Quaternion symmetry in relativistic molecular calculations: The Dirac–Hartree–Fock method

T. Saue, H. J Aa Jensen

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T. Saue[a] and H. J. Aa Jensen
Department of Chemistry, University of Southern Denmark—Main campus: Odense University, DK-5230 Odense M, Denmark

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A symmetry scheme based on the irreducible corepresentations of the full symmetry group of a molecular system is presented for use in relativistic calculations. Consideration of time-reversal symmetry leads to a reformulation of the Dirac–Hartree–Fock equations in terms of quaternion algebra. Further symmetry reductions due to molecular point group symmetry are then manifested by a descent to complex or real algebra. Spatial symmetry will be restricted to D_{2h} and subgroups, and it will be demonstrated that the Frobenius–Schur test can be used to characterize these groups as a whole. The resulting symmetry scheme automatically provides maximum point group and time-reversal symmetry reduction of the computational effort, also when the Fock matrix is constructed in a scalar basis, that is, from the same type of electron repulsion integrals over symmetry-adapted scalar basis functions as in nonrelativistic theory. An illustrative numerical example is given showing symmetry reductions comparable to the nonrelativistic case. © *1999 American Institute of Physics.* [S0021-9606(99)31637-8]

I. INTRODUCTION

Symmetry plays an important role both in the theoretical formulation and the computational implementation of molecular quantum mechanics. On the one hand, it elucidates theory, possibly leading to its reformulation in a more compact form. On the other hand, it may greatly reduce the computational effort in the implementation of theory.

The full symmetry group of a molecular system within the Born–Oppenheimer approximation consists of all unitary or antiunitary operators that commute with its electronic Hamiltonian.[1] Physically, the antiunitary operators involve time reversal, whereas rotations, reflections, and inversion of space and spin coordinates are unitary operators. As the product of two antiunitary operators is a unitary operator, we need to consider only one antiunitary operator, namely the time-reversal operator itself; all others can then be expressed as products of the time-reversal operator and a unitary operator.

In the nonrelativistic realm, the Hamiltonian is spin-free, allowing a separation of spin and spatial symmetry. In the relativistic realm, however, spin symmetry is lost and the single point groups are replaced by double groups.[2] These are constructed from the single groups by the introduction of an extra element $\overline{E}$, corresponding to a rotation of 2π about an arbitrary axis. This leads to a doubling of the number of elements, but in general not to a doubling of the number of irreducible representations (irreps). For instance, the single point group D_2 has four irreps, but in the corresponding double group only one extra irrep appears. The extra irreps are spanned by fermion functions and are therefore denoted fermion irreps. Correspondingly, the irreps of the single groups are termed boson irreps. When time reversal is included in the symmetry group as well, it is no longer possible to form representations such that the product of two operators is represented by the product of the corresponding representation matrices. However, it is still possible to form a system of matrices, a corepresentation, that may be broken down to irreducible forms.[1,3,4]

In this paper we consider the exploitation of symmetry in relativistic molecular calculations in the finite basis approximation when the Hamiltonian is totally symmetric with respect to time-reversal symmetry (this excludes external magnetic fields and nuclear spins). We shall specifically investigate the closed-shell Dirac–Hartree–Fock (DHF) method, and we shall concentrate on the dominating computational task, namely the construction of Fock matrices.

A straightforward implementation of symmetry in relativistic molecular calculations would be to construct a basis adapted to double group symmetry (see Refs. 5–8 and references therein), or, alternatively, to use projective (ray) representations.[9,10] We shall, however, pursue a somewhat different approach in which we work with the irreducible corepresentations of the full symmetry group. A characteristic feature of the symmetry scheme that we present is the transfer of symmetry information into the algebra of the problem at hand. Considering only time-reversal symmetry, the Dirac–Hartree–Fock problem can be efficiently treated using quaternion algebra.[11] In the nonrelativistic limit this corresponds to using orbitals instead of spin-orbitals. However, as we shall see, for some point groups the problem may be reduced to complex or real algebra, which leads to further considerable savings in computation time and memory requirements of approximately a factor two and four, respectively, compared to not invoking point group symmetry. This symmetry scheme allows us to work with scalar basis func-

[a]Current address: IRSAMC—LPQ, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France.

tions (so-called atomic orbitals) adapted to boson irreps rather than fermion irreps, just as in nonrelativistic calculations. This has the advantage that it allows us to work with conventional integral packages for nonrelativistic *ab initio* calculations (although small modifications to skip the integral classes not used is, of course, computationally highly beneficial) and, as we have seen above, there is more symmetry to exploit. Spatial symmetry will be restricted to D_{2h} and subgroups thereof. This is the set of all single point groups with no elements of order higher than two. We shall therefore denote them binary groups. The symmetry scheme presented in this article has been implemented in DIRAC,[11,12] a code for four-component relativistic molecular calculations which incorporates the nonrelativistic two-electron integral generator HERMIT.[13]

The article is organized as follows: In Sec. II we focus on time-reversal symmetry and reduce the Dirac equation to quaternion form. In Sec. III the structure of Dirac spinors is analyzed in terms of the boson irreps of the molecular point group. In Sec. IV we present the new symmetry scheme based on quaternion algebra that automatically provides maximum time reversal and point group symmetry reduction in computational implementations based on the finite basis approximation, with basis functions adapted to boson irreps, as in nonrelativistic implementations. The symmetry scheme is applied to the Dirac–Hartree–Fock problem and the computational gains are illustrated by a test case.

II. TIME-REVERSAL SYMMETRY

Our point of departure is the time-independent Dirac equation

$$\hat{h}_D\psi = E\psi; \quad \hat{h}_D = \beta' mc^2 + c(\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}) + \hat{V}, \tag{1}$$

where $\hat{h}_D$ is the Dirac operator in the field $\hat{V}$ of fixed nuclei with the zero point aligned with the nonrelativistic energy scale. The Dirac matrices $\boldsymbol{\alpha}$ and β' are given by

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix}; \quad \beta' = \begin{bmatrix} 0 & 0 \\ 0 & -2I_2 \end{bmatrix};$$

$$I_n - n\times n \ \text{identity matrix}. \tag{2}$$

The Pauli matrices $\boldsymbol{\sigma}$ are given in their standard representation,[14]

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{3}$$

Note that this corresponds to a specific choice of spin quantization, namely along the *z*-axis. This is never a problem in nonrelativistic calculations because the spin symmetry is completely decoupled from the spatial symmetry, and the spin may thus be quantized along an arbitrary axis, which conventionally is chosen to be the *z*-axis. Even though spin is not a good quantum number for relativistic systems, we shall see in this section how the Pauli spin matrices form a link between the Dirac equation, time-reversal symmetry, and quaternion algebra. We first briefly recapitulate salient features of quaternion algebra. Next we demonstrate how quaternion algebra naturally allows exploitation of time-reversal symmetry. Finally we apply these results to the Dirac equation given above.

A. Quaternion algebra and time-reversal symmetry

A quaternion number is given by

$$q = \sum_{\Lambda=0}^{3} v_\Lambda e_\Lambda = v_0 + v_1\check{\imath} + v_2\check{\jmath} + v_3\check{k}; \quad v_\Lambda \in \grave{R}. \tag{4}$$

In his landmark paper on ''magnetic electrons,'' [14] Pauli in a footnote refers to a remark by P. Jordan, stating that the algebra of the spin matrices times imaginary i is identical to that of the quaternion units $\check{\imath}, \check{\jmath}$, and $\check{k}$. In other words, we can make the isomorphous connection

$$e_1 = \check{\imath} \leftrightarrow i\sigma_z; \quad e_2 = \check{\jmath} \leftrightarrow i\sigma_y; \quad e_3 = \check{k} \leftrightarrow i\sigma_x. \tag{5}$$

This allows the expression of quaternion numbers as

$$q \equiv [s,\mathbf{v}] \leftrightarrow s + i(\tilde{\boldsymbol{\sigma}}\cdot\mathbf{v}), \tag{6}$$

where s can be considered the scalar part, $\mathbf{v}$ the vector part, and $\tilde{\boldsymbol{\sigma}} = (\sigma_z, \sigma_y, \sigma_x)$. Observe that there is a certain arbitrariness in the above connection in the sense that we can reassign the Pauli matrices to any cyclic permutation of the quaternion units. Accordingly, the quaternion units are equivalent, and in a complex number $a+ib$ the imaginary i may correspond to either $\check{\imath}, \check{\jmath}$, or $\check{k}$ without changing its algebraic properties [we shall later see that the specific choice in Eq. (6) corresponds to quantization of spin along the *z*-axis]. In view of this we shall term $s = v_0$ the real part and v_1, v_2, and v_3 the *i*-, *j*-, and *k*-imaginary parts, respectively, of a quaternion number.

The multiplication rule of the quaternion units is consequently in one-to-one correspondence to the multiplication rule of the spin matrices,[15]

$$\sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k; \Rightarrow e_i e_j = -\delta_{ij} - \epsilon_{ijk}e_k, \tag{7}$$

where ϵ_{ijk} is the Levi–Cevita symbol. Accordingly, the product of two quaternion numbers is

$$\begin{aligned} q_1 q_2 &= [s_1,\mathbf{v}_1][s_2,\mathbf{v}_2] \\ &= [(s_1 s_2 - \mathbf{v}_1\cdot\mathbf{v}_2),(s_2\mathbf{v}_1 + s_1\mathbf{v}_2 - \{\mathbf{v}_1\times\mathbf{v}_2\})]. \end{aligned} \tag{8}$$

The presence of the vector product in the vector part accounts for an important and troublesome facet of quaternion algebra, namely the noncommutivity under multiplication. We may add as an historical note that in the early days of quantum mechanics Dirac introduced the concept of *c*-numbers and *q*-numbers, where ''*c* stands for classical or maybe commuting'' and ''*q* stands for quantum or maybe queer.'' [16] Maybe they should stand for complex and quaternion?

The connection between quaternion algebra and time-reversal symmetry can be established in the following manner: In the four-component formalism the time-reversal operator $\hat{\mathcal{K}}$ has the explicit form[17]

$$\hat{\mathcal{K}} = -i[I_2\otimes\sigma_y]\hat{\mathcal{K}}_0, \tag{9}$$

where $\hat{\mathcal{K}}_0$ is the complex conjugation operator. Since we are concerned with fermion functions, we can alternatively define the time-reversal operator by its action on a fermion function ϕ,[18] that is

$$\hat{\mathcal{K}} a\phi = a^* \hat{\mathcal{K}}\phi; \quad \hat{\mathcal{K}}^2\phi = -\phi. \tag{10}$$

Using the notation $\hat{\mathcal{K}}\phi = \overline{\phi}$, then ϕ and $\overline{\phi}$ are said to form a Kramers pair. A Kramers restricted basis is formed by the union of a set of functions $\{\phi_i\}$ and their Kramers partners $\{\overline{\phi_i}\}$. Consider a Hermitian one-electron operator $\hat{O}$ which is symmetric under time reversal, that is $\hat{\mathcal{K}}\hat{O}\hat{\mathcal{K}}^{-1} = \hat{O}$. In a Kramers paired basis, the matrix representation of $\hat{O}$ then has the following structure:[18]

$$\mathbf{O} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & \mathbf{A}^* \end{bmatrix}; \quad \begin{matrix} \mathbf{A}^\dagger = \mathbf{A}; & A_{pq} = O_{pq} \\ \mathbf{B}^T = -\mathbf{B}; & B_{pq} = O_{p\bar{q}}. \end{matrix} \tag{11}$$

The matrix can be expanded in Pauli spin-matrices,

$$\begin{bmatrix} \mathbf{A}_R + i\mathbf{A}_I & \mathbf{B}_R + i\mathbf{B}_I \\ -\mathbf{B}_R + i\mathbf{B}_I & \mathbf{A}_R - i\mathbf{A}_I \end{bmatrix} = I_2 \otimes \mathbf{A}_R + [i\sigma_z] \otimes \mathbf{A}_I + [i\sigma_y] \otimes \mathbf{B}_R + [i\sigma_x] \otimes \mathbf{B}_I, \tag{12}$$

thus displaying a quaternion structure.

Since $\hat{O}$ is a Hermitian operator, its matrix may be diagonalized by a unitary transformation, giving real eigenvalues ε,

$$\mathbf{Oc} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{c}^\alpha \\ \mathbf{c}^\beta \end{bmatrix} = \varepsilon \begin{bmatrix} \mathbf{c}^\alpha \\ \mathbf{c}^\beta \end{bmatrix}. \tag{13}$$

Simple rearrangement[19] of this matrix equation gives

$$\mathbf{O}\overline{\mathbf{c}} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} -\mathbf{c}^{\beta *} \\ \mathbf{c}^{\alpha *} \end{bmatrix} = \varepsilon \begin{bmatrix} -\mathbf{c}^{\beta *} \\ \mathbf{c}^{\alpha *} \end{bmatrix}. \tag{14}$$

From the above manipulations we conclude that the matrix of a time-symmetric Hermitian operator $\hat{O}$ in a Kramers paired basis is doubly degenerate with eigenvectors related by time-reversal symmetry. The double-degeneracy of a time-symmetric matrix strongly suggests that it may be block-diagonalized into two parts. This is indeed possible, but only at the expense of going from complex to quaternion algebra,[18,20]

$$\mathbf{U}^\dagger \mathbf{O} \mathbf{U} = \begin{bmatrix} \mathbf{A} + \mathbf{B}\check{\jmath} & 0 \\ 0 & -\check{k}(\mathbf{A} + \mathbf{B}\check{\jmath})\check{k} \end{bmatrix}; \quad \mathbf{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mathbf{I} & \check{\jmath}\mathbf{I} \\ \check{\jmath}\mathbf{I} & \mathbf{I} \end{bmatrix}. \tag{15}$$

An analog (or rather its inverse) is known from numerical methods, in which the $n \times n$ complex Hermitian eigenvalue problem may be shown to be equivalent to a doubly degenerate $2n \times 2n$ real problem (see, for instance, Ref. 21). The eigenvalue problem Eq. (13) reduces to a quaternion eigenvalue equation of half the dimension,

$$[\mathbf{A} + \mathbf{B}\check{\jmath}][\mathbf{c}^\alpha - \mathbf{c}^{\beta *}\check{\jmath}] = \epsilon[\mathbf{c}^\alpha - \mathbf{c}^{\beta *}\check{\jmath}]. \tag{16}$$

Comparing this equation with Eq. (12) leads to the specific assignment of quaternion units we introduced in Eq. (5).

B. The quaternion Dirac equation

The Dirac operator in the molecular field (nuclear spins ignored) is symmetric under time reversal and can therefore be reduced to quaternion form. It turns out that the structure of the Dirac equation with respect to time-reversal symmetry is best displayed by a reordering of the Dirac 4-spinors such that components are grouped on spin labels (α, β) rather than large and small components (L,S),

$$\begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{bmatrix} \rightarrow \begin{bmatrix} \psi^{L\alpha} \\ \psi^{S\alpha} \\ \psi^{L\beta} \\ \psi^{S\beta} \end{bmatrix} = \begin{bmatrix} \psi^\alpha \\ \psi^\beta \end{bmatrix}. \tag{17}$$

With the reordered spinors, the time-reversal operator $\hat{\mathcal{K}}$ in Eq. (9) now has the explicit form

$$\hat{\mathcal{K}} = -i[\sigma_y \otimes I_2]\hat{\mathcal{K}}_0 = \begin{bmatrix} 0 & -I_2 \\ I_2 & 0 \end{bmatrix} \hat{\mathcal{K}}_0. \tag{18}$$

Application of this operator demonstrates explicitly that the eigenvectors $\mathbf{c}$ and $\overline{\mathbf{c}}$ in Eqs. (13) and (14) are related by time-reversal symmetry.

In the reordered form, the Dirac operator exhibits the time-symmetric form of Eq. (11),

$$\hat{h}_D = \begin{bmatrix} \hat{V} & -ic\hat{d}_z & 0 & -ic\hat{d}_- \\ -ic\hat{d}_z & -2mc^2 + \hat{V} & -ic\hat{d}_- & 0 \\ 0 & -ic\hat{d}_+ & \hat{V} & ic\hat{d}_z \\ -ic\hat{d}_+ & 0 & ic\hat{d}_z & -2mc^2 + \hat{V} \end{bmatrix};$$

$$\hat{d}_z = \frac{\partial}{\partial z} \quad \hat{d}_\pm = \frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}, \tag{19}$$

and the corresponding Dirac equation can therefore be written in two-component form using quaternion algebra (indicated by upper prescript Q),

$${}^Q\hat{h}_D\, {}^Q\psi = E\, {}^Q\psi, \tag{20}$$

where

$${}^Q\hat{h}_D = \left\{ \begin{bmatrix} \hat{V} & 0 \\ 0 & -2mc^2 + \hat{V} \end{bmatrix} - c\check{\imath} \begin{bmatrix} 0 & \hat{d}_z \\ \hat{d}_z & 0 \end{bmatrix} - c\check{\jmath} \begin{bmatrix} 0 & \hat{d}_y \\ \hat{d}_y & 0 \end{bmatrix} - c\check{k} \begin{bmatrix} 0 & \hat{d}_x \\ \hat{d}_x & 0 \end{bmatrix} \right\} \tag{21}$$

and

$${}^Q\psi = \psi^\alpha - \psi^{\beta *}\check{\jmath}. \tag{22}$$

The quaternion Dirac operator ${}^Q\hat{h}_D$ has an intriguing structure. The scalar potential enters the real part, whereas the kinetic energy part is spanned by the quaternion units $\check{\imath}, \check{\jmath}$, and $\check{k}$. The equivalence of quaternion units thus parallels the equivalence of the coordinate axes (x,y,z). The equivalence of the quaternion units also implies that the quaternion Dirac equation is unbiased with respect to choice of spin quantiza-

tion axis, contrary to the Dirac equation in standard form, where the form of the Pauli spin matrices refers to quantization along the *z*-axis.

III. SPINOR STRUCTURE

In the previous section we have seen that the time-reversal symmetry of the Dirac operator in the molecular field [Eq. (1)] allows solution of the corresponding eigenvalue problem by quaternion algebra. In this section we will consider spatial symmetry and discuss the structure of the Dirac spinors not in terms of fermion irreps, but rather boson irreps. In the next section we shall see that this opens up the possibility of further symmetry reductions in certain point groups whereby the two-component Dirac equation of Eq. (20) may be solved by real or complex algebra.

In terms of real scalar functions (''orbitals'' in nonrelativistic theory), any Dirac spinor has eight degrees of freedom, corresponding to the real and imaginary parts of the two large and the two small components. A given molecular 4-spinor belongs to a fermion irrep of the molecular double point group. However, as we shall show, each of the eight real scalar functions of the spinor belongs to a specific boson irrep.

We shall restrict the detailed discussion to the binary groups, that is D_{2h} and its subgroups. The binary groups are particularly simple to discuss since the single groups are all Abelian. Also, many computer codes limit point group symmetry to the binary groups using bit operations. The boson irreps of the binary groups are spanned by any scalar, the coordinates (x,y,z), the corresponding rotations (R_x,R_y,R_z), and the product of coordinates xyz. We shall denote the corresponding boson irreps Γ_0, Γ_q, Γ_{R_q}, and Γ_{xyz} $(q=x,y,z)$, respectively.

The Dirac equation in Eq. (1) can be transformed to two coupled equations by the method of elimination of the small component,

$$\left.\begin{aligned}&\left[\hat{V}+\frac{1}{2m}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\hat{B}(E)(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\right]\psi^L=E\psi^L\\&2mc\,\psi^S=\hat{B}(E)(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\psi^L\end{aligned}\right\}$$

$$\text{where}\quad \hat{B}(E)=\left[1+\frac{E-\hat{V}}{2mc^2}\right]^{-1}. \tag{23}$$

From the first line we can analyze the symmetry content of the two-component ψ^L in detail,

$$\Gamma_L=\begin{bmatrix}(\Gamma^R_{L\alpha},\Gamma^I_{L\alpha})\\(\Gamma^R_{L\beta},\Gamma^I_{L\beta})\end{bmatrix}, \tag{24}$$

where, for instance, $\Gamma^R_{L\alpha}$ refers to the symmetry of the real part of the $L\alpha$-component. Obviously the symmetry properties of the four real scalar functions in ψ^L are the same for relativistic four-component implementations and for relativistic two-component implementations, so this analysis is valid for both types of implementations. After the internal symmetry properties of ψ^L have been established, the internal symmetry properties of ψ^S follow from the second line in Eq. (23).

The potential $\hat{V}$ in the first line in Eq. (23) is diagonal and totally symmetric (as it defines the molecular point group) and does not give any information about the symmetry properties of the four real scalar functions in ψ^L. The second operator contains the energy-dependent operator $\hat{B}(E)$ which is totally symmetric and two operators of the form $(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$ that relate the symmetry of the four real scalar functions in ψ^L through the action of the Pauli spin matrices. We are not interested in the action of the momentum operator $\hat{\mathbf{p}}$ per se, only its symmetry content. Since the momentum operator transforms as the coordinates, we may express the structure of the second operator in terms of symmetry as

$$\begin{aligned}&[\boldsymbol{\sigma}\cdot(\Gamma^2_x,\Gamma^2_y,\Gamma^2_z)]\otimes\Gamma_0\otimes[\boldsymbol{\sigma}\cdot(\Gamma^1_x,\Gamma^1_y,\Gamma^1_z)]\\&=\begin{bmatrix}(\Gamma^2_x\Gamma^1_x+\Gamma^2_y\Gamma^1_y+\Gamma^2_z\Gamma^1_z)+i(\Gamma^2_x\Gamma^1_y-\Gamma^2_y\Gamma_x) & (\Gamma^2_z\Gamma^1_x-\Gamma^2_x\Gamma^1_z)+i(\Gamma^2_y\Gamma^1_z-\Gamma^2_z\Gamma^1_y)\\ -(\Gamma^2_z\Gamma^1_x-\Gamma^2_x\Gamma^1_z)+i(\Gamma^2_y\Gamma^1_z-\Gamma^2_z\Gamma^1_y) & (\Gamma^2_x\Gamma^1_x+\Gamma^2_y\Gamma^1_y+\Gamma^2_z\Gamma^1_z)-i(\Gamma^2_x\Gamma^1_y-\Gamma^2_y\Gamma^1_x)\end{bmatrix}=\begin{bmatrix}\Gamma_0+i\Gamma_{R_z} & \Gamma_{R_y}+i\Gamma_{R_x}\\ -\Gamma_{R_y}+i\Gamma_{R_x} & \Gamma_0-i\Gamma_{R_z}\end{bmatrix}.\end{aligned} \tag{25}$$

Note the quaternion structure [cf. Eq. (12)]. In the above equation we have introduced superscripts 1 and 2 to distinguish the two operators $(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$ involved in the direct product; otherwise, the antisymmetric part would vanish. This 2×2-matrix operator is totally symmetric in the double group and therefore it must leave the spinor structure in terms of boson irreps unchanged. In order to elucidate this spinor structure we consider a large component 2-spinor which is zero, except for the real part of the $L\alpha$-component which transforms as some irrep Γ_ϕ. From the above considerations we find the following distributions of boson irreps among the large components:

$$\begin{aligned}\Gamma_L&=\begin{bmatrix}\Gamma_0+i\Gamma_{R_z} & \Gamma_{R_y}+i\Gamma_{R_x}\\ -\Gamma_{R_y}+i\Gamma_{R_x} & \Gamma_0-i\Gamma_{R_z}\end{bmatrix}\otimes\begin{bmatrix}(\Gamma_\phi,0)\\(0,0)\end{bmatrix}\\&=\begin{bmatrix}(\Gamma_0,\Gamma_{R_z})\\(\Gamma_{R_y},\Gamma_{R_x})\end{bmatrix}\otimes\Gamma_\phi.\end{aligned} \tag{26}$$

This distribution of boson symmetries in the 2-spinor is invariant to repeated application of the operator in Eq. (25), and we have thus exposed the internal symmetry structure of the ψ_L 2-spinors.

More insight in the symmetry effect of the direct product in Eq. (25) can be obtained by inserting a specific choice of representatives of the given symmetry species,

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})=\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}+i\boldsymbol{\sigma}\cdot\hat{\mathbf{l}}. \tag{27}$$

The first term transforms as r^2 and therefore spans the totally symmetric irrep Γ_0, whereas the second term is essentially the spin-orbit operator, in which the components of the angular momentum operator $\hat{\mathbf{l}}$ transform as the rotations R_x, R_y, and R_z respectively. Note that with the choice $(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\times(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$, i.e., the nonrelativistic limit, we would lose the second term, which is the antisymmetric part of the direct product function.

The internal symmetry structure of the ψ_S 2-spinor is obtained from the symmetry content of the second line in Eq. (23),

$$\begin{aligned}\Gamma_S&=\begin{bmatrix}(\Gamma^R_{S\alpha},\Gamma^I_{S\alpha})\\(\Gamma^R_{S\beta},\Gamma^I_{S\beta})\end{bmatrix}\\&=[\boldsymbol{\sigma}\cdot(\Gamma_x,\Gamma_y,\Gamma_z)]\otimes\begin{bmatrix}(\Gamma^R_{L\alpha},\Gamma^I_{L\alpha})\\(\Gamma^R_{L\beta},\Gamma^I_{L\beta})\end{bmatrix}\\&=[\boldsymbol{\sigma}\cdot(\Gamma_x,\Gamma_y,\Gamma_z)]\otimes\begin{bmatrix}(\Gamma_0,\Gamma_{R_z})\\(\Gamma_{R_y},\Gamma_{R_x})\end{bmatrix}\otimes\Gamma_\phi\\&=\begin{bmatrix}(\Gamma_{xyz},\Gamma_z)\\(\Gamma_y,\Gamma_x)\end{bmatrix}\otimes\Gamma_\phi=\Gamma_{xyz}\otimes\Gamma_L.\end{aligned} \tag{28}$$

From this symmetry analysis we see that the quaternion formalism introduced in the previous section allows us to express the distribution of boson irreps amongst the real and imaginary parts of a 4-spinor in a compact form,

$$\Gamma_{Q_\psi}=\begin{bmatrix}\Gamma_{Q_\psi L}\\\Gamma_{Q_\psi S}\end{bmatrix}=\begin{bmatrix}[\Gamma_0,\ \boldsymbol{\Gamma}_{R_\mathbf{r}}]\\[\Gamma_{xyz},\ \boldsymbol{\Gamma}_\mathbf{r}]\end{bmatrix}\otimes\Gamma_\phi. \tag{29}$$

We observe that the three imaginary parts of the quaternion Dirac spinor are spanned by the symmetries of the coordinates or of the rotations. From the equivalence of the quaternion units it follows that the Dirac spinor in quaternion form has no preferred choice of quantization axis. On the basis of the above distribution we can immediately deduce a theoretically significant and computationally useful result for D_{2h} and subgroups. For a moment, let the choice $\Gamma_\phi=\Gamma_0$ represent our reference spinor. The choice of Γ_ϕ other than Γ_0 will generally introduce a redistribution of boson irreps. In some cases the original spinor can be recovered by the introduction of a quaternion phase factor; in other cases the choice of Γ_ϕ leads to a spinor qualitatively different from the reference spinor. The two cases are easily distinguished by observing that the two sets of boson irreps $\{\Gamma_0,\Gamma_\mathbf{r}\}$ and $\{\Gamma_{xyz},\Gamma_{R_\mathbf{r}}\}=\{\Gamma_0,\Gamma_\mathbf{r}\}\otimes\Gamma_{xyz}$ are identical in the absence of the operation of inversion. On the other hand, in the inversion group C_i irreps Γ_0 and Γ_{xyz} correspond to the gerade and ungerade irreps, respectively, so that in the presence of inversion the two sets respectively span the gerade and ungerade irreps. We observe that the Kramers partner of ${}^Q\psi$ corresponds to the choice $\Gamma_\phi=\Gamma_{R_y}$, which does not change the parity of the reference spinor. The symmetry content of the large and small components, on the other hand, is related by Γ_{xyz}, showing that they have different parity. In conclusion, we see that when we combine time-reversal symmetry with spatial symmetry limited to binary groups, there are at most two qualitatively different spinors in terms of symmetry content, corresponding—as we shall see in Sec. IV B—to two irreducible corepresentations solely distinguished by parity.

IV. THE FULL SYMMETRY GROUP

In the previous two sections we have investigated properties of the Dirac equation due to time reversal and spatial symmetry. In this section we shall combine the two symmetries, that is, we will work with corepresentations of the full symmetry group. We shall present a symmetry scheme that provides maximum point group and time-reversal symmetry reduction of the computational effort. This scheme will be applied to the Dirac–Hartree–Fock problem in a finite scalar basis. The basic features of the symmetry scheme are outlined in Sec. IV A. We proceed at first in a rather intuitive manner, but in Sec. IV B more rigour will be introduced by forming connections to the theory of irreducible corepresentations. Then, in Secs. IV C and IV D, the symmetry scheme is applied to the construction of the one- and two-electron Fock matrices, respectively. Finally, the possible symmetry reductions will be illustrated in Sec. IV E by a small test case, namely the F_2 molecule.

A. Application of symmetry to the DHF problem

In the quaternion formalism introduced in Sec. II, the Dirac–Hartree–Fock (DHF) equation has the form of the eigenvalue equation [Eq. (20)] with the quaternion Dirac operator replaced by a quaternion Fock operator. For further details the reader may consult Ref. 11. Solutions of this equation in the finite basis approximation may be obtained by separate expansion of the large and small components in a real basis

$$\begin{aligned}&{}^Q\psi_k=\begin{bmatrix}\boldsymbol{\chi}^L&0\\0&\boldsymbol{\chi}^S\end{bmatrix}\begin{bmatrix}{}^Q\mathbf{c}^L_k\\{}^Q\mathbf{c}^S_k\end{bmatrix};\\&{}^Qc^X=c^X_0+\check{\imath}c^X_1-\check{\jmath}c^X_2+\check{k}c^X_3\quad(X=L,S).\end{aligned} \tag{30}$$

We then obtain the quaternion DHF equations

$${}^Q\mathbf{F}\,{}^Q\mathbf{c}=\boldsymbol{\epsilon}\mathbf{S}\,{}^Q\mathbf{c};\quad S^{XY}_{ij}=\langle\chi^X_i|\chi^Y_j\rangle\delta_{XY};\quad {}^Q\mathbf{F}=\sum_{\Lambda=0}^{3}e_\Lambda\mathbf{F}_\Lambda, \tag{31}$$

where $\mathbf{S}$ is the (real) overlap matrix. The Fock matrix ${}^Q\mathbf{F}$ naturally splits into the one- and two-electron Fock matrices of one- and two-electron integral contributions, respectively.

The quaternion formulation of the DHF problem stems from the exploitation of time-reversal symmetry. In terms of the real algebra of a computational implementation, the construction of two real matrices, corresponding to the real and imaginary parts of the complex Hermitian Fock matrix, has

been replaced by the construction of four real matrices of half the dimension, thus reducing the operation count and memory requirement by a factor two. Furthermore, a quaternion diagonalization scheme may be employed. The use of quaternion diagonalizations (in terms of complex variables) for relativistic molecular DHF calculations was first advocated by N. Rösch.[20] A routine for quaternion diagonalization based on real variables[19] has been implemented in DIRAC and was found to speed up diagonalization by a factor six.

Further symmetry reductions may be obtained by invoking spatial symmetry. We assume that we work in a basis of real functions adapted to the boson irreps of the molecular point group. From the spinor structure in terms of boson irreps discussed in Sec. III, it is then clear that a given symmetry-adapted basis function can only contribute to certain positions in the Dirac spinor. If we choose $\Gamma_\phi = \Gamma_0$, the basis set expansion of a quaternion Dirac spinor may be written as

$$ {}^Q\psi = \begin{bmatrix} \sum_i \chi_i^L(\Gamma_i)\{c_{0i}^L(\Gamma_0) + c_{1i}^L(\Gamma_{R_z})\check{\imath} - c_{2i}^L(\Gamma_{R_y})\check{\jmath} + c_{3i}^L(\Gamma_{R_x})\check{k}\} \\ \sum_j \chi_j^S(\Gamma_j)\{c_{0j}^S(\Gamma_{xyz}) + c_{1j}^S(\Gamma_z)\check{\imath} - c_{2j}^S(\Gamma_y)\check{\jmath} + c_{3j}^S(\Gamma_x)\check{k}\} \end{bmatrix}, \tag{32} $$

where, e.g., $c_{0i}^L(\Gamma_0) = 0$ if $\Gamma_0 \neq \Gamma_i$. Each part of the quaternion coefficients corresponds to a certain position in the Dirac spinor and therefore to a particular boson irrep, as indicated in parentheses. Consider now a large component basis function of symmetry Γ_0. Clearly the number of nonzero contributions of the corresponding coefficient depends on the number of totally symmetric rotations. As the infinitesimal rotations R_x, R_y, and R_z are invariant under inversion, rotations about their own axes, and under reflection in the corresponding horizontal plane, only three possibilities exist,

(i) In groups with no mirror planes or rotations (C_1, C_i), all rotations are totally symmetric;
(ii) In groups with one rotation axis or one mirror plane (C_n, C_{nh}, S_n), only one rotation is totally symmetric;
(iii) For all other groups no rotations are totally symmetric.

For a basis function of irrep Γ_0, the classification above corresponds to a quaternion, complex, or real coefficient, respectively, in terms of nonzero contributions. This is an important result, because it means that the molecular point group symmetry effectively determines the algebra of the coefficient. For binary groups this result is straightforwardly extended to basis functions of any irrep χ_i. For these groups the relation $\Gamma_{R_x} \otimes \Gamma_{R_y} \otimes \Gamma_{R_z} = \Gamma_0$ holds, which implies

(i) when there is only one totally symmetric rotation, the other two rotations belong to the same irrep ($\neq \Gamma_0$); and
(ii) when there are no totally symmetric rotations, the three rotations belong to three different boson irreps.

Accordingly, when there are no totally symmetric rotations, the coefficients of basis functions of any boson irrep have only one nonzero contribution out of the four real variables in ${}^Q\mathbf{c}$. The coefficients are generally not real since they come with a quaternion unit. However, we will correct for this by shifting the quaternion unit over to the basis function ($\chi_\Gamma \rightarrow e_\Gamma \chi_\Gamma$), as will be demonstrated in Sec. IV C. For groups with only one totally symmetric rotation, equivalent shifts give strictly complex coefficients. This is the key step in the symmetry scheme presented in this paper: Each boson irrep will be associated with a quaternion unit. This corresponds to a transfer of symmetry information to algebra, and will allow symmetry reductions by reducing the algebra of the problem under study.

We have seen above that the binary groups can be classified according to the minimum algebra of expansion coefficients in the finite basis approximation. In the next section we shall see that this corresponds to a general classification of irreducible corepresentations in terms of the algebra of their representation matrices.

B. Irreducible corepresentations

In this section the results of the previous section will be put on a solid theoretical footing by making reference to the theory of irreducible representations.[1,3,4] When antiunitary operators are present in the symmetry group, it is no longer possible to form matrix representations so that the product of two group elements is represented by the product of the corresponding representation matrices. However, as shown by Wigner,[1] we may still form a set of matrices, a corepresentation, that may be broken down to irreducible forms.

Consider a set of functions $\{\phi_p^\gamma\}$ that span a fermion irrep γ of some (unitary) double group. We construct the set of Kramers partners $\{\phi_p^{\overline{\gamma}}\}$ by application of the time-reversal operator. It is straightforwardly shown that the fermion irreps γ and $\overline{\gamma}$ are related by complex conjugation, and they are further characterized by the Frobenius–Schur test,[3]

$$ \mathrm{FST} = \frac{1}{g}\sum_{\hat{G}} \chi^\gamma(\hat{G}^2) = \begin{cases} +1; & \text{real irrep} \\ 0; & \text{complex irrep} \\ -1; & \text{pseudoreal irrep} \end{cases}, \tag{33} $$

as will be discussed shortly (g is the order of the group). With regards to the sets $\{\phi_p^\gamma\}$ and $\{\phi_p^{\overline{\gamma}}\}$, they necessarily either span the same space or their intersection is void. Consider now the structure of the corresponding irreducible corepresentation of the full symmetry group, which is neces-

TABLE I. Classification of binary double groups. FST refers to the Frobenius–Schur test and T is the number of totally symmetric rotations.

	FST	T	
Quaternion groups	+1	3	C_1, C_i
Complex groups	0	1	C_2, C_s, C_{2h}
Real groups	−1	0	C_{2v}, D_2, D_{2h}

sarily spanned by the combined set $\{\phi_p^\gamma, \phi_{\bar{p}}^{\bar{\gamma}}\}$. To avoid linear dependencies in the case $\{\phi_p^\gamma\}=\{\phi_{\bar{p}}^{\bar{\gamma}}\}$, we assume that the set has been orthogonalized, but in such a manner that the Kramers pair structure has been preserved. For simplicity, superscripts γ and $\bar{\gamma}$ will be dropped in the following analysis. Acting with a general symmetry operation $\hat{G}$ (unitary or antiunitary), we obtain

$$\begin{aligned}\hat{G}\phi_q &= \sum_p \phi_p R_{pq}(\hat{G}) + \sum_{\bar{p}} \phi_{\bar{p}} R_{\bar{p}q}(\hat{G}),\\ \hat{G}\phi_{\bar{q}} &= \sum_p \phi_p R_{p\bar{q}}(\hat{G}) + \sum_{\bar{p}} \phi_{\bar{p}} R_{\bar{p}\bar{q}}(\hat{G}).\end{aligned} \tag{34}$$

Next we operate with the time-reversal operator on both sides in Eq. (34) to obtain

$$\begin{aligned}\hat{G}\phi_{\bar{q}} &= \sum_{\bar{p}} \phi_{\bar{p}} R^*_{pq}(\hat{G}) - \sum_p \phi_p R^*_{\bar{p}q}(\hat{G}),\\ -\hat{G}\phi_q &= \sum_{\bar{p}} \phi_{\bar{p}} R^*_{p\bar{q}}(\hat{G}) - \sum_p \phi_p R^*_{\bar{p}\bar{q}}(\hat{G}).\end{aligned} \tag{35}$$

This enables us to form the connections

$$R_{\bar{p}\bar{q}} = R^*_{pq}; \quad R_{\bar{p}q} = -R^*_{p\bar{q}}. \tag{36}$$

We have thus seen that the general structure of matrix corepresentations is

$$\hat{G}[\phi_q \phi_{\bar{q}}] = [\phi_p \phi_{\bar{p}}]\mathbf{R}(G) = [\phi_p \phi_{\bar{p}}]\begin{bmatrix} R_{pq} & R_{p\bar{q}} \\ -R^*_{p\bar{q}} & R^*_{pq}\end{bmatrix}. \tag{37}$$

This structure corresponds to the structure of the matrix of a time-symmetric operator $\hat{O}$ Eq. (11), and the matrix can therefore be block-diagonalized by a quaternion transformation Eq. (15). We shall shortly see that there are cases where the off-diagonal elements $R_{p\bar{q}}$ and $R_{\bar{p}q}$ are identically zero for unitary operators, such that matrix blocking is obtained without resorting to quaternion algebra. However, such automatic blocking is never obtained for antiunitary operators, as is immediately seen from the representation matrix of the time-reversal operator $\mathbf{R}(\hat{\mathcal{K}}) = \left[\begin{smallmatrix} 0 & -I \\ I & 0\end{smallmatrix}\right]$. In the quaternion representation, the time-reversal operator is represented by the quaternion unit $\check{j}$, whereas the representation matrices of the unitary subgroup are quaternion, complex, or real, depending on the distribution of Kramers partners among the irreps of the double point group,

(1) $\{\phi_p^\gamma\} \cap \{\phi_{\bar{p}}^{\bar{\gamma}}\} = 0$; FST $= +1$:
The Kramers partners are two equivalent bases for the same irrep ($\gamma = \bar{\gamma}$). For unitary operators, matrix elements $R_{p\bar{q}}$ and $R_{\bar{p}q}$ have to be zero, but in addition we may obtain $R_{pq} = R_{\bar{p}\bar{q}} = R^*_{pq}$ with proper alignment of the basis, that is by a suitable similarity transformation. Hence the representation matrices of irrep γ are real. On the other hand, the off-diagonal elements $O_{p\bar{q}}$ in the matrix of $\hat{O}$ are in general not zero, and the matrix can therefore only be block-diagonalized by a quaternion transformation.

(2) $\{\phi_p^\gamma\} \cap \{\phi_{\bar{p}}^{\bar{\gamma}}\} = 0$; FST $= +0$:
The Kramers partners span inequivalent irreps. Thus again matrix elements $R_{p\bar{q}}$ and $R_{p\bar{q}}$ have to be zero for unitary operators, and the irreducible corepresentation matrices are complex. The identical conclusion applies to the matrix of $\hat{O}$.

(3) $\{\phi_p^\gamma\} = \{\phi_{\bar{p}}^{\bar{\gamma}}\}$; FST $= -1$:
The Kramers partners are members of the same irrep ($\gamma = \bar{\gamma}$) and are rotated among each other under the unitary operations. The irreducible representation matrices are quaternion. On the other hand, the operator matrix is generally real. All matrix elements $O_{p\bar{q}}$ are zero by symmetry, whereas matrix elements O_{pq} are generally real.

We find that representation matrices and operator matrices are dualistic in the sense that real, complex, and pseudoreal (quaternion) irreps give quaternion, complex, and real operator matrices, respectively.

For binary groups, the above classification scheme applies to the group as a whole, as can be deduced from the Frobenius–Schur test: In the binary double groups $\hat{G}^2 = \bar{E}$ for rotations and reflections and $\hat{G}^2 = E$ for inversions and the element $\bar{E}$. This corresponds to a choice of Pauli gauge.[10] The Frobenius–Schur test thereby attains the simple form

$$\begin{aligned}\mathrm{FST} &= \frac{1}{g}\sum_{\hat{G}} \chi^\gamma(\hat{G}^2)\\ &= \frac{2}{g}[\chi(E)(1+n_I) + \chi(\bar{E})(n_C + n_\sigma)],\end{aligned} \tag{38}$$

where n_I, n_C, and n_σ are the number of inversions, rotations, and reflections, respectively, in the corresponding single point group. For fermion irreps we have $\chi(\bar{E}) = -\chi(E) = -n_\gamma$, leading to

$$\mathrm{FST} = \frac{1}{g}\sum_{\hat{G}} \chi^\gamma(\hat{G}^2) = \frac{2n_\gamma}{g}[(1+n_I) - (n_C + n_\sigma)]. \tag{39}$$

It follows that all fermion irreps of a given binary double group are of the same kind, so that the Frobenius–Schur test may be used to classify the group as a whole. The classification of the binary double groups into real, complex, and quaternion groups may be done by a simple count of symmetry operations. In fact, the Frobenius–Schur test can be replaced by a simple count T of totally symmetric rotations R_z, R_y, and R_x,

$$T = \begin{cases} 3; & \text{quaternion groups} \\ 1; & \text{complex groups} \\ 0; & \text{real groups}\end{cases}. \tag{40}$$

The classification of binary double groups is summarized in Table I. The classification corresponds exactly to the result of the previous section and demonstrates the link between symmetry and algebra. This link forms the basis for the symmetry scheme presented in this paper. Its application to the DHF problem will be demonstrated in the following.

C. Construction of the one-electron Fock matrix

In this section we will consider the one-electron Fock matrix which in the quaternion formalism is given by

$$ {}^{Q}\mathbf{F}^{[1]}=\begin{bmatrix} \mathbf{V}^{LL} & -c\check{\imath}\mathbf{D}_z^{LS}-c\check{\jmath}\mathbf{D}_y^{LS}-c\check{k}\mathbf{D}_x^{LS} \\ -c\check{\imath}\mathbf{D}_z^{SL}-c\check{\jmath}\mathbf{D}_y^{SL}-c\check{k}\mathbf{D}_x^{SL} & \mathbf{W}^{SS} \end{bmatrix}, \tag{41} $$

with the notation

$$ V_{\mu\nu}^{XY}=\langle\chi_\mu^X|\hat{V}|\chi_\nu^Y\rangle,\quad W_{\mu\nu}^{XY}=\langle\chi_\mu^X|\hat{V}-2c^2|\chi_\nu^Y\rangle,\quad D_{q,\mu\nu}^{XY}=\langle\chi_\mu^X|\frac{\partial}{\partial q}|\chi_\nu^Y\rangle. \tag{42} $$

When the operation of inversion is present in the molecular point group, the Fock matrix will split into two blocks corresponding to different parities ($\Gamma_\phi=\Gamma_0$ and $\Gamma_\phi=\Gamma_{xyz}$). When all rotations are totally symmetric, as in the groups C_1 and C_i, no further symmetry reductions are possible and the problem is solved by resorting to quaternion algebra. When there are only one or no totally symmetric rotations, further symmetry reductions are possible, as will be discussed presently. In the following, attention will be restricted to the block of the Fock matrix corresponding to $\Gamma_\phi=\Gamma_0$; the symmetry structure of the other block in groups with inversion symmetry is obtained by switching gerade and ungerade.

1. Real groups

We consider first the binary groups where no rotations are totally symmetric. This corresponds to the groups D_2, C_{2v}, and D_{2h}. In terms of contributions not zero by symmetry, the left-hand side of the DHF equations [Eq. (31)] can be written

$$ {}^{Q}\mathbf{F}^{[1]}\,{}^{Q}\mathbf{c}= \left[\begin{array}{c|cccc|cccc} & \multicolumn{4}{c|}{\text{Large components}} & \multicolumn{4}{c}{\text{Small components}} \\ & \Gamma_0 & \Gamma_{R_z} & \Gamma_{R_y} & \Gamma_{R_x} & \Gamma_{xyz} & \Gamma_z & \Gamma_y & \Gamma_x \\ \hline \Gamma_0 & \mathbf{V}^{LL} & 0 & 0 & 0 & 0 & -\check{\imath}c\mathbf{D}_z^{LS} & -\check{\jmath}c\mathbf{D}_y^{LS} & -\check{k}c\mathbf{D}_x^{LS} \\ \Gamma_{R_z} & 0 & \mathbf{V}^{LL} & 0 & 0 & -\check{\imath}c\mathbf{D}_z^{LS} & 0 & -\check{k}c\mathbf{D}_x^{LS} & -\check{\jmath}c\mathbf{D}_y^{LS} \\ \Gamma_{R_y} & 0 & 0 & \mathbf{V}^{LL} & 0 & -\check{\jmath}c\mathbf{D}_y^{LS} & -\check{k}c\mathbf{D}_x^{LS} & 0 & -\check{\imath}c\mathbf{D}_z^{LS} \\ \Gamma_{R_x} & 0 & 0 & 0 & \mathbf{V}^{LL} & -\check{k}c\mathbf{D}_x^{LS} & -\check{\jmath}c\mathbf{D}_y^{LS} & -\check{\imath}c\mathbf{D}_z^{LS} & 0 \\ \Gamma_{xyz} & 0 & -\check{\imath}c\mathbf{D}_z^{SL} & -\check{\jmath}c\mathbf{D}_y^{SL} & -\check{k}c\mathbf{D}_x^{SL} & \mathbf{W}^{SS} & 0 & 0 & 0 \\ \Gamma_z & -\check{\imath}c\mathbf{D}_z^{SL} & 0 & -\check{k}c\mathbf{D}_x^{SL} & -\check{\jmath}c\mathbf{D}_y^{SL} & 0 & \mathbf{W}^{SS} & 0 & 0 \\ \Gamma_y & -\check{\jmath}c\mathbf{D}_y^{SL} & -\check{k}c\mathbf{D}_x^{SL} & 0 & -\check{\imath}c\mathbf{D}_z^{SL} & 0 & 0 & \mathbf{W}^{SS} & 0 \\ T_x & -\check{k}c\mathbf{D}_x^{SL} & -\check{\jmath}c\mathbf{D}_y^{SL} & -\check{\imath}c\mathbf{D}_z^{SL} & 0 & 0 & 0 & 0 & \mathbf{W}^{SS} \end{array}\right] \left[\begin{array}{c} c_0^L \\ \check{\imath}c_1^L \\ -\check{\jmath}c_2^L \\ \check{k}c_3^L \\ c_0^S \\ \check{\imath}c_1^S \\ -\check{\jmath}c_2^S \\ \check{k}c_3^S \end{array}\right], \tag{43} $$

where basis functions have been ordered by boson irreps. In the present form, both the Fock matrix and coefficients are quaternion. However, we can make both matrix and coefficients real by a quaternion phase transfer, that is by shifting a quaternion phase from coefficients to basis functions. Formally, this is done by multiplying basis functions by a quaternion unit and corresponding coefficients by its complex conjugate. With the choice

$$ \begin{matrix} \chi_\Gamma^X\rightarrow e_\Gamma\chi_\Gamma^X \\ c_\Gamma^X\rightarrow e_\Gamma^* c_\Gamma^X \end{matrix}: \left\{\begin{array}{c|cccc} X=L & \Gamma_0 & \Gamma_{R_z} & \Gamma_{R_y} & \Gamma_{R_x} \\ X=S & \Gamma_{xyz} & \Gamma_z & \Gamma_y & \Gamma_x \\ \hline e_\Gamma & 1 & \hat{\imath} & \hat{\jmath} & k \end{array}\right., \tag{44} $$

Eq. (43) is transformed into

$$ {}^{R}\mathbf{F}^{[1]}\,{}^{R}\mathbf{c}= \left[\begin{array}{c|cccc|cccc} & \multicolumn{4}{c|}{\text{Large components}} & \multicolumn{4}{c}{\text{Small components}} \\ & \Gamma_0 & \Gamma_{R_z} & \Gamma_{R_y} & \Gamma_{R_x} & \Gamma_{xyz} & \Gamma_z & \Gamma_y & \Gamma_x \\ \hline \Gamma_0 & \mathbf{V}^{LL} & 0 & 0 & 0 & 0 & c\mathbf{D}_z^{LS} & c\mathbf{D}_y^{LS} & c\mathbf{D}_x^{LS} \\ \Gamma_{R_z} & 0 & \mathbf{V}^{LL} & 0 & 0 & -c\mathbf{D}_z^{LS} & 0 & c\mathbf{D}_x^{LS} & -c\mathbf{D}_y^{LS} \\ \Gamma_{R_y} & 0 & 0 & \mathbf{V}^{LL} & 0 & -c\mathbf{D}_y^{LS} & -c\mathbf{D}_x^{LS} & 0 & c\mathbf{D}_z^{LS} \\ \Gamma_{R_x} & 0 & 0 & 0 & \mathbf{V}^{LL} & -c\mathbf{D}_x^{LS} & c\mathbf{D}_y^{LS} & -c\mathbf{D}_z^{LS} & 0 \\ \Gamma_{xyz} & 0 & c\mathbf{D}_z^{SL} & c\mathbf{D}_y^{SL} & c\mathbf{D}_x^{SL} & \mathbf{W}^{SS} & 0 & 0 & 0 \\ \Gamma_z & -c\mathbf{D}_z^{SL} & 0 & c\mathbf{D}_x^{SL} & -c\mathbf{D}_y^{SL} & 0 & \mathbf{W}^{SS} & 0 & 0 \\ \Gamma_y & -c\mathbf{D}_y^{SL} & -c\mathbf{D}_x^{SL} & 0 & c\mathbf{D}_z^{SL} & 0 & 0 & \mathbf{W}^{SS} & 0 \\ \Gamma_x & -c\mathbf{D}_x^{SL} & c\mathbf{D}_y^{SL} & -c\mathbf{D}_z^{SL} & 0 & 0 & 0 & 0 & \mathbf{W}^{SS} \end{array}\right] \left[\begin{array}{c} c_0^L \\ c_1^L \\ -c_2^L \\ c_3^L \\ c_0^S \\ c_1^S \\ -c_2^S \\ c_3^S \end{array}\right] \tag{45} $$

By this operation four real matrices have been collapsed into one. This reduces the memory of the problem by a factor four and allows the solution of the eigenvalue equation entirely in terms of real algebra. For groups with inversion symmetry, the quaternion phases for basis functions in the block corresponding to $\Gamma_\phi = \Gamma_{xyz}$ are found by replacing the irreps in Eq. (44) by their direct products with Γ_{xyz}.

2. Complex groups

The groups C_s, C_2, and C_{2h} have one totally symmetric rotation. Three cases must be distinguished depending upon which rotation is totally symmetric. We consider first the case where Γ_{R_z} is totally symmetric. This implies $\Gamma_{R_x} = \Gamma_{R_y}$, $\Gamma_x = \Gamma_y$, and $\Gamma_z = \Gamma_{xyz}$. With the notation $q = \{x,y\}$, nonzero contributions to the left-hand side of the DHF equation are given by

$$
{}^{Q}\mathbf{F}^{[1]}\,{}^{Q}\mathbf{c} =
\left[\begin{array}{c|cc|cc}
 & \multicolumn{2}{c|}{\text{Large components}} & \multicolumn{2}{c}{\text{Small components}} \\
 & \Gamma_0 & \Gamma_{R_q} & \Gamma_{xyz} & \Gamma_q \\ \hline
\Gamma_0 & \mathbf{V}^{LL} & 0 & -\check{\imath}c\mathbf{D}_z^{LS} & -\check{\jmath}c\mathbf{D}_y^{LS} - \check{k}c\mathbf{D}_x^{LS} \\
\Gamma_{R_q} & 0 & \mathbf{V}^{LL} & -\check{\jmath}c\mathbf{D}_y^{LS} - \check{k}c\mathbf{D}_x^{LS} & -\check{\imath}c\mathbf{D}_z^{LS} \\
\Gamma_{xyz} & -\check{\imath}c\mathbf{D}_z^{SL} & -\check{\jmath}c\mathbf{D}_y^{SL} - \check{k}c\mathbf{D}_x^{SL} & \mathbf{W}^{SS} & 0 \\
\Gamma_q & -\check{\jmath}c\mathbf{D}_y^{SL} - \check{k}c\mathbf{D}_x^{SL} & -\check{\imath}c\mathbf{D}_z^{SL} & 0 & \mathbf{W}^{SS}
\end{array}\right]
\left[\begin{array}{c} c_0^L + \check{\imath}c_1^L \\ -\check{\jmath}c_2^L + \check{k}c_3^L \\ c_0^S + \check{\imath}c_1^S \\ \check{\jmath}c_2^S + \check{k}c_3^S \end{array}\right], \tag{46}
$$

in terms of basis functions ordered by boson irreps. The coefficients of the totally symmetric irrep Γ_0 are seen to be complex. To obtain complex coefficients for all irreps and a complex matrix we again introduce a quaternion phase transfer between coefficients and basis functions,

$$
\begin{array}{l}
\chi_\Gamma^X \rightarrow e_\Gamma \chi_\Gamma^X \\
c_\Gamma^X \rightarrow e_\Gamma^* c_\Gamma^X :
\end{array}
\left\{\begin{array}{c|ccc}
X=L & \Gamma_0 & \Gamma_{R_q} \\
X=S & \Gamma_{xyz} & \Gamma_q \\ \hline
e_\Gamma & 1 & \hat{k}
\end{array}\right., \tag{47}
$$

and we obtain

$$
{}^{C}\mathbf{F}^{[1]}\,{}^{C}\mathbf{c} =
\left[\begin{array}{c|cc|cc}
 & \multicolumn{2}{c|}{\text{Large components}} & \multicolumn{2}{c}{\text{Small components}} \\
 & \Gamma_0 & \Gamma_{R_q} & \Gamma_{xyz} & \Gamma_q \\ \hline
\Gamma_0 & \mathbf{V}^{LL} & 0 & -\check{\imath}c\mathbf{D}_z^{LS} & -\check{\imath}c\mathbf{D}_y^{LS} + c\mathbf{D}_x^{LS} \\
\Gamma_{R_q} & 0 & \mathbf{V}^{LL} & \check{\imath}c\mathbf{D}_y^{LS} - c\mathbf{D}_x^{LS} & \check{\imath}c\mathbf{D}_z^{LS} \\
\Gamma_{xyz} & -\check{\imath}c\mathbf{D}_z^{SL} & -\check{\imath}c\mathbf{D}_y^{SL} + c\mathbf{D}_x^{SL} & \mathbf{W}^{SS} & 0 \\
\Gamma_q & -\check{\imath}c\mathbf{D}_y^{SL} - c\mathbf{D}_x^{SL} & \check{\imath}c\mathbf{D}_z^{SL} & 0 & \mathbf{W}^{SS}
\end{array}\right]
\left[\begin{array}{c} c_0^L + \check{\imath}c_1^L \\ c_3^L - \check{\imath}c_2^L \\ c_0^S + \check{\imath}c_1^S \\ c_3^S - \check{\imath}c_2^S \end{array}\right]. \tag{48}
$$

Four real matrices have thereby been packed into two. Memory is reduced by a factor two and the problem can be handled by complex algebra. The cases with Γ_{R_x} or Γ_{R_y} being totally symmetric may be treated by defining other shifts of quaternion units, but a simpler solution is simply to relabel the quaternion units. Note, however, that the equivalent operation in the Dirac equation in standard form corresponds to a change of spin quantization axis.

3. Implementation

The computational implementation of the above symmetry scheme for the construction of the one-electron Fock matrix is straightforward. The quaternion phases introduced on the basis functions corresponds to a transformation of individual elements of the Fock matrix,

$${}^{Q}F_{\mu\nu;\Lambda} e_\Lambda \rightarrow {}^{S}F_{\mu\nu;\Gamma} e_\Gamma = {}^{Q}F_{\mu\nu;\Lambda} e_\mu^* e_\Lambda e_\nu; \quad e_\Gamma = e_{\mu\Lambda\nu}. \tag{49}$$

The quaternion triple product appearing in the above transformation can be reformulated as

$$e_\mu^* e_\Lambda e_\nu = \omega_\Lambda(\mu,\nu) e_{\mu\Lambda\nu}, \quad e_\mu e_\Lambda e_\nu^* = \overline{\omega}_\Lambda(\mu,\nu) e_{\mu\Lambda\nu}, \tag{50}$$

where $e_{\mu\Lambda\nu}$ is the product quaternion unit and $\omega_\Lambda(\mu,\nu)$ its phase (± 1). Note that the noncommutivity of quaternion multiplication is associated with the phase $\omega_\Lambda(\mu,\nu)$ and not the product quaternion unit $e_{\mu\Lambda\nu}$, so that, for instance, $e_{\mu\Lambda\mu} = e_\Lambda$. The symmetry reduced Fock matrix is now generated by taking a set of real one-electron integrals contrib-

uting to the matrix, inserting phases $\omega_\Lambda(\mu,\nu)$, and then assigning the integrals to the matrix indicated by $e_{\mu\Lambda\nu}$. The insertion of phases requires virtually no extra computational effort.

D. Construction of two-electron Fock matrix

The quaternion two-electron Fock matrix has the following form[11]:

$$\mathbf{F}_\Lambda^{[2]}=\begin{bmatrix}\mathbf{J}_0^L-\mathbf{K}_0^{LL} & -\mathbf{K}_0^{LS}\\ -\mathbf{K}_0^{SL} & \mathbf{J}_0^S-\mathbf{K}_0^{SS}\end{bmatrix}-\check{\imath}\begin{bmatrix}\mathbf{K}_1^{LL} & \mathbf{K}_1^{LS}\\ \mathbf{K}_1^{SL} & \mathbf{K}_1^{SS}\end{bmatrix}-\check{J}\begin{bmatrix}\mathbf{K}_2^{LL} & \mathbf{K}_2^{LS}\\ \mathbf{K}_2^{SL} & \mathbf{K}_2^{SS}\end{bmatrix}-\check{k}\begin{bmatrix}\mathbf{K}_3^{LL} & \mathbf{K}_3^{LS}\\ \mathbf{K}_3^{SL} & \mathbf{K}_3^{SS}\end{bmatrix}, \tag{51}$$

in terms of Coulomb and exchange contributions defined as

$$J_{\mu\nu;\Lambda}=\sum_{\kappa\lambda}\ (\mu\nu|\kappa\lambda)2D_{\lambda\kappa;\Lambda};$$
$$K_{\mu\nu;\Lambda}=\sum_{\kappa\lambda}\ (\mu\lambda|\kappa\nu)D_{\lambda\kappa;\Lambda}. \tag{52}$$

Due to the spinor structure in terms of boson irreps discussed in Sec. III, blocks of the density matrix (four real matrices) may be zero by symmetry. As the two-electron integrals are totally symmetric, the same structure is transferred to the two-electron Fock matrix. In the previous section we have seen how the introduction of quaternion phase shifts on basis functions leads to significant symmetry reductions for real and complex groups. The reader may straightforwardly verify that the equivalent transformation [Eq. (49)] of individual elements of the two-electron Fock matrix leads to identical symmetry reductions. However, the Coulomb and exchange contributions are expressed in terms of the original quaternion density matrix and not the density matrix of the phase transformed coefficients, and this must be corrected for.

We recall that the introduction of quaternion units on the basis functions $\chi_\mu\rightarrow e_\mu\chi_\mu$ leads to a corresponding phase shift of the coefficients ${}^Qc_{\mu i}\rightarrow{}^Sc_{\mu i}=e_\mu^*\,{}^Qc_{\mu i}$. The original quaternion density matrix is then replaced by

$${}^QD_{\lambda\kappa}=\sum_i^{occ}\ {}^Qc_{\lambda i}\,{}^Qc_{\kappa i}^*\rightarrow{}^SD_{\lambda\kappa}$$
$$=\sum_i^{occ}\ {}^Sc_{\lambda i}\,{}^Sc_{\kappa i}^*=e_\lambda^*\,{}^QD_{\lambda\kappa}e_\kappa. \tag{53}$$

Note that this transformation is contravariant with respect to the transformation of the Fock matrix Eq. (49). By using the transformation of the Fock matrix in Eq. (49), the Coulomb and exchange contributions can now be written in terms of the transformed density matrix as

$$[{}^SJ_{\mu\nu;\mu\Lambda\nu}]e_{\mu\Lambda\nu}=e_\mu^*[{}^QJ_{\mu\nu;\Lambda}e_\Lambda]e_\nu$$
$$=\sum_{\kappa\lambda}\ [(\mu\nu|\kappa\lambda)2\,{}^SD_{\lambda\kappa;\lambda\Lambda\kappa}]e_\mu^*e_\lambda e_{\mu\Lambda\nu}e_\kappa^*e_\nu,$$
$$[{}^SK_{\mu\nu;\mu\Lambda\nu}]e_{\mu\Lambda\nu}=e_\mu^*[{}^QK_{\mu\nu;\Lambda}e_\Lambda]e_\nu \tag{54}$$
$$=\sum_{\kappa\lambda}\ [(\mu\lambda|\kappa\nu)^SD_{\lambda\kappa;\lambda\Lambda\kappa}]e_\mu^*e_\lambda e_{\mu\Lambda\nu}e_\kappa^*e_\nu.$$

The same quaternion pentuplet product appears in both contributions and can be simplified in the following manner: A two-electron integral $(\mu\nu|\kappa\lambda)$ is zero unless the integrand is totally symmetric, i.e., $\Gamma_\mu\otimes\Gamma_\nu\otimes\Gamma_\kappa\otimes\Gamma_\lambda=\Gamma_0$. As each boson irrep is associated with a quaternion unit, the selection rule is reexpressed in algebraic terms as $e_\mu^*e_\nu e_\kappa^*e_\lambda=\Omega_0(\mu,\nu,\kappa,\lambda)$, where Ω_0 is a phase (±1). The above result allows us to rewrite the quaternion pentuplet product as

$$e_\mu^*e_\lambda e_\Gamma e_\kappa^*e_\nu=\Omega_\Gamma(\mu,\lambda,\kappa,\nu)e_\Gamma;$$
$$\text{where}\ \ e_\Gamma=e_{\mu\Lambda\nu}=e_{\lambda\Lambda\kappa}. \tag{55}$$

It is computationally intractable to work with phases defined in terms of four indices. However, a factorization is straightforwardly obtained,

$$e_\mu^*e_\lambda e_\Gamma e_\kappa^*e_\nu=e_\lambda^*e_\mu e_\Gamma e_\nu^*e_\kappa$$
$$=\overline{\omega}_\Gamma(\mu,\nu)e_\lambda^*e_{\mu\Gamma\nu}e_\kappa$$
$$=\overline{\omega}_\Gamma(\mu,\nu)\omega_{\lambda\Gamma\kappa}(\lambda,\kappa)e_\Gamma, \tag{56}$$

and the Coulomb and exchange contributions can be written as

$${}^SJ_{\mu\nu;\Gamma}e_\Gamma=\overline{\omega}_\Gamma(\mu,\nu)\sum_{\kappa\lambda}\ [(\mu\nu|\kappa\lambda)2\,{}^SD_{\lambda\kappa;\Gamma}]\omega_{\lambda\Gamma\kappa}(\lambda,\kappa),$$
$${}^SK_{\mu\nu;\Gamma}e_\Gamma=\overline{\omega}_\Gamma(\mu,\nu)\sum_{\kappa\lambda}\ [(\mu\lambda|\kappa\nu)^SD_{\lambda\kappa;\Gamma}]\omega_{\lambda\Gamma\kappa}(\lambda,\kappa). \tag{57}$$

The factorization of phases $\Omega_\Gamma(\mu,\lambda,\kappa,\nu)$ allows a two-step construction of Fock matrices. We first form an auxiliary density matrix,

$${}^SD'_{\lambda\kappa;\Gamma}=\omega_{\lambda\Gamma\kappa}(\lambda,\kappa)^SD_{\lambda\kappa;\Gamma}, \tag{58}$$

from which we construct an auxiliary Fock matrix ${}^S\mathbf{F}^{[2]\prime}$. The true Fock matrix is then recovered by

$${}^SF^{[2]}_{\mu\nu;\Gamma}=\overline{\omega}_\Gamma(\mu,\nu)^SF^{[2]}_{\mu\nu;\Gamma}. \tag{59}$$

Note that the component real matrices of the auxiliary density matrix are neither symmetric nor antisymmetric. However, each element of a component matrix has a specific symmetry about the diagonal, which means that in the construction of the auxiliary Fock matrix only half of the contributions need to be explicitly inserted, since the other half is recovered after symmetrization of the true Fock matrix. Again, the insertion of phases takes virtually no computational effort, whereas the reduction in the number of real matrices to be constructed gives considerable computational savings.

TABLE II. Test calculations on the F_2 molecule to illustrate symmetry reduction by the symmetry scheme outlined in the article. (*Q*—quaternion group, *C*—complex group, *R*—real group.)

Point group		Average CPU seconds		
		Per iteration	$F^{[2]}$-construction	Diagonalization
C_1	(*Q*)	108.94	102.44	1.30
C_2	(*C*)	61.30	58.65	0.48
C_{2v}	(*R*)	40.32	39.47	0.26
C_i	(*Q*)	75.60	73.29	0.34
C_{2h}	(*C*)	43.46	42.66	0.13
D_{2h}	(*R*)	27.39	27.11	0.08

E. Sample calculation

To illustrate the savings that are possible with the symmetry scheme outlined above, we have performed DHF calculations on the diatomic molecule F_2 using an uncontracted cc-pVDZ basis[22] (with one tight *p*-function added) and the DIRAC code.[11] For each fluorine atom the large components were expanded in a $9s5p1d$ basis, whereas the small components were expanded in a $5s10p5d1f$ basis generated by kinetic balance. The total basis set thereby comprised 210 functions. All calculations were carried out at bond distance of 135 pm.

The calculations were carried out using a conventional self-consistent field (SCF) scheme with two-electron integrals in symmetry-adapted basis stored on disk. An additional symmetry speedup is obtained in this case by noting that the Coulomb contributions Eq. (52) appear only in one of four real matrices in the quaternion two-electron Fock matrix Eq. (51) and only in *LL* and *SS* blocks corresponding to boson irrep Γ_0. By presorting two-electron atomic orbital (AO) integrals $(\mu\nu|\kappa\lambda)$ on the irrep of density $(\mu\nu)$, Coulomb contributions are calculated only for the set of integrals corresponding to $\Gamma_{\mu\nu}=\Gamma_0$. The F_2 molecule has been calculated in the quaternion group C_1, the complex group C_2, and the real group C_{2v}, the latter two chosen with the rotation axis along the molecular axis. The symmetry groups were chosen to give exactly the same number of two-electron integrals on disk (15.3 million), so that differences in CPU time could be attributed to the symmetry scheme alone. The above groups have only one irreducible corepresentation. A second series of calculations was carried out in which the operation of inversion was added to the above groups, giving the groups C_i, C_{2h}, and D_{2h}, respectively, and 11.4 million integrals on disk. The calculations were performed on a HP7200 workstation and the results are given in Table II.

The results confirm that the construction of the two-electron Fock matrix is the dominant computational task, accounting for more than 90% of the CPU time spent in each SCF iteration. Considering first the series of groups without inversion, we observe that when going from C_1 to C_2 symmetry, that is from quaternion to complex algebra, the $\mathbf{F}^{[2]}$ construction is speeded up by a factor 1.8 and diagonalization by a factor 2.7. When going to C_{2v}, that is real algebra, additional speedup factors 1.5 and 1.9 are observed for Fock-matrix construction and diagonalization, respectively. Identical trends are observed for the series of groups with inversion. Comparing now groups on the same level of algebra in the two series, we see that ratios between CPU times for Fock-matrix construction are identical to ratios between the number of two-electron integrals on disk. On the other hand, we observe a considerable speedup of diagonalization for groups with inversion. This is due to the blocking of the Fock matrix on the irreducible corepresentations of different parity. It should be kept in mind that the observed reductions in CPU times are accompanied by significant reductions in the memory needed for the calculation, as pointed out in Sec. IV C.

The results of the sample calculation can be compared to the results obtained by L. Visscher in Ref. 7, since the same test system and identical basis sets have been used. The results of L. Visscher have been obtained with the MOLFDIR code, which is based on the conventional four-component complex DHF operator rather than the two-component quaternion operator used in DIRAC. The Fock matrix is constructed in the basis of functions adapted to the molecular double point group, but a new method has been introduced that allows the use of real algebra for groups containing C_{2v} or D_2 as a subgroup. CPU times can not be compared directly since the calculations have been carried out on different computers and with different numbers of two-electron integrals on disk, but some important points can be noted: In the MOLFDIR calculations the CPU time for Fock-matrix construction is directly proportional to the number of two-electron integrals and independent of the algebra of the binary groups presented. In the DIRAC calculation, significant symmetry reductions are observed with reduction of the algebra of the group. Another observation of interest is that even for the group C_1 the CPU time for Fock-matrix diagonalization in the DIRAC run is only a small fraction of the time for Fock-matrix construction (less than 1.5%). In the MOLFDIR run the diagonalization at the C_1 level takes more time than the Fock-matrix construction. For higher groups the diagonalization time drops significantly with increased blocking of the Fock matrix and the possible use of real algebra. For larger systems, as pointed out by L. Visscher, the diagonalization becomes insignificant compared to Fock-matrix construction, unless this trend can be counterbalanced by efficient integral screening.[11]

V. CONCLUSION

This work exploits time reversal and point group symmetry in molecular relativistic calculations. Previously it has been shown that the time-dependent Dirac equation may be expressed in terms of complex quaternions.[23–25] We restrict ourselves to the time-independent case and the Dirac operator in the molecular field (nuclear spins neglected). The Dirac operator is then symmetric under time reversal and can thereby be reduced to two-component form in terms of real quaternions. A significant feature of the quaternion representation, in contrast to the customary complex four-component representation, is the complete equivalence between the *x*-, *y*-, and *z*-axes, as it should be. This equivalence is manifested here in the equivalence between the quaternion units $\check{\imath}, \check{\jmath}$, and $\check{k}$. When complex i is identified with quaternion $\check{\imath}$, the

quaternion wave function may be split up into α and β complex spin components, corresponding to the conventional choice of the *z*-axis as the principal rotation axis and the quantization of spin along this axis (quantization with S_z). However, we may equally well assign i to $\check{j}$ or $\check{k}$, which corresponds to quantization with S_y and S_x, respectively.

Time-reversal symmetry is combined with the molecular point group to form the full symmetry group. The binary groups (D_{2h} and subgroups) are found to have at most two irreducible corepresentations, distinguished by parity alone. The binary groups can furthermore be classified according to the algebra of their representation matrices in the quaternion representation. This classification is evidently linked to the Frobenius theorem restricting associative real division algebras to the real numbers, complex numbers, and quaternions (for an interesting discussion along these lines see Ref. 26). The relationship between symmetry and algebra is explored in a symmetry scheme where the central feature is the association of boson irreps with quaternion units, thus providing a transfer of symmetry information to the algebra of the problem at hand. Even though the derivation may seem somewhat involved, the computational implementation of the symmetry scheme is straightforward. Applied to the Dirac–Hartree–Fock method, it simply requires a pretabulation of phases $\omega_\Lambda(\mu,\nu)$ and $\overline{\omega}_\Lambda(\mu,\nu)$ [Eq. (50)] and then insertion of the appropriate phase ± 1 from these tables in the Fock and density matrices at various points during the execution of the program. The computational gains are significant both in terms of memory and CPU time, as illustrated by a simple test case. In summary, we obtain the same reduction in computational effort by using D_{2h} and subgroups instead of C_1 as in nonrelativistic calculations, namely roughly the number of boson irreps (so, for example, using C_{2v} instead of C_1 reduces the computational effort by approximately a factor of four).

The symmetry scheme presented in this paper may be extended to perturbations which are not symmetric with respect to point group or time-reversal symmetry. For real groups, such perturbations will, in our scheme, be transformed to *i*-imaginary, *j*-imaginary, or *k*-imaginary operators. In a forthcoming paper we shall analyze the implications of this for the calculation of molecular response properties with full use of point group symmetry.

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