

# New quantum number for the many-electron Dirac-Coulomb Hamiltonian

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By breaking the spin symmetry in the relativistic domain, a powerful tool in physical sciences was lost. In this work, we examine an alternative of spin symmetry for systems described by the many-electron Dirac-Coulomb Hamiltonian. We show that the square of many-electron operator  $\mathcal{K}_+$ , defined as a *sum* of individual single-electron time-reversal (TR) operators, is a linear Hermitian operator which commutes with the Dirac-Coulomb Hamiltonian in a finite Fock subspace. In contrast to the square of a standard unitary many-electron TR operator  $\mathcal{K}$ , the  $\mathcal{K}_+^2$  has a rich eigenspectrum having potential to substitute spin symmetry in the relativistic domain. We demonstrate that  $\mathcal{K}_+$  is connected to  $\mathcal{K}$  through an exponential mapping, in the same way as spin operators are mapped to the spin rotational group. Consequently, we call  $\mathcal{K}_+$  the generator of the many-electron TR symmetry. By diagonalizing the operator  $\mathcal{K}_+^2$  in the basis of Kramers-restricted Slater determinants, we introduce the relativistic variant of configuration state functions (CSF), denoted as Kramers CSF. A new quantum number associated with  $\mathcal{K}_+^2$  has potential to be used in many areas, for instance, (a) to design effective spin Hamiltonians for electron spin resonance spectroscopy of heavy-element containing systems; (b) to increase efficiency of methods for the solution of many-electron problems in relativistic computational chemistry and physics; (c) to define Kramers contamination in unrestricted density functional and Hartree-Fock theory as a relativistic analog of the spin contamination in the nonrelativistic domain.

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## I. INTRODUCTION

In experimental and theoretical science, it is of great importance to know the symmetry of the system studied. In spectroscopy, the choice of the effective Hamiltonian, used to fit the experimental data, is influenced (if not based) by the symmetry of the system. Similarly, taking symmetry into account in quantum computational science increases the efficiency and stability of computational methods.

In this work, our attention points towards symmetries of electronic systems in the absence of magnetic fields, while excluding symmetries associated with external electric fields such as point-group symmetry or translational symmetry given by clamped nuclei. To this class of symmetries we consider, for example, spin symmetry in nonrelativistic and time-reversal symmetry [1,2] in both the nonrelativistic and the Dirac four-component relativistic level of theory [3–5]. Here, the following general rule applies: all symmetries present at the higher level of theory appear also at lower level of theory or, in other words, going from a lower to a higher level of theory can lead to symmetry breaking.

Ideally, every study of a quantum system should use the highest possible level of theory. However, in practical applications, it is common to restrict the type of Hamiltonian and the representation of the wave function to make a given calculation feasible. The decision factor usually is the energy scale in combination with the accuracy needed for the problem under investigation. This work is aimed at the domain of relativistic quantum chemistry, and therefore we only consider theories which include spin-orbit (SO) interaction nonperturbatively

(two- or four-component) and partly theories without SO interaction (nonrelativistic or scalar relativistic). A quantum electrodynamics theory and other particle theories are beyond the scope of this study.

The nonrelativistic electronic structure theory with spin introduced *ad hoc* has been thoroughly investigated with respect to electron correlation, system dynamics, spectroscopic parameters, and the theory of spin itself has been worked out in great detail [6–12]. Eigenfunctions and eigenvalues of spin operators are well known and are successfully accommodated in different spectroscopies [13–15]. Nevertheless, spin symmetry is not appropriate for treating problems where SO effects become non-negligible since, in this case, spin is no longer a good quantum number. Although the time-reversal operator commutes with Hamiltonians accounting explicitly for SO coupling, it is an antilinear operator and therefore does not have eigenvalues and eigenvectors. For this reason, time-reversal symmetry has never played as important a role in atomic and molecular spectroscopy as spin symmetry. The same conclusions hold for the well-known generalization of the time-reversal operator to the many-electron case (constructed as a *product* of the one-electron time-reversal operators  $\mathcal{K}$ ) [16,17]. Although the square of  $\mathcal{K}$  becomes linear Hermitian operator and still commutes with the relativistic many-electron Hamiltonian, the quantum number associated with the operator contains very little information, as it is either +1 or –1 depending on the even or odd number of electrons in the system [16,17]. Therefore, even the  $\mathcal{K}^2$  can not substitute the role of the spin operators in relativistic theories.

Still, time-reversal (TR) symmetry has been shown to simplify the evaluation of matrix elements [18–29] and has been worked out in combination with double-group symmetry [3,30–33]. Nevertheless, the lack of useful quantum

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numbers for the many-fermion open-shell wave function in the framework of relativistic theories that account for spin-orbit coupling remains an obstacle. In the works of Bučinský *et al.* [34,35], a new operator  $\mathcal{K}_+$ , suitable for treating open-shell systems, has been proposed. This operator has originally been denoted as a *pseudo-time-reversal operator*. However, in this work we use the name *time-reversal generator* to emphasize the fact that it generates the TR operator  $\mathcal{K}$  in similar way as spin operators generate operators of spin rotations. The operator  $\mathcal{K}_+$  is constructed as a *sum* of individual one-electron time-reversal operators and its square produces quantum number with information which supersedes the well-known counterpart  $\mathcal{K}^2$ . Eigenfunctions (in the basis of Kramers-restricted Slater determinants) and eigenvalues of the  $\mathcal{K}_+^2$  operator have been presented previously for cases with up to four unpaired electrons with all possible Kramer determinants. However, these eigenfunctions were built phenomenologically and were not orthonormalized. Herein, we give additional insight into the relation between the many-electron  $\mathcal{K}$  and  $\mathcal{K}_+$  operators. Furthermore, we investigate the spectrum of the square of the time-reversal generator  $\mathcal{K}_+^2$  both for general wave functions and for the basis of Kramers-restricted determinants. We show the commutation relation between the Dirac-Coulomb Hamiltonian and the  $\mathcal{K}_+^2$  operator, thus introducing a new quantum number associated with  $\mathcal{K}_+^2$ . Finally, as one of the examples, we make a brief connection to non-Kramers doublets involved more than a half century in works related to Electron paramagnetic resonance or Mössbauer spectroscopy [36–41], magnetism [42–44], or conductivity theory [45–47].

The article is organized as follows. First, we give a general summary on time-reversal symmetry in the relativistic framework. We then define the time-reversal generator and formulate the eigenproblem theorem of the  $\mathcal{K}_+^2$  operator, followed by Sec. IV where we prove this theorem. In Sec. V, we show a paired structure of the eigenspectrum. Subsequently, we discuss a new quantum number of the Dirac-Coulomb Hamiltonian. Finally, a diagonalization method is employed to obtain the Kramers configuration state functions of the  $\mathcal{K}_+^2$  applied to cases with two (three) open shells. In Appendix I, we briefly discuss the cases with four and five unpaired electrons. In addition, we provide a simple FORTRAN program able to generate eigenfunctions up to 10 open-shell fermions.

## II. TIME-REVERSAL SYMMETRY

Many textbooks on quantum mechanics contain a detailed discussion of time-reversal symmetry and its applications [3,16,17]. In the following section, we summarize some of the well-known facts as a starting point for the discussion of the time-reversal generator in Secs. III–VII.

The one-electron Dirac operator in an external scalar potential  $V$  can be written in atomic units as [3–5]

$$D_i = c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i c^2 + V_i, \quad (1)$$

where  $c$  is the speed of light,  $\vec{\alpha}$  is the off-diagonal matrix operator constructed of gamma matrices in their standard representation  $\vec{\alpha} = \gamma_0 \vec{\gamma}$ ,  $\vec{p} = -i\vec{\nabla}$  is the momentum operator,

and  $\beta = \gamma_0$ . The subscript  $i$  represents the action of the operators on the  $i$ th electron.

The Dirac Hamiltonian (1) commutes with an one-electron time-reversal operator  $K_i$ , which reflects the fact that the time-dependent Dirac equation is invariant under time inversion

$$[D_i, K_i] = 0. \quad (2)$$

Fixing the arbitrariness in the phase of the time-reversal operator to  $-i$ ,  $K_i$  can be written as [2,3,20]

$$K_i = -i \Sigma_{y,i} K_{0,i}, \quad (3)$$

where  $K_{0,i}$  is the complex conjugation operator and  $\Sigma_{y,i}$  is the four-component spin  $y$  operator expressed via the Pauli matrix  $\sigma_y$  as

$$\Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}. \quad (4)$$

The time-reversal operator  $K_i$  is an antilinear unitary operator (also called antiunitary) satisfying

$$K_i(c_1 \psi + c_2 \phi) = c_1^* K_i \psi + c_2^* K_i \phi, \quad (5)$$

$$K_i^\dagger K_i = K_i K_i^\dagger = 1, \quad (6)$$

where  $c_1, c_2 \in \mathbb{C}$  and  $\psi, \phi \in [L^2(\mathbb{R}^3)]^4$  are four-spinors in the Hilbert space with the inner product

$$\langle \psi | \phi \rangle = \int \psi^\dagger \phi dV. \quad (7)$$

From the definition of an adjoint of antilinear operators

$$\langle K_i^\dagger \psi | \phi \rangle = \langle \psi | K_i \phi \rangle^* \quad (8)$$

it can be shown that the adjoint of the time-reversal operator has the form

$$K_i^\dagger = i \Sigma_{y,i} K_{0,i}, \quad (9)$$

which is consistent with the unitary condition in Eq. (6).

The closed form for the electron-electron interaction in the relativistic domain is not known, therefore, only approximate expressions are used. The commonly applied extensions of one-electron Dirac Hamiltonian to the many-electron case are the Dirac-Coulomb  $H^{\text{DC}}$  and Dirac-Coulomb-Breit  $H^{\text{DB}}$  Hamiltonians [48]

$$H^{\text{DC}} = \sum_i^N D_i + \sum_{i<j}^N \frac{1}{r_{ij}}, \quad (10)$$

$$H^{\text{DB}} = \sum_i^N D_i + \sum_{i<j}^N \left[ \frac{1}{r_{ij}} - \frac{\vec{\alpha}_i \cdot \vec{\alpha}_j}{2r_{ij}} + \frac{(\vec{\alpha}_i \cdot \vec{r}_{ij})(\vec{\alpha}_j \cdot \vec{r}_{ij})}{2r_{ij}^3} \right]. \quad (11)$$

Here,  $N$  is the number of electrons,  $\vec{r}_i$  is the position vector of the  $i$ th electron, and  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ .

The well-known extension of the one-electron time-reversal operator (3) to the many-electron case [16,17] can be written as

$$\mathcal{K} = \prod_i^N K_i. \quad (12)$$

It can be shown that  $\mathcal{K}$  is unitary in the sense of Eq. (C1) and commutes with the Hamiltonians (10) and (11):

$$\mathcal{K}^\dagger \mathcal{K} = \mathcal{K} \mathcal{K}^\dagger = \hat{1}, \quad (13)$$

$$[H^{\text{DC}}, \mathcal{K}] = 0, \quad (14)$$

$$[H^{\text{DB}}, \mathcal{K}] = 0. \quad (15)$$

These expressions reflect the fact that  $\mathcal{K}$  corresponds to a symmetry of the system described by the relativistic many-electron Hamiltonians, namely, time-reversal symmetry. However,  $\mathcal{K}$  is an antilinear operator, and thus cannot in general be represented as exponential of a linear Hermitian operator  $\mathcal{O}$ , i.e.,  $\mathcal{K} \neq e^{i\mathcal{O}}$ . Therefore, time-reversal symmetry cannot be directly associated with an observable quantity [3]. In Sec. IV, we show how the operator  $\mathcal{K}$  can be connected to the exponential of an antilinear operator.

The square of any antilinear operator becomes a linear operator, and in the case of  $\mathcal{K}$ , the commutation relations (14) and (15) of the original operator  $\mathcal{K}$  are preserved. Moreover, due to the simple relation between the one-electron time-reversal operator and its adjoint

$$K_i = -K_i^\dagger, \quad (16)$$

$\mathcal{K}^2$  becomes a Hermitian operator. Thus, we can write

$$\mathcal{K}^2(c_1\Psi + c_2\Phi) = c_1\mathcal{K}^2\Psi + c_2\mathcal{K}^2\Phi, \quad (17)$$

$$[H^X, \mathcal{K}] = 0 \Rightarrow [H^X, \mathcal{K}^2] = 0, \quad (18)$$

$$\mathcal{K}^2 = (\mathcal{K}^2)^\dagger, \quad (19)$$

where the  $N$ -electron wave functions  $\Psi$  and  $\Phi$  belong to the Fock subspace for  $N$  fermions,  $\Psi, \Phi \in S^-H^{\otimes N}$ ,  $H = [L^2(\mathbb{R}^3)]^4$ , with inner product defined in Appendix A,  $X = \text{DC, DB}$  and the operator  $S^-$  antisymmetrizes a tensor. In the following, capital Greek letters represent wave functions from the Fock subspace  $S^-H^{\otimes N}$ . Finally, utilizing the simple relation for the one-electron time-reversal operator

$$K_i^2 = -1, \quad (20)$$

it is straightforward to show that  $\mathcal{K}^2$  has the form

$$\mathcal{K}^2 = (-1)^N \hat{1} \quad (21)$$

with  $\hat{1}$  being the identity operator in  $S^-H^{\otimes N}$ .

Expressions (17)–(19) define conservation law for many-electron relativistic systems, with operator of symmetry

$$e^{i\theta\mathcal{K}^2} = e^{i\theta(-1)^N} \hat{1}. \quad (22)$$

Note that this operator just changes the phase of wave functions. The corresponding constant of motion

$$\frac{d}{dt} \langle \Psi | \mathcal{K}^2 | \Psi \rangle = 0 \quad (23)$$

represents the fact that the wave functions do not change their boson (+1) or fermion (−1) symmetry while evolving in time. An equivalent statement is that Hamiltonians  $H^{\text{DC}}$  and  $H^{\text{DB}}$

share eigenfunctions with the operator  $\mathcal{K}^2$ , giving rise to the quantum number  $\pm 1$  [16,17]:

$$H^X \Psi = E \Psi, \quad (24)$$

$$\mathcal{K}^2 \Psi = (-1)^N \Psi, \quad (25)$$

where  $X = \text{DC, DB}$ . Although these are fundamentally important observations, they are not as useful in spectroscopy as spin symmetries in the many-electron nonrelativistic domain.

In the next section, we define and describe some properties of the recently proposed operator  $\mathcal{K}_+^2$  [34,35], and consider in details its relation to  $\mathcal{K}$ . Unlike the  $\mathcal{K}^2$  operator, it has the potential to supplement the role of spin symmetry in the relativistic domain.

### III. TIME-REVERSAL GENERATOR

Bučinský *et al.* [34,35] recently proposed the many-electron operator

$$\mathcal{K}_+ = \sum_i^N K_i. \quad (26)$$

The operator in Eq. (26) is antilinear, but unlike  $\mathcal{K}$  it is not unitary [for the definition of  $\mathcal{K}_+^\dagger$ , see Eq. (C1)]:

$$\mathcal{K}_+^\dagger \mathcal{K}_+ = \mathcal{K}_+ \mathcal{K}_+^\dagger \neq 1, \quad (27)$$

thus, it does not represent a symmetry operation. However, as it is shown in Sec. IV, it is connected to  $\mathcal{K}$  through

$$\mathcal{K} = e^{\frac{\pi}{2}\mathcal{K}_+}. \quad (28)$$

This exponential mapping is in some aspects similar to the standard relation between a unitary operator  $\mathcal{U}$  and the corresponding Hermitian operator  $\mathcal{O}$ ,  $\mathcal{U} = e^{i\mathcal{O}}$ . If such operators commute with the Hamiltonian, the symmetry and conservation law of the system are defined by  $\mathcal{U}$  and  $\mathcal{O}$ , respectively. Thus, we call the operator  $\mathcal{K}_+$  a generator of the time-reversal operator  $\mathcal{K}$ , in analogy to the elements of the Lie algebra being infinitesimal generators of the Lie group. Unfortunately,  $\mathcal{K}_+$  is still an antilinear operator, and it can therefore not be associated with an observable quantity (it is not diagonalizable) even though it commutes with the Dirac-Coulomb Hamiltonian

$$[H^{\text{DC}}, \mathcal{K}_+] = 0, \quad (29)$$

$$[H^{\text{DB}}, \mathcal{K}_+] \neq 0. \quad (30)$$

For completeness, we also note that  $\mathcal{K}_+$  does not commute with the Dirac-Coulomb-Breit Hamiltonian. However, it can be shown that its square is a linear Hermitian operator [utilizing Eq. (16)] which still commutes with the Dirac-Coulomb Hamiltonian:

$$\mathcal{K}_+^2(c_1\Psi + c_2\Phi) = c_1\mathcal{K}_+^2\Psi + c_2\mathcal{K}_+^2\Phi, \quad (31)$$

$$[H^{\text{DC}}, \mathcal{K}_+] = 0 \Rightarrow [H^{\text{DC}}, \mathcal{K}_+^2] = 0, \quad (32)$$

$$\mathcal{K}_+^2 = (\mathcal{K}_+^2)^\dagger. \quad (33)$$

Therefore, it corresponds to an observable and as it turns out it has a much richer eigenvalue spectrum than  $\mathcal{K}^2$  [Eq. (25)]. In Sec. IV, we prove the following eigenvalue theorem:

$$\begin{aligned} \mathcal{K}_+^2 \Psi &= -k^2 \Psi, \quad k \in \mathbb{N}_0, \\ \text{odd } N &\Leftrightarrow \text{odd } k, \\ \text{even } N &\Leftrightarrow \text{even } k. \end{aligned} \quad (34)$$

Here,  $N$  refers to the total number of electrons in a system. When constructing the eigenfunction  $\Psi$  of  $\mathcal{K}_+^2$  as a specific linear combination of Slater determinants, where each determinant is composed of Kramers-restricted molecular orbitals (see Sec. VII), we observe that these eigenfunctions have a more refined eigenvalue spectrum and degeneracy

$$\begin{aligned} \mathcal{K}_+^2 \Psi(N, N_O) &= -k^2 \Psi(N, N_O), \\ \text{odd } N &\Leftrightarrow k = 1, 3, \dots, N_O, \\ \text{even } N &\Leftrightarrow k = 0, 2, \dots, N_O, \end{aligned} \quad (35)$$

where  $N_O$  is the number of unpaired electrons (open shells).

Note that in Eqs. (34) and (35), as well as in the following discussion, we omit the index  $k$  for the eigenfunction  $\Psi_k$  to simplify the notation. However, the reader should keep in mind that eigenfunctions  $\Psi$  always associate with a specific eigenvalue  $-k^2$ .

#### IV. EIGENSPECTRUM OF $\mathcal{K}_+^2$ OPERATOR

In this section, we prove the eigenvalue theorem (34) and establish the relation between the many-electron operators  $\mathcal{K}$  [Eq. (12)] and  $\mathcal{K}_+$  [Eq. (26)].

Since the operators  $\mathcal{K}_+^2$  and  $\mathcal{K}^2$  commute

$$[\mathcal{K}_+^2, \mathcal{K}^2] = 0 \quad (36)$$

and  $\mathcal{K}^2$  is just a scaled identity operator [Eq. (21)], both operators share the same set of eigenfunctions

$$\mathcal{K}_+^2 \Psi = \kappa \Psi, \quad (37)$$

$$\mathcal{K}^2 \Psi = (-1)^N \Psi. \quad (38)$$

Here, the eigenvalue  $\kappa$  is considered an unknown real number. In the following, we show that the form of eigenvalues  $\kappa$  [Eq. (34)] is a direct consequence of expressions (37) and (38).

Defining  $e^{\theta K_i}$  through the Taylor series expansion and utilizing repeatedly the property of the one-electron time-reversal operator (20), we can write (see Appendix B)

$$e^{\theta K_i} = \cos(\theta) + K_i \sin(\theta). \quad (39)$$

Choosing  $\theta = \pi/2$  or  $\theta = \pi$ , we get

$$e^{\frac{\pi}{2} K_i} = K_i, \quad (40)$$

$$e^{\pi K_i} = -1. \quad (41)$$

Employing Eq. (40) and the commutation relation  $[K_i, K_j] = 0$  in a many-fermion case, we can rewrite the time-reversal operator (12) as

$$\mathcal{K} = \prod_i^N K_i = \prod_i^N e^{\frac{\pi}{2} K_i} = e^{\frac{\pi}{2} \sum_i^N K_i}. \quad (42)$$

As a result, we obtain the relation (28) for many-fermion operators

$$\mathcal{K} = e^{\frac{\pi}{2} \mathcal{K}_+} \quad (43)$$

and similarly for their adjoint

$$\mathcal{K}^\dagger = e^{\frac{\pi}{2} \mathcal{K}_+^\dagger}. \quad (44)$$

Multiplying the last two equations and realizing that  $\mathcal{K}_+^\dagger = -\mathcal{K}_+$  [see Eq. (16)], the unitarity of  $\mathcal{K}$  can readily be obtained.

We now turn our attention to the square of the time-reversal operator  $\mathcal{K}$ :

$$\mathcal{K}^2 = e^{\pi \mathcal{K}_+} \quad (45)$$

since it provides us with the link between the eigenvalues of  $\mathcal{K}^2$  and  $\mathcal{K}_+^2$  operators. Applying Eq. (37), we obtain

$$\begin{aligned} e^{\pi \mathcal{K}_+} \Psi &= \left( 1 + \pi \mathcal{K}_+ + \frac{\pi^2}{2!} \mathcal{K}_+^2 + \dots \right) \Psi \\ &= \left( 1 + \frac{\pi^2}{2!} \kappa + \frac{\pi^4}{4!} \kappa^2 + \dots \right) \Psi \\ &\quad + \left( \pi + \frac{\pi^3}{3!} \kappa + \frac{\pi^5}{5!} \kappa^2 + \dots \right) \mathcal{K}_+ \Psi, \end{aligned} \quad (46)$$

and Eq. (38), we get

$$e^{\pi \mathcal{K}_+} \Psi = \mathcal{K}^2 \Psi = (-1)^N \Psi. \quad (47)$$

Combining the last two equations, we can write

$$\begin{aligned} (-1)^N \Psi &= \left( 1 + \frac{\pi^2}{2!} \kappa + \frac{\pi^4}{4!} \kappa^2 + \dots \right) \Psi \\ &\quad + \left( \pi + \frac{\pi^3}{3!} \kappa + \frac{\pi^5}{5!} \kappa^2 + \dots \right) \mathcal{K}_+ \Psi. \end{aligned} \quad (48)$$

It is worth to examine two possibilities of the action of  $\mathcal{K}_+$  on the wave function  $\Psi$ :

$$\mathcal{K}_+ \Psi = 0, \quad (49)$$

$$\mathcal{K}_+ \Psi \equiv \Phi. \quad (50)$$

In the first case, by substituting Eq. (49) into Eqs. (37) and (48), we immediately see that Eq. (49) is satisfied only for boson-type wave functions (even number of electrons)

$$\mathcal{K}_+ \Psi = 0 \quad \Rightarrow \quad \kappa = 0 \quad \Rightarrow \quad (-1)^N \Psi = \Psi. \quad (51)$$

In the second case, it is possible to show that the wave function  $\Phi$  is orthogonal to  $\Psi$ , but since  $\mathcal{K}_+$  is not unitary,  $\Phi$  is not normalized to one (for proof, see Appendix C):

$$\langle \Psi | \Phi \rangle = 0, \quad (52)$$

$$\langle \Phi | \Phi \rangle = -\kappa. \quad (53)$$

Integrating Eq. (48) with  $\langle \Psi |$  and  $\langle \Phi |$  we get two expressions

$$(-1)^N = 1 + \frac{\pi^2}{2!} \kappa + \frac{\pi^4}{4!} \kappa^2 + \dots, \quad (54)$$

$$0 = \pi \kappa + \frac{\pi^3}{3!} \kappa^2 + \frac{\pi^5}{5!} \kappa^3 + \dots. \quad (55)$$

Since  $\kappa$  is an eigenvalue of a Hermitian operator it must be real, and we can therefore examine  $\kappa$  being a positive or a negative real number. For this purpose, we use the ansatz  $\kappa = k^2$  and  $\kappa = -k^2$ , respectively.

In the case of  $\kappa = k^2$ , we get from Eqs. (54) and (55)

$$(-1)^N = \cosh(\pi k), \quad (56)$$

$$0 = k \sinh(\pi k), \quad (57)$$

which is satisfied only for  $k = 0$  and even number of electrons  $N$ . More interesting is the case of  $\kappa = -k^2$ , where we get

$$(-1)^N = \cos(\pi k), \quad (58)$$

$$0 = k \sin(\pi k), \quad (59)$$

which is satisfied for integer numbers ( $k \in \mathbb{Z}$ ) with the following rule:

$$\begin{aligned} \text{odd } N &\Leftrightarrow \text{odd } k, \\ \text{even } N &\Leftrightarrow \text{even } k. \end{aligned} \quad (60)$$

We can further restrict  $k$  to positive integers including zero  $k \in \mathbb{N}_0$  since both positive and negative  $k$  produce the same eigenvalues  $\kappa$ . Thus, we have proved the theorem (34).

## V. PAIRED EIGENFUNCTIONS OF THE $\mathcal{K}_+^2$ OPERATOR

In Sec. IV, we have seen that the time-reversal generator when acting on normalized wave functions  $\Psi$  produces a non-normalized wave function  $\Phi$  [see Eqs. (50) and (53)]. By choosing the definition in Eq. (50) to

$$\mathcal{K}_+ \Psi \equiv k \tilde{\Psi} \Rightarrow \langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1 \quad (61)$$

such that  $k > 0$  and  $-k^2$  is the eigenvalue of  $\Psi$  defined in Eq. (34), then  $\tilde{\Psi}$  is a normalized wave function. Applying operator  $\mathcal{K}_+$  on Eq. (61) and employing Eq. (34) we get

$$\mathcal{K}_+ \tilde{\Psi} = -k \Psi. \quad (62)$$

Note that the choice of right-hand side in Eq. (61) fixes the relative phase of wave functions  $\Psi$  and  $\tilde{\Psi}$ . The relations (61) and (62) between  $\Psi$  and  $\tilde{\Psi}$  have been observed previously for Kramers-restricted Slater determinants [35].

The wave functions  $\Psi$  and  $\tilde{\Psi}$  are normalized, orthogonal, and share the same eigenvalue (see Appendix C)

$$\begin{aligned} \mathcal{K}_+^2 \Psi &= -k^2 \Psi, \\ \mathcal{K}_+^2 \tilde{\Psi} &= -k^2 \tilde{\Psi}. \end{aligned} \quad (63)$$

The only exception arises for  $k = 0$ , for which  $\mathcal{K}_+ \Psi$  is zero and thus  $\tilde{\Psi}$  is not uniquely defined. Nevertheless, due to Eqs. (50) and (53), we can change the implication in expression (51) to an equivalence

$$[\mathcal{K}_+ \Psi = 0 \Leftrightarrow k = 0] \Rightarrow (-1)^N \Psi = \Psi. \quad (64)$$

As a result, for  $k \neq 0$  the eigenspectrum of  $\mathcal{K}_+^2$  is at least two times degenerate, where Eqs. (61) and (62) describe the connection between these degenerate wave functions. The pair structure (61)–(63) is similar to the Kramers pairs arising from the time-reversal symmetry operator  $\mathcal{K}$ , defined as

$$\mathcal{K} \Psi \equiv \bar{\Psi}. \quad (65)$$

From the form of the  $\mathcal{K}^2$  operator (21), it is clear that  $\bar{\Psi}$  has the same eigenvalue as  $\Psi$  and because  $\mathcal{K}$  is unitary,  $\bar{\Psi}$  remains normalized. Indeed, there is a close connection between these two paired structures (see Appendix D), where for  $k = 0$

$$\mathcal{K}_+ \Psi = 0 \quad \wedge \quad \Psi = \bar{\Psi} \quad (66)$$

and for  $k \neq 0$

$$\begin{pmatrix} \cos(\frac{\pi}{2}k) & \sin(\frac{\pi}{2}k) \\ -\sin(\frac{\pi}{2}k) & \cos(\frac{\pi}{2}k) \end{pmatrix} \begin{pmatrix} \Psi \\ \tilde{\Psi} \end{pmatrix} = \begin{pmatrix} \bar{\Psi} \\ \tilde{\bar{\Psi}} \end{pmatrix}. \quad (67)$$

In addition, because  $k$  is an integer, we arrive at the following two cases:

$$\begin{aligned} \text{even } k &\Rightarrow \cos\left(\frac{\pi}{2}k\right) \begin{pmatrix} \Psi \\ \tilde{\Psi} \end{pmatrix} = \begin{pmatrix} \bar{\Psi} \\ \tilde{\bar{\Psi}} \end{pmatrix}, \\ \text{odd } k &\Rightarrow \sin\left(\frac{\pi}{2}k\right) \begin{pmatrix} \tilde{\Psi} \\ -\Psi \end{pmatrix} = \begin{pmatrix} \bar{\Psi} \\ \tilde{\bar{\Psi}} \end{pmatrix}. \end{aligned} \quad (68)$$

The sine and cosine functions change only the sign of the wave functions, and can be ignored in the following discussion. Based on Eqs. (68), we conclude that for boson systems (even  $k$  and  $N$ ), the time-reversal operator produces the same wave function and for a fermion system (odd  $k$  and  $N$ ),  $\bar{\Psi}$  and  $\tilde{\bar{\Psi}}$  are equal. In other words, the wave function  $\tilde{\Psi}$  in the eigenspectrum of  $\mathcal{K}_+^2$  can be reached by operating both with  $\mathcal{K}_+$  and  $\mathcal{K}$  in the fermion case, but only with the  $\mathcal{K}_+$  operator in the boson case.

## VI. QUANTUM NUMBER OF THE MANY-ELECTRON DIRAC-COULOMB HAMILTONIAN

In the case of *infinite-dimensional* Hilbert spaces, two operators which commute do not in general produce the same set of eigenfunctions, and therefore wave functions  $\Psi$  in Eq. (34) are not necessarily eigenfunctions of the Dirac-Coulomb Hamiltonian, despite of the commutation relation (32). The existence of a common set of degenerate eigenfunctions of two commuting operators must be proved for each case separately. For example, the  $\mathcal{K}^2$  operator has the very simple form (21), and thus it is easy to see that it shares eigenfunctions with the many-electron relativistic Hamiltonians [Eqs. (24) and (25)] and  $\mathcal{K}_+^2$  operator [Eqs. (37) and (38)].

The form of the  $\mathcal{K}_+^2$  is not as trivial as  $\mathcal{K}^2$ , and the proof that the former operator shares eigenfunctions with the Dirac-Coulomb Hamiltonian is not known to the authors, despite the fact that they commute (32). However, if two operators commute in *finite-dimensional* Hilbert space it can be shown that they automatically share the same set of eigenvectors. Fortunately, this can be utilized for  $\mathcal{K}_+^2$  and  $H^{\text{DC}}$  operators when represented in Fock subspace  $F(M, N)$  (subspace of  $S^- H^{\otimes N}$ ):

$$[H^{\text{DC}}, \mathcal{K}_+^2] = 0, \quad (69)$$

where a finite-dimensional basis in  $F(M, N)$ , used to represent the operators in Eq. (69), contains all Kramers-restricted Slater determinants (KRSD) obtained by distributing  $N$  electrons among  $M$  four-spinors. The proof of relation (69), which assumes the use of an orthonormal restricted kinetically

balanced basis [49] to represent four-spinors, is given in Appendix E. Finally, we can conclude that commutation relation (69) leads to a new quantum number (34) for solutions of the Dirac-Coulomb Hamiltonian.

In the nonrelativistic theory, multiconfiguration post-Hartree-Fock methods often utilize linear combination of Slater determinants (configuration state functions [50]) as many-electron basis. These functions account for spin symmetry of the one-component Hamiltonians (being eigenfunctions of spin operators), potentially reducing the computational cost and simplifying the analysis of the solutions. In the relativistic domain, the spin symmetry is broken but since  $\mathcal{K}_+^2$  and  $H^{\text{DC}}$  share the same set of eigenvectors, the relativistic counterpart of configuration state functions (CSF) can be defined using eigenvectors of the  $\mathcal{K}_+^2$  operator instead. We denote these functions as Kramers configuration state functions (KCSF) and discuss their construction in Sec. VII. The biggest potential advantage of these functions as a many-electron basis lies in the ability to predict the structure of the matrix representation of the Dirac-Coulomb Hamiltonian and other operators  $\mathcal{O}$  in this basis. This can give rise to selection rules (forbidden or allowed transition) in the relativistic domain. However, a detailed study of such rules is beyond the scope of this work. Herein, we show only four simple examples.

As a first example, let us consider Hermitian time-reversal antisymmetric operators

$$\begin{aligned} \mathcal{O}^\dagger &= \mathcal{O}, \\ \mathcal{K}^\dagger \mathcal{O} \mathcal{K} &= -\mathcal{O}. \end{aligned} \quad (70)$$

A typical example are operators responsible for interaction with magnetic fields or operators for total spin. For an even number of electrons, it holds that the Kramers-partner wave function  $\bar{\Psi}$  is equal, up to a sign, to the wave function  $\Psi$  [see Eq. (68)]. It is then easy to show that the inner product of this wave function with the operator  $\mathcal{O}$  is zero (see Appendix F):

$$\text{even } N \Rightarrow \langle \Psi | \mathcal{O} | \Psi \rangle = 0. \quad (71)$$

Although this expression holds for an exact wave function of the Dirac-Coulomb Hamiltonian, it can be extended also to KCSF. As a consequence, the diagonal elements of magnetic field operators represented in the KCSF basis are strictly zero for even-electron systems.

Another example is the connection of paired wave functions  $\Psi$  and  $\bar{\Psi}$  [Eq. (61)] with eigenvalues of the Dirac-Coulomb Hamiltonian. In the case of  $k \neq 0$ , when combining the commutation relation (69) with the definition of the paired wave function (61) we obtain

$$H^{\text{DC}} \mathbf{C} = E \mathbf{C}, \quad (72)$$

$$H^{\text{DC}} \tilde{\mathbf{C}} = E \tilde{\mathbf{C}}, \quad (73)$$

where  $\mathbf{C}$  are expansion coefficients in the KRSD basis. The paired eigenvectors thus share the same eigenvalue of both Dirac-Coulomb and  $\mathcal{K}_+^2$  operators [see also Eq. (63)]. In other words, if an eigenvector of the  $H^{\text{DC}}$  Hamiltonian is associated with a nonzero quantum number  $-k^2$ , its energy level is at least two times degenerate. Consequently, if an eigenvector  $\mathbf{C}^{nd}$  is nondegenerate, then its quantum number  $-k^2$  is equal to zero,

which may happen only for systems with an even number of electrons [Eq. (64)], i.e.,

$$H^{\text{DC}} \mathbf{C}^{nd} = E^{nd} \mathbf{C}^{nd} \Rightarrow \mathcal{K}_+ \mathbf{C}^{nd} = 0 \Leftrightarrow \text{even } N. \quad (74)$$

Similarly, all energy levels are at least  $2n$  times degenerate ( $n \in \mathbb{N}$ ) for systems with an odd number of electrons, which is a well-known fact easy to prove facilitating the time-reversal operator  $\mathcal{K}$  [18]. We can also translate these statements to the nonrelativistic framework, where the energetically nondegenerate states are allowed only for systems with an even number of electrons, like for instance closed-shell or open-shell singlet states.

As a third example, let us consider a doubly degenerate state  $\{\Psi_1, \Psi_2\}$  of the Dirac-Coulomb Hamiltonian. According to the above discussion, these states have the same eigenvalue  $-k^2$  and behave under time-reversal symmetry as [see Eq. (68)]

$$\text{even } N \Rightarrow \mathcal{K} \Psi_i = \pm \Psi_i, \quad i = 1, 2 \quad (75)$$

$$\text{odd } N \Rightarrow \mathcal{K} \Psi_1 = \pm \Psi_2. \quad (76)$$

The matrix representation of any Hermitian operator in the basis of two wave functions, either degenerate as  $\{\Psi_1, \Psi_2\}$  or nondegenerate, can be expanded as a linear combination of the identity matrix and the Pauli matrices. For Hermitian time-reversal antisymmetric operators (70), only Pauli matrices contribute in the case of so-called Kramers doublet (76), and only the Pauli  $y$  matrix contributes in the case of so-called non-Kramers doublet (75) [36]. To prove the last statement, use expressions (75) and (76) and techniques from Appendix F.

As a fourth example, we consider an even-electron system and two arbitrary states of the Dirac-Coulomb Hamiltonian,  $\Psi_1$  and  $\Psi_2$ . These two wave functions are related by time-reversal symmetry via Eq. (75), thus, the expectation value of an operator  $\mathcal{O}$  [Eq. (70)] can be expressed as

$$\langle \Psi_1 | \mathcal{O} | \Psi_2 \rangle = \pm \langle \mathcal{K} \Psi_1 | \mathcal{O} | \mathcal{K} \Psi_2 \rangle = \mp \langle \Psi_1 | \mathcal{O} | \Psi_2 \rangle^*. \quad (77)$$

Therefore, if wave functions  $\Psi_1$  and  $\Psi_2$  transform under time-reversal symmetry with the same (different) sign the matrix element (77) is a pure imaginary (real) number. As a result for systems with even number of electrons, the matrix representations of operators responsible for magnetic interactions are either pure real or pure imaginary numbers on off diagonal (77) and zero on the diagonal (71). This can help to design effective spin Hamiltonians used to characterize the heavy-element containing systems.

Finally, we note that the previous findings also hold for any approximate two-component Hamiltonians involving the Coulomb operator for electron-electron interaction. All those Hamiltonians commute with two-component version of the  $\mathcal{K}_+^2$  operator and share the same set of eigenvectors. Also note that a time-reversal antisymmetric magnetic field operator breaks the commutation relation (69) since the  $\mathcal{K}_+^2$  operator has no special commutation or anticommutation relation with the magnetic field operator.

## VII. KRAMERS CONFIGURATION STATE FUNCTIONS

In the previous section, we have argued that in order to relate eigenfunctions of the Dirac-Coulomb and  $\mathcal{K}_+^2$  operators and thus introducing a new quantum number, we need to represent

both operators in the Fock subspace  $F(M, N)$ . Moreover, in any practical application of the quantum theory, the discretization of the infinite-dimensional problems is essential. In this section, we investigate the matrix representation of the  $\mathcal{K}_+^2$  operator in the Fock subspace  $F(M, N)$  in more details. The complete basis in  $F(M, N)$  contains all Kramers-restricted Slater determinants obtained by distributing  $N$  electrons among  $M$  four-spinors. Since a one-electron operator  $K_i$ , alike spin operators in the nonrelativistic theory, mixes only associated Kramers pairs, when investigating the  $\mathcal{K}_+^2$  eigenvectors it is sufficient to involve only determinants with a constant number of excitations (i.e., constant number of unpaired electrons). In other words,  $\mathcal{K}_+^2$  has a block-diagonal structure in the Fock subspace  $F(M, N)$ . Here, the reader is referred to Appendix G, where the form of the  $\mathcal{K}_+^2$  operator in the second quantization formalism is employed to prove this statement.

Let us consider a basis consisting of Kramers-restricted Slater determinants with  $N_O$  unpaired (open-shell) electrons  $\{\Phi_i(N_O)\}$ . Each Slater determinant is constructed from a set of Kramers paired four-spinors [51]. To indicate the Kramers paired structure of the spinor  $m$ , we use bar over the index ( $\bar{m}$ ). The  $\mathcal{K}_+^2$  operator for an  $N$ -electron system can be expressed as

$$\mathcal{K}_+^2 = -N\hat{1} + 2 \sum_{i < j}^N K_i K_j \quad (78)$$

and the definition of the matrix elements of  $\mathcal{K}_+^2$  in the  $\{\Phi_i(N_O)\}$  basis reads as

$$(\mathcal{K}_+^2)_{ij} = \langle \Phi_i | \mathcal{K}_+^2 | \Phi_j \rangle. \quad (79)$$

From the form of the  $\mathcal{K}_+^2$  operator (78) and the discussion in the previous sections, we can draw some general conclusions about the properties of the matrix elements (79):

(i) The matrix elements of  $\mathcal{K}_+^2$  operator in the basis of Kramers-restricted wave functions are real numbers, as can be easily seen from the second quantization form of  $\mathcal{K}_+$  (see Appendix G).

(ii) The diagonal elements have the simple form (see also Ref. [34])

$$(\mathcal{K}_+^2)_{ii} = -N_O. \quad (80)$$

(iii) The  $\{\Phi_i(N_O)\}$  manifold can be split into two sets based on the even ( $e$ ) and odd ( $o$ ) number of unpaired barred spinors in the determinants  $\{\Phi_i^e\}$  and  $\{\Phi_i^o\}$ , respectively. The inner product between these two sets is zero because  $\mathcal{K}_+^2$  contains either double  $K_i K_j$  or neutral  $K_i K_i = -1$  contributions [see Eq. (78)]

$$\langle \Phi_i^e | \mathcal{K}_+^2 | \Phi_j^o \rangle = 0. \quad (81)$$

(iv) For system with an odd number of electrons it holds

$$\text{odd } N \Rightarrow \langle \Phi_i^o | \mathcal{K}_+^2 | \Phi_j^o \rangle = \langle \Phi_i^e | \mathcal{K}_+^2 | \Phi_j^e \rangle. \quad (82)$$

To prove expression (82), one needs the connection between even and odd sets

$$\Phi_i^o = \mathcal{K} \Phi_i^e \quad (83)$$

techniques from Appendix C, the commutation relation  $[\mathcal{K}_+, \mathcal{K}] = 0$ , unitarity of  $\mathcal{K}$ , and real-valued matrix elements  $(\mathcal{K}_+^2)_{ij}$ .

(v) For  $k \neq 0$ , eigenvectors of  $\langle \Phi_i^x | \mathcal{K}_+^2 | \Phi_j^x \rangle$  corresponding to the even ( $x = e$ ) or odd ( $x = o$ ) set are related to each other by the  $\mathcal{K}_+$  operator (see discussion in Sec. V).

To build the Kramers configuration state functions one needs to diagonalize the matrix representation of the  $\mathcal{K}_+^2$  operator in the basis of Kramers-restricted Slater determinants  $\{\Phi_i(N_O)\}$ , where  $N_O$  denotes a particular number of unpaired electrons. Intermediate products  $\mathcal{K}_+^2 \Phi_j$  for two and three unpaired electrons are listed in Appendix H. Here, we only summarize and discuss the final matrix elements (79).

For two unpaired electrons, the basis consists of  $\{\Phi_{12}, \Phi_{\bar{1}\bar{2}}, \Phi_{\bar{1}2}, \Phi_{1\bar{2}}\}$ , and the matrix elements of the  $\mathcal{K}_+^2$  operator are

$$\begin{matrix} & 12 & \bar{1}\bar{2} & \bar{1}2 & 1\bar{2} \\ \begin{matrix} 12 \\ \bar{1}\bar{2} \\ \bar{1}2 \\ 1\bar{2} \end{matrix} & \begin{pmatrix} -2 & 2 & 0 & 0 \\ 2 & -2 & 0 & 0 \\ 0 & 0 & -2 & -2 \\ 0 & 0 & -2 & -2 \end{pmatrix} & & & \end{matrix} \quad (84)$$

As discussed earlier, the matrix (84) is real and has a block-diagonal structure with the diagonal elements equal to minus the number of unpaired electrons. After diagonalization of the matrix (84) we obtain the eigenvalues  $e_i$  and eigenfunctions  $\Psi_i$  in the following form:

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{2}}(\Phi_{12} - \Phi_{\bar{1}\bar{2}}), & e_1 &= -4, \\ \Psi_2 &= \frac{1}{\sqrt{2}}(\Phi_{\bar{1}\bar{2}} + \Phi_{12}), & e_2 &= -4, \\ \Psi_3 &= \frac{1}{\sqrt{2}}(\Phi_{12} + \Phi_{\bar{1}\bar{2}}), & e_3 &= 0, \\ \Psi_4 &= \frac{1}{\sqrt{2}}(\Phi_{\bar{1}\bar{2}} - \Phi_{12}), & e_4 &= 0. \end{aligned} \quad (85)$$

The wave functions in Eqs. (85) satisfy expressions (35), (71), and (77). The paired structure for system with an even number of electrons, as described in Sec. IV, can also be readily verified:

$$\begin{aligned} \mathcal{K}_+ \Psi_1 &= 2\Psi_2, \\ \mathcal{K}_+ \Psi_2 &= -2\Psi_1, \\ \mathcal{K}_+ \Psi_i &= 0, \quad i = 3, 4 \\ \mathcal{K} \Psi_i &= -\Psi_i, \quad i = 1, 2 \\ \mathcal{K} \Psi_i &= \Psi_i, \quad i = 3, 4. \end{aligned} \quad (86)$$

Thus, according to notation in Sec. IV we can write

$$\Psi_2 = \tilde{\Psi}_1. \quad (87)$$

For comparison, let us consider the three-electron open-shell case. Because the matrix (79) has the block-diagonal structure (81) with both (even and odd) blocks identical (82),

we can focus only on the even set  $\langle \Phi_i^e | \mathcal{K}_+^2 | \Phi_j^e \rangle$ :

$$\begin{array}{cccc} & 123 & \bar{1}\bar{2}\bar{3} & \bar{1}\bar{2}\bar{3} & \bar{1}\bar{2}\bar{3} \\ \begin{array}{c} 123 \\ \bar{1}\bar{2}\bar{3} \\ \bar{1}\bar{2}\bar{3} \\ 123 \end{array} & \begin{pmatrix} -3 & 2 & 2 & 2 \\ 2 & -3 & -2 & -2 \\ 2 & -2 & -3 & -2 \\ 2 & -2 & -2 & -3 \end{pmatrix} & & \end{array} \quad (88)$$

Again, the matrix elements are real and the diagonal is equal to minus the number of unpaired electrons. Diagonalization of this matrix leads directly to the set of eigenvalues  $\{-9, -1, -1, -1\}$  with the corresponding eigenvectors (in columns)

$$\begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 & 0 \\ -1/2 & \sqrt{3}/6 & 0 & \sqrt{6}/3 \\ -1/2 & \sqrt{3}/6 & \sqrt{2}/2 & -\sqrt{6}/6 \\ -1/2 & \sqrt{3}/6 & -\sqrt{2}/2 & -\sqrt{6}/6 \end{pmatrix}. \quad (89)$$

The triply degenerate eigenvectors in (89) have been chosen to mimic as close as possible the nonrelativistic  $S^2$  eigenvectors [see Eq. (96)]. To construct the eigenvectors for the odd manifold one can apply either of the operators  $\mathcal{K}_+$  and  $\mathcal{K}$  [see Sec. V and Eq. (83)]. Note that the eigenfunctions are orthonormal, in contrast to the previously reported eigenfunctions with eigenvalue  $-1$  [35].

In Appendix I, we provide explicit expressions for the case of four and five open shells and in Supplemental Material [53] we make available a program for obtaining the appropriate Kramers configuration state functions for cases of up to 10 unpaired electrons.

The discussion in Secs. III–VI is valid for systems described by Dirac-Coulomb and one-component nonrelativistic or scalar relativistic Hamiltonians. Since spin symmetry is valid in the one-component domain we can compare the eigenfunctions of both  $\mathcal{K}_+^2$  and  $S^2$  [6] operators in more detail. In one-component theory, the appropriate basis functions are spin-restricted Slater determinants  $\{\Phi^s\}$  in which  $S^2$  has the matrix form

$$(\mathcal{S}^2)_{ij} = \langle \Phi_i^s | \mathcal{S}^2 | \Phi_j^s \rangle. \quad (90)$$

Considering the case of two open-shell electrons  $\{\Phi_{12}^s, \Phi_{\bar{1}\bar{2}}^s, \Phi_{\bar{1}\bar{2}}^s, \Phi_{1\bar{2}}^s\}$  we obtain

$$\begin{array}{cccc} & 12 & \bar{1}\bar{2} & \bar{1}\bar{2} & \bar{1}\bar{2} \\ \begin{array}{c} 12 \\ \bar{1}\bar{2} \\ \bar{1}\bar{2} \\ \bar{1}\bar{2} \end{array} & \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} & & \end{array} \quad (91)$$

with eigenvalues and eigenvectors

$$\begin{aligned} \Psi^{1,1} &= \Phi_{12}^s, & e_1 &= 2, \\ \Psi^{1,-1} &= \Phi_{\bar{1}\bar{2}}^s, & e_2 &= 2, \\ \Psi^{1,0} &= \frac{1}{\sqrt{2}}(\Phi_{\bar{1}\bar{2}}^s + \Phi_{1\bar{2}}^s), & e_3 &= 2, \\ \Psi^{0,0} &= \frac{1}{\sqrt{2}}(\Phi_{\bar{1}\bar{2}}^s - \Phi_{1\bar{2}}^s), & e_4 &= 0. \end{aligned} \quad (92)$$

To be consistent with the previous discussion, we have used unbarred ( $\alpha$ ) and barred ( $\beta$ ) notation for the one-electron spinors. Comparing the eigenfunctions (92) and (85), we note that while the singlet  $\Psi^{0,0}$  and the low-spin triplet  $\Psi^{1,0}$  wave functions remain unchanged, we need to combine the high-spin

triplet wave functions  $\Psi^{1,1}$  and  $\Psi^{1,-1}$  to obtain the remaining eigenfunctions in Eq. (85). Interestingly, this behavior was already observed when representing one-electron operators in the second quantization formalism. The standard excitation operators in the nonrelativistic theory [52] are

$$\begin{aligned} \hat{T}_{pq}^{1,1} &= -a_p^\dagger a_q, \\ \hat{T}_{pq}^{1,-1} &= a_p^\dagger a_q, \\ \hat{T}_{pq}^{1,0} &= \frac{1}{\sqrt{2}}(a_p^\dagger a_q - a_p^\dagger a_{\bar{q}}), \\ \hat{S}_{pq}^{0,0} &= \frac{1}{\sqrt{2}}(a_p^\dagger a_q + a_p^\dagger a_{\bar{q}}). \end{aligned} \quad (93)$$

When these operators act on the two-electron closed-shell Slater determinant, spin-adapted wave functions (92) are created. On the other hand, the excitation operators used to describe the one-electron Dirac operator [51]

$$\begin{aligned} \hat{E}_{\bar{p}q}^- &= (a_{\bar{p}}^\dagger a_q + a_p^\dagger a_{\bar{q}}), \\ \hat{E}_{\bar{p}q}^+ &= (a_{\bar{p}}^\dagger a_q - a_p^\dagger a_{\bar{q}}), \\ \hat{E}_{pq}^- &= (a_p^\dagger a_q - a_{\bar{p}}^\dagger a_{\bar{q}}), \\ \hat{E}_{pq}^+ &= (a_p^\dagger a_q + a_{\bar{p}}^\dagger a_{\bar{q}}) \end{aligned} \quad (94)$$

create Kramers configuration state functions (85) (up to a normalization factor). For a definition of the creation and annihilation operators, see the corresponding literature [51,52]. Moreover, the equivalent of the triplet operators  $\hat{T}$  [Eq. (93)] in the nonrelativistic case, known as Cartesian components of triplet excitation operators [52], produce wave functions of  $\mathcal{K}_+^2$  [Eq. (85)]. This reflects the fact that both  $\mathcal{K}_+^2$  and  $S^2$  are appropriate operators for representing the symmetry in the nonrelativistic theory.

In the case of three open-shell electrons, the matrix representation of  $S^2$  has a block-diagonal form. Due to the block-diagonal structure, it is possible to construct two identical  $4 \times 4$  matrices. In the same basis as  $\mathcal{K}_+^2$  in Eq. (88), one of the matrices reads as

$$\begin{array}{cccc} & 123 & \bar{1}\bar{2}\bar{3} & \bar{1}\bar{2}\bar{3} & \bar{1}\bar{2}\bar{3} \\ \begin{array}{c} 123 \\ \bar{1}\bar{2}\bar{3} \\ \bar{1}\bar{2}\bar{3} \\ 123 \end{array} & \begin{pmatrix} 15/4 & 0 & 0 & 0 \\ 0 & 7/4 & 1 & 1 \\ 0 & 1 & 7/4 & 1 \\ 0 & 0 & 1 & 7/4 \end{pmatrix} & & \end{array} \quad (95)$$

The eigenspectrum of this matrix is doubly degenerate  $\{15/4, 15/4, 3/4, 3/4\}$  permitting the freedom of unitary rotation among the degenerate eigenvectors. It is customary to choose the eigenvectors corresponding to eigenvalue  $15/4$  being simultaneously eigenvectors of  $S_z$  operator with eigenvalues  $3/2$  and  $1/2$ . The remaining eigenvectors with  $S_z$  eigenvalue  $1/2$  were selected in their conventional form [6] (eigenvectors ordered in columns)

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 & \sqrt{6}/3 \\ 0 & 1/\sqrt{3} & \sqrt{2}/2 & -\sqrt{6}/6 \\ 0 & 1/\sqrt{3} & -\sqrt{2}/2 & -\sqrt{6}/6 \end{pmatrix}. \quad (96)$$

Similarly to the case of two open-shell electrons, two of the low-spin eigenvectors  $\Psi^{3/4, 1/2}$  are identical to eigenvectors of

the  $\mathcal{K}_+^2$  operator [see Eq. (89)]. On the other hand, to obtain remaining eigenfunctions of Eq. (89) we need to combine both low-spin  $\Psi^{15/4,1/2}$  and high-spin  $\Psi^{15/4,3/2}$  eigenvectors, and hence break the  $S_z$  symmetry.

### VIII. CONCLUSIONS

In this work, we have shown the connection between the recently proposed time-reversal generator [34,35]

$$\mathcal{K}_+ = \sum_i^N K_i \quad (97)$$

and the well-known unitary time-reversal operator  $\mathcal{K}$

$$\mathcal{K} = e^{\frac{\pi}{2}\mathcal{K}_+} \quad (98)$$

for the case of an  $N$ -electron system. Based on the relation (98), we have proved the eigenvalue theorem for the square of the time-reversal generator  $\mathcal{K}_+^2$  without the need of knowing an explicit form of its eigenfunctions

$$\begin{aligned} \mathcal{K}_+^2 \Psi &= -k^2 \Psi, \quad k \in \mathbb{N}_0, \\ \text{odd } N &\Leftrightarrow \text{odd } k, \\ \text{even } N &\Leftrightarrow \text{even } k. \end{aligned} \quad (99)$$

Since  $\mathcal{K}_+^2$  operator commutes with the Dirac-Coulomb (DC) Hamiltonian in the basis of Kramers-restricted Slater determinants

$$[\mathbf{H}^{\text{DC}}, \mathcal{K}_+^2] = 0, \quad (100)$$

the eigenvalues  $-k^2$  represent a new quantum number for the relativistic wave functions and give rise to a new type of symmetry in relativistic many-particle systems described by DC Hamiltonian

$$\mathbf{U} \equiv e^{i\theta\mathcal{K}_+^2}. \quad (101)$$

Furthermore, the time-reversal generator defines an orthonormal pair of wave functions  $\{\Psi, \tilde{\Psi}\}$  which are degenerate eigenfunctions of both DC Hamiltonian and the  $\mathcal{K}_+^2$  operator

$$\mathcal{K}_+ \Psi \equiv k \tilde{\Psi}. \quad (102)$$

We have shown the connection between the pair  $\{\Psi, \tilde{\Psi}\}$  and standard Kramers pair  $\{\Psi, \bar{\Psi}\}$ . It turns out that while for an odd-electron system  $\bar{\Psi} = \pm \tilde{\Psi}$ , for an even-electron system  $\Psi = \pm \bar{\Psi}$  and  $\tilde{\Psi} \neq \bar{\Psi}$ . From these relations several consequences arise and are related to matrix elements of operators  $\mathcal{O}$  responsible for interactions with magnetic fields and to the degeneracy of energy levels for the Dirac-Coulomb Hamiltonian. One especially interesting result holds for systems with an even number of electrons, where the matrix elements of  $\mathcal{O}$  in the basis of eigenfunctions (99) are zero on the diagonal and either pure real or pure imaginary on the off diagonal.

The general eigenvalue theorem (99) was confirmed analytically in the basis composed of Kramers-restricted Slater determinants with further restriction on the quantum number  $k$  to the number of the unpaired electrons. A program solving the eigenvalue problem (99) is provided within the Supplemental Material [53].

The symmetry and corresponding constants of motion presented here offer a comparable amount of information about the relativistic many-electron systems as the spin quantum numbers in nonrelativistic theory. We therefore believe that the new quantum number  $-k^2$  will prove useful in different areas of quantum physics. There are several applications we can foresee:

(i) Since we have now access to the quantum number  $-k^2$  [Eq. (99)], it is possible to measure the difference

$$-k^2 - \langle \Psi | \mathcal{K}_+^2 | \Psi \rangle \quad (103)$$

with  $\Psi$  obtained from the Kramers-unrestricted solutions of density functional theory (DFT) or Hartree-Fock theory (HF). We call the measure (103) *Kramers contamination*, in analogy to the spin contamination in nonrelativistic DFT and HF theories, where it is evaluated as the difference of the  $S(S+1)$  spin quantum number and the inner product of spin-unrestricted wave functions over  $S^2$  operator. The Kramers contamination has already been studied in the framework of two-component HF theory in the pilot work which introduced the time-reversal generator (97) [34].

(ii) Characterization of spectra for heavy-element containing compounds and selection rules based on symmetry generated by the  $\mathcal{K}_+^2$  operator.

(iii) Kramers configuration state functions (KCSF) as relativistic analogs of the nonrelativistic configuration state functions (known also as spin-adapted functions) [50].

(iv) Reduced computational effort associated with the evaluation of operator matrix elements in the KCSF basis.

(v) Relation between the symmetry generated by the  $\mathcal{K}_+^2$  operator and double-group symmetry.

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### APPENDIX A

We assume that Kramers-restricted Slater determinants  $\{\Phi_i\}$  constitute a complete basis in the Fock subspace  $S^- H^{\otimes N}$ . Thus, to define inner product of two wave functions  $\Psi, \Phi \in S^- H^{\otimes N}$ , it is sufficient to define the inner product between two determinants

$$\langle \Phi_i | \Phi_j \rangle = \frac{1}{N!} \sum_{\zeta, \xi=1}^{N!} P_L^\zeta P_R^\xi (-1)^{\zeta+\xi} \langle \phi_{i1} | \phi_{j1} \rangle \dots \langle \phi_{iN} | \phi_{jN} \rangle. \quad (\text{A1})$$

Here, the permutation operator  $P_L$  ( $P_R$ ) acts on the indices of bra (ket) functions, and the inner product of two one-electron wave functions  $\langle \phi_i | \phi_j \rangle$  is defined in Eq. (7).

### APPENDIX B

For clarity, we omit the index  $i$  in  $K_i$  in the following text. For a real number  $\theta$  we can then write

$$\begin{aligned} e^{\theta K} &= 1 + \theta K + \frac{\theta^2}{2!} K^2 + \frac{\theta^3}{3!} K^3 + \frac{\theta^4}{4!} K^4 + \frac{\theta^5}{5!} K^5 + \dots \\ &= 1 + \theta K + \frac{\theta^2}{2!} (-1) + \frac{\theta^3}{3!} (-K) + \frac{\theta^4}{4!} + \frac{\theta^5}{5!} K + \dots \\ &= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \dots\right) + K \left(\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \dots\right) \\ &= \cos(\theta) + K \sin(\theta), \end{aligned} \quad (\text{B1})$$

where we have used repeatedly expression (20).

### APPENDIX C

The definition of the adjoint of an antilinear operator in the Fock subspace  $S^- H^{\otimes N}$  reads as

$$\langle \mathcal{O}^\dagger \Lambda_1 | \Lambda_2 \rangle = \langle \Lambda_1 | \mathcal{O} \Lambda_2 \rangle^*. \quad (\text{C1})$$

Note, however, that Eq. (C1) is given in the perspective of Appendix A. In that case, the definition of the adjoint of operators  $\mathcal{K}$  and  $\mathcal{K}_+$  follows from the expression for the adjoint of a one-electron antilinear operator (8). Furthermore, it requires that the Kramers-restricted determinants constitute a complete basis in  $S^- H^{\otimes N}$  and are constructed from orthonormal four-spinors.

Taking into account the above definition of an adjoint, from Eqs. (16) and (26) it follows that

$$\mathcal{K}_+^\dagger = -\mathcal{K}_+. \quad (\text{C2})$$

Assuming that the wave function  $\Phi$  is a normalized eigenfunction of  $\mathcal{K}_+^2$

$$\mathcal{K}_+^2 \Phi = \kappa \Phi, \quad \langle \Phi | \Phi \rangle = 1, \quad (\text{C3})$$

and defining the action of the time-reversal generator

$$\mathcal{K}_+ \Phi = \tilde{\Phi}, \quad (\text{C4})$$

the following statements are straightforward to show

$$\begin{aligned} \langle \Phi | \tilde{\Phi} \rangle &= \langle \Phi | \mathcal{K}_+ \Phi \rangle = \langle \mathcal{K}_+^\dagger \Phi | \Phi \rangle^* \\ &= \langle \Phi | \mathcal{K}_+^\dagger \Phi \rangle = -\langle \Phi | \mathcal{K}_+ \Phi \rangle = -\langle \Phi | \tilde{\Phi} \rangle \\ &\Rightarrow \langle \Phi | \tilde{\Phi} \rangle = 0, \end{aligned} \quad (\text{C5})$$

$$\begin{aligned} \langle \tilde{\Phi} | \tilde{\Phi} \rangle &= \langle \mathcal{K}_+ \Phi | \mathcal{K}_+ \Phi \rangle = \langle \mathcal{K}_+^\dagger \mathcal{K}_+ \Phi | \Phi \rangle^* \\ &= \langle \Phi | \mathcal{K}_+^\dagger \mathcal{K}_+ \Phi \rangle = -\langle \Phi | \mathcal{K}_+^2 \Phi \rangle = -\kappa \langle \Phi | \Phi \rangle \\ &\Rightarrow \langle \tilde{\Phi} | \tilde{\Phi} \rangle = -\kappa, \end{aligned} \quad (\text{C6})$$

$$\begin{aligned} \mathcal{K}_+^2 \Phi &= \mathcal{K}_+ \tilde{\Phi} = \kappa \Phi, \\ \mathcal{K}_+^2 \tilde{\Phi} &= \kappa \mathcal{K}_+ \Phi \\ &\Rightarrow \mathcal{K}_+^2 \tilde{\Phi} = \kappa \tilde{\Phi}. \end{aligned} \quad (\text{C7})$$

### APPENDIX D

Starting from the connection between the  $\mathcal{K}$  and  $\mathcal{K}_+$  operators (43), using a Taylor expansion and eigenvalue Eq. (34), we get

$$\begin{aligned} \bar{\Psi} &= \mathcal{K} \Psi = e^{\frac{\pi}{2} \mathcal{K}_+} \Psi \\ &= \left[ 1 - \frac{1}{2!} \left(\frac{\pi}{2} k\right)^2 + \frac{1}{4!} \left(\frac{\pi}{2} k\right)^4 + \dots \right] \Psi \\ &\quad + \left[ \frac{\pi}{2} - \frac{1}{3!} \left(\frac{\pi}{2}\right)^3 k^2 + \frac{1}{5!} \left(\frac{\pi}{2}\right)^5 k^4 + \dots \right] \mathcal{K}_+ \Psi. \end{aligned} \quad (\text{D1})$$

For  $k = 0$ , the wave function  $\Psi$  and its Kramers pair  $\bar{\Psi}$  are identical:

$$k = 0 \Rightarrow \bar{\Psi} = \Psi, \quad (\text{D2})$$

where we used  $\mathcal{K}_+ \Psi = 0$  [see Eq. (64)].

Considering the definition of  $\tilde{\Psi}$  [Eq. (61)], we can rewrite expression (D1) for  $k \neq 0$  as

$$\begin{aligned} \bar{\Psi} &= \left[ \cos\left(\frac{\pi}{2} k\right) \hat{1} + \frac{1}{k} \sin\left(\frac{\pi}{2} k\right) \mathcal{K}_+ \right] \Psi \\ &= \cos\left(\frac{\pi}{2} k\right) \Psi + \sin\left(\frac{\pi}{2} k\right) \tilde{\Psi}. \end{aligned} \quad (\text{D3})$$

We can repeat the same procedure for  $\tilde{\Psi}$  since it shares the same eigenvalue  $-k^2$  with  $\Psi$ . After obtaining

$$\tilde{\bar{\Psi}} = \cos\left(\frac{\pi}{2} k\right) \tilde{\Psi} - \sin\left(\frac{\pi}{2} k\right) \Psi, \quad (\text{D4})$$

we can combine this expression with Eq. (D3) to get the final result in compact matrix form

$$\begin{pmatrix} \cos\left(\frac{\pi}{2} k\right) & \sin\left(\frac{\pi}{2} k\right) \\ -\sin\left(\frac{\pi}{2} k\right) & \cos\left(\frac{\pi}{2} k\right) \end{pmatrix} \begin{pmatrix} \Psi \\ \tilde{\Psi} \end{pmatrix} = \begin{pmatrix} \bar{\Psi} \\ \tilde{\bar{\Psi}} \end{pmatrix}. \quad (\text{D5})$$

### APPENDIX E

In this Appendix, we assume summation over repeated indices, bold symbols stand for  $2 \times 2$  or  $4 \times 4$  matrices depending on the context, and the following index notation is employed:  $\lambda, \tau, \mu$ , and  $\nu$  denote atomic basis functions and  $p, q, r, s$ , and  $t$  are molecular orbital functions.

The orthonormal restricted kinetically balanced (RKB) [49] basis can be expressed as

$$\mathbf{X}_\lambda = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2c} \vec{\sigma} \cdot \vec{p} \end{pmatrix} \chi_\tau \begin{pmatrix} S_{\tau\lambda}^{-\frac{1}{2}} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & 2c T_{\tau\lambda}^{-\frac{1}{2}} \mathbf{1} \end{pmatrix}, \quad (\text{E1})$$

where  $\chi_\tau$  stands for a Gaussian-type scalar function and

$$S_{\lambda\tau} = \langle \chi_\lambda | \chi_\tau \rangle, \quad (\text{E2})$$

$$T_{\lambda\tau} = \langle \chi_\lambda | p^2 | \chi_\tau \rangle. \quad (\text{E3})$$

Due to the fact that the RKB basis commutes with the one-electron time-reversal symmetry (TS) operator

$$[\mathbf{K}, \mathbf{X}_\lambda] = 0, \quad (\text{E4})$$

the matrix elements of the TS operator have the simple form

$$\mathbf{K}_{\lambda\tau} = \langle \mathbf{X}_\lambda | \mathbf{K} | \mathbf{X}_\tau \rangle = -i \Sigma_y K_0 \delta_{\lambda\tau}. \quad (\text{E5})$$

The one-electron Dirac operator (1) in the basis (E1) can be written as

$$\begin{aligned} \mathbf{D}_{\lambda\tau} &= \langle \mathbf{X}_\lambda | \mathbf{D} | \mathbf{X}_\tau \rangle \\ &= \begin{pmatrix} \left( c^2 \delta_{\lambda\tau} + S_{\lambda\mu}^{-\frac{1}{2}} V_{\mu\nu} S_{\nu\tau}^{-\frac{1}{2}} \right) \mathbf{1} & c S_{\lambda\mu}^{-\frac{1}{2}} T_{\mu\tau}^{\frac{1}{2}} \mathbf{1} \\ c T_{\lambda\mu}^{\frac{1}{2}} S_{\mu\tau}^{-\frac{1}{2}} \mathbf{1} & -c^2 \delta_{\lambda\tau} \mathbf{1} + T_{\lambda\mu}^{-\frac{1}{2}} \mathbf{W}_{\mu\nu} T_{\nu\tau}^{-\frac{1}{2}} \end{pmatrix}, \end{aligned} \quad (\text{E6})$$

where the external potential matrices are

$$V_{\lambda\tau} = \langle \chi_\lambda | V | \chi_\tau \rangle, \quad (\text{E7})$$

$$\mathbf{W}_{\lambda\tau} = \langle \vec{\sigma} \cdot \vec{p} \chi_\lambda | V | \vec{\sigma} \cdot \vec{p} \chi_\tau \rangle. \quad (\text{E8})$$

That the matrices in Eqs. (E5) and (E6) commute is seen by rewriting the matrix  $\mathbf{W}$  as

$$\mathbf{W}_{\lambda\tau} = \langle \nabla_l \chi_\lambda | V | \nabla_l \chi_\tau \rangle \mathbf{1} + i \varepsilon_{lmn} \langle \nabla_l \chi_\lambda | V | \nabla_m \chi_\tau \rangle \sigma_n \quad (\text{E9})$$

and realizing that

$$[-i\sigma_y K_0, i\vec{\sigma}] = 0. \quad (\text{E10})$$

We can thus write the commutation relation between the one-electron Dirac Hamiltonian and the time-reversal operator in the orthonormal RKB basis as

$$[\mathbf{K}, \mathbf{D}] = 0. \quad (\text{E11})$$

Since four-spinor molecular orbital coefficients

$$\varphi_p = \mathbf{X}_\lambda \mathbf{C}_{\lambda p} \quad (\text{E12})$$

act like a unitary transformation from an orthonormal atomic orbital basis  $\mathbf{X}_\lambda$  to an orthonormal molecular orbital basis  $\varphi_p$  we can write

$$K_{pq} D_{qr} - D_{pq} K_{qr} = 0. \quad (\text{E13})$$

Thanks to the fact that the Coulomb electron-electron interaction is represented by a real scalar operator and that the time-reversal operator commutes with the RKB basis (E4), the following identity holds:

$$K_{pq} g_{qrst} - g_{pqst} K_{qr} + g_{srpq} K_{qt} - K_{pq} g_{srqt} = 0, \quad (\text{E14})$$

where

$$g_{prst} = \iint r_{12}^{-1} \varphi_p^\dagger(1) \varphi_r(1) \varphi_s^\dagger(2) \varphi_t(2) dV_{12}. \quad (\text{E15})$$

Due to the identities (E13) and (E14), the Dirac-Coulomb Hamiltonian and the time-reversal generator commute in the Fock subspace  $F(M, N)$ :

$$[\hat{H}^{\text{DC}}, \hat{\mathcal{K}}_+] = 0, \quad (\text{E16})$$

where  $F(M, N)$  contains all Kramers-restricted Slater determinants obtained by distributing  $N$  electrons among  $M$  four-spinors, and the operators  $\hat{H}^{\text{DC}}$  and  $\hat{\mathcal{K}}_+$  have the standard form in the second quantization formalism [3,51].

Finally, we can write the commutation relations in the basis of the Kramers-restricted Slater determinants  $\{\Phi_i\}$  since these form the complete basis in  $F(M, N)$ :

$$(\hat{H}^{\text{DC}})_{ij} (\hat{\mathcal{K}}_+)_{jk} - (\hat{\mathcal{K}}_+)_{ij} (\hat{H}^{\text{DC}})_{jk} = 0. \quad (\text{E17})$$

## APPENDIX F

For Hermitian time-reversal antisymmetric operators

$$\mathcal{O}^\dagger = \mathcal{O}, \quad (\text{F1})$$

$$\mathcal{K}^\dagger \mathcal{O} \mathcal{K} = -\mathcal{O} \quad (\text{F2})$$

and wave functions  $\Psi$  for which it holds that

$$\bar{\Psi} \equiv \mathcal{K} \Psi = e^{i\omega} \Psi, \quad (\text{F3})$$

it follows

$$\begin{aligned} \langle \Psi | \mathcal{O} | \Psi \rangle &= \langle \bar{\Psi} | \mathcal{O} | \bar{\Psi} \rangle = \langle \mathcal{K} \Psi | \mathcal{O} | \mathcal{K} \Psi \rangle \\ &= \langle \Psi | \mathcal{K}^\dagger \mathcal{O} \mathcal{K} | \Psi \rangle^* = -\langle \Psi | \mathcal{O} | \Psi \rangle^* \\ &= -\langle \Psi | \mathcal{O} | \Psi \rangle \end{aligned} \quad (\text{F4})$$

$$\Rightarrow \langle \Psi | \mathcal{O} | \Psi \rangle = 0. \quad (\text{F5})$$

Note that  $e^{i\omega}$  is an arbitrary phase factor and we have assumed that  $\mathcal{O}$  is a linear operator.

## APPENDIX G

To express the operator  $\mathcal{K}_+$  in the second quantization formalism, we start from the general form of the one-particle operators [51]

$$\begin{aligned} \mathcal{K}_+ &= \sum_{pq} [(\mathcal{K}_+)_{pq} a_p^\dagger a_q + (\mathcal{K}_+)_{p\bar{q}} a_p^\dagger a_{\bar{q}} \\ &\quad + (\mathcal{K}_+)_{\bar{p}q} a_{\bar{p}}^\dagger a_q + (\mathcal{K}_+)_{\bar{p}\bar{q}} a_{\bar{p}}^\dagger a_{\bar{q}}]. \end{aligned} \quad (\text{G1})$$

Utilizing the definition of the barred index  $\phi_{\bar{p}} = K \phi_p$ , realizing that the square of the one-electron time-reversal operator equals minus one [Eq. (20)], and that we are working with orthonormal one-particle functions, we can write

$$\mathcal{K}_+ = \sum_p (a_{\bar{p}}^\dagger a_p - a_p^\dagger a_{\bar{p}}). \quad (\text{G2})$$

It is now easy to see that the operator in Eq. (G2) mixes only determinants with the same number of unpaired electrons and that doubly occupied Kramers pairs are ignored. Finally, we note that the same observations hold for the square of the time-reversal generator.

## APPENDIX H

In the case of two open-shell electrons, the action of  $\mathcal{K}_+^2$  on the Slater determinant basis reads as

$$\begin{aligned} \mathcal{K}_+^2 \Psi_{12} &= -2\Psi_{12} + 2\Psi_{\bar{1}\bar{2}}, \\ \mathcal{K}_+^2 \Psi_{\bar{1}\bar{2}} &= 2\Psi_{12} - 2\Psi_{\bar{1}\bar{2}}, \\ \mathcal{K}_+^2 \Psi_{1\bar{2}} &= -2\Psi_{1\bar{2}} - 2\Psi_{\bar{1}2}, \\ \mathcal{K}_+^2 \Psi_{\bar{1}2} &= -2\Psi_{\bar{1}2} - 2\Psi_{1\bar{2}}. \end{aligned} \quad (\text{H1})$$

For the case of three open-shell electrons, we have chosen just the even manifold for our considerations since the odd manifold can be easily constructed applying the time-reversal

operator  $\mathcal{K}$  on the following expressions:

$$\begin{aligned}\mathcal{K}_+^2 \Psi_{123} &= -3\Psi_{123} + 2\Psi_{\bar{1}\bar{2}\bar{3}} + 2\Psi_{\bar{1}\bar{2}\bar{3}} + 2\Psi_{\bar{1}\bar{2}\bar{3}}, \\ \mathcal{K}_+^2 \Psi_{\bar{1}\bar{2}\bar{3}} &= 2\Psi_{123} - 3\Psi_{\bar{1}\bar{2}\bar{3}} - 2\Psi_{\bar{1}\bar{2}\bar{3}} - 2\Psi_{\bar{1}\bar{2}\bar{3}}, \\ \mathcal{K}_+^2 \Psi_{\bar{1}\bar{2}\bar{3}} &= 2\Psi_{123} - 2\Psi_{\bar{1}\bar{2}\bar{3}} - 3\Psi_{\bar{1}\bar{2}\bar{3}} - 2\Psi_{\bar{1}\bar{2}\bar{3}}, \\ \mathcal{K}_+^2 \Psi_{\bar{1}\bar{2}\bar{3}} &= 2\Psi_{123} - 2\Psi_{\bar{1}\bar{2}\bar{3}} - 2\Psi_{\bar{1}\bar{2}\bar{3}} - 3\Psi_{\bar{1}\bar{2}\bar{3}}.\end{aligned}\tag{H2}$$

### APPENDIX I

In the case of four unpaired electrons, the basis of determinants can be splitted into two separate independent branches of matrix representation of TR generator squared

$$\{\Phi_{1234}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}\}\tag{I1}$$

and

$$\{\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}\}.\tag{I2}$$

The even (odd) basis contains exclusively determinants with even (odd) number of barred spinors.

For illustration we will consider the action of TR generator squared in the form

$$\mathcal{K}_+^2 = -4\hat{1} + 2 \sum_{i<j} K_i K_j\tag{I3}$$

on the following four determinants  $\Phi_{1234}$ ,  $\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}$ ,  $\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}$ , and  $\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}$ :

$$\begin{aligned}\mathcal{K}_+^2 \Phi_{1234} &= -4\Phi_{1234} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 0\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \\ \mathcal{K}_+^2 \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} &= +2\Phi_{1234} - 4\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 0\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \\ \mathcal{K}_+^2 \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} &= -4\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 0\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}, \\ \mathcal{K}_+^2 \Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} &= +2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} + 0\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 4\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}} - 2\Phi_{\bar{1}\bar{2}\bar{3}\bar{4}}.\end{aligned}\tag{I4}$$

Thus, we will obtain the following matrix representation of the  $\langle \Phi_x | \mathcal{K}_+^2 | \Phi_y \rangle$  products for the even basis manifold:

$$\begin{array}{cccccccc} & 1234 & \bar{1}\bar{2}\bar{3}\bar{4} & \bar{1}\bar{2}\bar{3}\bar{4} & \bar{1}\bar{2}\bar{3}\bar{4} & \bar{1}\bar{2}\bar{3}\bar{4} & \bar{1}\bar{2}\bar{3}\bar{4} & \bar{1}\bar{2}\bar{3}\bar{4} \\ \begin{array}{l} 1234 \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \\ \bar{1}\bar{2}\bar{3}\bar{4} \end{array} & \begin{pmatrix} -4 & 2 & 2 & 2 & 2 & 2 & 2 & 0 \\ 2 & -4 & -2 & -2 & -2 & -2 & 0 & 2 \\ 2 & -2 & -4 & -2 & -2 & 0 & -2 & 2 \\ 2 & -2 & -2 & -4 & 0 & -2 & -2 & 2 \\ 2 & -2 & -2 & 0 & -4 & -2 & -2 & 2 \\ 2 & -2 & 0 & -2 & -2 & -4 & -2 & 2 \\ 2 & 0 & -2 & -2 & -2 & -2 & -4 & 2 \\ 0 & 2 & 2 & 2 & 2 & 2 & 2 & -4 \end{pmatrix} & \end{array}\tag{I5}$$

with eigenvalues equal to

$$\{-16, -4, -4, -4, -4, 0, 0, 0\}^T\tag{I6}$$

and the eigenvector coefficients (ordered in columns)

$$\begin{pmatrix} -0.35355339 & 0.60199155 & 0.00000000 & -0.05524348 & 0.36681649 & 0.06127536 & 0.60927828 & 0.00503067 \\ 0.35355339 & 0.36496952 & 0.05988493 & -0.02197086 & -0.60226931 & -0.24113491 & 0.23364026 & -0.51211931 \\ 0.35355339 & -0.06618721 & 0.28381790 & -0.64415204 & 0.01161054 & -0.29172449 & 0.23048191 & 0.48659522 \\ 0.35355339 & 0.00476227 & -0.64487300 & -0.28554088 & -0.05081864 & 0.59413476 & 0.14515612 & 0.03055476 \\ 0.35355339 & -0.00476227 & 0.64487300 & 0.28554088 & 0.05081864 & 0.59413476 & 0.14515612 & 0.03055476 \\ 0.35355339 & 0.06618721 & -0.28381790 & 0.64415204 & -0.01161054 & -0.29172449 & 0.23048191 & 0.48659522 \\ 0.35355339 & -0.36496952 & -0.05988493 & 0.02197086 & 0.60226931 & -0.24113491 & 0.23364026 & -0.51211931 \\ -0.35355339 & -0.60199155 & 0.00000000 & 0.05524348 & -0.36681648 & 0.06127536 & 0.60927828 & 0.00503067 \end{pmatrix}.\tag{I7}$$

The odd basis has the following matrix representation:

$$\begin{array}{c}
 \bar{1}234 \quad \bar{1}\bar{2}34 \quad 1\bar{2}\bar{3}4 \quad 123\bar{4} \quad \bar{1}\bar{2}\bar{3}4 \quad \bar{1}\bar{2}\bar{3}\bar{4} \quad \bar{1}2\bar{3}\bar{4} \quad \bar{1}\bar{2}\bar{3}4 \\
 \begin{array}{c}
 \bar{1}234 \\
 \bar{1}\bar{2}34 \\
 1\bar{2}\bar{3}4 \\
 123\bar{4} \\
 \bar{1}\bar{2}\bar{3}4 \\
 \bar{1}\bar{2}\bar{3}\bar{4} \\
 \bar{1}2\bar{3}\bar{4} \\
 1\bar{2}\bar{3}4
 \end{array}
 \begin{pmatrix}
 -4 & -2 & -2 & -2 & 2 & 2 & 2 & 0 \\
 -2 & -4 & -2 & -2 & 2 & 2 & 0 & 2 \\
 -2 & -2 & -4 & -2 & 2 & 0 & 2 & 2 \\
 -2 & -2 & -2 & -4 & 0 & 2 & 2 & 2 \\
 2 & 2 & 2 & 0 & -4 & -2 & -2 & -2 \\
 2 & 2 & 0 & 2 & -2 & -4 & -2 & -2 \\
 2 & 0 & 2 & 2 & -2 & -2 & -4 & -2 \\
 0 & 2 & 2 & 2 & -2 & -2 & -2 & -4
 \end{pmatrix}
 \end{array} \quad (18)$$

with eigenvalues equal to

$$\{-16, -4, -4, -4, -4, 0, 0, 0\}^T \quad (19)$$

and the appropriate coefficients (ordered in columns)

$$\begin{pmatrix}
 0.35355339 & -0.60199155 & 0.00000000 & 0.05524348 & 0.36681649 & -0.06127536 & -0.60927828 & -0.00503067 \\
 0.35355339 & 0.36496952 & -0.05988493 & -0.02197086 & 0.60226931 & -0.24113491 & 0.23364026 & -0.51211931 \\
 0.35355339 & -0.06618721 & -0.28381790 & -0.64415204 & -0.01161054 & -0.29172449 & 0.23048191 & 0.48659522 \\
 0.35355339 & 0.00476227 & 0.64487300 & -0.28554088 & 0.05081864 & 0.59413476 & 0.14515612 & 0.03055476 \\
 -0.35355339 & 0.00476227 & 0.64487300 & -0.28554088 & 0.05081864 & -0.59413476 & -0.14515612 & -0.03055476 \\
 -0.35355339 & -0.06618721 & -0.28381790 & -0.64415204 & -0.01161054 & 0.29172449 & -0.23048191 & -0.48659522 \\
 -0.35355339 & 0.36496952 & -0.05988493 & -0.02197086 & 0.60226931 & 0.24113491 & -0.23364026 & 0.51211931 \\
 -0.35355339 & -0.60199155 & 0.00000000 & 0.05524348 & 0.36681648 & 0.06127536 & 0.60927828 & 0.00503067
 \end{pmatrix}. \quad (110)$$

For the five open-shell electrons case (considering only the even barred basis manifold) we will obtain the following matrix representation:

$$\begin{array}{c}
 12345 \quad \bar{1}\bar{2}345 \quad \bar{1}2\bar{3}45 \quad \bar{1}\bar{2}\bar{3}45 \quad \bar{1}234\bar{5} \quad 1\bar{2}\bar{3}4\bar{5} \quad 1\bar{2}34\bar{5} \quad \bar{1}\bar{2}\bar{3}4\bar{5} \quad 1\bar{2}\bar{3}4\bar{5} \quad 1\bar{2}34\bar{5} \quad 1\bar{2}\bar{3}4\bar{5} \quad \bar{1}\bar{2}\bar{3}4\bar{5} \quad \bar{1}\bar{2}\bar{3}4\bar{5} \quad \bar{1}\bar{2}\bar{3}4\bar{5} \quad \bar{1}\bar{2}\bar{3}4\bar{5} \quad 1\bar{2}\bar{3}4\bar{5} \\
 \begin{array}{c}
 12345 \\
 \bar{1}\bar{2}345 \\
 \bar{1}\bar{2}\bar{3}45 \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}2\bar{3}4\bar{5} \\
 1\bar{2}\bar{3}4\bar{5} \\
 1\bar{2}34\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 1\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 \bar{1}\bar{2}\bar{3}4\bar{5} \\
 1\bar{2}\bar{3}4\bar{5}
 \end{array}
 \begin{pmatrix}
 -5 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 0 & 0 & 0 & 0 & 0 \\
 2 & -5 & -2 & -2 & -2 & -2 & -2 & -2 & 0 & 0 & 0 & 2 & 2 & 2 & 0 & 0 \\
 2 & -2 & -5 & -2 & -2 & -2 & 0 & 0 & -2 & -2 & 0 & 2 & 2 & 0 & 2 & 0 \\
 2 & -2 & -2 & -5 & -2 & 0 & -2 & 0 & -2 & 0 & -2 & 2 & 0 & 2 & 2 & 0 \\
 2 & -2 & -2 & -2 & -5 & 0 & 0 & -2 & 0 & -2 & -2 & 0 & 2 & 2 & 2 & 0 \\
 2 & -2 & -2 & 0 & 0 & -5 & -2 & -2 & -2 & 0 & -2 & 2 & 2 & 0 & 0 & 2 \\
 2 & -2 & 0 & -2 & 0 & -2 & -5 & -2 & -2 & 0 & -2 & 2 & 0 & 2 & 0 & 2 \\
 2 & -2 & 0 & 0 & -2 & -2 & -2 & -5 & 0 & -2 & -2 & 0 & 2 & 2 & 0 & 2 \\
 2 & 0 & -2 & -2 & 0 & -2 & -2 & 0 & -5 & -2 & -2 & 2 & 0 & 0 & 2 & 2 \\
 2 & 0 & -2 & 0 & -2 & -2 & 0 & -2 & -2 & -5 & -2 & 0 & 2 & 0 & 2 & 2 \\
 2 & 0 & 0 & -2 & -2 & 0 & -2 & -2 & -2 & -5 & 0 & 0 & 2 & 2 & 2 & 2 \\
 0 & 2 & 2 & 2 & 0 & 2 & 2 & 0 & 2 & 0 & 0 & -5 & -2 & -2 & -2 & -2 \\
 0 & 2 & 2 & 0 & 2 & 2 & 0 & 2 & 0 & 2 & 0 & -2 & -5 & -2 & -2 & -2 \\
 0 & 2 & 0 & 2 & 2 & 0 & 2 & 2 & 0 & 0 & 2 & -2 & -2 & -5 & -2 & -2 \\
 0 & 0 & 2 & 2 & 2 & 0 & 0 & 0 & 2 & 2 & 2 & -2 & -2 & -2 & -5 & -2 \\
 0 & 0 & 0 & 0 & 0 & 2 & 2 & 2 & 2 & 2 & 2 & -2 & -2 & -2 & -2 & -5
 \end{pmatrix}
 \end{array} \quad (111)$$

with eigenvalues being equal to

$$\{-25, 5 \times (-9), 10 \times (-1)\}^T. \quad (112)$$

The matrix representation of  $\mathcal{K}_+^2$  in the odd basis manifold (83) of the five open-shell case is identical to Eq. (111) [see Eq. (82)]. The eigenvectors of the five open-shell case are not shown for brevity. The interested reader might use the attached FORTRAN code [53] to obtain eigenfunctions and eigenvalues of  $\mathcal{K}_+^2$  for cases with up to 10 unpaired electrons.

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- [53] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevA.94.052104> for FORTRAN program to generate Kramers configuration state functions for cases of up to 10 unpaired electrons.