DIRAC–COULOMB HAMILTONIAN IN *N*-ELECTRON MODEL SPACES

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

Relations between matrices representing non-relativistic and relativistic *N*-electron Hamiltonians in *N*-electron model spaces are analyzed. The model spaces are defined as the antisymmetric parts of products of the *N*-th Kronecker power of either a two-dimensional (the non-relativistic case) or four-dimensional (the relativistic case) spinor space and of an orbital (or configurational) space. The explicit relation between the matrices corresponding to the relativistic and non-relativistic cases is derived and its practical implications are briefly discussed.

Keywords: Quantum chemistry; *Ab initio* methods; Relativistic effects; Dirac equation; Pauli equation; Configuration interaction; Symmetric group approach.

The structure of an antisymmetric model space, appropriate for representation of an *N*-electron Hamiltonian, depends on two main factors: the specific symmetry imposed upon the model space and the structure of the spin space. The ways the first of these factors may be implemented are the subject of many analyses and have been described in numerous works (*e.g.* refs[1–5]). In brief, they may be reduced to a requirement that the model space is chosen to be an eigenspace of the operators which commute with the Hamiltonian and/or a carrier space of a representation of the invariance group of the Hamiltonian. The structure of the spin space depends on the spinor properties of the pertinent one-electron wavefunctions: two-component in the non-relativistic Pauli model and four-component in the relativistic Dirac theory. Properly taking into account the second factor is inherent in all algorithms of construction of the Hamiltonian matrix. Consequently, there exist two sets of methods and of the corresponding algorithms: those based on using the two-component Pauli spinors[2] and those based on the four-component Dirac spinors (also referred to as bi-spinors)[6].

In a vast majority of implementations the formulations using two-component spinors are exploited. During the last decade several works were concerned with construction of methods in which the four-component-spinor space is expressed in terms of products of the two-component-spinor spaces and, consequently, the methods of construction of the Hamiltonian matrix developed for the two-component spinors, after some modifications, might be applied[7–9]. Also the present work belongs to this category. However, we use a new separation scheme of the Dirac bi-spinors. All previous authors, except for a brief note by Moshinsky and Sharma[10], expressed the Dirac bi-spinor as a direct sum of two two-component parts: the "large" (composed of two large components) and the "small" (composed of two small components) parts. In the present paper the bi-spinors are split in an entirely different way: the Dirac bi-spinor is expressed as a direct product of two two-component quantities, one of which is the same as the Pauli spinor. Though the present approach assigns certain hierarchy to the two-component spaces, it allows us for a more symmetric way of approaching the problem of construction of the Hamiltonian matrix in a basis of relativistic wavefunctions. In particular, we derive some explicit relations between the Hamiltonian matrix constructed in a space composed of products of bi-spinors and matrices constructed in spaces based on products of the Pauli spinors. As a practical consequence, a matrix representing the relativistic Dirac Hamiltonian may be constructed using slightly modified algorithms designed for construction of the Hamiltonian matrices in the non-relativistic models.

Atomic units are used in this paper. However, if the clarity of presentation is increased by explicit using of some physical constants we set $\mathfrak{m}$ and $\mathfrak{e}$ for the electron mass and charge, respectively. The velocity of light is denoted $\mathfrak{c} \approx 137$.

THEORY

Basic Definitions and Concepts

Let $\{\varphi_j(\boldsymbol{r}_1)\}_{j=1}^{\infty}$ be a complete set of linearly-independent scalar functions. Since we are concerned with a description of discrete states, we may assume, without any loss of generality, that the basis is orthonormal. Let $\mathcal{R}^1$ be the one-particle Hilbert space spanned by this basis. A non-relativistic wavefunction (spin-orbital) describing a stationary state of a single electron may be expressed as

$$\phi^{ab}(\boldsymbol{x}_1) = \begin{pmatrix}1\\0\end{pmatrix}\varphi^{a}(\boldsymbol{r}_1) + \begin{pmatrix}0\\1\end{pmatrix}\varphi^{b}(\boldsymbol{r}_1)\ , \tag{1}$$

where

$$\begin{pmatrix}1\\0\end{pmatrix} \equiv e_{a}\ , \qquad \begin{pmatrix}0\\1\end{pmatrix} \equiv e_{b} \tag{2}$$

are the eigenvectors of the spin projection operator and φ^a, $\varphi^b \in \mathcal{R}^1$ are the orbitals associated with the respective spin projections (frequently, in the so called *restricted* methods, $\varphi^a = \varphi^b$ is assumed). In the coordinate representation, $\boldsymbol{r}_1$ is the position vector and $\boldsymbol{x}_1$ stands collectively for the position and spin coordinates of the electron. Consequently, the corresponding one-electron model space, referred to hereafter as the *Pauli space* $\mathcal{P}$, may be expressed as

$$\mathcal{P} \equiv \mathcal{H}^1_{\mathrm{nr}} = \mathcal{V}^1_{\sigma} \otimes \mathcal{R}^1\ , \tag{3}$$

where $\mathcal{V}^1_{\sigma}$ is a two-dimensional one-electron spin space spanned by $\{e_a, e_b\}$.

In the relativistic (Dirac) theory, a one-electron wavefunction is represented by a bi-spinor and may be expressed as

$$\psi(\mathbf{1}) = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}\varphi^{al}(\boldsymbol{r}_1) + \begin{pmatrix}0\\1\\0\\0\end{pmatrix}\varphi^{bl}(\boldsymbol{r}_1) + \begin{pmatrix}0\\0\\1\\0\end{pmatrix}\varphi^{as}(\boldsymbol{r}_1) + \begin{pmatrix}0\\0\\0\\1\end{pmatrix}\varphi^{bs}(\boldsymbol{r}_1)\ , \tag{4}$$

where the argument **1** in $\psi(\mathbf{1})$ refers to the spinor and position coordinates of the electron. Alternatively, Eq. (*4*) may be expressed as

$$\psi(\mathbf{1}) = \sum_{c=\mathrm{l,s}} \sum_{\sigma=\mathrm{a,b}} [\tilde{e}_c \otimes e_{\sigma}]\varphi^{\sigma c}(\boldsymbol{r}_1)\ , \tag{5}$$

where $\varphi^{\sigma c}(\boldsymbol{r}_1) \in \mathcal{R}^1$ and

$$\tilde{e}_{\mathrm{l}} = \begin{pmatrix}1\\0\end{pmatrix}, \qquad \tilde{e}_{\mathrm{s}} = \begin{pmatrix}0\\1\end{pmatrix} \tag{6}$$

are orthonormal basis vectors in a two-dimensional space $\mathcal{V}^1_c$ referred to as the *space of large and small components* of the wavefunction[11]. It is obvious

that spaces $\mathcal{V}_c^1$ and $\mathcal{V}_\sigma^1$ are isomorphic. The corresponding one-electron model space, referred to hereafter as the *Dirac space* $\mathcal{D}$, may be expressed as

$$\mathcal{D} \equiv \mathcal{H}_{\mathrm{rel}}^1 = \mathcal{V}_c^1 \otimes \mathcal{V}_\sigma^1 \otimes \mathcal{R}^1 = \mathcal{V}_c^1 \otimes \mathcal{H}_{\mathrm{nr}}^1 = \mathcal{V}^1 \otimes \mathcal{R}^1, \tag{7}$$

where

$$\mathcal{V}^1 = \mathcal{V}_c^1 \otimes \mathcal{V}_\sigma^1 \tag{8}$$

is the four-dimensional, one-electron, bi-spinor space.

The bi-spinor space $\mathcal{V}^1$ may also be represented as

$$\mathcal{V}^1 = \mathcal{V}_\sigma^1 \otimes \mathcal{V}_c^1 . \tag{9}$$

This representation, canonically equivalent to the one given by Eq. (*8*), is of particular interest and importance though, surprisingly, has not been exploited in practical calculations. Due to Eq. (*9*), the Dirac space may be decomposed in a way analogous to the decomposition (*3*) of the Pauli space:

$$\mathcal{H}_{\mathrm{rel}}^1 = \mathcal{V}_\sigma^1 \otimes \mathcal{Q}^1 , \tag{10}$$

where

$$\mathcal{Q}^1 = \mathcal{V}_c^1 \otimes \mathcal{R}^1 \tag{11}$$

corresponds to $\mathcal{R}^1$ of the non-relativistic theory.

The *N*-electron space is defined as the antisymmetric part of the *N*-fold Kronecker product of the one-electron space. Thus, in the non-relativistic case

$$\mathcal{H}_{\mathrm{nr}}^N = [\mathcal{H}_{\mathrm{nr}}^{1\,\otimes N}]^{\mathrm{A}} \tag{12}$$

and in the relativistic case

$$\mathcal{H}_{\mathrm{rel}}^N = [\mathcal{H}_{\mathrm{rel}}^{1\,\otimes N}]^{\mathrm{A}}, \tag{13}$$

where the superscript A stands for the antisymmetry. The *N*-electron spaces, composed of the orbital and of the spinor spaces combined in a way described by Eqs (*12*) and (*13*) are equivalent to the *N*-electron subspaces of

the Fock space[1]. In the non-relativistic case, there are two canonically equivalent ways of representing the *N*-electron subspace of the Fock space. In the first

$$\mathcal{H}^N_{\mathrm{nr}} = [(\mathcal{V}^1_\sigma \otimes \mathcal{R}^1)^{\otimes N}]^{\mathrm{A}} \tag{14}$$

and in the second

$$\mathcal{H}^N_{\mathrm{nr}} = [(\mathcal{V}^1_\sigma)^{\otimes N} \otimes (\mathcal{R}^1)^{\otimes N}]^{\mathrm{A}}. \tag{15}$$

From this equivalence one may derive the so called *duality of Weyl*[2] and, in consequence, two approaches to the non-relativistic theory of many-electron systems known, respectively, as the *unitary group approach*[3] and the *symmetric group approach* (SGA)[4]. In the relativistic case

$$\mathcal{H}^N_{\mathrm{rel}} = [(\mathcal{V}^1_c \otimes \mathcal{H}^1_{\mathrm{nr}})^{\otimes N}]^{\mathrm{A}}. \tag{16}$$

This representation of $\mathcal{H}^N_{\mathrm{rel}}$, corresponding to the *unitary group approach* of the non-relativistic theory, is commonly used in relativistic calculations in which the wavefunctions are expressed as linear combinations of Slater determinants built from the one-electron Dirac bi-spinors[6]. A canonically equivalent representation, analogous to Eq. (*15*) is

$$\mathcal{H}^N_{\mathrm{rel}} = [(\mathcal{V}^1_c)^{\otimes N} \otimes (\mathcal{H}^1_{\mathrm{nr}})^{\otimes N}]^{\mathrm{A}} . \tag{17}$$

Two other equivalent representations may be written as

$$\mathcal{H}^N_{\mathrm{rel}} = [(\mathcal{V}^1_c)^{\otimes N} \otimes (\mathcal{V}^1_\sigma)^{\otimes N} \otimes (\mathcal{R}^1)^{\otimes N}]^{\mathrm{A}} = [(\mathcal{V}^1)^{\otimes N} \otimes (\mathcal{R}^1)^{\otimes N}]^{\mathrm{A}}. \tag{18}$$

Finally, Eq. (*10*) implies that

$$\mathcal{H}^N_{\mathrm{rel}} = [(\mathcal{V}^1_\sigma)^{\otimes N} \otimes (\mathcal{Q}^1)^{\otimes N}]^{\mathrm{A}} . \tag{19}$$

The last representation may be used as a starting point for construction of a relativistic analogue to the symmetric group approach to spin-dependent

configuration interaction method[12]. Its consequences will be discussed later in this work.

In practical calculations, the complete (and infinite) Hilbert space $\mathcal{R}^1$ is replaced by a finite-dimensional orbital space. In consequence, $\mathcal{H}^N_{\mathrm{rel}}$ and $\mathcal{H}^N_{\mathrm{nr}}$ become finite-dimensional model spaces often referred to as the *full configuration interaction spaces*[1]. In order to better compensate the truncation of the basis set of the one-particle functions, one may introduce an *N*-particle orbital model space $\mathcal{R}^N$ which is not expressible as the *N*-th Kronecker power of a finite-dimensional one-particle space. The best known example is the space which defines the *method of superposition of correlated configurations* also known as the *Hylleraas configuration interaction method* (see, *e.g.*, ref.[13] and references therein). In such a case, in Eqs (*15*) and (*18*) we substitute a general orbital space $\mathcal{R}^N$ for $(\mathcal{R}^1)^{\otimes N}$.

In this paper we study relations between matrix representations of two kinds of *N*-electron Hamiltonians: $\hat{H}^{\mathrm{P}}(\boldsymbol{x}_1,\boldsymbol{x}_2,...,\boldsymbol{x}_N)$ (a Pauli-type, nonrelativistic and spin-dependent) and $\hat{H}^{\mathrm{D}}(\mathbf{1},\mathbf{2},...,\boldsymbol{N})$ (a Dirac-type, relativistic). The Hamiltonians are defined on $\mathcal{H}^N_{\mathrm{nr}}$ and $\mathcal{H}^N_{\mathrm{rel}}$, respectively. Our aim is to compare the matrix representations of these Hamiltonians in the model spaces described, respectively, by Eqs (*15*) and (*19*).

One Electron

The one-electron Dirac Hamiltonian is defined on the Dirac space $\mathcal{H}^1_{\mathrm{rel}}$ and may be expressed as

$$\hat{H}^{\mathrm{D}}_1(\mathbf{1}) = \hat{I}_c \otimes \hat{H}^{\mathrm{D}}_{\mathrm{A}}(\boldsymbol{x}_1) + \hat{\beta} \otimes \hat{H}^{\mathrm{D}}_{\mathrm{B}}(\boldsymbol{x}_1) + \hat{\alpha} \otimes \hat{H}^{\mathrm{D}}_{\mathrm{C}}(\boldsymbol{x}_1)\,, \tag{20}$$

where

$$\hat{I}_c = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \hat{\beta} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{\alpha} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{21}$$

are defined on the large and small component space $\mathcal{V}^1_c$. The remaining operators, *i.e.*,

$$\hat{H}^{\mathrm{D}}_{\mathrm{A}} = \hat{I}_\sigma \otimes \hat{\upsilon}(\boldsymbol{r}_1)\,, \quad \hat{H}^{\mathrm{D}}_{\mathrm{B}} = \hat{I}_\sigma \otimes \mathfrak{m}\mathfrak{c}^2 \hat{I}_{\mathrm{r}} \tag{22}$$

and

$$\hat{H}^{\mathrm{D}}_{\mathrm{C}} = \mathfrak{c} \sum_{m=-1}^{1} \hat{\sigma}^{\dagger}_m \otimes \hat{\pi}_m(\boldsymbol{r}_1)\,, \tag{23}$$

where $\hat{I}_\sigma$ and $\hat{\sigma}_m$ represent, respectively, the unit matrix and the Pauli spin matrices, $\hat{I}_r$ is the unit operator in $\mathcal{R}^1$, $\hat{\upsilon}$ is an external scalar potential, mc^2 is the rest energy, and $\hat{\pi}_m$ is the *k*-th component of the generalized momentum, are defined on the Pauli space. We assume that the Pauli matrices are in the standard form, *i.e.*

$$\hat{\sigma}_0 = \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{\sigma}_{+1} = \frac{1}{\sqrt{2}}(\hat{\sigma}_x + \mathrm{i}\hat{\sigma}_y) = \begin{bmatrix} 0 & \sqrt{2} \\ 0 & 0 \end{bmatrix} \tag{24}$$

and $\hat{\sigma}_{-1} = \hat{\sigma}_{+1}^\dagger$. Accordingly, the components of the generalized momentum are defined as

$$\hat{\pi}_0 = \hat{p}_z - e\hat{A}_z\,, \quad \hat{\pi}_{+1} = \frac{1}{\sqrt{2}}[(\hat{p}_x + \mathrm{i}\hat{p}_y) - e(\hat{A}_x + \mathrm{i}\hat{A}_y)], \quad \hat{\pi}_{-1} = \hat{\pi}_{+1}^\dagger\,, \tag{25}$$

where $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{A}}$ are, respectively, the momentum and the vector potential operators. Let us note that operators $\hat{I}_r$, $\hat{\upsilon}$ and $\hat{\pi}$ act on $\mathcal{R}^1$ while $\hat{I}_\sigma$ and $\hat{\sigma}_m$ are defined on the spin space $\mathcal{V}_\sigma^1$. Equation (*20*) may be rewritten as

$$\hat{H}_1^{\mathrm{D}}(\mathbf{1}) = \begin{bmatrix} \hat{h}_{\mathrm{ll}}^{\mathrm{D}}(\boldsymbol{x}_1) & \hat{h}_{\mathrm{ls}}^{\mathrm{D}}(\boldsymbol{x}_1) \\ \hat{h}_{\mathrm{sl}}^{\mathrm{D}}(\boldsymbol{x}_1) & \hat{h}_{\mathrm{ss}}^{\mathrm{D}}(\boldsymbol{x}_1) \end{bmatrix}, \tag{26}$$

where $\hat{h}_{\mathrm{ll}}^{\mathrm{D}} = \hat{H}_{\mathrm{A}}^{\mathrm{D}} + \hat{H}_{\mathrm{B}}^{\mathrm{D}}$, $\hat{h}_{\mathrm{ss}}^{\mathrm{D}} = \hat{H}_{\mathrm{A}}^{\mathrm{D}} - \hat{H}_{\mathrm{B}}^{\mathrm{D}}$ and $\hat{h}_{\mathrm{ls}}^{\mathrm{D}} = (\hat{h}_{\mathrm{sl}}^{\mathrm{D}})^\dagger = \hat{H}_{\mathrm{C}}^{\mathrm{D}}$. Hence we may write

$$\mathcal{H}_{\mathrm{rel}}^1 = \mathcal{H}_{\mathrm{rel,l}}^1 \otimes \mathcal{H}_{\mathrm{rel,s}}^1\,, \tag{27}$$

and, since $\hat{h}_{cc'}^{\mathrm{D}}$ act on the Pauli space, $\mathcal{H}_{\mathrm{rel},c}^1 = \tilde{e}_c \otimes \mathcal{H}_{\mathrm{nr}}^1$, $c \in \{\mathrm{l},\mathrm{s}\}$.

If the Dirac space is decomposed according to Eq. (*10*), then the Dirac Hamiltonian (*20*) may be expressed in the form

$$\hat{H}_1^{\mathrm{D}}(\mathbf{1}) = \hat{I}_\sigma \otimes \hat{H}_0^{\mathrm{D}}(\tilde{\boldsymbol{x}}_1) + \sum_{m=-1}^{1} \hat{\sigma}_m^\dagger \otimes \hat{B}_m^{\mathrm{D}}(\tilde{\boldsymbol{x}}_1)\,, \tag{28}$$

where $\tilde{\boldsymbol{x}}_1$ stands collectively for the position and large-small-component-space coordinates of the electron,

$$\hat{H}_0^{\mathrm{D}}(\tilde{\boldsymbol{x}}_1) = \hat{I}_c \otimes \hat{\upsilon}(\boldsymbol{r}_1) + \mathrm{mc}^2 \hat{\beta} \otimes \hat{I}_r = \begin{bmatrix} \hat{\upsilon} + \mathrm{mc}^2 & 0 \\ 0 & \hat{\upsilon} - \mathrm{mc}^2 \end{bmatrix} \tag{29}$$

and

$$\hat{B}_m^{\mathrm{D}}(\tilde{\boldsymbol{x}}_1) = \mathrm{c}\hat{\alpha} \otimes \hat{\pi}_m = \mathrm{c}\begin{bmatrix} 0 & \hat{\pi}_m \\ \hat{\pi}_m & 0 \end{bmatrix}. \tag{30}$$

The corresponding eigenvalue equation may be written as

$$\begin{bmatrix} \hat{H}_0^{\mathrm{D}}(\boldsymbol{x}_1) + \hat{B}_0^{\mathrm{D}}(\boldsymbol{x}_1) - E & \sqrt{2}\hat{B}_{-1}^{\mathrm{D}}(\boldsymbol{x}_1) \\ \sqrt{2}\hat{B}_{+1}^{\mathrm{D}}(\boldsymbol{x}_1) & \hat{H}_0^{\mathrm{D}}(\boldsymbol{x}_1) - \hat{B}_0^{\mathrm{D}}(\boldsymbol{x}_1) - E \end{bmatrix} \begin{bmatrix} \phi^{\mathrm{a}}(\boldsymbol{x}_1) \\ \phi^{\mathrm{b}}(\boldsymbol{x}_1) \end{bmatrix} = 0\,, \tag{31}$$

where $E = \mathcal{E} + \mathrm{mc}^2$ is the energy and

$$\phi^{\mathrm{a}}(\boldsymbol{x}_1) = \begin{bmatrix} \varphi^{\mathrm{al}}(\boldsymbol{r}_1) \\ \varphi^{\mathrm{as}}(\boldsymbol{r}_1) \end{bmatrix}, \quad \phi^{\mathrm{b}}(\boldsymbol{x}_1) = \begin{bmatrix} \varphi^{\mathrm{bl}}(\boldsymbol{r}_1) \\ \varphi^{\mathrm{bs}}(\boldsymbol{r}_1) \end{bmatrix}. \tag{32}$$

In this case, instead of Eq. (*27*) we have

$$\mathcal{H}_{\mathrm{rel}}^1 = \mathcal{H}_{\mathrm{rel,a}}^1 \oplus \mathcal{H}_{\mathrm{rel,b}}^1 = e_{\mathrm{a}} \otimes \mathcal{Q}^1 \oplus e_{\mathrm{b}} \otimes \mathcal{Q}^1. \tag{33}$$

The non-relativistic limit of Eq. (*31*) may easily be obtained by the substitution[14]

$$\hat{\upsilon} - (\mathrm{mc}^2 + E)\hat{I}_r = \hat{\upsilon} - (2\mathrm{mc}^2 + \mathcal{E})\hat{I}_r \rightarrow -2\mathrm{mc}^2\hat{I}_r\,. \tag{34}$$

Under this substitution, the small components may be expressed in terms of the large ones as

$$\varphi^{\mathrm{as}} = \frac{1}{2\mathrm{mc}}(\hat{\pi}_0\varphi^{\mathrm{al}} + \sqrt{2}\hat{\pi}_{-1}\varphi^{\mathrm{bl}}), \quad \varphi^{\mathrm{bs}} = \frac{1}{2\mathrm{mc}}(\sqrt{2}\hat{\pi}_{+1}\varphi^{\mathrm{al}} - \hat{\pi}_0\varphi^{\mathrm{bl}})\,, \tag{35}$$

and, consequently, eliminated from Eq. (*31*). The resulting non-relativistic, two-component, equation reads

$$\begin{bmatrix} \hat{H}_0^{\mathrm{P}}(\boldsymbol{r}_1) + \hat{B}_0^{\mathrm{P}}(\boldsymbol{r}_1) - \mathcal{E} & \sqrt{2}\hat{B}_{-1}^{\mathrm{P}}(\boldsymbol{r}_1) \\ \sqrt{2}\hat{B}_{+1}^{\mathrm{P}}(\boldsymbol{r}_1) & \hat{H}_0^{\mathrm{P}}(\boldsymbol{r}_1) - \hat{B}_0^{\mathrm{P}}(\boldsymbol{r}_1) - \mathcal{E} \end{bmatrix} \begin{bmatrix} \varphi^{\mathrm{al}}(\boldsymbol{r}_1) \\ \varphi^{\mathrm{bl}}(\boldsymbol{r}_1) \end{bmatrix} = 0 \,, \tag{36}$$

where

$$\hat{H}_0^{\mathrm{P}} = \hat{\upsilon} + \frac{1}{2\mathfrak{m}} \hat{\boldsymbol{\pi}}^2 \,, \tag{37}$$

and

$$\hat{B}_0^{\mathrm{P}} = \frac{1}{2\mathfrak{m}} [\hat{\pi}_{+1}, \hat{\pi}_{-1}] \,, \quad \hat{B}_{+1}^{\mathrm{P}} = \frac{1}{2\mathfrak{m}} [\hat{\pi}_{-1}, \hat{\pi}_0] \,, \quad \hat{B}_{-1}^{\mathrm{P}} = \frac{1}{2\mathfrak{m}} [\hat{\pi}_0, \hat{\pi}_{+1}] \,,$$

or, in a more compact form,

$$\hat{\boldsymbol{B}}^{\mathrm{P}} = \frac{1}{2\mathfrak{m}} \hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}} \,. \tag{38}$$

Except for definitions of specific symbols, the structure of this equation is the same as that of its relativistic counterpart (*31*). In particular, the non-relativistic Hamiltonian associated with Eq. (*36*) may be written as

$$\hat{H}_1^{\mathrm{P}}(\boldsymbol{x}_1) = \hat{I}_\sigma \otimes \hat{H}_0^{\mathrm{P}}(\boldsymbol{r}_1) + \sum_{m=-1}^{1} \hat{\sigma}_m^\dagger \otimes \hat{B}_m^{\mathrm{P}}(\boldsymbol{r}_1) \,, \tag{39}$$

analogous to the Dirac Hamiltonian defined in Eq. (*28*). Consequently, in analogy to Eq. (*33*), the space $\mathcal{H}_{\mathrm{nr}}^1$ over which $\hat{H}^{\mathrm{P}}$ is defined may be, alternatively to Eq. (*3*), decomposed as

$$\mathcal{H}_{\mathrm{nr}}^1 = \mathcal{H}_{\mathrm{nr,a}}^1 \oplus \mathcal{H}_{\mathrm{nr,b}}^1 = e_{\mathrm{a}} \otimes \mathcal{R}^1 \oplus e_{\mathrm{b}} \otimes \mathcal{R}^1 . \tag{40}$$

Let us assume that the basis in $\mathcal{R}^1$ is finite, *i.e.* the orbital space is selected as a finite-dimensional subspace of the complete Hilbert space. In such a case the subspaces of $\mathcal{R}^1$ associated with each of the components of the wavefunction may be different. Assume that in the finite basis

$$\mathcal{H}_{\mathrm{nr}}^1 = e_{\mathrm{a}} \otimes \mathcal{R}_{\mathrm{a}}^1 \oplus e_{\mathrm{b}} \otimes \mathcal{R}_{\mathrm{b}}^1 \,, \tag{41}$$

where $\mathcal{R}_{\mathrm{a}}^1$ and $\mathcal{R}_{\mathrm{b}}^1$ are spanned, respectively, by

$$\{\boldsymbol{\varphi}^{\mathrm{a}}\} = \{\varphi_j^{\mathrm{a}}(\boldsymbol{r}_1)\}_{j=1}^{d_{\mathrm{a}}} \quad \text{and} \quad \{\boldsymbol{\varphi}^{\mathrm{b}}\} = \{\varphi_j^{\mathrm{b}}(\boldsymbol{r}_1)\}_{j=1}^{d_{\mathrm{b}}} \ . \tag{42}$$

The corresponding basis in $\mathcal{Q}^1$ is given by

$$\{\boldsymbol{\phi}^{\mathrm{a}}\} \equiv \{\phi_j^{\mathrm{a}}\}_{j=1}^{2d_{\mathrm{a}}} = \{\tilde{e}_1 \otimes \varphi_i^{\mathrm{a}}\}_{i=1}^{d_{\mathrm{a}}} \cup \{\tilde{e}_{\mathrm{s}} \otimes \varphi_i^{\mathrm{a}}\}_{i=1}^{d_{\mathrm{a}}} \tag{43}$$

and

$$\{\boldsymbol{\phi}^{\mathrm{b}}\} \equiv \{\phi_j^{\mathrm{b}}\}_{j=1}^{2d_{\mathrm{b}}} = \{\tilde{e}_1 \otimes \varphi_i^{\mathrm{b}}\}_{i=1}^{d_{\mathrm{b}}} \cup \{\tilde{e}_{\mathrm{s}} \otimes \varphi_i^{\mathrm{b}}\}_{i=1}^{d_{\mathrm{b}}} \ , \tag{44}$$

where, for simplicity, we assumed that the large- and small-component bases are the same. According to Eqs (*5*), (*10*), (*43*) and (*44*), the resulting Dirac space is spanned by $d = 2(d_{\mathrm{a}} + d_{\mathrm{b}})$ bi-spinors

$$\{\boldsymbol{\psi}\} = e_{\mathrm{a}} \otimes \{\boldsymbol{\phi}^{\mathrm{a}}\} \cup e_{\mathrm{b}} \otimes \{\boldsymbol{\phi}^{\mathrm{b}}\} \ . \tag{45}$$

The Hamiltonian $\hat{H}^{\mathrm{R}}$, where R = D, P, is represented by the matrix

$$\boldsymbol{H}^{\mathrm{R}} = [\{\boldsymbol{f}^{\mathrm{a}}\},\{\boldsymbol{f}^{\mathrm{b}}\}|\hat{H}_1^{\mathrm{R}}|\{\boldsymbol{f}^{\mathrm{a}}\},\{\boldsymbol{f}^{\mathrm{b}}\}] = \begin{bmatrix} \boldsymbol{h}_{\mathrm{aa}}^{\mathrm{R}} & \boldsymbol{h}_{\mathrm{ab}}^{\mathrm{R}} \\ \boldsymbol{h}_{\mathrm{ba}}^{\mathrm{R}} & \boldsymbol{h}_{\mathrm{bb}}^{\mathrm{R}} \end{bmatrix}, \tag{46}$$

where $\boldsymbol{f} = \boldsymbol{\varphi}/\boldsymbol{\phi}$ if R = D/P,

$$\begin{aligned} \boldsymbol{h}_{\mathrm{aa}}^{\mathrm{R}} &= [\{\boldsymbol{f}^{\mathrm{a}}\}|\hat{H}_0^{\mathrm{R}} + \hat{B}_0^{\mathrm{R}}|\{\boldsymbol{f}^{\mathrm{a}}\}], \quad \boldsymbol{h}_{\mathrm{bb}}^{\mathrm{R}} = [\{\boldsymbol{f}^{\mathrm{b}}\}|\hat{H}_0^{\mathrm{R}} - \hat{B}_0^{\mathrm{R}}|\{\boldsymbol{f}^{\mathrm{b}}\}], \\ \boldsymbol{h}_{\mathrm{ab}}^{\mathrm{P}} &= (\boldsymbol{h}_{\mathrm{ba}}^{\mathrm{P}})^{\dagger} = [\{\boldsymbol{f}^{\mathrm{a}}\}|\hat{B}_{+1}^{\mathrm{R}}|\{\boldsymbol{f}^{\mathrm{b}}\}] \ , \end{aligned} \tag{47}$$

and $\boldsymbol{h}_{\sigma\sigma'}^{\mathrm{R}}(\sigma,\sigma' \in \{\mathrm{a},\mathrm{b}\})$ are blocks of elements

$$(\boldsymbol{h}_{\sigma\sigma'}^{\mathrm{R}})_{jj'} = \langle f_j^{\sigma}|\hat{h}_{\sigma\sigma'}^{\mathrm{R}}|f_{j'}^{\sigma'}\rangle \tag{48}$$

of dimensions $d_\sigma \times d_{\sigma'}$ in the non-relativistic (Pauli) model (*cf.* Eq. (*42*)) and $2d_\sigma \times 2d_{\sigma'}$ in the relativistic (Dirac) model (*cf.* Eqs (*43*) and (*44*)). Another

important difference between the Dirac and the Pauli models is the structure of the Hamiltonian. In the Pauli model, $\hat{H}_0^{\mathrm{P}}$ and $\hat{B}_m^{\mathrm{P}}$ are one-component quantities while in the Dirac model $\hat{H}_0^{\mathrm{D}}$ and $\hat{B}_m^{\mathrm{D}}$ are 2 × 2 matrices.

N-Electrons

By augmenting the one-electron Hamiltonians to the *N*-electron space, one obtains their simplest *N*-electron generalizations in which interactions between electrons are neglected. If the interaction in a relativistic system (augmented Eq. (*28*)) or in a non-relativistic system (augmented Eq. (*39*)) is described by the scalar Coulomb potential $\hat{H}_2(r_{ij}) = \mathrm{e}^2/r_{ij}$, where r_{ij} is the interelectron distance, then the resulting *N*-electron Hamiltonians are known, respectively, as Dirac–Coulomb and Pauli–Coulomb Hamiltonians. If the interaction potentials include the Breit terms, then the resulting Hamiltonians are referred to as Dirac–Breit and Pauli–Breit, respectively. In this paper we shall restrict our discussion to Dirac–Coulomb and Pauli–Coulomb Hamiltonians. A generalization for the cases of Dirac–Breit and Pauli–Breit is conceptually straightforward though technically rather cumbersome. In order to simplify the discussion whenever possible, we shall use the symbol $\hat{H}$ to denote both Dirac–Coulomb and Pauli–Coulomb Hamiltonians.

The *N*-electron Hamiltonian may be expressed as

$$\hat{H}_N(\boldsymbol{\rho}) = \sum_{i=1}^{N} \hat{I}^{\otimes(i-1)} \otimes \hat{H}_1(\rho_i) \otimes \hat{I}^{\otimes(N-i)} + \hat{I}^{\otimes N} G \,, \tag{49}$$

where

$$G = \sum_{i>j}^{N} \hat{H}_2(r_{ij})$$

is a scalar function describing interactions between electrons, $\hat{I}$ is the identity operator defined on the space of the Hamiltonian, ρ_i is the appropriate variable describing the electron, and $\boldsymbol{\rho}$ stands collectively for $\rho_1, \rho_2, \ldots, \rho_N$. The Hamiltonian is symmetric in electron coordinates, *i.e.* it commutes with the permutation operators $\hat{P}$ of the electron coordinates. Since $\hat{H}_1$ explicitly depends on the Pauli spin matrices, the Hamiltonian does not commute with the total spin operators. Nevertheless, it proves to be convenient to construct the matrix representing the Hamiltonian in a model space $\mathcal{H}^N$ with $(\mathcal{V}_\sigma^1)^{\otimes N}$ decomposed onto eigenspaces $\mathcal{V}_{SM}^N$ of the total spin operators

$\hat{S}^2$ and $\hat{S}_z$, *i.e.* onto carrier spaces for the irreducible representations of the symmetric group $\mathcal{S}_N$ (refs[12,15,16]). Then, we express the N-electron spin space as

$$(\mathcal{V}_\sigma^1)^{\otimes N} = \bigoplus_S \bigoplus_{M=-S}^{S} \mathcal{V}_{SM}^N \ , \qquad (50)$$

where S and N label nonequivalent irreducible representations, and M is the counting index for labeling irreducible representations which appear $(2S + 1)$ times in $(\mathcal{V}_\sigma^1)^{\otimes N}$. The approach in which the spin space is separated from the rest of the model space and decomposed according to Eq. (*50*) is specific for SGA and has been used to construct matrices representing Pauli–Coulomb Hamiltonians in N-electron model spaces[2,15,17]. In this note we generalize this approach for the case of the Dirac–Coulomb Hamiltonian.

The N-electron basis in $(\mathcal{V}_\sigma^1)^{\otimes N}$ may be taken as the set of 2^N different products of the one-electron spin functions (*2*)

$$\Theta_k^M(\boldsymbol{\sigma}) \equiv \Theta_k^M(\sigma_1, \sigma_2, \ldots, \sigma_N) = \bigotimes_{j=1}^{N} \sigma_j \ , \quad \sigma_j = e_a \ , \ e_b \ , \qquad (51)$$

where $M = (N_a - N_b)/2$ and N_a and N_b are equal, respectively, to the numbers of the one-electron spin functions e_a and e_b in the product (*51*). Then, Θ_k^M are eigenfunctions of $\hat{S}_z$ to the eigenvalue M. As one can easily see,

$$\hat{P}\Theta_k^M(\boldsymbol{\sigma}) = \sum_{i=1}^{g} Z(P)_{ik} \Theta_i^M(\boldsymbol{\sigma}) \ , \qquad (52)$$

where

$$g \equiv g(M, N) = \binom{N}{M + N/2}$$

is the dimension of the subspace of $(\mathcal{V}_\sigma^1)^{\otimes N}$ corresponding to the given M. The set of $N!$ matrices $\boldsymbol{Z}(P)$ forms a (reducible) representation of $\mathcal{S}_N$. Matrices $\boldsymbol{Z}(P)$ are easy to construct and have very simple structure: in each row and in each column one element is equal to 1 and the remaining ones are equal to 0. By taking an appropriate unitary transformation of the products Θ_k, one may construct a set of eigenfunctions of the total spin operators $\hat{S}^2$ and

$\hat{S}_z$, *i.e.* the bases in $\mathcal{V}_{SM}^N \in (\mathcal{V}_\sigma^1)^{\otimes N}$ (see ref.[16] for details). The resulting functions, Θ_k^{SM}, span carrier spaces for irreducible representations of $\mathcal{S}_N$, *i.e.*

$$\hat{P}\Theta_k^{SM}(\boldsymbol{\sigma}) = \sum_{j=1}^{f} V_S^N(P)_{jk}\Theta_j^{SM}(\boldsymbol{\sigma}) , \tag{53}$$

where $\boldsymbol{V}_S^N$ are the matrices of these representations and

$$f \equiv f(S,N) = \frac{2S+1}{N+1}\binom{N+1}{N/2-S} \tag{54}$$

is their dimension. The representations generated by Θ_k^{SM} correspond to two-row Young shapes with $x = (N/2) + S$ boxes in the first row and $y = (N/2) - S$ boxes in the second row[16].

In a similar way one may construct a basis in $(\mathcal{V}_c^1)^{\otimes N}$. Then, the primitive N-electron basis may be defined as

$$\Xi_k^{\mathfrak{M}}(\boldsymbol{c}) \equiv \Xi_k^{\mathfrak{M}}(c_1, c_1, \ldots, c_N) = \bigotimes_{j=1}^{N} c_j , \quad c_j = \tilde{e}_1 , \ \tilde{e}_s \tag{55}$$

with, in analogy to Eq. (*51*), $\mathfrak{M} = (N_l - N_s)/2$, where N_l and N_s are, respectively, the numbers of large and small components in the product. Let us note that $N = N_l + N_s$ and, consequently,

$$N_l = \mathfrak{M} + \frac{N}{2} . \tag{56}$$

Therefore the value of $\mathfrak{M}$ may be used as a measure of the significance of a term containing a specific function $\Xi_k^{\mathfrak{M}}$ in a transition to the non-relativistic limit. The basis (*55*) may also be adapted to $\mathcal{S}_N$ resulting in N-electron functions $\Xi_k^{\mathfrak{S}\mathfrak{M}}$ with $\mathfrak{M} = -\mathfrak{S}, -\mathfrak{S}+1, \ldots, \mathfrak{S}$ and $k = 1, 2, \ldots, f(\mathfrak{S},N)$ (more details may be found in ref.[18]). The transformation properties of $\Xi_k^{\mathfrak{M}}$ and of $\Xi_k^{\mathfrak{S}\mathfrak{M}}$ are the same as the ones of Θ_k^M (Eq. (*52*)) and of Θ_k^{SM} (Eq. (*53*)), respectively.

The antisymmetric and spin-adapted basis in $\mathcal{H}_{nr}^N$ is given by

$$\Psi_{k,\lambda}^{SM}(\boldsymbol{\sigma},\boldsymbol{r}) = \hat{A}[\Theta_k^{SM}(\boldsymbol{\sigma}) \otimes R_\lambda(\boldsymbol{r})] , \tag{57}$$

where $R_\lambda(\boldsymbol{r})$ is a basis function in $\mathcal{R}^N$

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_P \epsilon(P)\hat{P} \tag{58}$$

is the antisymmetrization operator and $\epsilon(P) = \pm 1$ is the parity of $\hat{P}$. The analogous basis in $\mathcal{H}^N_{\mathrm{rel}}$ may be defined as

$$\tilde{\Psi}^{SM,\mathfrak{M}}_{k,n\lambda}(\boldsymbol{\sigma},\boldsymbol{c},\boldsymbol{r}) = \hat{A}[\Theta^{SM}_k(\boldsymbol{\sigma}) \otimes \tilde{R}^{\mathfrak{M}}_{n\lambda}(\boldsymbol{c},\boldsymbol{r})] , \tag{59}$$

where

$$\tilde{R}^{\mathfrak{M}}_{n\lambda}(\boldsymbol{c},\boldsymbol{r}) = \Xi^{\mathfrak{M}}_n(\boldsymbol{c}) \otimes R_\lambda(\boldsymbol{r}) \tag{60}$$

and $n = 1, 2, \ldots, g(\mathfrak{M},N)$.

Now let us evaluate matrix elements of the spin-dependent non-relativistic N-electron Hamiltonian

$$H^{\lambda\lambda'}_{\kappa\kappa'} \equiv \langle \Psi^{SM}_{k,\lambda} | \hat{H}^{\mathrm{P}}_N | \Psi^{S'M'}_{k',\lambda'} \rangle . \tag{61}$$

After using Eq. (*53*), the matrix element may be expressed as

$$H^{\lambda\lambda'}_{\kappa\kappa'} = \sum_P \epsilon(P) \langle R_\lambda | \langle \Theta^{SM}_k | \hat{P}\hat{H}^{\mathrm{P}}_N | \Theta^{S'M'}_{k'} \rangle | R_{\lambda'} \rangle , \tag{62}$$

where $\kappa = \{k,S,M\}$, $\kappa' = \{k',S',M'\}$; the external bracket symbolizes integration over the electron coordinates and the internal one – over spin variables. Substituting the explicit form of the Hamiltonian (Eqs (*39*) and (*49*)) to Eq. (*62*), we can split the general matrix element expression

$$H^{\lambda\lambda'}_{\kappa\kappa'} = \sum_{i=1}^{N} H_1(i)^{\lambda\lambda'}_{\kappa\kappa'} + \sum_{i>j}^{N} H_2(i,j)^{\lambda\lambda'}_{\kappa\kappa'} \tag{63}$$

to the one-electron contributions

$$H_1(i)^{\lambda\lambda'}_{\kappa\kappa'} = H_{10}(i)^{\lambda\lambda'}_{\kappa\kappa'} + \sum_{m=-1}^{1} H^m_{11}(i)^{\lambda\lambda'}_{\kappa\kappa'} \tag{64}$$

and the two-electron contributions

$$H_2(i,j)^{\lambda\lambda'}_{\kappa\kappa'} = \sum_P \epsilon(P) V_S^N(P)_{kk'} X_2^{ij}(P)^{\lambda\lambda'} \delta_{SS'} \delta_{MM'} , \tag{65}$$

where

$$X_2^{ij}(P)^{\lambda\lambda'} = \langle (\hat{P}^{-1} R_\lambda) | \hat{H}_2(r_{ij}) | R_{\lambda'} \rangle . \tag{66}$$

The one-electron contributions, according to Eq. (*39*), may be expressed as

$$H_{10}(i)^{\lambda\lambda'}_{\kappa\kappa'} = \sum_P \epsilon(P) V_S^N(P)_{kk'} X_1^i(P)^{\lambda\lambda'} \delta_{SS'} \delta_{MM'} \tag{67}$$

$$H_{11}^m(i)^{\lambda\lambda'}_{\kappa\kappa'} = \sum_P \epsilon(P) W_m^i(P)_{\kappa\kappa'} Y_{1m}^i(P)^{\lambda\lambda'} , \tag{68}$$

where

$$X_1^i(P)^{\lambda\lambda'} = \langle (\hat{P}^{-1} R_\lambda) | \hat{H}_0^{\mathrm{p}}(\boldsymbol{r}_i) | R_{\lambda'} \rangle \tag{69}$$

$$Y_{1m}^i(P)^{\lambda\lambda'} = \langle (\hat{P}^{-1} R_\lambda) | \hat{B}_m^{\mathrm{p}}(\boldsymbol{r}_i)^\dagger | R_{\lambda'} \rangle \tag{70}$$

$$W_m^i(P)_{\kappa\kappa'} = \langle \Theta_k^{SM} | \hat{P} \hat{\sigma}_m^i | \Theta_{k'}^{S'M'} \rangle \tag{71}$$

and

$$\hat{\sigma}_m^i = \hat{I}^{\otimes(i-1)} \otimes \hat{\sigma}_m \otimes \hat{I}^{\otimes(N-1)} . \tag{72}$$

Let us note that $W_m^i(P)_{\kappa\kappa'} = 0$ if either $|S - S'| > 1$ or $|M - M'| > 1$.

This approach is reduced to the CI method for spin-dependent Hamiltonians if the basis in $\mathcal{R}^N$ is constructed from products of one-electron orbitals, *i.e.* if

$$\mathcal{R}^N = (\mathcal{R}^1)^{\otimes N} \tag{73}$$

(see refs[12,15] for details). Integrals over the orbital space (Eqs (*66*), (*69*) and (*70*)) are then reduced to simple one- (Eqs (*69*) and (*70*)) and two-electron (Eq. (*66*)) integrals. If the one-electron basis is orthogonal, then most of the contributions given by Eqs (*66*), (*69*) and (*70*) vanish. However, the formalism presented is much more general. It is valid for an arbitrary square-integrable basis functions in $\mathcal{R}^N$, including explicitly correlated ones. Detailed discussion of specific cases is highly technical, involves rather tedious algebra and will be presented elsewhere.

It is most important that a very similar formalism applies also in the relativistic case. The relativistic counterpart of Eq. (*62*) may be obtained by combining Eq. (*59*) with the Hamiltonians (*28*) and (*49*):

$$\tilde{H}^{\lambda\lambda'}_{\mu\mu'} = \sum_P \epsilon(P) \langle \tilde{R}^{\mathfrak{M}}_{n\lambda} | \langle \Theta^{SM}_k | \hat{P}\hat{H} | \Theta^{S'M'}_{k'} \rangle | \tilde{R}^{\mathfrak{M}}_{n'\lambda'} \rangle \,, \tag{74}$$

where $\mu = \{k,S,M,n,\mathfrak{M}\}$, $\mu' = \{k',S',M',n',\mathfrak{M}'\}$. Then the relativistic analogs to Eqs (*63*)–(*70*), are obtained by the replacement of symbols H by $\tilde{H}$, changing the subscripts $\kappa\kappa'$ to $\mu\mu'$ and by redefining X and Y integrals in the following way:

$$X^{ij}_2(P)^{\lambda\lambda'} \rightarrow \tilde{X}^{ij}_2(P)^{\lambda\lambda'}_{\nu\nu'} = \langle (\hat{P}^{-1}\tilde{R}^{\mathfrak{M}}_{n\lambda}) | \hat{H}_2(r_{ij}) | \tilde{R}^{\mathfrak{M}'}_{n'\lambda'} \rangle \tag{75}$$

$$X^{i}_1(P)^{\lambda\lambda'} \rightarrow \tilde{X}^{i}_1(P)^{\lambda\lambda'}_{\nu\nu'} = \langle (\hat{P}^{-1}\tilde{R}^{\mathfrak{M}}_{n\lambda}) | \hat{H}^{\mathrm{D}}_0(\boldsymbol{x}_i) | \tilde{R}^{\mathfrak{M}'}_{n'\lambda'} \rangle \tag{76}$$

$$Y^{i}_{1m}(P)^{\lambda\lambda'} \rightarrow \tilde{Y}^{i}_{1m}(P)^{\lambda\lambda'}_{\nu\nu'} = \langle (\hat{P}^{-1}\tilde{R}^{\mathfrak{M}}_{n\lambda}) | \tilde{B}^{\mathrm{D}}_m(\boldsymbol{x}_i)^{\dagger} | \tilde{R}^{\mathfrak{M}'}_{n'\lambda'} \rangle \,, \tag{77}$$

where $\nu = \{n,\mathfrak{M}\}$, $\nu' = \{n',\mathfrak{M}'\}$. Thus, instead of Eqs (*65*), (*67*) and (*68*), we have, respectively,

$$\tilde{H}_2(i,j)^{\lambda\lambda'}_{\mu\mu'} = \sum_P \epsilon(P) V^N_S(P)_{kk'} \tilde{X}^{ij}_2(P)^{\lambda\lambda'}_{\nu\nu'} \delta_{SS'} \delta_{MM'} \tag{78}$$

$$\tilde{H}_{10}(i)^{\lambda\lambda'}_{\mu\mu'} = \sum_P \epsilon(P) V^N_S(P)_{kk'} \tilde{X}^{i}_1(P)^{\lambda\lambda'}_{\nu\nu'} \delta_{SS'} \delta_{MM'} \tag{79}$$

$$\tilde{H}_{11}^{m}(i)_{\mu\mu'}^{\lambda\lambda'} = \sum_{P} \epsilon(P) W_{m}^{i}(P)_{\mu\mu'} \tilde{Y}_{1m}^{i}(P)_{\nu\nu'}^{\lambda\lambda'} \,. \tag{80}$$

Let us note that for a given pair $\{\lambda,\lambda'\}$ in the non-relativistic case, $X_2^{ij}(P)^{\lambda\lambda'}$, $X_1^{i}(P)^{\lambda\lambda'}$ and $Y_{1m}^{i}(P)^{\lambda\lambda'}$ are single numbers while their relativistic counterparts, respectively $\tilde{X}_2^{ij}(P)_{\nu\nu'}^{\lambda\lambda'}$, $\tilde{X}_1^{i}(P)_{\nu\nu'}^{\lambda\lambda'}$ and $\tilde{Y}_{1m}^{i}(P)_{\nu\nu'}^{\lambda\lambda'}$, are $2^N \times 2^N$ arrays. In particular, from Eqs (*60*) and (*75*)–(*77*) one gets

$$\tilde{X}_2^{ij}(P)_{\nu\nu'}^{\lambda\lambda'} = \langle \Xi_n^{\mathfrak{M}} | \hat{P} | \Xi_{n'}^{\mathfrak{M}'} \rangle \langle (\hat{P}^{-1} R_\lambda) | \hat{H}_2(r_{ij}) | R_{\lambda'} \rangle \tag{81}$$

$$\begin{aligned} \tilde{X}_1^{i}(P)_{\nu\nu'}^{\lambda\lambda'} &= \langle \Xi_n^{\mathfrak{M}} | \hat{P} | \Xi_{n'}^{\mathfrak{M}'} \rangle \langle (\hat{P}^{-1} R_\lambda) | \hat{\upsilon}(\boldsymbol{r}_i) | R_{\lambda'} \rangle + \\ &+ \mathfrak{m}\mathfrak{c}^2 \langle \Xi_n^{\mathfrak{M}} | \hat{P}\beta^i | \Xi_{n'}^{\mathfrak{M}'} \rangle \langle (\hat{P}^{-1} R_\lambda) R_{\lambda'} \rangle \end{aligned} \tag{82}$$

$$\tilde{Y}_{1m}^{i}(P)_{\nu\nu'}^{\lambda\lambda'} = \mathfrak{c} \langle \Xi_n^{\mathfrak{M}} | \hat{P}\alpha^i | \Xi_{n'}^{\mathfrak{M}'} \rangle \langle (\hat{P}^{-1} R_\lambda) | \hat{\pi}_m(\boldsymbol{r}_i)^\dagger | R_{\lambda'} \rangle \,, \tag{83}$$

where

$$\omega^i = \hat{I}^{\otimes(i-1)} \otimes \omega \otimes \hat{I}^{\otimes(N-i)} \tag{84}$$

with $\omega = \alpha, \beta$. Therefore, in Eqs (*78*)–(*80*) each matrix element of either $\boldsymbol{V}_S^N$ or $\boldsymbol{W}_m^i$ matrix has to be multiplied by the appropriate $2^N \times 2^N$ matrix giving a $4^N \times 4^N$ matrix as the result. The evaluation of matrices $\tilde{Z}(\Omega)_{nn'} = \langle \Xi_n^{\mathfrak{M}} | \hat{\Omega} | \Xi_{n'}^{\mathfrak{M}'} \rangle$, where $\hat{\Omega} = \hat{P}$, $\hat{P}\beta^i$, $\hat{P}\alpha^i$ is very simple. In all cases, in each row and in each column one element is equal to ±1 and the remaining ones are 0. If $\Omega = \hat{P}$, then $\tilde{Z}(\Omega)_{nn'} = Z(P)_{nn'}$, where $\boldsymbol{Z}(P)$ is defined in Eq. (*52*). The elements in $\tilde{\boldsymbol{Z}}(\hat{P}\alpha^i)$ are the same as in $\tilde{\boldsymbol{Z}}(\hat{P})$ except for two pairs of elements being transposed. Finally, the non-zero elements in $\tilde{\boldsymbol{Z}}(\hat{P}\beta^i)$ are located in the same positions as in $\tilde{\boldsymbol{Z}}(\hat{P})$ except that half of them is equal to –1 rather than 1. More details concerning structure of $\tilde{\boldsymbol{Z}}(\hat{\Omega})$ may be found in ref.[18]

CONCLUSIONS

The decomposition of the 4^N-dimensional N-electron Dirac spinor space to a product of two isomorphic 2^N-dimensional spaces $(\mathcal{V}_\sigma^1)^{\otimes N}$ and $(\mathcal{V}_c)^{\otimes N}$ leads to an approach in which the problem of construction of a matrix representing $\hat{H}_N^{\mathrm{D}}$ in an N-electron model space is reduced to a much better elaborated problem of construction of a matrix representing spin-dependent operators in the non-relativistic theory based on Pauli two-component spinors. In particular, computer programs designed for a treatment of spin-dependent operators within a Pauli-type formalism may be, by only some minor modifications, adapted to the corresponding Dirac–Coulomb approach.

The ideas presented in this paper may be a starting point for development of a variety of approaches to relativistic theories of N-electron systems, ranging from all kinds of CI methods to approaches in which explicitly correlated variational functions are used. Since the method allows for a clear separation of the algorithms for a generation (either evaluation or reading from a file) of the integrals over the coordinate space from the algorithms which generate the coefficients with which these integrals appear in Hamiltonian matrix elements (known as the *coupling constants*), it is particularly suitable for implementations within direct CI methods. In particular, Eqs (*75*)–(*83*) allow for an assignment of blocks of the coupling constants to specific integrals over the coordinate space.

One of the most important and difficult aspects of CI is designing criteria for truncation of the expansions. The problem is particularly severe in the case of relativistic approaches. When the basis in $(\mathcal{V}_\sigma^1)^{\otimes N}$ is spin-adapted, then a criterion involving spin multiplicity may be very useful. In the lowest approximation, only these parts of the coupling constant matrices may be included that correspond to a given spin S. Next, the parts of the matrices corresponding to S and to $S \pm 1$ may be included. In higher approximations, consecutive blocks of the coupling constant matrices may be added. Similarly, depending upon the quantities of interest, parts of the coupling constant matrices corresponding to specific values of M may be included. In general, the use of the spin-adapted basis even in the cases in which spin is not a good quantum number gives a deeper insight into the structure of the wavefunction and allows for easier selection of the most important components of the CI wave function. At the same time, the spin adaptation does not bring any substantial complexity to the algorithm.

The most “exotic”, since it has no non-relativistic counterpart, is the space of large and small components, $(\mathcal{V}_c^1)^{\otimes N}$. Formally, it is isomorphic to the spin space $(\mathcal{V}_\sigma^1)^{\otimes N}$. However its physical meaning is entirely different.

Its subspace corresponding to a specific $\mathfrak{M}$ contains wavefunctions with a given ratio of large/small components in one-electron spinors. The authors are not aware of any physical meaning of $\mathcal{S}_N$-adapted subspaces of $(\mathcal{V}_c^1)^{\otimes N}$. Therefore, in this paper, we do not perform any $\mathcal{S}_N$ adaptation of this space (though such an adaptation is not associated with any formal difficulty). The N-electron space of large and small components may be truncated at a certain value of $\mathfrak{M}$ (in particular, only the subspaces corresponding to $\mathfrak{M} = N/2$, $N/2 - 1$ are involved in constructing the non-relativistic limit). One has to remember that this truncation is not trivial: also the Hamiltonian has to be changed accordingly.

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