -block elements and compared with the CASSI-SO¹⁹ method. Through the examination of total energy difference and occupations in the relevant spinors, the characteristic of KRCASSCF is also analyzed.

The paper is organized as follows. In Sec. II, the underlying theory is presented, followed by the details of implementation in Sec. III. Applications of the present KRCASSCF implementation to the lower p -block atoms are given in Sec. IV. Finally, the conclusion is given in Sec. V.

II. THEORY

All equations are written in atomic unit. The indices p, q, \dots refer to general spinors, $i, \bar{i}, j, \bar{j}, \dots$ to particular spinors of Kramers pairs, while m, n, u, v correspond to non-specific spinors of Kramers pairs.

A. Two-component Hamiltonian with SOREP

The two-component n valence electron Hamiltonian with SOREP is expressed as⁵

$$\hat{H} = \sum_I \hat{h}_I + \sum_{I>J} \frac{1}{r_{IJ}} + h_{\text{nuc}}, \quad (1)$$

$$\hat{h}_I = -\frac{1}{2} \nabla_I^2 + \sum_A \left[-\frac{Z_A^{\text{eff}}}{r_{IA}} + \hat{U}_A^{\text{SOREP}} \right], \quad (2)$$

where I, J denote the valence electrons, A denotes the nucleus, Z_A^{eff} and \hat{U}_A^{SOREP} are the effective charge and the SOREP of the core A , and h_{nuc} is the nuclear repulsion energy. The \hat{U}^{SOREP} for an atom is defined as³

$$\hat{U}^{\text{SOREP}} = \sum_{l=0}^{\infty} \sum_{j=|l-1/2|}^{l+1/2} U_{ij}^{\text{SOREP}}(r) \sum_{m=-j}^j |l j m\rangle \langle l j m|, \quad (3)$$

where l and j denote the orbital and the total angular momentum quantum number, m denotes the magnetic quantum numbers for the given j , and $|l j m\rangle \langle l j m|$ is the two-component projection operator. The first summation of above equation is often constrained to certain angular momentum L , at which the contribution from the higher angular momenta are summed into a single term or neglected entirely. The scalar relativistic (spin-free) effects, mostly from mass-velocity and Darwin terms, and the spin-orbit coupling effects can be conveniently treated in the framework of the two-component SOREP by rewriting Eq. (3) as the sum of (spin-orbit)-averaged RECP (AREP), which replaces the core electrons and also incorporates the scalar relativistic effects, and an effective one-electron spin-orbit operator:^{5,20}

$$\hat{U}^{\text{SOREP}} = \hat{U}^{\text{AREP}} + \hat{H}^{\text{SO}}, \quad (4)$$

with

$$\hat{U}^{\text{AREP}} = U_L^{\text{AREP}}(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^l \times [U_l^{\text{AREP}}(r) - U_L^{\text{AREP}}(r)] |l m\rangle \langle l m|, \quad (5)$$

$$\hat{H}^{\text{SO}} = \hat{s} \cdot \sum_{l=1}^L \frac{2}{2l+1} \Delta U_l^{\text{SOREP}}(r) \times \sum_{m=-l}^l \sum_{m'=-l}^l |l m\rangle \langle l m| \hat{l} |l m'\rangle \langle l m'|, \quad (6)$$

where $U_l^{\text{AREP}}(r) = (2l+1)^{-1} [l \cdot U_{l,l-1/2}^{\text{SOREP}}(r) + (l+1) \cdot U_{l,l+1/2}^{\text{SOREP}}(r)]$ and $\Delta U_l^{\text{SOREP}}(r) = U_{l,l+1/2}^{\text{SOREP}}(r) - U_{l,l-1/2}^{\text{SOREP}}(r)$. The spin-orbit integrals of \hat{H}^{SO} are purely imaginary²¹ and contribute to spin off-diagonal matrix elements, inducing the one-electron wavefunctions to be composed by mixture of α and β spin functions, and hence, two-component. On the other hand, the omission of \hat{H}^{SO} in the calculation corresponds the one-component scalar relativistic approach and shares the non-relativistic methodology. More details of SOREP are described in Refs. 22 and 23.

In the relativistic regime, the spin symmetry for orbitals in the nonrelativistic or scalar relativistic theory is no longer valid and replaced by time-reversal (also known as Kramers) symmetry, leading to the relativistic extension of spin-restricted Hartree-Fock (RHF) into Kramers restricted (KR)HF method.^{6,24-26} The time-reversal operator can be written in an anti-unitary form for an electron as²⁷

$$\hat{T} = -i \sigma_y \hat{K}_0, \quad (7)$$

where σ_y is the Pauli y -matrix applied on the spin part and \hat{K}_0 is the complex conjugation operator acting on the orbital part. Then, two-component Fock equation is given by²⁴

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & -\mathbf{F}^{\beta\alpha*} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\alpha\alpha*} \end{pmatrix} \begin{pmatrix} \mathbf{c}_i^\alpha \\ \mathbf{c}_i^\beta \end{pmatrix} = \varepsilon_i \begin{pmatrix} \mathbf{c}_i^\alpha \\ \mathbf{c}_i^\beta \end{pmatrix}, \quad (8)$$

where \mathbf{F} is the two-component Fock matrix, the one-electron eigenvector \mathbf{c} is called spinor, and the eigenvalue ε is the spinor energy. The spin diagonal $\mathbf{F}^{\alpha\alpha}$ is a hermitian matrix, while the spin off-diagonal $\mathbf{F}^{\beta\alpha}$ is a complex anti-symmetric

matrix and nonzero by direct results of the spin-orbit integrals and additional two-electron exchange integrals. The spinors of KRHF form the doubly degenerate pairs called Kramers pairs related through Eq. (7) as

$$\hat{T} |i\rangle = \hat{T} \begin{pmatrix} \mathbf{c}_i^\alpha \\ \mathbf{c}_i^\beta \end{pmatrix} = \begin{pmatrix} -\mathbf{c}_i^{\beta*} \\ \mathbf{c}_i^{\alpha*} \end{pmatrix} = |\bar{i}\rangle. \quad (9)$$

Since the spin-orbit coupling is introduced in the atomic bases and treated self-consistently, KRHF can be regarded as the *jj*-coupling approach. The KRHF wavefunction is a single Slater determinant composed of Kramers pairs and has been widely employed as a starting point for elaborate correlated methods.^{14,28,29}

B. Fundamentals of KRCASSCF

The basic idea of nonrelativistic MCSCF,³⁰ which is a simultaneous optimization of both configuration and orbital spaces, is retained in the relativistic two-component case, but the reformulation is necessary since (i) the real orbital becomes the complex spinor, which is doubled in size and requires complex arithmetic operations, and (ii) the excitations and the rotations between barred and unbarred spinors are allowed, giving rise to larger matrix dimensions and complications in the mathematical expressions.

The relativistic MCSCF trial wavefunction is expressed as the linear combination of *n*-electron functions such as determinants composed of the spinors from an initial KRHF calculation:

$$|0\rangle = \sum_{\mathbf{m}} C_{\mathbf{m}} |\mathbf{m}\rangle. \quad (10)$$

Then, the optimized wavefunction can be obtained by applying the unitary transformation

$$|0'\rangle = \hat{U} |0\rangle, \quad (11)$$

$$\hat{U} = \exp(\hat{A}) \exp(\hat{S}), \quad (12)$$

where \hat{A} and \hat{S} are the anti-Hermitian spinor and configuration transformation operators, respectively, for the optimizations of the spinor coefficients in the determinants and the corresponding configuration coefficients in Eq. (10). Note that the CI method can be regarded as a special case of MCSCF, for which the orbitals (or spinors) are kept frozen. The operator \hat{A} can be written in terms of spinor rotation parameters and elementary spinor excitation operators as

$$\hat{A} = \sum_{p>q} [a_{pq} \hat{E}_{pq} - a_{pq}^* \hat{E}_{qp}], \quad (13)$$

$$\hat{E}_{pq} = \hat{a}_p^\dagger \hat{a}_q, \quad (14)$$

where \hat{a}^\dagger and \hat{a} are the elementary creation and annihilation operators in the spinor space. Note the anti-Hermiticity relation in the rotation parameters in Eq. (13). In the determination of these parameters, the elimination of the redundant and undesired rotations including inactive-inactive, active-active and

external-external are crucial for minimizing numerical problems during the rotation.⁹ The operator \hat{S} is defined by

$$\hat{S} = \sum_{K \neq 0} (s_{K0} |K\rangle \langle 0| - s_{K0}^* |0\rangle \langle K|), \quad (15)$$

where $|K\rangle$ is the orthogonal complement to the wavefunction $|0\rangle$.

The convergence in MCSCF wavefunction is reached by locating the stationary point of the energy hypersurface, i.e., $(\partial E/\partial a)_0 = 0$ and $(\partial E/\partial s)_0 = 0$. If the spinors and the configurations are optimized simultaneously during the iterations, this is called one-step method. The coupling between \hat{A} and \hat{S} may be neglected altogether, resulting in the two-step procedure,^{31,32} which is frequently used in practice due to its much simpler form. In the two-step procedure, the configurations are first optimized with a fixed spinor space followed by the rotation in the spinor space with the pre-optimized but fixed configurations. The same procedure is iterated until the convergence of MCSCF wavefunction. In this paper, we will only consider the two-step procedure employing the second-order Newton-Raphson method for the spinor rotation, and hence the procedure is quadratic only in the spinor space.

The relativistic MCSCF energy, at a point of iterations, is given by

$$E(\mathbf{a}, \mathbf{s}) = \langle 0' | \hat{H} | 0' \rangle = \langle 0 | \exp(-\hat{S}) \exp(-\hat{A}) \hat{H} \exp(\hat{A}) \exp(\hat{S}) | 0 \rangle, \quad (16)$$

and Baker-Campbell-Hausdorff expansion to second-order leads to

$$E(\mathbf{a}, \mathbf{s}) \simeq \langle 0 | \hat{H} | 0 \rangle + \langle 0 | [\hat{H}, \hat{A}] | 0 \rangle + \langle 0 | [\hat{H}, \hat{S}] | 0 \rangle + \frac{1}{2} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle + \frac{1}{2} \langle 0 | [[\hat{H}, \hat{S}], \hat{S}] | 0 \rangle + \langle 0 | [[\hat{H}, \hat{A}], \hat{S}] | 0 \rangle. \quad (17)$$

For the expressions of the expectation values of above commutators, which will be used in the expansion of derivatives in Secs. II D and II E, it is most convenient to rewrite the Hamiltonian (1) in the second quantization as

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q + h_{\text{nuc}}, \quad (18)$$

with

$$h_{pq} = \iint \phi_p^*(\mathbf{r}_1, \sigma_1) \hat{h}_1 \phi_q(\mathbf{r}_1, \sigma_1) d\mathbf{r}_1 d\sigma_1, \quad (19)$$

$$g_{pqrs} = \iiint \phi_p^*(\mathbf{r}_1, \sigma_1) \phi_r^*(\mathbf{r}_2, \sigma_2) r_{12}^{-1} \phi_q(\mathbf{r}_1, \sigma_1) \times \phi_s(\mathbf{r}_2, \sigma_2) d\mathbf{r}_1 d\sigma_1 d\mathbf{r}_2 d\sigma_2, \quad (20)$$

where ϕ refers the spinor and σ denotes the spin variable. The one- and two-electron molecular spinor integrals, Eqs. (19) and (20), respectively, can be obtained by the complex two- and four-index transformation outlined in Ref. 33.

As noted earlier, the specification of the orbital space determines the particular MCSCF scheme. The KRCASSCF method, which we consider in this paper, divides the spinor space into three groups: inactive, active, and external spaces,

where the inactive and external spaces have full and zero occupations, respectively, and the active space can have varying occupation number. Therefore, the occupation number n_{occ} for a Kramers pair in each space is $n_{\text{occ}} = 2$ for the inactive, $0 < n_{\text{occ}} < 2$ for the active, and $n_{\text{occ}} = 0$ for the external space. The additional spaces, the frozen core and the deleted virtual spaces can be also defined in order to reduce the computational cost.

C. Spinor rotation under Kramers symmetry

The spinor variation can be regarded as a rotation in the vector space spanned by the spinors and is written as

$$\Phi^{\text{new}} = \Phi^{\text{old}} \exp(\mathbf{A}), \quad (21)$$

where Φ is a row vector containing Kramers pairs, i.e., $\Phi = [\Phi_+ \Phi_-] = [\phi_1 \cdots \phi_M \phi_{\bar{1}} \cdots \phi_{\bar{M}}]$ where M is the total number of Kramers pairs. Since the unitary transformation given by Eq. (21) should leave the rotated spinors under time-reversal symmetry, the following relations between the elements of the anti-Hermitian rotation matrix \mathbf{A} can be obtained:¹²

$$a_{ij} = a_{i\bar{j}}^*, \quad (22)$$

$$a_{i\bar{j}} = -a_{ij}^*. \quad (22a)$$

Making use of these, and by breaking the summation to adapt Kramers pairs, i.e., $\Sigma_p^{2M} \rightarrow \Sigma_i^M + \Sigma_{\bar{i}}^M$, we can rewrite Eq. (13) as

$$\hat{A} = \sum_{i>j} [a_{ij}(\hat{E}_{ij} - \hat{E}_{\bar{j}\bar{i}}) - a_{i\bar{j}}^*(\hat{E}_{ji} - \hat{E}_{\bar{i}\bar{j}}) + a_{\bar{i}j}(\hat{E}_{\bar{i}j} + \hat{E}_{\bar{j}\bar{i}}) - a_{\bar{i}j}^*(\hat{E}_{\bar{j}\bar{i}} + \hat{E}_{\bar{i}j}) + a_{\bar{i}\bar{i}}\hat{E}_{\bar{i}\bar{i}} - a_{ii}^*\hat{E}_{ii}]. \quad (23)$$

Here, the four sets of rotation parameters constructs the rotation matrix \mathbf{A} as

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{++} & -\mathbf{A}_{-+}^* \\ \mathbf{A}_{-+} & \mathbf{A}_{++}^* \end{pmatrix}. \quad (24)$$

Note that the submatrices \mathbf{A}_{++} and \mathbf{A}_{-+} are anti-Hermitian and complex-symmetric, respectively. In the nonrelativistic limit, the subscripts $+$ and $-$ correspond to α and β spin, respectively, and $\mathbf{A}_{\alpha\beta} = \mathbf{A}_{\beta\alpha} = \mathbf{0}$ since the orbitals with different spin function simply cannot mix due to the orthogonality. However, since the two-component spinor is basically the linear combination of α and β functions, the mixing between $+$ and $-$ spinors does occur and gives rise to the additional off-diagonal rotation parameters compared with the nonrelativistic case. The matrix exponential $\exp(\mathbf{A})$ can be calculated either using the power expansion or the method by Dalgaard and Jørgensen,³² which elegantly obtains the matrix exponential by the diagonalization of the Hermitian matrix $[-\mathbf{A}^2]$. The quaternion algebra^{26,34} can be employed in the manipulation of \mathbf{A} , since the structure of matrix resembles the quaternion.

At fixed configurations, the Taylor expansion of MCSCF energy at the zero point in the energy hypersurface spanned

by the spinor variables is

$$E(\mathbf{a}) = E(\mathbf{0}) + \mathbf{g}^\dagger \mathbf{a} + \frac{1}{2} \mathbf{a}^\dagger \mathbf{H} \mathbf{a} + \cdots, \quad (25)$$

where \mathbf{g} and \mathbf{H} are the gradient and Hessian with respect to spinor rotation parameters \mathbf{a} , the vector arrangement of the rotation matrix \mathbf{A} . The truncation of above equation to second-order and setting $dE/d\mathbf{a} = 0$ lead to the second-order Newton-Raphson equation,

$$\mathbf{a} = -\mathbf{H}^{-1} \mathbf{g}, \quad (26)$$

for the calculation of the rotation parameters. To solve above equation, 4 gradient vectors and 16 Hessian matrices according to the four types of rotations are required, however, as will be shown later in this section, the number of gradients and Hessians elements that are required can be reduced to $\frac{1}{2}$ and $\frac{1}{4}$, respectively, using the time-reversal symmetry.

D. Spinor gradient

The spinor gradient vector at a point can be partitioned into 4 vectors according to the types of the rotation parameters as

$$\mathbf{g} = \left[\left(\frac{\partial E}{\partial a_{ij}} \right)_0 \quad \left(\frac{\partial E}{\partial a_{i\bar{j}}^*} \right)_0 \quad \left(\frac{\partial E}{\partial a_{\bar{i}j}} \right)_0 \quad \left(\frac{\partial E}{\partial a_{\bar{i}\bar{j}}^*} \right)_0 \right]^T, \quad (27)$$

Note the restriction $i > j$ by Eq. (23) and the 4-fold increase in the dimension from the nonrelativistic case. Direct differentiation of the MCSCF energy given by Eq. (17) leads to

$$g_{ij}^{(1)} = \frac{\partial}{\partial a_{ij}} \langle 0 | [\hat{H}, \hat{A}] | 0 \rangle = \langle 0 | [\hat{H}, \hat{E}_{ij}] - [\hat{H}, \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (28)$$

$$g_{i\bar{j}}^{(2)} = \frac{\partial}{\partial a_{i\bar{j}}^*} \langle 0 | [\hat{H}, \hat{A}] | 0 \rangle = \langle 0 | [\hat{H}, \hat{E}_{i\bar{j}}] - [\hat{H}, \hat{E}_{\bar{j}i}] | 0 \rangle, \quad (28a)$$

$$g_{\bar{i}j}^{(3)} = \frac{\partial}{\partial a_{\bar{i}j}} \langle 0 | [\hat{H}, \hat{A}] | 0 \rangle = \langle 0 | [\hat{H}, \hat{E}_{\bar{i}j}] + [\hat{H}, \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (28b)$$

$$g_{\bar{i}\bar{j}}^{(4)} = \frac{\partial}{\partial a_{\bar{i}\bar{j}}^*} \langle 0 | [\hat{H}, \hat{A}] | 0 \rangle = \langle 0 | -[\hat{H}, \hat{E}_{\bar{i}\bar{j}}] - [\hat{H}, \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (28c)$$

where the superscript denotes the location in the \mathbf{g} vector. The gradients are given by the sum or the difference of the commutator $[\hat{H}, \hat{E}_{mn}]$. Using the anti-commutation relations of elementary operators,³⁵ the expectation value of this commutator can be written as

$$\langle 0 | [\hat{H}, \hat{E}_{mn}] | 0 \rangle = \sum_p [h_{pm} D_{pn} - (h_{pn} D_{pm})^*] + \sum_{pqr} [g_{pgrm} d_{pqrn} - (g_{pqrn} d_{pqrm})^*], \quad (29)$$

where

$$D_{pq} = \langle 0 | \hat{E}_{pq} | 0 \rangle, \quad (30)$$

$$d_{pqrs} = \langle 0 | a_p^\dagger a_r^\dagger a_s a_q | 0 \rangle, \quad (31)$$

refer the first- and second-order reduced density matrix elements, respectively. The expressions for other commutators entering Eqs. (28)–(28c) can be obtained by an appropriate interchange of indices. Also, the permutation of indices in Eq. (29) gives

$$\langle 0 | [\hat{H}, \hat{E}_{mn}] | 0 \rangle = -\langle 0 | [\hat{H}, \hat{E}_{nm}] | 0 \rangle^*, \quad (32)$$

which leads to the relations within the \mathbf{g} vector:

$$g_{ij}^{(1)} = (g_{ij}^{(2)})^*, \quad (33)$$

$$g_{ij}^{(3)} = (g_{ij}^{(4)})^*. \quad (33a)$$

Thus, only two gradient vectors, $\mathbf{g}^{(1)}$ and $\mathbf{g}^{(3)}$ are distinct and required to be calculated, and the evaluation of the various types of Eq. (29) with differing time-reversal notations are the central quantities composing the gradients. By defining the intermediate

$$F_{mn} = \sum_p h_{pm} D_{pn} + \sum_{pqr} g_{pqrm} d_{pqrn}, \quad (34)$$

and with Eq. (29), the final working expressions for the nonredundant gradients are

$$g_{ij}^{(1)} = F_{ij} - F_{ji}^* - F_{\bar{j}\bar{i}} + F_{\bar{i}\bar{j}}^*, \quad (35)$$

$$g_{ij}^{(3)} = F_{\bar{i}\bar{j}} - F_{\bar{j}\bar{i}}^* + F_{\bar{j}\bar{i}} - F_{\bar{i}\bar{j}}^*. \quad (35a)$$

We note the similarity of Eq. (34) to the nonrelativistic MCSCF Fock-type matrix, however, such decomposition is only used here for sake of simplification and computational reduction, since it does not reduce to the Fock matrix as in nonrelativistic case. Therefore, by computing the four types of \mathbf{F} matrix entering Eqs. (35) and (35a), the gradients can be easily calculated.

E. Spinor Hessian

Like the spinor gradient, the spinor Hessian matrix at a point in the energy hypersurface, appearing in Eq. (25), can be partitioned into 4 by 4 submatrices according to the rotation parameters as

$$\mathbf{H} = \begin{bmatrix} \left(\frac{\partial^2 E}{\partial a_{ij} \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij} \partial a_{kl}^*} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij} \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij} \partial a_{kl}^*} \right)_0 \\ \left(\frac{\partial^2 E}{\partial a_{ij}^* \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij}^* \partial a_{kl}^*} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij}^* \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{ij}^* \partial a_{kl}^*} \right)_0 \\ \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}} \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}} \partial a_{kl}^*} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}} \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}} \partial a_{kl}^*} \right)_0 \\ \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}}^* \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}}^* \partial a_{kl}^*} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}}^* \partial a_{kl}} \right)_0 & \left(\frac{\partial^2 E}{\partial a_{\bar{i}\bar{j}}^* \partial a_{kl}^*} \right)_0 \end{bmatrix}. \quad (36)$$

Again, note the restrictions $i > j$ and $k > l$, and since the dimension is four times larger compared with the nonrelativistic case and the elements are complex-numbered, the increase in the storage of \mathbf{H} is thus 32 times. The matrix elements are given by the second derivatives of MCSCF energy with respect to the rotation parameters:

$$\begin{aligned} H_{ij,kl}^{(1,1)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij} \partial a_{kl}} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\ &= \frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{ij}], \hat{E}_{kl}] + [[\hat{H}, \hat{E}_{kl}], \hat{E}_{ij}] \\ &\quad - [[\hat{H}, \hat{E}_{ij}], \hat{E}_{\bar{l}\bar{k}}] - [[\hat{H}, \hat{E}_{\bar{l}\bar{k}}], \hat{E}_{ij}] \\ &\quad - [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{kl}] - [[\hat{H}, \hat{E}_{kl}], \hat{E}_{\bar{j}\bar{i}}] \\ &\quad + [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{\bar{l}\bar{k}}] + [[\hat{H}, \hat{E}_{\bar{l}\bar{k}}], \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (37) \end{aligned}$$

$$\begin{aligned} H_{ij,kl}^{(1,2)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij} \partial a_{kl}^*} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\ &= \frac{1}{2} \langle 0 | - [[\hat{H}, \hat{E}_{ij}], \hat{E}_{lk}] - [[\hat{H}, \hat{E}_{lk}], \hat{E}_{ij}] \\ &\quad + [[\hat{H}, \hat{E}_{ij}], \hat{E}_{\bar{k}\bar{l}}] + [[\hat{H}, \hat{E}_{\bar{k}\bar{l}}], \hat{E}_{ij}] \\ &\quad + [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{lk}] + [[\hat{H}, \hat{E}_{lk}], \hat{E}_{\bar{j}\bar{i}}] \\ &\quad - [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{\bar{k}\bar{l}}] - [[\hat{H}, \hat{E}_{\bar{k}\bar{l}}], \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (37a) \end{aligned}$$

$$\begin{aligned} H_{ij,kl}^{(1,3)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij} \partial a_{kl}} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\ &= \frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{ij}], \hat{E}_{kl}] + [[\hat{H}, \hat{E}_{kl}], \hat{E}_{ij}] \\ &\quad + [[\hat{H}, \hat{E}_{ij}], \hat{E}_{\bar{l}\bar{k}}] + [[\hat{H}, \hat{E}_{\bar{l}\bar{k}}], \hat{E}_{ij}] \\ &\quad - [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{kl}] - [[\hat{H}, \hat{E}_{kl}], \hat{E}_{\bar{j}\bar{i}}] \\ &\quad - [[\hat{H}, \hat{E}_{\bar{j}\bar{i}}], \hat{E}_{\bar{l}\bar{k}}] - [[\hat{H}, \hat{E}_{\bar{l}\bar{k}}], \hat{E}_{\bar{j}\bar{i}}] | 0 \rangle, \quad (37b) \end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(4,2)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij}^* \partial a_{kl}^*} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\
&= \frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{lk}] + [[\hat{H}, \hat{E}_{lk}], \hat{E}_{i\bar{j}}] \\
&\quad - [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{k\bar{l}}] - [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{i\bar{j}}] \\
&\quad + [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{lk}] + [[\hat{H}, \hat{E}_{lk}], \hat{E}_{j\bar{i}}] \\
&\quad - [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{k\bar{l}}] - [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{j\bar{i}}] | 0 \rangle, \quad (37m)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(4,3)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij}^* \partial a_{kl}^*} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\
&= \frac{1}{2} \langle 0 | - [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{k\bar{l}}] - [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{i\bar{j}}] \\
&\quad - [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{lk}] - [[\hat{H}, \hat{E}_{lk}], \hat{E}_{i\bar{j}}] \\
&\quad - [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{k\bar{l}}] - [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{j\bar{i}}] \\
&\quad - [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{lk}] - [[\hat{H}, \hat{E}_{lk}], \hat{E}_{j\bar{i}}] | 0 \rangle, \quad (37n)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(4,4)} &= \frac{1}{2} \frac{\partial^2}{\partial a_{ij}^* \partial a_{kl}^*} \langle 0 | [[\hat{H}, \hat{A}], \hat{A}] | 0 \rangle \\
&= \frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{k\bar{l}}] + [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{i\bar{j}}] \\
&\quad + [[\hat{H}, \hat{E}_{i\bar{j}}], \hat{E}_{l\bar{k}}] + [[\hat{H}, \hat{E}_{l\bar{k}}], \hat{E}_{i\bar{j}}] \\
&\quad + [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{k\bar{l}}] + [[\hat{H}, \hat{E}_{k\bar{l}}], \hat{E}_{j\bar{i}}] \\
&\quad + [[\hat{H}, \hat{E}_{j\bar{i}}], \hat{E}_{l\bar{k}}] + [[\hat{H}, \hat{E}_{l\bar{k}}], \hat{E}_{j\bar{i}}] | 0 \rangle, \quad (37o)
\end{aligned}$$

where the superscript denotes the location in Eq. (36). After some algebra in the second quantization, we obtain for the symmetric sum of the nested commutators entering Eqs. (37)–(37o) the following expression:

$$\begin{aligned}
&\frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{mn}], \hat{E}_{uv}] + [[\hat{H}, \hat{E}_{uv}], \hat{E}_{mn}] | 0 \rangle \\
&= \frac{1}{2} \{ \delta_{nu} (F_{mv} + F_{vm}^*) + \delta_{mv} (F_{un} + F_{nu}^*) \} \\
&\quad - h_{nu} D_{mv} - (h_{mv} D_{nu})^* + \sum_{pq} [g_{pmqu} d_{pnqv} + (g_{pnqv} d_{pmqu})^*] \\
&\quad + \sum_{pq} [(g_{pmvq} - g_{pqvm}) d_{pqun} + \{(g_{pnqu} - g_{pqun}) d_{pqvm}\}^*]. \quad (38)
\end{aligned}$$

By interchanging one or more indices with their time-reversal pair, the expressions for other similar sums in Eqs. (37)–(37o) can be obtained. Using that Eq. (38) is symmetric with respect to the interchange of the excitation operators and the following relation:

$$\begin{aligned}
&\langle 0 | [[\hat{H}, \hat{E}_{mn}], \hat{E}_{uv}] + [[\hat{H}, \hat{E}_{uv}], \hat{E}_{mn}] | 0 \rangle \\
&= \langle 0 | [[\hat{H}, \hat{E}_{nm}], \hat{E}_{vu}] + [[\hat{H}, \hat{E}_{vu}], \hat{E}_{nm}] | 0 \rangle^*, \quad (39)
\end{aligned}$$

the elements of the \mathbf{H} matrix are related as follows:

$$H_{ij,kl}^{(1,1)} = H_{kl,ij}^{(1,1)} = (H_{ij,kl}^{(2,2)})^*, \quad (40)$$

$$H_{ij,kl}^{(1,2)} = (H_{kl,ij}^{(1,2)})^* = (H_{ij,kl}^{(2,1)})^*, \quad (40a)$$

$$H_{ij,kl}^{(1,3)} = H_{kl,ij}^{(3,1)} = (H_{ij,kl}^{(2,4)})^* = (H_{kl,ij}^{(4,2)})^*, \quad (40b)$$

$$H_{ij,kl}^{(1,4)} = (H_{kl,ij}^{(3,2)})^* = (H_{ij,kl}^{(2,3)})^* = H_{kl,ij}^{(4,1)}, \quad (40c)$$

$$H_{ij,kl}^{(3,3)} = H_{kl,ij}^{(3,3)} = (H_{ij,kl}^{(4,4)})^*, \quad (40d)$$

$$H_{ij,kl}^{(3,4)} = (H_{kl,ij}^{(3,4)})^* = (H_{ij,kl}^{(4,3)})^*. \quad (40e)$$

The first and second rows of Eq. (36) are related by complex conjugation, and likewise for the third and fourth rows. Additionally, the upper triangular elements of the submatrices are also related to the lower parts as shown above. Also, the \mathbf{H} matrix is overall symmetric, which is a natural feature of the Hessian. Therefore, the nonredundant Hessian elements are the lower triangular elements of the submatrices comprising the first and third rows of \mathbf{H} , and therefore, the computational effort for \mathbf{H} is reduced to $\frac{1}{4}$. Furthermore, Eq. (38) can be separated into two parts:

$$\begin{aligned}
&\frac{1}{2} \langle 0 | [[\hat{H}, \hat{E}_{mn}], \hat{E}_{uv}] + [[\hat{H}, \hat{E}_{uv}], \hat{E}_{mn}] | 0 \rangle \\
&= B_{mn,uv} + B_{nm,vu}^*, \quad (41)
\end{aligned}$$

where

$$\begin{aligned}
B_{mn,uv} &= \frac{1}{2} (\delta_{nu} F_{mv} + \delta_{mv} F_{un}) - h_{nu} D_{mv} \\
&\quad + \sum_{pq} [g_{pmqu} d_{pnqv} + (g_{pmvq} - g_{pqvm}) d_{pqun}], \quad (42)
\end{aligned}$$

in analogy to defining Eq. (34) for the spinor gradients. Substituting Eq. (42) into Eqs. (37)–(37o) with the consideration of the relations provided by Eqs. (40)–(40e), the lower-triangular elements of the nonredundant Hessian submatrices can be written as

$$\begin{aligned}
H_{ij,kl}^{(1,1)} &= B_{ij,kl} + B_{ji,lk}^* - B_{ij,l\bar{k}} - B_{ji,\bar{k}l}^* - B_{j\bar{i},kl} \\
&\quad - B_{i\bar{j},lk}^* + B_{j\bar{i},l\bar{k}} + B_{i\bar{j},k\bar{l}}^*, \quad (43)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(1,2)} &= -B_{ij,lk} - B_{ji,kl}^* + B_{ij,k\bar{l}} + B_{ji,\bar{l}k}^* + B_{j\bar{i},lk} \\
&\quad + B_{i\bar{j},kl}^* - B_{j\bar{i},k\bar{l}} - B_{i\bar{j},l\bar{k}}^*, \quad (43a)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(1,3)} &= B_{ij,k\bar{l}} + B_{ji,\bar{l}k}^* + B_{ij,l\bar{k}} + B_{ji,\bar{k}l}^* - B_{j\bar{i},kl} \\
&\quad - B_{i\bar{j},l\bar{k}}^* - B_{j\bar{i},l\bar{k}} - B_{i\bar{j},k\bar{l}}^*, \quad (43b)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(1,4)} &= -B_{ij,k\bar{l}} - B_{ji,\bar{l}k}^* - B_{ij,l\bar{k}} - B_{ji,\bar{k}l}^* + B_{j\bar{i},kl} \\
&\quad + B_{i\bar{j},lk}^* + B_{j\bar{i},l\bar{k}} + B_{i\bar{j},k\bar{l}}^*, \quad (43c)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(3,1)} &= B_{i\bar{j},kl} + B_{j\bar{i},lk}^* - B_{i\bar{j},l\bar{k}} - B_{j\bar{i},\bar{k}l}^* + B_{j\bar{i},kl} \\
&\quad + B_{i\bar{j},lk}^* - B_{j\bar{i},l\bar{k}} - B_{i\bar{j},k\bar{l}}^*, \quad (43d)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(3,2)} &= -B_{i\bar{j},lk} - B_{j\bar{i},kl}^* + B_{i\bar{j},k\bar{l}} + B_{j\bar{i},\bar{l}k}^* - B_{j\bar{i},lk} \\
&\quad - B_{i\bar{j},kl}^* + B_{j\bar{i},k\bar{l}} + B_{i\bar{j},l\bar{k}}^*, \quad (43e)
\end{aligned}$$

$$\begin{aligned}
H_{ij,kl}^{(3,3)} &= B_{i\bar{j},k\bar{l}} + B_{j\bar{i},\bar{l}k}^* + B_{i\bar{j},l\bar{k}} + B_{j\bar{i},\bar{k}l}^* + B_{j\bar{i},kl} \\
&\quad + B_{i\bar{j},l\bar{k}}^* + B_{j\bar{i},l\bar{k}} + B_{i\bar{j},k\bar{l}}^*, \quad (43f)
\end{aligned}$$

$$H_{ij,kl}^{(3,4)} = -B_{i\bar{j},k\bar{l}} - B_{i\bar{j},l\bar{k}}^* - B_{i\bar{j},l\bar{k}} - B_{j\bar{i},k\bar{l}}^* - B_{j\bar{i},k\bar{l}} - B_{i\bar{j},l\bar{k}}^* - B_{j\bar{i},l\bar{k}} - B_{i\bar{j},k\bar{l}}^* \quad (43g)$$

$$\begin{pmatrix} \text{Re}[\mathbf{H}^{(1,1)} + \mathbf{H}^{(1,2)}] & -\text{Im}[\mathbf{H}^{(1,1)} - \mathbf{H}^{(1,2)}] & \text{Re}[\mathbf{H}^{(1,3)} + \mathbf{H}^{(1,4)}] & -\text{Im}[\mathbf{H}^{(1,3)} - \mathbf{H}^{(1,4)}] \\ \text{Im}[\mathbf{H}^{(1,1)} + \mathbf{H}^{(1,2)}] & \text{Re}[\mathbf{H}^{(1,1)} - \mathbf{H}^{(1,2)}] & \text{Im}[\mathbf{H}^{(1,3)} + \mathbf{H}^{(1,4)}] & \text{Re}[\mathbf{H}^{(1,3)} - \mathbf{H}^{(1,4)}] \\ \text{Re}[\mathbf{H}^{(3,1)} + \mathbf{H}^{(3,2)}] & -\text{Im}[\mathbf{H}^{(3,1)} - \mathbf{H}^{(3,2)}] & \text{Re}[\mathbf{H}^{(3,3)} + \mathbf{H}^{(3,4)}] & -\text{Im}[\mathbf{H}^{(3,3)} - \mathbf{H}^{(3,4)}] \\ \text{Im}[\mathbf{H}^{(3,1)} + \mathbf{H}^{(3,2)}] & \text{Re}[\mathbf{H}^{(3,1)} - \mathbf{H}^{(3,2)}] & \text{Im}[\mathbf{H}^{(3,3)} + \mathbf{H}^{(3,4)}] & \text{Re}[\mathbf{H}^{(3,3)} - \mathbf{H}^{(3,4)}] \end{pmatrix} \times \begin{pmatrix} \text{Re}[\mathbf{a}^{(1)}] \\ \text{Im}[\mathbf{a}^{(1)}] \\ \text{Re}[\mathbf{a}^{(3)}] \\ \text{Im}[\mathbf{a}^{(3)}] \end{pmatrix} = - \begin{pmatrix} \text{Re}[\mathbf{g}^{(1)}] \\ \text{Im}[\mathbf{g}^{(1)}] \\ \text{Re}[\mathbf{g}^{(3)}] \\ \text{Im}[\mathbf{g}^{(3)}] \end{pmatrix}, \quad (44)$$

where $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(3)}$ are the vector forms of the lower triangular elements of the matrices \mathbf{A}_{++} and \mathbf{A}_{-+} in Eq. (24), respectively. Therefore, in the actual implementation, it is the matrix part of above equation that is required, instead of the full Hessian matrix \mathbf{H} , and its element can be easily obtained by the combinations provided by Eqs. (43)–(43g).

F. Configuration optimization

In the two-step procedure, the configurations of frozen spinors are optimized by the *full*-CI procedure within the KR-CASSCF active space, i.e., by the KRCASCI, which solves the CI eigenvalue equation based on the orthonormal two-component spinors,

$$\mathbf{H}\mathbf{C} = \mathbf{C}E, \quad (45)$$

where \mathbf{H} is the CI matrix, \mathbf{C} is the CI coefficients matrix and E is the diagonal matrix constituting the CI energies. Although the determinants, which form the bases of the KR-CI wavefunction, are generated via the unrestricted excitations between barred and unbarred spinors, the Kramers restricted formalism is retained by the use of one- and two-electron integrals over the two-component Kramers pairs given in Eqs. (19) and (20) in the construction of CI matrix. The matrix elements $H_{mn} = \langle \mathbf{m} | \hat{H} | \mathbf{n} \rangle$ are evaluated using Slater's rules,³⁶ in which the nonzero matrix elements occur between the determinants that differ by at most two spinors.

Since the calculations of the lowest few CI states relevant to KRCASSCF calculations are necessary or the dimension of CI matrix can be too large, a direct CI algorithm based on Davidson diagonalization³⁷ that has been modified for Hermitian matrix is employed. With the optimized CI coefficients, the reduced density matrix elements, Eqs. (30) and (31), are computed for usage in the stage of spinor rotation:

$$D_{pq} = \sum_{\mathbf{m}\mathbf{n}} C_{\mathbf{m}}^* C_{\mathbf{n}} \langle \mathbf{m} | \hat{a}_p^\dagger \hat{a}_q | \mathbf{n} \rangle, \quad (46)$$

In solving the Newton-Raphson equation, using Eqs. (33) and (33a), and (40)–(40e) in Eq. (26), then, by rearranging into real and imaginary parts, Eq. (26) can be rewritten in the form of a real linear equation:

$$d_{pqrs} = \sum_{\mathbf{m}\mathbf{n}} C_{\mathbf{m}}^* C_{\mathbf{n}} \langle \mathbf{m} | a_p^\dagger a_r^\dagger a_s a_q | \mathbf{n} \rangle. \quad (47)$$

Note that the expectation values of the number conserving operators in above equations can have three possible values: -1 , 0 , or 1 . Usually the active space is small enough that the reduced density matrices can be stored in the core memory.

III. IMPLEMENTATION

The KRCASSCF approach described in Sec. II is implemented into KPACK,³⁸ the relativistic two-component *ab initio* electronic structure program package developed by the authors. The routines for the spinor rotation are written entirely in the standard-compliant Fortran 95/2003 language as the rest of package. Also, an extension to the existing KR-CI routines is made in order to enable the computation of the reduced density matrices. The present implementation does not yet support the use of (double) point group symmetry.

A. Algorithm

We employ the two-step procedure in convergence of KRCASSCF wavefunction, in which the stationary point in both the configuration and the spinor spaces is reached by an iterative loop of a sequential execution of the configuration and the spinor optimizations. The sequence of the current implementation of KRCASSCF can be summarized as follows:

- (i) Define molecule. Choose basis sets. Specify KR-CASSCF inactive, active and external spaces. Start the calculation. Find the initial spinor guess by solving the two-component Fock equation, Eq. (8), i.e., KRHF.
- (ii) Transform the atomic orbital integrals to a molecular spinor basis with the current spinor set, i.e., calculate Eqs. (19) and (20). Perform KRCASCI [Eq. (45)] to obtain the configuration coefficients. Calculate the first-and

second-order reduced density matrices, Eqs. (46) and (47).

- (iii) Generate 4 types of \mathbf{F} matrix, Eq. (34). Use these to evaluate the gradients using Eqs. (35) and (35a).
- (iv) Check the convergence for gradient and energy. If converged, stop the iterations and exit.
- (v) Generate 64 types of B , Eq. (42), for the given Hessian indices to avoid storing massive \mathbf{B} matrices. Use these to evaluate the Hessian matrix element using Eqs. (43)–(43g). Repeat for all indices.
- (vi) Solve the second-order Newton-Raphson equation, Eq. (44), and obtain the spinor rotation parameters. Compute the matrix exponential of rotation matrix, $\exp(\mathbf{A})$. Update the spinor set by Eq. (21). Return to step (ii).

B. Comparison with previous implementation

Table I shows the practical speedups compared to the previous implementation for a construction of the spinor Hessian matrix, which predominates the computation time, with respect to the size of active space for the state-specific KR-CASSCF calculation performed for the ground state of the Pb atom. Note that, by simply counting the number of Hessian elements to be evaluated, a nominal speedup by a factor of 2 can be expected by the inclusion of time-reversal symmetry. However, even for the minimal active space (6s6p) calculation, the measured speedup is 2.4 times, exceeding the prediction and reaches 4.1 times for the larger active space of 17 Kramers pairs (up to 8p). This extra speedup of the present code may be attributed to that the \mathbf{F} matrix given by Eq. (34) has replaced some parts in the calculation of Hessian elements in Eqs. (42)–(43g), leading to a reduction of the computational effort, and renders the present method superior for the larger active space calculations. Lastly, the present formulation facilitates the implementation effort substantially as writing routines for the intermediates, Eqs. (34) and (42), will suffice for the computation of energy derivatives in the spinor space.

While the application of the previous implementation was restricted to the state-specific KRCASSCF calculations for the atoms and molecules with nondegenerate ground state, the present implementation has extend the capability to the

TABLE I. Wall times (in seconds) for the calculation of Hessian matrix in a single spinor optimization step of KRCASSCF for the Pb atom^a with 4 active electrons. Both the previous and present codes were compiled using PGI compilers (release 13.3) with the default optimization level. A 3.3GHz single core of the i7-3960X CPU was used.

Active space	(#Electrons, #Kramers pairs)	Previous code ^b	This work	Speedup
6s6p	(4,4)	2.8	1.2	2.4 times
6s6p7s	(4,5)	6.5	2.4	2.7 times
6s6p7s7p	(4,8)	36.9	11.8	3.1 times
6s6p6d7s7p	(4,13)	193.7	51.7	3.7 times
6s6p6d7s7p8s	(4,14)	239.4	63.3	3.8 times
6s6p6d7s7p8s8p	(4,17)	411.1	101.4	4.1 times

^aSOREP(ECP78MDF) and the uncontracted [6s6p2d] basis set were used, Ref. 40.

^bFrom Ref. 14.

calculation of excited states and open-shell systems, and the state-average scheme for degenerate states can also be employed.

IV. APPLICATION

Atomic calculations are carried out for the lower p -block atoms, 5p through 7p-block, for which the scheme of spin-orbit coupling ranges from *intermediate*- to *jj*-coupling, to verify the correctness of implementation and assess the accuracy.

A. Computational details

All two-component KRHF and KRCASSCF calculations are performed using the KPACK package,³⁸ and the MOLPRO package³⁹ is used for the spin-orbit complete active space state interaction (CASSI-SO) calculation, in which the spin-orbit coupling is included using the CASSCF state interaction. Both methods use the active space of outermost valence shells: 5s5p for In through Xe, 6s6p for Tl through Rn, and 7s7p for E113 through E118. Apart from the use of RECP, no frozen core or deleted virtual approximation is employed; all orbitals (or spinors) below and above the active space are included in the inactive and the external space, respectively. All calculations are carried out in C_1 symmetry.

The atomic ground and excited states arising from the valence p^n configuration are considered in this work, and the resulting levels by the *LS*- and *jj*-coupling schemes are summarized in Table II. The CASSI-SO approach is available through the state-average scheme because more than one *LS* term can contribute to the (spin-orbit)-*J*-levels. Using AREP only, first the CASSCF energy for average of all *LS* terms of various multiplicity belonging to the p^n configurations is optimized, and then, with these reference spin-free CASSCF wavefunctions, the *J*-levels are calculated by a diagonalization of the matrix over the spin-free states with the SOREP spin-orbit operator. The state-average scheme is also applied to the KRCASSCF calculations, even though the state-specific scheme is also possible in this case, to bring the two methods close for comparison. Here, the spin-orbit levels are already determined by the implicit *jj*-coupling, so the KRCASSCF directly optimizes the energy average of the *J*-levels of interest. Hence, KRCASSCF is a true MCSCF procedure, while CASSI-SO merely seeks the spin-orbit coupling between the scalar relativistic CASSCF states. We note that,

TABLE II. Spin-orbit levels arising from the p^n configurations.

Configurations	<i>LS</i> -coupling	<i>jj</i> -coupling
p^1, p^5	$^2P_{1/2,3/2}$	$(1/2)_{1/2}$ $(3/2)_{3/2}$
p^2, p^4	$^3P_{0,1,2}$ 1D_2 1S_0	$(1/2, 1/2)_0$ $(1/2, 3/2)_{1,2}$ $(3/2, 3/2)_{0,2}$
p^3	$^4S_{3/2}$ $^2D_{3/2,5/2}$ $^2P_{1/2,3/2}$	$(1/2, 1/2, 3/2)_{3/2}$ $(1/2, 3/2, 3/2)_{1/2, 3/2, 5/2}$ $(3/2, 3/2, 3/2)_{3/2}$

TABLE III. Excitation energies (in eV) arising from the p^n configurations for the $5p$, $6p$, and $7p$ atoms.

Initial	Final	$5p$			$6p$			$7p$				
		CASSI-SO	KRCASSCF	Expt. ^a	CASSI-SO	KRCASSCF	Expt. ^a	CASSI-SO	KRCASSCF	MRCI ^b	FSCC ^c	FSCC ^d
<i>In, Tl, and E113</i>												
(1/2) _{1/2}	(3/2) _{3/2}	0.274	0.230	0.274	0.929	0.823	0.966	2.397	2.884	2.965	2.793	2.878
<i>Sn, Pb, and Fl</i>												
(1/2,1/2) ₀	(1/2,3/2) ₁	0.190	0.181	0.210	0.836	0.849	0.969	2.861	3.221	3.383	3.266	2.687
	(1/2,3/2) ₂	0.408	0.398	0.425	1.282	1.310	1.320	3.411	3.682	3.703	3.593	3.045
	(3/2,3/2) ₂	1.323	1.314	1.068	2.552	2.625	2.660	6.642	7.830		7.557	
	(3/2,3/2) ₀	2.213	2.204	2.128	3.602	3.677	3.653	7.804	8.840		8.408	
<i>Sb, Bi, and E115</i>												
(1/2,1/2,3/2) _{3/2}	(1/2,3/2,3/2) _{3/2}	1.512	1.504	1.055	1.533	1.558	1.416	3.750	4.544	4.616		
	(1/2,3/2,3/2) _{5/2}	1.683	1.685	1.222	2.120	2.177	1.914	4.546	5.187	5.101		
	(1/2,3/2,3/2) _{1/2}	2.343	2.345	2.033	2.875	2.929	2.686	5.426	5.999			
	(3/2,3/2,3/2) _{3/2}	2.558	2.567	2.289	3.995	4.209	4.112	9.228	11.231			
<i>Te, Po, and E116</i>												
(3/2,3/2) ₂	(3/2,3/2) ₀	0.565	0.578	0.583	0.988	1.012	0.932	1.219	1.139	0.915		0.838
	(1/2,3/2) ₁	0.540	0.558	0.589	1.829	2.025	2.087	5.236	6.570	6.441		
	(1/2,3/2) ₂	1.558	1.574	1.309	2.688	2.864	2.688	5.999	7.158			
	(1/2,1/2) ₀	2.796	2.827	2.876	5.016	5.438	5.296	11.727	14.804			
<i>I, At, and E117</i>												
(3/2) _{3/2}	(1/2) _{1/2}	0.901	0.939	0.943	2.593	2.886	2.800 ^e	6.816	8.523	8.213		
MAE ^f		0.165	0.163		0.122	0.116		0.714 ^g	0.135 ^g			
MD ^h		0.015			0.125			1.051				

^aExperiments, Ref. 46.^bAll-electron four-component MRCISD with Dirac-Coulomb Hamiltonian, Refs. 47 and 48.^cAll-electron four-component Fock-space coupled cluster, Refs. 49 and 50.^dSOREP based two-component Fock-space coupled cluster, Ref. 42.^eAll-electron two-component DFT(B3LYP) with the sixth-order Douglas-Kroll Hamiltonian, Ref. 54.^fMean absolute error, relative to experiments.^gCalculated relative to MRCI results.^hMean difference between CASSI-SO and KRCASSCF.

as far as the same basis is used, both methods will converge to the same energy at the *full*-CI limit, which is, however, not feasible in practice.

The small-core energy-adjusted SOREPs of Stuttgart/Cologne group are employed for the atoms: ECP28MDF⁴⁰ for the $5p$, ECP60MDF⁴¹ for the $6p$, and ECP92MDFB^{42,43} for the $7p$ -block. The ECP92MDFB also includes the low-frequency Breit contribution. The basis sets of polarized valence double-zeta quality are used. An improvement by using larger bases is little when the active space only includes the outermost shell, since the optimization of the inactive and external spaces will not directly contribute to the CASSCF energy. The uncontracted $[8s8p6d]$ basis sets^{44,45} are used with ECP28MDF and ECP60MDF to provide a sufficient flexibility for the two-component calculations because the contraction is based on one-component calculations. With ECP92MDFB, the accompanying contracted basis sets are used, $[12s11p9d1f]/(4s3p2d1f)$ for the CASSI-SO and $[12s11p9d1f]/(4s5p3d1f)$ for the KRCASSCF calculations; for these basis sets, the primitives and contractions were optimized separately for one- and two-component calculations.

B. Excitation energy

Spin-orbit coupling, in particular, plays an important role in the excited state energy levels, since the stabilization or destabilization of spinors will directly affect the excitation energy, and therefore, for accurate results, both ground and excited states should be treated equally in terms of spin-orbit coupling and electron correlation, preferably by multi-configurational or multi-reference level of theory. In Table III, the KRCASSCF excitation energies for the $5p$, $6p$, and $7p$ atoms are listed, and the energies by CASSI-SO method are also presented for comparison purposes. The *jj*-coupling scheme is more pertinent to the electronic structure of heavy atoms and hence, will be used to denote the states throughout this section.

For excitation energies of the $5p$ atoms, on average, the errors in both methods, relative to the experiment,⁴⁶ is about 0.16 eV, while the difference between the two methods is only 0.02 eV. The small difference implies that the two methods, which differ in the stage of the spin-orbit treatment, show near convergence, at least, in energy. The mechanism of CASSI-SO closely resembles the *LS*-coupling scheme (and also the

intermediate-coupling if a sufficient number of states are introduced to interact), a good performance is thus expected for such coupling cases as in the $5p$ atoms, for which one might deem the KRCASSCF unfit due to the inherent *jj*-coupling within one-electron functions. However, the near convergence between the two methods suggests that the KRCASSCF has retrieved the weak spin-orbit coupling via the spinor optimization, which leads to a significant mixing of the *jj*-coupled functions as observed in the spinor occupations (see Sec. IV D). Similar characteristic has been previously reported by the KRCASSCF calculation of the ground state of group-14 elements.³⁸ The nature of errors, in the case of $5p$, is similar for both methods, and stems mostly from the lack of dynamical correlation as the correlated space being the outermost valence shell, scarcely enough for the important static correlation.

Although the $6p$ elements are known to be close to the *jj*-coupling scheme, the quality of KRCASSCF appears to be quite similar to the CASSI-SO, as indicated by both errors being about 0.12 eV, but there is a significant increase in the value of mean difference from the $5p$, which now reaches 0.13 eV, implying some departure in the energy convergence between the two methods. Here, the CASSI-SO suffers from the additional source of error caused by the inadequacy of scalar relativistic orbitals, and the similar magnitudes of errors shown for the $6p$ atoms indicate that the two types of errors, one from spin-orbit and the other from dynamical correlation, are not additive, at least, for the excitation energy. In other words, there is some sort of error cancelation occurred to produce the final error of CASSI-SO to be similar to the error by correlation shown for the KRCASSCF. This suggests that, for heavy atoms of the $6p$, because the spin-orbit coupling and the electron correlation can be strongly intertwined, an additional computation for the dynamical correlation upon CASSI-SO may not reduce the spin-orbit errors, which can be as large, implied by the value of mean difference.

The results of the KRCASSCF calculations on the $7p$ atoms are compared with the multi-reference (MR)CI results of Dyall,^{47,48} the Fock-space coupled cluster (FSCC) results of Eliav and co-workers,^{49,50} and the SOREP-FSCC results of Hangele *et al.*,⁴² since no experimental atomic excitation energy of superheavy elements has been reported to date. Many of the excitations of $7p$ atoms calculated in present work have not yet been calculated before, probably due to the complicated nature of open-shell in the relativistic regime where multi-configurational approach is essential. Moreover, most of excitation energies within the p^n configuration for the second half atoms of $7p$ -block are not the lowest excitations as in lighter homologues, since a promotion from the $7p_{3/2}$ to the $8s$ or $8p_{1/2}$ spinor takes less energy than to promote from the $7p_{1/2}$ to the $7p_{3/2}$ spinor.⁴⁷ The KRCASSCF excitation energies are within about 0.14 eV of the MRCI results, showing a consistent value of error throughout the lower p -block, and outperforms the CASSI-SO, which not only greatly underestimates the excitations, producing a large error of about 0.7 eV but also fails to address the large spin-orbit coupling effectively even though all terms responsible for the spin-orbit coupling within the $7p$ orbital are brought in for the state interaction. Moreover, it is conspicuous in the results that the

excitations reflect the pure *jj*-coupling scheme, so the excitation energies belonging to the same *jj*-configuration are placed in nearby energy, e.g., for Fl, the $(1/2,3/2)_{1,2}$ states are within 3.2–3.7 eV, while the $(3/2,3/2)_{2,0}$ states in 7.8–8.8 eV.

C. Spin-orbit energy

The self-consistent treatment of spin-orbit coupling always lowers the total energy. In most cases, the energy lowering can occur directly by occupying the stabilized spinors, for instance, the group-13 and group-14 atoms. An indirect energy lowering also takes place since an additional spin degree of freedom is introduced in the one-electron functions. The effect of the latter is insignificant for lighter atoms, but grows dramatically for the heavier ones; it can be seen from the difference in the total energies of AREP-HF and KRHF of the inert gases, which amounts 0.056 a.u. for Xe, 0.354 a.u. for Rn, and becomes nearly 2 a.u. for E118. The overall spin-orbit energy lowering, whether it is likely overestimated in the *jj*-coupling or completely neglected in the *LS*-coupling approach in the SCF step, should afford the total energies in close agreement, if corrected properly in *a posteriori* stage.

In this respect, Table IV lists the two types of spin-orbit energies of the ground states: The Δ_{LS} defined as $E_{\text{CASSCF}} - E_{\text{CASSI-SO}}$ indicates the spin-orbit energy recovered by the state interaction between the spin-free *LS* terms, and the Δ_{jj}^{LS} defined as $E_{\text{CASSI-SO}} - E_{\text{KRCASSCF}}$ determines the convergence or divergence of the two methods in terms of the total energy. In the results, the value of Δ_{LS} alternates across a period and is largest for the p^2 and p^4 configurations for all cases, and the averages are 0.009 a.u. for the $5p$, 0.032 a.u. for the $6p$, and 0.105 a.u. for the $7p$ atoms, indicating the obvious increase in the degree of spin-orbit coupling as descending down a group. The values of Δ_{jj}^{LS} are generally larger than Δ_{LS} by an order of magnitude and also increase significantly down in a group, reaching over 1 a.u. for the $7p$ atoms. The occurrence of such large divergence indicates that the CASSI-SO is, again, not able to recover the strong spin-orbit coupling effectively, whereas comparably small Δ_{jj}^{LS} for the $5p$ atoms proves the capability of KRCASSCF to describe the weak spin-orbit coupling as well. These are in line with the findings in Sec. IV B.

We also note that the Δ_{jj}^{LS} increases almost linearly from left to right across a period. As atomic number increases in

TABLE IV. Spin-orbit energies (Δ_{LS}^a and Δ_{jj}^{LSb} in a.u.) of the ground state for the $5p$, $6p$, and $7p$ atoms.

Group	$5p$		$6p$		$7p$	
	Δ_{LS}	Δ_{jj}^{LS}	Δ_{LS}	Δ_{jj}^{LS}	Δ_{LS}	Δ_{jj}^{LS}
13	0.007	0.021	0.023	0.180	0.059	1.081
14	0.012	0.021	0.046	0.228	0.147	1.209
15	0.002	0.029	0.020	0.257	0.111	1.397
16	0.011	0.033	0.042	0.289	0.124	1.585
17	0.011	0.037	0.032	0.319	0.084	1.772

^a $\Delta_{LS} = E_{\text{CASSCF}} - E_{\text{CASSI-SO}}$.

^b $\Delta_{jj}^{LS} = E_{\text{CASSI-SO}} - E_{\text{KRCASSCF}}$.

TABLE V. Occupations of the $p_{1/2}$ and $p_{3/2}$ valence spinors in the ground and excited states of the $5p$, $6p$, and $7p$ atoms.^a

State	$5p$		$6p$		$7p$	
	$p_{1/2}$	$p_{3/2}$	$p_{1/2}$	$p_{3/2}$	$p_{1/2}$	$p_{3/2}$
<i>In, Tl, and E113</i>						
$(1/2)_{1/2}$	1.000	0.057	1.000	0.029	1.000	0.005
$(3/2)_{3/2}$	0.034	1.028	0.029	1.013	0.025	1.002
<i>Sn, Pb, and Fl</i>						
$(1/2,1/2)_0$	1.615	0.409	1.874	0.141	1.985	0.018
$(1/2,3/2)_1$	1.000	1.024	1.000	1.012	1.000	1.002
$(1/2,3/2)_2$	0.539	1.488	0.878	1.135	0.993	1.009
$(3/2,3/2)_2$	0.491	1.537	0.147	1.877	0.029	1.993
$(3/2,3/2)_0$	0.411	1.682	0.149	1.905	0.037	1.990
<i>Sb, Bi, and E115</i>						
$(1/2,1/2,3/2)_{3/2}$	1.216	1.784	1.715	1.289	1.984	1.017
$(1/2,3/2,3/2)_{3/2}$	1.489	1.517	1.211	1.792	1.007	1.993
$(1/2,3/2,3/2)_{5/2}$	1.000	2.000	1.000	2.000	1.000	2.000
$(1/2,3/2,3/2)_{1/2}$	1.000	2.042	1.000	2.021	1.000	2.004
$(3/2,3/2,3/2)_{3/2}$	0.320	2.720	0.096	2.930	0.029	2.992
<i>Te, Po, and Lv</i>						
$(3/2,3/2)_2$	1.856	2.144	1.966	2.034	1.997	2.003
$(3/2,3/2)_0$	1.099	2.902	1.873	2.137	1.992	2.011
$(1/2,3/2)_1$	1.000	3.000	1.000	3.000	1.000	3.000
$(1/2,3/2)_2$	1.144	2.856	1.034	2.966	1.003	2.997
$(1/2,1/2)_0$	0.725	3.330	0.147	3.882	0.027	3.993
<i>I, At, and E117</i>						
$(3/2)_{3/2}$	2.000	3.000	2.000	3.000	2.000	3.000
$(1/2)_{1/2}$	1.000	4.000	1.000	4.000	1.000	4.000
δ_{jj}^b	0.470		0.130		0.013	

^aOccupation of the $s_{1/2}$ spinor is greater than 1.9 for all cases, i.e., it is almost closed-shell, and hence is omitted for clarity.

^bMean deviation of occupations of the $np_{1/2,3/2}$ spinors ($n = 5-7$) from pure jj -coupling occupations. Singly occurring J -levels within the p^n configurations are not included, see text for details.

a period, the effect of spin-orbit coupling consequently increases approximately as Z^4 ; however, the introduction of spin-orbit coupling via the CASSI-SO method appears rather limited to a certain amount for the given period that such additional increments in the degree of spin-orbit coupling cannot be accounted for. This explains the observed trend of somewhat deteriorating accuracy of the CASSI-SO in the excitation energy for the heavier elements in the same period.

D. Occupation number

The occupation numbers, obtained by the diagonal elements of the first-order reduced density matrix, give an insight into the composition of the respective wavefunction. In Table V, the occupations of the $p_{1/2}$ and $p_{3/2}$ spinors are given. The deviation from the pure jj -coupling scheme is denoted as δ_{jj} for the $5p$, $6p$ and $7p$ atoms and defined as the average departure of the KRCASSCF occupation from the corresponding jj -coupled occupation. In the table, the states, $(1/2)_{1/2}$, $(3/2)_{3/2}$ for the p^1 , p^5 , $(1/2,3/2)_1$ for the p^2 , p^4 , and $(1/2,3/2,3/2)_{1/2,5/2}$ for the p^3 atoms appear to obey the jj -

coupling scheme very nicely. These J -levels occur uniquely within the expansion of a given p^n configuration, and the slight mixing is from the $s_{1/2}$ spinor included in the current active space. The occupations of these states have been excluded in the calculation of δ_{jj} .

The δ_{jj} is shown to decrease rapidly as descending down a group, reaching almost zero (pure jj -coupling) for the $7p$ atoms, whereas a considerable excitation of about half electron is observed for the $5p$ atoms in effort to describe the weak spin-orbit coupling properly from the jj -coupled one-electron functions. Therefore, the success of the correct calculation of the ground and excited states in KRCASSCF for various strengths of spin-orbit coupling is mainly due to the spinor optimization that brings the spinors close to mix.

E. Ionization potential

It is well-known that as the spin-orbit coupling strengthens, the $p_{1/2}$ spinor is stabilized to give a higher ionization potential for the p^2 species than the p^3 , while in the nonrelativistic limit, the ionization potential of the p^3 to be higher than the p^4 due to the extra stability induced by unpaired spins, and this change in the trend is reproduced qualitatively in the KRCASSCF results. Table VI lists the ionization potentials of the lower p -block elements calculated by the KRCASSCF and CASSI-SO methods. Both errors (underestimation) for the $5p$ and $6p$ atoms, relative to the experiments,⁵¹ are about 0.9–1.0 eV with a difference between the two methods less than 0.1 eV. This is an expected convergence as the energy convergence in the ground state has already been discussed in Sec. IV C. The KRCASSCF performs slightly better by smaller error and also predicts the ionization potential of Pb to be lower than Bi, where the CASSI-SO has failed to capture. The underestimation in the calculated ionization potentials can be attributed to the lack of dynamical correlations. Assuming that all the static correlation is treated in the present calculations, the inclusion of dynamical correlation will lower the energy of a neutral atom more than a singly positive cation since the correlation energy of the neutral atom should be larger due to an additional electron. The ionization potentials calculated by a composite method using the same SOREP for the $5p$ and $6p$ atoms has been reported to be within 0.16 eV error of the experiment.⁵²

The ionization potentials for the $7p$ atoms are compared with the relativistic CISDT results,⁴⁷ and the FSCC results.^{42,49,50,53} As stated above, the present calculations underestimate the ionization potential by 0.63 eV for the KRCASSCF, and the large error (1.37 eV) of CASSI-SO indicates that the spin-orbit relaxation effect is not consistently described here for the different ionic states. For the KRCASSCF results, there is a gradual increase in the error across the $7p$ -block period from 0.46 eV (E113) to 0.76 eV (E118), which implies the increase in dynamical correlation that has not been included in the calculation. Taking the CISDT results as a reference, the excitations to the $(3/2,3/2)_0$ state for Fl, the $(1/2,3/2,3/2)_{1/2}$ and $(3/2,3/2,3/2)_{3/2}$ states for E115, the $(1/2,3/2)_2$ and $(1/2,1/2)_0$ states for Lv, and the $(1/2)_{1/2}$ state for E117 are above the ionization limit.

TABLE VI. Ionization potentials (in eV) of the $5p$, $6p$, and $7p$ atoms.

Group	$5p$			$6p$			$7p$				
	CASSI-SO	KRCASSCF	Expt. ^a	CASSI-SO	KRCASSCF	Expt. ^a	CASSI-SO	KRCASSCF	CISDT ^b	FSCC ^c	FSCC ^d
13	4.854	4.829	5.786	5.134	5.112	6.108	5.838	6.762	7.220	7.306	7.282
14	6.569	6.587	7.344	6.527	6.639	7.417	7.184	7.869	8.433	8.538	7.276
15	7.918	7.918	8.608	6.535	6.558	7.286	4.235	4.766	5.342	5.583	4.690
16	7.824	7.842	9.010	7.313	7.413	8.414	5.211	5.989	6.629		5.893
17	9.435	9.444	10.451	8.276	8.348	9.350 ^e	5.836	6.625	7.380		
18	11.258	11.259	12.130	9.796	9.850	10.749	7.119	7.888	8.648		8.846
MAE ^f	0.912	0.908		0.957	0.900		1.371 ^g	0.626 ^g			
MD ^h	0.012			0.064			0.746				

^aExperiments, Ref. 51.^bAll-electron four-component CISDT with Dirac-Coulomb Hamiltonian, Ref. 47.^cAll-electron four-component Fock-space coupled cluster, Refs. 49, 53, and 50.^dSOREP based two-component Fock-space coupled cluster, Ref. 42.^eMulti-configuration Dirac-Fock, Ref. 55.^fMean absolute error, relative to experiments.^gCalculated relative to CISDT results.^hMean difference between CASSI-SO and KRCASSCF.

V. CONCLUSION

The KRCASSCF method in the framework of two-component SOREP is presented and the underlying theory has been revised in terms of completeness with a full consideration of time-reversal symmetry. By the construction of spinor rotation operator with the elementary excitation operator, the expressions of the gradient and Hessian were derived in simpler forms, which can be efficiently calculated through suitable decomposition methods. Although the second-order Newton-Raphson method employed for the optimization of spinors only provides quadratic convergence in the spinor space, in our experience with the implementation, the overall convergence was almost quadratic, as far as the initial guess wavefunction is provided near the stationary point in the energy hypersurface. The application showed that the KRCASSCF is a versatile tool for both closed- and open-shell systems and is able to provide consistent results for both extremes of the LS and jj -coupling schemes of spin-orbit coupling through the *intermediate*-coupling region.

In our formulation, we presume that the SOREP is in use; however, the present scheme is applicable to any two-component spinors. Although highly symmetric atoms were considered in this paper for demonstration purposes, at the current stage of development the implementation largely focuses on the efficient calculations for systems with low symmetry requiring the variational treatment of spin-orbit coupling. Efforts are also being made to add the dynamical correlation upon KRCASSCF reference state through the multi-reference configuration interaction or the second-order perturbation theory. Such approaches are expected to create a significant synergy effect in obtaining highly accurate results.

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